REMOVAL AND SEPARATION OF LEAD, COPPER AND CADMIUM FROM WATER SOLUTIONS USING RESIN ADSORPTION

By

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ABSTRACT

Heavy metals including lead, copper, and cadmium existing in various industrial effluents create severe environmental impacts around the world. There are various technologies applied for the treatment of wastewaters bearing toxic metals such as ultrafiltration, solvent extraction, precipitation, reverse osmosis, and resin adsorption via ion exchange or chelating bonding. Removal and separation of heavy metals have been the subject of many studies, but few of them systematically investigated various resins at the same time and the acting mechanism of functional group types in details. The current research bridged this gap with the following novel works : (1) experimental investigation and molecular simulation of uptake of cadmium ions from aqueous solution using resins with sulphonic /phosphonic functional groups; (2) removal/ recovery of single copper and lead ions from water system with comprehensive studies of the influences of pH, adsorption time, resin dosage, concentrations, as well as adsorption kinetics, thermodynamics and resin elution process; (3) experimental investigation of the separation of lead and copper ions from acidic binary solution, systematic studies on various operational conditions at different measurement ranges, as well as kinetics, isotherms, thermodynamics and elution studies. The results from the research demonstrated the potency for removal of lead, copper, and cadmium as well as lead-copper separation from wastewaters by the use of resin adsorption via ion exchange or chelating bonding. More resin structure-performance studies will be conducted in the future for efficient metal removal/recovery from wastewaters, secondary resources, or even ocean waters.

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NOMENCLATURES

D2EHPA	Di-ethylhexylphosphate
DFT	Density functional theory
DHLL	Debye Huckel Limiting Law equation
DI	Deionized
DTMPPA	Di(2,4,4-trimethylpentyl)-phosphinic acid
DVB	Divinylbenzene
EPA	Environmental Protection Agency
HCl	Hydrochloric
HM	Heavy metal
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
IDA	Iminodiacetic acid
IPD	Intra-particle diffusion equation
ICP-EOS	Inductively Couple Plasma Optical Emission Spectroscopy
MBD	Mixed bed
MWCNT	Multi-Walled Carbon Nanotube
MCCM	Mesoporous Carbons Coated Monolith
PBT	Persistent bio-accumulative toxic
SAC	Strong acid cation
WHO	World Health Organization
WDXRF	Wavelength dispersive X-ray fluorescence
B3LYP	Becke, 3-parameter, Lee–Yang–Parr

MBR	Mixed bed resins
IPD	Intra-particle diffusion equation
MBR	Mixed bed resins
PFO	Pseudo First Order equation
PSO	Pseudo Second Order equation
SAR	Strong anion exchange resins
PS	Polystyrene
LUMO	Lowest Unoccupied Molecular Orbital
SCR	Strong cation exchange resins
SIR	Solvent impregnated resin
WAR	Weak anion exchange resins
WCR	Weak cation exchange resins
C_o	Initial concentration (mg/L)
Ce	Final concentration (mg/L)
x_R	Amount of metal per gram of resin (g M^+/ g resin)
M^+	Metal ion
w	Amount of resin used in adsorption experiments (g).
v	Volume of sample in adsorption experiments. (mL)
Q^0	Adsorption capacity (mg/g)
b	Energy of adsorption (l/mg)
M	Total amount of resin in grams (g)
K_a	Thermodynamic equilibrium constant
K_F	Freundlich equilibrium constant

K_L	Langmuir equilibrium constant
K_T	Temkin isotherm constant (l/g)
B	Heat of sorption constant (J/mol).
K_D	Distribution constant
k_1	First order rate constant
k_2	Second order rate constant
k_p	rate constant of IDP
$q_{\mathrm{e\ cal}}$	Adsorption capacity at equilibrium calculated theoretically
q_{e}	Adsorption capacity of adsorbent at equilibrium
q_{max}	Maximum adsorption capacity of adsorbent
$q_{\mathrm{e\ exp}}$	Adsorption capacity at equilibrium obtained experimentally
q_{t}	Adsorbate uptake per mass of adsorbent at given time
SCF	Self-Consistent Field
ΔG°	Change in Gibbs free energy
ΔH°	Change in Enthalpy
ΔS°	Change in Entropy
R	Ideal gas constant [8.315 J/mol K]
T	Temperature
ε_{o}	electronic energy

Chapter 1

Introduction

1.1 Background

Removal of heavy metals (HM) such as lead, copper and cadmium from industrial and municipal wastewater is a common waste treatment process. Lead is present in earth crust with only 0.00002 % [1]. The total world production of lead in 2019 was 4,800,000 metric tonnes and was 4,500,000 metric tonnes in 2020. This decrease was due to power shortages and COVID-related restrictions. The main release sources for lead in the environment are from human activities and industrial processes such as battery manufacturing, soldering and alloys, paint pigments, and automobiles [2, 3]. Lead damages enzymes, kidneys, liver, and nervous system [4, 5]. According to the WHO 2017 guideline, the maximum allowable limit is 0.01 mg/L [6].

Cadmium exists in nature in the form of compounds. The main compounds are CdS and $CdCO_3$. The world production of cadmium in 2019 was 26800 metric tonnes, and in 2020 was 24500 metric tonnes. This decrease is for the same reason as mentioned above [7]. The major sources of cadmium exposure are mining processes, alloys manufacturing, batteries, fertilizers, and pigments [8, 9, 10, 11]. Cadmium causes many health problems, including kidney damage and compositional changes of bones and blood, and diarrhea [8, 9, 11, 12]. The maximum acceptable limit of cadmium in water is 0.005 mg/L as recommended by the WHO 2017 guideline [6].

Copper usually exists in the sulphide form in the earth's crust. [13]. Fertilizers, electronic industries, pigments, metal cleaning, refineries and municipal wastewater are the main sources of copper waste [14, 15]. The total world production of smelter copper and refined copper in 2020 were 17,500,000 metric tonnes and 24,900,000 metric tonnes respectively [7]. Although copper is an essential element for several enzymes, its exposure in high doses causes poisoning, mucosal irritation, kidney and liver damage, and nervous system problems [14, 16]. The highest permissible concentration by the WHO 2017guideline is 1.0 mg/L [6].

Lead and copper often coexist in sulfides ore bodies. Cadmium usually coexists with zinc and lead sulfide minerals. Separation of heavy metals is also very important from environmental and economic aspects. Therefore, the recovery and removal of heavy metals have great significances in research and industrial sectors. The composition of wastewaters is different according to the nature of industrial activities, as shown in Table 1.1. In this research, to verify the efficiency of the explored resins for removal and separation of lead, copper and cadmium, they are tested at different concentrations of metal ions.

Table1.1: Composition of different industrial effluents, (mg/L).

Ions	**Leach of electronic scrap** [17]	**Electroplating industrial** [18]	**A television recycling factory** [19]
Pb^{2+}	80	116.42	6000
Cu^{2+}	14940	NA	NA
Cd^{2+}	0.5	964.16	NA
Ni^{2+}	560	NA	NA
Zn^{2+}	5.6	16.11	1350
SO_4^{2-}	NA	1228.52	3258

The existence of lead, copper and cadmium and other heavy metals in wastewaters brings up concerns and interests of many researchers as regards to their removal from a single solution, while the separation of these metals attracts less attention, as seen in the literature.

Copper and lead are separated from stripping and rinsing solutions generated from electronic industries effluents [20, 21]. Separation of Cu^{2+} and Pb^{2+} ions from aqueous solutions by a diethylenediamine (DETA)-functionalized polymeric adsorbent was investigated by [22]. Cu^{2+} and Pb^{2+} were also separated from an aqueous solution in fixed bed columns by manganese oxide coated zeolite [23].

Many methods were proposed for removal and separation of heavy metals from wastewater. These methods include evaporation, precipitation, liquid extraction, and membrane filtration [24, 25]. However, these techniques have some disadvantages such as high operational costs, disposal, and the amount of used energy [26, 27].

As efficient separation technology, in resin adsorption processes, selective ion exchange or chelating resins can be used to pick up a certain metal ion via adsorption from a solution mixture which contains different metals. Moreover, these adsorbents can be regenerated. In this work, resin adsorption processes are chosen to remove samples of lead, copper and cadmium ions from an acidic water solution, as presented in Chapters 3, 4 and 5. Separating these metals from binary mixtures, is presented in Chapters 6. The process has become widely used for removal and separation of heavy metals from wastewater due to many advantages, including high treatment capacity, removal efficiency, simplicity of use, and cost savings [28-30].

1.2 Scope of work

This research presents removal of single metal, i.e., lead, copper and cadmium from simulated wastewaters using commercial resins. Also, the separation of binary metals from solutions is explored. The wastewater was synthetically prepared in the lab by dissolving appropriate amounts of metal salts in specific volumes of deionized water. Wavelength dispersive X-ray fluorescence spectroscopy and Inductively Coupled Plasma (ICP) analysis were used for determination of the concentrations of selected heavy metal ions. The experiments were designed and conducted using a batch technique.

Twenty-seven resins with sixteen different functional groups which are obtained from different manufacturing companies were tested as shown in Table 1.2. They are classified in three main classes, including cation acid resins (strong acid and weak acid), anion base resins (strong base and weak base), and chelating resins.

The operational conditions that affect the adsorption of selected metals on the explored resins including resin dosage, pH, adsorption time, initial metal solution concentration, and temperature, were studied at different ranges. Isotherm, kinetics, and thermodynamics studies were conducted to help in the design of an adsorption system in wastewater treatment. In addition, desorption/elution studies were preformed to investigate the recycling of the adsorbents.

Table1.2: Commercial resins used in this thesis.

Functional group	**Resin**	**Matrix**	**Delivery form**	**Bead size (mm)**	**Total capacity (equiv./L)**	**Supplier**
1.Sulfonic	Dowex G-26	S-DVB (gel)	H^+	0.650 ± 50	2	Dow
	Amberlite IR-120 H	S-DVB (gel)	H^+	0.620–0.830	>1.8	Sigma-Aldrich
2.Iminodiacetic	Purolite S930 plus	PS-DVB (macroporous)	Na^+	0.425–1.0	50 g Cu/L	Purolite
	Lewatit monoplusTP207	PS-DVB (macroporous)	H^+	0.61 (±0.05)	2	Lanxess
	Amberlite IRC784I	PS-DVB (macroporous)	Na^+	0.50–0.65	>1.35	Roham& Haas
	Lewatit monoplus TP208	PS-DVB (macroporous)	Na^+	0.4–1.25	2.9	Lanxess
	Purolite S930EPlus	PS-DVB (macroporous)	Na^+	0.425–1.0	50 g Cu/L	Purolite
3.Aminophosphonic	SIR 500	S-DVB (macroporous)	Na^+	0.297–1.19	>1.4	ResinTech
	Amberlite IRC747	PS-DVB (macroporous)	Na^+	0.520–0.660	1.75	Dow
	Purolite S940	PS-DVB (macroporous)	Na^+	0.425–0.850	20 g Ca/L	Purolite
	Purolite S950plus	PS-DVB (macroporous)	Na^+	0.425–0.850	24 g Ca/L	Purolite
	Puromet™ MTS9500	PS-DVB (macroporous)	Na^+	0.30–1.2	26 g Ca/L	Purolite
4.Aminomethylphosphonic	Lewatit monoplus TP 260	PS-DVB (macroporous)	Na^+	0.63 (±0.05)	2.4	Lanxess
5.Phosphonic and Sulfonic	Purolite MTS 9570	PS-DVB (macroporous)	H^+	0.315–0.850	18 g Fe/L	Purolite
6.Bis-picolylamine	Lewatit MDS TP220	PS-DVB (macroporous)	FB form	0.62(±0.05)	5 g Cu/L	Lanxess
7.Carboxilic	Dowex Mac-3	PA (macroporous)	H^+	0.30–1.2	3.8	Dow
	WAG RTI 26600	PA-DVB (gel)	H^+	0.297–1.19	>4.0	ResinTech
8.N-methylglucamine	Purolite S108	PS-DVB (macroporous)	FB form	0.425–0.630	0.6	Purolite
9.Di-2-ethylhexylphosphat (D2EHPA)	Lewatit vp oc 1026	PS-DVB (macroporous)	-	0.31-1.65	13 g Zn/L	Lanxess
10.Thiourea	Lewatit monoplusTP214	PS-DVB (macroporous)	-	0.55 (±0.05)	1.1	Lanxess
	PuroliteMTS9140	PS-DVB (macroporous)	-	0.30–1.2	1.0	Purolite
11.Trimethyl ammonium	Amberjet 4400 Cl	PS-DVB (gel)	Cl^-	0.53-0.63	1.4	Roham& Haas
12.Isothiouronium	Purolite MTS9200	PS-DVB (macroporous)	H^+	0.30–1.2	275 g Hg/L	Purolite
13.Amidoxime	Puromet™ MTS9100	PA-DVB (gel)	FB form	0.30–1.2	40 g Cu/L	Purolite
14.Thiol	Puromet™ MTS9240	PS-DVB (macroporous)	H^+	0.30–1.00	200 g Hg/L	Purolite
15.Sulphonic and Trimethyl ammonium	Amberlite™ IRN150	S-DVB (gel)	H^+&OH^-	0.60 - 0.70 0.58- 0.68	≥ 1.90&≥ 1.20	Roham& Haas
16.Sulfonic / Trimethylamine	ResinTech MBD-15 SC	S-DVB (gel)	H^+&OH	0.297-1.19	0.57	ResinTech

1.3 Research Objectives

The overall objective of this research is to remove and separate lead, copper and cadmium efficiently from wastewaters using resins with specific functional groups. Figure 1.1 outlines the tasks conducted to achieve the research objectives. The research goal is achieved through the following research tasks:

I. Find an effective resin for the removal of Cd(II) ions from single solution.

II. Find a highly efficient resin for the removal of Cu(II) ions from a single solution.

III. Find a resin with high performance for the removal of Pb(II) ions from a single solution.

IV. Find an effective resin to separate Cu(II) and Pb(II) from a binary solution.

V. Study the mechanism of Cd^{2+}ion adsorption onto resins using a molecular simulation method.

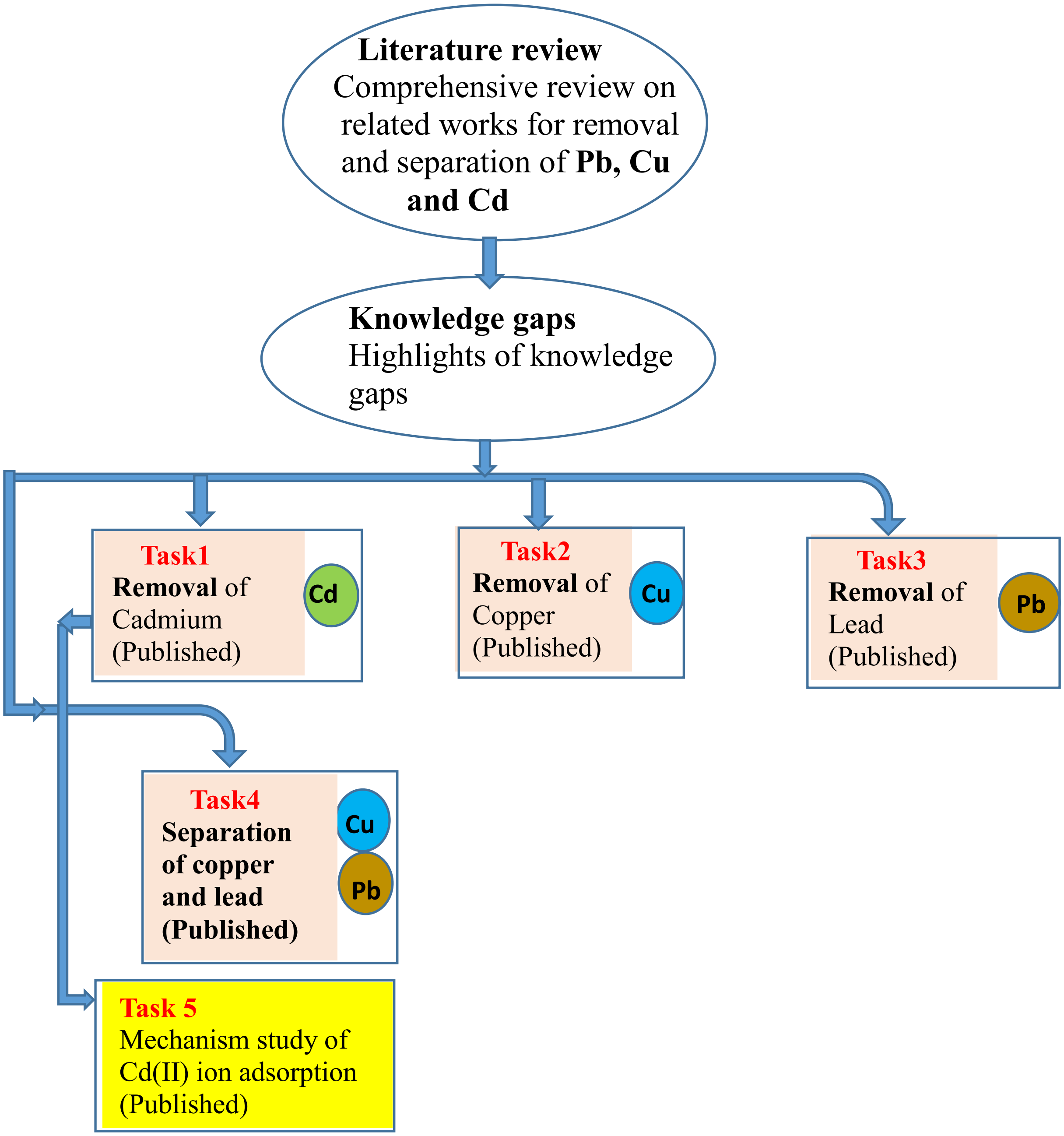


Figure 1.1: Research tasks.

1.4 Contributions and novelty of the current work

Presently, there is no theoretical standard for the choice of resins for removal and separation of metals in water solutions. The scientific contributions and novelties of this doctoral work are highlighted as follows:

- Development of a patent. The invention relates to the removal of cadmium ions with resin fibers bearing sulfonic acid group from aqueous systems, including but not limited to industrial wastewater, contaminated water streams in commercial and agricultural production, and polluted rivers and lakes. A novel adsorption process using low dimensional styrene-divinylbenzene (SDVB) resins (i.e., resin fibers) bearing sulfonic acid group fabricated through electrospinning and sulfonation method demonstrated excellent efficiency for Cd(II) ion removal from aqueous systems under desired conditions. The loaded resin could be recycled with a customized elution process using hydrochloric acid solution, sodium citrate solution, or a mixture of hydrochloric acid and sodium citrate solution.
- The scientific discovery that the removal of lead, copper and cadmium ions from a single water solution can be achieved efficiently by using Dowex G-26 resin with sulfonic group and Purolite MTS 9570 resin with both phosphonic and sulfonic groups.
- Experimental findings that the separation of Cu(II) and Pb(II) from wastewater by using Puromet™ MTS 9140 resin with thiourea group has a strong adsorption preference to Cu (II) over Pb(II).

1.5 Organization of the thesis

This doctoral thesis is written in a manuscript-based format. Hence, the outcomes of the doctoral work are presented in eight journal articles. Figure 1.2 shows the structure of the thesis. The introduction and conclusion are presented in Chapters 1 and 8, respectively. Chapters 2 to 7 are developed based on the submitted and to be submitted papers to peer-reviewed journals.

Chapter 2 comprises a comprehensive review of the relevant previous studies. This chapter is completed and ready to be submitted for publication.

Chapter 3 presents the uptake of cadmium ions from aqueous solution using sulphonic/ phosphonic acid functionalization resins. The chapter is published in *Can J Chem Eng. 2022;1–9.*

Chapter 4 presents removal of copper ions from a water solution using a batch method; the studies of the influence of operational parameters, isotherm models, and desorption/elution are involved. This chapter is published in *Can J Chem Eng. 2022.*

Chapter 5 presents comprehensive studies of the recovery of lead ions from water system and the influence of pH, adsorption time, resin dosage, concentrations, and thermodynamics on the recovery process. This chapter is published in the *Journal of Minerals 2022; 12, 1312.*

Chapter 6 presents separation of binary lead and copper ions from an acidic solution. Systemic studies were conducted for various operational conditions at different measurement ranges. Ion exchange isotherms and kinetic studies were also conducted. This chapter is published in *ACS Omega 2022, 7, 15, 13042–13049.*

Chapter 7 presents a mechanism study of Cd(II) ion adsorption onto resins with sulfonic/ phosphonic groups using electronic structure methods. This chapter is published in the *Journal of Molecular Liquids 2022, 358, 119199.*

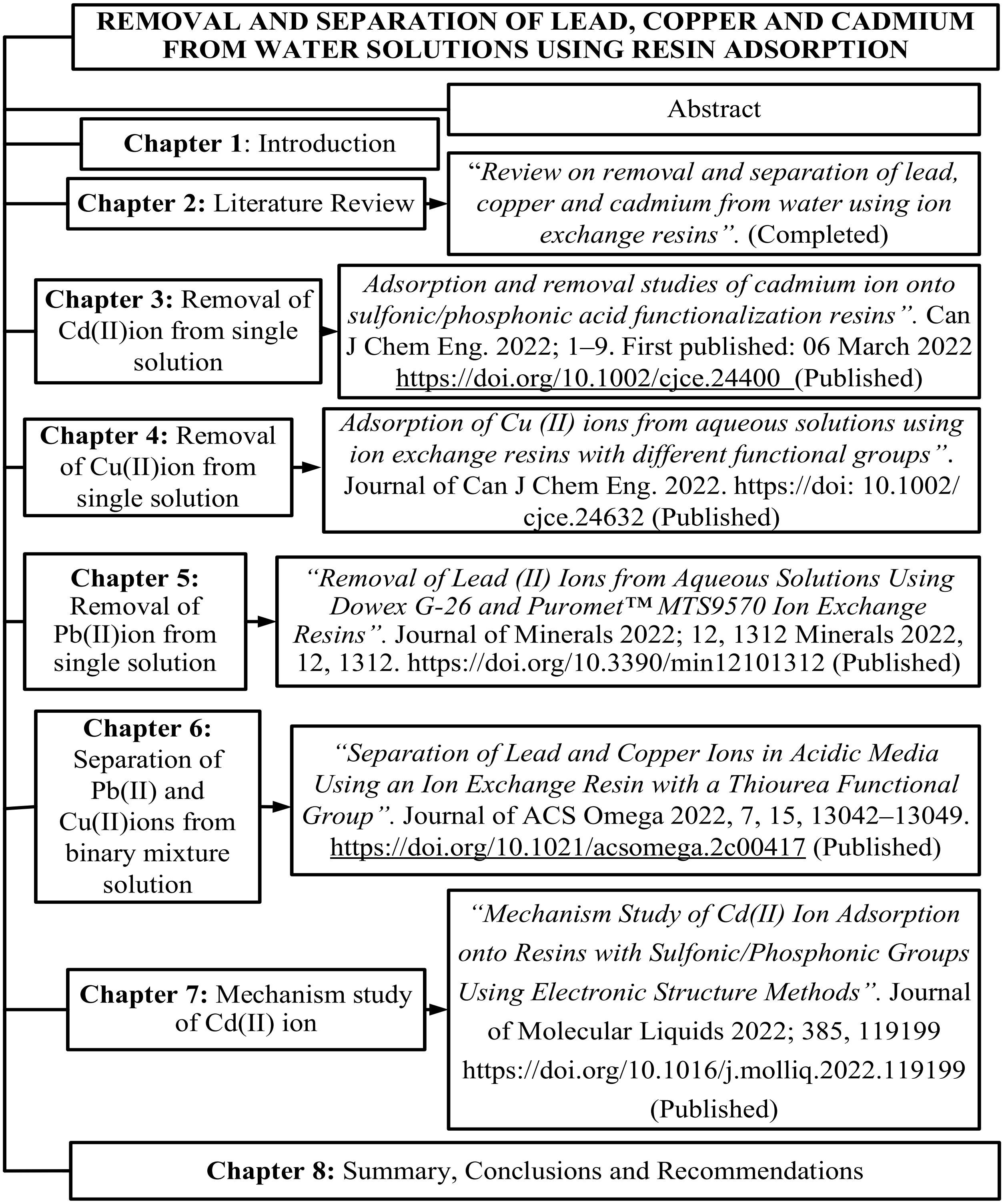


Figure 1.2: Organization of the doctoral thesis

1.6 Co-Authorship Statement

The principal author of this thesis, Salem Elfeghe, acted as the primary author of all the chapters included in this thesis (except chapter 9 as second author), and performed all the experimental works and analysis except where otherwise noted. Dr. Yahui Zhang, who acted as the principal supervisor of this thesis, provided technical guidance and all additional supports needed in the thesis supervision.

References

[1] D.Morales, B. Rivas, ''Poly(2-acrylamidoglycolic acid-co-2-acrylamide-2-methyl-1-propane sulfonic acid) and poly(2-acrylamidoglycolic acid-co-4-styrene sodium sulfonate): synthesis ,characterization, and properties for use in the removal of Cd(II), Hg(II), Zn(II), and Pb(II)'' . *Polymer Bulletin, 2015,72, 339–352. DOI 10.1007/s00289-014-1277-0.*

[2] P.Thu, T.Thanh, H. Phi, S.Kim, V.Vo, ''Adsorption of lead from water by thiol-unctionalized SBA-15 silicas". *Journal of Materials Science, 2010,45, 2952–2957. Doi 10.1007/s10853-01 0-4288-8.*

[3] E.Ramírez, S.Burillo, C.Díaz, G.Roa, B.Bilyeu, ''Use of pH-sensitive polymer hydrogels in lead removal from aqueous solution". *Journal of Hazardous Materials 2011,192, 432–439. Doi:10.1016/j.jhazmat.2011.04.109.*

[4] R.Brooks, M.Bahadory, F.Tovia, H.Rostami, ''Removal of lead from contaminated water". *International Journal of Soil, Sediment and Water2010, 3, 1-13. https://scholarworks.umass.edu/intljssw/vol3/iss2/14*

[5] Fu Fenglian, Qi Wang, ''Removal of heavy metal ions from wastewaters": A review, *Journal*

of Environmental Management 2011, 92,407-418. [*https://doi.org/10.1016/j.jenvman.2010.11.011*](https://doi.org/10.1016/j.jenvman.2010.11.011)

[6] World Health Organization. guidline for drinking-water quality (fourth edi). *World Health Organization.2017. https://www.who.int/publications/i/item/9789241549950.*

[7] N. Idoine, E. Raycraft, R. Shaw, S. Hobbs, E. Deady, P. Everett, E. Evans, A. Mills, World mineral production 2016–2020, *British geological survey. ISBN 978-0-85272-795-9 (Website Version).*

[8] P.Vaughan, M.Bruns, C. Beck, M. Cochran, ‘‘Removal efficiency of heavy metals using various resins and natural materials”. *Journal of Applied Sciences. 2012, 12, (19), 2065-2070. DOI: 10.3923/jas.2012.2065.2070.*

[9] M.Moosavirad, R. Sarikhani, E. Shahsavani, Z. Mohammadi, ‘‘Removal of some heavy metals from inorganic industrial wastewaters by ion exchange method”. *Journal of Water Chemistry and Technology, 2015,37, 191–199. DOI: 10.3103/S1063455X15040074*.

[10] K. Bedoui, I. Abbes, E. Srasra, ‘‘Removal of cadmium (II) from aqueous solution using pure smectite and Lewatit S 100: the effect of time and metal concentration”. *Desalination 2008. 223, 269–273. doi:10.1016/j.desal.2007.02.078.*

[11] Y. Ho, A. Ofomaja, ‘‘Biosorption thermodynamics of cadmium on coconut copra meal as Biosorbent”. *Biochemical Engineering Journal 2006, 30,117–123.* [*https://doi.org/10.1016/j.bej.2006.02.012*](https://doi.org/10.1016/j.bej.2006.02.012).

[12] D.Mohan, Jr. Charles, M. Bricka, F.Smith, B.Yancey, J.Mohammad, P. Steele, M.Franco, V.Serrano, H.Gong, ‘‘Sorption of arsenic, cadmium, and lead by chars produced from

fast pyrolysis of wood and bark during bio-oil production". *Journal of Colloid and Interface Science 310 (2007) 57–73. https://doi.org/10.1016/j.jcis.2007.01.020.*

[13] Z.Hubicki, D.Kołodyńska, ''Selective Removal of Heavy Metal Ions from Waters and Wastewaters Using Ion Exchange Methods", *chapter 8, Ion Exchange Technologies, INTECH, open access book. http://dx.doi.org/10.5772/51040.*

[14] S.Rengaraj, Y.Kim, C.Joo, J.Yi, ''Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: kinetics and equilibrium". *Journal of Colloid and Interface Science 2004, 273, 14–21. doi:10.1016/j.jcis.2004.01.007.*

[15] M. Jha, N. Nguyen, J.Lee, J. Jeong, J.Yoo, ''Adsorption of copper from the sulphate solution of low copper contents using the cationic resin Amberlite IR 120*". Journal of Hazardous Materials 2009,164, 948–953. https://doi.org/10.1016/j.jhazmat.2008.08.103*.

[16] S.Rengaraj, J.Yeon, Y.Kimb, Y.Jung, Y.Ha, W.Kim, ''Adsorption characteristics of Cu(II) onto ion exchange resins 252H and 1500H: Kinetics, isotherms and error analysis". *Journal of Hazardous Materials 2007, 143, 469–477.https://doi.org/10.1016/j.jhazmat.2006.09.064.*

[17] N. Nguyen, J.Lee, H.Huynh, J. Jeong, ''Extraction and Separation of Cadmium from the Chloride Solution of E-Waste Using Cyanex 923 Impregnated Amberlite XAD-7HP Resin". *Materials Transactions, 2015, 56, 1294 -1301.*https://doi.org/10.2320/matertrans.M2015137.

[18] R. Navarro, K.Tatsumi, K. Sumi, M.Matsumura, ''Role of anions on heavy metal sorption of a cellulose modified with poly(glycidyl methacrylate) and polyethyleneimine". *Water Research 2001, 35, 2724–2730. https://doi.org/10.1016/S0043-1354 (00)00546-7*

[19] A.Mengistie, T. Rao, A.Rao, M.Singanan, ''Removal of lead(II) ions from aqueous

solutions using activated carbon from Militia ferruginea plant leaves". *Bull. Chem. Soc. Ethiop. 2008, 22, 349-360. DOI: 10.4314/bcse.v22i3.61207*

[20] J.Lee, H.Song, J.Yoo, ‘‘Present status of the recycling of waste electrical and electronic equipment in Korea". *Resources, Conservation and Recycling2007, 50,380-397. https://doi.org/10.1016/j.resconrec.2007.01.010*

[21] R.Nekouei, F.Pahlevani, M.Assefi, S.Maroufi, V.Sahajwalla, ‘‘Selective isolation of heavy metals from spent electronic waste solution by macroporous ion-exchange resins". *Journal of Hazardous Materials 2019, 371, 389-396. https://doi.org/10.1016/j.jhazmat.2019.03.013*

[22] C.Liu, R.Bai, Q. Ly, ‘‘Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: Behaviors and mechanisms", *Water research 2008, 42, 1511– 15. https://doi.org/10.1016/j.watres.2007.10.031*

[23] R.Han, W. Zou, H. Li, Y.Li, J.Shi , ‘‘Copper(II) and lead(II) removal from aqueous solution in fixed-bed columns by manganese oxide coated zeolite". *Journal of Hazardous Materials, 2006, B137, 934–942. doi:10.1016/j.jhazmat.2006.03.016*

[24] L. Zhou, S. Pan, X. Chen, Y. Zhao, B. Zou, M. Jin, ‘‘Kinetics and thermodynamics studies of pentachlorophenol adsorption on covalently functionalized Fe3O4@SiO2–MWCNTs core–shell magnetic microspheres", *Chem. Eng. J. 2014, 257, 10–19. https://doi.org/10.1016/j.cej.2014.07.060*

[25] M.Arbabi, N. Golshani, ‘‘Removal of copper ions Cu(II) from industrial wastewater: A review of removal methods". *International Journal of Epidemiologic Research, 2016, 3, 283- 293. http://ijer.skums.ac.ir › article_19084*

[26] N. Dizgea, B.Keskinler, H. Barlas, ‘‘Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin”. *Journal of Hazardous Materials 2009.167, 915–926. https://doi.org/10.1016/j.jhazmat.2009.01.073*

[27] M.Arbabi, N. Golshani, ‘‘Removal of copper ions Cu(II) from industrial wastewater: A review of removal methods”. *International Journal of Epidemiologic Research, 2016, 3, 283-293. Corpus ID: 52219731*

[28] S.Rengaraj, Y.Kim, C. Joo, K.Choi, J.Yi, ‘‘Batch Adsorptive Removal of Copper Ions in Aqueous Solutions by Ion Exchange Resins: 1200H and IRN97H”. *Korean J. Chem. Eng.2004, 21,187-194. https://doi.org/10.1007/BF02705397*

[29] P. Ling, F. Liu, L. Li, X. Jing, B. Yin, K. Chen, A.Li, ‘‘Adsorption of divalent heavy metal ions onto IDA-chelating resins: Simulation of physicochemical structures and elucidation of interaction mechanisms”. *Talanta 2010, 81,424–432. doi:10.1016/j.talanta.2009.12.019*

[30] Y. Zhang, Q. Liu, L.Li, ‘‘Removal of iron from synthetic copper leach solution using a hydroxyl-oxime chelating resin”. *Hydrometallurgy2016, 164,154–158. http://dx.doi.org/10.1016/j.hydromet.2016.06.00*

Chapter 2

Review on removal and separation of lead, copper and cadmium from water using resins with functional groups

Preface

This chapter has been completed and now being reviewed for submission to a journal for publication. ***.*** *I and my co-author; Yahui Zhang produced the work. I am the main author. I designed, gathered all the information and conducted the literature review. Dr. Yahui Zhang supervised the design of the literature review and reviewed the manuscript.*

Abstract

In many countries heavy metals including lead, copper, and cadmium that exist in most of the industrial effluents create severe environmental impacts. There are various technologies normally applied for the treatment of wastewater bearing toxic metals such as ultrafiltration, solvent extraction, precipitation, reverse osmosis, and resin adsorption including ion exchange. Removal and separation of heavy metal have been the subject of several literature reviews, but few of them explicitly classified the resins used and their function group types in details. The main goal of this review is to bridge this gap.

This review is organized by the following scientific and technological perspectives, (i) Which resins with specific functional groups are more effective for the removal and separation of lead, copper and cadmium ions from water solutions? (ii) What are the limitations of new adsorbents and how to overcome these limitations? This paper summarizes the literature on removal and separation of lead, copper and cadmium from water systems by resin adsorption processes based on ion exchange (cationic or anionic) and chelating resins.

The literature survey shows that chelating resins and strong acid resins are most used. While the resins of weak acid, strong anion, and weak anion categories have few applications. The work reveals the necessity of developing more new adsorbents for the removal and separation of the studied metals.

Keywords: *heavy metals*, *environment*, *wastewater, ion exchange, chelating resins*

2.1-Introduction

Removal of heavy metals from water is a very important subject for academic and industrial sectors due to their toxic effects on the environment. Heavy metals have a high impact even at low concentrations. In this study, researches on removal and separation of three heavy metals including lead, copper and cadmium from water systems are reviewed**.**

Lead is a raw material used by many industries such as batteries, dyes, leaded glass, gasoline additives, paintings, and explosive materials [1,2]. Lead is considered a toxic heavy metal in water recourses, which is generated from many sources such as mining and metallurgy industries, battery manufacturing, chemical, and petrochemical industries. Lead hazards are assigned by their exposure limit. Lead is toxic and hazardous to most forms of life. Lead chronically affects the human body primarily through neurological disorders, particularly in fetuses and in children [3]. Maximum concertation levels in drinking water are 0.01 mg/L as determined in the Guideline 2017 provided by World Health Organization (WHO) [4].

Copper is used in electrical engineering, construction, machinery works, transportation, and weapons. It is a very useful element to keep neural systems functioning, but when exceeding its acceptable limits, it causes diseases such as Alzheimer, Parkinson, and amyotrophic lateral sclerosis. Copper becomes toxic in its sulphate form and is discharged from iron and steel factories, and mining industry effluents [5, 6]. The highest allowable limit for copper in drinking water is 2mg/L according to the WHO guideline 2017 [4].

Cadmium is a metal of group (II) in the periodic table. Cadmium widely exists in the wastewater of many industrial units such as electroplating plants, dye factories, fertilizer plants, plastic and battery factories. Cadmium is considered as a very toxic metal due to its high solubility [7]. Cadmium causes hazards to the human body such as cancer, damage to kidneys, lungs and liver, and Itai-Itai disease [8]. The permissible limit of cadmium in drinking water is 0.003 mg/L as reported in the WHO guidelines 2017 [4].

There are serval techniques applied for the uptake and separation of lead, copper, cadmium and other heavy metal ions such as adsorption, ion exchange, membrane, filtration, electrodialysis, reverse osmosis, ultrafiltration and photocatalysis [9]. In this paper, resin adsorption including ion exchange processes are chosen for lead, copper and cadmium removal and separation from different aqueous solutions because it is considered to have the advantages of low remnant metal concentration and regeneration of resins [10].

2.2 Ion exchange process

Ion exchange is defined as a process which involves an exchange of ions between an electrolyte solution (liquid phase) and similarly charged ions immobilized in an ion exchange material (solid phase, e.g., resins), through a reversible stoichiometric ion exchange reaction [11,12].

Researches in ion exchange started in the 18th century, when Thomson and Way discovered the ability to cultivate soil by exchanging different ions such as NH_4^+ towards Ca(II) and Mg(II). In the 19th century, ion exchange techniques started growing. Adams and Holmes (1935) revealed that synthetic resins had ion exchange properties [13]. The most significant development for ion exchangers started when d'Alelio (1945) introduced polymerization instead of polycondensation in resin preparation. They succeeded in integrating SOH_3 function group with cross–linked polystyrene exchangers [13]. The most important events in ion exchange developments are summarized in Table 2.1.

Ion exchange materials are the core ion exchange processes. These materials involve polymers and minerals. For polymers, cationic or anionic resins, and membranes are used depending on their industrial applications [11]. Ion exchange resins are solid (usually as beads) and insoluble high molecular weight polyelectrolytes which can exchange their mobile ions for ions of equal charge from the surrounding medium. The resulting ion exchange is reversible and stoichiometric with the displacement of ionic species in solutions/media by another on the exchanger [13]. The ion exchange process can be used as a complementary technique in wastewater treatment system for HM removal [14, 15]. Some researchers applied natural materials as low-cost adsorbents for the removal of heavy metals, but the efficiency of these adsorbents is lower than the efficiency of ion exchange resins [16, 17].

Determining the optimal operating conditions for adsorption process parameter is significant for the design of wastewater treatment process [18, 19]. Many research works have been focused on synthesis of new adsorbents by developing the existing commercial resins to obtain functional groups that have high selectivity for metal ions [20, 21]. Some of the resins applied in this thesis have also been used recently by other researchers who also confirmed their efficiency for metal ions removal/recovery [22- 24].

Resin efficiency is dependent on some physical properties which involves cross-linking degree, porosity, and acid/base strength, degree of stability, purity and particle size [25]. Some of these physical properties for selected commercial resins are presented in Table 2.2.

Table 2.1: The most important events in ion exchange developments.

Year	Event
1850	Discovery of ion exchange phenomena (Thompson and Way).
1858	Introducing Ion exchange as a reversible process (Henneberg and Stohmann).
1870	Success in converting Lucite into analcime (Lemberg).
1905	First use of zeolite in water softening (Robert Gans).
1913	Manufacturing of first commercial zeolites (Permute Co.).
1935	Discovering synthetic resins have ion- exchange properties (Adams and Holmes).
1945	Replacement of polymerization instead of polycondensation in resin preparation (D'Alelio).
1950	Development of weak acidic cationic -exchange resins by polymerization of methacrylic acid and divinylbenzene.
1965	Introducing new macroreticular polymeric adsorbents.
1970	First use of commercial resins Amberlite IRA743.
1980 - 1999	Introducing bi-functional resins.
>2000	Development of new resins.

Table 2.2: Physical properties for some commercial resins *(Rohm and Haas, Purolite, Dow)*.

Properties **/resin**	**Matrix**	**Structure**	**Commercial form**	**Total capacity**	**Moisture content**	**Bead size mm**	**Max temp. limit ºC**	**pH range**	**source**
Amberlite IR120 H Strong Acid	PS-DVB	gel	H+	≥1.80 eq/L (H+ form)	53- 58 % (H+ form)	0.620 - 0.830	135	0-14	Rohm and Haas
Purolite C-104 Weak Acid	PS-DVB	Gel	H+	3.8eq/L	45- 55 %	0.60-0.85	120	0-14	Purolite
Amberlite IRA402 Cl Strong Base	PS-DVB	gel,	Cl^-	≥ 1.20 eq/L (Cl- form)	49- 60 % (Cl- form)	0.600 - 0.750	60	0-14	Rohm and Haas
Amberlite IRA96 Weak Base	PS-DVB	Macro porous	Freebase	1.25eq/L	59- 65 %	0.55-0.75	100	0-7	Dow
Purolite S950 Chelating resin	chelating	Macro porous	Na^+	24 g/L	60-68 %	0.60-0.85	90	6-11 Na form 2-6 H Form)	Purolite

2.3 Types of Ion-exchange Resins

Ion exchange resins involve two main classes, i.e., cation exchange resins (strong & weak acid cations), and anion exchange resins (strong & weak base anions) [25].

2.3.1 Cation exchange resins

2.3.1.1 Strong Acid Cation Exchange Resins

These types of ion exchangers characterised with strong acid functional groups such as sulfonic acid group (-SO_3H), (shown in Figure 2.1). It is produced from divinylbenzene matrix and synthesized by sulfonation of copolymer beads with H_2SO_4, SO_3, $H_2SO_4 \cdot (SO_3)_x$ or HSO_3Cl. There are many challenges associated with the production of these types of resins in the sulfonation process, such as producing undamaged crack-free beads. The exchangers must also be completely converted from H^+ form to Na^+ form by introducing sodium hydroxide in order to be used safely, particularly in water softening to avoid equipment corrosion [13]. Strong acid cation exchange processes, as presented by Ghinwa M. Naja and Bohumil Volesky [26], has the following general reaction.

$$RSO_3^- H^+ + Na^+ \rightleftharpoons RSO_3^- Na^+ + H^+ \tag{2.1}$$

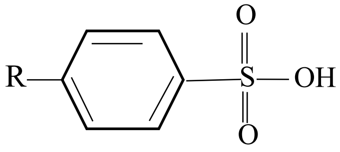


Figure 2.1: Strong acid functional group

This class involves many types of commercial resins which have been used in the removal of lead, cadmium, copper and other heavy metal ions by many researchers.

Demirbas et al., [27] studied the separation of Cu(II), Pb(II), and Cd(II) from aqueous media by using Amberlite IR-120 bearing sulfonic acid group. The results showed that the resin had the highest adsorption capacity of 201.1mmol g^{-1} for Cd^{2+}, 50.9 mmol g^{-1} for Cu^{2+} and 19.6 mmol g^{-1} for Pb^{2+}. The highest recovery of >99% was obtained at pH 9 and 0.1g of resin dose. Kocaoba

[28] reported a comparative study between Amberlite IR 120 and a natural zeolite for the removal of Pb(II) and Cd(II) from aqueous solutions. Optimum operational conditions were obtained at a concentration of 20 mg/L, pH 5, a contact time of 60 min, and an adsorbent dose of 0.5g. The results demonstrated that both adsorbents have good performances, and 99% extraction of Pb(II) and Cd(II) from wastewater.

Tabatabaei et al. [29] also conducted a comparative study for the removal of lead from aqueous solutions using Amberlite IR-120 and natural zeolite. The experiments involving different sizes of zeolite, one size of Amberlite, and different lead concentrations ranging from 40 to 1250 ppm. The study results demonstrated that the most influential parameters on absorption were the concentration of metal ions and zeolite size. The highest uptake efficiency of Amberlite for Pb^{2+} was 99% at 1000 mgl^{-1} and the lowest removal efficiency of zeolite for Pb^{2+} was 88.99% at 40 mgl^{-1}. Absorption of Pb^{2+} by zeolite was found to be less than Amberlite IR-120.

Amberlite IR-120 was analyzed by Carmona et al., [30] for ion-exchange equilibria of lead ions in aqueous systems. The experiments were conducted at a temperatures range of 283-323 K with solution concentration of 0.1eqL^{-1}. The experimental results revealed that equilibrium behavior was slightly affected by the reaction temperature, and the selected resin had a high removal capacity for lead.

Purolite C100 cation exchange resin was investigated by Badawy et al., [31] for removal and recovery of Pb(II) ions from binary mixtures. Batch and column techniques were applied for Pb(II) ions separation from Fe(III), Al(III), and Ba(II) solutions. The experimental results showed that Pb(II) ion was absorbed faster than other ions, thus it was removed before strong adsorption of other competitive adsorbed ions. The results confirmed that ammonium acetate ($NH_4CH_3\ CO_2$)

was a good eluent for Pb(II) cations extracted from Ba(II) or Al(III) solutions. Also, Abo-Farha et al., [32] used Purolite C100 for the separation of lead from aqueous solutions. Batch methods were conducted with metal concentrations between 2.65 and 265mgl^{-1} and 1g of resin dose at 25°C.The study confirmed that the distribution coefficient was indirectly proportional to metal concentrations. The results shown that the ionic radius influenced the loaded resin amount. The valence of cationic ions also influenced electrostatic interaction. The resin affinity for metal ions removal was following the order: $Ce^{4+} > Fe^{3+} > Pb^{2+}$.

Cation exchanger D-001 was investigated by Su et al., [33] for the uptake of lead and cadmium ions from aqueous systems. Batch experiments were employed at different pH ranges, concentrations, and the existence of Ca^{2+}, Na^{+}, K^{+}, and Mg^{2+} ions. The distribution ratio (Kd) of Pb^{2+} onto the sorbent at different initial Ca^{2+}/ Mg^{2+} ratios in solutions was studied. The results indicated that effective metal sorption onto D-001 is mainly due to electrostatic interaction. The study demonstrated that heavy metal removal by D-001 exhibits lower selective sorption in the presence of Ca^{2+} at high concentration levels.

EL-Said [34] tested the removal of iron from binary mixtures of lead and copper using Lewatit S100 resin. The adsorbent had been enhanced on neutral red dye at pH range 3.0 ± 0.5. The separation of selected metal was obtained with respect to its distribution coefficients with five different solutions at 25°C. Fe^{3+} ions were selected for separation from a synthetic mixture of Pb^{2+}, and Cu^{2+} solution. The results showed that the recovery % for Fe^{3+} were 97.67 and 96.88 with Pb(II), Cu(II) ions respectively when using 200 mL of 3M HNO_3 as eluent.

Dowex 50 W was investigated by Hamdzah et al. [35] for the removal of lead from battery manufacturing effluent discharge in Malaysia. The results showed maximum adsorption capacity was 92.3% at a resin amount of 0.3g, pH 6.5, and 75mintues of contact time. In another study by Pehlivan and Altun [36], Dowex 50W was used for the removal of of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous systems. The results showed that the highest recoveries for Cu^{2+} and Cd^{2+} were 97%, and 80% for Pb^{2+} found at high pH ranges. The ion exchange capacity of a sorbed metal ion was found to be 424,146 and 269 mg/g dry resin for lead, copper, and cadmium, respectively.

Dowex 50WX8 hydrogen was used for the evaluation of lead, copper, and cadmium removal from Iranian industrial wastewater by Moosavirad et al., [37]. Industrial effluent for six factories and one coal mine were studied. The effluent composition consisted of (0.061-0.21) ppm Cd^{2+}, (0.175-0.75) ppm Pb^{2+}, and (0.053-0.243) ppm Cu^{2+}. Sorbent capacities were 45, 50 and 60 mg/g for Cu^{2+}, Cd^{2+} and Pb^{2+} respectively. The removal rates (%) for all metal ions from all the factories were 97-100% under the best-operating conditions of pH 5, flow rate 4 of mL/min, and 2g of adsorbent.

Removal of Pb^{2+} from aqueous media using 732-CR resin with sulfonic acid group in Na^+ form was studied by Guo et al., [38], and Qian et al., [39]. The highest exchange capacity of 732-CR for lead was 484.0 mg g^{-1} at 35°C. The results confirmed that 732 resin was great for Pb^{2+} uptake from water systems.

Zewail and Yousef [40] conducted study for the removal of Pb^{2+} ions from water. In the experiments, they applied batch conical air spouted vessel in the presence of Amberjet 1200 in Na^+ form. The results indicated that the resin removal efficiency was 99% for lead. However, the uptake capacity was slightly affected by an increase in the initial metal concentrations (800-1300 ppm). The results revealed that Amberjet 1200 had high adsorption for Pb^{2+} ions.

Bożęcka et al. [41] examined the characteristics of C 160 bearing sulfonic acid group resin for the removal of lead, cadmium, and copper ions from nitrate solutions. Experiments were employed at 0.5g of adsorbent, heavy metal concentrations range of (6.25-109.39) mg/L, with constant pH value and at an ionic strength of 0.02 mol/L. the results confirmed the ability of the resin to remove lead ions with purification range (92-99%). The resin sorption capacities were 468.42, 112.17, and 31.76 mg/g for Cu^{2+}, Pb^{2+} and Cd^{2+}, respectively. The study reported that C 160 resin was very effective for Pb^{2+}ions.

Summary of commercial strong acid cation exchange resins used for removal and separation of lead, copper and cadmium in the literature is presented in Table 2.3.

Table 2.3: Summary of strong acid cation exchange resins literature.

Reference	Adsorbent	Function group	Metal ions removal	Technique	Sorbent capacities mg/g	Isotherm	Kinetics	Reaction
Demirbas et al. (2005)[27]	Amberlite IR-120	Sulfonic acid	Cu^{2+}, Cd^2,Pb^{2+}	AAS	(50;201;19.6)	Freundlich	N/A	N/A
Pehlivan et al. (2006)[37]	Dowex 50W	Sulfonic acid	Cu^{2+}, Cd^2,Pb^{2+}	AAS	(146;269; 424)	Langmuir	first-order rate kinetics	endothermic
Kocaoba et al. (2007)[28]	Amberlite IR 120 and natural zeolite (dolomite)	Sulfonic acid	Pb^{2+}, Cd^{2+}	XRF	(2.4;0.58) (44.9;3.2)	Freundlich and Langmuir	N/A	spontaneous and endothermic
Carmona et al. (2008)[30]	Amberlite IR-120 H form	Sulfonic acid	Pb^{2+}	ICP-AES	(576.2)	N/A	N/A	spontaneous and endothermic
Abo-Farha et al. (2009)[32]	Purolite C100	Sulfonic acid	Pb^{2+}	AAS	(10.43)	D–R& Langmuir	N/A	N/A
Guo et al. (2013)[39]	732-CR Na form	Sulfonic acid	Pb^{2+}	AAS	(396.8)	Langmuir	pseudo-first order	spontaneous and endothermic
Tabatabaei et al. (2013)[29]	Amberlite (IR-120) and natural Zeolite	Sulfonic acid	Pb^{2+}	AAS	(62;35)	N/A	N/A	N/A
Moosavirad et al. (2015)[38]	Dowex 50WX8	Sulfonic acid	Cu^{2+}, Cd^2,Pb^{2+}	FAAS	(45; 50; 60)	Langmuir	N/A	N/A
Zewail et al. (2015) [41]	Amberjet 1200 Na form	Sulfonic acid	Pb^{2+}	AAS	(61)	N/A	pseudo second order	N/A
Bożęcka et al. (2016) [42]	(C 160)	Sulfonic acid	Pb^{2+}, Cd^2, Cu^{2+}	UV-VIS spectroscopy	(112; 31; 468)	Langmuir	N/A	N/A
Lia Qian et al. (2016) [40]	732 cation-exchange	Sulfonic acid	Pb^{2+}	EDS	(484)	Langmuir	Nernst-Planck	spontaneous and exothermic

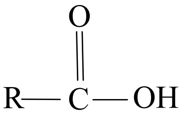
2.3.1.2 Weak Acid Cation Exchange Resins

Resins with carboxyl function group (COOH) are representative weak acid cation exchange resins, as shown in Figure 2.2. Their behaviour is similar to weak organic acids which are weakly dissociated. The dissociation degree of these types of resins are significantly impacted by the pH of the solution. Thus, resin capacity considers the solution pH dependent. Usually weak acid resins have an optimum capacity below pH 6.0[25].The carboxyl cation adsorbents are usually convenient for the uptake of cations from basic solutions.

The working mechanism of weak acid cation exchange resins have been presented by Ghinwa M. Naja and Bohumil Volesky [26] with the following general reaction:

$$RCOOH \rightleftharpoons RCO_2^- + H^+ \tag{2.2}$$

$$RCOOH + HCO_2^- + Na^+ \rightleftharpoons RCO_2^- Na^+ + H_2O + CO_2 \tag{2.3}$$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Figure 2.2: Weak acid function group.

Commercial weak acid cation exchangers had fewer studies in comparison to strong acid cation exchangers in the removal of heavy metal ions from water.

Sublet et al., [42] designed a new water filter for removal of lead <10 µg/L concertation from drinking water. Weak acid cation exchange resin (IMAC HP333) and ten other resins have been examined. Results showed that the resin had low adsorption capacity for Pb^{2+} at pH 6.5.

The efficiency of Amberlite IRC-50/IRC-86 resins for the uptake of lead, copper and cadmium from CO_2- H_2O solution in a fixed bed column was assessed by Silva and Brunner [43]. The experimental results showed that the adsorption efficiency of IRC-86 resin was higher than that of IRC-50 resin for the removal of selected metals ions. Temperature had insignificant impact on adsorption process efficiency but had strong influence on desorption process performance. Metal concentrations had a remarkable effect on sorption of metal ions.

The performance of Lewatit CNP 80 resin for the removal of small amounts of lead, copper, and cadmium from aqueous media was investigated by Pehlivan and Altun [44]. The obtained results were compared with other weakly acidic resins and chelating resin Lewatit TP 207. A constant volume of selected metals solutions with different amounts of adsorbent was taken for exchange equilibrium analysis. Lewatit CNP80 achieved the highest extraction of 98%, 99% and 95% for Cu^{2+}, Cd^{2+} and Pb^{2+}, respectively achieved at pH range 7-9. Adsorption quantities were 424, 146 and 269 mg/g dry resin for Pb(II), Cu(II) and Cd(II) respectively. The results indicated that Lewatit CNP 80 resin was more effective than Lewatit TP 207 resin for the uptake of the metals.

In another study Pb^{2+} removal from a battery manufacturing effluent using Lewatit CNP80 resin was examined by Vergili et al., [2]. The results indicated that the adsorption efficiency was 83.3% for lead at the best operating condition of 287 K, resin dose of 0.1 g, and contact time of 6 hours. Column experiments confirmed that regeneration process could be developed for this type of resin.

Purolite C-104 resin (PS-DVB (gel) and Lewatit CNP-80 resin (PA-DVB (macroporous) for removal of single solutions of cadmium and lead from aqueous systems in the presence of acid

(GA) as a complexing agent were investigated by Jachuła et al., [45]. Experimental sorption capacities of Purolite C-104 were 40.18 mg/g for Cd(II), and 94 mg/g for Pb(II), while sorption capacities of Lewatit CNP-80 were 16.02 mg/g for Cd(II) and 70.81mg/g for Pb(II).

Xiong and Yao [46] studied the adsorption characteristics of 110-H resin for Pb^{2+} removal in acid and alkaline system. The best operational condition for the adsorption process was obtained at pH 6.49. The adsorption capacity was 485 mgg^{-1} resin at 25°C. The lead was eluted by 0.025 mol/L of hydrochloric acid.

Table 2.4: Summary of weak acid cation exchange resins literature.

Reference	**Adsorbent**	**Function group**	**Metal ions removal**	**Technique**	**Sorbent Capacities mg/g**	**Isotherm**	**Kinetics**	**Reaction**
Sublet et al. (2003)[42]	IMAC HP333	carboxylic acid	Pb^{2+}	ICP-MS	(9)	N/A	N/A	N/A
Pehlivan et al. (2007) [44]	Lewatit CNP80	carboxylic acid	Pb^{2+},Cu^{2+}, Cd^{2+}	AAS	(424;146; 269)	Langmuir	First-order	N/A
Xiong and Yao (2008) [46]	(110-H)	carboxylic acid	Pb^{2+}	Spectro photometer	(485)	Langmuir	N/A	endothermic-spontaneous
Jachuła (2010)[33]	Purolite C-104/Lewatit CNP-80	carboxylic acid	Cd^{2+}, Pb^{2}	AAS	(34.05;12.04) (89.95;68.21)	Freundlich and Langmuir	pseudo second-order	N/A
Vergili et al. (2017)[2]	Lewatit CNP80	carboxylic acid	Pb^{2+}	AAS	(1.877)	N/A	pseudo second-order	Endothermic

2.4.2 Anion exchange resins

2.4.2.1 Strong base anion exchangers

These types of anion exchangers are produced by the chloromethylaton of styrene-divinylbenzene copolymers followed by conversion with amines. The produced exchangers are characterised with extreme stability and have a high exchange capacity. These exchangers have the ability to exchange negatively charged metal oxide groups, silicate and carbonate. They can be converted from their chloride form to their OH^- form by introducing NaOH. Type I exchangers are obtained by trimethylamine conversion, and Type II are produced by dimethylaminoethanol [13].

The typical reaction for strong base resins was introduced by Ghinwa M. Naja and Bohumil Volesky [26] as follow:

$$RNH\text{–}OH + NaCl \rightleftharpoons RNH\text{–}Cl + NaOH \tag{2.4}$$

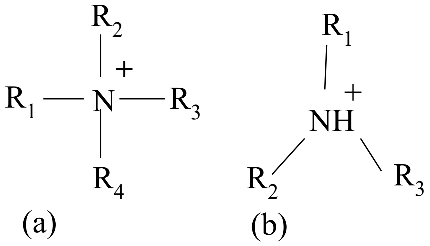


Figure 2.3: (a) Quaternary amine and (b) trimethyl ammonium functional groups.

Strong base anion exchange commercial resins have been investigated in the adsorption of lead, copper and cadmium from aqueous media by some researchers.

Diniz et al., [47] investigated MSA-1 and AG1-X8 resins (strong bases) for the removal of copper, and lead ions from a manganese chloride solution for a battery factory in Brazil. The results showed that for Cu^{2+} at 4 hours of contact time, and at initial concentration of 100 ppm, the final Cu^{2+} concentration of 100 ppm and 90 ppm was obtained for MSA-1 and AG1-XP, respectively. While for Pb^{2+} at same contact time, initial concentration 40 ppm, the final Pb^{2+} concentration was 37 ppm and 27.5 ppm for MSA-1 and AG1-XP, respectively. The study confirmed that both resins were very weak for removal of selected metals ions, which is understandable as the dissociated resin groups and the metal ions both have positive charges. Only cation not anion exchange resins should be used.

Juang et al., [48] examined Amberlite IRA-400 resin with Cl^- form for the adsorption of Cu(II)–EDTA complexed anions with and without formaldehyde. The experiments were run at ranges of solution pH 1- 6, temperature 15-35°C, and concentration 1.0 - 6.0 % and 0 - 6 vol % for Cu(II) and HCHO, respectively. The optimum results obtained at solution pH of 6. HCHO concentration of vol 3%, and 35°C.

The sorption performance of Amberlite IRA 458 resin, and Amberlite IRA 958 resin for Cu^{2+}, Pb^{2+} and Cd^{2+} ions from industrial effluents in the presence of complexing agents (EDTA, NTA, HEDTA, DTPA, and IDA) was studied by Kołodyńska & Hubicki [49]. Results indicated that the uptake of selected heavy metals in the existence of EDTA, NTA and IDA were significantly dependent on contact time and pH values. Both resins can be used for the uptake of heavy metal ions with complexing agents from aqueous systems, at pH range 4 - 8. The affinity of both resins for the metal ions are as follows: Cu(II) >Pb(II) > Cd(II).

Uptake of copper, lead, and cadmium from aqueous solutions was studied by Kołodyńska [50] in the presence of the chelating agent N, N-bis (carboxymethyl) glutamic acid using Lewatit Mono Plus MP 500 and Amberlite IRA 958 resins. Batch tests were employed in the existence of Ca^{2+}, Mg^{2+}, Cl^-, $SO4^{2-}$, and NO_3^- ions. Results indicated that a pH of 9.0 was the optimum conditions for adsorption process. The highest sorption capacity obtained for Pb^{2+}on Amberlite IRA 958 was 99.80 mgg^{-1}, while for Cu^{2+} complexes was 81.62 mg g^{-1} on Lewatit MonoPlus MP 500. Column studies revealed that 99% of sorption was achieved for Cu^{2+}- GLDA complexes by using 1M/L HCl as a regeneration agent.

Amberlite IRA 402 resin with a trimethyl ammonium functional group and Amberlite IRA458 resin with quaternary ammonium functional group were examined by Kołodyńska [51] for removal of Cu^{2+} and Pb^{2+} from wastewater in the existence of chelating agent N,N-bis (carboxymethyl) glutamic acid (GLDA) and with interfering ions (Ca^{2+}, Mg^{2+}, Cl^{-}, $SO4^{2-}$, and NO_3^{-}). Adsorption quantities in the presence of GLDA at concentration 0.001 M/L for Cu^{2+} and Pb^{2+} on IRA 402 were 5.79 and 19.32 mg/g respectively, while on IRA 458 were 5.68 and 19.12 mg/g, respectively.

Kołodyńska [52] conducted a comparative study between four strong base anions resins (Amberjet 4200, Amberjet 4400, Amberjet 4600, and Purolite A 520E) to analyze sorption efficiency for the removal of Cu(II),Pb(II) and Cd(II) ions with ethylenediamine-N,N′-disuccinic acid (EDDS) in the M(II):EDDS=1:1 system. The highest sorption capacity of these anion exchangers was for Cu^{2+}, with adsorption equilibrium attained at 30-60 min. Results revealed that the type of anion exchanger influenced the sorption process. The maximum adsorption capacities for Pb^{2+} and Cd^{2+} ions obtained by using Amberjet 4200, while for Cu^{2+} achieved by using Purolite A 520E. The best desorption was preformed by using 1 M HCl solution.

A comparative study between four strong basic anion resins, i.e., Amberlite IRA 402, Lewatit MonoPlus MP 500, Amberlite IRA 458, and Amberlite IRA 958 for the removal of Pb^{2+}, Cu^{2+} and Cd^{2+} from aqueous solutions in the presence of chelating agent ethylenediamine-N,N′-disuccinic acid (EDDS) was studied by Kołodyńska [53]. Results indicated that the sorption capacity for the selected adsorbents were dependent on initial solution pH, temperature, and the concentration of complexes. Sorption equilibrium was achieved at 20 - 30 min. Amberlite 402 had the best sorption capacities among the resins. The highest sorption capacities for this resin were 104.2, 119.5, and 134.9 mg/g for Cu^{2+}, Cd^{2+} and Pb^{2+}, respectively.

Comparative study between three strong basic anion exchangers Amberjet 4200, Amberjet 4600, and Purolite A 520E, for the removal of Pb^{+2}and Cu^{+2} ions in the existence of methylglycinediacetic acid (MGDA) as a complexing agent conducted by Jachuła et al., [54]. The sorption efficiency of the three resins were influenced by the concentrations of the metal ions. Maximum equilibrium capacities (q_0) for the sorption of Pb(II) complexes were: 66.23, 45.45 and 56.6 mg/g on Amberjet 4200, Amberjet 4600, and Purolite A 520E.

Table 2.5: Summary of strong base anion exchange resins literature.

reference	Adsorbent	Function group	Metal ions removal	Technique	Sorbent capacities mg/g	Isotherm	Kinetics	Reaction
Kołodynska and Hubicka (2009)[49]	Amberlite IRA458, Amberlite IRA 958	N+R3/ Quaternary Ammonium	Cu^{2+}, Pb^{2+}, Cd^{2+}	AAS	(6.1;20.5;11.2) (6.6;20.7;11.2)	N/A	pseudo second-order	N/A
Kołodyńska (2010) [50]	Lewatit Mono Plus MP 500, Amberlite IRA958, Diaion CR-20	Quaternary Amine	Cu$^{2+,}$ Cd^{2+} , Pb^{2+}	AAS	(81.6;44.2; n/s) (39.2; n/s;99.80) (12.3; n/s;11.9)	Dubinin–Radushkevich	pseudo second-order	endothermic
Kołodyńska (2011) [51]	Amberlite IRA 402, Amberlite IRA 458	Quaternary Ammonium/ N+R3	Cu^{2+}, Pb^{2+}	AAS	(5.79;19.32) (5.68;19.12)	Langmuir	Ho ,and McKay	endothermic and spontaneous
Kołodyńska (2011) [52]	Amberlite IRA 402, LewatitMonoPlus MP 500, Amberlite IRA 458, Amberlite IRA 958	Trimethyl Ammonium/ Quaternary Amine/N+R3/ Quaternary Amine	Cu^{2+} ,Cd^{2+} , Pb^{2+}	AAS	(104.1;119.5;135) (77.8;116.5;120.2) (89.2;106.3;106.3) (64.9;81.3;86.2)	Langmuir	pseudo second-order model	endothermic and spontaneous.
Jachuła et al.(2012) [54]	Amberjet 4200, Amberjet 4600, Purolite A 520E	Quaternary Ammonium	Cu^{2+}, Pb^{2+}	AAS	(18.37;47.71) (20.17;41.06) (16.21;45.31)	Langmuir	pseudo second-order	endothermic and spontaneous

2.4.2.2. Weak base anion exchangers

Weak base anion exchangers involve resins with functional groups of $–N^+H_2$= NH, and C=N. Styrene-divinylbenzene polymers produced by the chlormethylation reaction and then followed with amination which leads to the weak basic anion exchanger. These types of resins have low basicity, thus only anions of strong acids, such as HCl or H_2SO_4, can be exchanged effectively; while anions of weaker acids, such as SiO_3^- or HCO_3^-, are not sufficiently exchanged. These anion exchange resins can be converted into the OH^- form by using base materials such as Na_2CO_3 or NH_4OH. [13]

This class of anion adsorbents has been studied by Srikanth et al. [25] and they follow this reaction:

$$R–NH_2 + HCl \rightleftharpoons R–NH_3Cl \qquad (2.5)$$

The efficiencies commercial weak base anion exchange resins have been examined in the removal of lead, copper, and cadmium from aqueous systems in small scale studies.

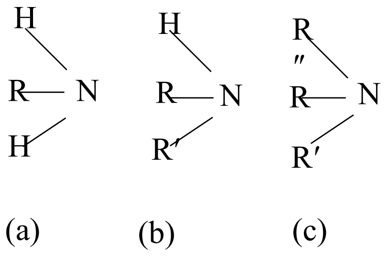
Kołodyńska and Hubicka [55] investigated the sorption performance of Amberlite IRA 67 resin for Cu^{2+}, Pb^{2+} and Cd^{2+} from industrial effluent in the presence of complexing agents (EDTA , NTA, HEDTA, DTPA, and IDA). Results indicated that uptake of selected heavy metals in the existence of EDTA, NTA and IDA was significantly dependent on contact time and pH values. Adsorption quantities at pH 2 to 6 were 6.15, 20.20 and 11.04 mg/g for Cu(II), Pb(II) and Cd(II), respectively.

Efficiency of the Lewatit FO 36 resin bearing a FeO (OH) functional group for Pb^{2+} removal from aqueous media was evaluated by Ahmadi et al., [56].The maximum adsorption capacity for

Pb^{2+} by the adsorbent was 62.5 mmol/g at optimum experimental conditions of pH 7, resin dosage 0.04 g/L and contact time 6 minutes.

Purolite A830 weak base resin applied for separation of Cu^{2+}, Cd^{2+} and Pb^{2+} from wastewater in the presence of methylglycinediacetic acid (MGDA) by Jachula and Hubicki [57]. Results showed that resin sorption efficiency for Cd^{2+} and Pb^{2+} was influenced by pH at the range of 6 -11. The Maximum sorption capacities with MGDA were 23.8, 43.29, and 24.15 mg/g for Cu(II), Cd(II), and Pb(II), respectively.

Kołodynska et al., [58] have conducted a comparative study between Lewatit FO 36 and Purolite Arsen X^{np} for the removal of Cu^{2+} , Cd^{2+} and Pb^{2+} ions from aqueous solutions with and without the existence of a complexing agent S,S-(ethylenediamine N, No^{-}disuccinic) acid (S, S^{-} EDDS) and the accompanying Cl^{-}, NO$_3^{-}$ and SO4^{2-} ions. Results showed that the sorption capacities of both adsorbents were dependent on metal ion concentrations in the solution. At the existence of accompanying ions, Purolite Arsen X^{np} had a higher sorption capacity for Cu^{2+} and Cd^{2+}ions than Lewatit FO36, while for Pb^{2+} Lewatit FO36 had a higher sorption capacity.



(a) (b) (c)

Figure 2.4 :(a) Primary amine. (b) Secondary amine and. (c) Tertiary amine functional groups.

Table 2.6: Summary of weak base anion exchange resins literature.

Reference	Adsorbent	Function group	Metal ions removal	Technique	Sorbent capacities mg/g	Isotherm	Kinetics	Reaction
Jachula and Hubicki (2013) [57]	Purolite A830	Complex Amine	Cu^{2+}, Cd^{2+}, Pb^{2}	AAS	(33.6;84.5 ;28.0)	Langmuir	Pseudo second order	N/A
Kołodynska and Hubicka (2009)[55]	Amberlite IRA 67	tertiary amine	Cu^{2+}, Pb^{2}, Cd^{2+}	AAS	(6.1;20.2; 11.0)	N/A	Pseudo second order	N/A
Ahmadi et al. (2011)[56]	Lewatit FO 36	FeO (OH)	Pb	FAAS	(12950)	Freundlich	Pseudo second order	N/A
Kołodynska et al. (2015) [58]	Lewatit FO 36	FeO (OH)	Cu^{2+}, Cd^{2+}, Pb^{2}	AAS	(21.7; 50;139)	Freundlich and Langmuir	Pseudo second order	N/A

2.5.3 Selective chelating resins

Chelating resins are a group of materials that have complexing or chelating groups on their surface [59]. These function groups own properties of specific reagents and their specificity depend on the chemical structures of the resin itself. Chelating resins have different types of chelating groups such as Amidoxime, Amino phosphonate, Iminodiacetate, Diphosphonate, Bis(2-picolyl) amine, 2-picolyl-2-hydroxypropyl amine, and oligoamine.

Garg et al., [59] outlined the advantages of using these types of resins over conventional methods in the extraction of metal ions. These advantages, include: (i) High possibility of selection and determination of metal ions when a chelating resin has a ligand possessing high selectivity to the targeted metal ion. (ii) An easy phase separation method. (iii) An economical method, because only a small amount of ligand and extraction solvent are used. (iv)Determination of trace metal ions at very low concentrations (ppb) can be obtained due to enrichment of targeted ions in the solid phase. (v) Visible estimations of metal ion concentrations can be achieved from the solid phase colour intensity. (vi). The technique can be considered ecofriendly due to restriction of the usage of carcinogenic organic solvents. Most resins with different chelating ligands are synthesized in the laboratory and few are commercially available [59].

2.5.3.1 Commercial chelating resins

Commercial chelating resins have been studied by many academics and professionals for their ability to remove lead, copper, and cadmium ions from water media. This class of resins include different functional groups in their structures, as shown in Figure 2.5.

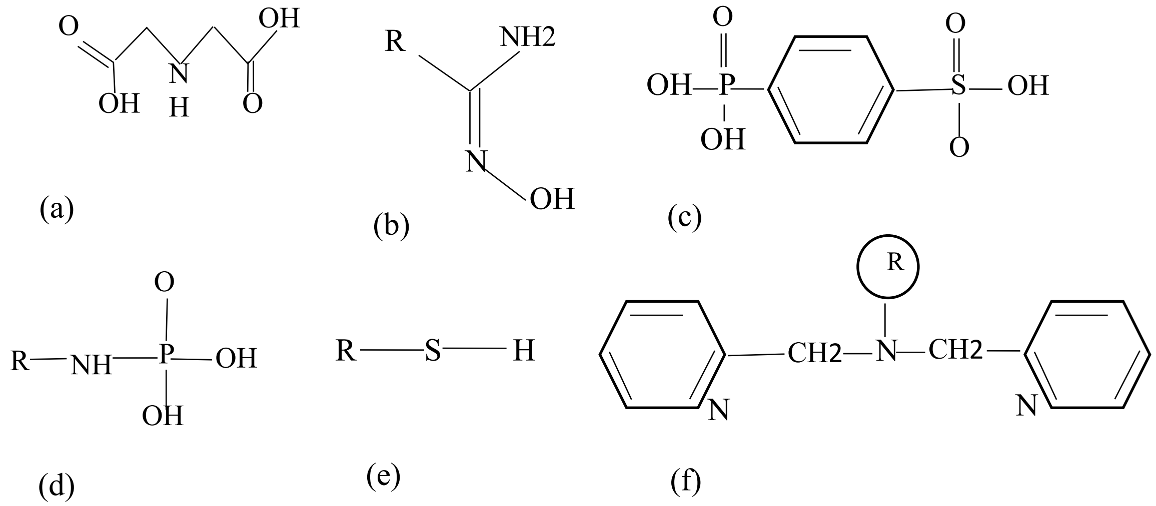


Figure 2.5: Chelating resin’s functional groups (a) Iminodiacetic, (b) Amidoxime, (c) sulfonic/phosphonic, (d) Aminophosphonic, (e) Thiol, and (f) Bis-picolylamine.

Removal of Pb^{2+}, Cu^{2+}, and Cd^{2+} from drinking water (rich in calcium and magnesium ions) using Lewatit TP-207 resin with an iminodiacetic acid functional group was examined by Korngold et al., [60]. At the bed volume of 500 mL/hr, the inlet Cu(II), Pb(II) and Cd(II) concentrations were 1.241, 0.50, 3.53 ppm, and the obtained outlet concentrations were 0.046, 0.012, 0.000 ppm for Cu(II), Pb(II) and Cd(II), respectively. The resin was regenerated with 3 M of hydrogen chloride or nitric acid. Experimental results proved that the recycled resin removed heavy metals when their concentrations in the water solution were below 6 ppm.

Diniz et al. [61] conducted a comparative study for commercial resins Dowex (M-4195) with a bis-picolylamine function group, and Amberlite® IRC718 with an iminodiacetic acid functional group for removal of copper and lead ions from acidic chloride solutions. After a batch contact time of 4 hours for initial concentration of 100 ppm for Cu(II), the final concentration obtained was 2.5 and 90 ppm for M-4195 and IRC-718 adsorption, respectively. For an initial concentration 40 ppm for Pb(II), the final concentration was 35, and 40 ppm for M-4195 and IRC-718, respectively. Results revealed that a bis-picolylamine function group resin was more effective for Cu(II) removal.

A comparative study to investigate the performance of Duolite GT-73 resin with a thiol functional group and Amberlite IRC-748 resin with an iminodiacetic function group was performed by Vilensky et al., [62] for the removal of Cd^{2+}, Cu^{2+}, and Pb^{2+} ions from contaminated groundwater samples in the existence of $CaCl_2$ and clay. The results showed that the adsorbents reduced the concentrations of selected metals significantly. The initial concentrations of metals in the column feed solutions were 0.50 ppm when using Duolite GT-73 at pH 7.13 and were 1.0 ppm while using Amberlite IRC-748 at pH 6.50. The obtained column final concentrations of the metals were 0.005 ppm and 0.003ppm for Cd(II) using Duolite GT-73 and Amberlite IRC-748 respectively, while the concentrations of Cu(II) and Pb(II) were below the detection limits of the ICP-AES.

Yebra et al., [63] studied the adsorption and elution of Pb^{2+} using Amberlite XAD-4 impregnated and 1-(2-pyridylazo) - 2-naphthol as a complexing agent from sea water samples in Spain. Sorption capacity of the resin was 0.96 µmol Pb(II)/g dry resin. The results showed that flowrate and the eluent volume were important factors.

The effect of pH on the adsorption of Cu^{2+} and Pb^{2+} from concentrated chloride solutions using chelating resin Dowex (M-4195) was investigated by Diniz et al., [64]. The experimental results confirmed that at Cl^- concentrations of 3.6 M, the adsorbent had a high affinity and adsorption capacity for Cu^{2+} ions even at low pH values, i.e., the adsorption rate at low pH values; the adsorption was found independent on the resin protonation degree. The study revealed that there was an indirect relation between Cl^- concentration and resin theoretical adsorption.

Removal of Cu^{2+}, Pb^{2+} and Cd^{2+} from seawater and wastewater samples after preconcentration using Amberlite XAD-16 resin with a chelating agent hexamethyleneammo nium-hexamethy lenedithio carbamate (HMA-HMDTC), and an NH_3/ NH_4Cl buffer solution was examined by Tokalioglu et al., [65]. Recovery percentages obtained for all metals were more than 95% at optimum experimental conditions.

Weak base chelating macroporous resin Dowex M-4195 with a Bis-Picolylamine functional group for removal of Cu^{2+} and Pb^{2+} ions from $MnCl_2$ leach solutions from a battery factory in Brazil was examined by Diniz et al., [66]. The effluent solution composition consists of 85mg/L of Cu(II) and 40 mg/L of Pb(II). Column experiments were used for eluting Cu^{2+} and Pb^{2+} ions with 4M of NH_4OH and 1M of H_2SO_4, respectively. The removal efficiency for copper was 74.7% and was 7.2% for lead. The study showed that the eluents used were not able to remove both metal ions completely, hence using complexing agent was recommended.

Removal and recovery of lead ions from binary mixtures (Fe^{3+}, Ca^{2+}, Mg^{2+}, and Ni^{2+}) of wastewater samples in India, using weak acid chelating resin Amberlite IRC 718 carrying an iminodiacetate functional group was investigated by Agrawal and Sahu [67]. The experimental results revealed a high difference of distribution coefficient rates, which caused metal ion separation from the binary mixtures. The adsorption capacity of the resin was 26, 46, 47, 51 and 409 mg/g for Mg(II), Ca(II), Fe(III), Ni(II), and Pb(II) respectively. Column experiments confirmed that metal recoveries were in the range of 98-99.6% for all metals.

Separation of Pb^{2+} ions from environmental samples using Amberlite XAD-1180/Pyrocatechol violet (PV) was studied by Soylak et al., [68]. The results showed that the recoveries for the spiked analysts were higher than 95% at pH range of 8-9 by using 1M of HNO_3 and 2M of HCl. The study reported that limit of detection (LOD) for lead was 0.37 μgl^{-1}.

Jachuła et al., [45] have conducted a comparative study between chelating ion exchangers with three different function groups chelating. i.e., Iminodiacetic (Purolite S-930 and Wofatit-20), Aminophosphonic (Purolite S-940) and Polyamine (Diaion CR-20) for the removal of Cd^{2+} and Pb^{2+} from aqueous systems by introducing glycolic acid (GA) as a complexing agent. The sorption capacities for the Cd (II)–GA (1:2) system were 103.6, 34.23, 133.2 and 32.33 mg/g for Purolite S-930, Wofatit MC-50, Purolite S-940, and Diaion CR-20, respectively. While the sorption capacities for the Pb (II)–GA (1:2) system were 243.39, 332.80, and 62.41mg/g for Purolite S-930, Purolite S-940, and Diaion CR-20, respectively.

Amberlite IRC748, resin with an iminodiacetic function group for the uptake of lead and cadmium ions from aqueous systems was investigated by Su et al., [33]. Batch tests were applied at different pH values, metal concentrations, and with the existence of Ca^{2+}, Na^{+}, K^{+}, and Mg^{2+} ions. The results confirmed that effective metal sorption onto Amberlite IRC 748 was obtained through the complex formation between metal ions and the iminodiacetic group. Highest Pb^{2+} removal was 55% at Pb^{2+}/ Ca^{2+} concentration ratios of 1-25 at pH 3 to 3.3, and maximum Cd^{2+} removal was 100% at Cd^{2+}/ Ca^{2+} concentration ratios of 1 and at pH 3.8 to 4.

Jachuła et al., [54] conducted a comparative study for commercial chelating resins involving Purolite S-920 with a Thiouronium functional group, Purolite S-930, and Lewatit TP-208 with an iminodiacetate function group for the uptake of Pb^{2+} ions from aqueous systems in the presence of methylglycinediacetic acid (MGDA) as a complexing agent**.** The maximum adsorption capacity for Purolite S-920 and PuroliteS-930 was obtained at a pH over 5, while for Lewatit TP-208 adsorption capacity increased at pH range of 1 to 5. Desorption studies revealed that 93.2% of Pb^{2+} was recovered by Lewatit TP-208.

Lead extraction from drinking water systems using a chelating resin Purolite S-930 with iminodiacetic acid functional groups was investigated by Merganpour et al., [69]. The results showed that the most effective factors on Pb^{2+} extraction from aqueous solutions was the resin column height, while pH had less effect. The resin had an ability to elute 95.42% of dissolved lead adsorbed at optimum operating conditions during 3 weeks of a service period. The mean uptake ratio for Pb(II) removal from water was 91.27% (up to 22 μg/L). Similar results were obtained by by Kor et al. [70].

2.5.3.2 New chelating resins

New chelating resins involve those which are prepared in laboratories by researchers in order to improve their properties for heavy metal removal and separation. New chelating resins have been prepared, investigated, and widely applied in the removal and separation of heavy metals.

Wang et al., [71] employed an iminodiacetic acid chelating group with a weak acid ion exchange resin in order to get a bi-function ion exchange resin for the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions by adsorptions. Experimental work revealed that the quantity of lead ions adsorbed was higher than that of cadmium ions adsorbed when the amount of the used chelating group becomes more than half of the equilibrium value. Adsorption efficiency of lead ions increased with increasing the chelating group range from 0.08 to 0.31 mmol/mmol COOH at a pH range of 2.5 to 0.5.

Vilensky et al., [62] investigated the performance of two solvent impregnated resins SIR1and SIR12, which were prepared from Amberlite IRA-96 for the removal of Cd^{2+}, Cu^{2+} and Pb^{2+} from polluted groundwater samples in the existence of $CaCl_2$ and clay. Column experiments were performed for desorption study. Initial concentrations of metals in feed solutions in column experiments on SR1 and SR2 were 1ppm for Cd^{2+}, Cu^{2+} and Pb^{2+}at pH 7.01, and the obtained outlet concentrations of metals in column experiments on SR1were 0.001, 0.003 and 0.001 ppm and on SR2 were 0.005, 0.003 and 0.001 ppm for Cd^{2+}, Cu^{2+} and Pb^{2+}, respectively.

Prabhakaran and Subramanian [72] developed a new bi-function chelating polymer using Amberlite XAD-16 modified from a (N-(3,4-dihydroxy) benzyl)-4-amino,3-hydroxynapthalene-1-sulphonic acid for the removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from different water samples. The results showed that the adsorption capacities of the developed chelating polymers were 85, 182, and 130 mg/g for Cd^{2+}, Pb^{2+} and Cu^{2+} respectively. Desorption studies revealed that the selected metals were eluted effectively from new synthesized polymers by using 2 M of HCl/HNO_3. The results demonstrated that the new resins still need more research on selectivity, accessibility and other parameters.

Prabhakaran and Subramanian [73] also developed a new chelating polymer using Amberlite XAD-16 functionalized with a (1,3-dimethyl-3-aminopropan-1-ol) for the removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions. The results showed that the best pH values for the sorption of Pb(II), Cu(II) and Cd(II) ions were 6.0 -7.0; 6.5 -7.5 and 7.5-8.5, respectively. The adsorption capacities of the resin were 47.66, 15.91, and 23.61 mg/g for Pb^{2+}, Cu^{2+} and Cd^{2+}, respectively. A preconcentration value of 300 was obtained for Cu(II) and Cd(II), while a value of 500 was obtained for Pb(II). The metal recovery was more than 98% for all selected metal ions with 4.0 M of HCl as eluting agent except for Cu(II) with 6.0 M of HCl.

Removal of lead ions from solutions containing base metals using a new polydithiocarbomate **c**helating resin supported on XAD-2 polystyrene for the separation process was studied by Roy et al., [74]. The results showed that this resin had 39 and 26 mg/g resin sorption capacity for Cu(II) and Pb(II), respectively at pH range 4 to 5. The metal recovery (%) in the presence of 10 ppm of Na^{+}, Mg^{2+} and Ca^{2+} ions was 98.6% and 98.5%, for Pb(II) and Cu(II), respectively. The study reported that the synthesized adsorbent has higher sorption efficiency than commercial chelating resins.

Amberlite IR- 400 resin with naphthol blue black for the separation of cadmium, copper, and lead ions in synthetic and pharmaceutical mixtures was developed by Nabi et al., [75]. The results revealed that the highest metal removal by naphthol blue–black was directly proportional to resin loading till 1.569×10^{-3} mol/0.4 g resin at pH 6. The removal was pH and temperature dependent. The highest distribution coefficients (Kd) for Cd(II) and Pb(II) were 1418 and 300, respectively using 0.1M trichloroacetic acid and the maximum Kd for Cu(II) was 420 using 0.1M acetic acid.

Uptake of Cu^{2+} and Pb^{2+} ions using polymeric diethylenetriamine adsorbent (P-DETA) from aqueous media was evaluated by Liu et al., [76]. Their results indicated that in the single system P-DETA had a slightly higher adsorption removal capacity for Pb^{2+} than that for Cu^{2+} ions), while in the binary system, the adsorbent had higher removal efficiency for Cu^{2+} ions than for Pb^{2+} ions due to the higher electronegativity that copper ions own. Their results showed that the metal adsorption is directly proportional to pH. The highest adsorptions were 1.16 and 1.32 mmol/g for Cu(II) and Pb(II), respectively obtained at pH of 5 and contact time of 60 minutes.

Separation of Pb^{2+}, Cu^{2+} and Cd^{2+} metal ions from aqueous solutions using new resin acrylonitrile (AN)–divinylbenzene (DVB)–methylacrylate (MA) developed from suspension polymerization in the existence of toluene as a diluent, and benzoylperoxide (BPO) as an initiator was studied by Nilchi et al., [77], The results showed that the sorption equilibrium was obtained within 40 minutes, and the resin had low affinity for Pb^{2+}, Cu^{2+} and Cd^{2+}. The recovery percentage at pH 5 was less than 45% for all metals. The study revealed that the metal ion adsorption was directly proportional to metal concentrations. The maximum adsorption capacity achieved at a metal concentration of 20 mmol/L was 2279, 381.2 and 337.2 mg/g resin for Pb(II), Cu(II), and Cd(II), respectively.

Performance of Amberlite IR-400 resin doped with titan yellow, a chelating agent for the separation of lead, copper, and cadmium from binary solution containing (Hg^{2+}; Sn^{4+}; Bi^{3+}) ions was studied by Khan et al., [78]. The results showed that the best sorption conditions were achieved at pH 6 and at 5 hours of contact time. Column experiments were carried out to study desorption processes using different eluents. Elution results showed that over 95% of Pb^{2+}, Cu^{2+} and Cd^{2+} ions was recovered from the binary mixtures. The research work demonstrated that the resin can be applied for toxic metal separation and for metal removal from an industrial effluent.

Parmanik et al., [79] examined removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions using a new chelating polymer containing (2-methoxy-1-imidazolylazobenze) functional group. An AAS method was applied for analyzing Cu^{2+} and Pb^{2+} ions at pH 3, while a radiotracer technique was used for the detection of Cd^{2+} ions employing 115 Cd^{2+} detectors as spike at pH 5. The limit of detection (LOD) corresponded to three standard deviation was 0.08 mg/L.

A new resin, TC4 (tetraester calyx 4 arene) for the removal of Pb(II) from aqueous solutions was prepared by Solangi et al.,[80] The resin was made by diazotization reaction of TC4 with Amberlite XAD-4 in the existence of $NaNO_2$ in acidic solution. The results indicated that, maximum sorption capacity 1018µmol/g was obtained at pH 6.5, temperature of 35°C and adsorption time of 160 minutes.

A novel chelating resin, D401 with a sulfonic functional group for the removal of lead from aqueous solutions was developed by Fei et al., [81] Their results indicated that the optimum experimental conditions were at a Pb^{2+} concentration range of 200 to 400 mg/L, pH 4 to 5, temperature 333K, and a resin dose 206 mg/g. Adsorption capacity ranges of the developed chelating resin for Pb^{2+} was 77% -100%.

Removal of Pb^{2+} ions from an aqueous phase using developed mesoporous silica (SBA-15), grafted with a thiol functional group was investigated by Thu et al., [82] Batch adsorption experiments were conducted on SBA-15 samples for Pb^{2+} with primary concentration of 200 ppm, temperature 30°C and pH range 2.5 to 4. Adsorption capacity for Pb^{2+} was 39.37mg/g. Regeneration of adsorbent can be done by using HCl.

Kamel et al., [83] examined the removal of Pb^{2+} ions from aqueous systems using a synthesized ion exchange resin of para-phenol containing ($-SO_3H^-$) and ($-COOH^-$) functional groups. The new exchanger was made by polycondensation of dioxaloyl para sulphanilamide and phenol while introducing 60% H_2SO_4 by weight of reactant in the presence of $C_2H_4O_2$ at temperature 60°C. The results confirmed that the new resin had ability to remove Pb^{2+} ions. Sorption capacity value for Pb^{2+} was 18.60 mg/g at initial Pb^{2+} concentration of 0.012 mol/L.

A comparative study between three PS-DVB copolymers (RM-l, RM-m, and RM-h) with different porosity for Pb^{2+} removal from aqueous systems was conducted by Souza et al. [84]. The new copolymers were synthesized using $PCl_3/AlCl_3$ in an aromatic electrophilic substitution reaction. The results showed that the resins were very effective at pH 6 and after ½ hour of contact time. Pb^{2+}removal percentages were in the range of 97-99 %. RM-1 resin had higher efficiency than the other two copolymers in removing Pb^{2+} ions from water systems.

Gurnule et al. [85] studied the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions in contaminated ground water in India using a new copolymer chelating resin, o-amino phenol and dithiooxamide with formaldehyde (o-APDF) for separation processes. The study confirmed that the distribution ratio of metals on resin increased by increasing the pH value. The selectivity of the copolymer for Cu^{2+} was the highest, while Cd^{2+} and Pb^{2+} ions have a lower distribution ratio at pH range 4 to 6 due to low stability constants. The results revealed that the rate of metal ion removal was dependent on the concentrations of the metal ions in the water solutions. The time required for the removal of various metal ions was metal nature dependent. It was observed that Cu^{2+} required 5 hours of time where Pb^{2+} and Cd^{2+} required 6 hours to reach equilibrium. Quantity of Cu^{2+} ions taken up by the developed copolymer increased with increasing concentrations of the NaCl, $NaNO_3$ and $NaClO_4$ electrolytes. While the uptake of Cd(II) and Pb(II) ions decreased with increasing electrolytes concentrations. In the existence of sulphate ions, the uptakes of all selected metals by the o-APDF copolymer were decreased by the increasing concentrations of the electrolyte, the researchers attributed this to stability constants.

A chelating copolymer resin (2,4-DHBEDF) which has phenolic and amino functional groups for the removal of Cu^{2+} and Pb^{2+} from different electrolytes was developed by Gurnule & Dhote [86]. The study revealed that the rate of metal ion uptake was time dependent, after 6 hours, the rate of uptake for Pb^{2+} was 85% and that for Cu^{2+} was 49.5%. The distribution ratio was found to be directly proportional to pH, the distribution ratio was 2874.1 for Pb^{2+} and 184.2 for Cu^{2+} at pH 6.5. The removal of Cu(II) and Pb(II) ions increased with the increasing of NO_3^-, Cl^- and ClO_4^- ion concentrations. They decreased with increasing SO_4^{2-} ion concentrations.

Dhore et al., [87] investigated the removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from different electrolytes (nitrate chloride, chlorate, and sulfate) using synthesized terpolymer resin, 4-ASAUF. The new adsorbent was produced by condensation of 4-aminosalicylicacid (4-ASA) and urea (U) with formaldehyde (F) in the presence of 2M HCl. The results showed that the rate of metal ion removal was a function of time following the order: Cu^{2+} (0:57) > Cd^{2+} (1:10) ≈ Pb^{2+} (1:19). The rates of metal ion removal at pH range of 4.5 - 6 and contact time 5 - 6 hours were 89, 93, and 95% for Cu^{2+}, Pb^{2+} and Cd^{2+}, respectively. Metal uptake increased with the increase in all electrolyte concentrations except with sulfate.

Kalaivani et al., [88] investigated the application of new modified poly (6-(ethoxybenzot hiazole acryl-amide) (PEBTA) for recovery of Cu(II) and Zn(II) from water system. The results showed that the maximum adsorption capacities were 273.5 mg/g for Cu(II) and 216.4 mg/g for Zn(II) at pH 6.

A new iminodiacetate chelating resin CPN-IDA was developed by El-bahy [89]. The chelating resin was made by reaction of poly (acrylonitrile-co-N, N'-methylenebisacrylamide) with etheylenediamine and sodium chloroacetate. The new synthesized resin was investigated for the removal of Cu(II), Cd(II) and Pb(II) ions from aqueous systems. The results showed that the resin adsorption capacity at 25°C were 154.42, 216.95 and 300.44mg/g for Cu^{2+}, Cd^{2+} and Pb^{2+}, respectively. 0.2M HNO_3 followed by 0.2M NaOH can be used for resin regeneration.

The adsorption characteristics of a new resin (ID301) for removing Cu^{2+}, Pb^{2+} and Cd^{2+} ions from aqueous solutions were investigated by An et al., [90]. The results showed that both pH, and temperature effected the adsorption capacity. The adsorption capacities of the new resin for Cu (II), Pb(II) and Cd(II) were 4.48, 2.99 and 2.26 mmol/g, respectively, obtained at 25°C and pH 5.

Kołodyńska et al., [91] studied the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous systems using new carbonaceous adsorbents W1 KPS, W2 KPS, D1 CC3 and D2 CC3. The new adsorbents were made from consumed resins. The results showed that W1 KPS had a higher affinity for heavy metal ions than W2 KPS. The sorption capacity was directly proportional to the initial concentrations of solution and contact time. Sorption capacities of D2 and CC3 were higher than that of D1 CC3. The highest adsorption was found at pH 5.0.

2.6 Conclusion

Resource industries in many countries around the world still impact the environment negatively due to heavy metals disposal to rivers, lakes, and other ecosystems. This work reviewed applications of adsorption processes including ion exchange using different types of resins to remove and separate toxic metals including copper, lead, and cadmium in various water systems.

As seen in the literature, studies have been conducted using resins with various functional groups for the removal of lead, copper, and cadmium from aqueous solutions. Most of the studies focus on certain resins, for example Amberlite IRA-120 and Dowex 50 with sulfonic acid functional group accounted for about 40%. However, these resins had a high affinity for most heavy metals.

In comparison with the resins bearing sulfonic acid functional group, the examined resins with carboxylic functional resins have shown relatively less affinity for the adsorption of the studied metals. Around 50% of the studies for lead, copper, and cadmium uptake were preformed using Lewatit® CNP 80 resin in this class.

The researches conducted using Amberlite IRA 402 and Amberlite IRA 958 resins for removal and separation of toxic metals represented 80% of the strong base anion exchangers category. The sorption capacity of these adsorbents reaches 120 mg/g as mentioned in the literature.

Weak basic anion exchangers have a good potential for the removal of heavy metals. This class of resins has low research attention similar to weak acid cation exchange resins.

Commercial chelating resins are characterized by various functional groups, iminodiacetic, bis-picolylamine, thiol, thiouronium, amidoxime, aminophosphonic, and polyamine. As seen in the literature, about 50% of the articles of this class addressed the application of iminodiacetic functional group resins.

The extractions of heavy metals using new adsorbents have attracted many researchers in the last twenty years, around 39% of the studied focused on the investigation of new high-efficiency adsorbents for heavy metal removal. The majority of the researches were performed to develop commercial resins by introducing or adding new functional groups. Most of these new resins have good selectivity for removal and separation of metal ions. On the other hand, these new adsorbents still need more work to be available commercially. Finally, finding more efficient adsorbents for removal and separation of lead, copper, cadmium, and other heavy metal ions from aqueous systems is so important in order to protect the environment from toxic metal pollution.

The knowledge gaps found in this review and as presented in the previous chapter were addressed through the following research achievements:

I. Determined an effective resin for the removal of Cd(II) ions from a single solution.

II. Found a highly efficient resin for the removal of Cu(II) ions from a single solution.

III. Found a resin with high performance for the removal of Pb(II) ions from a single solution.

IV. Determined an effective resin to separate Cu(II) and Pb(II) from a binary solution.

V. Studied the mechanism of Cd(II) ion adsorption onto resins using a molecular simulation method.

Table 2.7: Summary of commercial and new chelating ion exchange resins literature (desorption process).

Reference	**Adsorbent**	**Complexing Agent**	**Metal ions removal**	**Technique**	**Eluent**	**pH**	**PF(1)**	**DL µg/L (2)**	**RSD % (3)**
Tokalioglu et al., (2002)[65]	Amberlite XAD-16	(HMA-HMDTC)	Cu^{2+}, Pb^{2}, Cd^{2+}	FAAS	0.001-1M/L HNO_3	9	150,75	0.006-0.277	0.8-2.9%
Yebra et al. (2002)[63]	Amberlite XAD-4	1(2pyridylazo-2-naphthol)	Pb^{2}	AAS-FAAS	0.5M/L HCl	8	1248	0.005	4.0-3.1%
Prabhakaran and Subramanian (2003)[72]	Amberlite XAD-16	1,3-dimethyl-3-aminopropan-1-ol	Pb^{2}, Cu^{2+}, Cd^{2+}	FAAS	4M/L HCl	6-8.5	500-400-300	20-25-10	0.62-3.23
Prabhakaran and Subramanian (2003)[73]	XAD-16 (AXAD-16	(N-(3,4-dihydroxy)benzyl)-4amino,3-hydroxynapthalene-1-sulphonic	Cd^{2+}, Pb^{2}, Cu^{2+}	FAAS	2M/L HCl, HNO_3	6-7.5	234-300	2-6.5	2.10-2.21
Diniz et al., (2005)[66]	Dowex M-4195	Bis(2-pyridylmethyl	Cu^{2+} , Pb^{2}	AAS	1M/L H_2SO_4, 4M/L NH_4OH	1- 7	32.,10	0.1-.04	4.1
Soylak et al., (2006)[68]	Amberlite XAD-1180	Pyrocatechol violet	Pb^{2}, Cd^{2+}	FAAS	1M/L HNO_3	8-9	100	0.20-0.73	< 10
Parmanik et al., (2009)[79]	New chelating polymer	2-methoxy-1-imidazolylazo benze)	Cd^{2+}, Pb^{2}, Cu^{2+}	AAS	5-4M/L HCl	3- 5	0.1-2.4	80 for Pb	<7

Table 2.8: Summary of commercial & new chelating ion exchange resins literature (adsorption process).

Reference	Adsorbent	Function group	Metal ions removal	Technique	Sorbent capacities mg/g	Isotherm	Kinetics	Reaction
Nilchi et al., (2008)[77]	AN-DBV-MA	R-C(=NOH) NR^1R^2	Cu^{2+}, $Pb^{2,}$ Cd^{2+}	ICP	(381;2279; 337.2)	N/A	N/A	N/A
Liu et al., (2008)[76]	P-DETA	$R-NH_2$	Cu^{2+}, Pb^2	ICP	(73.7; 273.5)	Langmuir	N/A	N/A
Xiong & Yao, (2009)[46]	Polystyrene-triethylenetetramine resin (PS-TETA)	$-NH(CH_2CH_2NH)_2CH_2CH_2NH-$	Cd^{2+} , Pb^2	FAAS	(212.8; 147.1)	Langmuir	Thomas	N/A
Solangi et al., (2009)[80]	TC4 (tetraester calyx 4 arene)	$R- SO_3$ R-COO	Pb^2	AAS	(20.7)	Freundlich, Langmuir, and D–R	pseudo-first and second-order	exothermic and spontaneous
Thu et al., (2010)[82]	SBA-15	R-SH	Pb^2	AAS	(39.37)	Langmuir	N/A	N/A
Jachuła et al., (2010)[33]	Purolite S-930, Purolite S-940, Purolite S-950, Diaion CR-20, and Wofatit MC-50	$HN(CH_2CO_2H)_2$ $C_{12}H_20 N_5O_6 P_2 SC_{12} H_20 N5O_6 P_2 S$ $HN(CH_2CO_2H)_2$	Cd^{2+} , Pb^2	AAS	(103.6; 133.2; 32.3; 34.2) (243.3; 332.8; 62.41;n/a)	Langmuir Freundlich	pseudo-second-order	N/A
Kamel et al., (2011)[83]	Para-phenol	-COOH- & HSO_3H+	Pb^2	ICP-AES	(18.65)	Freundlich and D-R	pseudo-second-order	N/A
Jachuła et al.,(2012b) [54]	Purolite S-920, Purolite S-930 Lewatit TP-208	CH_5N_2S $HN(CH_2CO_2H)_2$ $HN(CH_2CO_2H)_2$	Pb^2	AAS	(53.01; 77.4; 58.2)	Langmuir, Freundlich Temkin and Dubinin-Raduskevih	pseudo-second-order	N/A
S.El-Bahy &Z. El-Bahy, (2016) [89]	CPN-IDA	$HN(CH_2CO_2H)_2$	Cu^{2+}, Cd^{2+} , Pb^2	AAS	(154.4;216.95;300.4)	Langmuir	pseudo-second-order	N/A
An et al., (2017)[90]	ID301	$HN(CH_2CO_2H)_2$	Cu^{2+}, Pb^2 Cd^{2+}	AAS	(284.69;619.53;254.05)	Langmuir	pseudo-second-order	spontaneous endothermic

References

[1] J.Jachuła, D. Kołodyńska, Z. Hubicki, ‘‘Methylglycinediacetic Acid as a New Complexing Agent for Removal of Heavy Metal Ions from Industrial Wastewater’’. *Solvent Extraction and Ion Exchange*, 2012,*30*, 181. *https://doi.org/10.1080/07366299.2011.581088*

[2] I.Vergili, Z. Gönder,Y. Kaya, G. Gürdağ, S. Çavuş, ‘‘Sorption of Pb(II) from battery industry wastewater using a weak acid cation exchange resin’’. Process *Safety and Environmental Protection, 2017,107, 498. http://dx.doi.org/10.1016/j.psep.2017.03.018*

[3] O. Okareh, A. Adeolu, ‘‘Removal of Lead Ion from Industrial Effluent Using Plantain (Musa Paradisiaca) Wastes’’. *British Journal of Applied Science and Technology, 2015, 8, 267. DOI: 10.9734/BJAST/2015/16989*

[4] World Health Organization. guidline for drinking-water quality (fourth edi). *World Health Organization.2017. https://www.who.int/publications/i/item/9789241549950*

[5] L.Gaetke, K. Chow, ‘‘Copper toxicity, oxidative stress, and antioxidant nutrients’’. *Toxicology,2003,189,147. https://doi. 10.1016/s0300-483x(03)00159-8*

[6] B.Ashish, K. Neeti, K.Himanshu, ‘‘Copper Toxicity: A Comprehensive Study’’. *Research Journal of Recent Sciences Res.J.Recent.Sci, 2013,2, 58. ISSN, 2277, p.2502.*

[7] M.Benavides, S.Gallego, M.Tomaro, ‘‘cadmium toxity in plants’’. *Braz.j.Plant Physiol, 2005,17, 21. https://doi.org/10.1590/S1677-04202005000100003*

[8] J.Godt, F.Scheidig, C. Grosse-Siestrup, V.Esche, P. Brandenburg, A. Reich, A. Groneberg, ‘‘The toxicity of cadmium and resulting hazards for human health’’. *Journal of Occupational*

Medicine and toxicology,2006,1,22. doi: 10.1186/1745-6673-1–22

[9] S.K. Gunatilake, ‘‘Methods of Removing Heavy Metals from Industrial Wastewater’’ Journal *of Multidisciplinary Engineering Science Studies (JMESS).2015, 1, 12–18, Corpus ID: 42117809.*

[10] M. Rosocka, ‘‘A review on methods of regeneration of spent pickling solutions from steel Processing’’. *Journal of Hazardous Materials, 2010, 177, 57– 69 https://doi.org/10.1016/j.jhazmat.2009.12.043*.

[11] I. Luqman, Ion Exchange Technology II Applications, Springer Science Business Media *B.V. 2012, DOI 10.1007/978-94-007-4026-6.*

[12] P.R.Haddad, Ion exchange| Overview, *Encyclopedia of Analytical Science (Second Edition) 2005, Pages 440–446. https://doi.org/10.1016/B0-12-369397-7/00283-1*.

[13] K.Dorfner, ion exchangers, properties and applications. *annarbor science and Toxicology*, *1972,1, 1. ISBN 10: 0250975017 / ISBN 13: 9780250975013*

[14] C.Zhao, R.Ge, Y. Zhen, Y.Wang, Z.Li, Y.Shi, X. Chen, ‘‘A hybrid process of coprecipitation-Induced crystallization-capacitive deionization-ion exchange process for heavy metals removal from hypersaline ternary precursor wastewater’’. *Chemical Engineering Journal 2019. 378, 122136. https://doi.org/10.1016/j.cej.2019.122136*

[15] J.Chu, J.Kang, S.Park, C.Lee, ‘‘Application of the anion-exchange resin as a complementary technique to remove residual cyanide complexes in industrial plating wastewater after conventional treatment’’. *Environmental Science and Pollution Research (2020) 27:41688–41701 https://doi.org/10.1007/s11356-020-10162-y.*

[16] V. Dev, K. Nair, G.Baburaj, K. Krishnan, ‘‘Pushing the boundaries of heavy metal adsorption: A commentary on strategies to improve adsorption efficiency and modulate process mechanisms’’. *Colloid and Interface Science Communications 2022, 49,100626. https://doi.org/10.1016/j.colcom.2022.100626*

[17] M. Ullah, R.Nazir, M. Khan, W.Khan, M. Shah, S. Afridi, A. Zada, ‘‘the effective removal of heavy metals from water by activated carbon adsorbents of Albizia lebbeck and Melia azedarach seed shells’’. *Soil and Water Research 2020, 15, 30–37. https://doi.org/10.17221/212/2018-SWR*.

[18] A.Hamidian, S.Esfandeh, Y.Zhang, M.Yang, ‘‘Simulation and optimization of nanomaterials application for heavy metal removal from aqueous solutions’’. *Inorganic and Nano-metal Chemistry 2019, Vol. 49, No. 7, 217–230. https://doi.org/10.1080/24701556.2019.1653321*.

[19] L.Costa, L.Ribeiro, G. Hidalgo, L.Féris, ‘‘Determination of optimal operating parameters for tetracycline removal by adsorption from synthetic and real aqueous solutions’’. *Journal of Environmental Science and Health, Part A 2020, Vol. 55, No. 14, 1615–1623. https://doi.org/10.1080/10934529.2020.1829887*

[20] A.Murray, B.Örmeci, ‘‘Use of polymeric sub-micron ion-exchange resins for removal of lead, copper, zinc, and nickel from natural waters’’, *Journal of Environmental Sciences 2019, 75, 247–254. https://doi.org/10.1016/j.jes.2018.03.035.*

[21] E. Sikora,V. Hajdu,G.Muránszky,K. Katona,I.Kocserha,T.Kanazawa,B. Fiser, B.Viskolcz, L.Vanyorek, ‘‘Application of ion-exchange resin beads to produce magnetic adsorbents’’. *Chemical Papers (2021) 75:1187–1195 https://doi.org/10.1007/s11696-020-01376-y*

[22] R.Nekouei, F.Pahlevani, M.Assefi, S.Maroufi, V. Sahajwalla, ‘‘Selective isolation of heavy metals from spent electronic waste solution by macroporous ion-exchange resins’’. *Journal of Hazardous Materials 2019, 371,389–396. https://doi.org/10.1016/j.jhazmat.2019.03.013*

[23] J.Bezzina, L.Ruder, R.Dawson, M.Ogden, ‘‘Ion exchange removal of Cu(II), Fe(II), Pb(II) and Zn(II) from acid extracted sewage sludge e Resin screening in weak acid media’’, *Water Research 2019,158, 257–267. https://doi.org/10.1016/j.watres.2019.04.042.*

[24] M.Rahman, M.Sarjadi, S.Guerin, S.Sarkar, Poly (amidoxime) Resins for Efficient and Eco-friendly Metal Extraction’’. *ACS Appl. Polym. Mater. 2022, 4, 2216−2232. https://doi.org/10.1021/acsapm.1c01716*

[25] V.Srikanth, A. Sunil, S. Rao, U. Uhumwangho, V. Ramana Murthy, (2010). ‘‘Ion-Exchange Resins as Controlled Drug Delivery Carriers’’. *Journal of Scientific Research, 2010,2,597. DOI: 10.3329/jsr.v2i3.4991*

[26] G.Naja and B.Volesky. ‘‘Treatment of metal-bearing effluents: removal and recovery’’. chapter 9 ,2009, *In Hand book on Heavy metals in the environment*, Wang, LK., Chen, J.P., Hung, Y.T. and Shammas, N.K., eds. *Taylor & Francis and CRC Press, Boca Raton, FL, pgs.247–291. E Book ISBN9781315117423*

[27] A.Demirbas, E.Pehlivan, F.Gode, T.Altun, G. Arslan, G. ‘‘Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin’’. *Journal of Colloid and Interface Science, 2005,282, 20–25. doi:10.1016/j.jcis.2004.08.147*

[28] S.Kocaoba, ‘‘Comparison of Amberlite IR 120 and dolomite’s performances for removal of heavy metals’’. *Journal of Hazardous Materials, 2007,147, 488–496*

doi:10.1016/j.jcis.2004.08.147

[29] H.Tabatabaei, M. Asemanrafat, M.Nousahdi, ‘‘Removal of Lead from aqueous phase using Amberlite and natural Zeolite’’, *E3S Web of Conferences 2013,13010, 3–6. https://doi.org/10.1051/e3sconf/20130113010*

[30] M.Carmona, J.Warchoł, A. Lucas, F.Rodriguez, ‘‘Ion-Exchange Equilibria of Pb^{2+}, Ni^{2+}, and Cr^{2+}Ions for H^+ on Amberlite IR-120 Resin’’. *Journal of Chemical &Engineering Data,2008,53, 1325–1331. https://doi.org/10.1021/je8000552*

[31] A.Badawy, A. El-Bayaa, Y. Abdel-Aal, E. Garamon, ‘‘Chromatographic separations and recovery of lead ions from a synthetic binary mixtures of some heavy metal using cation exchange resin’’. *Journal of Hazardous Materials, 2009,166, 1266–1271. doi:10.1016/j.jhazmat.2008.12.044*

[32] A.Abo-Farha, Y. Abdel-Aal, A. Ashour, E. Garamon, ‘‘Removal of some heavy metal cations by synthetic resin purolite C100’’. *Journal of Hazardous Materials, 2009,169, 190–194 https://doi.org/10.1016/j.jhazmat.2009.03.086*

[33] Q.Su, B. Pan, S.Wan, W. Zhang, L. Lv, ‘‘Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium, and zinc ions from water’’. J*ournal of Colloid and Interface Science, 2010,349,607–612 doi:10.1016/j.jcis.2010.05.052*

[34] A.G.EL-Said, ‘‘Colume Chromatographic Separation of Fe(III) at Trace Levels in Various Synthetic Binary Mixtures by Cation – Exchange Resin Impregnated with Neutral Red Dye’’. *New York Science Journal, 2011,4, 5–13. http://www.sciencepub.net/newyork.*

[35] M.Hamdzah, M.Nasef, T. Hadibarata, G.Olsson, H. Hassan, N. Rusli, ‘‘ optimization of

parameters affecting adsorption of Ni Zn and Pb on dowex 50 W resin using response surface methodology approach''. *Journal of Enviromental Science and Technology, 2013,6, 106–118. doi:10.3923/jest.2013.106.118*

[36] E.Pehlivan, T.Altun, T, ''The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin''. *Journal of Hazardous Materials, 2006,134, 149–156. doi:10.1016/j.jhazmat.2005.10.052*

[37] M.Moosavirad, R. Sarikhani, E. Shahsavani, Z. Mohammadi, ''Removal of some heavy metals from inorganic industrial wastewaters by ion exchange method''. *Journal of Water Chemistry and Technology, 2015,37, 191–199. DOI: 10.3103/S1063455X15040074*

[38] H.Guo, Y. Ren, X. Sun, Y. Xu, X. Li, T. Zhang, D.Liu, ''Removal of Pb^{2+} from aqueous solutions by a high-efficiency resin''. *Applied Surface Science, 2013,283, 660–667. http://dx.doi.org/10.1016/j.apsusc.2013.06.161*

[39] J.Qian, Z. Zeng, W. Xue, Q. Guo, ''Lead removal from aqueous solutions by 732 cation-exchange resin''. *Canadian Journal of Chemical Engineering, 2016,94, 142–150. DOI 10.1002/cjce.22363*

[40] T.Zewail, S. Yousef, N. S. ''Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed''. *Alexandria Engineering Journal, 2015,54, 83–90. http://dx.doi.org/10.1016/j.aej.2014.11.008*

[41] A.Bożęcka, M. Orlof-Naturalna, S.Sanak-Rydlewska, ''Removal of lead, cadmium and copper ions from aqueous solutions by using ion exchange resin C 160''. *Gospodarka Surowcami Mineralnymi, 2016,32, 129–140. DOI 10.1515/gospo-2016-0033*

[42] R.Sublet, O. Simonnot, A. Boireau, M. Sardin, M. ‘‘Selection of an adsorbent for lead removal from drinking water by a point-of-use treatment device’’. *Water Research, 2003,37, 4904–4912. doi:10.1016/j.watres.2003.08.010*

[43] L.Silva, G.Brunner, ‘‘Desorption of heavy metals from ion exchange resin with water and carbon dioxide’’. *Brazilian Jounaul of Chemical Engineering, 2006,23,213–218. https://doi.org/10.1590/S0104-66322006000200008*

[44] E.Pehlivan, T.Altun, ‘‘Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions from aqueous solution by Lewatit CNP 80’’. *Journal of Hazardous Materials, 2007,140, 299–307. doi:10.1016/j.jhazmat.2006.09.011*

[45] J.Jachuła, D. Kołodyńska, Z. Hubicki, Z. ‘‘Removal of Cd(II) and Pb(II) complexes with glycolic acid from aqueous solutions on different ion exchangers’’. *Canadian Journal of Chemistry, 2010,88, 540–547. doi:10.1139/V10-027*

[46] C.Xiong, C. Yao, ‘‘Adsorption behavior of gel-type weak acid resin (110-H) for Pb^{2+}’’. *Transactions of Nonferrous Metals Society of China (English Edition), 2008,18,1290–1294. https://doi.org/10.1016/S1003-6326(08)60219-8*

[47] C.Diniz, M.Doyle, H. Martins, ‘‘Uptake of heavy metals by chelating resins from acidic manganese chloride solution’’. *Minerals and Metallurgical Processing,2000, 17, 217–222. https://doi.org/10.1007/BF03403237*

[48]R. Juan, S.Lin, H.Kao, M. Theng ‘‘Effect of formaldehyde on Cu(II) removal from synthetic complexed solutions by ion exchange’’. *Chemosphere 2005,1355-1360 https://doi.org/10.1016/j.chemosphere.2004.11.074*

[49] D.Kołodyńska, H. Hubicka, ‘‘Polyacrylate anion exchangers in sorption of heavy metal ions with non-biodegradable complexing agents’’. *Chemical Engineering Journal, 2009,150,308–315.* *https://doi.org/10.1016/j.cej.2009.01.003*

[50] D.Kołodyńska, ‘‘The effect of the novel complexing agent in removal of heavy metal ions from waters and wastewaters’’. *Chemical Engineering Journal, 2010,165, 835–845. https://doi.org/10.1016/j.cej.2010.10.028*

[51] D.Kołodyǹska, ‘‘Green complexing agent - EDDS in removal of heavy metal ions on strongly basic anion exchangers’’. *Desalination, 2011,280, 44–57. https://doi.org/10.1016/j.desal.2011.06.060*

[52] D.Kołodyńska, ‘‘Application of strongly basic anion exchangers for removal of heavy metal ions in the presence of green chelating agent’’. *Chemical Engineering Journal,2011, 168, 994–1007.* *https://doi.org/10.1016/j.cej.2011.01.073*

[53] D.Kołodyńska, D. Cu(II), Zn(II), Co(II) and Pb(II) removal in the presence of the complexing agent of a new generation’’. *Desalination, 2011,267,175–183.* *https://doi.org/10.1016/j.desal.2010.09.022*

[54] J.Jachuła, D.Kołodyńska, Z. Hubicki, Z. ‘‘Sorption of Zn(II) and Pb(II) ions in the presence of the biodegradable complexing agent of a new generation’’. *Chemical Engineering Research and Design, 2012,90, 1671–1679. https://doi.org/10.1016/j.cherd.2012.01.015*

[55] D.Kołodyńska, Z. Hubicki, ‘‘Application of novel complexing agent in sorption of heavy metal ions from wastewaters on ion exchangers of various types’’. *Annales UMCS, Chemistry, 2009,64,1. DOI: 10.2478/v10063-008-0017-4*

[56] M.Ahmadi, P.Teymouri, A. Setodeh, S.Mortazavi, A. Asgari, ‘‘Adsorption of Pb(II) from aqueous solution onto lewatit FO36 nano resin: Equilibrium and kinetic studies’’. *Environmental Engineering and Management Journal, 2011,10, 1579–1587. DOI:10.30638/eemj.2011.219*

[57] J.chula, Z. Hubicki. ‘‘Sorption of heavy metal complexes with MGDA on the macroporous anionexchangerPuroliteA830’’.*Chemik,2013,67,693–700. https://bibliotekanauki.pl/articles/1216010*

[58] D.Kołodyńska, M. Kowalczyk, Z.Hubicki, V. Shvets, V. Golub, ‘‘Effect of accompanying ions and ethylenediaminedisuccinic acid on heavy metals sorption using hybrid materials Lewatit FO 36 and Purolite Arsen Xnp’’. *Chemical Engineering Journal, 2015,276, 376–387. https://doi.org/10.1016/j.cej.2015.04.088*

[59] B.S.Garg, 1R.K.Sharma, N.Bhojak, S.Mittal, ‘‘Chelating Resins and Their Applications in the Analysis of Trace Metal Ions’’. *Microchemical Journal, 1999, 61, 94–114. https://doi.org/10.1006/mchj.1998.1681*

[60] E.Korngold, S. Belfer, C. Urtizberea, ‘‘Removal of heavy metals from tap water by a cation exchanger’’, *Desalination,1996,104, 197–201 https://doi.org/10.1016/0011-9164(96)00042-2*

[61] V.Diniz, T. Ciminelli, M. Doyle, ‘‘The use of the chelating resin Dowex M-4195 in the adsorption of selected heavy metal ions from manganese solutions’’. *Hydrometallurgy, 2005,78, 147–155. doi:10.1016/j.hydromet.2004.12.007*

[62] Y.Vilensky, B. Berkowitz, A. Warshawsky, ‘‘In situ remediation of groundwater ontaminated

by heavy- and transition-metal ions by selective ion-exchange methods''. *Environmental Science and Technology, 2002,36, 1851–1855.* *https://doi.org/10.1021/es010313+*

[63] M.Yebra, L. Rodrı´guez, L. Puig, A. Moreno-Cid, ''Application of a Field Flow Preconcentration System with a Minicolumn Packed with Amberlite XAD-4=1-(2-pyridylazo)-2-naphthol and a Flow Injection-Flame Atomic Absorption Spectrometric System for Lead Determination in Sea Water Microchim''. *Acta 2002,140, 219–225. https://doi.org/10.1007/s00604-002-0918-4*

[64] C.Diniz, M.Doyle, T.Ciminelli, ''Effect of pH on the adsorption of selected heavy metal ions from concentrated chloride solutions by the chelating resin Dowex M-4195''. *Separation Science and Technology, 2002,37, 3169–3185. https://doi.org/10.1081/SS-120006155*

[65] S.Tokalioglu, S.Kartal, L. Elci, ''Determination of Trace Metals in Waters by FAAS after Enrichment as Metal-HMDTC Complexes Using Solid Phase Extraction''. *Bull.Korean Chem.Soc, 2002,23, 693–698. https://doi.org/10.5012/bkcs.2002.23.5.693*

[66] V.Diniz, T. Ciminelli, M. Doyle, ''The use of the chelating resin Dowex M-4195 in the adsorption of selected heavy metal ions from manganese solutions''. *Hydrometallurgy, 2005,78, 147–155. doi:10.1016/j.hydromet.2004.12.007*

[67] A.Agrawal, K. Sahu, ''Separation and recovery of lead from a mixture of some heavy metals using Amberlite IRC 718 chelating resin''. *Journal of Hazardous Materials, 2006,133,299–303. doi:10.1016/j.jhazmat.2005.08.029*

[68] M.Soylak, M. Tuzen, I. Narin, ''Solid phase extraction of iron and lead in environmental matricesonamberlite-1180/PV''*Quim.Nova,2006,29,203–207.*

https://doi.org/10.1590/S0100-40422006000200005

[69] M.Merganpour, G. Nekuonam, A. Tomaj, Y.Kor, H. Safari, ‘‘Efficiency of lead removal from drinking water using cationic resin Purolite’’. *Environmental Health Engineering and Management Journal*, 2015,2, 41–45. *http://creativecommons.org/licenses/by/4.0*

[70] Y.Kor, A.Merganpour, M.Vakili, M. Farrokhi, Z. Soughi, R. Ayobi, B.Amirlkhanlo, ‘‘Investigation of High Removal Efficiency of Lead Using Purolite S-930 Resin in Aqueous Solution’’.*Journal of Veterinary Dentistry2015,3,204–212.* *https://www.researchgate.net/publication/283661728*

[71] C.Wang, C.Chang, C.Chen, ‘‘Study on Metal Ion Adsorption of Bifunctional Chelating / Ion-Exchange Resins’’.*Macromol.Chem.Phys.,2001,202,882–890.* *https://doi.org/10.1002/1521-3935(20010301)202:6<882::AID-MACP882>3.0.CO;2-K*

[72] D.Prabhakaran, M. Subramanian,‘‘A new chelating sorbent for metal ion extraction under high saline conditions".*Talanta,2003,59,1277-1236. DOI: 10.1016/S0039-9140(03)00030-4*

[73] D. Prabhakaran, M.S. Subramanian, ‘‘Enhanced metal extractive behavior using dual mechanism bifunctional polymer: an effective metal chelatogen’’, *Talanta 2003, 61, 431-437. DOI: 10.1016/S0039-9140(03)00307-2*

[74] P.Roy, A. Rawat, V.Choudhary, P.Rai, ‘‘Removal of heavy metal ions using polydithioc arba mate resin supported on polystyrene’’. *Indian Journal of Chemical Technology,2004 ,11, 51–58. https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/4228438*

[75] S.Nabi, M. Naushad, A. Khan, ‘‘Sorption studies of metal ions on naphthol blue-black modified Amberlite IR-400 anion exchange resin: Separation and determination of metal ion

contents of pharmaceutical preparation''. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2006,280, 66–70. doi:10.1016/j.colsurfa.2006.01.031*

[76] C.Liu, R. Bai, Q.San Ly, ''Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: Behaviors and mechanisms''. *Water Research, 2008,42, 1511–522. DOI: 10.1016/j.watres.2007.10.031*

[77] A.Nilchi, A.Babalou, R. Rafiee, H. Sid Kalal, ''Adsorption properties of amidoxime resins for separation of metal ions from aqueous systems''. *Reactive and Functional Polymers, 2008,68, 1663–1668. doi:10.1016/j.reactfunctpolym.2008.09.011*

[78] A.Khan, S.Khan, S. Ganai, ''Role of chemically modified organic resin in selective separation of Hg^{2+} from other metal ions, *Conference paper. First Annual National Seminar of the Indian Society of Toxicology on "Human Toxicology and Environmental Health: New Frontiers and Future Challenges*'', *Aligarh, India, 22 February 2009. 2009, 1, 127–133, http://www.biolmedonline.com/Articles*

[79] S.Pramanik, S.Sarkar, H.Paul,P.Chattopadhyay, '' A new chelating polymer with 2-metho xy -1-imidazolylazobenzene functionality for determination of lead(II) and iron(III) '', *Indian Journal of Chemistry 2009,48,30–37. https://www.researchgate.net/publication/237710378*

[80] I.Solangi, S. Memon,M. Bhanger, ''Synthesis and application of a highly efficient tetraester calix[4]arene based resin for the removal of $Pb^{2+}$from aqueous environment''. *Analytica Chimica Acta, 2009,638, 146–153. doi:10.1016/j.aca.2009.02.026*

[81] W.Fei, W.Lian-jun, L. Jian-sheng, S. Xiu-yun, Z. Liang, '' Synthesis of modified D401 chelating resin and its adsorption properties for Pb^{2+}'' . *J. Cent. South Univ. Technol, 2009,16,*

0575–0580 DOI: 10.1007/s11771−009−0096−1

[82] P.Thu, T.Thanh, H. Phi, S.Kim, V.Vo, ‘‘Adsorption of lead from water by thiol-unctionalized SBA-15 silicas’’. *Journal of Materials Science, 2010,45, 2952–2957. DOI 10.1007/s10853-010-4288-8*

[83] N.Kamel,E. Sayyah, A. Abdel-aal, ‘‘Removal of Lead , Cobalt and Manganese from Aqueous Solutions using a new Modified Synthetic Ion Exchanger’’, *Archives of Applied Science Research, 2011,3,448–464. http://scholarsresearchlibrary.com/archive.html*

[84] M.Souza, L.de Santa Maria, M. Costa, W. Hui, L. Costa, H. Araujo Filho, S. Amico, ‘‘Synthesis, characterization and evaluation of phosphorylated resins in the removal of Pb^{2+} from aqueous solutions’’. *Polymer Bulletin, 2011,67,237–249. DOI 10.1007/s00289-010-0373-z*

[85] W.Gurnule, S.Katkamwar, ‘‘Selective Removal of Toxic Metal Ions From Waste Water Using Phenol-Formaldehyde Type Chelating Resins’’.*Rasayan J.Chem. 2012,5, 365–375. http://www.rasayanjournal.com*

[86] W.Gurnule, S. Dhote, ‘‘Preparation, characterization and chelating ion-exchange properties of copolymer resin derived from 2,4-Dihydroxy benzoic acid, ethylene diamine and formaldehyde’’. *Der Pharma Chemica, 2012,4, 791–799. http://derpharmachemica.com/archive.html*

[87] M.Dhore, S. Butoliya,A. Zade, ‘‘Removal of Toxic Metal Ions from Water Using Chelating Terpolymer Resin as a Function of Different Concentration Time and pH’’, *ISRN Polymer Science, 2014,1-11,http://dx.doi.org/10.1155/2014/873520*

[88] S. Kalaivani, T. Vidhyadevi, A. Murugesan, K.Thiruvengadaravi, D. Anuradha, S.sivanesan

, L. Ravikumar, ‘‘The use of new modified poly (acrylamide) chelating resin with pendent benzothiazole groups containing donor atoms in the removal of heavy metal ions from aqueous solutions’’. *Water Resources and Industry 2014, 5, 21–35.* *http://dx.doi.org/10.1016/j.wri.2014.04.001*

[89] S.El-Bahy, Z.El-Bahy, ‘‘Synthesis and characterization of a new iminodiacetate chelating resin for removal of toxic heavy metal ions from aqueous solution by batch and fixed bed column methods’’. *Korean Journal of Chemical Engineering, 2016,33, 2492–2501. https://doi.org/10.1007/s11814-016-0070-1*

[90] F.An, R. Wu, M. Li, T.Hu, J.Gao, Z. Yuan, ‘‘Adsorption of heavy metal ions by iminodiacetic acid functionalized D301 resin: Kinetics, isotherms and thermodynamics’’. *Reactive and Functional Polymers,2017, 118, 42 http://dx.doi.org/10.1016/j.reactfunctpolym.2017.07.005*

[91] D.Kołodyńska, J. Krukowska-Bąk, J. Kazmierczak-Razna, R. Pietrzak, ‘‘Uptake of heavy metal ions from aqueous solutions by sorbents obtained from the spent ion exchange resins. *Microporous and Mesoporous Materials, 2017,244, 127–136. https://doi.org/10.1016/j.micromeso.2017.02.040*

Chapter 3

Adsorption and removal studies of cadmium ion onto sulfonic/phosphonic acid functionalization resins

Preface

A version of this chapter has been published in the **Can J Chem Eng. 2022; 1–9.** *I produced the work alongside my co-authors; Yahui Zhang, and* Shams Anwar. *I am the main author. I conducted all lab experiments, calculated parameters for isotherms, kinetic and dynamic studies. I prepared the first draft of the manuscript and subsequently revised the manuscript based on the co-authors' and peer review feedback. Co-author, Yahui Zhang assisted in the development of concept, design of methodology, reviewing and editing the draft, and reviewing and revising the new version of the manuscript. Co-author,* Shams Anwar, *supported in the data and process analysis, reviewing and editing the draft, reviewing and revising the new version of the manuscript.*

Abstract

Cadmium is a persistent bio-accumulative toxic metallic element, which causes hazardous impacts on living species, water, and the environment. This paper presents the study of cadmium ion removal from aqueous solutions in batch experiments using 22 ion exchange resins with different functional groups. It was found that Dowex G-26 resin with a sulphonic functional group and Puromet™ MTS9570 resin with sulphonic and phosphonic functional groups had excellent performance for Cd(II) ion removal. The effects of resin dosage, adsorption time, initial concentration of cadmium, and initial pH of solution on cadmium removal were investigated systematically using Dowex G-26 and Puromet™ MTS9570 resins. Maximum cadmium removal rates of 99.2% and 98.9% were achieved for G-26 and MTS9570, respectively, at an initial cadmium concentration of 1000 mg/L, an initial solution pH of 5.0, an adsorption time of 30 min, and a 0.01 g/mL resin dosage for G-26, and a 0.025 g/mL resin dosage for MTS9570. The ion-exchange adsorption process was fast, and it reached equilibrium after 30 min of adsorption. The results obtained show that both resins performed well for the removal of Cd(II) ions from weakly acidic solutions. Langmuir, Freundlich, and Temkin isotherms models were employed to investigate and understand the adsorption characteristics. The results showed that the studied adsorption processes fitted well to the Langmuir adsorption isotherm. From the Langmuir adsorption isotherm, the maximum adsorption capacities of Cd(II) were found to be 78.125 and 51.020 mg/g for G-26 and MTS9570, respectively. This research provides an efficient systemic approach for cadmium ion removal from aqueous solutions.

Keywords: adsorption isotherms, cadmium, ion-exchange resins, removal, sulphonic acid group

3.1 Introduction

In modern society, rapid industrial development has resulted in a high level of wastewater discharged containing heavy metal ions, which are not biodegradable. They remain indefinitely in the ecological systems and in food chains, exposing human health and the ecosystem to a high threat [1-3]. In particular, Cd(II) ions emerge as one of the most hazardous heavy metal species in foods and the environment due to their ability to alter various organs and tissues following either acute or chronic exposure [4]. Cadmium and its compounds are highly toxic, which cause hazards to the human body such as damage to the cardiovascular, renal, respiratory, gastrointestinal, neurological, and reproductive systems [5, 6], especially due to their high water solubility [7]. Cadmium metal is primarily employed as an anticorrosive, as an electroplate on steel electronic parts, and as neutron shielding and control rods for nuclear reactors. Water may be contaminated with cadmium due to cadmium impurities in galvanized pipes, water heaters, water coolers, and taps containing cadmium. Even a very low concentration of cadmium can be harmful to the environment and human health [8, 9]. According to the World Health Organization (WHO) guidelines (2017), the permissible limit of cadmium in drinking water is 3μg/L[10]. One characteristic of cadmium toxicity is that it is a persistent bioaccumulative toxic (PBT) substance, which makes it more harmful to the environment and human beings. Thus, minimizing the waste hazards and removal of cadmium have become one of the most important concerns for many researchers in environmental protection [11].

There are several techniques such as adsorption [12], ion exchange, membrane, filtration, electro-sorption, reverse osmosis, ultrafiltration, and photocatalysis applied for the removal of cadmium and other heavy metal ions from the water system [13-17]. Among these technologies, the ion exchange process is one of the most efficient methods for thorough cadmium removal from different aqueous solutions because it has advantages, such as being effective at a low metal concentration, simple operation, low cost, and easy regeneration of resins [18, 19]. Ion exchange resins (beads) are solid and insolubilized high-molecular-weight polyelectrolytes that can exchange their mobile ions for ions of the same charge from the surrounding medium according to an electric charge balance. The resulting ion exchange is reversible and stoichiometric with the displacement of ionic species by another on the exchanger [20, 21].

$$nR{-}SO_3H + M^{n+} \rightarrow (R{-}SO_3{-})nM + nH^+ \qquad (R1)$$

$$nR{-}COOH + M^{n+} \rightarrow (R{-}COO{-})nM + nH^+ \qquad (R2)$$

The ion exchange resins studied for cadmium removal from aqueous solutions are strong acid resins with sulphonic acid groups ($-SO_3H$), such as Amberlite IR 120, Lewatit SP-112, Dowex Marathon C, Dowex 50W, and Dowex 50WX8; weak acid resins with carboxylic groups such as Purolite C-104 and Lewatit CNP-80; weak acid and chelating resins with iminodiacetic acid (IDA) groups such as Purolite S-930, Wofatit MC-50, Amberlite IRC 718, and Lewatit TP 207, acid; chelating resins with amino-phosphonic groups such as Purolite S-940 and Purolite S-950; and chelating resins with amino groups such as Diaion CR-20 [22,23]. In the (weak) acid and chelating resins with IDA or aminophosphonic function groups, the multivalent counter ions, that is, metal ions, are bound not only by electrostatic but also by coordinative forces.

Taha studied the ion exchange of Cd(II), U(VI), Mn(II), Cu(II), and Zn(II) from multi-component phosphoric acid solutions using Dowex Marathon C resin, which is a gel type strong acidic cation exchange resin with a polystyrene divinylbenzene (DVB) matrix and a sulphonic acid group. The effects of critical parameters on the ion exchange process such as contact time, initial metal ion concentration, resin dose, and concentration of phosphoric acid were investigated. It was found that the ion exchange process reached equilibrium within 240 min for the five metal ions studied. Successful removal of metal ions from crude phosphoric acid suggests that the Marathon C resin could be used in removing toxic metal ions from crude phosphoric acids used in phosphate fertilizer production [24].

Pehlivan and Altun studied the ion exchange of Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} from aqueous solutions with Dowex 50W synthetic resin [25]. The structural polymeric backbone of the resin is styrene cross-linked with DVB, functionalized with sulphonic acid group in sodium form as the ion exchange site. It has been observed that the selectivity of $-SO_3H$ group of the resin increases with atomic number, valency, and degree of ionization of the exchanged metals, that is, metal selectivity follows the order: $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. They also reported that Lewatit CNP80 resins made from acrylic polymers, cross-linked with DVB and functionalized with carboxylic group (–COOH), can be economically used for the removal of Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} from wastewaters at pH >5.0 [26].

Moosavirad et al., [27], reported the removal of heavy metals such as Cd(II), Cu(II), Zn(II), Ni(II), and Pb(II) from wastewaters in several industrial areas of Kerman, Iran, using Dowex 50WX8 (H^+) resin bearing a sulphonic acid group on the styrene backbone, and found that the exchanger resin is very effective in lowering the metal content of wastewaters. Maximum heavy metal ion exchange on Dowex 50WX8 (H^+) resin was achieved at a pH range of 4.0–6.0 [27].

Kocaoba [22] found that the Amberlite IR-120 resins with styrene matrix and sulphonic acid group ($–SO_3H$) were efficient adsorbents for Cd(II) removal from aqueous solutions, and the resin in Na^+ form was more effective. The optimum solution pH for metal removal is around pH 5.5. More than 99% of Cd(II) ions can be removed at sufficient resin dosage [28,29].

Being a bio-accumulative toxic metal to the environment and human health, the removal of cadmium from aqueous systems is a common and indispensable task. As an efficient technology, ion exchange processes have been studied using various resins by researchers. However, usually only a few different resins were explored in each research reported. Resin efficiency depends on its chemical–physical properties, which involve chemical activities of functional groups, acid/base strength, crosslinking degree, porosity, degree of stability, purity, particle size, and, of course, operation parameters such as medium pH, contact time, and agitation [30]. Currently, there are no known criteria for selecting resins with functional groups for Cd^{2+}removal and little knowledge of the effects of different functional groups on Cd(II) sorption. In this study, 22 resins with different functional groups such as sulphonic, iminodiacetic, amino-phosphonic, sulphonic/trimethylamine, amino-methyl-phosphonic, and phosphonic/sulphonic groups have been explored and compared for cadmium ion exchange to discover the reactivity and preference of resins with specific groups to Cd(II) adsorption. Resins with ideal Cd(II) removal such as G-26 and MTS9570 have been investigated systematically considering the influences of operation parameters, that is, resin dosage, ion exchange time, initial concentration of cadmium, and initial pH of solutions. Classic adsorption isotherms, that is, Langmuir, Freundlich, and Temkin models, are employed to discuss the equilibrium characteristics of Cd(II) adsorption.

3.2 Materials and Method

The resins with different functional groups used in this study are listed in Table 3.1. Cadmium nitrate tetra-hydrate $Cd(NO_3)_2 \cdot 4H_2O$ (bought from Alfa Aesar Canada) and deionized (DI) water were employed for preparing solutions with various Cd(II) concentrations. Briefly, 0.1 mol/L HCl and 1% NaOH solutions were used for pH adjustment. All chemicals used in testing were analytical reagent-grade.

Resins were initially washed in DI water at 150 rpm on a reciprocating platform shaker (model Promax 2020, Heidol pH Instruments GmbH & Co. KG) for 1 h. Then the resins were activated with a solution of 10% (v/v) HCl and agitated at 150 rpm for 24 h. Subsequently, the resins were washed twice in DI water at 150 rpm for 1 h and dried at 20°C for 72 h. Before each experiment, the corresponding amount of dried resin for testing was weighted and placed in an individual flask with DI water for 1 h to allow initial swelling. The resin was then filtered and placed in a 125 mL flask containing 20 ml of cadmium solution with a specific concentration and pH. The samples were agitated on the reciprocating shaker at 150 rpm for a specific amount of time at room temperature.

Table 3.1: Ion exchangers and their properties.

Typical properties					
Ion exchanger	**Matrix**	**Active groups**	**Delivery form**	**Bed size (mm)**	**Total capacity (equiv./L)**
Dowex G-26	S-DVB(gel)	Sulfonic	H^+	0.650 ± 50	2
Amberlite IR-120 H	S-DVB(gel)	Sulfonic	H^+	0.620-0.830	>1.8
Purolite S930 plus	PS-DVB(macroporous)	Iminodiacetic	Na^+	0.425 - 1.0	50 g Cu/L
Lewatit monoplusTP207	PS-DVB(macroporous)	Iminodiacetic	H^+	0.61 (+/- 0.05)	2
Amberlite IRC784I	PS-DVB(macroporous)	Iminodiacetic	Na^+	0.50 - 0.65	≥ 1.35
Lewatit monoplus TP208	PS-DBV(macroporous)	Iminodiacetic	Na^+	0.4-1.25	2.9
Purolite S930EPlus	PS-DVB(macroporous)	Iminodiacetic	Na^+	0.425 - 1.0	50 g Cu/L
SIR 500	S-DVB(macroporous)	Aminophosphonic	Na^+	0.297-1.19	>1.4
Amberlite IRC747	PS-DVB(macroporous)	Aminophosphonic	Na^+	0.520 - 0.660	1.75
Purolite S940	PS-DVB(macroporous)	Aminophosphonic	Na^+	0.425 - 0.850	20 g Ca/L
Purolite S950plus	PS-DVB(macroporous)	Aminophosphonic	Na^+	0.425 – 0.850	24 g Ca/L
Lewatit monoplus TP 260	PS-DVB(macroporous)	Aminomethylphosphonic	Na^+	0.63 (+/- 0.05	2.4
Purolite MTS 9570	PS-DVB(macroporous)	Phosphonic and Sulfonic	H^+	0.315 - 0.850	18 g Fe/L
Lewatit MDS TP220	PS-DVB(macroporous)	Bis-picolylamine	FB Form	0.62(+/- 0.05)	5 g Cu/L
Dowex Mac-3	PA (macroporous)	Carboxilic	H^+	0.30 – 1.2	3.8
WAG RTI 26600	PA-DVB(gel)	Carboxilic	H^+	0.297-1.19	>4.0
Purolite S108	PS-DVB(macroporous)	N-methylglucamine	FB Form	0.425 - 0.630	0.6
Lewatit vp oc 1026	PS-DVB(macroporous)	Di-2-ethylhexylphosphat	_	0.31-1.65	13 g Zn/L
Lewatit monoplusTP214	PS-DVB(macroporous)	Thiourea	_	0.55 (+/- 0.05)	1.1
PuroliteMTS9140	PS-DVB(macroporous)	Thiourea	_	0.30 - 1.2	1
Amberjet 4400Cl	PS-DVB(gel)	Trimethyl ammonium	Cl^-	0.53 – 0.63	1.4
Purolite MTS9200	PS-DVB(macroporous)	Isothiouronium	H^+	0.30 - 1.2	275 g Hg/L

The metal concentrations before and after an ion exchange experiment were determined using wavelength dispersive X-ray fluorescence spectroscopy (Supermini200, Rigaku Co.), and their difference was used for the calculation of metal ion exchange. The batch ion-exchange experiments were performed in triplicate. The reproducibility deviation of the measurements was within 5%.

The removal percentage of Cd(II) and ion exchange capacities of the G-26 and MTS9570 resins were calculated, respectively, using Equations (3.1) and (3.2).

$$\% \text{ removal of Cd (II) ions} = \frac{(C_i - C_o)}{C_i} \text{ x } 100 \qquad (3.1)$$

$$Q_t = \frac{(C_i - C_e)V/1000}{W} \qquad (3.2)$$

where C_i, C_o and C_e are the initial, final, and equilibrium concentrations of Cd(II) in mg/L, respectively; and Q_t is the ion exchange capacity of the resin in mg/g at time *t; V* is the volume of Cd(II) solution in ml; and *W* is the total amount of resin in g.

3.3 Results and Discussion

3.3.1 Exploration of Cd removal using resins with various functional groups

To explore the reactivity and preference of resins with specific functional groups to Cd(II) ion exchange, 22 resins with different groups such as sulphonic, iminodiacetic, amino-phosphonic, sulphonic/trimethylamine, aminomethyl-phosphonic, and phosphonic/sulphonic groups have been tested and compared. The resin dosage varies in the range of 0.1-0.5 g (i.e, 5 -25g/L) with other fixed conditions, that is, pH 5.0, room temperature of 20°C, a shaking speed of 150 rpm, an adsorption time of 2 h, and a metal concentration of 1000 mg/L.

It is found that 13 resins with sulphonic, iminodiacetic, amino-phosphonic, amino-methyl-phosphonic, phosphonic/ sulphonic functional groups have a high adsorption rate for Cd(II) ions, as shown in Figure 3.1. However, nine resins with functional groups, including iso-thiouronium, thiourea, bis-picolylamine, carboxylic, N-methylglucamine, trimethylammonium, and di-ethylhexylphosphate (D2EHPA) have relatively low adsorption performance for cadmium ions (Figure 3.2).

Among these resins, Dowex G-26 hydrogen forms a resin with a sulphonic group, which is a strong acid resin, and exhibits ideal Cd(II) removal performance, and the MTS9570 resin, which is the only one with both sulphonic and phosphonic functional groups, also has an excellent cadmium removal rate. It is of significance to understand how these two functional groups affect the adsorption of Cd^{2+} ions. Therefore, in this work, G-26 and MTS9570 resins (schematic structures shown in Figure 3.3) have been selected for systematic study on the influences of operation parameters, that is, adsorption time, resin dosage, medium pH, agitation, and initial metal ion concentration, on Cd(II) removal from aqueous solutions.

Dowex G-26 resin was studied for copper removal from industrial wastewater [31]. Puromet™ MTS9570 has good removal performance for antimony, bismuth, and iron ions as reported by Purolite Co. It was studied for ferric ion removal from a copper electrowinning electrolyte containing antimony and bismuth [32]. MTS9570 resin was also used for the extraction of Co(II), and other metals in the chloride media [33].

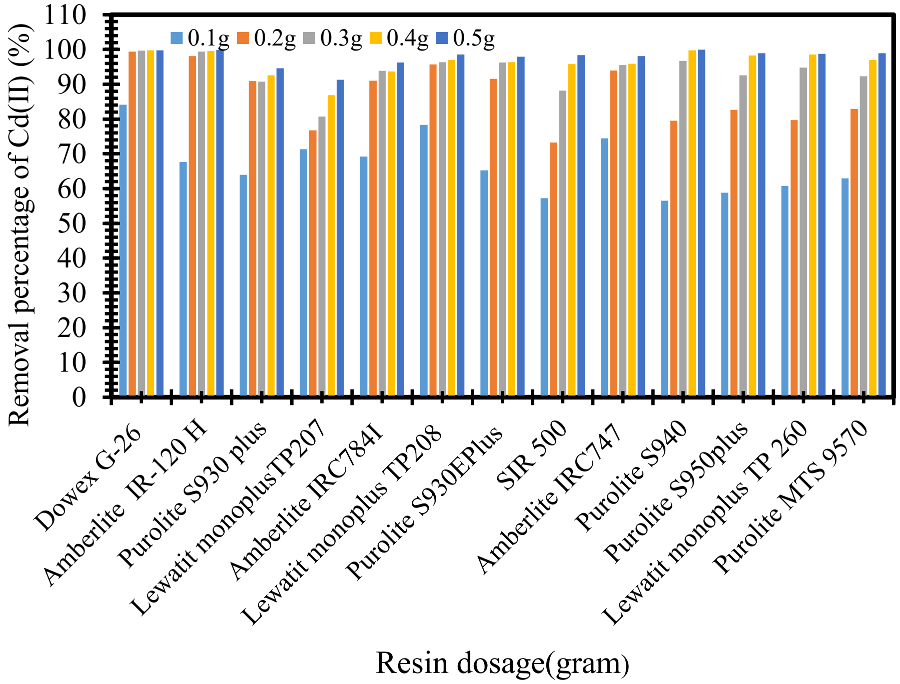


Figure 3.1: Resins with high removal rate of Cd(II).

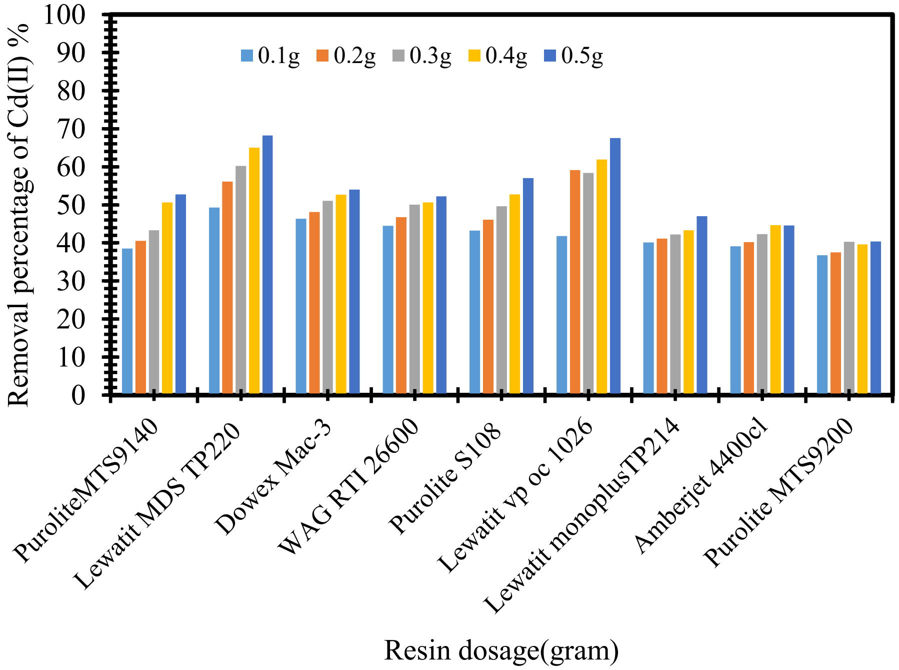


Figure 3.2: Resins with low removal rate of Cd(II).

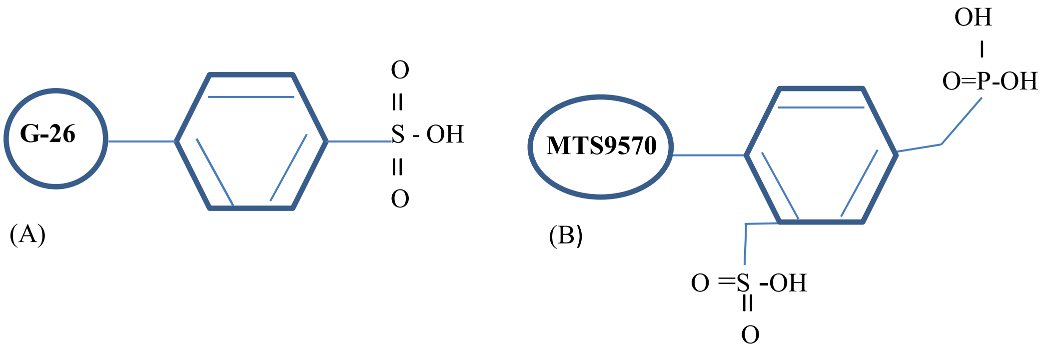


Figure 3.3: (A) G-26 resin with sulfonic functional group, (B) MTS 9570 resin with sulfonic and phosphonic functional groups.

3.3.2 Effect of adsorption time

The effect of adsorption time on Cd(II) removal was tested at the conditions of pH 5.0, room temperature of 20°C, shaking speed of 150 rpm, metal concentration of 1000 mg/L, and 0.5 g resin in 20 mL of metal solution. As shown in Figure 3.4, the removal percentage of Cd(II) ions increases with extending adsorption time. Adsorption equilibrium was achieved within 30 min of adsorption time for both resins. A further increase in contact time had no effect on cadmium adsorption on both resins.

3.3.3 Effect of resin dosage

The influence of adsorbent amount on the adsorption of cadmium from the aqueous solution containing 1000 ppm cadmium was studied at room temperature, pH 5, a shaking speed of 150 rpm, and an adsorption time of 30 min. Resin dosage was varied from 0.1- 0.5 g in a 20 mL solution. The results (shown in Figure 3.5) indicate that the removal percentage of Cd(II) was 99.2% at 0.2 g resin dosage for G-26. Further increase in the resin amount did not improve the cadmium removal percentage. This result is in good agreement with what was reported by Jha et al., [31]. The removal percentage of Cd(II) increased from 62.9%–98.9% with the resin range increasing from 0.1- 0.5 g for MTS9570. The increase in cadmium removal percentage with resin amount is due to the availability of active surface sites for adsorption. Therefore, optimum adsorbent amounts were chosen as 0.2 and 0.5 g for G-26 and MTS9570 for forthcoming tests, respectively.

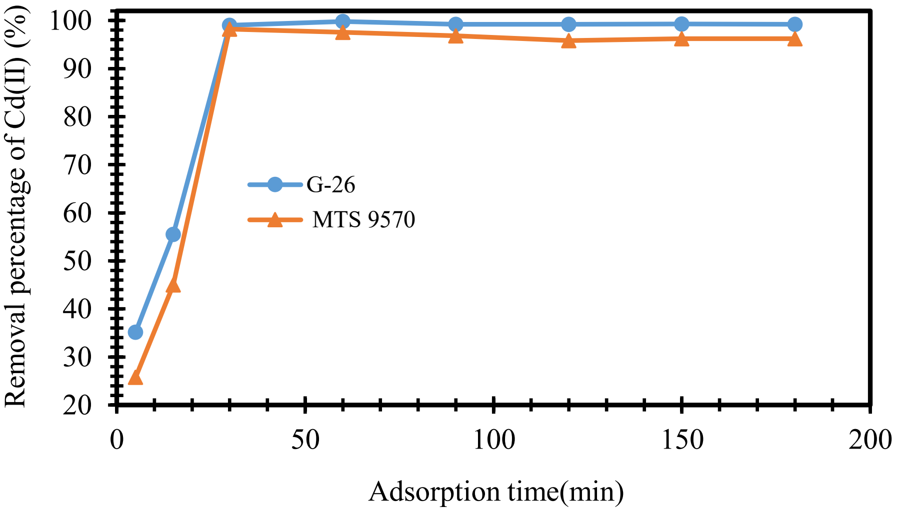


Figure 3.4: Effect of adsorption time on removal rate of Cd(II) using G-26 and MTS9570.

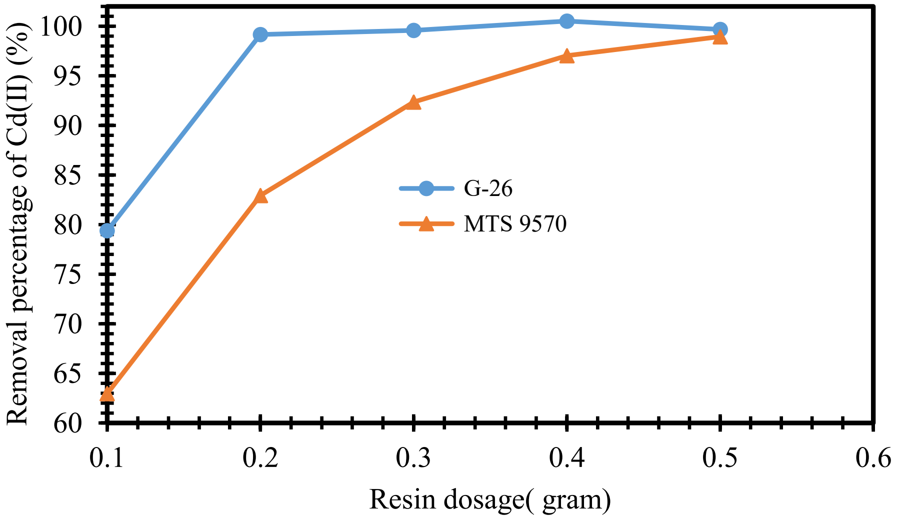


Figure 3.5: Effect of resin dosage on removal rate of Cd(II) using G-26 and MTS9570.

3.3.4 Effect of pH

The effect of pH on cadmium adsorption from a solution containing 1000 ppm cadmium was studied using fixed resin dosages, that is, 0.2 g for G-26 and 0.5 g for MTS9570, at room temperature, a shaking speed of 150 rpm, and an adsorption time of 30 min. The results (presented in Figure 3.6) show that the adsorption percentage of cadmium increased from 93% at pH 1.5 to 99.2% at pH 5.0 on G-26 and that the adsorption percentage of cadmium increased from 83.7% at pH 1.5 to 98.9% at pH 5.0 on MTS9570. The increase in pH leads to higher H^+ dissociation in the functional groups, which results in a higher cadmium removal percentage. Precipitation of cadmium was observed at pH >5.5. Therefore, in the subsequent tests, the solution was kept at pH 5.0.

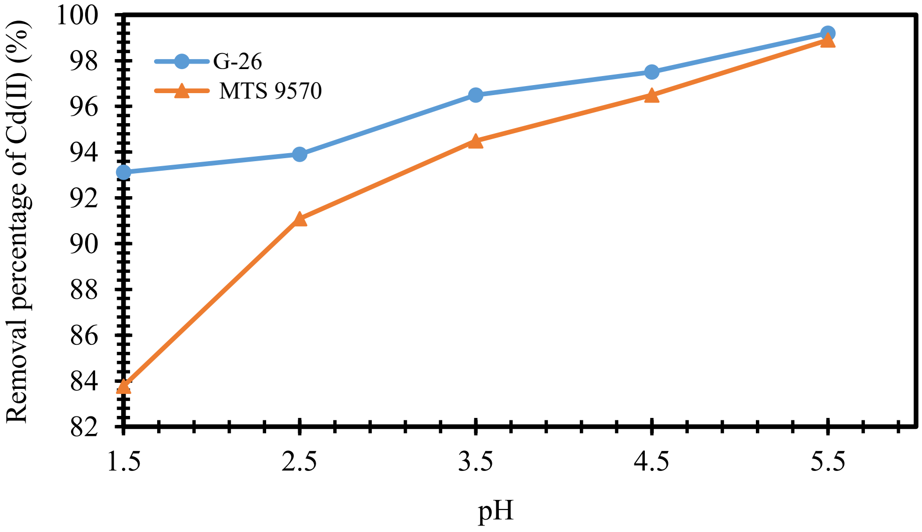


Figure 3.6: Effect of pH on removal rate of Cd(II) using G-26 and MTS9570.

3.3.5 Effect of initial metal ion concentration

The influence of the initial metal concentration on the adsorption process was studied by using 100 -1400 mg/L cadmium solution at pH 5.0, room temperature, a shaking speed of 150 rpm, and an adsorption time of 30 min. The resin dosage was 0.2 g for G-26 and 0.5 g for MTS9570. As shown in Figure 3.7, the removal percentage of Cd(II) decreases slightly with the increase in initial Cd(II) concentration. This is due to relatively fewer adsorption sites on the resins with an increasing initial metal concentration. The present result is in accordance with that reported by Zewail and Yousef [34].

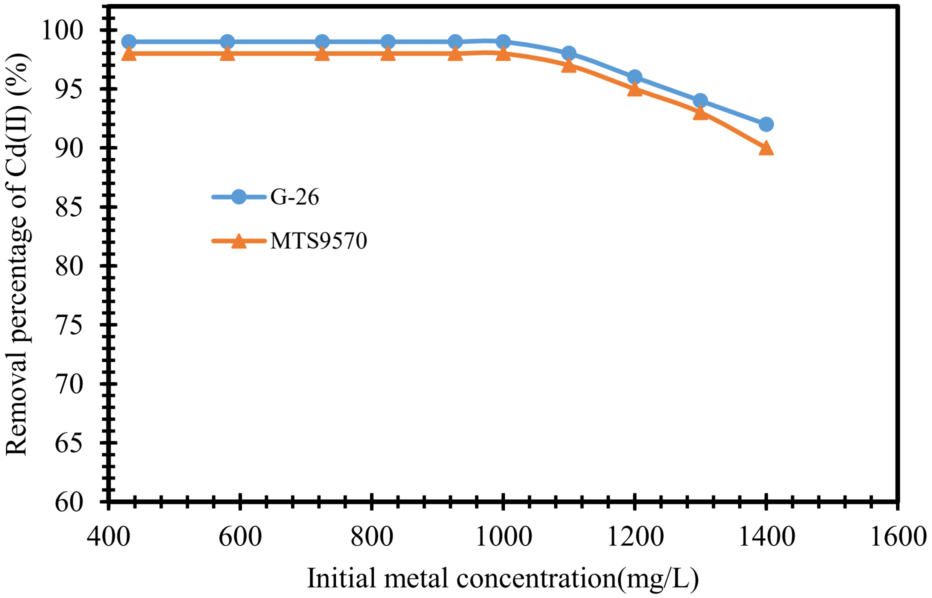


Figure 3.7: Effect of initial metal concentration on removal rate of Cd(II) using G-26 and MTS9570.

3.3.6 Adsorption isotherms

The adsorption isotherm provides information on sorption mechanisms, as well as how pollutants are absorbed [35]. They also provide information about the adsorbent capacity, which is one of the most important parameters in the design of an adsorption system [36]. Various adsorption parameters related to the adsorption models are determined and reported in order to understand the adsorption nature. An adsorption isotherm model can be used to determine the distribution of a solute between the adsorbent phase and the liquid phase at equilibrium and to predict the adsorption capacity of the adsorbent [37]. A variety of adsorption isotherms models, including Langmuir [38], Freundlich [39], and Temkin [40], were examined in detail [41,42].

The Langmuir adsorption isotherm represents the monolayer uniform adsorption of adsorbate metal ions on the surface of the adsorbent (i.e., resin). The linear form of the Langmuir isotherm equation is represented as follow: [43, 44]

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{3.3}$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), Q^0(mg/g) and *b*(L/mg) are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

Freundlich model assumes heterogeneous surfaces. The linear form of Freundlich isotherm equation is represented as follow [39].

$$log q_e = log K_F + \frac{1}{n} log C_e \tag{3.4}$$

Where K_F is the adsorption equilibrium constant, which relates to the adsorbent capacity, and *1/n* is the parameter relating to adsorption intensity.

Temkin isotherm model based on the interaction between adsorbate and adsorbent, which causes heat of adsorption due to repulsions forces. The linear form of Temkin equation is given by the following expression [40].

$$q_e = \mathrm{B} \ln (K_T) + \mathrm{B} \ln (C_e) ; \quad \mathrm{B} = \frac{RT}{b_T} \tag{3.5}$$

where K_T (L/g) and *B* (J/mol) are the Temkin and the heat of sorption constants, respectively.

R = universal gas constant (8.314J/mol/K), and *T*= Temperature at 298.15K.

In this study, Langmuir, Freundlich and Temkin models are employed to understand the equilibrium characteristics of Cd(II) adsorption on Dowex G-26 and MTS9570 resins, which are shown in Figures 3.8, 3.9, and 3.10. The Langmuir, Freundlich and Temkin isotherm parameters for the adsorption of cadmium (II) ions onto resins, which are calculated using isotherm equations and their correlation coefficients, are listed in Table 3.2. Comparison of the correlation coefficients values R^2 showed that the adsorption of Cd(II) onto G-26 and MTS9570 resins fitted better to the Langmuir model (R^2 = 0.9881 - 0.9939) than the Freundlich (R^2 = 0.9879 - 0.9863) and Temkin models (R^2 = 0.9731- 0.9666). This means monolayer uniform adsorption mechanism is the best description for Cd(II) adsorption onto the surface of G-26 and MTS9570 resins. According to Langmuir isotherm, the maximum Cd(II) adsorption capacity of resin was 78.125 mg/g for G-26 and 51.02 mg/g for MTS9570, respectively.

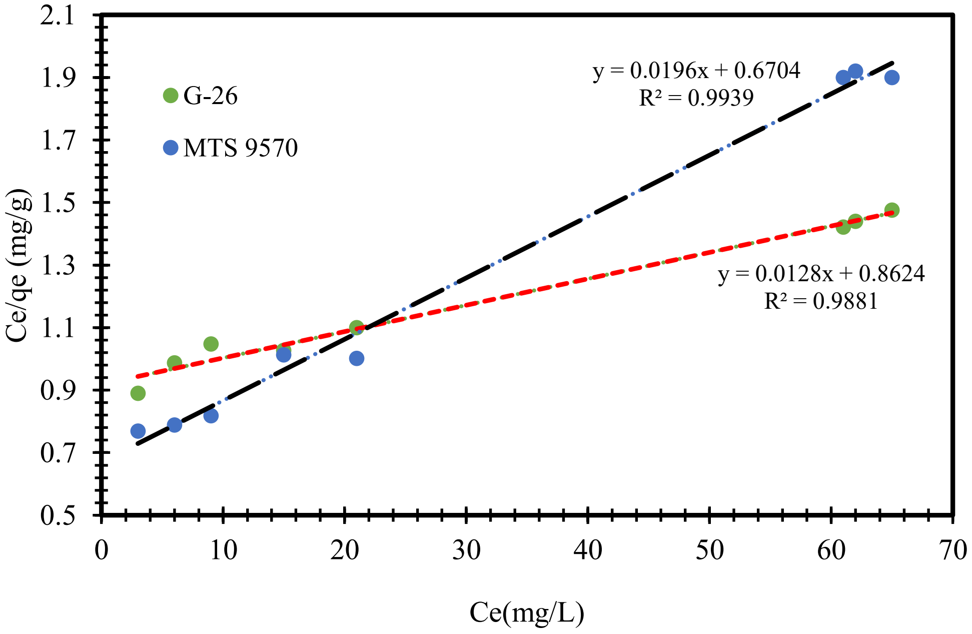


Figure 3.8: Langmuir isotherm of Cd(II) adsorption on G-26 and MTS9570.

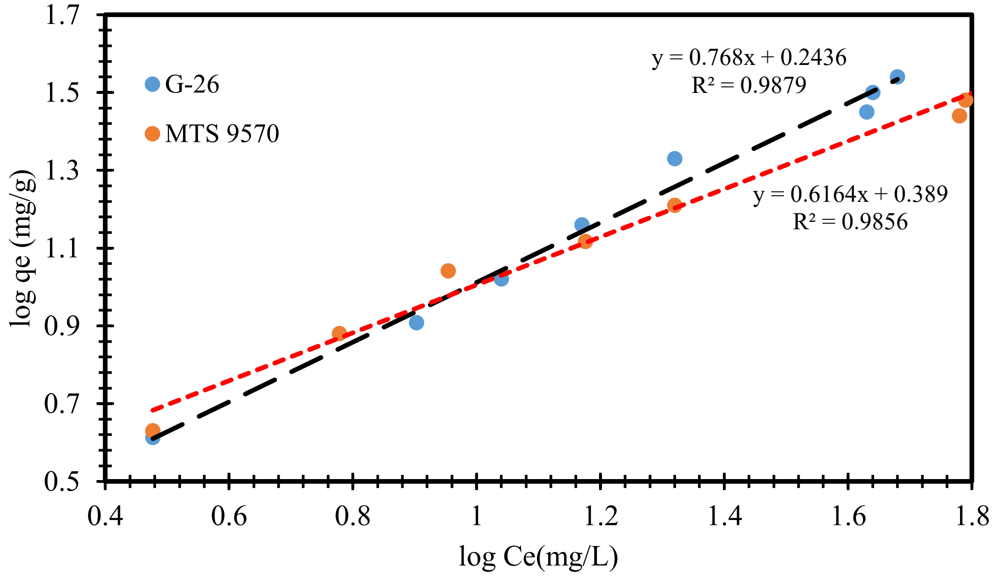


Figure 3.9: Freundlich isotherm of Cd(II) adsorption on G-26 and MTS9570.

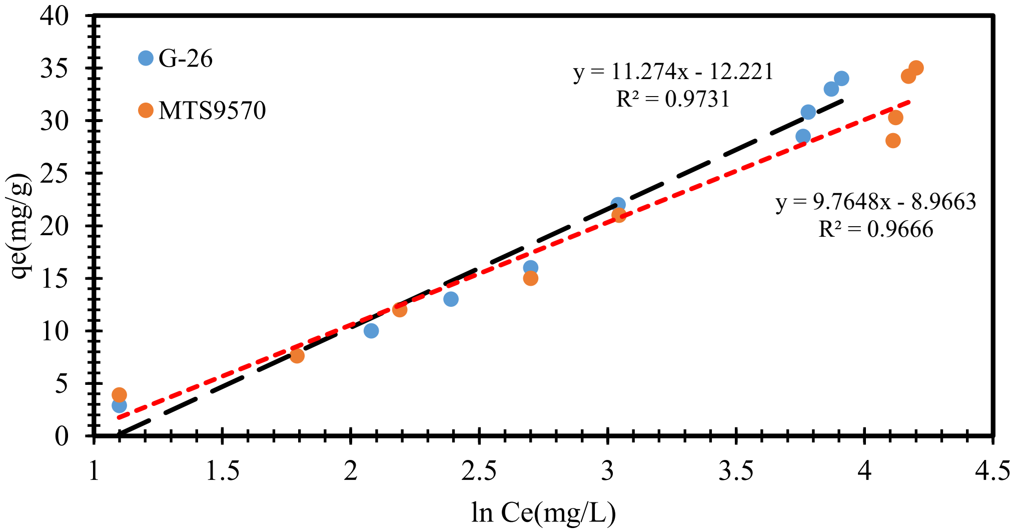


Figure 3.10: Temkin isotherm of Cd(II) adsorption on G-26 and MTS9570.

Table 3.2: The isotherm parameters for Cd(II) adsorption on G-26 and MTS9570.

Isotherm	**G-26**	**MTS9570**
Langmuir isotherm		
Q^0 (mg/g)	78.125	50.02
b (L/mg)	0.0148	0.029
R^2	0.9881	0.9939
Freundlich isotherm		
K_F (mg/g)	1.70	2.39
n	1..27	1.59
R^2	0.9879	0.9863
Temkin isotherm		
b_T	219.8	253.8
B	11.27	9.76
R^2	0.9731	0.9666

A comparison of G-26 and MTS9570 resins with some other adsorbents for Cd(II) adsorption reported in recent references is summarized in Table 3.3. The MTS9570 and G-26 resins investigated in this study are evidently superior to the previously reported adsorbents in cadmium ion adsorption. Therefore, they have very good potential for application in removing Cd(II) from aqueous solutions. The Comparison of Cd(II) removal rate using G-26 and MTS9570 is shown in Figure 3.11. It can be seen that G-26 resin has higher Cd(II) removal rate than MTS9570 resin at low dosages. For G-26 resin, the Cd(II) removal rate is close to 100% at the dosage of 0.01g/ml, while, for MTS9570 resin, it needs the dosage above 0.025g/ml. This may be deduced that sulfonic acid group is more efficient than phosphonic acid group for bonding and adsorbing Cd(II) ions. In molecular simulation using electronic structure methods, it is found that resin unit with sulfonic group are spontaneous for Cd(II) ion adsorption. While resin unit with phosphonic groups are not thermodynamically favorable for Cd(II) ion adsorption. Therefore, these observations are appealing to carry out details' simulation through further an individual study.

Table 3.3: Comparison of maximum adsorption capacity of Dowex G-26 and Puromet™ MTS9570 resins with some other adsorbents for Cd(II) adsorption.

Adsorbent	**Sorption capacity for Cd(II) (mg/g)**	**Conditions**	**References**
Waste Plastic	31.92	pH = 5.5, 25°C	[45]
Lewatit MonoPlus MP 64	21.93	pH = 5.8 and 6.4, 25°C	[46]
1,8-DAN/XAD-4	19.16	pH = 7, 25°C	[47]
PIDA1	33.7	pH = 0.5-2.5,25°C	[48]
PIDA2	29.2	pH = 0.5-2.5,25°C	[48]
PIDA3	32.6	pH = 0.5-2.5,25°C	[48]
PIDA4	22.48	pH = 0.5-2.5,25°C	[48]
PAA	16.86	pH = 0.5-2.5,25°C	[48]
FeO3@APS@AA-CO-CA	29.6	pH = 5.5, 25°C	[49]
Na-Mt	22.4	pH = 4, 25°C	[50]
Ca-Mt	17.8	pH = 4, 25°C	[50]
C160	31.76	pH = 4.1, 25°C	[51]
Dowex 50W	27.65	pH = 8-9, 25°C	[25]
CR-20	35.7	pH = 4-6, 25°C	[23]
MC-50	36.3	pH = 4-6, 25°C	[23]
CNP-80	16.02	pH = 4-6, 25°C	[23]
Dowex G-26	***78.125***	***pH = 5.0, 20°C***	***This work***
Puromet™ MTS9570	***51.02***	***pH = 5.0, 20°C***	***This work***

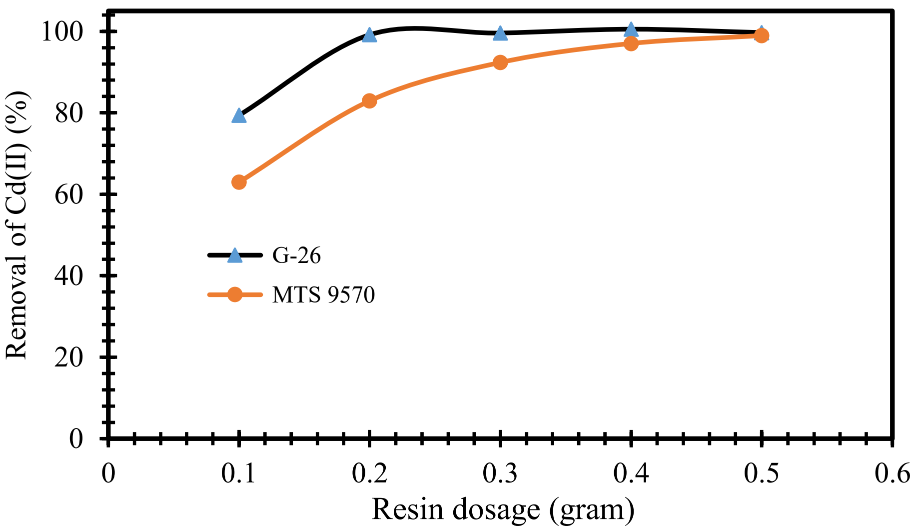


Figure 3.11: Comparison of Cd(II) removal rate using G-26 and MTS9570.

3.4 Conclusions

The removal of cadmium ions from aqueous solutions has been conducted using 22 ion exchange resins with different functional groups. This study provides an efficient systemic approach for cadmium ion removal from aqueous solutions. Batch experiment results show that Dowex G-26 resin with a sulphonic functional group and Puromet™ MTS9570 resin with both sulphonic and phosphonic functionality groups can efficiently remove Cd(II) present in aqueous solutions. The ion-exchange of Cd(II) was dependent on the time of contact, adsorbent dosage, pH level, and initial metal concentrations. At an initial metal concentration of 1000 mg/L, an adsorption time of 30 min, and an initial pH of 5.0, a maximum cadmium removal rate of 99.2% was achieved for G-26 at 0.01g/mL resin dosage; similarly, a maximum cadmium removal rate of 98.9% was achieved for MTS9570 at 0.025 g/mL resin dosage. The results obtained show that among the 22 resins investigated, the two resins with sulphonic groups, that is, G-26 and MTS9570, have the strongest adsorption affinity for Cd(II) ions.

The Langmuir, Freundlich, and Temkin adsorption models were used for the mathematical description of the adsorption of Cd(II) ions onto resins. The result showed that the studied adsorption processes fitted well to the Langmuir adsorption isotherm, which means monolayer uniform adsorption well describes the mechanism for Cd(II) adsorption onto the surface of G-26 and MTS9570 resins. From the Langmuir isotherm, the maximum Cd(II) adsorption capacity of the resin was 78.125 mg/g for G-26 and 51.02 mg/g for MTS9570.

The presented study led to an invention [52], which relates to the removal of cadmium ions using resin fibers bearing sulfonic acid group from aqueous systems, including but not limited to industrial wastewater, contaminated water streams in commercial and agricultural production, and polluted rivers and lakes. A novel adsorption process using low dimensional styrene-divinylbenzene (SDVB) resins (i.e., resin fibers) bearing sulfonic acid group fabricated through electrospinning and sulfonation method demonstrated excellent efficiency for Cd(II) ion removal from aqueous systems under desired conditions. The loaded resin could be recycled with a customized elution process using hydrochloric acid solution, sodium citrate solution, or a mixture of them.

References

[1] S. Anwar, F. Khan, S. Caines, R. Abbassi, Y. Zhang, ''Influence of chloride and pH on the pitting mechanism of Zn-Ni alloy coating in sodium chloride solutions''. *Can.J. Chem. Eng. 2021, 99, 680–694.* *https://doi.org/10.1002/cjce.23920*

[2] A. Benettayeb, A. Morsli, K. Z. Elwakeel, M. F. Hamza, E.Guibal, ''Recovery of Heavy Metal Ions Using Magnetic Glycine-Modified Chitosan—Application to Aqueous Solutions and Tailing Leachate''.*Appl. Sci. 2021, 11, 8377.* *https://doi.org/10.3390/app11188377*

[3] M.Awual, M.Hasan, A.Asiri, M.Rahman, ‘‘Cleaning the arsenic(V) contaminated water for safe-guarding the public health using novel composite material’’.*Compos. Part B-Eng. 2019, 17115, 294 – 301.* https://doi.org/10.1016/j.compositesb.2019.05.078

[4] M. Alvand, F. Shemirani, ‘‘preconcentration of trace cadmium ion using magnetic graphene nanoparticles as an efficient adsorbent’’.*Microchim. Acta 2014, 18,181–184.* https://doi.org/10.1007/s00604-013-1094-4

[5] J. Godt, F. Scheidig, C. Grosse-Siestrup, V. Esche, P.Brandenburg, A. Reich, D. A. Groneberg, ‘‘The toxicity of cadmium and resulting hazards for human health’’. *J. Occup. Med. Toxicol. 2006, 1: 22, 1– 6.* https://doi.org/10.1186/1745-6673-1-22

[6] G. Genchi, M. S. Sinicropi, G. Lauria, A. Carocci, A. Catalano, ‘‘the Effects of Cadmium Toxicity’’. *Int. J. Env. Res. Pub. He. 2020, 17(11), 3782.*

https://doi.org/10.3390/ijerph17113782

[7] M. Benavides, S. Gallego, M. Tomaro, ‘‘Cadmium toxicity in plants’’.*Brazilian Journal of Plant Physiology 2005, 17, 21.* https://doi.org/10.1590/S1677-04202005000100003

[8] N. Siva Kumar, V. Dharmendra, V. Sreenivasulu, M. Asif, A. A. Ibrahim, V. Balaram, ‘‘Separation and Pre-Concentration of Pb and Cd in Water Samples Using 3-(2-hydroxyphenyl)-1H-1,2,4-triazole-5(4H)-thione (HTT) and Their Determination by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)*’’Metals 2017, 7(7), 240.* https://doi.org/10.3390/met7070240

[9] S. Kaur, K. Kaur, A. Kaur, J. Singh Aulakh, ‘‘$SiO_2@Fe_3O_4$-SB nano-hybrids as nanosorbent for preconcentration of cadmium ions from environmental water samples’’.*Journal of*

Environmental Chemical Engineering 2020, 8, 103448. https://doi.org/10.1016/j.jece.2019.103448

[10] World Health Organization Ed., Guideline for Drinking-Water Quality, 4th ed., *World Health Organization, Geneva, Switzerland 2017.*

[11] T. K. Sen, M. V. Sarzali, ''Removal of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminium oxide (Al_2O_3): A kinetic and equilibrium study''.*Chem. Eng. J. 2008, 142, 256 –262.* https://doi.org/10.1016/j.cej.2007.12.001

[12] D. Bulgariu, L. Bulgariu, ''Potential use of alkaline treated algae waste biomass as sustainable biosorbent for clean recovery of cadmium(II) from aqueous media: batch and column studies'' *J. Clean. Prod. 2016, 112, 4525–4533.* https://doi.org/10.1016/j.jclepro.2015.05.124

[13] M. A. Naeem, M. Imran, M. Amjad, G. Abbas, M. Tahir, B. Murtaza, A. Zakir, M. Shahid, L. Bulgariu, I. Ahmad, ''Batch and Column Scale Removal of Cadmium from Water Using Raw and Acid Activated Wheat Straw Biochar''. *Water 2019, 11(7), 1438.* https://doi.org/10.3390/w11071438

[14] P. Sanga, Y. Iradukunda, J. C. Munyemana, ''Recycling of Alum from Water Treatment Residue and Reuse It as a Flocculating Agent for Raw Water Treatment''. *Journal of Geosciences and Environment Protection 2018, 6, 216–226.* https://doi.org/10.4236/gep.2018.612018

[15] A. Hashem, G. M. Taha, A. J. Fletcher, L. A. Mohamed, S. H. Samaha, ''Highly Efficient Adsorption of Cd(II) onto Carboxylated Camelthorn Biomass: Applicability of Three-Parameter Isotherm Models, Kinetics, and Mechanism''. *J. Polym. Environ. 2021, 29, 1630–*

1642.https://doi.org/10.1007/s10924-020-01991-6

[16] R. Rajumon, S. P. Aravind, S. Bhuvaneshwari, J. Ranjitha, P. Mohanraj, ‘‘Removal of cadmium heavy metal ions from wastewater by electrosorption using modified activated carbon felt electrodes’’.*Water Sci. Technol. 2020, 82(7), 1430–1444. https://doi.org/10.2166/wst.2020.425*

[17] J. Zhao, R. Su, A. Fieramosca, W. Zhao, W. Du, X. Liu, C. Diederichs, D. Sanvitto, T. C. H. Liew, Q. Xiong, ‘‘Ultralow Threshold Polariton Condensate in a Monolayer Semiconductor Microcavity at Room Temperature’’. *Nano Lett. 2021, 221, 3331–3339. https://doi.org/10.1021/acs.nanolett.1c01162*

[18] N. Kansara, L. Bhati, M. Narang, R. Vaishnavi, ‘‘Wastewater treatment by ion exchange method: a review of past and recent researches’’ *Environmental Science: An Indian Journal 2016, 12, 143–150.*

[19] S. Jiang, H. Sun, H. Wang, B. P. Ladewig, Z. Yao, ‘‘A comprehensive review on the synthesis and applications of ion exchange membranes’’.*Chemosphere 2021, 282, 130817. https://doi.org/10.1016/j.chemosphere.2021.130817*

[20] K. Dorfner, (1972) Ion Exchangers, Properties and Applications, *Ann Arbor Science, Newton, 177.*

[21] R. A. Silva, K. Hawboldt, Y. Zhang, ‘‘Application of resins with functional groups in the separation of metal ions/species – a review’’.*Min. Proc. Ext. Met. Rev. 2018, 39, 395–413. https://doi.org/10.1080/08827508.2018.1459619*

[22] S. Kocaoba, ‘‘Behaviour of Cadmium(II) Ions on Cation-Exchange Resins’’.*Adsorpt. Sci.*

Technol. 2003, 21, 831–840. https://doi.org/10.1260/02636170360744083

[23] J. Jachuła, D. Kołodynska, Z. Hubicki, ‘‘Removal of Cd(II) and Pb(II) complexes with glycolic acid from aqueous solutions on different ion exchangers’’.*Can. J. Chem. 2010, 88, 540–547.* https://doi.org/10.1139/V10-027

[24] M. H. Taha, ‘‘Sorption of U(VI), Mn (II), Cu(II), Zn(II), and Cd(II) from multi-component phosphoric acid solutions using Marathon C resin’’.*Environ. Sci. Pollut. R. 2021, 28, 12475–12489.* https://doi.org/10.1007/s11356-020-11256-3

[25] E. Pehlivan, T. Altun, ‘‘The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin’’.*J. Hazard. Mater. 2006, 134, 149–156.* https://doi.org/10.1016/j.jhazmat.2005.10.052

[26] E. Pehlivan, T. Altun,‘‘Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions from aqueous solution by Lewatit CNP 80’’ *J. Hazard. Mater. 2007, 140, 299–307.* https://doi.org/10.1016/j.jhazmat.2006.09.011

[27] S. M. Moosavirad, R. Sarikhani, E. Shahsavani, S. Z. Mohammadi, ‘‘Removal of some heavy metals from inorganic industrial wastewaters by ion exchange method’’. *J. Water Chem. Technol. 2015, 37, 191–199.* https://doi.org/10.3103/S1063455X15040074

[28] S. Kocaoba, G. Akcin, ‘‘Removal of chromium (III) and cadmium (II) from aqueous solutions' *Desalination 2005, 180, 151–156.* https://doi.org/10.1016/j.desal.2004.12.034

[29] S. Kocaoba, ‘‘Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals’’. *J. Hazard. Mater. 2007, 147, 488–496.* https://doi.org/10.1016/j.jhazmat.2007.01.037

[30] M. V. Srikanth, S. A. Sunil, N. S. Rao, M. U. Uhumwangho, K. V. Ramana Murthy, ‘‘ Review Ion-Exchange Resins as Controlled Drug Delivery Carriers’’. *Journal of Scientific Research 2010, 2, 597–611. Doi:10.3329/jsr.v2i3.4991*

[31] M. K. Jha, N. Van Nguyen, J. C. Lee, J. Jeong, J. M. Yoo, ‘‘ Adsorption of copper from the sulphate solution of low copper contents using the cationic resin Amberlite IR 120’’.*J. Hazard. Mater. 2009, 164, 948–953. https://doi.org/10.1016/j.jhazmat.2008.08.103*

[32] B. McKevitt, D. Dreisinger, ‘‘A comparison of various ion exchange resins for the removal of ferric ions from copper electrowinning electrolyte solutions Part II: Electrolytes containing antimony and bismuth’’. *Hydrometallurgy 2009, 98, 122–127.*

https://doi.org/10.1016/j.hydromet.2009.04.007

[33] A. J. Canner, S. E. Pepper, M. Hayer, M. D. Ogden, ‘‘Removal of radionuclides from a HCl steel decontamination stream using chelating ion exchange resins – Initial studies’’.*Prog. Nucl. Energ. 2018, 104, 271–277. https://doi.org/10.1016/j.pnucene.2017.10.007*

[34] T. M. Zewail, N. S. Yousef, ‘‘Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed’’.*Alexandria Engineering Journal 2015, 54, 83–90. https://doi.org/10.1016/j.aej.2014.11.008*

[35] E. C. Nnadozie, P. A. Ajibade, ‘‘Data for experimental and calculated values of the adsorption of Pb(II) and Cr(VI) on APTES functionalized magnetite biochar using Langmuir, Freundlich and Temkin equations’’. *Data in Brief 2020, 32, 106292. https://doi.org/10.1016/j.dib.2020.106292*

[36] N. Dizge, B. Keskinler, H. Barlas, ‘‘Sorption of Ni(II) ions from aqueous solution by Lewatit

cation-exchange resin''. *J. Hazard. Mater. 2009, 167, 915–926.* *https://doi.org/10.1016/j.jhazmat.2009.01.073*

[37] M.Hoque, Y.Yamauchi, R. Naidu, R. Holze, R. Saidur, Q. Qu, M. Rahman, N.Torad, M. Hossain, M. Kim, J. Kim, S. Ahmad, A. Rehman, M.Firoz, U.Luba, S.Chowdhury, A.N. Chowdhury, ''A Facile Synthesis of Hematite Nanorods from Rice Starch and Their Application to Pb(II) Ions Removal''. *Chemistry Select 2019, 4, 3730–3736.* *https://doi.org/10.1002/slct.201802462*

[38] I.Langmuir, ''the Constitution and Fundamental Properties of Solids and Liquids''. Part I Solids. *J. Am. Chem. Soc. 1916, 38, 2221–2295.* *https://doi.org/10.1021/ja02268a002*

[39] H.M.F.Freundlich, ''Uber die Adsorption in Losungen''.*Phys. Chem. 1906, 57, 385–470.*

[40] M.Temkin, V. Pyzhev, ''Kinetics of Ammonia Synthesis on Promoted Iron Catalysts''. *Acta Physicochim. URSS 1940, 12, 327–356.*

[41] C. S. T. Araújo, I. L. S. Almeida, H. C. Rezende, S. M. L. O.Marcionilio, J. J. L. Léon, T. N. de Matos, ''Elucidation of mechanism involved in adsorption of Pb(II) onto lobeira fruit (Solanum lycocarpum) using Langmuir, Freundlich and Temkin isotherms''. *Microchem. J. 2018,137, 348–354.* *https://doi.org/10.1016/j.microc.2017.11.009*

[42] G. C. Saha, M. I. U. Hoque, M. A. M. Miah, R. Holze, D. A.Chowdhury, S. Khandaker, S. Chowdhury, ''Biosorptive removal of lead from aqueous solutions onto Taro (Colocasiaesculenta (L.) Schott) as a low cost bioadsorbent: Characterization, equilibria, kinetics and biosorption-mechanism studies''. *Journal of Environmental Chemical Engineering 2017, 5, 2151–2161.* *https://doi.org/10.1016/j.jece.2017.04.013*

[43] S. Mustapha, D.Shuaib, M.Ndamitso, M. Etsuyankpa, A. Sumaila, U.Mohammed, M.B. Nasirudeen, ‘‘Adsorption isotherm, kinetic and thermodynamic studies for the removal of Pb(II), Cd(II), Zn(II) and Cu(II) ions from aqueous solutions using Albizia lebbeck pods’’.*Applied Water Science 2019, 9, 142.*https://doi.org/10.1007/s13201-019-1021-x

[44]H.I.Meléndez-Ortiz,B. Puente-Urbina,J. A.Mercado-Silva, L.García-Uriostegui, ‘‘Adsorption performance of mesoporous silicas towards a cationic dye. Influence of mesostructure on adsorption capacity’’. *Int. J. Appl. Ceram. Tec. 2019, 16, 1533–1543.* https://doi.org/10.1111/ijac.13179

[45] I. Bekri-Abbes, S. Bayoudh, M. Baklouti, ‘‘Converting Waste Polystyrene into Adsorbent: Potential Use in the Removal of Lead and Cadmium Ions from Aqueous Solution’’. *J. Polym. Environ.2006, 14, 249–256.* https://doi.org/10.1007/s10924-006-0018-3

[46] D. Kołodynska, Z. Hubicki, ‘‘Application of novel complexing agent in sorption of heavy metal ions from wastewaters on ion exchangers of various types’’. *Annales UMCS, Chemistry 2009, 64,227–245. DOI: 10.2478/v10063-008-0017-4*

[47] M.Hoque, D.Chowdhury, R. Holze, A. Chowdhury, M. Azam, ‘‘Modification of Amberlite XAD-4 resin with 1,8-diaminonaphthalene3 for solid phase extraction of copper, cadmium and lead, and its4 application to determination of these metals in dairy cow’s milk’’ *Journal of Environmental Chemical Engineering 2015, 3, 831–842.* https://doi.org/10.1016/j.jece.2015.03.020

[48] C. Wang, C. Chang, C. Chen, ‘‘Study on Metal Ion Adsorption of Bifunctional Chelating/Ion-Exchange Resins’’. *Macromol. Chem. Phys. 2001,202, 882–890.*

[49] F. Ge, M. M. Li, H. Ye, B. X. Zhao,‘‘Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic *nanoparticles’’ J. Hazard. Mater. 2012, 211–212, 366–372.* https://doi.org/10.1016/j.jhazmat.2011.12.013

[50] C. Chen, H. Liu, T. Chen, D. Chen, R. L. Frost, ‘‘An insight into the removal of Pb(II), Cu(II), Co(II), Cd(II), Zn(II), Ag(I), Hg(I), Cr(VI) by Na(I)-montmorillonite and Ca(II)-montmorillonite *’’Appl. Clay Sci.2015, 118, 239–247.* https://doi.org/10.1016/j.clay.2015.09.004

[51] A. Bożęcka, M. Orlof-Naturalna, S. Sanak-Rydlewska, ‘‘Removal of lead, cadmium and copper ions from aqueous solutions by using ion exchange resin C 160’’. *Gospod. Surowcami Min. 2016, 32,129–139.* https://doi.org/10.1515/gospo-2016-0033

[52] H. Zeng, Z. Zhao, Y. Zhang, S. Elfeghe, “Removal of cadmium from aqueous systems using resin fibers bearing sulfonic acid group”, *US Patent* Application No. 63/610,975, Date 12/15/2023.

Chapter 4

Adsorption of Cu(II) ions from aqueous solutions using ion exchange resins with different functional groups

Preface

A version of this chapter has been published in the **Can J Chem Eng. 2022.** *I produced the work alongside my co-authors; Yahui Zhang,* Lesley James *and* Shams Anwar. *I am the main author. I conducted all lab experiments, calculated parameters for isotherms, kinetic and dynamic studies. I prepared the first draft of the manuscript and subsequently revised the manuscript based on the co-authors' and peer review feedback. Co-author, Yahui Zhang assisted in the development of concept, design of methodology, reviewing and editing the draft, and reviewing and revising the new version of the manuscript. Co-author,* Lesley James *supported in the project supervision, Co-author,* Shams Anwar *supported in the data and process analysis, reviewing and editing the draft, reviewing and revising the new version of the manuscript.*

Abstract

The extraction of heavy metals from industrial effluents using efficient adsorbents is crucial for wastewater treatment and beneficial for metal recycling. In this study, the removal of Cu(II) from an acidic solution by commercial resins Dowex G-26 and Puromet™ MTS9570 was investigated. The influence of contact time, solution concentration, pH, temperature, and resin dosage on the adsorption process were studied with batch technique. The optimum adsorption conditions were obtained at a concentration of 1100 mg/L Cu^{2+}, contact time of 30 min, pH 3.5 and the resin dosage of 0.025g/mL for removal of 99.9% and 90% of copper ions by G-26 and MTS9570, respectively. The experimental data of copper adsorption were analyzed using the

Langmuir, Freundlich, and Temkin isotherm models. The highest metal uptakes of 41.67 and 37.70 mg/g were observed for Dowex G-26 and MTS9570, respectively. It was found that both resins had higher adsorption capacities than the substances reported in the literature. The adsorption kinetic studies showed that the copper adsorption process could be better described by the pseudo-second- order model. Adsorption occurs spontaneously under endothermic conditions, which indicates the endothermic nature of the process.

Keywords: adsorption isotherms, copper(II), desorption, ion-exchange resins, kinetics, wastewater

4.1 Introduction

Water pollution of heavy metals is ever-increasing due to the discharge of industrial effluents[1].The extraction of heavy metals from these effluents using efficient adsorbents is crucial for wastewater treatment and beneficial for metal recycling. Heavy metals in wastewater are mainly being emitted from hydrometallurgy, electroplating, tanning, artificial fertilizers, herbicide production, dyeing, textile, motor, as well as energetic industries [2-5]. Heavy metals such as Cr(III,VI), As(III,V), Cd(II), Pb(II), Cu(II), Zn(II) and Hg(II) can endanger the environment and living organisms [6-12]. Among the various wastewater treatment technologies available, ion exchange is one of the most commonly used processes [13-15]. The main advantages of this method are the recovery of valuable metals, selectivity, reduced sludge production, and conformity with discharge specifications. The application of anion exchange resins is justified for specific wastewaters that contain heavy metal ions along with complexing agents [16].

The removal of dissolved metals through ion exchange onto low-cost media such as synthetic resins can be an attractive and inexpensive process [17, 18]. Heavy metals have caused increased concern for human health and aquatic ecosystems. Ion exchangers are used in a wide variety of industrial processes. Heavy metal cations can be recovered from wastewater through the use of inorganic substances [19]. Sulfonated styrene-divinylbenzene copolymers provide strong acidic cation exchangers in modern ion exchangers, such as the styrene-divinylbenzene copolymer. The heavy metal-selective ion exchangers, which have a sufficiently high affinity for heavy metals, can be used to eliminate heavy metals selectively. In industrial wastewater treatment, however, this method has not been adapted extensively. Waste streams can be cleaned effectively with ion exchange [18-24]. Metals in various environmental samples can be identified using various separation techniques, including solvent extraction, ion exchange, co-precipitation, membrane processes, and sorption [25-27]. In the treatment of industrial wastewater, ion exchange is one of the most popular methods [28, 29].

Copper is an important component for construction, machinery works, transportation, and weapons, and is a vital part of keeping the nervous system functioning [30]. However, when it exceeds its acceptable limit, it can cause diseases, including Alzheimer's, Parkinson's, and amyotrophic lateral sclerosis. The sulphate form of copper is toxic and is discharged from iron and steel plants, and in mining effluents [31, 32]. The highest allowable limit for copper in drinking water according to the WHO guideline of 2017 is 2 mg/L [33].

There have been several studies conducted on the exchange capacity of Cu(II) ions from acidic aqueous solutions with two different types of commercial resins. Pehlivan and Altun [17] studied the effect of various parameters on Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} ion exchange on Dowex 50W synthetic resin. The maximum recovery rates of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} were observed at pH ranges 8-9 for batch-sorbent Dowex 50W. In terms of metal ions sorbed, the amounts calculated were 4.1, 4.6, 4.7, 4.8, and 4.7 equiv/gram dry resin for Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+}, respectively. An optimum set of conditions was used to test the method's precision. As the series progressed, the selectivity increased: $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. Increasing the atomic number, valence, and degree of ionization of exchanged metals increases the selectivity of the $–SO_3H$ group of the resin. A new compounding agent was evaluated by Dorota Kolodyńska [1] in the treatment of waters and wastewaters for heavy metal removal. A novel chemical reagent, N, Nbis(carboxymethyl)glutamic acid (GLDA), was used to remove Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) from domestic water and industrial wastes. A batch and column study was conducted to examine the effects of contact time, concentrations, pH, temperature, and interference ions on the sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with GLDA on ion exchangers Lewatit MonoPlus MP 500, Amberlite IRA 958, and Diaion CR-20. The pseudo second-order equation shows that sorption is favoured with a pH of 9.0.

Wang et al., [34] used waste amidoxime chelating resin for adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) ions in solution to remove and recover these metals. The batch experiments explored the effects of the initial metal ions concentration, contact time, temperature, and solution pH on the adsorption performance of the metal ions. Results indicated that pH 4 was optimum. An adsorption isotherm consistent with the Langmuir model was determined by kinetic studies. The adsorption process corresponded with the pseudo-second-order kinetic model. The adsorption capacity of the resin for Pb^{2+}, Cu^{2+}, $Zn^{2+}$and Cd^{2+} measured at room temperature was 114.6, 93.4, 24.4 and 20.7 mg/g, respectively.

There have been many studies on adsorption of copper ions using various ion exchange resins, including Dowex 50W, which was invented by Pehlivan and Altun [17]. Purolite C-104 and Lewatit CNP-80, which were investigated by Jha et al.[35], and Lewatit Mono Plus MP 500 and Amberlite IRA 958, which were explored by Kołodyńska [1].

In this study, the comparison of the exchange capacity of Cu(II) ions from acidic aqueous solutions with a new two different commercial resins, Dowex G-26 with a sulfonic function group, and Puromet™ MTS9570 with a phosphonic and sulfonic function group were investigated by batch technique. The effects of experimental parameters, including agitation time, solution pH, metal ion concentration, amount of adsorbent, and temperature, and adsorption isotherms, were studied in order to obtain the optimum conditions for maximum removal of Cu(II) ions from an acidic aqueous solution.

4.2 Experimental Details

4.2.1. Materials

Commercial synthetic resins Dowex G-26 (Sigma Aldrich) in hydrogen form and Puromet™ MTS9570 (Purolite US), Copper sulfate pentahydrate $CuSO_4.5\ H_2O$ were purchased from A&C American Chemicals Ltd. (Québec-Canada). The properties of the resins are given in Table 1. All the chemicals used to prepare reagent solutions were of analytical reagent grade.

4.2.2. Apparatus

Instruments used in this study were as follows: A wavelength dispersive X-ray fluorescence (WDXRF) spectrometer (model Supermini200) was used for metal concentration analysis; an electric shaker (model Promax 2020) was used for adsorption tests with 20 ml solutions in 125 mL flasks. The pH measurements were performed with a pH Meter (model Orion Star A211).

Table 4.1: Physical and chemical properties of resins.

Characteristics	G-26	MTS9570
Matrix	Styrene-DVB	Polystyrene- DVB
Ionic form as shipped	H^+ form	H^+ form
Functional group	Sulfonic	Phosphonic and Sulfonic
Appearance	uniform particle size	Spherical Beads
Structure	gel	Macroporous
Capacity	2.0 eq/L	18 g/L
Bed size	0.65mm ± 0.05	0.315 – 0.850 mm
Uniformity Coefficient	1.1	1.4
Water retention	45 – 52%	55 - 70 %
Specific Gravity	1.22 g/mL	1.12 g/mL

4.2.3 Experimental procedure

4.2.3.1 Preparation of resins

Before using the resins in the adsorption experiments, the ion-exchange resins were well washed with distilled water three times to remove all impurities. They were then dried at room temperature for 18 days. The dried resins were stored in dry bottles and were used for further experiments.

4.2.3.2 Adsorption studies

A standard solution of copper (1100 ppm) was prepared by dissolving a 4.322g of copper sulfate pentahydrate $CuSO_4.5\ H_2O$ in 1000 ml distilled water and the pH was adjusted by adding 0.1mol/L HCl. The adsorption performances of G-26 and MTS 9570 for Cu^{2+} ions were investigated by batch experiments at different temperatures. Batch sorption experiments were conducted at a constant volume of 20 ml metal ions solution and using different doses of dry resins, from 0.005 to 0.03 g/mL. The adsorption behaviour of metal ions by the adsorbents was studied in the pH range of 1.5 - 4.5. The solution pH was adjusted by 0.1 mol/L HCl. Samples of metal solution and resins in 125 mL flasks were shaken in an electric shaker at different contact times, ranging from 5 to 180 min and at the fixed speed of 150 rpm. After reaching the equilibrium stage, the solution was filtered and analyzed by XRF. The batch adsorption experiments were performed in triplicate. The reproducibility of the measurements was within 5%. The adsorption capacities of G-26, and MTS9570 exchangers and the percentage removal of Cu(II), were calculated using the following Equations, (4.1) and (4.2), respectively.

$$Q = \frac{(C_i - C_e)V/1000}{M} \tag{4.1}$$

And % removal of Cu (II) ions = $\frac{(C_i - C_o)}{C_i}$ x 100 (4.2)

where Q is the adsorption capacity in mg/g at time t, C_i, C_o and C_e are the initial, final and equilibrium concentrations of Cu(II) in mg/L, respectively, V is the volume of Cu(II) solution in ml and, M is the total amount of resin in grams (g).

4.2.3.3 Desorption studies

Desorption is an important stage of the adsorption processes, where the adsorbent will be regenerated, and metal ions can be potentially recovered.

The elution behaviour of Cu(II) ions adsorbed on G-26 and MTS9570 resins was studied using a 15% v/v HCl solution at various elution time and HCl solution volume at room temperature (20°C). The desorption percentage is calculated from the following equation:

% Desorption of Cu(II) ions = $\boldsymbol{\frac{(C_o.V)}{q.m}}$ **x 100** (4.3) where C_o (mg/L) is the final copper concentration in the metal solution at desorption equilibrium; V (L) is the HCl volume; q (mg/g) is the initial amount of copper ions bound per unit weight of resin; and m (g) is the amount of resin.

4.3 Result and Discussions

4.3.1 Exploration of Cu removal using resins

Selection of the proper resins for the removal of copper ions from acidic solution is investigated. A good adsorbent must have good mechanical and kinetic characteristics in order to have high adsorption of metal ions [8]. In this work, a series of adsorption experiments was conducted for adsorption of copper ions from an acidic system at constant operating conditions of pH, temperature, adsorption time, agitation speed and metal concentration. Various commercial resins with different functions groups from different suppliers were tested at the dosage range of 0.005-0.025 g/mL.

As shown in Figure 4.1, fifteen resins with functions groups, including sulfonic (IR120 H and G-26), amino-phosphonic (SIR 500, S940, S950 plus, and IRC747), iminodiacetic (TP208, TP207, S930EPlus, IRC784Iand S930 plus), Aminomethylphosphonic (TP260), bis-picolylamine (TP220), sulfonic / trimethylamine (MBD-15-SC), and sulfonic/phosphonic (MTS9570), have high adsorption rates for Cu^{2+} ions.

Figure 4.2 presents eight resins with functions groups, including N-methylglucamine (S108), carboxylic (WAG RTI 26600 and Mac-3), thiourea (MTS9140 and TP214), di-ethylhexyl phos phat (Lewatit vp oc 1026), isothiouronium (MTS9200), and trimethyl ammonium (Amberjet 4400 Cl) which have low adsorption performance for cadmium ions. In this research, adsorption studies on the removal of Cu^{2+}ions from acidic solution of two different resins, Dowex G-26 and MTS 9570, with two different functional groups, have been chosen from the high adsorption class.

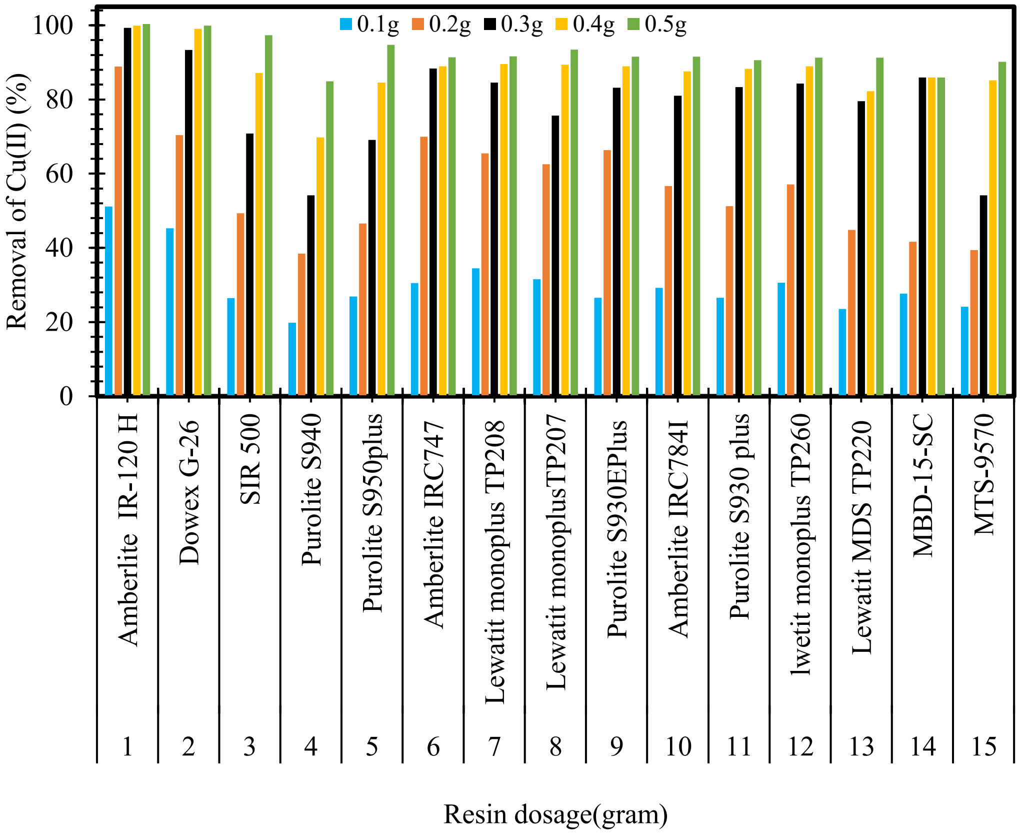


Figure 4.1: Resins with high removal rate of Cu(II).

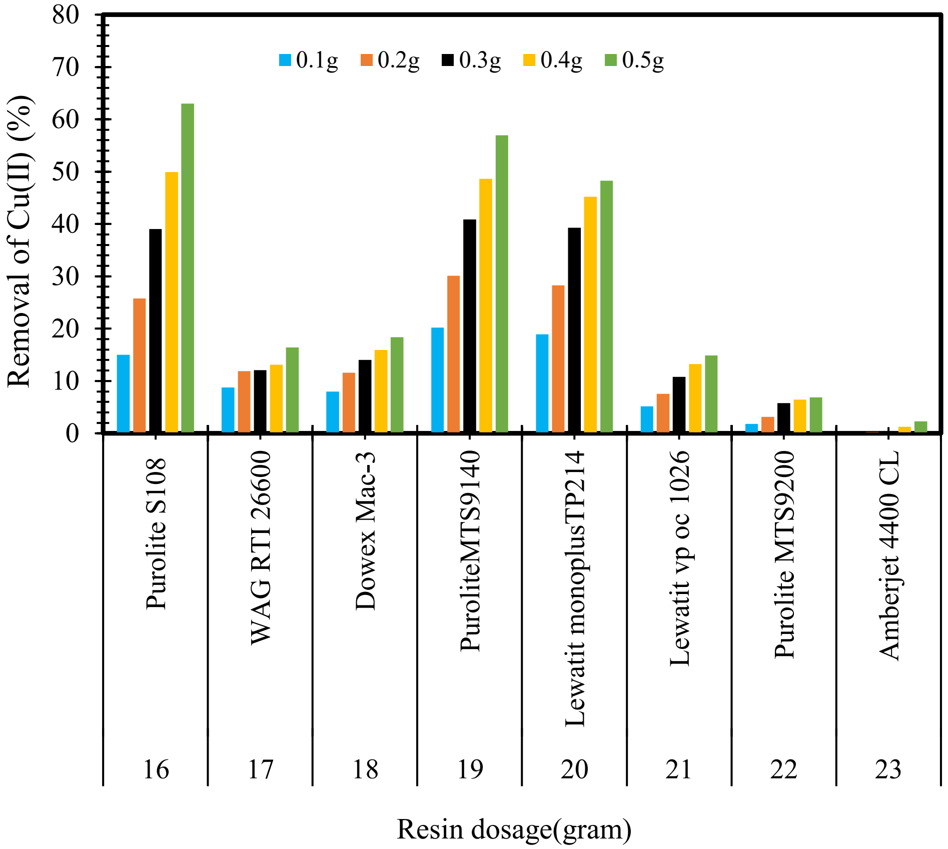


Figure 4.2: Resins with low removal rate of Cu(II).

4.3.2 Effect of agitation time

A series of adsorption time studies for copper ions was carried out with the initial metal concentration of 1100 mg/L at 20±1°C. The adsorption experiments were conducted at time periods from 5 to 180 min, in pH 3.5 and 0.025g/mL of resins. Figure 4.3 shows the removal % of Cu^{2+} ions adsorbed as a function of contact time. It can be seen that equilibrium uptake for both resins occurred after 30 min. The same equilibrium times were obtained in other work for removal of Cu^{2+} using these two resins by the authors. However, the removal of Cu^{2+} ions for the resins was 99.9% and 90% for G-26 and MTS9570, respectively.

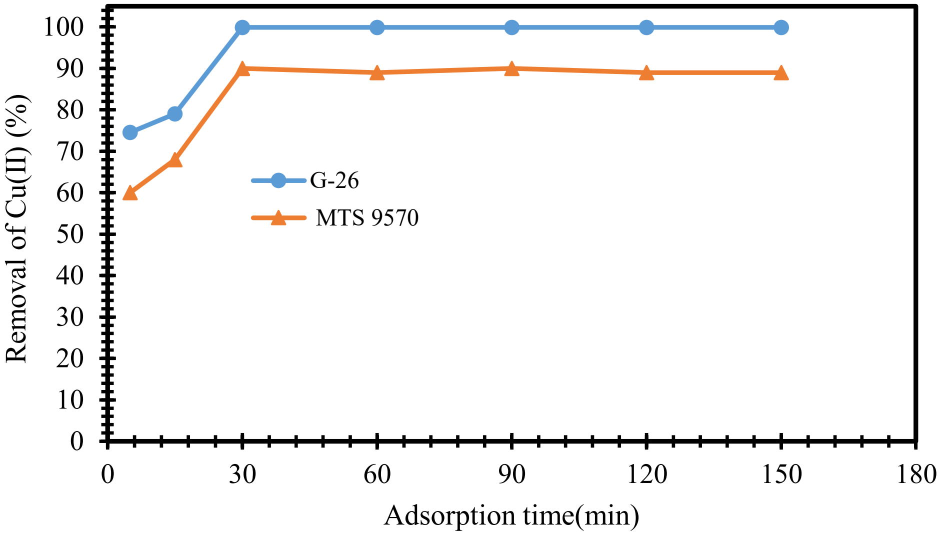


Figure 4.3: Effect of agitation time on adsorption of Cu(II) using G-26 and MTS9570 exchange resins.

4.3.3 Effect of resin dosage

Figure 4.4 represents the removal of copper as a function of resin dosage by G-26 and MTS9570 resins at the solution pH of 3.5, and 1100 mg/L concentration. Resins amounts varied from 0.005 to 0.03 g/mL resin and equilibrated for 30 minutes. The removal percentage of Cu(II) was directly proportional to the adsorbent dosage; this can be attributed to the availability of surface area. The maximum adsorption of copper of 99.9% for G-26 and 90% for MTS9570 was obtained at 0.025g/mL of resin dosage. Further increase in resin does not improve the adsorption efficiency of copper from the solution, and this agrees with results reported by Rengaraj et al.[36]. The optimum adsorbent amount for further adsorption experiments was chosen as 0.025 g/mL for both resins.

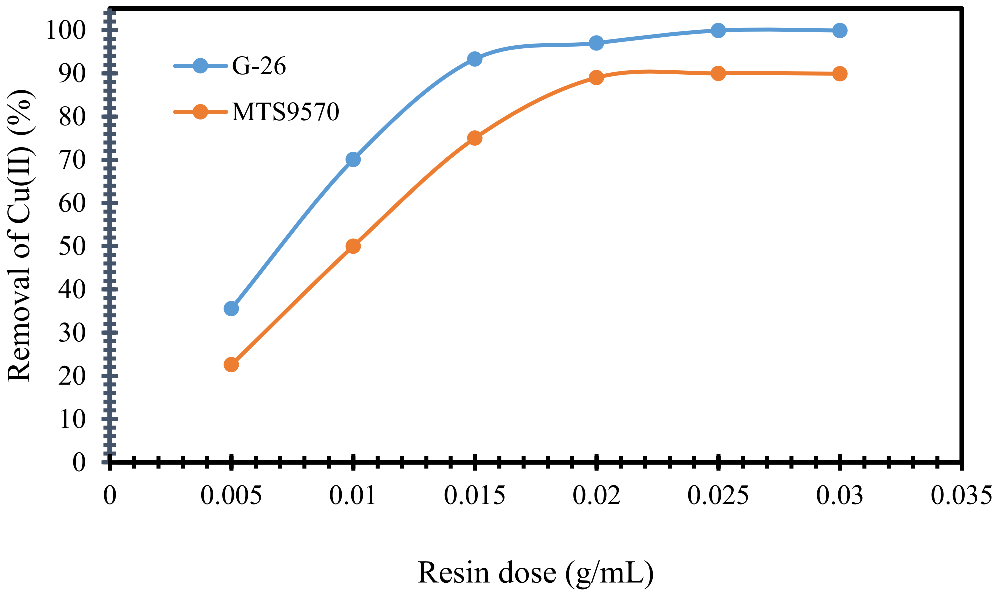


Figure 4.4: Effect of resin dosage on adsorption of Cu(II) using G-26 and MTS9570 exchange resins.

4.3.4 Effect of pH

The solution pH presents one of the most important parameters affecting metal ions adsorption, because of a strong competition between hydrogen ions and metal ions. The effects of initial pH on the removal of Cu(II) by G-26 and MTS9570 ion exchange resins were investigated by adjusting the pH in a range of 1.5 - 4.5. The results presented in Figure 4.5 show that copper adsorption increased with increasing pH. The optimum pH for copper adsorption was obtained at pH 3.5 for both resins. The low adsorption of copper ions at a lower pH value can be attributed to the high metal concentration and mobility of hydrogen ions, according to Jha et al.,[37].

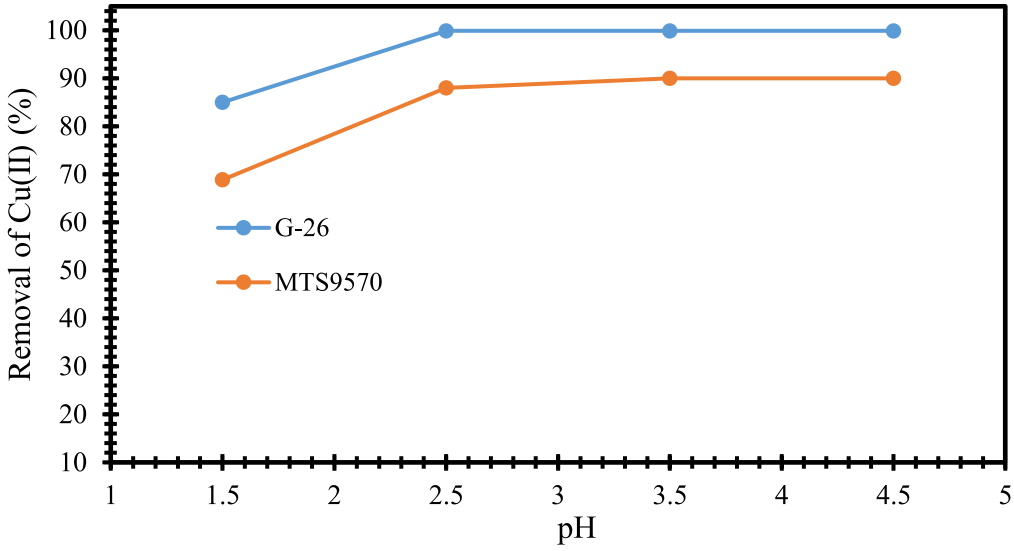


Figure 4.5: Effect of pH on adsorption of Cu(II) using G-26 and MTS9570 exchange resins.

4.3.5 Effect of temperature

The effect of temperature on Cu(II) removal for both resins was studied at different temperatures 20,40,60 and 80°C as shown in Figure 4.6.

Figure 4.6 shows the relationship between the extent of adsorption and temperature. The removal efficiencies increased slightly with increases in temperature, which suggests an endothermic process of divalent cations onto both resins [17]. The influence of temperature was relatively low, which can be explained by the fact that the removal mechanism is merely that of ion exchange. The uptake of Cu(II) ions on G-26 and MTS9570 increases slightly with increasing temperature; this indicates the monolayer coverage of the surface area of both resins by Cu(II) ions.

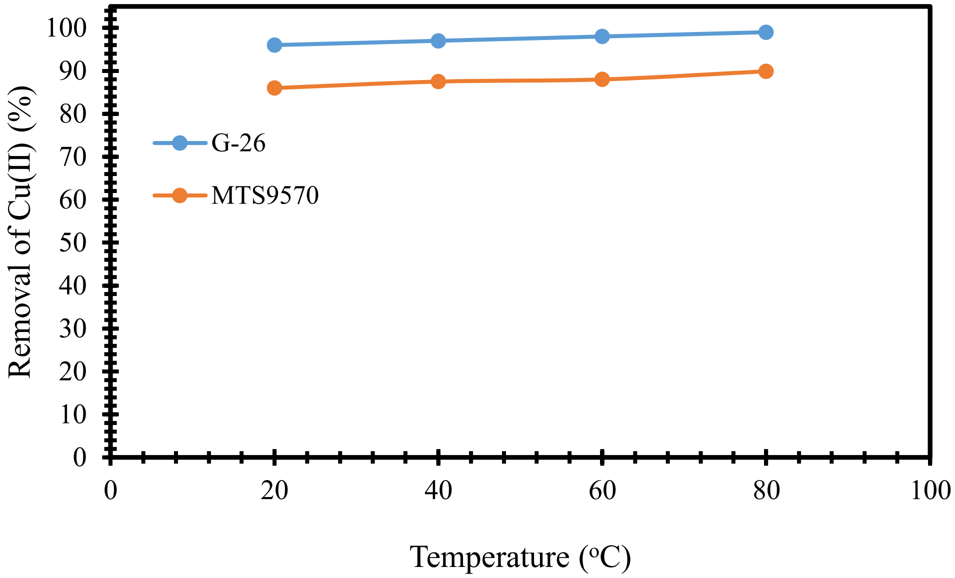


Figure 4.6: Effect of temperature on adsorption of Cu(II) using G-26 and MTS9570 exchange resins.

4.3.6 Effect of initial metal ion concentration

The adsorption experiments of Cu(II) ions were carried out at the initial concentration range of (80 -1400 mg/L), with pH values of 3.5 for both resins, a temperature of 293 K, and 30 min of contact time for both resins. As shown in Figure 4.7, at the range (80 -1100 mg/L) of initial metal concentrations, the metals adsorption percentages of Cu^{2+} remain constant at 99.9% and 90% for G-26 and MTS9570, respectively. Then it starts to decrease. This decrease of adsorption efficiency of resins with an increase of Cu^{2+} concentration can be attributed to a low surface area for the ion exchange process being available (Zewail and Yousef) [38].

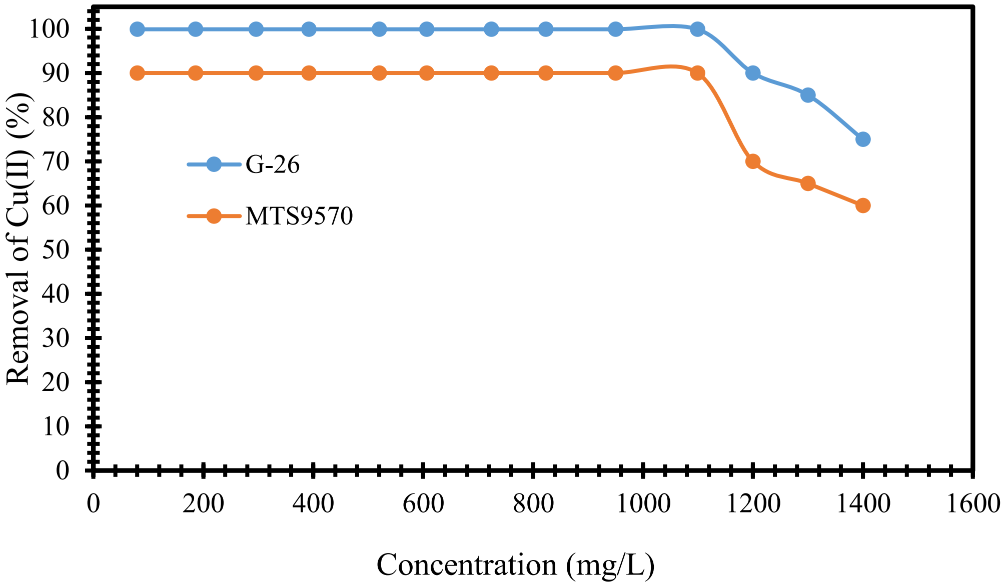


Figure 4.7: Effect of concentration on adsorption of Cu(II) using G-26 and MTS9570 exchange resins.

4.3.7 Adsorption isotherms

The adsorption experimental equilibrium data are commonly described by an isotherm model, the parameters of which express the relationship between the resin adsorption capacity (mg/g) and metal concentration (mg/L). In order to verify the performance of G-26 and MTS 9570 resins in adsorption of Cu(II) ions, Langmuir [39], Freundlich [40], and Temkin[41] equations are used.

The Langmuir adsorption isotherm describes a monolayer uniform adsorption of adsorbate metal ions on the surface of the adsorbent. The linear form of the Langmuir isotherm equation is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad (4.4)$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), Q^0(mg/g) and b (L/mg) are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

In Table 4.4, q_e of the G-26 and MTS9570 resins for copper(II) sorption are compared with other adsorbents reported in the literature. The adsorption capacity of G-26 and MTS9570 for copper(II) is more than that of other adsorbents, therefore they have very good potential for removing copper(II) from aqueous solutions.

The Freundlich model is based on heterogeneous surfaces. The linear form of the Freundlich isotherm equation is represented as follows:

$$log q_e = log K_F + \frac{1}{n} log C_e \tag{4.5}$$

where K_F is the adsorption equilibrium constant related to the adsorbent capacity, and *1/n* is the parameter related to the adsorption intensity.

The Temkin isotherm assumes that the interaction between adsorbate and adsorbent which causes the heating of adsorption is due to repulsion forces. The linear form of the Temkin equation is given by the following equation.

$$q_e = \mathrm{B} \ln (K_T) + \mathrm{B} \ln (C_e) \tag{4.6}$$

And $\mathrm{B} = \frac{RT}{b_T}$

where K_T (L/g) , and B (J/mol) are the Temkin isotherm and heat of sorption constants, respectively. R= universal gas constant (8.314J/mol/K), and T= Temperature at 298K.

The Langmuir, Freundlich, and Temkin isotherms of the adsorption of Cu(II) on G-26 and MTS9570 are presented in Figures 4.8 - 4.10, respectively. The Langmuir, Freundlich and Temkin isotherm parameters for adsorption of copper(II) ions onto chelating resins are calculated by using isotherms, and their correlation coefficients are listed in Table 4.2. Comparison of the correlation coefficients values shows that adsorption of Cu(II) onto G-26 and MTS9570 resins is fitted better by the Langmuir model (R^2 = 0.9991- 0.9981) than Freundlich (R^2 = 0.9896 - 0.9966) and Temkin models (R^2 = 0.9819 - 0.9744). The highest copper adsorption capacities of 41.66 and 37.7 mg/g were observed for Dowex G-26 and MTS9570, respectively. A comparison of adsorption capacity of G-26 and MTS9570 resins with those of different types of adsorbents in recent references is shown in Table 4.3. The data presented in Table 4.3 reveal that, generally, the resins examined in this study have a better efficiency for copper ions' adsorption than the previously reported adsorbents. Thus, they have very good prospective application for removing Cu(II) from aqueous solutions. The Langmuir, Freundlich, and Temkin isotherm of the adsorption of Cu(II) on G-26 and MTS9570 as presented in Figures 4.8 - 4.10.

Table 4.2: The isotherm parameters for Cu(II), on G-26 and MTS9570.

	G-26	MTS9570
Langmuir isotherm		
Q^0 (mg/g)	41.666	37.7
b (L/mg)	0.25	0.27
R^2	0.999	0.998
Freundlich isotherm		
K_F (mg/g)	19.16	20.52
n	6.1	8.4
R^2	0.989	0.996
Temkin isotherm		
b_T	156.9	165.7
B	15.79	14.79
R^2	0.981	0.974

Table 4.3: Comparison of maximum adsorption capacity of G-26 and MTS9570 resins with some other adsorbents for the adsorption of Cu(II).

Adsorbent	**Sorption capacity for Cu(II)(mg/g)**	**Conditions**	**References**
Amberlite IR-120	21.86	pH = 8, 20°C	[42]
Amberjet 1500H	24.57	pH = 5.8,25°C	[43]
Amberjet 252H	11.74	pH = 5.8,25°C	[43]
1200H	26.73	pH = 5.8,25°C	[44]
Purolite A830	32.76	pH = 7-9, 25°C	[45]
Ca-Mt	6.61	pH = 4, NA	[45]
Na-Mt	9.66	pH = 4, NA	[46]
1,8-DAN/XAD-4	13.98	pH = 6-7, NA	[47]
Lewatit MonoPlus MP 64	26.52	pH = 6-9, 25°C	[47]
Purolite S-920	29.52	pH = 6-9, 25°C	[49]
CR-10	26.88	pH = 5, 25°C	[48]
CR-15	16.52	pH = 5, 25°C	[48]
G-26	41.66	pH = 3.5, 20°C	This work
MTS9570	37.7	pH = 3.5, 20°C	This work

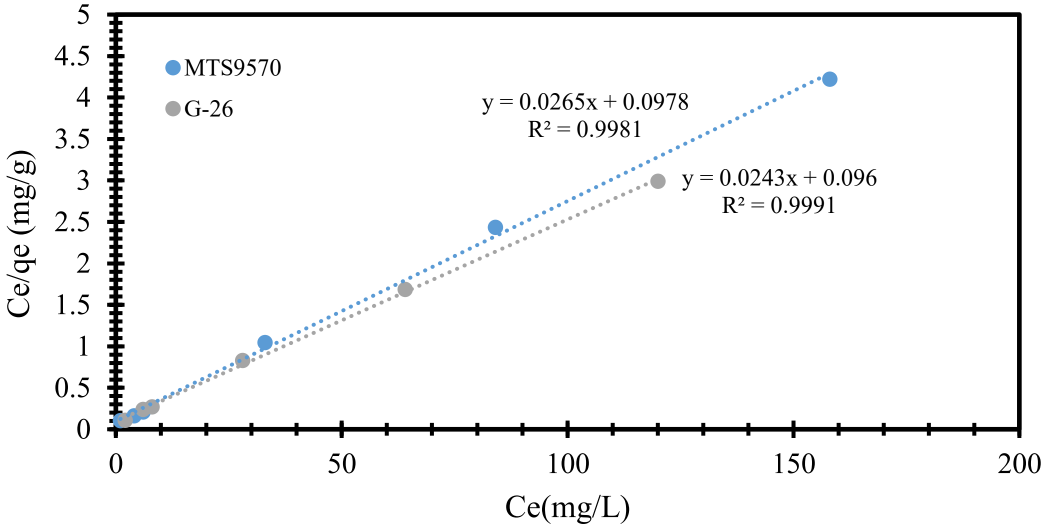


Figure 4.8: Langmuir isotherm of Cu(II) adsorption on G-26 and MTS9570.

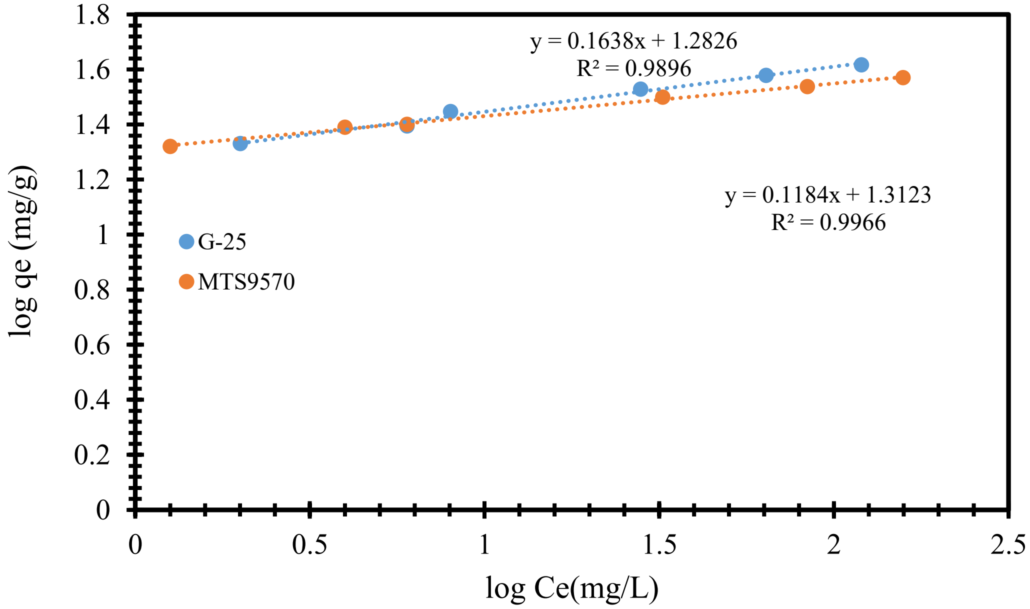


Figure 4.9: Freundlich isotherm of Cu(II) adsorption on G-26 and MTS9570.

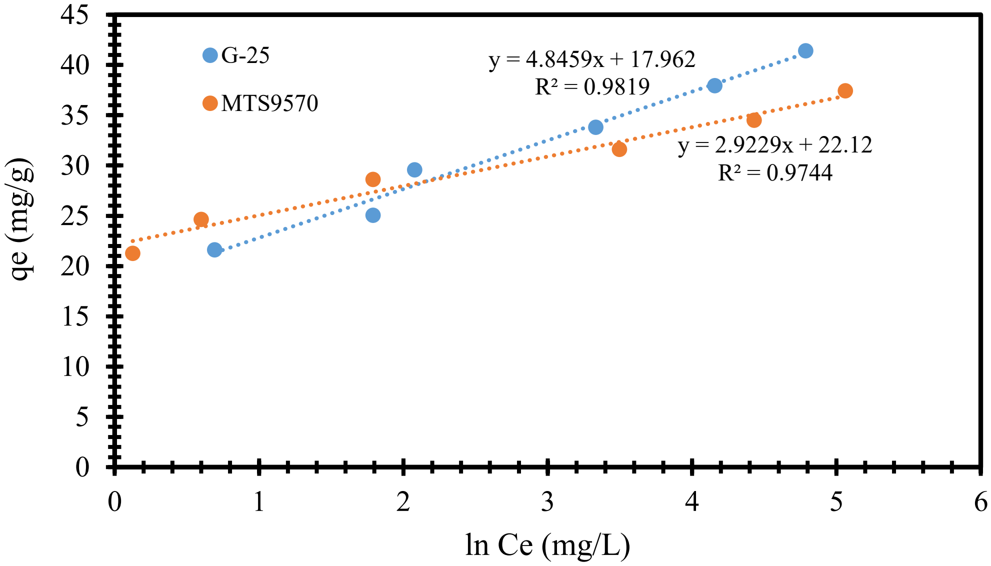


Figure 4.10: Temkin isotherm of Cu(II) adsorption on G-26 and MTS9570.

4.3.8 Adsorption kinetics

The adsorption kinetics of Cu(II) ions with G-26 and MTS9570 were investigated using Lagergren pseudo first order and pseudo-second-order models, for equations (4.7) and (4.8), respectively.

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \qquad (4.7)$$

where q_t, q_e are the amounts of the metal ions adsorbed (mg/g) at equilibrium and at contact time t (min), respectively; k_1 (min^{-1}) is the first order rate constant. The plots of ln $(q_e - q_t)$ versus t were presented in Figure 4.11, and the rate constants (k_1) and calculated equilibrium adsorption capacities, q_e (cal.), were depicted in Table 4.4.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (4.8)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo second-order adsorption reaction. The plots of $\frac{t}{q_t}$ versus t are shown in Figure 4.12 and the rate constants (k_2) and calculated equilibrium adsorption capacities, q_e (cal.) are presented in Table 4.4. From Table 4.4, it can be observed that the calculated equilibrium adsorption capacities, q_e (cal.) of the pseudo-first order kinetic model were not in accordance with the experimental adsorption capacities q_e (exp.). Moreover, R^2 of the plots for copper ions were not good (0.352, 0.256) for G-26 and MTS9570, respectively. Therefore, it is suggested that the adsorption of Cu(II) onto selected resins cannot be described by the pseudo first order model. As for the pseudo-second-order model, R^2 for the slopes were close to one for both resins and the calculated q_e values were close to the experimental q_e values. It was possible that the adsorption of Cu(II) onto G-26 and MTS9570 exchangers followed a pseudo-second order kinetics.

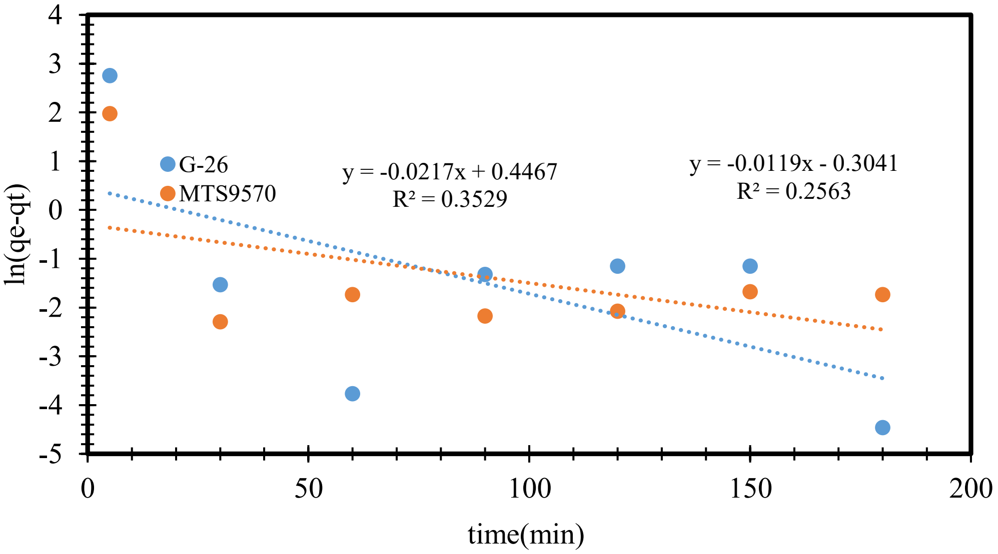


Figure 4.11: Pseudo first order for adsorption of Cu(II) onto G-26 and MTS9570 exchange resins.

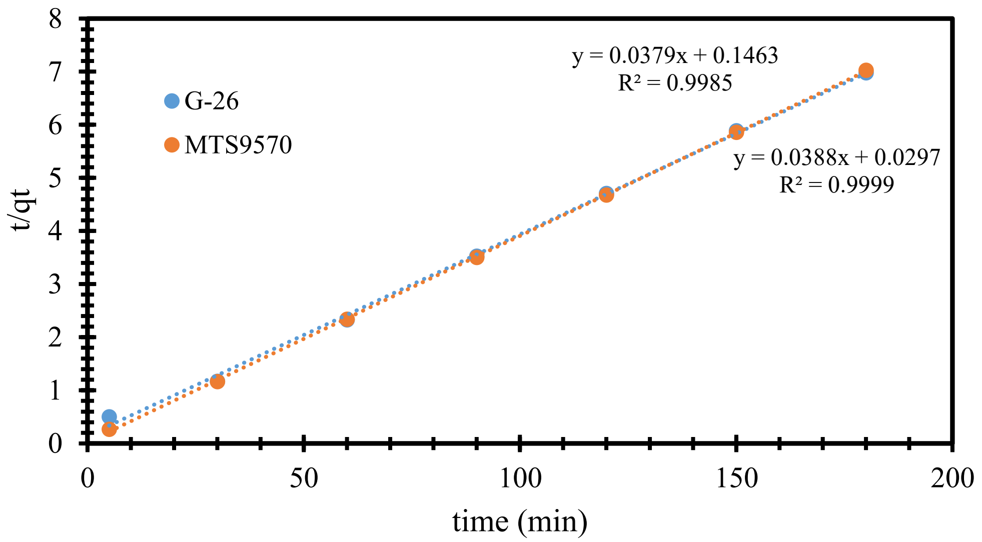


Figure 4.12: Pseudo second order for adsorption of Cu(II) onto G-26and MTS9570 exchange resin.

Table 4.4: Kinetic parameters for the simultaneous removal of Cu(II) ions onto G-26 and MTS9570.

	G-26	**MTS9570**
Equations		
Pseudo first order		
q_e , exp (mg/g)	25.8	25.8
q_e, cal (mg/g)	1.563	0.737
k1 (m^{-1})	-0.00012	-0.00066
R^2	0.352	0.2563
Pseudo second order		
q_e, exp (mg/g)	25.8	25.8
q_e, cal (mg/g)	26.38	25.77
k2 (g/mg min)	0.00981	0.05068
R^2	0.9985	0.9999

4.3.9 Thermodynamic evaluation of the process

In order to investigate the influence of temperature on the adsorption process, thermodynamic parameters such as standard free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$) were determined, using the following equations:

$$\Delta G° = -RT \ln K_D \tag{4.9}$$

$$\Delta G° = \Delta H° - T \cdot \Delta S\ ° \tag{4.10}$$

OR

$$\ln K_D = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{4.11}$$

where K_D is a dimensionless adsorption equilibrium constant calculated from the Langmuir equation , R is the universal gas constant (8.314 J/mol/K), and T is the adsorption temperature (K).The values of $\Delta H°(k\mathrm{J/mol})$and $\Delta S°$ (J/mol) could be obtained from the slope and interception of a linear plot between ln K_D versus *1/T*.

The Langmuir constant K_L can easily be converted to dimensionless adsorption equilibrium constant K_D as shown in in equation (4.12) [50, 51].

$$\mathrm{K_D} = 55.5\ (1000)\ (\mathrm{M_W})(\mathrm{K_L}) \tag{4.12}$$

$$K_L = \frac{q_e}{C_e}$$

where M_W is the molecular weight of solute, the factor 55.5 ($\mathrm{mL^3}$/mol mol/ $\mathrm{mL^3}$) is dimensionless and it is the number of moles of pure water per litre of solution. It is obtained by dividing ~1000 g/L by 18 g/mol. Multiplying by this factor makes equations (4.12) dimensionless. This was recommended by Milonjic [50] and then developed by Liu [51]. The calculated values of thermodynamic parameters are listed in Table 4.5.

The negative value of $\Delta G°$for the adsorption of Cu(II) indicates a spontaneous process, and the positive values of $\Delta H°$ (25.5 and 18.4 kJ/mol for G-26 and MTS9570, respectively) verify the endothermic nature of the adsorption process which corresponds with the temperature tests. The positive value of entropy indicates an increase of randomness at the solid-solution interface during the fixation of Cu^{2+} ions on the active sites of the resins.

Table 4.5: Thermodynamic parameters for the adsorption of Cu(II) on G-26 and MTS9570.

Resin	ΔG (kJ mol^{-1})						
	293 K	303 K	313 K	353 K	ΔH (kJ mol^{-1})	ΔS (J/ mol)	R^2
G-26	-21.45	-22.9	-24.38	-25.84	25.51	141.01	0.9916
MTS9570	-16.35	-18.19	-20.39	-23.58	18.41	117.73	0.9344

4.3.10 Desorption studies

Desorption test results confirmed that ideal metal removal % can be achieved in 20 min for both resins as shown in Figure 4.13. As shown in Figure 4.14, the optimum volume of the eluent is 40 mL. In order to evaluate the resin efficiency for adsorption/desorption of copper ions, experiments were performed using the same resin for adsorption/desorption in three cycles. The results are listed in Table 4.6. After the first adsorption-desorption cycle, G-26 beads were completely regenerated, but MTS9570 beads lost some uptake capacity. The desorption ratio of sulfonic resin G-26 was almost 100%, while the desorption ratio of phosphonic sulfonic resin MTS9570 decreased to 74%, as shown in Table 4.6. This might be attributed to resin structure and property difference. G-26 resin has gel type structure), while MTS9570 resin has macroporous type structure, as shown in Table 4.1. Generally, Gel resins are characterized as having smaller pores, which lead to a higher initial exchange capacity. The obtained result agrees with the result reported by Volesky [49].

Table 4.6: Adsorption and desorption cycles of Cu(II) on G-26 and MTS9570.

Resin	**Cu(II) Removal %**			**Cu(II) Recovery %**		
	Adsorption cycle			**Elution cycle**		
	First adsorption	Second adsorption	Third adsorption	First elution	Second elution	Third elution
G-26	100	100	100	100	100	100
MTS9570	90	70	70	94	75	74

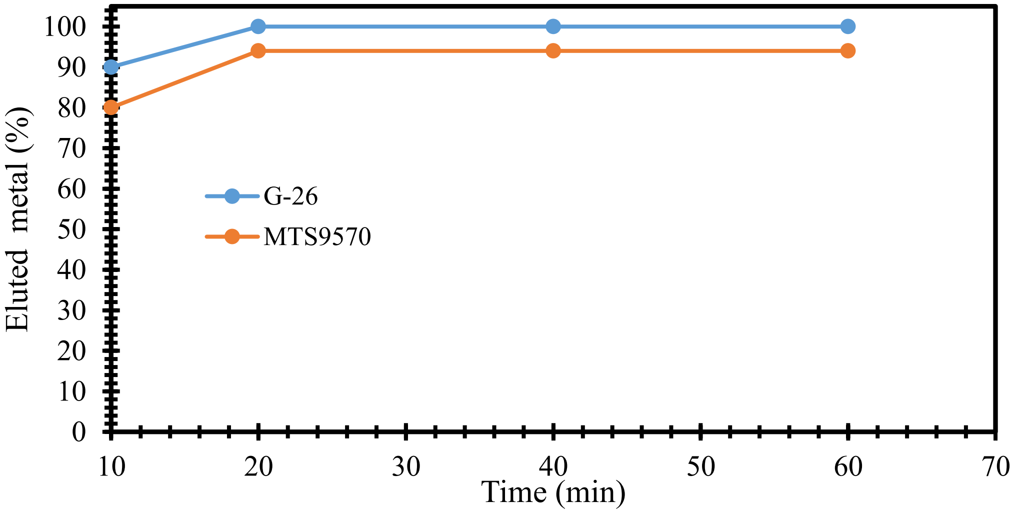


Figure 4.11: Effect of time on desorption of G-26 and MTS9570 resins.

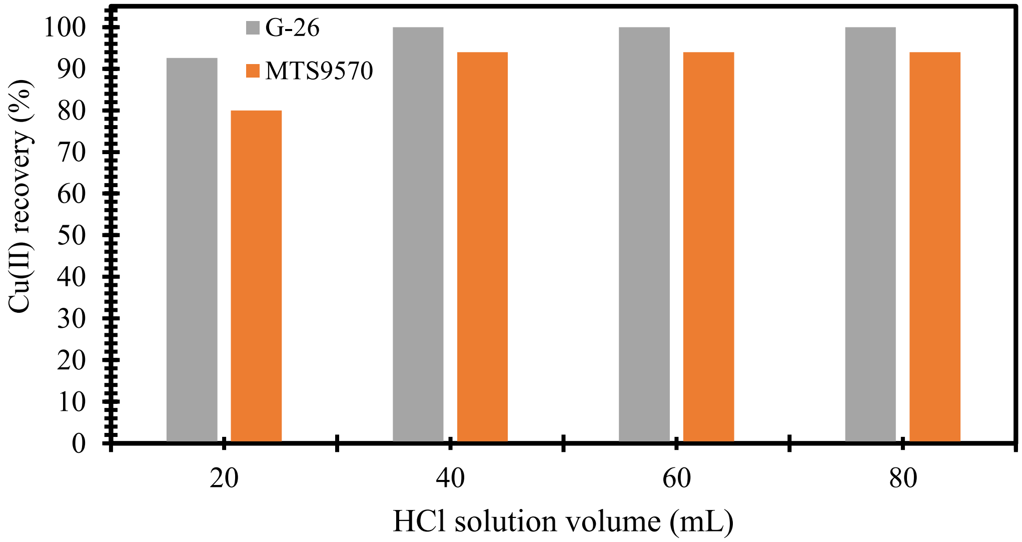


Figure 4.12: Elution of G-26 and MTS9570 at different volumes of (15% v/v) HCl concentration, 0.5 g of resins dosage, 20 minutes agitation time, and at room temperature.

4.4. Conclusion

The removal of copper from acidic solution using G-26 and MTS9570 resins has been studied in this work. Batch adsorption tests were conducted for analyzing the effects of operation factors, i.e., contact time, ionic strength, resin dosage, pH, and temperature, on copper removal. Adsorption experimental results verified a higher efficiency for both resins compared to the adsorbents of previous works. Optimum conditions were obtained at a Cu^{2+} concentration of 80-1100 mg/L, contact time of 30 min, and 0.025g/mL of resin and pH 3.5 for both resins. The sorption capacity of sulfonic resin G-26 for Cu(II) ions was 41.6 mg/g, a little superior to that of phosphonic and sulfonic resin MTS9570 (37.7 mg/g). This may be due to the competition and unequal ability between the double functional groups of MTS9570 resin for the adsorption of Cu^{2+} ions. Langmuir isotherm fits the adsorption data better than Freundlich and Temkin isotherms as shown by the adsorption coefficients.

The kinetic experiments showed that the pseudo-second-order kinetic model fit the adsorption data best. Thermodynamic analysis suggested that the spontaneous adsorption process of copper ions onto both resins is endothermic in nature. The adsorption/desorption studies demonstrated that the performance of G-26 resin is better than that of MTS9570 resin and can be prospective for being applied in the treatment of copper- bearing wastewater.

References

[1] D. Kołodyńska, ''The effect of the novel complexing agent in removal of heavy metal ions from waters and waste waters''. *Chem. Eng. J. 2010, 165, 835–845.* *https://doi.org/10.1016/j.cej.2010.10.028*

[2] S. Anwar, Y. Zhang, and F. Khan, "Electrodeposition of Zn-Ni Alloy and Zn-Ni-TiO2 Nano-Composite Corrosion Resistance Coatings from Ammonium Citrate Stabilize Bath," *Process Saf. Environ. Prot.*, 2020

[3] S. Anwar, F. Khan, S. Caines, R. Abbassi, Y. Zhang, ''Influence of chloride and pH on the pitting mechanism of Zn-Ni alloy coating in sodium chloride solutions''. *Can. J. Chem. Eng. 2021, 99, 680–694.* *https://doi.org/10.1002/cjce.23920*

[4] A. Elhemmali, S. Anwar, Y. Zhang, J. Shirokoff, ''A comparison of oil-water separation by gravity and electrolysis separation process''. *Sep. Sci. Technol. 2021, 56, 359–373.* *https://doi.org/10.1080/01496395.2020.1713812*

[5] D. Kołodyńska, J. Krukowska-Bąk, J. Kazmierczak-Razna, R. Pietrzak, ''Uptake of heavy metal ions from aqueous solutions by sorbents obtained from the spent ion exchange resins''. *Microporous Mesoporous Mater. 2017, 244, 127–136.*

https://doi.org/10.1016/j.micromeso.2017.02.040

[6] R. G. Riley, J. M. Zachara, F. J. Wobber, Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research, *US Department of Energy, Office of Energy Research, Subsurface Science Program, Washington, DC 1992*.

[7] E.-M. Burkhardt, S. Meißner, D. Merten, G. Büchel, K. Küsel, "Heavy metal retention and microbial activities in geochemical barriers formed in glacial sediments subjacent to a former uranium mining leaching heap'' .*Geochemistry 2009,69, 21–34..* https://doi.org/10.1016/j.chemer.2008.12.003

[8] H. Bolton, L. Xun, D. C. Girvin, "Biodegradation of Synthetic Chelating Agents," *Environmental Microbe-Metal Interactions, 2014*.

[9] C. S. T. Araújo, I. L. S. Almeida, H. C. Rezende, S. M. L. O. Marcionilio, J. J. L. Léon, T. N. de Matos, "Elucidation of mechanism involved in adsorption of Pb(II) onto lobeira fruit (Solanum lycocarpum) using Langmuir, Freundlich and Temkin isotherms''.*Microchem. J. 2018, 137, 348–354.* https://doi.org/10.1016/j.microc.2017.11.009

[10] G. Saha, M. Hoque, M. Miah, R. Holze, D. Chowdhury, S. Khandaker, S. Chowdhury, "Biosorptive removal of lead from aqueous solutions onto Taro (Colocasiaesculenta (L.) Schott) as a low cost bioadsorbent: Characterization, equilibria, kinetics and biosorption-mechanism studies''. *J. Environ. Chem. Eng. 2017, 5, 2151–2162.* https://doi.org/10.1016/j.jece.2017.04.013

[11] E. C. Nnadozie, P. A. Ajibade, "Data for experimental and calculated values of the adsorption of Pb(II) and Cr(VI) on APTES functionalized magnetite biochar using

Langmuir, Freundlich and Temkin equations''. *Data Br. 2020, 32,106292* *https://doi.org/10.1016/j.dib.2020.106292*

[12] S. Rengaraj, J. Yeon, Y. Kim, Y. Jung, Y. K. Ha, W. H. Kim, "Adsorption characteristics of Cu(II) onto ion exchange resins 252H and 1500H: Kinetics, isotherms and error analysis''. *J. Hazard. Mater. 2007, 143, 469–477. https://doi.org/10.1016/j.jhazmat.2006.09.064*

[13] S. Elfeghe, S. Anwar, Y. Zhang, "Adsorption and removal studies of cadmium ion onto sulphonic/phosphonic acid functionalization resins''.*Can J Chem Eng, 2022, 100, 3006–3014. https://doi.org /10.1002/cjce.24400*

[14] S. Wu, K. Zhang, X. Wang, Y. Jia, B. Sun, T. Luo, F. Meng, Z. Jin, D. Lin, W. Shen, L. Kong, J. Liu, "Enhanced adsorption of cadmium ions by 3D sulfonated reduced graphene oxide''.*Chem. Eng. J. 2015, 262, 1292–1302. https://doi.org/10.1016/j.cej.2014.10.092*

[15] M. R. Awual, "A facile composite material for enhanced cadmium(II) ion capturing from wastewater''. *J. Environ. Chem. Eng. 2019, 7, 103378. https://doi.org/10.1016/j.jece.2019.103378*

[16] R.S.I. Amer, "Simplified removal of chelated metals*''Met. Finish. 2004, 102, 36–40. https://doi.org/10.1016/S0026-0576(04)90237-1*

[17] E.Pehlivan, T. Altun, ''The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic *resin''J. Hazard.Mater. 2006, 134,149–156. https://doi.org/10.1016/j.jhazmat.2005.10.052*

[18] V. K. Gupta, ''Equilibrium Uptake, Sorption Dynamics, Process Development, and Column Operations for the Removal of Copper and Nickel from Aqueous Solution and Wastewater

Using Activated Slag, a Low-Cost Adsorbent''. *Ind. Eng. Chem. Res. 1998, 37, 192–202.* *https://doi.org/10.1021/ie9703898*

[19] S. Kaur, K. Kaur, A. Kaur, J. Aulakh, ''SiO2@Fe3O4-SB nano-hybrids as nanosorbent for preconcentration of cadmium ions from environmental water samples'' *J. Environ. Chem. Eng. 2020, 103448.* *https://doi.org/10.1016/j.jece.2019.103448*

[20] M. Pesavento, R. Biesuz, ''Sorption of divalent metal ions on an iminodiacetic resin from artificial seawater''. *Anal. Chim. Acta 1997, 346, 381–391.* *https://doi.org/10.1016/S0003-2670(97)90083-0*

[21] D. B. Singh, D. C. Rupainwar, G. Prasad, K. C. Jayaprakas, ''Studies on the Cd(II) removal from water by adsorption''. *J. Hazard. Mater. 1998, 60, 29–40.* *https://doi.org/10.1016/S0304-3894(97)00071-X*

[22] Ş. Tokalioğlu, Ş. Kartal, ''Preconcentration of lron(III), Lead(II), Cobalt(II) and Chromium (III) on Amberlite XAD-1180 Resin Loaded with 4-(2-Pyridylazo)-resorcinol (PAR) and Their Determination by FAAS''.*Bull. Korean Chem. Soc. 2006, 27, 1293–1296.* *https://doi.org/10.5012/BKCS.2006.27.9.129*

[23] J. T. Jasper, Y. Yang, M. Hoffmann, ''Toxic Byproduct Formation during electrochemical Treatment of Latrine Wastewater''. *Environ. Sci. Technol. 2017, 51, 7111-71119.* *https://doi.org/10.1021/acs.est.7b01002*

[24] S. Verbych, N. Hilal, G. Sorokin, M. Leaper, Ion Exchange Extraction of Heavy Metal Ions from Wastewater''.*Sep. Sci. Technol. 2004, 39, 2031–2040.* *https://doi.org/10.1081/SS-120039317*

[25] P. A. Sule, J. D. Ingle, ‘‘Determination of the speciation of chromium with an automated two-column ion-exchange system’’.*Anal. Chim. Acta 1996, 326, 85–93.* *https://doi.org/10.1016/0003-2670(96)00041-4*

[26] M. I. Khan, L. Wu, A. N. Mondal, Z. Yao, L. Ge, T. Xu, ‘‘Adsorption of methyl orange from aqueous solution on anion exchange membranes: Adsorption kinetics and equilibrium’’. *Membr.Water Treat. 2016, 7, 23–38.* *http://dx.doi.org/10.12989/mwt.2016.7.1.023*

[27] H. Leinonen, J. Lehto, ‘‘Ion-exchange of nickel by iminodiacetic acid chelating resin Chelex 100’’.*React. Funct. Polym. 2000, 43, 1–6.* *https://doi.org/10.1016/S1381-5148(98)00082-0*

[28] Ş. Kartal, Ş. Tokahoğlu, B. Özkan, ‘‘Speciation of Cr(III)/Cr(VI) in tannery waste waters by using ion-exchange resins’’. *Bull. Korean Chem. Soc. 2006, 27, 694–698.* *https://doi.org/10.5012/BKCS.2006.27.5.694*

[29] T. Sumida, A. Sabarudin, M. Oshima, S. Motomizu, ‘‘Speciation of Chromium in Seawater by ICP-AES with Dual Mini-columns Containing Chelating Resin’’.*Anal. Sci. 2006, 22, 161–164.* https://doi.org/10.2116/analsci.22.161

[30] I. Bleotu, E. N. Dragoi, M. Mureşeanu, S. A. Dorneanu, ‘‘Removal of Cu(II) ions from aqueous solutions by an ion-exchange process: Modeling and optimization’’. *Environ. Prog. Sustain. Energy 2018, 37, 605–612.* https://doi.org/10.1002/ep.12793

[31] L. M. Gaetke, C. K. Chow, ‘‘Copper toxicity, oxidative stress, and antioxidant nutrients’’ *Toxicology 2003, 189, 147. Doi: 10.1016/s0300-483x(03)00159-8*

[32] B. Ashish, K. Neeti, K. Himanshu, ‘‘Copper Toxicity: A Comprehensive Study’’. *Res.J. Recent.Sci 2013, 2, 58–67.*

[33] N. Graham, Guidelines for Drinking-Water Quality, 2nd Edition, Addendum to Volume 1 – Recommendations, *World Health Organisation, Geneva, 1998, 36 pages, 4th ed., Vol. 1, World Health Organization, Geneva, Switzerland 1999.*

[34] G.Wang, Y.Wenchao, C. Zheng, C.He, Y.Yang, T.Fujita, ‘‘Characterization of Waste Amidoxime Chelating Resin and Its Reutilization Performance in Adsorption of Pb(II), Cu(II), Cd(II) and Zn(II) Ions’’. *Metals 2022, 12 (1), 149.* *https://doi.org/10.3390/met12010149*

[35] M. K. Jha, N. Van Nguyen, J. Chun Lee, J. Jeong, J. M. Yoo, ‘‘Adsorption of copper from the sulphate solution of low copper contents using the cationic resin Amberlite IR 120’’ *J. Hazard. Mater. 2009, 164, 948–953.* *https://doi.org/10.1016/j.jhazmat.2008.08.103*

[36] R. Ferreira, In : A Book on Ion Exchange, Adsorption and Solvent Extraction ISBN : 978-Equilibrium and Kinetic Studies in adsorption of toxic metals ions. *Vicente de Oliveira Sousa Neto 1, Giselle Santiago Cabral Raulino 2, 2013.*

[37] M. K. Jha, R. R. Upadhyay, J. chun Lee, V. Kumar, ‘‘Treatment of rayon waste effluent for the removal of Zn and Ca using Indion BSR resin’’.*Desalination 2008, 228, 97–107.* *https://doi.org/10.1016/j.desal.2007.08.010*

[38] T. M. Zewail, N. S. Yousef, ‘‘Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed’’. *Alexandria Eng. J. 2015, 54, 83–90.* *https://doi.org/10.1016/j.aej.2014.11.008*

[39] I.Langmuir, ‘‘the Constitution and Fundamental Properties of Solids and Liquids’’. Part I Solids. *J. Am. Chem. Soc. 1916, 38, 2221–2295.* https://doi.org/10.1021/ja02268a002.

[40] H.M.F.Freundlich, ‘‘Uber die Adsorption in Losungen’’. *Phys. Chem. 1906, 57, 385–470.*

[41] M.Temkin, V. Pyzhev, ‘‘Kinetics of Ammonia Synthesis on Promoted Iron Catalysts’’. *Acta Physicochim. URSS 1940, 12, 327–356.*

[42] A.Demirbas, E.Pehlivan, F. Gode, T. Altun, G. Arslan, ‘‘Adsorption of Cu(II), Zn(II), Ni (II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin’’ *J. Colloid Interface Sci. 2005, 282, 20–25.* https://doi.org/10.1016/j.jcis.2004.08.147

[43] S. Rengaraj, Y. Kim, C. K. Joo, K. Choi, J. Yi, ‘‘Batch adsorptive removal of copper ions in aqueous solutions by ion exchange resins: 1200H and IRN97H’’. *Korean J. Chem. Eng. 2004, 21, 187–194.* https://doi.org/10.1007/BF02705397

[44] J.Jachua, Z. Hubicki, ‘‘Sorption of heavy metal complexes with MGDA on the macroporous anion exchanger Purolite A830’’. *CHEMIK 2013, 67, 693–700*

[45] C.Chen, H. Liu, T.Chen, D. Chen, R. Frost, ‘‘An insight into the removal of Pb(II),Cu(II), , Co(II), Cd(II), Zn(II), Ag(I), Hg(I), Cr(VI) by Na(I)-montmorillonite and Ca(II)-Montmorillonite’’. *Appl. Clay Sci. 2015, 118, 239–247.* https://doi.org/10.1016/j.clay.2015.09.004

[46] M.I.U.Hoque, D.A. Chowdhury, R. Holze, A.N. Chowdhury, M.S. Azam, ‘‘Modification of Amberlite XAD-4 resin with 1,8-diaminonaphthalene for solid phase extraction of copper, cadmium and lead, and its application to determination of these metals in dairy cow’s milk’’. *J. Environ. Chem. Eng.2015, 3, 831–842.*https://doi.org/10.1016/j.jece.2015.03.020

[47] D. Kołodyńska, Z. Hubicki, ‘‘Application of novel complexing agent in sorption of heavy metal ions from wastewaters on ion exchangers of various types’’. *Ann. UMCS, Chem.2009, 64.227–245. DOI: 10.2478/v10063-008-0017-4*

[48] M. V. Dinu, E. S. Dragan, ‘‘Heavy metals adsorption on some iminodiacetate chelating resins as a function of the adsorption parameters”. *React. Funct. Polym. 2008, 68, 1346–1354. https://doi.org/10.1016/j.reactfunctpolym.2008.06.011*

[49] B.Volesky, J. Weber, J.M. Park, ‘‘Continuous-flow metal biosorption in a regenerable Sargassum column’’.*Water Res. 2003, 37,297–306. https://doi.org/10.1016/S0043-1354(02)00282-8*

[50] S.K. Milonjic, A consideration of the correct calculation of thermodynamic parameters of adsorption, J. Serb. Chem. Soc. 72 (12) (2007) 1363–1367. *DOI:10.2298/JSC0712363M*

[51] Y. Liu, Is the free energy change of adsorption correctly calculated? J. Chem.Eng. Data 54 (7) (2009) 1981–1985. *https://doi.org/10.1021/je800661q*

Chapter 5

Removal of Lead (II) Ions from Aqueous Solutions Using Dowex G-26 and Puromet™ MTS9570 Ion Exchange Resins

Preface

A version of this chapter has been published in the ***Journal of*** **Minerals** ***2022; 12, 1312.*** *I produced the work alongside my co-authors; Yahui Zhang,* Lesley James, Qiuyue Sheng and Abbas Mamudu. *I am the main author. I conducted all lab experiments, calculated parameters for isotherms, kinetic and dynamic studies. I prepared the first draft of the manuscript and subsequently revised the manuscript based on the co-authors' and peer review feedback. Co-author, Yahui Zhang assisted in the development of concept, design of methodology, reviewing and editing the draft, and reviewing and revising the new version of the manuscript. Co-author,* Lesley James *supported in the project supervision, Co-author,* Qiuyue Sheng *supported in the data and process analysis, reviewing and editing the draft, reviewing and revising the new version of the manuscript. Co-author,* Abbas Mamudu *supported in data analysis and reviewing and editing the draft, reviewing and revising the new version of the manuscript.*

Abstract

This study presents Pb(II) recovery/removal from water solutions using two different commercial ion-exchange resins, i.e., Dowex G-26 with sulfonic functional group and Puromet™ MTS9570 with sulfonic and phosphonic functional groups. Overall, 100% Pb(II) recovery/removal by both resins was obtained at solution pH 3.5, resin dosage 25 g/L, adsorption time 30 min, room temperature, and initial Pb(II) concentration 1000 mg/L. Langmuir, Freundlich, and Temkin isotherms were used to model the experimental data. The mechanism of the adsorption process was investigated using kinetic and thermodynamic models. The experimental data fitted very well with the pseudo-second-order kinetic model, and thermodynamic analysis showed that the adsorption of Pb(II) from acidic solution onto both resins was a spontaneous and endothermic process in nature. Regeneration of the resins loaded with lead ions was tested for three cycles to evaluate the resin recyclability. Good stability of G-26 and performance degradation of MTS9570 resin was observed.

Keywords: Pb(II); ion-exchange resins; regeneration; isotherms; kinetics; thermodynamics

5.1 Introduction

With more demands for modern industrial products, heavy-metals consumption is widely increased in many fields. Their environmental impacts bring up serious concern because of their toxicity and non-degradability. Exposure to these pollutants can be harmful to human and environmental species [1-4]. Lead is one of the toxic metals and is discharged from different industrial activities such as mining, metals production, battery industry, and fuels combustion [5-7]. Lead's existence in water recourses can cause different diseases such as hepatitis and anemia [8-11]. According to the World Health Organization (WHO) guideline 2017, the maximum acceptable concentration for lead in drinking water is 0.01 mg/L [12-14]. Therefore, lead removal from wastewaters has become an important task, which also has the benefit of lead metal recovery.

Several remediation techniques have been used for lead recovery/removal from wastewater, such as chemical precipitation, electrodialysis, electrolysis, reverse osmosis, adsorption, and ion exchange [15-19]. Among these technologies, resin adsorption is one of the most suitable methods for the removal of lead and other toxic metals from aqueous solution due to its low cost, process simplicity, low remnant metal concentration, and high efficiency.

Various resins with different functional groups such as strong acid cation (SAC) resins with sulfonic acid group (-SO_3H), including Amberlite IR-120, Dowex 50W, Purolite C100, Lewatit SP-112, D-001, 732-CR, Dowex 50WX8, Amberjet 1200 Na^+, and C 160; weak acid cation (WAC) resins with carboxylic acid group (-COOH) such as Amberlite IRC-50/IRC-86, Lewatit CNP 80, and Purolite C-104; weak acid and chelating resins with iminodiacetic acid groups such as Purolite S-930, Amberlite IRC718, and Lewatit TP207; and acid and chelating resins with amino-phosphonic groups such as Purolite S-940 and Purolite S-950 were studied for lead removal from aqueous solutions [20-23].

Qian et al., [24] studied the kinetics and thermodynamics of lead removal from aqueous solution using 732 cation-exchange resin with sulfonic acid group in hydrogen type in the temperature range of 298–328 K and Pb(II) concentration range of 0.005-0.05 mol/L. The experimental results show that the adsorption isotherm data agreed closely with the Langmuir isotherm and the maximum monolayer exchange for Pb(II) was 484.0 mg/g at 308 K. Thermodynamic studies demonstrate that the adsorption of Pb(II) onto 732-CR is spontaneous and exothermic in nature. This resin was also tested by Guo et al., for removing lead from aqueous solutions [25]. The maximum sorption capacity of Pb(II) at pH 4.0 was 396.8 mg/g resin from their study. Tabatabaei et al., [26] investigated removal of lead from aqueous system using Amberlite IR-120 with sulfonic acid group and compared its efficiency with natural zeolite.

Vergili et al., [27] investigated the performance of WAC resin Lewatit CNP80 with carboxylic (–COOH) functional group for Pb(II) removal from battery industry wastewater. The Pb(II) removal efficiency in batch experiments was found to be 83.3% at 25 °C, with resin dosage of 2 g/L in 6 h contact time. The Pb(II) removal efficiency could increase slightly from 83% to 87% with increase in temperature. A similar study was reported by Xiong and Yao using resin

(110-H) with carboxylic group for Pb(II) adsorption in HAc-NaAc medium, obtaining the maximum lead adsorption capacity of 485 mg/g at pH 6.7 and 298 K [28].

Thu et al., [29] synthesized thiol-functionalized mesoporous silicas by co-condensation of tetraethoxysilane and varying contents of 3-mercaptopropyltrimethoxysilane in acidic medium with the block copolymer Pluronic 123 as a structure directing agent. Adsorption of lead from water by the thiol-functionalized silicas was studied. The maximum adsorption capacity was 0.19 mmol Pb per gram of adsorbent at 90 min contact time with initial Pb(II) concentration 200 mg/L and temperature 30°C. The adsorption efficiency of the lead-reloaded sample can reach 80% after five cycles of adsorption-elution compared with the fresh ones.

Removal of lead using Purolite S-930 resin with iminodiacetic functional group in aqueous solution was studied by Merganpour et al. [30]. The column adsorption results concluded that 91.12% of mean lead removal ratio from drinking water containing up to 22 μg/L Pb^{2+} can be achieved using Purolite S-930 during 21-day service at pH 6.5, which demonstrates an economic and technically feasible lead-removal process.

Ren et al. [31] reported a comparison study of Pb(II) adsorption on XC-72 carbon black and multi-walled carbon nanotubes (MWCNTs). The load of Pb(II) was 125.0 mg/g and 17.5 mg/g on XC-72 and MWCNTs, respectively, at pH 6.0 and 293 K temperature.

The performance of G-26 and MTS9570 resins have been examined by us for removing Cd(II) ions successfully from acidic solutions. Maximum cadmium-removal rates of 99.2% and 98.9% were achieved for G-26 and MTS9570, respectively, at 30 min of adsorption, 5.0 of initial solution pH, 1000 mg/L of initial metal concentration, and 0.01 g/mL of resin dosage for G-26 and 0.025 g/mL of resin dosage for MTS9570 [32,33]. As lead and cadmium are both persistent bio-accumulative toxic (PBT) metals, and they often coexist in nature, comparative study of G-26 and

MTS9570 for Pb(II) removal from aqueous solution was conducted in this work for a co-removal process in the future. The research involves exploratory experiments using twenty-three resins with different functional groups. The adsorption process using G-26 and MTS9570 was evaluated with adsorption isotherms, kinetic, and thermodynamic studies at different operation conditions.

5.2 Experimental Details

5.2.1 Materials

All the chemicals used to prepare Pb(II) solutions were of analytical reagent grade. Commercial synthetic resins Dowex G-26 in hydrogen form and Puromet™ MTS9570 were supplied by DuPont™ and Purolite US, respectively. Lead nitrate $Pb(NO_3)_2$ (obtained from A&C American Chemicals Ltd., Montreal, Canada) was used to prepare 1000 mg/L stock standard solution. The working standard solutions were prepared by the dilution of appropriate volumes of the stock standard solution with deionized water. Solution pH was adjusted with 0.1 mol/L HCl or 1% NaOH solutions. The properties of the resins are given in Table 5.1.

5.2.2. Apparatus

Instruments used in this study were as follows: Inductively coupled plasma (ICP) spectroscopy was used for metal concentration analysis; an electric shaker (model Promax 2020, Heidolph Instruments GmbH & Co. KG, Schwabach, Germany) was used for adsorption tests with 20 mL solutions in 125mL flasks. The solution pH was measured with a pH meter (model Orion Star A211).

Table 5.1: Physical and chemical properties of resins [32].

Characteristics	**G-26**	**MTS9570**
Matrix	Styrene-DVB	Polystyrene- DVB
Ionic form as shipped	H^+ form	H^+ form
Functional group	Sulfonic	Phosphonic and Sulfonic
Appearance	uniform particle size	Spherical Beads
Structure	gel	Macroporous
Capacity	2.0 eq/L	18 g/L
Bed size	0.65mm ± 0.05	0.315 – 0.850mm
Uniformity Coefficient	1.1	1.4
Water retention	45 – 52%	55 - 70 %
Specific Gravity	1.22 g/mL	1.12 g/mL

5.2.3. Experimental procedure

5.2.3.1. Activation of Resins

Before experiments, resins were initially washed in DI water at 150 rpm on a reciprocating platform shaker for 1 h. Then, they were activated with a solution of 10% (*v*/*v*) HCl and agitated at 150 rpm for 24 h. Subsequently, the resins were washed two times in DI water at 150 rpm for 1 h and dried at room temperature for 7 days. The dried resins were stored in dry bottles and were used for future experiments.

5.2.3.2. Adsorption studies

A standard solution of lead (1000 ppm) was prepared by dissolving a weighed amount of lead nitrate salt in distilled water, and the pH was adjusted by adding 0.1 mol/L HCl. The adsorption performances of G-26 and MTS 9570 for Pb(II) ions were investigated by batch experiments at different temperatures. Batch adsorption experiments were conducted at a constant volume of 20 mL metal ions solution and using different doses of dry resins, i.e., from 0.1 to 0.5 g/mL. The adsorption behavior of metal ions by the adsorbents was studied in the pH range of 1.5-5.5. Samples of metal solution and resins in 125 mL flasks were shaken in an electric shaker at different contact times ranging from 5 to 180 min and at the fixed speed of 150 rpm. After reaching the equilibrium stage, the solution was filtered and analyzed with XRF. The batch adsorption experiments were performed in triplicate and adopted the average value. The errors of the measurements were within 10%. The adsorption capacities of G-26 and MTS9570 exchangers and the removal percentage of Pb(II) were calculated using the following Equations (5.1) and (5.2), respectively.

$$Q = \frac{(C_i - C_e)V/1000}{M} \quad (5.1)$$

$$\text{And \% removal of Pb(II) ions} = \frac{(C_i - C_o)}{C_i} \text{ x } 100 \quad (5.2)$$

where Q is the adsorption capacity in mg/g at time t; C_i, C_o, and C_e are the initial, final, and equilibrium concentrations of Pb(II) in mg/L, respectively; V is the volume of Pb (II) solution in ml, and M is the total amount of resin in grams (g).

5.3 Results and discussion

5.3.1 Exploration of Pb Recovery/Removal Using Resins

There are many commercial resins available from different manufacturing companies. These resins have different chemical and physical properties. To explore the suitable resin for Pb(II) uptake, twenty-three resins were tested, which have different functional groups. The exploration process was conducted at resin amounts ranging from 0.1 g to 0.5 g at 20 mL constant volume metal solution, 180 min adsorption time, 150 adsorption speed, 1000 mg/L solution concentration, pH 3.5, and 20 ± 1°C room temperature.

Figure 5.1 illustrates fourteen resins that have a Pb(II)-removal percentage above or close to 90%. These resins mainly contain sulfonic, phosphonic/sulfonic, amino/phosphonic, iminodisatic, bis-picolylamine, or sulfonic/trimethylamine group(s), while the other nine resins with functional group(s) of iso-thiouronium, carboxylic, N-methylglucamine, di-ethylhexylphosphate (D2EHPA), thiourea, aminomethylphosphonic, or trimethyl ammonium have relatively low adsorption performance for lead ions (Figure 5.2). Among the twenty-three resins tested, Dowex G-26 resin with sulfonic group and Purolite MTS 9570 resin with phosphonic/sulfonic groups were selected. These two resins have been tested by the same author, and they had high efficiency for removal of cadmium and copper as well [32].

5.3.2 Effect of agitation time

A series of adsorption time tests for lead recovery/removal were carried out with the initial metal concentration of 1000 mg/L, resin dose 0.5 g, and shaking speed 150 rpm at pH 3.5 and room temperature. The removal percentage of adsorbed lead(II) ions onto both resins increased with time, as shown in Figure 5.3. It can be found that the adsorption time necessary to reach equilibrium was within 30 min. Further increase in time had no effect on the adsorption of lead for both exchangers. The uptake percentage for Pb(II) increased from 49.3% to 100% and from 45.8%

to 100% for G-26 and MTS9570, respectively. Further, 30 min adsorption time was adopted for subsequent tests.

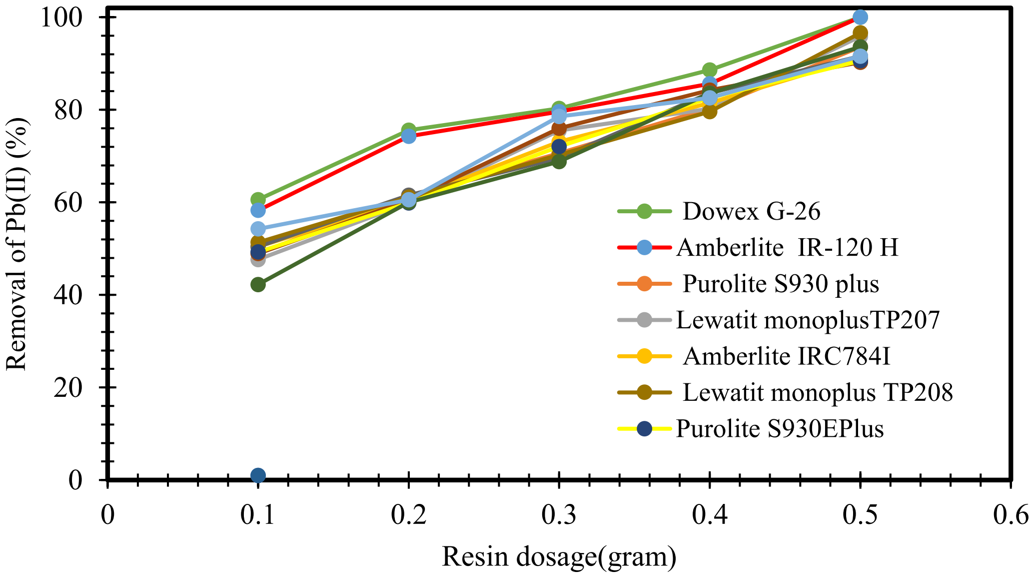


Figure5.1.Cont

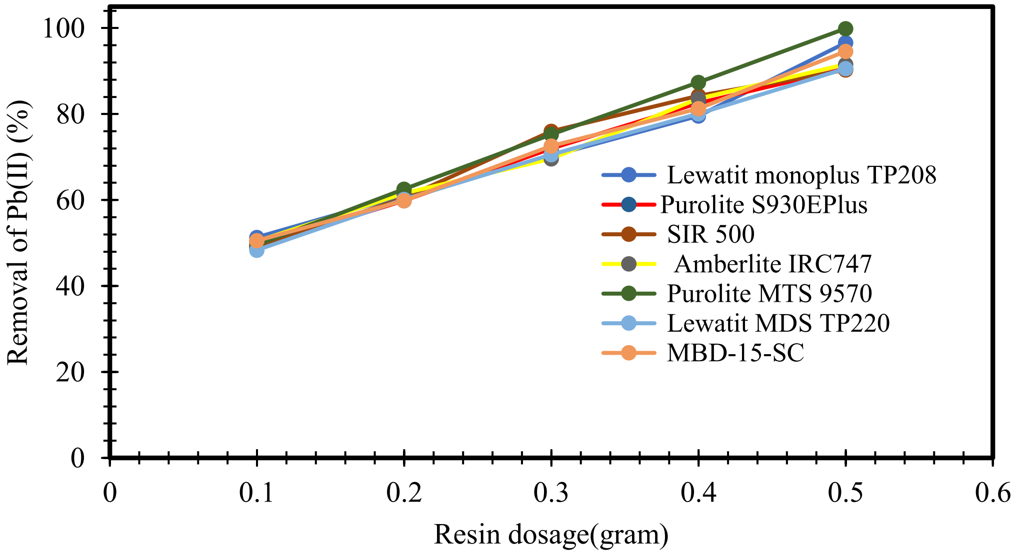


Figure 5.1: Resins with high removal rate of Pb(II) at 30 min contact time,150rpm agitation speed,20ml volume,pH4, concentration 1000 mg/L, and temperature 20°C.(a) Purolite S940,

Lewatit monoplus TP207, Amberlite IR-120H, Dowex G-26, Purolite S930 Plus, Amberlite IRC7841, and Purolite S950Plus resin. (b) Lewatit monoplus TP208, SIR500, Lewatit MDS TP220, Purolite MTS9570, MDB-15-SC, and Amberlite IRC 747 resin.

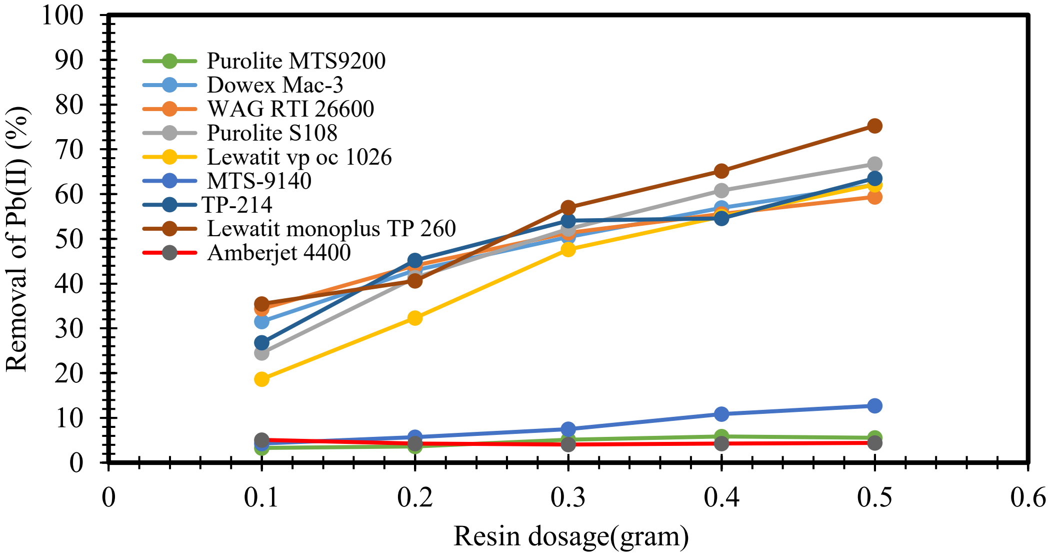


Figure 5.2: Resins with low removal rate of Pb(II) at 30 min contact time,150 rpm agitation speed,20 ml volume,pH4.5, concentration 1000 mg/L, and temperature 20°C.

5.3.3 Effect of adsorbent dose

Figure 5.4 presents the removal of Pb(II) by G-26 and MTS9570 as a function of resin dosage. Resin dosage was varied from 5 to 30 g/L, while other conditions were the same as in the adsorption time tests. Increasing resin dosage increased the removal percentage of Pb(II). When the resin dosage increased to 25 g/L, Pb(II)-removal rates were close to 100% for both resins. This indicates that both resins can be used as adsorbents to remove Pb(II) ions effectively, and 25 g/L resin dosage was used for subsequent tests.

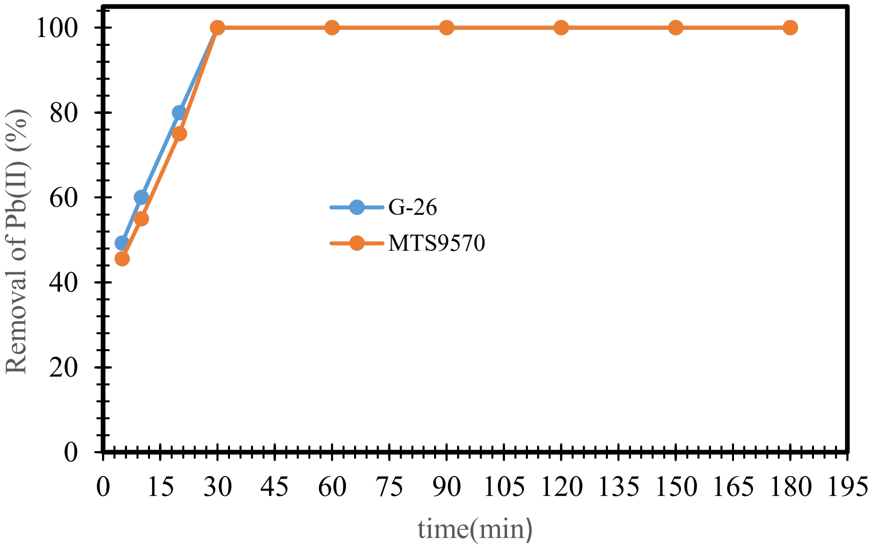


Figure 5.3: Effect of agitation time on adsorption of Pb(II) using G-26 and MTS9570 exchange resin 0.5 g of resin dosage (i.e.25g/L), 30 min contact time,150 rpm agitation speed, pH3.5, concentration 1000 mg/L, and temperature 20°C.

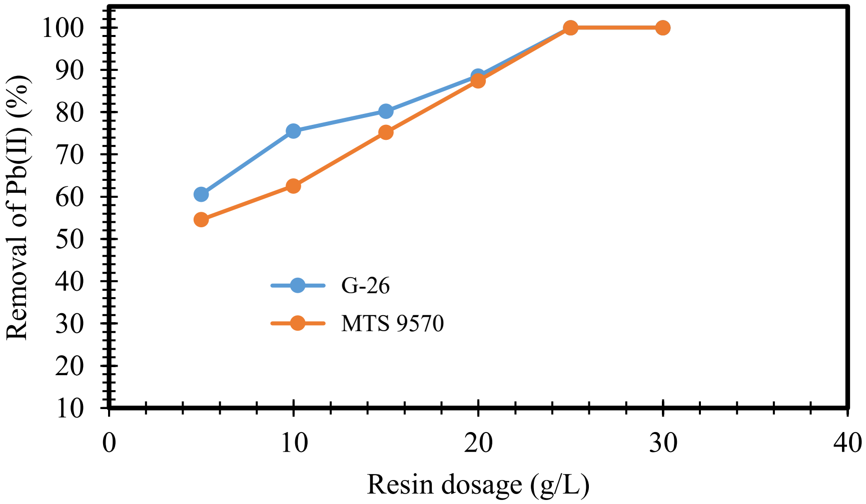


Figure 5.4: Effect of resin dosage on adsorption of Pb(II) using G-26 and MTS9570 exchange resin at 30 min contact time,150 rpm agitation speed, pH3.5, concentration 1000 mg/L, and temperature 20°C.

5.3.4 Effect of pH

The influence of pH on the removal of Pb(II) was investigated at pH range 1.5-5.5, while other conditions were the same as in the adsorbent dosage tests. As seen from Figure 5.5, pH does not have a significant effect on the adsorption of Pb(II) onto G-26 resin in the entire explored pH range (1.5-5.5). The removal rate of Pb(II) was slightly low at pH 1.5 for MTS9570. Precipitation of lead was observed at pH > 5.5. Therefore, in the subsequent experiments, the solution pH was kept at 3.5.

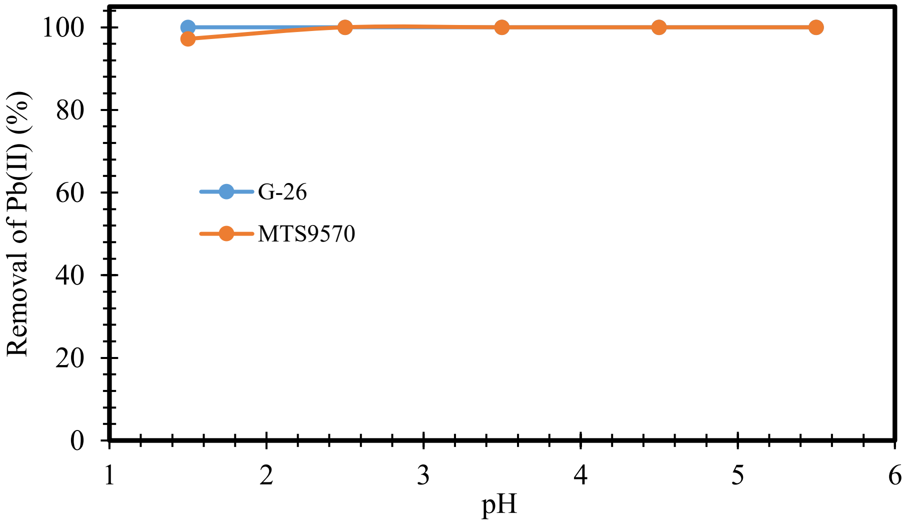


Figure 5.5: Effect of pH on adsorption of Pb(II) using G-26 and MTS9570 exchange resin at 0.5 g of resin dosage (i.e.25g/L) , 30 min contact time,150 rpm agitation speed, concentration 1000 mg/L, and temperature 20°C.

5.3.5 Effect of temperature

Adsorption experiments were conducted at four different temperatures (20, 40, 60, and 80 °C) to study the performance of the selected resins on the adsorption of lead ions. As shown in Figure

5.6, the removal percentage of Pb(II) increased with the rising temperature, which indicates that the adsorption of Pb(II) ions onto G-26 and MTS9570 resins is endothermic in nature.

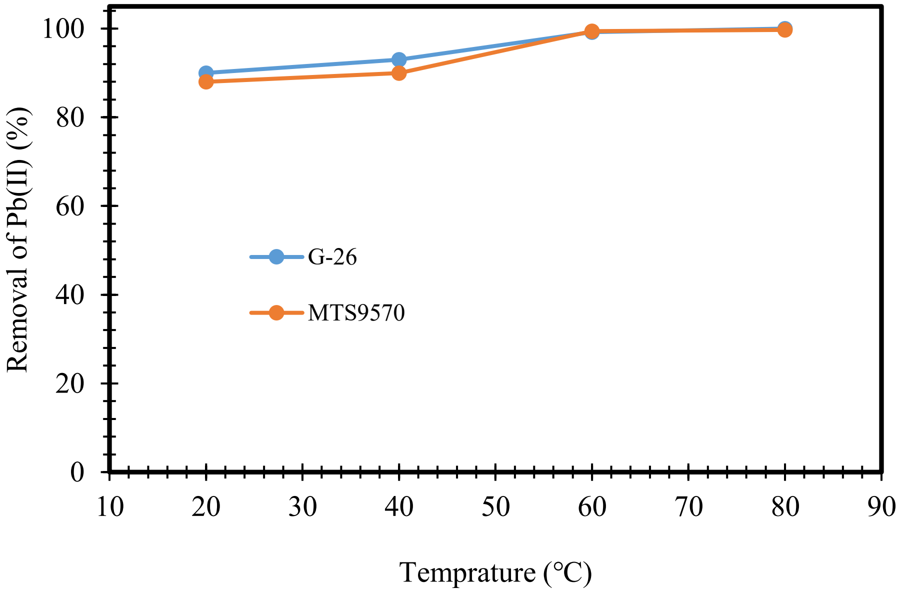


Figure 5.6: Effect of temperature on adsorption of Pb(II) using G-26 and MTS9570 exchange resin at 0.5 g of resin dosage (i.e.25g/L), 30 min contact time, 150 rpm agitation speed, pH3.5, and concentration 1000 mg/L.

5.3.6 Effect of initial metal ion concentration

Effect of initial metal concentration on Pb(II) adsorption onto G-26 and MTS9570 resins was explored at 20°C (shown in Figure 5.7). The removal percentages of 100 -1000 mg/L. At the high metal concentration of 1200 mg/L, the removal percentage of Pb^{2+} decreased, which is due to no availability of favorable sites for adsorption on the resin beads. The result obtained of this work is consistent to results reported by Al Anber et al., [34] and Elfeghe et al., [32].

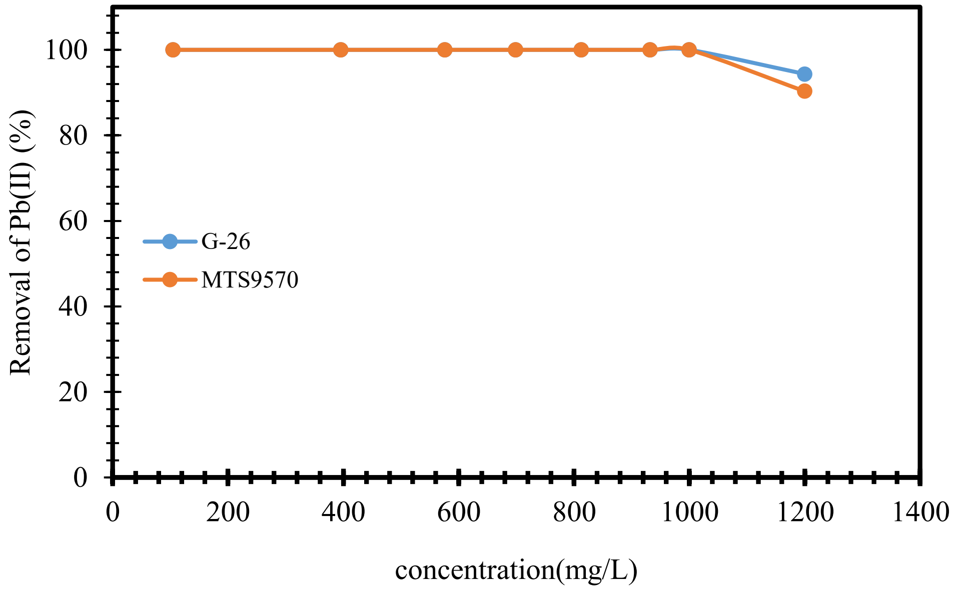


Figure 5.7: Effect of concentration on adsorption of Pb(II) using G-26 and MTS9570 exchange resin at 0.5 g of resin dosage (i.e.25g/L) , 30 min contact time,150 rpm agitation speed, pH3.5 and temperature 20°C.

5.3.7 Adsorption isotherms

The sorption isotherms play an important role in the design of adsorption systems. Three popular isotherm models, i.e., Langmuir [35], Freundlich [36], and Temkin [37] isotherms, were applied for the equilibrium modelling of Pb(II) adsorption on the resins.

The Langmuir isotherm is commonly used to describe monolayer sorption at equilibrium, and the linear form is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{5.3}$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), and Q^0(mg/g) and b (L/mg) are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

The Freundlich model assumes adsorption on heterogeneous surfaces. The linear form of the Freundlich isotherm equation is represented as follows:

$$log q_e = log K_F + \frac{1}{n} log C_e \tag{5.4}$$

where K_F is the adsorption equilibrium constant relating to the adsorbent capacity, and *1/n* is the parameter relating the adsorption intensity.

The Temkin isotherm is based on the interaction between adsorbate and adsorbent, which causes heat of adsorption due to repulsions forces. The linear form of the Temkin equation is given by the following equation:

$$q_e = \mathrm{B} \ln (K_T) + \mathrm{B} \ln (C_e) \tag{5.5}$$

And $\mathrm{B} = \frac{RT}{b_T}$

where $\mathrm{K_T}$ (L/g), and B (J/mol) are the Temkin and heat of sorption constants, respectively. R = universal gas constant (8.314 J/mol/K), and T = Temperature at 298K.

The Langmuir, Freundlich, and Temkin isotherm parameters for the adsorption of lead (II) onto G-26 and MTS9570 resins were calculated by using isotherms and their correlation coefficients and listed in Table 5.2. Comparison of the correlation coefficients values shows that the adsorption of Pb(II) onto G-26 and MTS9570 resins is fitted better by Langmuir model (R^2 = 0.9973–0.9906) and Freundlich than Temkin models (R^2 = 0.9806–0.9943 and R^2 = 0.9681–0.9557). The Langmuir, Freundlich, and Temkin isotherms of the adsorption of Pb(II) on G-26 and MTS9570 are presented in Figures 5.8–5.10, respectively. The maximum adsorption capacities of G-26 and

MTS 9570 resins are excellent compared with some other adsorbents for the adsorption of Pb(II) (Table 5.3).

Table 5.2: The isotherm parameters for Pb(II) adsorption on G-26 and MTS9570.

	G-26	**MTS9570**
Langmuir isotherm		
Q^0 (mg/g)	45.45	38.46
b (L/mg)	0.082	0.221
R^2	0.9973	0.9906
Freundlich isotherm		
K_F (mg/g)	19.16	20.52
n	5.740	7.450
R^2	0.9806	0.9943
Temkin isotherm		
b_T	294.9	669.6
B	8.40	3.70
R^2	0.9681	0.9557

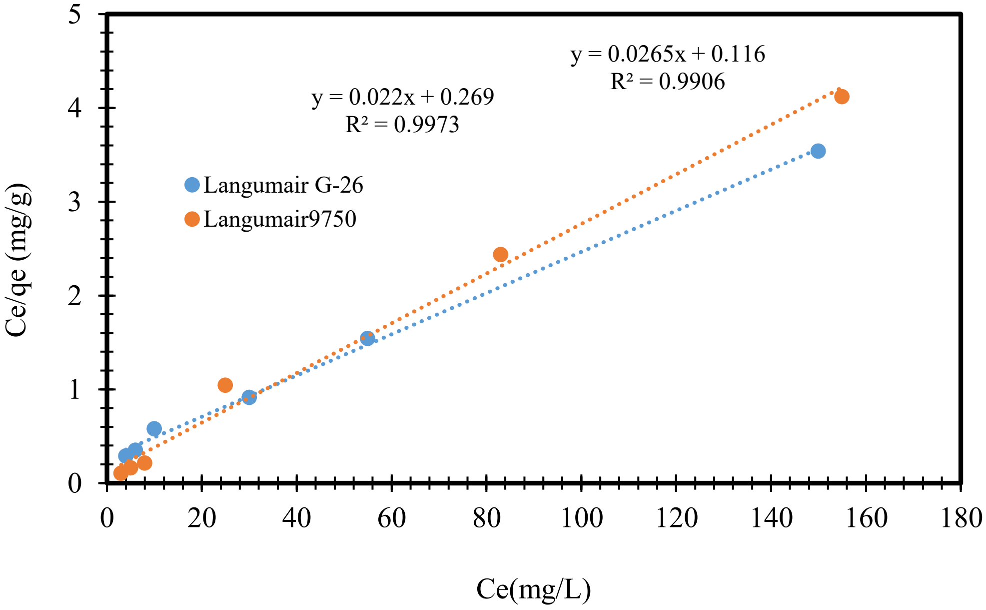


Figure 5.8: Langmuir isotherm of Pb(II) adsorption on G-26 and MTS9570.

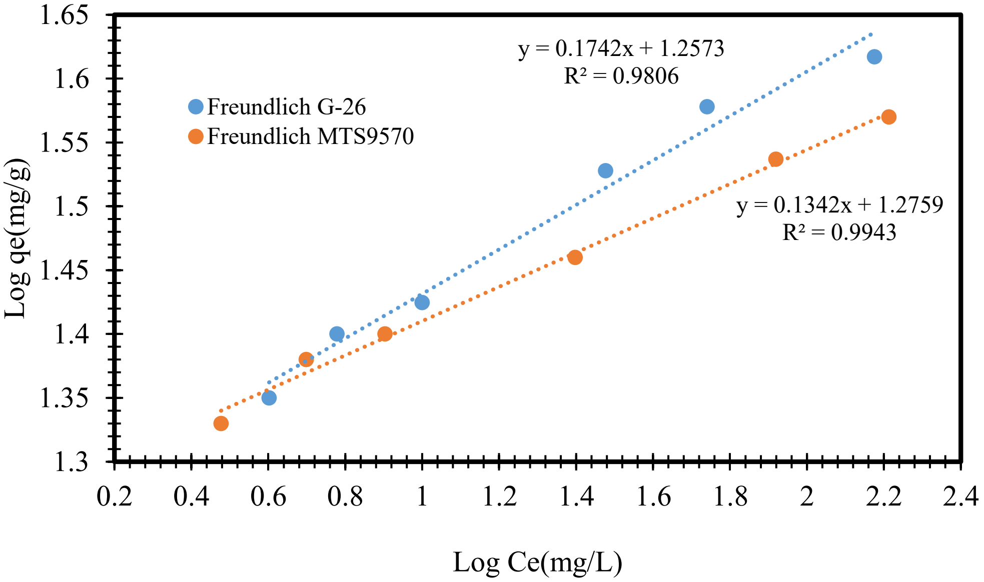


Figure. 5.9. Freundlich isotherm of Pb(II) adsorption on G-26 and MTS9570.

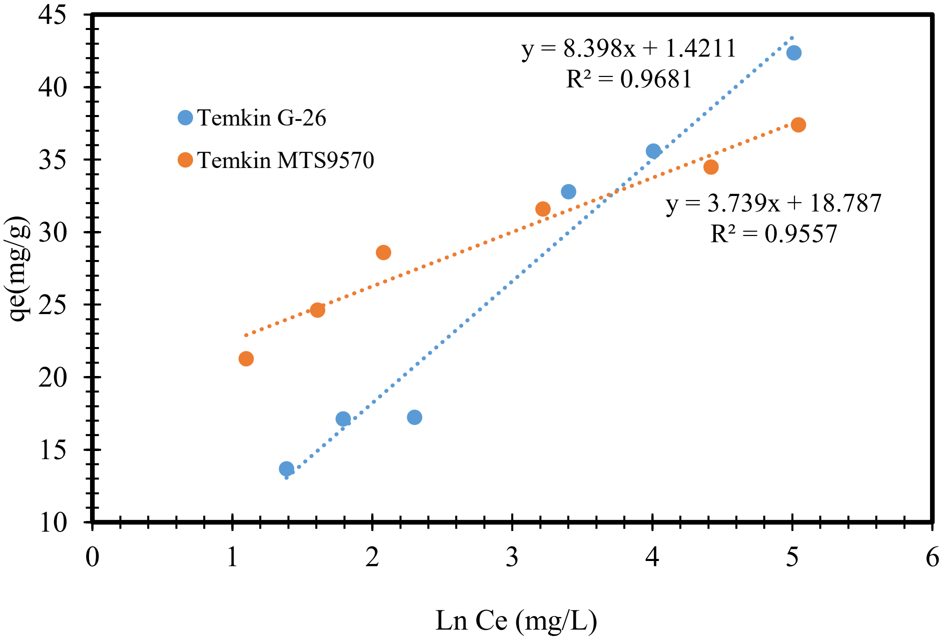


Figure 5.10: Temkin isotherm of Pb(II) adsorption on G-26 and MTS9570.

Table 5.3: Comparison of maximum adsorption capacity of G-26 and MTS9570 resins with some other adsorbents for the adsorption of Pb(II).

Adsorbent	Sorption Capacity for Cu (II) (mg/g)	Conditions	References
SBA-15	41.50	pH = 2.5–4, 30°C	[29]
MWCNT	17.54	pH = 6.5, 20°C	[31]
APTS-SBA-15-AB	43.50	pH =6.0, 60°C	[38]
MCCM	45.50	pH = 6.0, 30°C	[39]
1,8-DAN/XAD-4	29.01	pH = 6.0–7.0, 20°C	[40]
Copolymer 2- hydroxyethyl methacrylate	31.50	pH = 6.0–7.0, 20°C	[41]
Crosslinked chitosan with epichlorohydrin	34.13	pH = 7.0, NA	[42]
Purolite C100	9.64	pH = NA, 25°C	[43]
Amberlite XAD-2 functionalized with Tiron	12.60	pH = 4.0-.5.5, 25°C	[44]
Purolite A830	30.61	pH = 7.0–9.0, 50°C	[45]
Bentonite	28.00	pH = 6.0–9.0, 25°C	[46]
Zeolite	24.40	pH = 9.0, 20°C	[47]
G-26	45.45	pH = 3.5, 20°C	This work
MTS9570	38.46	pH = 3.5, 20°C	This work

5.3.8 Adsorption kinetics

The kinetics for the adsorption of Pb(II) onto G-26 and MTS9570 resins were investigated using Lagergren pseudo-first-order and pseudo-second-order models, represented by Equations (5.6) and (5.7), respectively [48,49].

$$\ln (q_e - q_t) = \ln (q_e) - \frac{k_1 t}{2.303} \tag{5.6}$$

where q_t and q_e are the amounts of metal ions adsorbed (mg/g) at equilibrium and at contact time t (min), respectively; k_1 (min^{-1}) is the first-order rate constant. The plots of ln $(q_e - q_t)$ versus t are presented in Figure 5.11, and the rate constants (k_1) are listed in Table 5.4.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2\, q_e^2} \tag{5.7}$$

where k_2 (g/mg/min) is the rate constant of pseudo-second-order adsorption. The plots of $\frac{t}{q_t}$ versus t are shown in Figure 5.12, and the rate constants (k_2) are presented in Table 5.4. Pseudo-first-order and pseudo-second-order parameters are listed in Table 4. The results clearly show that R^2 values of the second-order kinetic model for both resins are closer to 1 than the results obtained from the first-order kinetic model. Therefore, the adsorption behavior of Pb(II) onto the resins fits the second-order kinetics. G-26 and MTS9570 resins have about the same order of magnitude for the adsorption rates even if they are characterized by different functional groups.

Table 5.4: Kinetic parameters for the adsorption of Pb(II) ions onto G-26 and MTS9570.

	G-26	**MTS9570**
Equations		
Pseudo-first-order		
q_e, exp (mg/g)	41.80	42.00
q_e, cal (mg/g)	3.49	2.513
k1 (m^{-1})	−0.00017	−0.00020
R^2	0.7243	0.9090
Pseudo-second-order		
q_e, cal (mg/g)	42.50	42.10
k2 (g/mg min)	0.00896	0.0362
R^2	0.9994	0.9999

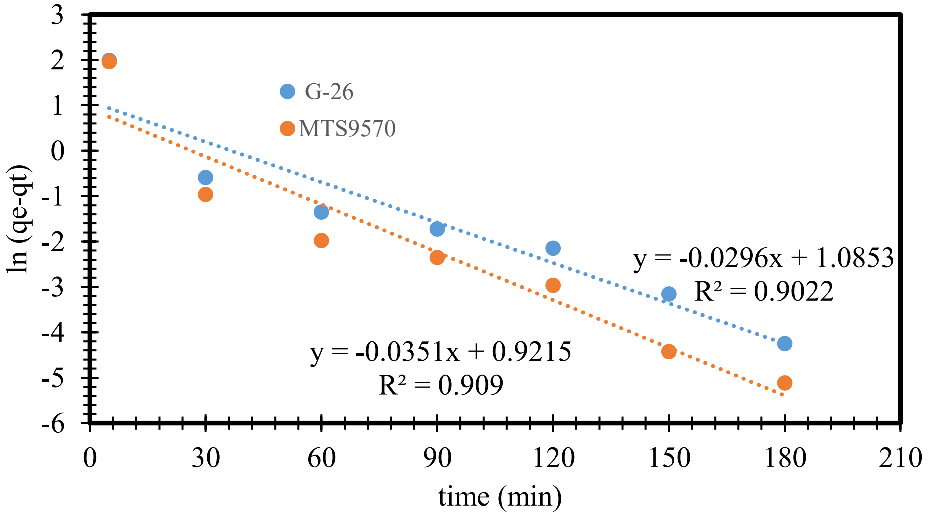


Figure 5.13: Pseudo- first -order for adsorption of Pb(II) onto G-26 andMTS9570 exchange resins.

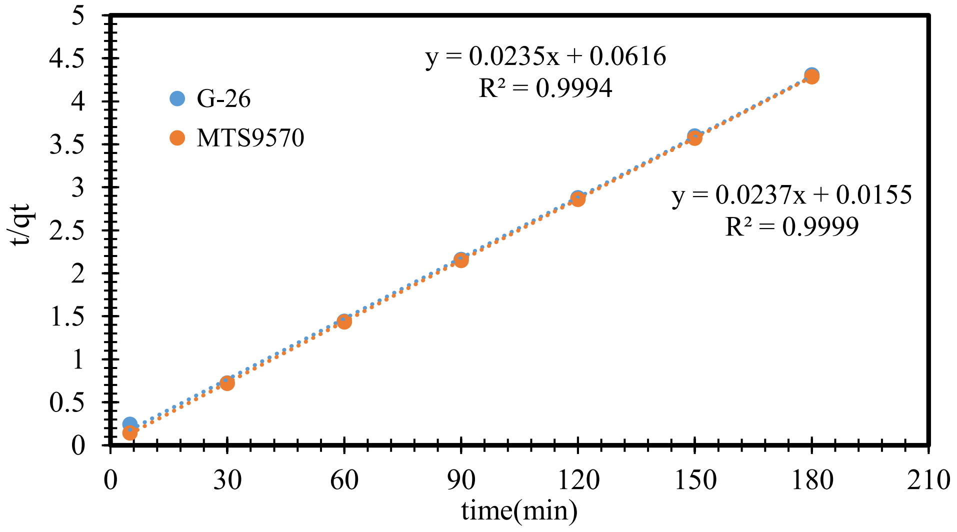


Figure 5.14: pseudo second-order for adsorption of Pb(II) onto G-26and MTS9570 exchange resins.

5.3.9 Thermodynamic evaluation of the process

Thermodynamic parameters such as standard free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$) are very important for analyzing the nature of an ion-exchange process [50]. To estimate these parameters, the influence of temperature on the adsorption process was studied.

The thermodynamic parameters including $\Delta G°$, $\Delta H°$, and $\Delta S°$ were determined, using the following equations:

$$\Delta G° = -RT \ln K_D \quad , K_L = \frac{q_e}{C_e} \tag{5.8}$$

$$\Delta G° = \Delta H° - T \cdot \Delta S° \tag{5.9}$$

OR

$$\ln K_D = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{5.10}$$

where K_D is a dimensionless distribution coefficient calculated from the Langmuir equation as mentioned earlier in Chapter 4, R is the universal gas constant (8.314 J/mol/K), and T is absolute temperature (K). The values of $\Delta H°$and $\Delta S°$ could be obtained from the slope and intercept of the linear plot between $\ln K_D$ versus $1/T$. The calculated values of thermodynamic parameters are listed in Table 5.5.

Table 5.5: Thermodynamic parameters for the adsorption of Pb(II) on G-26 and MTS9570.

Resin	ΔG (kJ mol^{-1})						
	293 K	303 K	313 K	353 K	ΔH (kJ mol^{-1})	ΔS (J/ mol)	R^2
G-26	-22.38	-25.36	-30.93	-35.25	42.30	219.07	0.9645
MTS9570	-22.23	-24.41	-28.75	-33.19	38.65	183.32	0.9266

The negative values for free energy change $\Delta G°$ confirm the feasibility and spontaneous process for Pb(II) adsorption onto both resins, and the positive values of $\Delta H°$ (42.3 and 38.6 kJ/mol for G-26 and MTS9570, respectively) indicate the endothermic nature of the adsorption process. The higher value of TΔS than ΔH suggests that the adsorption process is enthalpy-driven [51].

5.3.10 Desorption studies

The recyclability of the sorbent is one of the most important factors in wastewater treatment [52]. In this work, the regeneration and reuse of the ion exchangers were investigated. For the elution of Pb^{2+} from G-26 and MTS9570 resins, various electrolytes volumes of HCl, HNO_3, CH_3COOH, and $C_2H_2O_4$ were tested at room temperature. It was observed that the best elution result was obtained using 40 mL volume of HCl with 15% (v/v) concentration and 20 min of elution time for the 0.5 g loaded resin, as shown in Figure 5.13. The adsorption-desorption cycle was repeated three times using the same resin, and the results are presented in Table 5.6.

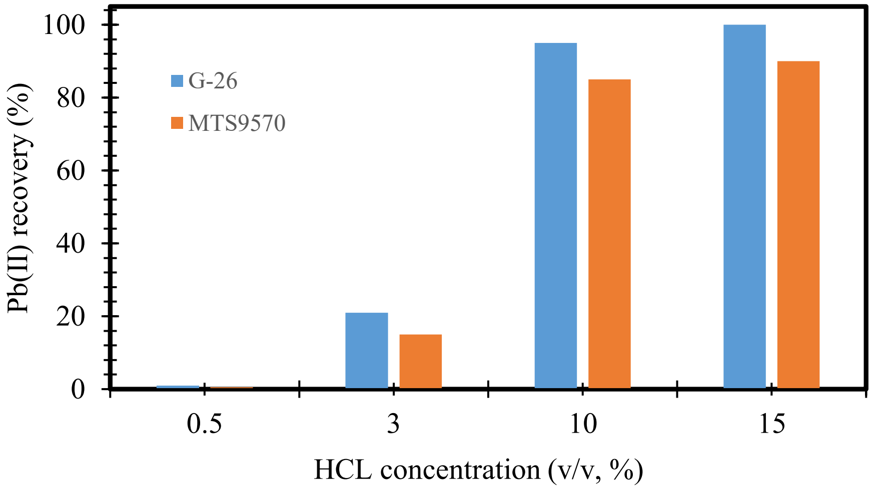


Figure 5.13: Elution of G-26 and MTS9570 at different HCl concentrations (*v/v*) at 0.5 g of resin dosage, 30 min agitation time, 40 mL volume, and at room temperature.

Table 5.6: Adsorption and desorption cycles of Pb(II) on G-26 and MTS9570 resins.

Resin	**Pb(II) Removal %**			**Pb(II) Recovery %**		
	Adsorption Cycle			**Elution Cycle**		
	First Adsorption	**Second Adsorption**	**Third Adsorption**	**First Elution**	**Second Elution**	**Third Elution**
G-26	100	100	100	100	100	100
MTS9570	100	97	96	90	86	76

Table 5.6 shows excellent stability of G-26 resin in all the three cycles, with 100% for adsorption and 100% for elution of Pb(II) ions. While, for the MTS9570 resin, the adsorption percentage was 100, 97, and 96 in the first cycle, second cycle, and third cycle, respectively, the elution efficiency was 90%, 86%, and 76% in the first cycle, second cycle, and third cycle, respectively. This result agrees with the earlier results of Volesky [53]. The performance degradation of MTS9570 resin might be due to its macroporous S-DVB structure (low surface area) and negative swelling factor (−5%) as well. Swelling is an important parameter for the completion of adsorption reaction [54].

Negative swelling factor means volume shrink, which leads to specific surface area adsorption-site decrease.

5.4 Conclusion

This work presents an investigation on the performance of G-26 and MTS9570 resins for the adsorption of lead ions from synthesized wastewater. The resin dosage, pH of solution, contact time, initial metal concentration, and temperature were the main operation parameters that affected the adsorption of Pb(II). For all the systems studied, the pseudo-second-order chemical reaction kinetics provided the best correlation of the experimental data for both resins. The Langmuir model better described the adsorption equilibrium. The maximum adsorption capacities to Pb(II) were 45.45 and 38.46 mg/g for G-26 and MTS9570, respectively. The negative value of free energy $\Delta G°$and the positive value of $\Delta H°$ obtained indicate that the adsorption process is spontaneous and endothermic in nature.

The resin recycling study shows that the most efficient Pb(II) desorption for both resins was obtained using 40 mL volume of HCl with 15% (v/v) concentration and 20 min of elution time at room temperature. Results of consecutive adsorption/desorption studies show that G-26 resin exhibited excellent stability in all the three cycles, with 100% recovery for adsorption and 100% efficiency for elution of Pb(II) ions. Furthermore for the MTS9570 resin, its performance degradation might be due to its macroporous S-DVB structure (low surface area) and negative swelling factor. Gel-structure resin G-26 is more effective than macroporous-structure resin (MTS9570) for the removal/recovery of lead ions from wastewater.

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References

[1] Y.H.Zhang, ‘‘100 years of Pb deposition and transport in soils in Champaign, Illinois, USA’’. *Water Air Soil Pollut. 2003, 146, 197–210.https://doi.org/10.1023/A:1023957226204*.

[2] A.Selvi, A.Rajasekar, J.Theerthagiri, A. Ananthaselvam, K. Sathishkumar, J. Madhavan, P. Rahman, ‘‘Integrated remediation processes toward heavy metal removal/recovery from various environments—A review’’. *Front.Environ. Sci. 2019, 00066, 1–15. https://doi.org/10.3389/fenvs.2019.00066*

[3] S.Ahuja, B.G.Loganathan, ‘‘Contaminants in Our Water: Identification and Remediation Methods’’. *American Chemical Society: Washington, DC, USA, 2020.*

[4] N.A.A.Qasem, R.H. Mohammed, D.U, ‘‘Removal of heavy metal ions from wastewater: A comprehensive and critical review’’. *NPJ Clean Water 2021, 36, 1–15. https://doi.org/10.1038/s41545-021-00127-0.*

[5] M.L.Rahman, M.S. Sarjadi, S. Guerin, S.M. Sarkar, ‘‘Poly (amidoxime) Resins for Efficient and Eco-friendly Metal Extraction’’. *ACS Appl. Polym. Mater. 2022, 4, 2216–2232.*

[6] G.S.S.Sunder, A. Rohanifar, N.Alipourasiabi, J.G. Lawrence, J.R. Kirchhoff, ‘‘Synthesis and Characterization of Poly(pyrrole-1- carboxylic acid) for Preconcentration and Determination

of Rare Earth Elements and Heavy Metals in Water Matrices''.*ACS Appl. Mater. Interfaces 2021, 13, 34782–34792.* *https://doi.org/10.1021/acsami.1c05061*

[7] F.X.Chu, C. Liu, H. Wu, X. Liu, ''Advances in Chelating Resins for Adsorption of Heavy Metal Ions'', *Ind. Eng. Chem. Res. 2022, 61, 11309–11328.* *https://doi.org/10.1021/acs.iecr.2c01353*

[8] T.Chen,H. Li,H. Wang,X. Zou,H. Liu,D. Chen, Y. Zhou, ''Removal of Pb(II) from Aqueous Solutions by Periclase/Calcite Nanocomposites'',*Water. Air Soil Pollut. 2019, 230, 299–314. https://doi.org/10.1007/s11270-019-4354-z*

[9] A.Lalmi,K. Bouhidel, B. Sahraoui, C.E.H Anfif, ''Removal of lead from polluted waters using ion exchange resin with $Ca(NO_3)_2$ for elution''.*Hydrometallurgy 2018, 178, 287–293.* *https://doi.org/10.1016/j.hydromet.2018.05.009*

[10] N.Wang, M. Bora, H. Song, K. Tao, J. Wu,L. Hu,J. Liao,S. Lin,M.S Triantafyllou, X. Li, ''Hyaluronic Acid Methacrylate Hydrogel-Modified Electrochemical Device for Adsorptive Removal of Lead(II)''.*Biosensors 2022, 12, 714.* *https://doi.org/10.3390/bios12090714*

[11] H.Ren,B. Li, M. Neckenig, D. Wu, Y. Li, Y. Ma, X. Li, N. Zhang, . ''Efficient lead ion removal from water by a novel chitosan gel-based sorbent modified with glutamic acid ionic liquid'', *Carbohydr. Polym. 2019, 207, 737–746.* *https://doi.org/10.1016/j.carbpol.2018.12.043*

[12] World Health Organization. ''Guidline for Drinking-Water Quality, 4th ed.; World Health Organization'': *Geneva, Switzerland, 2017.*

[13] G. Sunder, S. Adhikari, A.Rohanifar, A.Poudel, J. Kirchhoff, ''volution of environmentally

friendly strategies for metal extraction''.*Separations 2020, 7, 4.* *https://doi.org/10.3390/separations7010004*

[14] S.Elfeghe, Q. Sheng, Y. Zhang, ''Separation of Lead and Copper Ions in Acidic Media Using an Ion-Exchange Resin with a Thiourea Functional Group''. *ACS Omega 2022, 7, 13042–13049. https://doi.org/10.1021/acsomega.2c00417*

[15] J.Acharya, J.N. Sahu, J.R Mohanty, B.C. Meikap, ''Removal of lead (II) from wastewater by activated carbon developedfrom tamarind wood by zinc chloride activation''.*Chem. Eng. J. 2009, 149, 249–262. https://doi.org/10.1016/j.cej.2008.10.029*

[16] A.Abou-Shady, C. Peng, J. Bi, H. Xu, O.J Almeria, '' Recovery of Pb(II) and removal of NO3− from aqueous solutions using integrated electrodialysis electrolysis, and adsorption Process''.*Desalination 2012, 286, 304–315. https://doi.org/10.1016/j.desal.2011.11.041*

[17] C.V Gherasim, J. Krivcik, P. Mikulasek, ''Investigation of batch electrodialysis process for Removal of lead ions from aqueous solutions''.*Chem. Eng. J. 2014, 256, 324–334.* *https://doi.org/10.1016/j.cej.2014.06.094*

[18] C.A.Bessel, K. Laubernds, N.M. Rodriguez, R.T.K. Baker, ''Graphite nanofibers as an Electrode for fuel cell applications''. *J. Phys.Chem. B 2001, 105, 1115–1518.* *https://doi.org/10.1021/jp003280d*

[19] A.Rohanifar, N. Alipourasiabi, G, Shyam Sunder, J.Lawrence, J.R. Kirchhoff, ''Reversible Chelating polymer for determination of heavy metals by dispersive micro solid- phase extraction with ICP-MS''. *Mikrochim. Acta 2020, 187, 339.* *https://doi.org/10.1007/s00604-020-04308-5*

[20] E.Maranón, Y. Fernández, L. Castrillón, ‘‘Ion exchange treatment of rinse water generated in the galvanizing process’’.*Water Environ. Res. 2005, 77, 3054–3058.* *https://doi.org/10.2175/106143005X73947*

[21] E.Pehlivan, T. Altun, ‘‘The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin’’. *J. Hazard. Mater. B 2006, 134, 149–156. https://doi.org/10.1016/j.jhazmat.2005.10.052*

[22] S. Cavaco, S. Fernandes, M.Quina, L.Ferreira, ‘‘Removal of chromium from electroplating industry effluentsby ion exchange resins’’. *J. Hazard. Mater. 2007, 144,634-638.* *https://doi.org/10.1016/j.jhazmat.2007.01.087*

[23] R.M.P.Silva, J.P.H Manso, J.R.C Rodrigues, R.J.L Lagoa, ‘‘Acomparative study of alginate beads and an ion exchangers in for the removal of heavy metals from a metal plating effluent *J. Environ. Sci. Health A 2008, 43, 1311–1317.https://doi.org/10.1080/10934520802177953*

[24] J.Qian, Z. Zeng, W. Xue, Q. Guo, ‘‘Lead removal from aqueous solutions by 732 cation-exchange resin’’. *Can. J. Chem. Eng. 2016, 94, 142–150. https://doi.org/10.1002/cjce.22363*

[25] H.Guo, Y.Ren, X. Sun, Y. Xu, ‘‘Removal of Pb^{2+} from aqueous solutions by a high-efficiency resin’’. *Appl. Surf. Sci. 2013, 283,660–667.* *https://doi.org/10.1016/j.apsusc.2013.06.161*

[26] S.H.Tabatabaei, M. Asemanrafat, M. Nousahdi, ‘‘Removal of Lead from aqueous phase using Amberlite and natural Zeolite’’. *E3SWeb Conf. 2013, 1, 13010.* *https://doi.org/10.1051/e3sconf/20130113010*

[27] I.Vergili, ‘‘Sorption of Pb (II) from battery industry wastewater using a weak acid cation

exchange resin''. *Process Saf. Environ. Prot.2017, 107, 498–507.* *https://doi.org/10.1016/j.psep.2017.03.018*

[28] C.Xiong, C. Yao, ''Adsorption behavior of gel-type weak acid resin (110-H) for Pb2+''. *Trans. Nonferr. Met. Soc. China 2008, 18, 1290–1294.* *https://doi.org/10.1016/S1003-6326(08)60219-8*

[29] P.T.T.Thu, T.T. Thanh, H.N.Phi, S.J. Kim, V. Vo, ''Adsorption of lead from water by thiol functionalized SBA-15 silicas''. *J. Mater.Sci. 2010, 45, 2952–2957.* *https://doi.org/10.1007/s10853-010-4288-8*

[30] A.Merganpour, G. Nekuonam, O.A. Tomaj, Y. Kor, H. Safari, ''Efficiency of lead removal from drinking water using cationic resin Purolite''.*Environ. Health Eng. Manag. J.2015, 2, 41–45.* *http://eprints.kmu.ac.ir/id/eprint/22171*

[31] X.Ren, D.Shao, S.Yang, J.Hu, G.D. Sheng, X.Tan, X.Wang, ''Comparative study of Pb(II) sorption on XC-72 carbon and multi-walled carbon nanotubes from aqueous solutions''. *Chem. Eng. J. 2011,170, 170–177.* *https://doi.org/10.1016/j.cej.2011.03.050*

[32] S.Elfeghe, S. Anwar, Y. Zhang, ''Adsorption and removal studies of cadmium ion onto Sulfonic/phosphonic acid functionalization resins''. *J. Chem. Eng. 2022, 100, 3006–3014.* *https://doi.org/10.1002/cjce.24400*

[33] Y.Zhang, S. Elfeghe, Z.D Tang, ''Mechanism study of Cd(II) ion adsorption onto resins with sulfonic/phosphonic groups using electronic structure methods''. *J. Mol. Liq. 2022, 358, 119199.* *https://doi.org/10.1016/j.molliq.2022.119199*

[34] M.Al-Anber, Z.A. Al-Anber, ''Utilization of natural zeolite as ion-exchange and sorbent

material in the removal of iron''. *Desalination 2007, 225, 70–81.* *https://doi.org/10.1016/j.desal.2007.07.006*

[35] I.Langmuir, ''the Constitution and Fundamental Properties of Solids and Liquids''. Part I Solids. *J. Am. Chem. Soc. 1916, 38, 2221–2295.* *https://doi.org/10.1021/ja02268a002*

[36] H.M.F.Freundlich, ''Uber die Adsorption in Losungen''.*Phys. Chem. 1906, 57, 385–470.*

[37] M.Temkin, V. Pyzhev, ''Kinetics of Ammonia Synthesis on Promoted Iron Catalysts''. *Acta Physicochim. URSS 1940, 12, 327–356.*

[38] E.Da'na, A. Sayari, 'Adsorption of heavy metals on amine-functionalized SBA-15 prepared Co-condensation: Applications to real water samples''.*Desalination 2012, 285, 62-67.* *https://doi.org/10.1016/j.desal.2011.09.034*

[39] X.Luo, J. Zeng, S.Liu, L. Zhang, ''An effective and recyclable adsorbent for the removal of Heavy metal ions from aqueous system: Magnetic chitosan/cellulose microspheres''. Bioresour. *Technol. 2015, 194, 403–406.* *https://doi.org/10.1016/j.biortech.2015.07.044*

[40] M.I.U.Hoque, D.A. Chowdhury, R. Holze, A.N. Chowdhury, M.S. Azam, ''Modification of Amberlite XAD-4 resin with 1,8-diaminonaphthalene for solid phase extraction of copper, cadmium and lead, and its application to determination of these metals in dairy cow's milk'' *.J. Environ. Chem. Eng.2015, 3, 831–842.* *https://doi.org/10.1016/j.jece.2015.03.020*

[41] O.Moradi, M. Aghaie, K. Zare, M. Monajjemi, H. Aghaie, ''The study of adsorption characteristics Cu^{2+} and Pb^{2+} ions onto PHEMA and P(MMA-HEMA) surfaces from aqueous single solution''. *J. Hazard. Mater. 2009, 170, 673–679.* *https://doi.org/10.1016/j.jhazmat.2009.05.012*

[42] A.H.Chen, S.C. Liu, C.Y.Chen, ‘‘Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin’’.*J. Hazard. Mater. 2008, 154, 184–191.* *https://doi.org/10.1016/j.jhazmat.2007.10.009*

[43] S.A. Abo-Farha, A.Y. Abdel-Aal, I.A. Ashour, S.E. Garamon, ‘‘Removal of some heavy metal cations by synthetic resin purolite C100’’.*J. Hazard. Mater. 2009, 169,190–194. DOI:* *10.1016/j.jhazmat.2009.03.086*

[44] M.Kumar, D.P.S. Rathore, A.K. Singh, ‘‘Metal ion enrichment with Amberlite XAD-2 functionalized with Tiron: Analytical applications’’. *Analyst 2000, 125, 1221–1226.* *https://doi.org/10.1039/B000858N*

[45] J.Jachua, Z. Hubicki, ‘‘Sorption of heavy metal complexes with MGDA on the macroporous anion exchanger Purolite A830’’. *CHEMIK 2013, 67, 693–700.*

[46] C.M.Futalan, C.C. Kan, M.L. Dalida, K.J. Hsien, C. Pascua, M.W.Wan, ‘‘Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentoni’’ *Carbohydr. Polym. 2011, 83, 528–536.* *https://doi.org/10.1016/j.carbpol.2010.08.013*

[47] F.Sharifipour, S. Hojati, A. Landi, A.F. Cano, ‘‘Kinetics and Thermodynamics of Lead Adsorption from Aqueous Solutions onto Iranian Sepiolite and Zeolite’’. *Int. J. Environ. Res. 2015, 9, 1001–1010. Doi.10.22059/IJER.2015.988*

[48] S.Lagergren, Zur theorie der sogenannten adsorption geloster stoffe. K. Sven. Vetensk. Handl. *1898, 24, 1–39.*

[49] Y.S.Ho, G. McKay, ‘‘Pseudo-second order model for sorption processes’’. *Process Biochem. 1999, 34, 451–465.* *https://doi.org/10.1016/S0032-9592(98)00112-5*

[50] M.Ahmadi, P. Teymouri, A. Setodeh, ‘‘Adsorption of Pb (II) from aqueous solution onto lewatit for 36 nano resin: Equilibrium and kinetic studies’’. *Environ. Eng. Manag. J. 2011, 10, 1579–1587. http://omicron.ch.tuiasi.ro/EEMJ/*

[51] F.Q.An, R.Y. Wu, M. Li, T.P. Hu, J.F. Gao, Z.G. Yuan, ‘‘Adsorption of heavy metal ions by iminodiacetic acid functionalized D301 resin: Kinetics, isotherms and thermodynamic’’. *React. Funct. Polym. 2017, 118, 42–50.* *https://doi.org/10.1016/j.reactfunctpolym.2017.07.005*

[52] N.Burham, ‘‘Separation and preconcentration system for lead and cadmium determination in natural samples using 2-aminoacetylthiophenol modified polyurethane foam’’. *Desalination 2009, 249, 1199–1205. https://doi.org/10.1016/j.desal.2009.04.009*

[53] B.Volesky, J. Weber, J.M. Park, ‘‘Continuous-flow metal biosorption in a regenerable Sargassum column’’. *Water Res. 2003, 37,297–306.* *https://doi.org/10.1016/S0043-1354(02)00282-8*

[54] V.G.Teixeira, F.M.B. Coutinho, F.R.M. Petrocínioa, A.S. Gomesa, ‘‘Determination of accessible chloromethyl groups in chloromethylated styrene-divinylbenzene copolymers’’ *.J. Braz. Chem. Soc. 2005, 16, 951–956.* *https://doi.org/10.1590/S0103-50532005000600010*

Chapter 6

Separation of Lead and Copper Ions in Acidic Media Using Resin with a Thiourea Functional Group

Preface

A version of this chapter has been published in the ***Journal of ACS Omega*** **2022, 7, 15, 13042–13049.** *I produced the work alongside my co-authors; Yahui Zhang and Qiuyue Sheng. I am the main author. I conducted all lab experiments, calculated parameters for isotherms, kinetic and dynamic studies. I prepared the first draft of the manuscript and subsequently revised the manuscript based on the co-authors' and peer review feedback. Co-author, Yahui Zhang assisted in the development of concept, design of methodology, reviewing and editing the draft, and reviewing and revising the new version of the manuscript. Co-author,* Qiuyue Sheng *supported in the data and process analysis, reviewing and editing the draft, reviewing and revising the new version of the manuscript.*

Abstract

This research studied the selective separation of lead and copper ions in acidic solutions using Puromet MTS 9140 resin with a thiourea functional group. The effects of operation parameters, that is, resin dosage, solution pH, adsorption time, metal concentration, and temperature, on metal adsorption were investigated using batch-test protocols. Adsorption experimental data were analyzed with Langmuir, Freundlich, and Temkin models. The results demonstrate that the MTS 9140 resin has adsorption selectivity for copper ions over lead ions. The adsorption recovery of Cu^{2+} exceeded 95%, while Pb^{2+} coloading was under 19% with MTS 9140 resin dosage of 0.070 g/mL in the pH range of 2.5 to 4.5. The kinetic studies showed that the adsorption process could be better described by the pseudo-second-order model for lead and copper ions. The temperature dependence indicates the endothermic nature of the adsorption process. The resin also showed potential application as an effective adsorbent for removing heavy metal ions in water or wastewater treatment.

Keywords: Adsorption; Resins; Copper and lead; Kinetics; Separation

6.1 Introduction

Heavy metal ions are hazardous environmental pollutants, which can be toxic even at very low concentrations, hence posing great challenges to researchers addressing environmental degradation. Lead and copper ions are two of these environmental pollutants and are commonly present in industrial effluents from processes such as electroplating, chemical, petrochemical, and metallurgical operations [1]. Many different technologies are being used for treating wastewaters, such as precipitation, sedimentation, membrane filtration, electrochemical techniques, and and ion exchange [2,3]. Among these methods, resin adsorption is considered to be the best process choice in many applications because it has high selectivity and can treat a large wastewater volume [4].

Numerous studies have been conducted on the removal and separation of toxic metals using different resins possessing various functional group [5-7]. A resin with a sulfonic functional group, for example, has been studied by Demirbas et. al. [8]. They studied the ion-exchange mechanism of metal ions on Amberlite IR-120-sulfonated resin and investigated the influence of resin dosage, pH, and temperature. In addition, Pehlivan et al [9]. reported the ion-exchange properties of Dowex 50 W resin toward Cu^{2+}, Zn^{2+}, Ni^{2+}, $Cd^{2+}$and Pb^{2+}, and the equilibrium ion-exchange capacity of resin for metal ions was explored using Freundlich and Langmuir isotherms. The resins with carboxylic functional groups were examined by Silva and Brunner [10]. They found that the efficiency of the IRC-50 resin was lower than that of the IRC-86 resin for the adsorption of Cd^{2+}, Cu^{2+}, and Pb^{2+}, and the sorption of metal ions depended strongly on the feed concentration. The Dow M-4195 resin with a quaternary ammonium function group has been studied by Diniz et al., [11]. The production of pure manganese chloride solution with the Dow M-4195 resin from an acidic manganese chloride leach solution contaminated by Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, and Fe^{3+} was demonstrated. Also, a resin with a tertiary amine functional group was tested by Jachuła et al [12].

The separation of Cu(II) and Pb(II) in the water system is a common practice in hydrometallurgy [13,14]. However, currently, there is no theoretical standard for the choice of resins for a selective Cu(II) and Pb(II) separation in water solutions. It is well known that thiourea has strong complexing power to gold ions [15,16]. As reported by Purolite Co., commercial polymeric exchanger Puromet MTS 9140 with a thiourea functional group was efficient for Au recovery. As copper and gold are both group IB metals in the periodic table, it may also have an adsorption preference for copper ions. Therefore, Puromet MTS 9140 and some commercial resins with various functional groups from different suppliers have been explored for such purposes. It was found that Puromet MTS 9140 with a thiourea group had a strong adsorption preference for Cu(II) over Pb(II). Resins with a thiourea functional group are rarely reported to be used in the separation and recovery of Cu(II) and Pb(II). In this work, a systematic study on the selective separation of copper from lead in a water system using Puromet MTS 9140 resin has been conducted. Batch experiments were performed at different conditions of solution pH, resin dosage, metal concentration, and adsorption time in order to investigate the resin adsorption performance.

6.2. Materials and Methods

6.2.1. Materials and Instruments

The macroporous polystyrenic chelating resin MTS 9140 with a thiourea group used in the experiments was supplied by Purolite USA. It contains three major structure units: p-thiourea-styrene, othiourea-styrene, and m-thiourea-styrene. Their molecular structures, built with Gauss View 6.1.1 software, are illustrated in Figure 6.1.

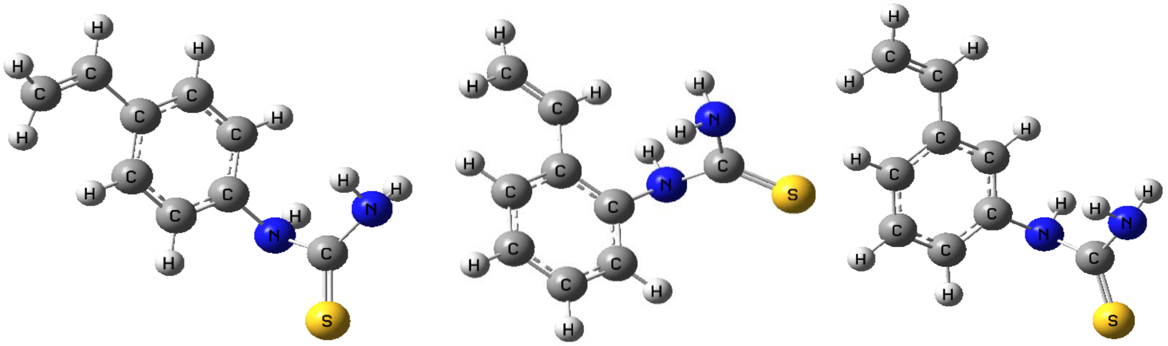


Figure 6.1: Three major structure units in MTS 9140 resin: p-thiourea-styrene, o-thiourea-styrene, and m-thiourea-styrene (from left to right). (Blue: N, Yellow: S, Dark gray: C, Gray: H).

Its physical and chemical properties, as reported by the suppliers, are shown in Table 6.1. Other commercial resins were also provided by their producers. Before using for the adsorption test, the resin was washed several times with deionized water to remove impurities, dried at room temperature for 10 days to constant mass, and stored safely in the lab for further experiments. Cupric chloride, $CuCl_2•2H_2O$, was purchased from A&C American Chemicals Ltd (Quebec,´Canada), and lead nitrate, $Pb(NO_3)_2$, was obtained from ACP Chemicals Inc. (Quebec, Canada). A wavelength dispersive X-´ ray fluorescence (WDXRF) spectrometer (model Supermini

200) was used for the metal concentration analysis, an orbital shaker (model Promax 2020) was employed for adsorption tests with 20 mL of solutions in 125 mL flasks, and an Orion Star A211 pH meter was used for the solution pH measurement.

Table 6.1: 1-Physical and chemical properties of MTS 9140 resin.

Characteristics	Physical form	Shipping weight	Particle size	Specific Gravity
Values	Spherical Beads	690 - 730 g/L	300 - 1200 μm	1.12
Characteristics	Matrix	Functional group	Total exchange	Temperature Limit
Values	Polystyrene DVB	Thiourea	1 eq/L	100 °C

6.2.2. Experimental Procedures

To find the most selective resin for the separation of Cu(II) and Pb(II) in the water system, a number of commercial resins with different functional groups from various suppliers have been tested at the dosage range of 0.005- 0.025 g/mL in a 20 mL solution containing 1800 mg/L Pb(II) and 1200 mg/L Cu(II) with pH 4.5 in a one-stage 2 h adsorption.

Due to the low density of Puromet MTS 9140 resin, the resin cannot be totally submerged in the 20 mL water solution when the resin amount is over 1 g. Therefore, systematic adsorption batch tests with Puromet MTS 9140 resin were performed in two stages by shaking 125 mL flasks on an electrical shaker for a period of 2 h in each stage, as shown in Figure 6.2. Unless otherwise specified, the experiments were conducted at 20 ± 1 °C, with a shaking speed of 150 rpm, using 0.6 g dry resin in the1st adsorption stage and 0.8 g dry resin for the 2nd adsorption stage added in a 20 mL solution containing 1800 mg/L Pb(II) and 1200 mg/L Cu(II) with pH 4.5. After each adsorption stage, the resin was filtered out, and the metal concentration in the remaining solution was measured by X-ray fluorescence (XRF). For single metal adsorption tests, separate 1800 mg/L

Pb(II) solution and 1200 mg/L Cu(II) solution with pH 4.5 were used following a similar procedure, as mentioned above. The average value of duplicate experiments was taken. The reproducibility deviation of the measurements was within 10.0%.

The metal recovery was calculated through the difference between the initial metal concentration in the solution and the final concentration in the filtrate after adsorption. The following formula was used to calculate metal removal efficiency (%).

$$\text{Removal } (\%) = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (6.1)$$

where C_i and C_f are the initial and final concentrations of the studied metal ions, respectively.

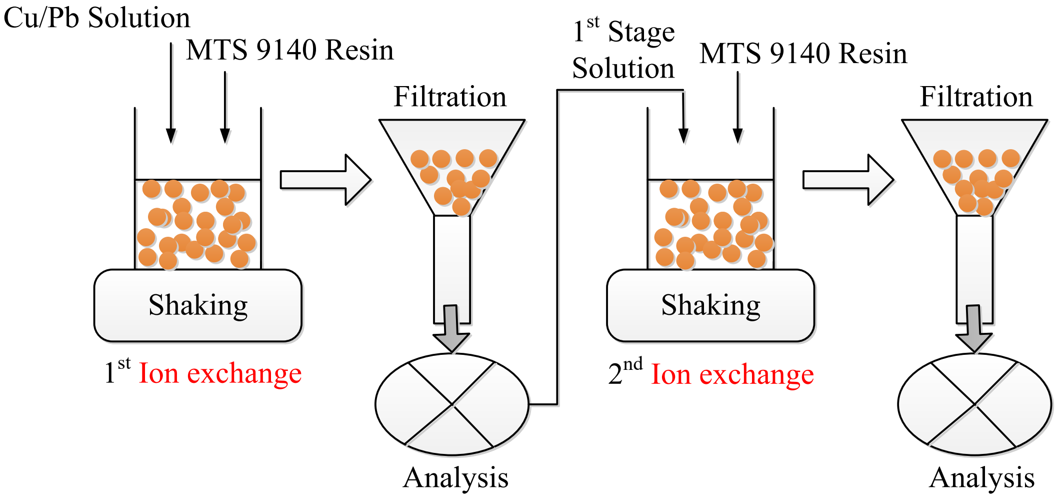


Figure 6.2: Flow sheet of metal adsorption process using MTS 9140 resin.

6.3. Results and Discussion

6.3.1. Exploration of Resins for the Cu- and Pb Selective Separation

In the adsorption process, selection of proper exchange resins for the metal separation is one of the biggest challenges due to the availability of various commercial adsorbents. The efficiency of the adsorption system is controlled by resin selectivity [17]. Various commercial resins with different functional groups from different suppliers have been tested at the dosage range of 0.005 - 0.025 g/mL in a 20 mL solution, which contains 1800 mg/L Pb(II) and 1200 mg/L Cu(II) with pH 4.5, in a one-stage ion exchange. The experimental results shown in Table 6.2 indicate that most of the studied resins have a high ion-exchange affinity for both the metals, for example, Lewatit MonoPlus TP208 and Amberlite IRC747 had a 99.9% removal rate for both Cu(II) and Pb(II) ions. They could be applied in the removal of both the metals from the water system, which is very important from the perspective of environmental remediation and protection. Of course, further studies are required. The possibility of Pb^{2+} and Cu^{2+} separation may be achieved by using Dowex Mac-3, WAG RTI 26600, Lewatit VP OC 1026, and Purolite MTS 9140 resins, which have large differences in the adsorption preference between Cu(II) and Pb(II). Owing to the largest recovery difference for Cu(II) and Pb(II) ions, the MTS 9140 resin was chosen for copper and lead separation in this study by improving its performance with two adsorption stages, as mentioned above. Systematic adsorption experiments were conducted for the separation of lead and copper ions from an acidic water solution at different operating conditions of the pH, temperature, adsorption time, agitation speed, and metal concentration.

Table 6.2: Resins explored for the adsorption of Pb^{2+} and Cu^{2+} ions (Resin dosage 0.025 g/mL).

Function group	Resin	Pb^{2+}%	Cu^{2+}%
Sulfonic	Dowex G-26	99.9	96
	Amberlite IR-120 H	96	85
Iminodiacetic	Purolite S930 plus	93	99
	Lewatit monoplusTP207	96	96
	Amberlite IRC784I	87	97
	Lewatit monoplus TP208	99.9	99.9
	Purolite S930EPlus	79	90
Aminophosphonic	SIR 500	91	84
	Amberlite IRC747	99.9	99.9
	Purolite S940	79	58
	Purolite S950plus	91	78
	Puromet™ MTS 9500	88	73
Aminomethylphosphonic	Lewatit monoplus TP 260	97	96
Phosphonic and Sulfonic	Purolite MTS 9570	87	45
Bis-picolylamine	Lewatit MDS TP220	98	93
Carboxilic	Dowex Mac-3	31	4
	WAG RTI 26600	34	3
N-methylglucamine	Purolite S108	34	62
Di-2-ethylhexylphosphat (D2EHPA)	Lewatit vp oc 1026	37	3
Thiourea	Lewatit monoplusTP214	69	43
	Purolite MTS 9140	3	43
Trimethyl ammonium	Amberjet 4400 Cl	2	0
Isothiouronium	Purolite MTS 9200	4	7
Amidoxime	Puromet™ MTS 9100	43	25
Thiol	Puromet™ MTS 9240	36	23
Sulphonic and Trimethylammonium	Amberlite™ IRN150	77	34

6.3.2. Effect of the Resin Dosage

The effect of the MTS 9140 resin dosage on adsorption recovery of Pb^{2+} and Cu^{2+} from the water solution was tested in the range of 0.005- 0.070 g/mL resin while keeping the other parameters constant as described in Section 6.2.2. The adsorption results demonstrate that both metal recoveries increase with the resin dosage. The adsorption recovery was 3.64% for Pb^{2+} and

41.68% for Cu^{2+} at 0.03 g/mL resin dosage (1st. adsorption stage, Figure 6.3a). Recovery increased to 15 and 99% for Pb^{2+} and Cu^{2+}, respectively, at 0.07 g/mL resin dosage after the 2nd stage adsorption (Figure 6.3b).

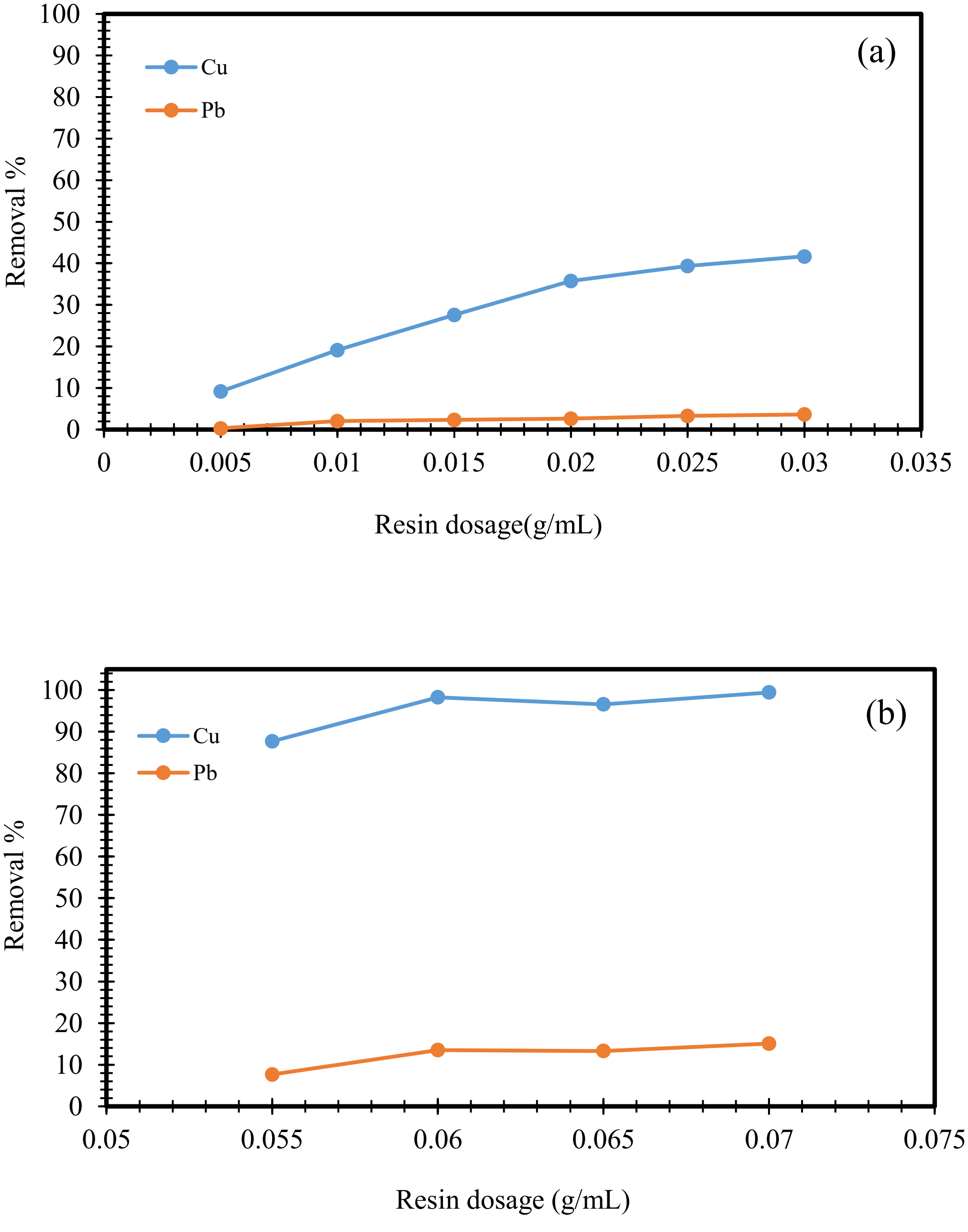


Figure 6.3: Effect of the resin dosage on Pb(II) and Cu(II) recoveries in binary metal solution in the 1st (a) and 2nd (b) adsorption stage.

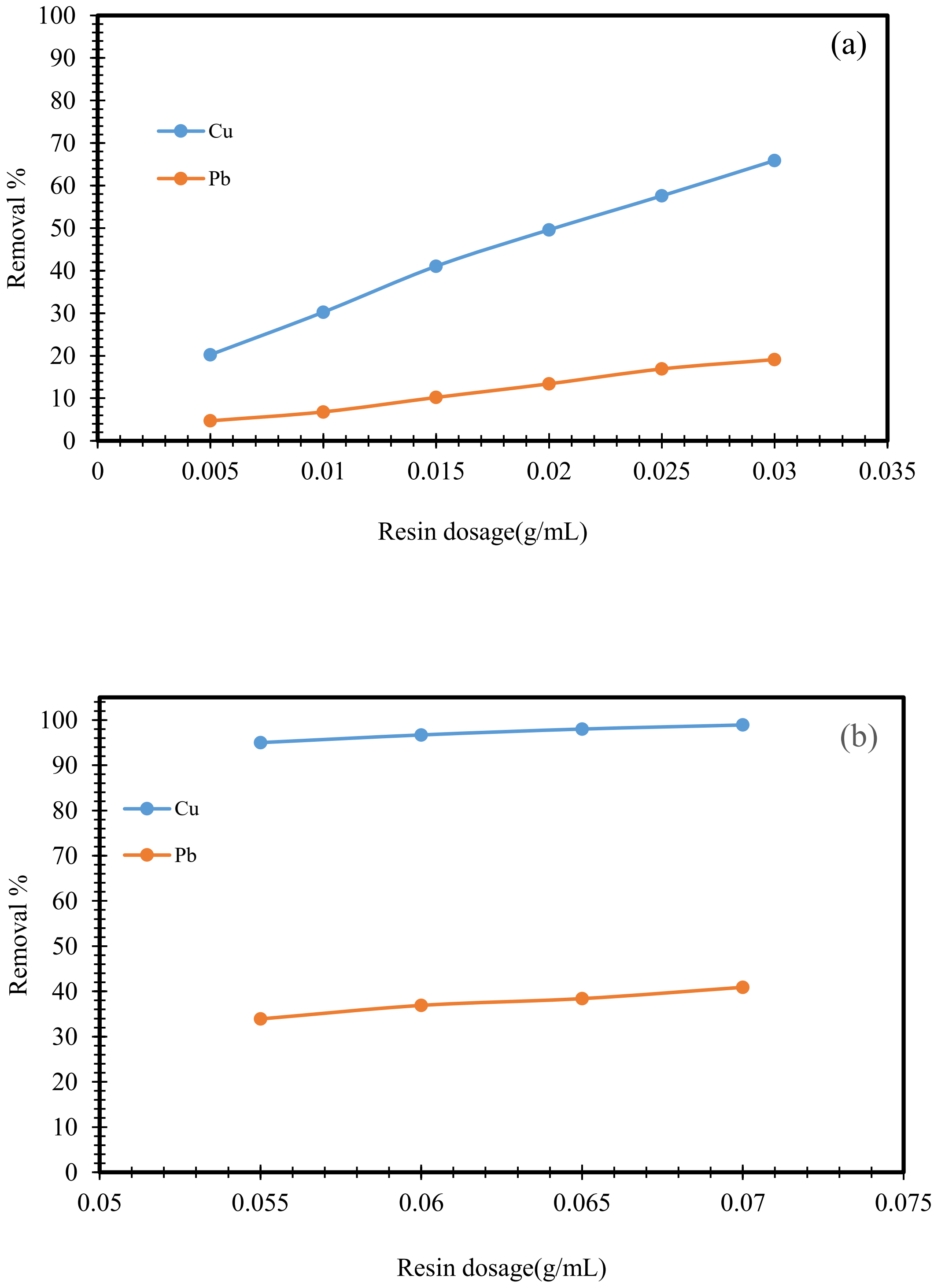


Figure 6.4: Effect of the resin dosage on Pb(II) and Cu(II) recoveries in the single metal solution in the 1st (a) and 2nd (b) adsorption stage.

To help understand the adsorption mechanism of Pb(II) and Cu(II) in the binary metal solution, the adsorption of Pb(II) and Cu(II) with the MTS 9140 resin in a single 1800 mg/L Pb (II) solution and single 1200 mg/L Cu(II) solution was studied as shown in Figure 6.4a,b. It was found that the adsorption recoveries for both Pb(II) and Cu(II) in the single metal solution were higher than those in the binary solution. Especially for Pb(II), its recovery can be over 40% at the resin dosage of 0.070 g/mL. This is because the MTS 9140 resin has a stronger adsorption preference for Cu(II) over Pb(II), and there are more adsorption sites for Pb(II) in the single metal solution.

6.3.3. Effect of pH

The effect of pH on the recovery of Pb(II) and Cu(II) ions was studied in the range of 1.5 to 4.5, and the results are shown in Figure 6. 5a, b. The maximum recovery of Pb was at pH 1.5 in the 1st stage adsorption, which agrees with the earlier results [18]. Between pH 2.5 and 4.5, Pb^{2+} recovery was constant in the range of 8%. Cu^{2+} recovery was in the range of 43 to 45% and did not change much with pH. During the 2nd stage, the recovery for Cu^{2+} increased to 98% and was quite stable across the whole pH range. Precipitation of copper was observed at pH > 5. Therefore, the solution pH was kept at 4.5 in the subsequent tests.

6.3.4. Effect of Temperature

The influence of temperature on adsorption of Cu(II) and Pb(II) ions on the MTS 9140 resin was studied at 20, 40, 60, and 80°C. The recovery of Pb^{2+} ions is not affected remarkably by temperature in both the first and second adsorption stages, while the adsorption recovery for Cu^{2+} ions increased with a temperature rise. Cu^{2+} recovery increased quickly to 73% at 80°C in the first adsorption stage and reached 100% at 60 and 80°C in the second adsorption stage, as shown in

Figure 6.6a, b. This may be attributed to the endothermic character of this adsorption process as temperature increment favors an endothermic reaction thermodynamically.

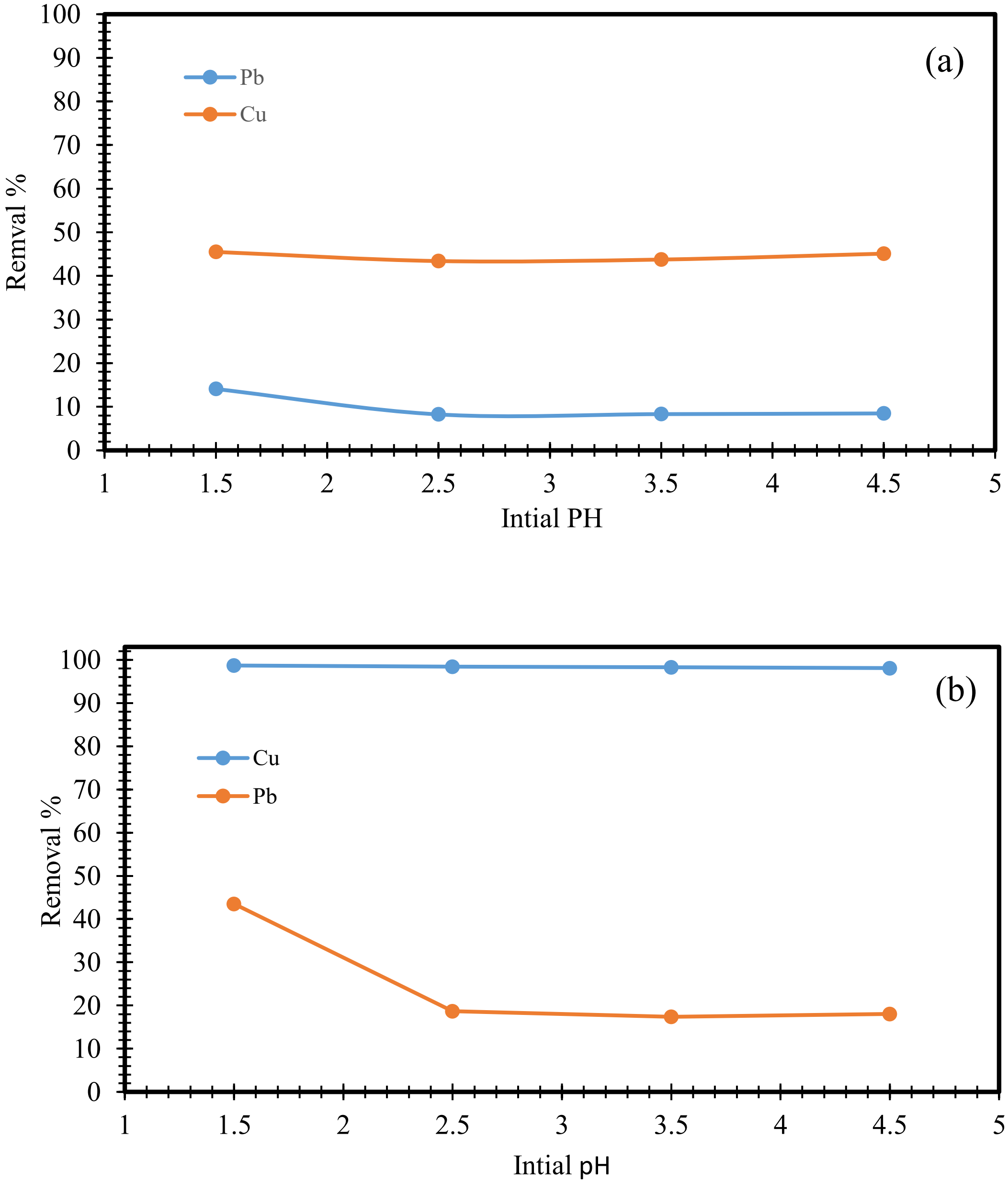


Figure 6.5: Effect of pH on Pb(II) and Cu(II) recoveries in the 1st (a) and 2nd (b) adsorption stage.

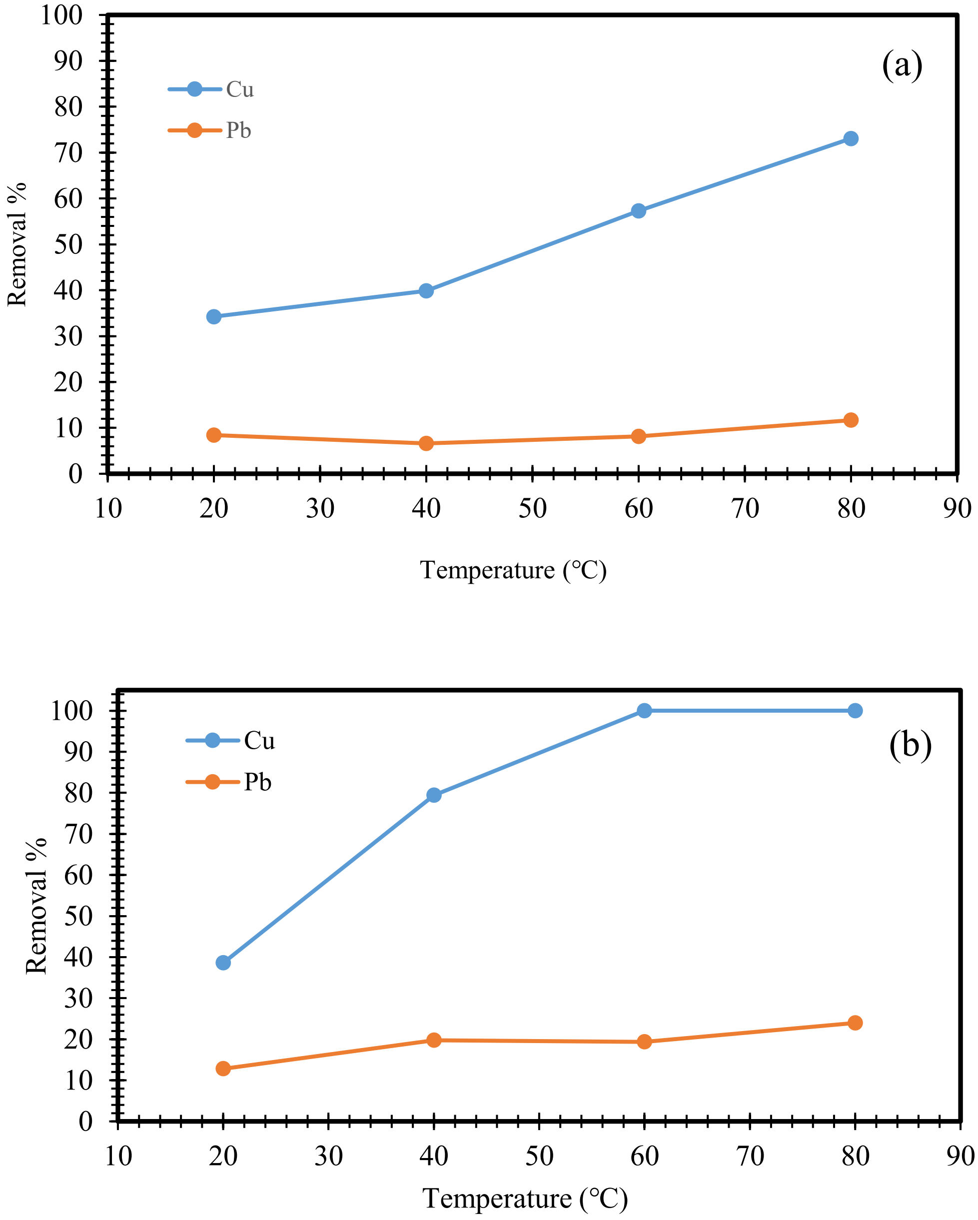


Figure 6.6: Effect of Temperature on Pb(II) and Cu(II) recoveries in the 1st (a) and 2nd (b) adsorption stage.

6.3.5. Effect of adsorption Time

Adsorption time has an important effect on the recovery/removal of toxic metals using resins. The influence of contact time on Pb^{2+} and Cu^{2+} recoveries was tested up to 180 min, and the results are shown in Figure 6.7a, b. The metal recoveries increase with time. Adsorption attains equilibrium in 30 min for lead and 90 min for copper. The metal removal percentage from water in the 1st stage adsorption was about 7% for Pb^{2+} and 42% for Cu^{2+}, while in the 2nd stage adsorption, the cumulative recovery increased to 17 and 97% for Pb^{2+} and Cu^{2+}, respectively. Therefore, the MTS 9140 resin has a remarkable adsorption selectivity for Cu(II) over Pb(II).

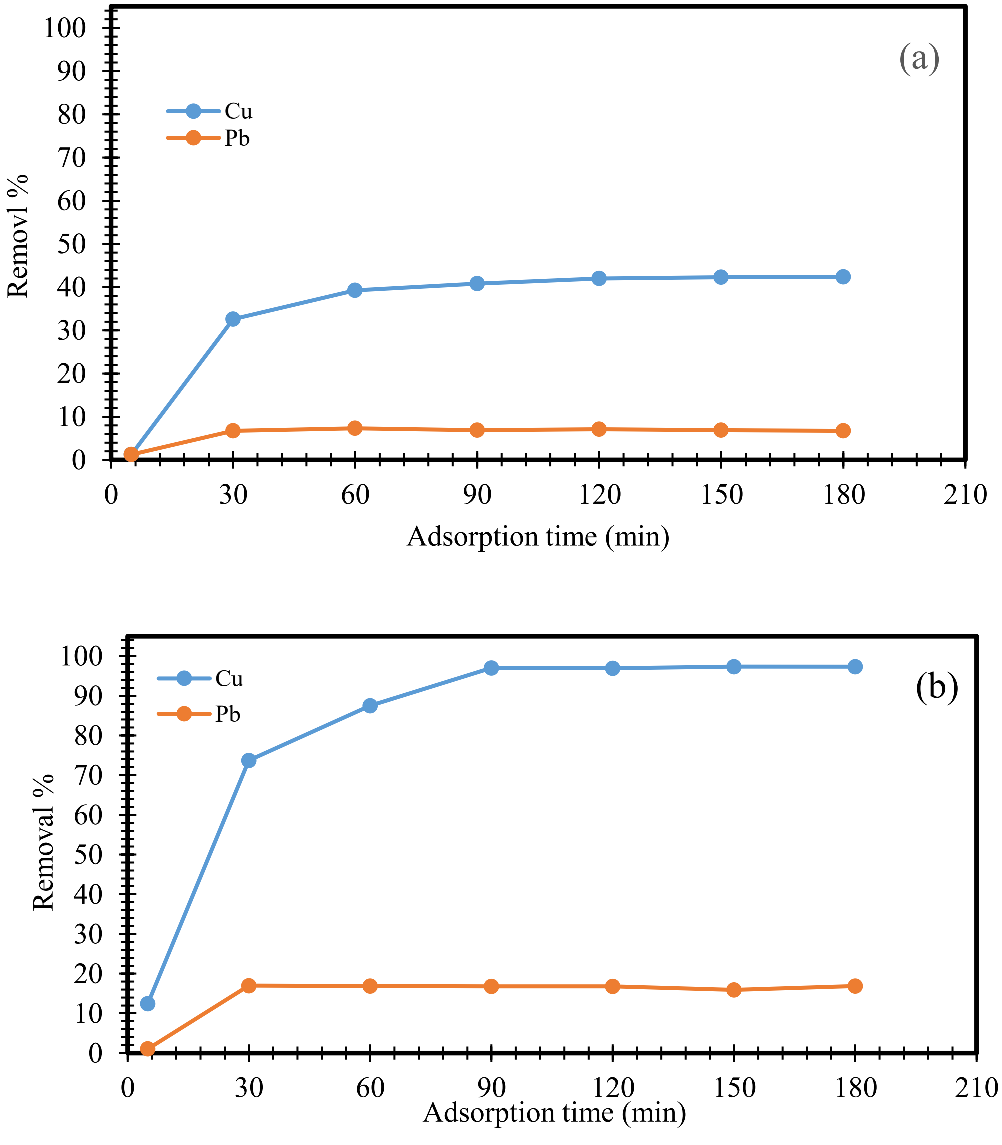
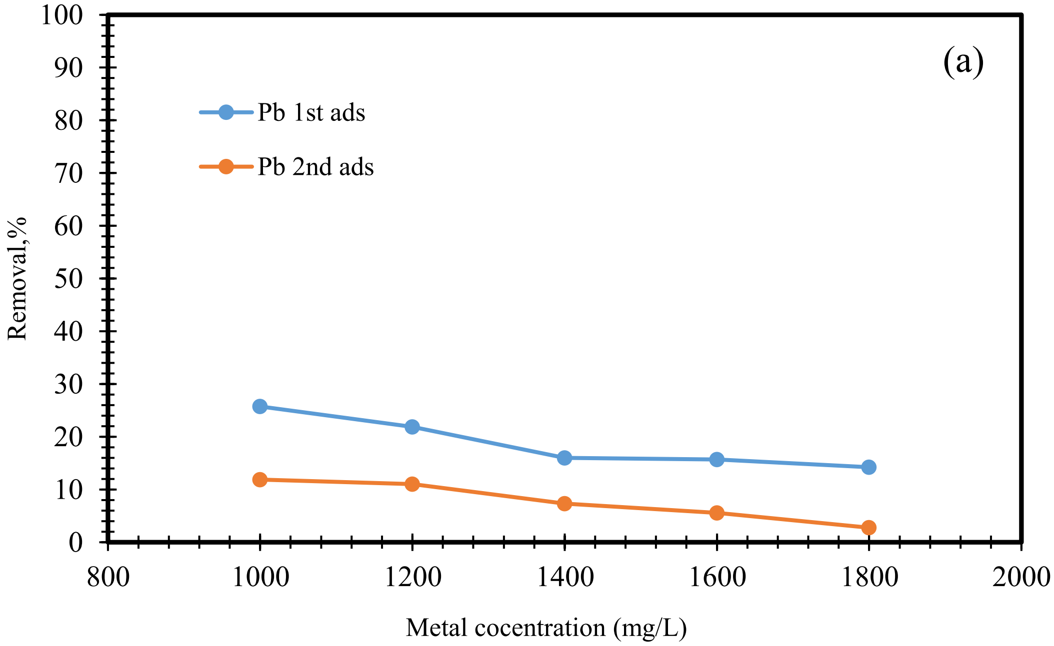


Figure 6.7: Effect of contact time on Pb(II) and Cu(II) recoveries in the 1st. (a) and 2nd. (b) adsorption stage.

6.3.6. Effect of the Initial Metal Ion Concentration

The effect of the initial metal ion concentration on Pb(II) and Cu(II) recoveries in the first and second adsorption stages is shown in Figure 6.8a, b. Lead recovery decreases slightly with the increase in the initial Pb^{2+} concentration. However, Cu^{2+} recovery at the 1st adsorption stage decreases remarkably at high initial Cu^{2+} concentrations. The slight dependence of Pb^{2+} recovery on initial Pb^{2+} concentrations may refer to the higher affinity of the MTS 9140 resin to Cu^{2+} ions over Pb^{2+} ions, while the decrease of Cu^{2+} recovery at a high concentration in the 1st adsorption stage is due to insufficient adsorption sites on resin at a high concentration of metal ions. This result has a similar trend to what was revealed by Zewail & Yousef [19].



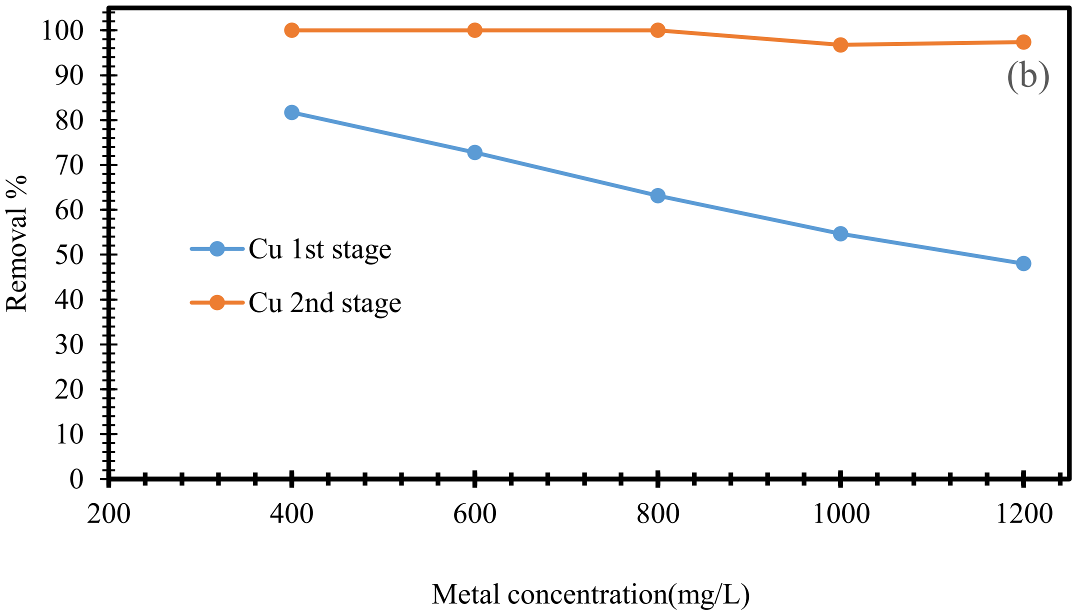


Figure 6.8: Effect of the initial metal concentration on adsorption of Pb(II) (a) and Cu(II) (b).

6.3.7. Adsorption Isotherms

The adsorption isotherms could be explained by Langmuir [20], Freundlich [21] and Temkin [22] models. The linear forms of these isotherm models are represented with Eqs. 6.2−6.4, respectively. Langmuir equation.

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{6.2}$$

where q_e is the equilibrium adsorption capacity of ions on the exchanger (mg/g); C_e, the equilibrium ion concentration in solution (mg/L); Q^0, the maximum capacity of the adsorbent (mg/g); and b, the Langmuir adsorption constant (L/mg).

Freundlich equation

$$logq_e = logK_F + \frac{1}{n}logC_e \tag{6.3}$$

where the equilibrium capacity (q_e) and C_e are defined in the above model, K_F is the Freundlich constant (L/mg), and n is the heterogeneity factor.

Temkin equation,

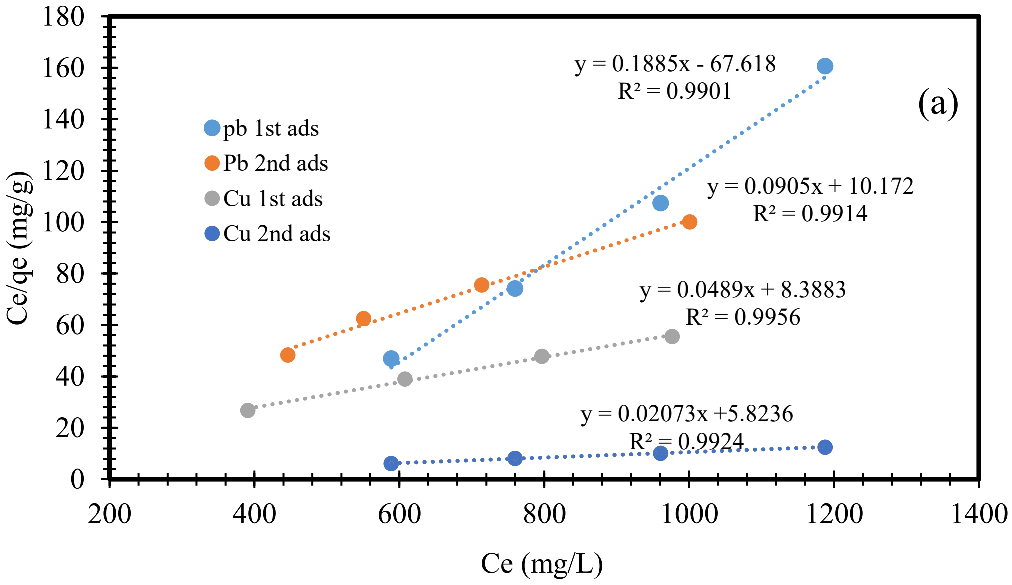
$$q_e = \text{B} \ln (K_T) + \text{B} \ln (C_e) ; \quad \text{B} = \frac{RT}{b_T} \tag{6.4}$$

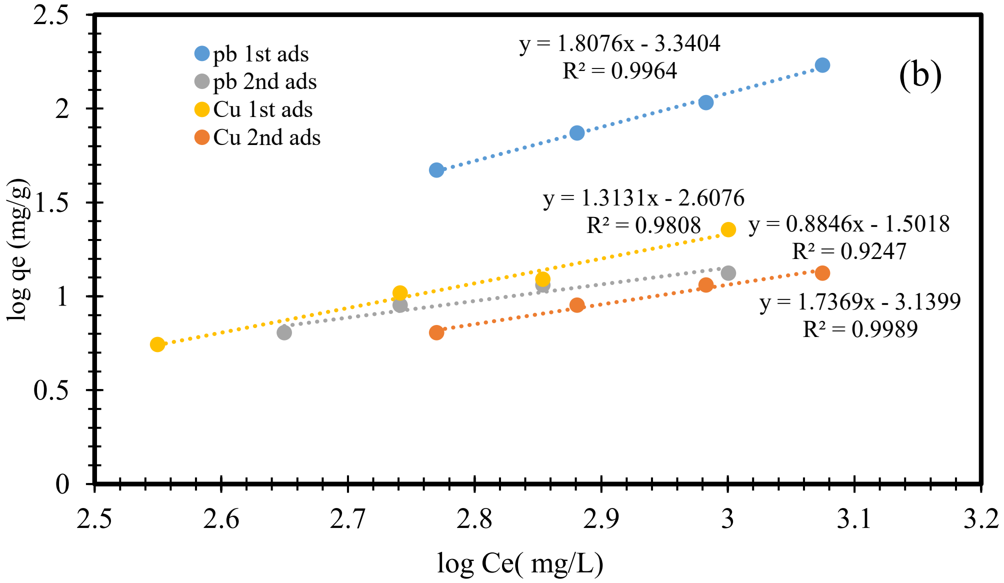
where K_T (L/g) and B (J/mol) are the Temkin and the heat of sorption constants, respectively.

R = universal gas constant (8.314 J/mol/K), and T = Temperature at 298 K.

All isotherm equations evaluated from the linear plots are presented in Figure 6.9 a-c, and their calculated parameters are listed in Table 6.3.

Compared with the other two adsorption isotherms, the R^2 values for both metal ions in the Langmuir adsorption isotherm were all above 0.99 (very close to 1), as shown in Table 6.3, which means the Langmuir isotherm model fits the adsorption process best for both Cu(II) and Pb(II) ions. The values of the Freundlich adsorption isotherm constant, n, were 0.553/0.966 and 4.91/1.38 for Pb(II) and Cu(II), respectively. All the values were within 0 -10, indicating that the sorption of lead and copper ions by the MTS 9140 macroporous resin was favorable. As shown in Table 6.4, the maximum adsorption capacity Q^0values of MTS 9140 are higher than many adsorbents reported in the literature, especially for the removal of copper ions.


(a)
pb 1st ads
Pb 2nd ads
Cu 1st ads
Cu 2nd ads
y = 0.1885x - 67.618
R² = 0.9901
y = 0.0905x + 10.172
R² = 0.9914
y = 0.0489x + 8.3883
R² = 0.9956
y = 0.02073x +5.8236
R² = 0.9924
Ce/qe (mg/g)
0
20
40
60
80
100
120
140
160
180
200
400
600
800
1000
1200
1400
Ce (mg/L)


(b)
pb 1st ads
pb 2nd ads
Cu 1st ads
Cu 2nd ads
y = 1.8076x - 3.3404
R² = 0.9964
y = 1.3131x - 2.6076
R² = 0.9808
y = 0.8846x - 1.5018
R² = 0.9247
y = 1.7369x - 3.1399
R² = 0.9989
log qe (mg/g)
0
0.5
1
1.5
2
2.5
2.5
2.6
2.7
2.8
2.9
3
3.1
3.2
log Ce(mg/L)

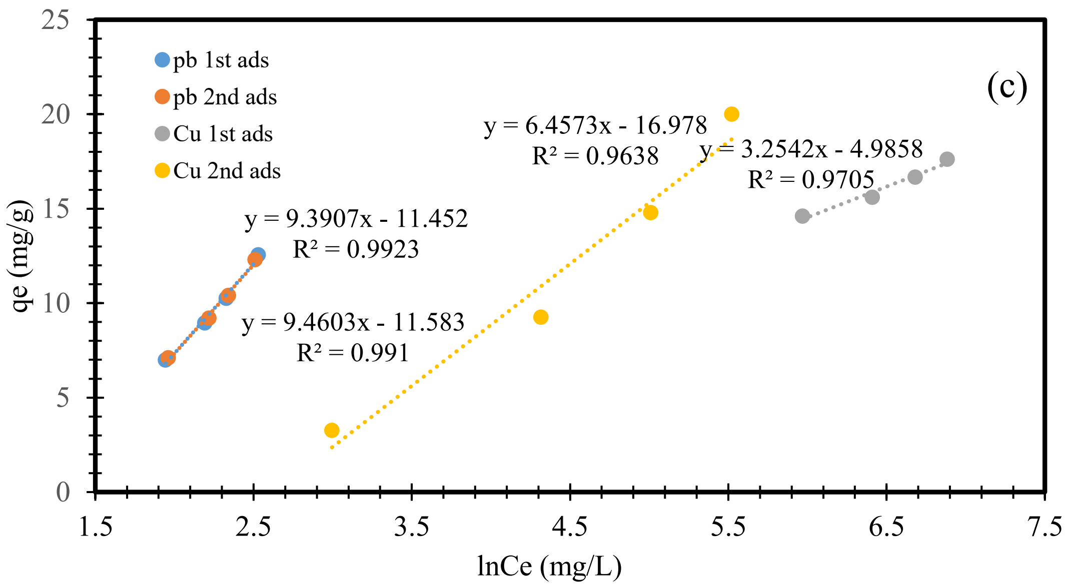


Figure 6.9: Langmuir isotherm (a), Freundlich isotherm (b), and Temkin isotherm (c) of Pb(II) and Cu(II) adsorption on the MTS 9140 resin.

Table 6.3: Isotherm Parameters for Pb(II) and Cu(II) adsorption on the MTS 9140 Resin.

Isotherm	**First ads. stage**		**Second ads stage**	
	Pb^{2+}	**Cu^{2+}**	**Pb^{2+}**	**Cu^{2+}**
Langmuir				
Q^0 (mg/g)	5.30	26.30	11.05	37.03
b (L/g)	0.0027	0.0046	0.0084	0.0045
R^2	0.9901	0.9956	0.9914	0.9924
Freundlich				
K_F	0.00045	4.286	0.01379	2.59
n	0.553	4.91	0.966	1.38
R^2	0.9964	0.9808	0.9247	0.9989
Temkin				
b_T	261.89	761.39	263.8	384.1
B	9.4603	3.254	9.3907	6.547
R^2	0.991	0.9704	0.9923	0.9638

Table 6.4: Comparison of the Maximum Adsorption Capacity of the MTS 9140 Resin with Some Other Adsorbents for Pb(II) and Cu(II) Adsorption.

Adsorbent	Metal ions	Reported sorption capacity(mg/g)	Conditions	References
Na-Mt	Pb(II) and Cu(II)	53.8 and 9.53	pH = 6.5, Na	[23]
Ca-Mt	Pb(II) and Cu(II)	34.2 and 6.61	pH = 6.5, Na	[23]
Dowex 50W	Pb(II) and Cu(II)	45.5 and 20.2	pH = 6.7 and 5.0, 25°C	[9]
Amidoxime chelating resin (AO AN/MA)	Pb(II) and Cu(II)	12.4 and 127.7	pH 3.0, 25°C	[24]
Sugar beet pulp	Pb(II) and Cu(II)	36 and 20.9	pH = 5.5, 35°C	[25]
Activated carbon (ac) granular AC	Pb(II) and Cu(II)	8.28 and 5.59	pH = 5, 30°C	[26]
Dithiocarbamated-Spororpollenin (DTC-S)	Pb(II) and Cu(II)	44.6 and 17.15	pH = 5.5, 20°C	[27]
Polystyrene microspheres	Pb(II) and Cu(II)	6.17 and 3.76	pH = 5.5, 20°C	[28]
Magnetic GO (simultaneous adsorption)	Pb(II) and Cu(II)	27.7 and 18.3	pH = 4.0, Na	[29]
Silica-supported Dithiocarbamate	Pb(II) and Cu(II)	70.04 and 20.3	pH = 6.0, 60°C	[30]
1,8-DAN/XAD-4	Pb(II) and Cu(II)	29.01 and 13.98	pH = 6−7, Na	[31]
MTS 9140	Pb(II) and Cu(II)	11.05 and 37.07	pH = 4.5, 20°C	**this study**

6.3.8. Adsorption Kinetics of Cu(II) and Pb(II)

A pseudo-first-order and a pseudo-second-order kinetic model were applied to study the mechanism of the two adsorption stages. The pseudo-first-order and the pseudo-second-order rates are expressed as Eqs. 6.5 and 6.6, respectively [32].

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \tag{6.5}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2\, q_e^2} \tag{6.6}$$

where q_t and q_e are the amounts of metal adsorbed at time t and equilibrium (mg/g), respectively, and k_1 is the first-order rate constant (min^{-1}). The slopes and intercepts of the plots of ln (q_e - q_t) versus contact time (t) were used to determine the first-order rate constant k_1 and equilibrium adsorption capacity (q_e), as shown in Figure 6.10a,b for both the metals in the 1st and 2nd adsorption stages, respectively.

k_2 is the second-order rate constant (mg/g min). The k_2 and q_e values were calculated from the slope and intercept of the linear plot of t/qt versus t, as shown in Figure 6.11a,b for Pb^{2+} and Cu^{2+} in the 1st and 2nd adsorption stages, respectively. A comparison of the results with the correlation coefficients for the kinetic models is presented in Table 6.5. The correlation coefficients for the pseudo-second-order kinetic model for Pb^{2+} and Cu^{2+} in the two adsorption stages (1st stage 0.9986, 0.9996; 2nd stage 0.9982, 0.9985) were high and close to 1, and closer values of q_e exp and q_e cal show that the data fit well with the pseudo-second-order model, which suggests a chemical adsorption process.

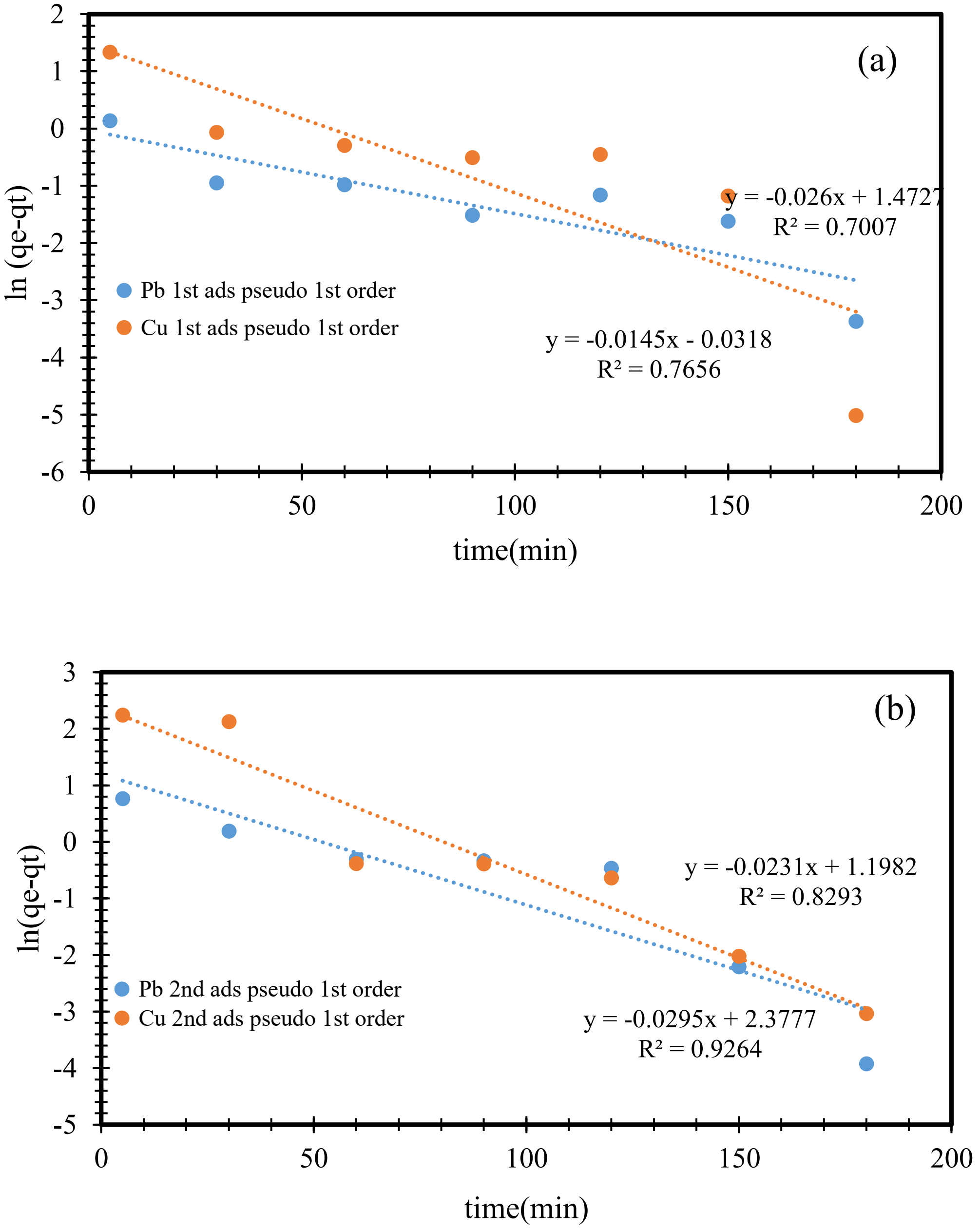


Figure 6.10: Pseudo-first order for adsorption of Pb(II) and Cu(II) onto the MTS 9140 resin for the 1st. (a) and 2nd. (b) adsorption stage

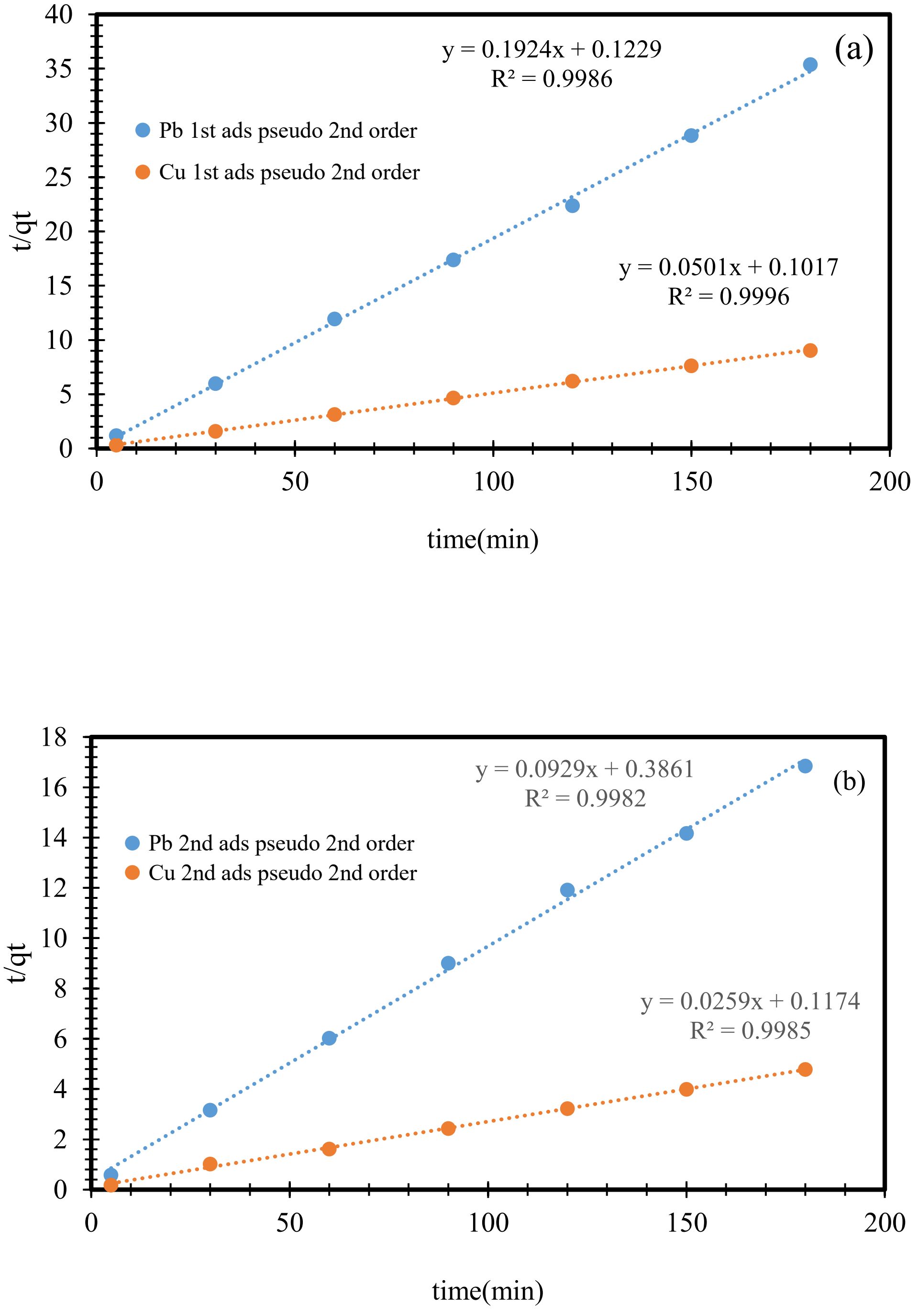


Figure 6.11: Pseudo-second order for adsorption of Pb(II) and Cu(II) onto the MTS 9140 resin for the 1st. (a) and 2nd. (b) adsorption stage.

Table 6.5: Kinetic Parameters for the Simultaneous Adsorption of Pb(II) and Cu(II) Ions Onto MTS 9140.

Equations	1st ads. stage		2nd ads. stage	
	Pb^{2+}	Cu^{2+}	Pb^{2+}	Cu^{2+}
Pseudo-first order				
q_e, exp (mg/g)	5.40	19.96	10.70	37.70
q_e, cal (mg/g)	0.9687	4.36	3.314	10.77
k_1(m-1)	-0.000081	-0.00014	-0.00013	-0.00016
R^2	0.7660	0.7007	0.8290	0.9264
Pseudo-second order				
q_e, cal (mg/g)	5.19	19.96	10.76	38.60
k_2(g/mg, min)	0.3012	0.0246	0.0223	0.00571
R^2	0.9986	0.9996	0.9982	0.9985

6.4 Conclusions

Puromet MTS 9140 resin with a thiourea group, which was rarely used in the separation of Cu(II) and Pb(II) in a water system, was found to have a strong adsorption preference for Cu(II) over Pb(II). In this work, a systematic study on the selective separation of copper from lead using Puromet MTS 9140 exchange equilibrium in 30 min for Pb(II) and 90 min for Cu(II) with initial concentrations of 1800 mg/L Pb^{2+} and 1200 mg/L Cu^{2+}. Metal recovery increased with a temperature rise, especially for Cu^{2+} adsorption, which may be attributed to the endothermic nature of the adsorption process. A 97% recovery for copper and 17% recovery for lead was obtained at the resin dosage of 0.07 g/mL and pH 4.5 after a two-stage adsorption, which demonstrated that the MTS 9140 resin had an excellent adsorption selectivity to Cu(II) over Pb(II). Langmuir, Freundlich, and Temkin isotherm models were constructed for analyzing the adsorption of Cu(II) and Pb(II) ions on the resin. The Langmuir isotherm was the best fit for both the metal ions. Adsorption kinetics analysis showed that the adsorption process complied with the pseudo-second order kinetic model.

In this study, it was also found that Lewatit monoplus TP208 and Amberlite IRC747 resins had a high adsorption affinity for both Cu(II) and Pb(II) ions. They could be applied in the removal of both the metals from a water system for environmental remediation and protection. Further studies are required.

Acknowledgement

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References

[1] C.Liu, R.Bai, Q. San, ‘‘Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: Behaviors and mechanisms’’. *Water Res. 2008, 42, 1511–1522. https://doi.org/10.1016/j.watres.2007.10.031*

[2] I. M. M.Kenawy, M. A. H.Hafez, M. A. Akl, R. R. Lashein, ‘‘Determination by AAS of Some Trace Heavy Metal Ions in Some Natural and Biological Samples after Their Preconcentration Using Newly Chemically Modified Chloromethylated Polystyrene-PAN Ion-Exchanger ’’. *Anal, Sci. 2000, 16, 493–500. https://doi.org/10.2116/analsci.16.493*

[3] L.Bulgariu, D. J. Bulgariu, ‘‘functionalized soy waste biomass - A novel environmental-friendly biosorbent for the removal of heavy metals from aqueous solution’’.*Cleaner Prod. 2018, 197, 875–885. https://doi.org/10.1016/j.jclepro.2018.06.261*

[4] S. A. Abo-Farha, A. Y. Abdel-Aal, I.A. Ashour, S.E. Garamon, ‘‘Removal of some heavy metal cations by synthetic resin purolite C100’’. *J. Hazard. Mater. 2009, 169, 190–194.* *https://doi.org/10.1016/j.jhazmat.2009.03.086*

[5] W.B.Gurnule, S.S.Katkamwar, ‘‘Selective removal of toxic metal ions from waste water using phenol-formaldehyde type chelating resins’’. *J. Chem. 2012, 5, 365–375.* *http://www.rasayanjournal.com*

[6] G.E.Moore, K.A. Kraus, ‘‘Adsorption of iron by anion exchange resins from hydrochloric acid solutions’’ *J. Am. Chem. Soc. 1950, 72, 5792–5793* https://doi.org/10.1021/ja01168a549

[7] W.B.Gurnule, K.Vajpai, A.D. Belsare, ‘‘Selective removal of toxic metal ions from waste water using polymeric resin and its composite’’.*Mater. Today: Proc. 2020, 36, 642–648.* *https://doi.org/10.1016/j.matpr.2020.04.372*

[8] A.Demirbas, E.Pehlivan, F. Gode, T. Altun, G. Arslan, ‘‘Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin’’. *J. Colloid Interface Sci. 2005, 282, 20–25.* *https://doi.org/10.1016/j.jcis.2004.08.147*

[9] E.Pehlivan, T. Altun, ‘‘The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin’. *J. Hazard. Mater. 2006, 134,149–156.* *https://doi.org/10.1016/j.jhazmat.2005.10.052*

[10] D.L.Silva, G. Brunner, ‘‘Desorption of heavy metals from ion exchange resin with water and carbon dioxide’’. *J. Chem. Eng. 2006, 23, 213–218.* *https://doi.org/10.1590/S0104-66322006000200008*

[11] C.V.Diniz, F.M. Doyle, A.H. Martins, ‘‘Uptake of heavy metals by chelating resins from

acidic manganese chloride solution''. *Miner. Metall. Process. 2000, 17, 217–222. https://doi.org/10.1007/BF03403237*

[12] J.Jachuła, D. Kołodynska, Z. Hubicki, ''Removal of Cd(II) and Pb(II) complexes with glycolic acid from aqueous solutions on different ion exchangers''. *Can. J. Chem. 2010, 88, 540–547. https://doi.org/10.1139/V10-027*

[13] P.Szczepanski, H. Guo, K. Dzieszkowski, Z. Rafin, W.́Kujawski, ''New reactive ionic liquids as carriers in polymer inclusion membranes for transport and separation of Cd(II), Cu(II), Pb(II), and Zn(II) ions from chloride aqueous solutions''.*J. Membr.Sci. 2021, 638, 119674. https://doi.org/10.1016/j.memsci.2021.119674*

[14] D.Mendil, M. Karatas, M. Tuzen, ''Separation and preconcentration of Cu(II), Pb(II), Zn(II), Fe(III) and Cr(III) ions with coprecipitation method without carrier element and their determination in food and water samples''.*Food Chem. 2015, 177, 320–324. https://doi.org/10.1016/j.foodchem.2015.01.008*

[15] J.Liu, C. Jin, C.Wang, ''Hyperbranched thiourea-grafted electrospun polyacrylonitrile fibers for efficient and selective gold recovery''. *J. Colloid Interface Sci. 2019, 561, 449–458. https://doi.org/10.1016/j.jcis.2019.11.016*

[16] X.Yang, M. S.Moats, J. D.Miller, X.Wang, X.Shi, H. Xu, ''Thiourea–thiocyanate leaching system for gold''. *Hydrometallurgy 2011, 106, 58–63. https://doi.org/10.1016/j.hydromet.2010.11.018*

[17] I.Luqman, Ion Exchange Technology I. *Theory and Mater; Springer, 2012.*

[18] D. V.Morales, B. L. Rivas, ''Poly(2-acrylamidoglycolic acid-co-2-acrylamide-2-methyl-1-

propane sulfonic acid) and poly(2-acrylamidoglycolic acid-co-4-styrene sodium sulfonate): synthesis, characterization, and properties for use in the removal of Cd(II), Hg(II), Zn(II), and Pb(II)''. *Polym. Bull. 2015, 72, 339–352. https://doi.org/10.1007/s00289-014-1277-0*

[19] T. M. Zewail, N. S. Yousef, ''Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed''.*Alexandria Engineering Journal 2015, 54, 83–90.* *https://doi.org/10.1016/j.aej.2014.11.008*

[20] I. Langmuir, ''the Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids''*.J. Am. Chem. Soc. 1916, 38, 2221– 2295.https://doi.org/10.1021/ja02268a002*

[21] H. M. F. Freundlich, ''Über die Adsorption in Lösungen''*.J. Phys. Chem. 1906, 57, 385–470.* *https://doi.org/10.1515/zpch-1907-5723*

[22] M. I. Temkin, V. Pyzhev, ''Kinetics of Ammonia Synthesis on Promoted Iron Catalysts''. *Acta Physicochim. URS. 1940, 12, 327–356.*

[23] C.Chen, H. Liu, T. Chen, D. Chen, ''An insight into the removal of Pb(II), Cu(II), Co(II), Cd(II), Zn(II), Ag(I), Hg(I), Cr(VI) by Na(I)-montmorillonite and Ca(II)-Montmorillonite'' *Appl. Clay Sci. 2015, 118, 239–247. https://doi.org/10.1016/j.clay.2015.09.004*

[24] S.M.El-Bahy, Z.M. El-Bahy, ''Synthesis and characterization of a new iminodiacetate chelating resin for removal of toxic heavy metal ions from aqueous solution by batch and fixed bed column methods''. *Korean J. Chem. Eng. 2016, 33, 2492–2501.* *https://doi.org/10.1007/s11814-016-0070-1*

[25] Z.Reddad, C.Gerente, Y.Andres, P.Le Cloirec, ''Adsorption of Several Metal Ions onto a Low-Cost Biosorbent: Kinetic and Equilibrium Studies''*.Environ. Sci. Technol. 2002, 36,*

2067–2073. https://doi.org/10.1021/es0102989

[26] H.An, B. Park, D. Kim, ''Crab shell for the removal of heavy metals from aqueous solution''. *Water Res. 2001, 35, 3551–3556.* https://doi.org/10.1016/S0043-1354(01)00099-9

(27) N.Ünlü, M.Ersoz, ''Removal of heavy metal ions by using dithiocarbamated- sporopollenin''. *Sep. Purif. Technol. 2007, 52, 461–469.* https://doi.org/10.1016/j.seppur.2006.05.026

[28] A.Denizli, K. Kesenci, Y. Arica, E.Piskin, ''Dithiocarbamate-incorporated monosize polystyrene microspheres for selective removal of mercury ions''.*React. Funct. Polym. 2000, 44, 235–243.* https://doi.org/10.1016/S1381-5148(99)00099-1

[29] R.Dorabei, S.Ferdowsi, A.Barzin, A. Tadjarodi, ''Highly efficient simultaneous ultrasonic assisted adsorption of Pb^{2+}, Cd^{2+}, Ni^{2+} and Cu^{2+} ions from aqueous solutions by graphene oxide modified with 2, 2′-dipyridylamine: Central composite design optimization '' *Ultrason. Sonochem. 2016, 32, 265–276.* https://doi.org/10.1016/j.ultsonch.2016.03.020

[30] F.Ge, M. Li, H. Ye, B. Zhao, ''Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles''. *J. Hazard. Mater. 2012, 211−212, 366–372.* https://doi.org/10.1016/j.jhazmat.2011.12.013

[31] M.I.U.Hoque, D.A. Chowdhury, R. Holze, A.N. Chowdhury, M.S Azam, ''Modification of Amberlite XAD-4 resin with 1, 8-diaminonaphthalene for solid phase extraction of copper, cadmium and lead, and its application to determination of these metals in dairy cow's milk''. *Chem. Eng. 2015, 3, 831–842.* https://doi.org/10.1016/j.jece.2015.03.020

[32] E.Haribabu, Y.D. Upadhya, S.N. Upadhyay, ''Removal of phenols from effluents by fly ash''. *Int. J. Environ. Stud. 1993, 43,169–176.https://doi.org/10.1080/00207239308710824*

Chapter 7

Mechanism Study of Cd(II) Ion Adsorption onto Resins with Sulfonic/Phosphonic Groups Using Electronic Structure Methods

Preface

A version of this chapter has been published in the **Journal of Molecular Liquids 2022; 385, 119199.** *I produced the work alongside my co-authors; Yahui Zhang* and Zhidong Tang*. I am the co- author. I conducted all lab experiments, and provid the data. Yahui Zhang assisted in the development of concept, design of methodology, reviewing and editing the draft, and reviewing and revising the new version of the manuscript. Co-author,Zhidong Tang supported in the project supervision, Co-author,* Zhidong Tang *supported in the data and process analysis, reviewing and editing the draft, reviewing and revising the new version of the manuscript.*

Abstract

Cadmium is a persistent bio-accumulative toxic metallic element causing hazardous impacts on environment. Through adsorption tests, it was found that Dowex G-26 resin with sulfonic group and Puromet™ MTS9570 resin with both sulfonic and phosphonic groups had excellent performance for Cd(II) ion removal from aqueous solution. To understand the adsorption mechanism of Cd(II) ion onto Dowex G-26 and Puromet™ MTS9570 resins, a density functional theory (DFT) B3LYP (Becke, 3-parameter, Lee–Yang–Parr) method and an *ab initio* Hartree-Fock (HF) method were employed to calculate the electronic structure properties including Mulliken population analysis, Mulliken charges of atoms, the energies of frontier orbitals, total electronic energy $\mathcal{E}_0$, enthalpy ΔH°_{f}, and free energy ΔG°_{f} of fourteen possible structural units with sulfonic or phosphonic group in these two resins and their interaction with Cd(II) ion. The hydration of

Cd(II) ion was considered during the simulation of the interaction of Cd(II) ion with the structural units. The calculation results of the electronic properties were of more reasonable significance of physics when simulating with HF method compared to B3LYP DFT method. HF method is a more suitable and reliable electronic structure theory for analyzing metal ion adsorption systems. The major reaction of Cd(II) ion adsorption onto G-26 and MTS9570 resins were presented.

KEYWORDS

Cadmium, ion-exchange resins, adsorption, molecular simulation, electronic structure theory, Hartree-Fock method, B3LYP DFT method.

Synopsis

Cadmium(Cd) is a persistent bio-accumulative toxic (PBT) metallic element causing severe hazards on environment and human being.

7.1 Introduction

Cadmium (Cd) is a metal of group 12 (IIB) in the periodic table with the atomic number 48 and outer –shell electron configuration of $4d^{10}5s^2$, which justifies Cd(II) is its common metal ion form. Cadmium is a soft, malleable, bluish white metal, usually occurs in low content in zinc, lead and copper ores in nature [1,2]. As a persistent bio-accumulative toxic (PBT) metallic element, cadmium can cause severe hazards on environment, human being and other living species [3,4].Water may be contaminated with cadmium due to usage of metallic products containing cadmium impurities such as galvanized pipes, water heaters, water coolers and taps, combustion of coal containing cadmium [5-7], and mining and metallurgy activities. A very low-level concentration of cadmium can be harmful to the environment and human health [8,9]. As per the World Health Organization (WHO) Guidelines 2017, the permissible limit of cadmium in drinking water is 3 μg/L [10].

Ion exchange process is an efficient method for thorough cadmium removal from aqueous systems, and lots of relevant researches have been published [11-22]. It has advantages, such as being effective at low metal concentration, simple operation, low cost, and the resins used can be regenerated. However, there are no known criteria for selecting resins with functional groups for Cd^{2+} removal and little knowledge of the effect of specific functional groups on Cd(II) sorption. Twenty-two resins with different functional groups such as sulfonic, phosphonic/sulfonic, iminodiacetic, amino-phosphonic, sulfonic/trimethylamine, and amino-methyl-phosphonic groups have been explored to discover the reactivity and preference of resins with specific groups to Cd(II) adsorption in our research [23]. It was found that Dowex G-26 resin with sulfonic ($-SO_2OH$) functional group and Puromet™ MTS9570 resin with both sulfonic and phosphonic ($-PO(OH)_2$) functional groups had excellent performance for Cd(II) ions adsorption. To understand the mechanism of Cd(II) ion adsorption onto these resins with sulfonic and sulfonic/phosphonic groups, molecular simulation study has been conducted in this work.

Generally, there are two broad areas of computational chemistry devoted to the structure of molecules and their chemical reactivity, i.e., molecular mechanics and electronic structure theory [24]. In molecular mechanics simulations, the laws of classical physics are employed to predict the structures and properties of chemical molecules. They are available in many computer programs e.g., MM3, HyperChem, Quanta, Sybyl, and Alchemy. Each molecular mechanics method is characterized by its particular force field. Molecular mechanics calculations do not explicitly treat the electron in a molecular system. Instead, they perform computations based on the interactions among the nuclei. Electronic effects are implicitly included in force fields through paramatrization. However, electronic structure methods use the laws of quantum mechanics rather than classical physics as the basis for their computations. It is known that quantum mechanics states the energy and other properties of a molecule may be obtained by solving the Schrödinger equation:

$$H\Psi = E\Psi$$

However, for even the smallest systems, exact solutions to Schrödinger equation are not computationally practical. Electronic structure methods are characterised by their various mathematical approximations to its solution. There are two major classes of electronic structure methods: semi-empirical methods, such as AM1, MINDO/3 and PM3, and *ab initio* methods. Unlike molecular mechanics and semi-empirical methods, *ab initio* methods use no experimental parameters in their computations. Instead, they are based solely on the laws of quantum mechanics, and on several basic physical constants. *Ab initio* means “from first principles" or "from the beginning”. Recent decades, a third class of electronic structure methods named density functional theory (DFT) methods have been widely adopted. DFT methods are attractive because they include the effects of electron correlation and cost less computational resources. Theoretically, *ab initio* and DFT methods are more logically rigorous than semi-empirical methods.

As it is of theoretical significance to understand the bonding properties between Cd(II) ions and the functional groups on resins, which involves the electronic structure in the adsorption system, in this work, two popular electronic structure methods, i.e., Hartree-Fock (HF) calculation (an *ab initio* method) [25-27] and B3LYP (Becke, 3-parameter, Lee–Yang–Parr) DFT method,[28-30] are employed to study the adsorption interaction between Cd(II) ions and resins with sulfonic/phosphonic groups. Some researchers have studied adsorption systems using molecular simulations [31-37]. However, rare publications are found in simulating metal ion adsorption with electronic structure theory and considering the hydration of metal ions in water systems through literature search [34-37]. In this paper, the hydration of Cd(II) ions was considered and the metal ion adsorption system was simulated using electronic structure methods. The electronic structure properties including Mulliken population analysis, Mulliken charges of atoms, the energies of frontier orbitals, total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f of fourteen possible structural units with sulfonic/phosphonic groups in the aforementioned two resins and their interaction with Cd(II) ion were calculated using B3LYP DFT and HF methods to understand the adsorption mechanism of Cd(II) ion onto the resins.

7.2 Methodology

7.2.1 Simulation Model

Ion exchange resins (beads) are solid and insolubilized high molecular weight polyelectrolytes, which can exchange their mobile ions for ions of same charge from the surrounding medium according to electric charge balance. The resulting ion exchange is reversible and stochiometric with the displacement of ionic species on the resin by another in solution [338,39]. As stable status, the metal ions and hydrogen ions in water are in the form of hydrated ions. A Cd(II) ion will form an octahedral complex with six water molecules, i.e., $[Cd(H_2O)_6]^{2+}$[40], and hydrogen ions exist as H_3O^+.For Dowex G-26 resin with sulfonic functional group and Puromet™ MTS9570 resin with both sulfonic and phosphonic functional groups, their interaction with Cd(II) ions at single structural unit can be expressed as:

$$R{-}SO_2OH + [Cd(H_2O)_6]^{2+} \rightarrow [R{-}SO_3{-}\ Cd]^{1+} + H_3O^+ + 5H_2O \tag{7.1}$$

$$R{-}PO(OH)_2 + [Cd(H_2O)_6]^{2+} \rightarrow [R{-}PO_3{-}\ Cd] + 2H_3O^+ + 5H_2O \tag{7.2}$$

By calculating the enthalpy ΔH°_f and free energy ΔG°_f of each component in equations (7.1) and (7.2), we can analyze the enthalpy change ΔH° and free energy change ΔG° of Cd(II) adsorption onto the resins.

The properties of Puromet™ MTS9570 and Dowex G-26 resins are summarized in Table 7.1 according to the information given by the resin suppliers. The matrix of Puromet™ MTS9570 resin is a macroporous copolymer of polystyrene (PS) crosslinked with divinylbenzene (DVB) having large pores (approximately 20 to 100 nm when hydrated), and that of Dowex G-26 resin is a copolymer of PS crosslinked with DVB in gel form having smaller pores (approximately 1 to 2 nm when hydrated). Therefore, the structural units of polymer matrixes of both G-26 and MTS9570 resins are styrene and divinylbenzene (mainly para-divinylbenzene and meta-divinylbenzene) [41]. The electronic structure properties of 14 possible structural units with sulfonic/phosphonic groups of these two resins, i.e., 2-phenyl-ethylene sulfonic acid, 3-vinyl-benzenesulfonic acid, 4-vinyl-benzenesulfonic acid, 2-(4-vinylphenyl)-ethylene sulfonic acid, 2-(3-vinyl-phenyl)-ethylene sulfonic acid, 3,5-divinyl-benzenesulfonic acid, 2,4-divinyl-benzenesulfonic acid, 2-phenyl-ethylene phosphonic acid, 3- vinyl-benzenephosphonic acid, 4-vinyl-benzenephosphonic acid, 2-(3-vinyl-phenyl)-ethylene phosphonic acid, 2-(4-vinyl-phenyl)-ethylenephosphonic acid,3,5-divinyl-benzenephosphonicacid, and 2,4-divinyl-benzenephosphonic acid, and the models of their interaction with hydrated Cd(II) ion were simulated to understand the adsorption mechanism of Cd(II) ion onto the resins.

Table 7.1: Ion exchange resins and their properties.

Typical properties					
Resin	**Matrix**	**Functional groups**	**Delivery forms**	**Bead size (mm)**	**Total capacity (equiv./L)**
MTS 9570	PS-DVB (macroporous)	Phosphonic and Sulfonic	H^+	0.315 - 0.850	18 g Fe/L
G-26	PS-DVB (gel)	Sulfonic	H^+	0.650 ± 50	2

7.2.2 Simulation Methods

In this work, Gauss View (version 6.1.1) software was used to build up the geometries of the molecular models for simulation. Gaussian (2016 version) software was employed to study the electronic structure properties of 14 possible structure units mentioned above and their interaction with hydrated Cd(II) ion using both B3LYP DFT and HF methods. As cadmium is a fifth-row metal element in the periodic table, STO-3G orbital basis set was adopted to conduct the quantum chemistry calculation to obtain normal determination for all components involved in equations (7.1) and (7.2). Geometry optimization was done using HF method with STO-3G basis set for all the components except cadmium aqua ion $[Cd(H_2O)_6]^{2+}$ before formal calculation. The calculated major indexes, e.g., Mulliken population/charges, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), total electronic energy ε_o, enthalpy ΔH°_f and free energies ΔG°_f were employed to analyze the adsorption process and comparison of the HFand B3LYP DFT methods.

7.3 Results and Discussion

7.3.1 Molecular simulation of structural units with sulfonic acid group

As aforementioned, the structural units of polymer matrixes of both G-26 and MTS9570 resins are styrene and divinylbenzene (mainly para-divinylbenzene and meta-divinylbenzene) [41]. To study the adsorption mechanism of hydrated Cd(II) ion onto the resins, the electronic structure properties of 14 possible structural units with sulfonic or phosphonic group of these two resins and the models of their interaction with Cd(II) ion were calculated using both B3LYP DFT and HFmethods.

The molecular structure of 2-phenyl-ethylene sulfonic acid built with Gauss View is illustrated in Fig. 7.1. The Mulliken charges of atoms, Mulliken population analysis for bonding between atoms, and the energies of frontier orbitals HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f calculated are listed in Table 7.2a, 7.2b and 7.2c, respectively. As can be seen from Table 7.2a, all the C and O atoms have negative charges, while H and S atoms possess positive charges. The H atom in sulfonic acid group possess much higher positive charge than those H atoms connected to C atoms. For the sulfonic acid group, S atom has more positive charge and O atoms have more negative charges from HF method calculation than those obtained from B3LYP method calculation. From Table 7.2b, the Mulliken population for bonding between the C-S calculated with the self-consistent field (SCF) density method of HF theory is larger than that calculated with B3LYP DFT theory. In Table 9.2c, the HOMO energy is negative while the LUMO energy is positive from the calculation of both methods. This complies with their significance of physics. The total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f calculated will be used to analyze the Cd(II) adsorption reaction represented in Equation (7.1).

Due to the mobility of the structural units bearing sulfonic group fixed on the resins and steric effect, they may only form the 1:1 complex with the metal ions, unlike the free solvent extractants which can form n:1(n = 1, 2, 3, 4 or 6) complexes in solvent extraction. Fig. 7.2 shows the model of the product of Cd(II) ion interacting with 2-phenyl-ethylene sulfonic acid. In this model, Cd(II) ion is shared by the three O atoms in sulfonic group, not just bonded with the O atom of hydroxyl group. The Mulliken charges of atoms, population analysis for bonding between atoms, and the energies of HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f calculated using B3LYP and HF methods are listed in Table 7.3a, 7.3b and 7.3c, respectively. As can be seen from Table 3a, all the O and most C atoms have negative charges, while Cd, H and S atoms possess positive charges. Cd atom has more positive charge and O atoms in sulfonic acid group have more negative charges from HF method calculation than those obtained from B3LYP method calculation. From Table 3b, the electron population for bond between C-S calculated with HF method is larger than that calculated with B3LYP method. One interesting result is that the electron populations between Cd and O atoms are even higher than those between S and O atoms in sulfonic group, which means the bonding between O-Cd is very strong. For the systems of structure units with sulfonic group, similar results were obtained. To maintain a reasonable length of this paper, the Mulliken charges of atoms and electronic population analysis for bonding between atoms will not be listed for the subsequent sulfonic group containing systems. In Table 3c, the LUMO energy is negative from the calculation of both methods, but the LUMO energy calculated with HF method is less negative. The total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f calculated will be used to analyze the Cd(II) adsorption reaction represented in Equation (7.1).

Similarly, the electronic structure properties of other structural units with sulfonic group, i.e., 3-vinyl-benzenesulfonic acid, 4- vinyl-benzenesulfonic acid, 2-(4-vinyl-phenyl)-ethylene sulfonic acid, 2-(3-vinyl-phenyl)-ethylene sulfonic acid, 3,5-divinyl-benzenesulfonic acid, and 2,4-divinyl-benzenesulfonic acid, and the models of their interaction with hydrated Cd(II) ion were simulated to understand the adsorption mechanism of Cd(II) ion onto the resins. The results are summarized in Supplemental Material.

Table 7.2a: Calculated Mulliken charges of atoms (2-phenyl-ethylene sulfonic acid).

B3LYP method	HF Method
1 C -0.081205	1 C -0.063662
2 C -0.074497	2 C -0.052328
3 C -0.003667	3 C -0.002093
4 C -0.076182	4 C -0.054179
5 C -0.080432	5 C -0.062713
6 C -0.077185	6 C -0.053839
7 H 0.088119	7 H 0.071131
8 H 0.087184	8 H 0.070926
9 H 0.085527	9 H 0.069138
10 H 0.087461	10 H 0.070356
11 H 0.087765	11 H 0.071567
12 C -0.068052	12 C -0.022154
13 H 0.100231	13 H 0.098166
14 C -0.233954	14 C -0.229461
15 H 0.095008	15 H 0.088824
16 S 1.245228	16 S 1.387263
17 O -0.497842	17 O -0.591096
18 O -0.484291	18 O -0.581135
19 O -0.405741	19 O -0.433839
20 H 0.206525	20 H 0.219128
Sum of Mulliken charges = 0.0	Sum of Mulliken charges = 0.0

Table 7.2b: Calculated population analysis for bonding between two connected atoms (2-phenylethylene sulfonic acid).

Bonding	Population (B3LYP method)	Population (HF method
C3-C12	0.410149	0.410149
C12-C14	0.588100	0.592640
C14-S16	0.159107	0.222035
S16-O17	0.159996	0.155617
S16-O18	0.169292	0.162868
S16-O19	0.072232	0.123924

Table 7.2c: Calculated energies of HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy $\Delta H°_f$, and free energy $\Delta G°_f$ (2-phenyl-ethylene sulfonic acid).

	B3LYP method	**HF method**
E_{HOMO}	-0.12191	-0.27813
E_{LUMO}	0.03058	0.18509
Total electronic energy $\mathcal{E}_0$	-921.7402366	-918.1095607
Enthalpy ΔH_f (298.15K)	-921.7402366	-917.932044
Free Energies ΔG_f (298.15K)	-921.61907	-917.977201

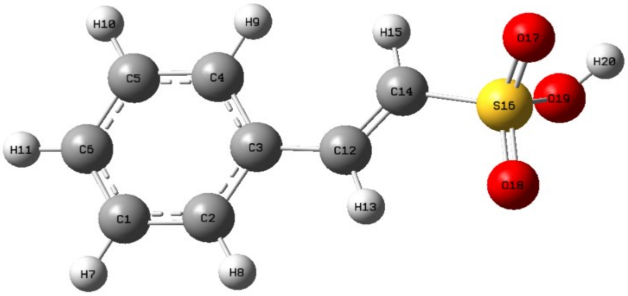

Figure7.1: Molecular structure of 2-phenyl-ethylenesulfonic acid

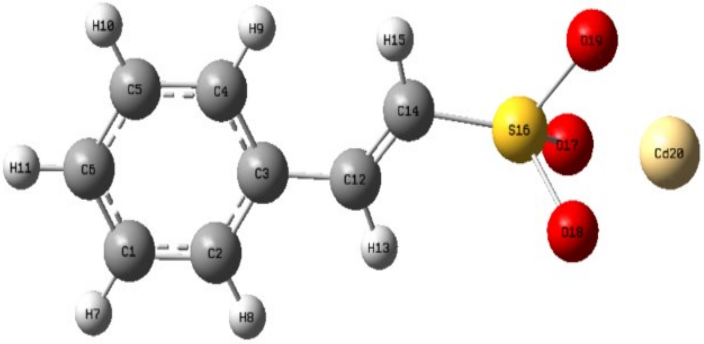

Figure 7.2 Molecular structure of the product of Cd(II) ion interacting with 2-phenyl-ethylene sulfonic acid.

Table 7.3a: Calculated Mulliken charges of atoms (product of Cd(II) ion interacting with 2-phenyl-ethylene sulfonic acid).

B3LYP method	**HF method**
1 C -0.068147	1 C -0.056854
2 C -0.060529	2 C -0.042776
3 C -0.001779	3 C -0.006893
4 C -0.064429	4 C -0.045994
5 C -0.067438	5 C -0.055903
6 C -0.054505	6 C -0.037027
7 H 0.107707	7 H 0.084184
8 H 0.096842	8 H 0.074038
9 H 0.090381	9 H 0.069581
10 H 0.106480	10 H 0.083218
11 H 0.110144	11 H 0.087607
12 C -0.027809	12 C 0.010181
13 H 0.119937	13 H 0.101793
14 C -0.160740	14 C -0.145450
15 H 0.144027	15 H 0.125283
16 S 0.736000	16 S 0.628832
17 O -0.249548	17 O -0.293009
18 O -0.249580	18 O -0.293069
19 O -0.248032	19 O -0.291963
20 Cd 0.741019	20 Cd 1.004220
Sum of Mulliken charges = 1.0	Sum of Mulliken charges = 1.0

Table 7.3b: Calculated population analysis for bonding between two connected atoms (product of Cd(II) ion interacting with 2-phenyl-ethylene sulfonic acid).

Bonding	Population (B3LYP method)	Population (HF method)
C3-C12	0.414357	0.405341
C12-C14	0.584089	0.590730
C14-S16	0.227669	0.256825
S16-O17	0.116411	0.112366
S16-O18	0.116427	0.112384
S16-O19	0.119350	0.114287
S16-Cd20	-0.086368	-0.116550
O17-Cd20	0.139803	0.141657
O18-Cd20	0.139808	0.141670
O19-Cd20	0.139238	0.141454

Table 7.3c: Calculated energies of HOMO and LUMO, total electronic energy $\mathcal{E}_0$, enthalpy ΔH_f, and free energy ΔGf (product of Cd(II) ion interacting with 2-phenyl-ethylene sulfonic acid).

	B3LYP method	HF method
E_{HOMO}	-0.27285	-0.38021
E_{LUMO}	-0.17516	-0.03734
Total electronic energy $\mathcal{E}_0$	-6334.761636	-6329.274553
Enthalpy ΔH_f(298.15K)	-6334.607614	-6329.107376
Free Energies ΔG_f (298.15K)	-6334.655207	-6329.15856

7.3.2. Molecular simulation of structural units with phosphoric acid group

The molecular structure of 2-phenyl-ethylene phosphonic acid is illustrated in Fig. 7.3. The Mulliken charges of atoms, Mulliken population analysis for bonding between atoms, and the energies of HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f,, and free energy ΔG°_f calculated using B3LYP and HF methods are listed in Table 7.4a, 7.4b and79.4c, respectively. As can be seen from Table 7.4a, all the C and O atoms have negative charges, while H and P atoms possess positive charges. The H atom in phosphonic acid group possess much higher positive charge than those H atoms connected to C atoms. For the phosphonic group, P atom has more positive charge and O atoms have more negative charges from HF method calculation than those obtained from B3LYP method calculation. From Table 7.4b, the Mulliken population for bonding between two atoms calculated with HF method is close to that calculated with B3LYP method. In Table 7.4c, the HOMO energy is negative while the LUMO energy is positive from the calculation of both methods. This complies with their significance of physics. The total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f calculated will be used to analyze the Cd(II) adsorption reaction represented in Equation (7.2).

Fig. 7.4 illustrates the model of the product of Cd(II) ion interacting with 2-phenyl-ethylene phosphonic acid. In this model, Cd(II) ion is shared by the three O atoms in phosphonic group, not just bonded with the O atoms of two hydroxyl groups. The Mulliken charges of atoms, population analysis for bonding between atoms, and the energies of HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_fcalculated using B3LYP and HF methods are listed in Table 7.5a, 7.5b and 7.5c, respectively. As can be seen from Table 7.5a, all the O and most C atoms have negative charges, while Cd, H and P atoms possess positive charges. Cd and P have more positive charge and O atoms in phosphonic acid group have more negative charges from HF method calculation than those obtained from B3LYP method calculation. From Table 7.5b, the Mulliken population for bonding between two atoms calculated with HF method is close to that calculated with B3LYP method. The electron populations between Cd and O atoms are smaller than those between P and O atoms in phosphonic group, which is opposite to the sulfonic group containing systems. For the systems of structure units with phosphonic group, similar results were obtained. To maintain a reasonable volume of this paper, the Mulliken charges of atoms and electronic population analysis for bonding between atoms will not be listed in the subsequent phosphonic group containing systems. In Table 7.5c, the LUMO energy is negative from the calculation of both methods, but the LUMO energy calculated with HF method is less negative. The total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f calculated will be used to analyze the Cd(II) adsorption reaction represented in Equation (7.2).

Similarly, other structural unit systems with phosphonic acid group, i.e., 3-vinyl-benzenephosphonic acid, 4-vinyl-benzenephosphonic acid, 2-(3-vinyl-phenyl)-ethylene phosphonic acid, 2-(4-vinyl-phenyl)-ethylene phosphonic acid, 3,5-divinyl-benzenephosphonic acid, and 2,4-divinyl-benzenephosphonic acid, have also been studied. The results are summarized in Supplemental Material [41].

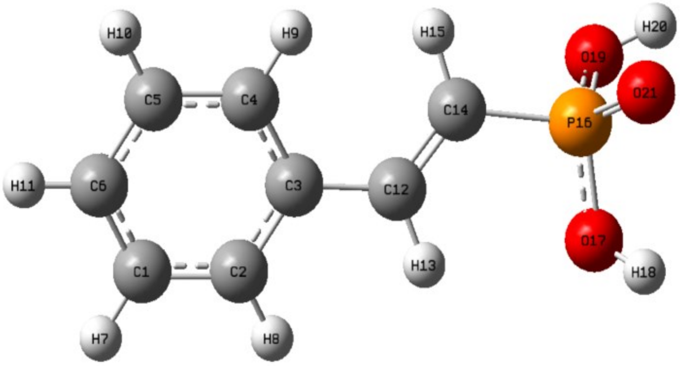

Figure7.3: Molecular structure of 2-phenyl-ethylene phosphonic acid.

Table 7.4a: Calculated Mulliken charges of atoms (2-phenyl-ethylene phosphonic acid).

B3LYP method	**HF method**
1 C -0.082757	1 C -0.064394
2 C -0.078053	2 C -0.058330
3 C -0.004796	3 C -0.000975
4 C -0.078737	4 C -0.058794
5 C -0.081861	5 C -0.063340
6 C -0.080412	6 C -0.059036
7 H 0.085106	7 H 0.067353
8 H 0.083423	8 H 0.065542
9 H 0.084581	9 H 0.067584
10 H 0.084974	10 H 0.067299
11 H 0.084980	11 H 0.067773
12 C -0.072184	12 C -0.036993
13 H 0.088746	13 H 0.076337
14 C -0.261671	14 C -0.265833
15 H 0.085825	15 H 0.073768
16 P 1.149434	16 P 1.332106
17 O -0.443203	17 O -0.491011
18 H 0.207135	18 H 0.207009
19 O -0.440773	19 O -0.488179
20 H 0.206009	20 H 0.205167
21 O -0.535765	21 O -0.643053
Sum of Mulliken charges = 0.0	Sum of Mulliken charges = 0.0

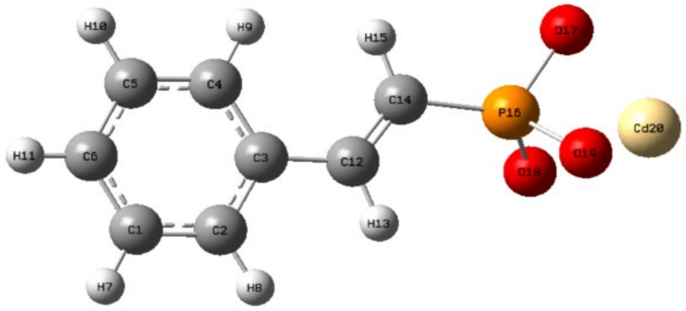

Figure 7.4: Molecular structure of the product of Cd(II) ion interacting with 2-phenyl-ethylene phosphonic acid.

Table 7.4b: Calculated population analysis for bonding between two connected atoms (2-phenylethylene phosphonic acid).

Bonding	Population (B3LYP method)	Population (HF method)
C3-C12	0.415164	0.408640
C12-C14	0.583188	0.589099
C14-P16	0.255273	0.286012
P16-O17	0.158319	0.189811
P16-O19	0.161351	0.191096
P16-O21	0.267075	0.254753
O17-H18	0.253903	0.265770
O19-H20	0.253492	0.265352

Table 7.4c: Calculated energies of HOMO and LUMO, total electronic energy $\mathcal{E}_0$, enthalpy ΔH_f, and free energy ΔGf (2-phenyl-ethylene phosphonic acid).

Frontier orbit energy	B3LYP method	HF method
E_{HOMO}	-0.10635	-0.25585
E_{LUMO}	0.04553	0.20595
Total electronic energy $\mathcal{E}_0$	-866.326554	-862.7441716
Enthalpy ΔHf (298.15K)	-866.15154	-862.55342
Free Energies ΔGf (298.15K)	-866.193386	-862.598111

Table 7.5a: Calculated Mulliken charges of atoms (product of Cd(II) ion interacting with 2-phenyl-ethylene phosphonic acid).

B3LYP method			**HF method**		
1	C	-0.080811	1	C	-0.063598
2	C	-0.075910	2	C	-0.058591
3	C	-0.002891	3	C	0.001719
4	C	-0.076844	4	C	-0.059347
5	C	-0.079977	5	C	-0.062624
6	C	-0.077973	6	C	-0.059478
7	H	0.085203	7	H	0.065117
8	H	0.083957	8	H	0.064346
9	H	0.083447	9	H	0.065321
10	H	0.084944	10	H	0.064972
11	H	0.085048	11	H	0.065237
12	C	-0.064108	12	C	-0.037566
13	H	0.088588	13	H	0.069651
14	C	-0.228734	14	C	-0.227609
15	H	0.094755	15	H	0.075436
16	P	0.828407	16	P	0.889158
17	O	-0.408466	17	O	-0.499666
18	O	-0.406553	18	O	-0.496484
19	O	-0.406567	19	O	-0.496500
20	Cd	0.474485	20	Cd	0.700507
Sum of Mulliken charges = 0.0			Sum of Mulliken charges = 0.0		

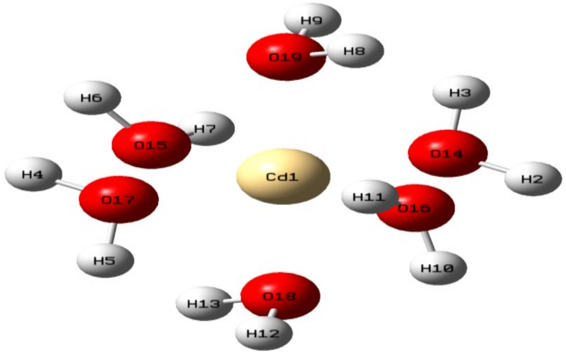

Figure 7.5: Structure of cadmium aqua ion $[Cd(H_2O)_6]^2$

Table 7.5b: Calculated population analysis for bonding between two connected atoms (product of Cd(II) ion interacting with 2-phenyl-ethylene phosphonic acid).

Bonding	**Population (B3LYP method)**	**Population (HF method)**
C3-C12	0.408835	0.402800
C12-C14	0.589331	0.594648
C14-P16	0.261613	0.284136
P16-O17	0.169951	0.185584
P16-O18	0.166793	0.182833
P16-O19	0.166799	0.182837
P16-Cd20	-0.152931	-0.204771
O17-Cd20	0.151882	0.161793
O18-Cd20	0.151547	0.161432
O19-Cd20	0.151546	0.161431

Table 7.5c: Calculated energies of HOMO and LUMO, total electronic energy $\mathcal{E}_0$, enthalpy ΔH_f, and free energy ΔGf (product of Cd(II) ion interacting with 2-phenyl-ethylene phosphonic acid).

Frontier orbit energy	**B3LYP method**	**HF method**
E_{HOMO}	-0.04085	-0.20841
E_{LUMO}	0.02012	0.16248
Total electronic energy $\mathcal{E}_0$	-6278.743892	-6273.240276
Enthalpy ΔH_f (298.15K)	-6278.58825	-6273.070946
Free Energies ΔG_f (298.15K)	-6278.635216	-6273.121477

7.3.3. Molecular simulation of hydrated Cd(II) ion, hydrated hydrogen ion and water molecule

In water solution, a Cd(II) ion usually forms an octahedral complex with six water molecules, i.e., $[Cd(H_2O)_6]^{2+}$ (Fig.7.5), to take the lowest energy status. [40] The energy of the five 4d orbitals of a free Cd(II) ion in spherical environment will split into two energy levels in the octahedral crystal field, i.e., d_{xy}, d_{xz} and d_{yz} orbitals with symmetry designation t_{2g} and d_{z^2} and $d_{x^2-y^2}$orbitals with symmetry designation e_g, as shown in Fig. 7.6. As a Cd(II) ion has the outer layer electronic configuration of $4d^{10}$, all the 4d orbitals are fully occupied, which means the $[Cd(H_2O)_6]^{2+}$ system can be calculated with restricted HF method.

The structure of hydrated Cd(II) ion $[Cd(H_2O)_6]^{2+}$ was built with Gauss View as shown in Fig.7. 5. The Mulliken charges of atoms, Mulliken population analysis for bonding between atoms, and the energies of HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy ΔG°_f calculated using B3LYP and HF methods are listed in Table 7.6a, 7.6b and 7.6c, respectively. As can be seen from Table 6a, all the O atoms have negative charges, while Cd and H atoms possess positive charges. Cd have more positive charge and O atoms have more negative charges from HF method calculation than those obtained from B3LYP method calculation. From Table 7.6b, the Mulliken population for bonding between Cd and O atoms calculated with HF method is lower than that calculated with B3LYP method. Compared to the above calculation results in the systems of interaction of Cd(II) ion with organic compounds containing sulfonic or phosphonic group, the Mulliken population for bonding between Cd and O atoms in this system is lower, which means the bonding between Cd and O atoms in cadmium aqua ion is weaker. In Table 7.6c, the LUMO energy is negative from the calculation of both methods, but the LUMO energy calculated with HF method is less negative. The total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f, and free energy

$\Delta G°_f$ calculated will be used to analyze the Cd(II) adsorption reactions represented in Equations (7.1) and (7.2).

The structure of hydrated hydrogen ion H_3O^+ is illustrated in Fig. 7.7. The Mulliken charges of atoms, Mulliken population analysis for bonding between atoms, and the energies of HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy $\Delta H°_f$, and free energy $\Delta G°_f$ calculated using B3LYP and HF methods are listed in Table 7.7a, 7.7b and 7.7c, respectively. As seen from Table 7.7a, the O atom has negative charge, and all the H atoms possess the same positive charges, which reflects the structural symmetry of hydronium ion. Similarly, the Mulliken population for bonding between O and H atoms are the same (Table 7.7b). In Table 7.7c, the LUMO energy is negative from the calculation with B3LYP method, but the LUMO energy calculated with HF method is positive, which complies with the physics significance of LUMO. The total electronic energy $\mathcal{E}_o$, enthalpy $\Delta H°_f$, and free energy $\Delta G°_f$ calculated will be used to analyze the Cd(II) adsorption reactions represented in Equations (7.1) and (7.2).

The structure of H_2O molecule is shown in Fig. 7.8. The Mulliken charges of atoms, Mulliken population analysis for bonding between atoms, and the energies of HOMO and LUMO, total electronic energy $\mathcal{E}_o$, enthalpy $\Delta H°_f$, and free energy $\Delta G°_f$ calculated using B3LYP and HF methods are listed in Table 8a, 8b and 8c, respectively. Similar to hydronium ion H_3O^+ , the H atoms possess the same positive charges (Table 7.8a) and the Mulliken population for bonding between O and H atoms are the same (Table 7.8b), which reflects the structural symmetry of water molecule. In Table 8c, the LUMO energy is negative from the calculation using B3LYP method, but the LUMO energy calculated using HF method is positive, which complies with the physics significance of LUMO. The total electronic energy $\mathcal{E}_o$, enthalpy $\Delta H°_f$, and free energy $\Delta G°_f$

calculated will be used to analyze the Cd(II) adsorption reactions represented in Equations (7.1) and (7.2).

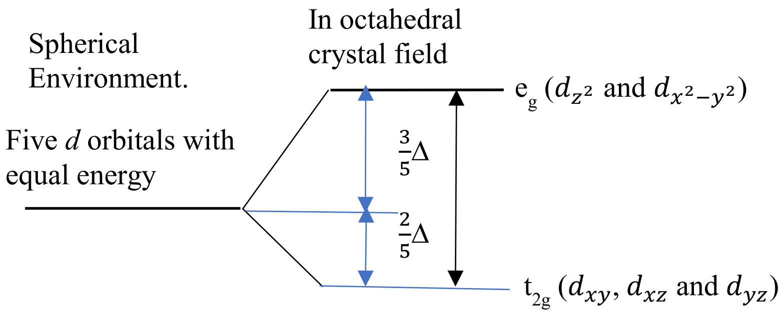

Figure 7.6: Energy splitting of five 4d orbitals in [Cd(H$_2$O)$_6$]^2

Table 7.6a: Calculated Mulliken charges of atoms ([Cd(H$_2$O)$_6$]$^{2+}$).

B3LYP method	HF method
1 Cd 0.617642	1 Cd 0.872845
2 H 0.256640	2 H 0.255694
3 H 0.228288	3 H 0.224521
4 H 0.250596	4 H 0.249801
5 H 0.232031	5 H 0.229570
6 H 0.242777	6 H 0.239944
7 H 0.251884	7 H 0.250360
8 H 0.251892	8 H 0.251118
9 H 0.231496	9 H 0.228828
10 H 0.243891	10 H 0.241657
11 H 0.250505	11 H 0.248715
12 H 0.227504	12 H 0.223596
13 H 0.256408	13 H 0.255545
14 O -0.254038	14 O -0.292173
15 O -0.262174	15 O -0.301160
16 O -0.262632	16 O -0.301631
17 O -0.254523	17 O -0.292709
18 O -0.253334	18 O -0.291413
19 O -0.254855	19 O -0.293105
Sum of Mulliken charges =2.0	Sum of Mulliken charges =2.0

Table 7.6b: Calculated population analysis for bonding between two connected atoms ($[Cd(H_2O)_6]^{2+}$

Bonding	Population (B3LYP method)	Population (HF method)
Cd1-O14	0.119224	0.107350
Cd1-O15	0.119572	0.107697
Cd1-O16	0.119094	0.107418
Cd1-O17	0.117520	0.106423
Cd1-O18	0.118954	0.107135
Cd1-O19	0.117609	0.106449

Table 7.6c: Calculated energies of HOMO and LUMO, total electronic energy $\mathcal{E}_0$, enthalpy ΔH_f, and free energy ΔGf ($[Cd(H_2O)_6]^{2+}$).

	B3LYP method	HF method
E_{HOMO}	-0.37308	-0.63002
E_{LUMO}	-0.20265	-0.00476
Total electronic energy $\mathcal{E}_0$	-5865.367782	-5861.291483
Enthalpy ΔHf (298.15K)	-5865.198908	-5861.102786
Free Energies ΔGf (298.15K)	-5865.252179	-5861.154855

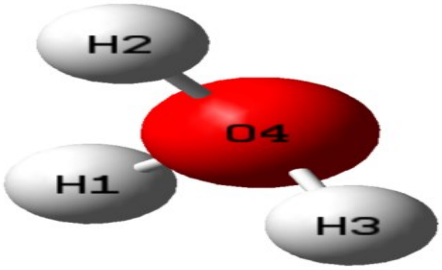

Figure 7.7: Structure of hydronium ion H_3O^+

Table 7.7a: Calculated Mulliken charges of atoms (H_3O^+)

B3LYP method	HF method
1 H 0.417804	1 H 0.421728
2 H 0.417804	2 H 0.421728
3 H 0.417804	3 H 0.421728
4 O -0.253413	4 O -0.265183
Sum of Mulliken charges = 1.0	Sum of Mulliken charges = 1.0

Table 7.7b: Calculated population analysis for bonding between two connected atoms (H_3O^+).

Bonding	Population (B3LYP method)	Population (HF method)
H1-O4	0.282095	0.282749
H2-O4	0.282095	0.282749
H3-O4	0.282095	0.282749

Table 7.7c: Calculated energies of HOMO and LUMO, total electronic energy $\mathcal{E}_0$, enthalpy ΔH_f, and free energy ΔG_f (H_3O^+).

	B3LYP method	HF method
E_{HOMO}	-0.69475	-0.93398
E_{LUMO}	-0.11637	0.11872
Total electronic energy $\mathcal{E}_0$	-75.67450917	-75.32498442
Enthalpy ΔH_f (298.15K)	-75.630889	-75.278771
Free Energies ΔG_f (298.15K)	-75.653691	-75.30064

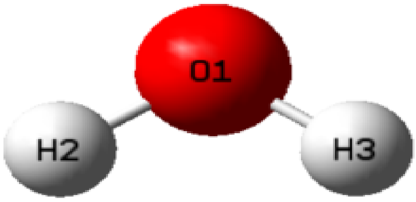

Figure 7.8: Molecular structure of H_2O.

Table 7.8a: Calculated Mulliken charges of atoms (H_2O).

B3LYP method	HF method
1 O -0.373756	1 O -0.372541
2 H 0.186878	2 H 0.186270
3 H 0.186878	3 H 0.186270
Sum of Mulliken charges = 0.0	Sum of Mulliken charges = 0.0

Table 7.8b: Calculated population analysis for bonding between two connected atoms (H_2O).

Bonding	Population (B3LYP method)	Population (HF method)
H2-O1	0.258010	0.266646
H3-O1	0.258010	0.266646

Table 7.8c: Calculated energies of HOMO and LUMO, total electronic energy $\mathcal{E}_0$, enthalpy ΔH_f, and free energy ΔG_f (H_2O).

	B3LYP method	HF method
E_{HOMO}	-0.14044	-0.38694
E_{LUMO}	0.34549	0.59290
Total electronic energy $\mathcal{E}_0$	-75.31001343	-74.96070251
Enthalpy ΔH_f (298.15K)	-75.282019	-74.931519
Free Energies ΔG_f (298.15K)	-75.303413	-74.952912

7.3.4. Molecular simulation of adsorption of hydrated Cd(II) ion

Based on the above calculations of species involved in Cd(II) adsorption reaction (7.1) or (7.2), the total electronic energy change $\Delta\mathcal{E}_o$, enthalpy change $\Delta H°$ and free energy change $\Delta G°$ of Cd(II) adsorption reaction calculated using B3LYP and HF methods are listed in Table 7.9a and 7.9b, respectively.

From Table 9.9a, it can be seen all the free energy changes ΔG° of Cd(II) adsorption reactions calculated using B3LYP method are positive, which means the adsorption of Cd(II) ions onto G-26 and MTS9570 resins are not thermodynamically favorable. This is not consistent to the adsorption tests [23]. Therefore, the molecular simulation of Cd(II) adsorption analyzed with B3LYP method does not resonate the experimental results.

In Table 7.9b, most of the free energy changes ΔG° of Cd(II) ion interactions with structural units containing sulfonic acid group (except for 2-(3-vinyl-phenyl)-ethylene sulfonic acid) are negative while calculated using HF method, which means the interactions of Cd(II) ion with structural units containing sulfonic group are spontaneous processes, i.e., thermodynamically favorable. This is consistent to the adsorption test results [23]. Besides the free energy changes ΔG°, most of the total electronic energy change $\Delta \mathcal{E}_o$ and enthalpy change ΔH° of Cd(II) ion interactions with structural units containing sulfonic acid group are also negative or have a small value. However, all the free energy changes ΔG° of Cd(II) ion interactions with structural units containing phosphonic acid group are positive while calculated with HF method, which means the interactions of Cd(II) ion with structural units containing phosphonic group are not thermodynamically favorable.

7.3.5. Interpretation of Cd(II) ion adsorption tests with molecular simulation study

The Cd(II) adsorption test results using G-26 and MTS9570 resins are listed in Table 7.10. As can be seen, G-26 resin containing only sulfonic group has higher Cd(II) removal percentage than MTS9570 resin containing both sulfonic and phosphonic groups at low resin dosages. For G-26 resin, the Cd(II) removal rate is close to 100% at the dosage of 0.3 g/ml. While, for MTS9570 resin, it needs the dosage above 0.5 g/ml. Combining with the molecular simulation results, it demonstrates that sulfonic acid group is more efficient than phosphonic acid group for bonding and adsorbing Cd(II) ions. The major Cd(II) adsorption reaction onto G-26 and MTS9570 resins can be represented with Equation (7.1).

7.4. Conclusions

To understand the adsorption mechanism of Cd(II) ion onto Dowex G-26 resin with sulfonic group and Puromet™ MTS9570 resin with both sulfonic and phosphonic groups, the electronic structure properties including Mulliken population analysis, Mulliken charges of atoms, the energies of frontier orbitals, total electronic energy $\mathcal{E}_o$, enthalpy ΔH°_f , and free energy ΔG°_f of fourteen possible structural units with sulfonic/phosphonic groups in these two resins and their interaction with Cd(II) ion were calculated using both B3LYP and HF methods.

For the interaction of Cd(II) ion with structural units bearing sulfonic group, the electron populations between Cd and O atoms are even higher than those between S and O atoms in sulfonic group, which means the bonding between O-Cd is very strong. Opposite to the sulfonic group containing systems, the electron populations between Cd and O atoms are smaller than those between P and O atoms in phosphonic group bearing systems.

The hydration of Cd(II) ion ($[Cd(H_2O)_6]^{2+}$)was considered when simulating the interaction of Cd(II) ion with the structural units containing sulfonic or phosphonic group.

All the free energy changes ΔG° of Cd(II) adsorption reactions calculated using B3LYP method are positive, which means the adsorption of Cd(II) ions onto G-26 and MTS9570 resins are not thermodynamically favorable. This does not resonate the experimental results.

The free energy changes ΔG° of Cd(II) ion interactions with most structural units containing sulfonic acid group (except for2-(3-vinyl-phenyl)-ethylene sulfonic acid) are negative while calculated using HF method, which means the interactions of Cd(II) ion with structural units containing sulfonic group are thermodynamically favorable processes. This is consistent to the adsorption test results. However, all the free energy changes $\Delta G°$ of Cd(II) ion interactions with structural units containing phosphonic acid group are positive while calculated using HF method, which means the interactions of Cd(II) ion with structural units containing phosphonic group are not thermodynamically favorable.

The calculation results of the energies of frontier orbitals (HOMO and LUMO), total electronic energy $\mathcal{E}_o$, enthalpy $\Delta H°_f$, and free energy $\Delta G°_f$ were of more reasonable significance of physics when simulating with HF method compared to B3LYP DFT method. In this study, HF method is a better electronic structure theory for simulating metal ion adsorption systems.

The molecular simulation results demonstrate that sulfonic acid group is more efficient than phosphonic acid group for bonding and adsorbing Cd(II) ions. The major Cd(II) adsorption reaction onto G-26 and MTS9570 resins can be represented with the equation:

$$R - SO_2OH + [Cd(H_2O)_6]^{2+} \longrightarrow [R\text{-}SO_3\text{-}Cd]^+ + H_3O + 5\ H_2O$$

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References

[1] J. Oliva, J. De Pablo, J.-L. Cortina, J. Cama, C. Ayora, ‘‘Removal of cadmium, copper, nickel, cobalt and mercury from water by Apatite IITM: Columnexperiments’’, *J. Hazard. Mater. 2011, 194. 312–323.*

[2] H. Liu, H. Gao, M. Long, H. Fu, P.J.J. Alvarez, Q. Li, S. Zheng, X. Qu, D. Zhu, ‘‘Sunlight Promotes Fast Release of Hazardous Cadmium from Widely-UsedCommercial Cadmium Pigment’’, *Environ. Sci. Technol. 2017, 51, 6877–6886.*

[3] L.N. Suvarapu, S.-O. Baek, ‘‘Determination of heavy metals in the ambientatmosphere: A review’’, *Toxicol. Ind. Health 33 (2017) 79–96, https://doi.org/10.1177/0748233716654827.*

[4] S. Kaur, K. Kaur, A. Kaur, J. Singh Aulakh, ‘‘SiO2@Fe3O4-SB nano-hybrids asnanosorbent for preconcentration of cadmium ions from environmental watersamples’’, *J. Environ. Chem. Eng. 2020, 8, 103448.*

[5] S. Cheng, G. Liu, Y. Liu, D. Wu, ‘‘Cadmium in Chinese coals: Abundance,distribution, occurrence, and environmental effects’’, *Hum. Ecol. Risk Assess. 2019, 25, 527–547.*

[6] R. Deep, ‘‘Bioaccumulation of mercury, arsenic, cadmium, and lead in plantsgrown on coal mine soil’’, *Hum. Ecol. Risk Assess. 2019, 25, 659–671, https://doi.org/10.1080/10807039.2018.1447360.*

[7] W. Cui, Q. Meng, Q. Feng, L. Zhou, Y. Cui, W. Li, ‘‘Occurrence and release of cadmium, chromium, and lead from stone coal combustion’’, *International journal of coal science & technology 2019,6, 586–594.*

[8] G. Genchi, M. S. Sinicropi, G. Lauria, et al. ‘‘The effects of cadmium toxicity’’. *Int. J.Env. Res. Public Health 2020, 17, 3782. https://doi.org/10.3390/ijerph17113782*

[9] M. Benavides, S. Gallego, M. Tomaro, ‘‘Cadmium toxicity in plants’’. *Braz.j, Plant physiol. 2005, 17, 21–34, https://doi.org/10.1590/S1677-04202005000100003.*

[10] J.A. Cotruvo, 2017 WHO Guidelines for Drinking Water Quality: First Addendum to the

Fourth Edition, *Journal AWWA 2017,109, 44–51.*

[11] S. Kocaoba, ‘‘Behaviour of Cadmium(II) Ions on Cation-Exchange Resins’’,*Adsorpt. Sci. Technol. 2003, 21, 831–840.*

[12] J. Jachuła, D. Kołodyn´ ska, Z. Hubicki, ‘‘Removal of Cd(II) and Pb(II) complexeswith glycolic acid from aqueous solutions on different ion exchanger’’, *Can. J.Chem. 2010, 88, 540, https://doi.org/10.1139/V10-027.*

[13] M.H. Taha, ‘‘Sorption of U(VI), Mn (II), Cu(II), Zn(II), and Cd(II) from multicomponent phosphoric acid solutions using MARATHON C resin’’, *Environ. Sci.Pollut. Res. 2021, 28, 12475–12489, https://doi.org/10.1007/s11356-020-11256-3.*

[14] E. Pehlivan, T. Altun, ‘‘The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin’’, *J.Hazard Mater. 2006,134, 149–156, https://doi.org/10.1016/j.jhazmat.2005.10.052.*

[15] E. Pehlivan, T. Altun, ‘‘Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} ions from aqueous solution by Lewatit CNP 80’’, *J. Hazard. Mater. 2007,140, 299–307, https://doi.org/10.1016/j.jhazmat.2006.09.011.*

[16] S.M. Moosavirad, R. Sarikhani, E. Shahsavani, S.Z. Mohammadi, ‘‘Removal ofsome heavy metals from inorganic industrial wastewaters by ion exchange method’’, *J. Water Chem. Technol. 2015, 37, 191–199.*

[17] S. Kocaoba, G. Akcin, ‘‘Removal of chromium (III) and cadmium (II) fromaqueous solutions’’, *Desalination 2005,180, 151–156, https://doi.org/10.1016/j.desal.2004.12.034*

[18] S. Kocaoba, ‘‘Comparison of Amberlite IR 120 and dolomite’s performances for removal of

heavy metals'', *J. Hazard. Mater. 2007,147, 488–496, https://doi.org/10.1016/j.jhazmat.2007.01.037.*

[19] N. Kansara, L. Bhati, M. Narang, et al., ''Wastewater treatment by ion exchange method: a review of past and recent researches'', *ESAIJ (Environmental Science,An Indian J.) 2016, 12, 143–150.*

[20] S. Jiang, H. Sun, H. Wang, B.P. Ladewig, Z. Yao, ''A comprehensive review on the synthesis and applications of ion exchange membranes'', *Chemosphere 2021,282, 130817.*

[21] H. Li, H. Ji, X. Cui, X. Che, Q. Zhang, J. Zhong, R. Jin, L. Wang, Y.i. Luo, ''Kinetics, thermodynamics, and equilibrium of As(III), Cd(II), Cu(II) and Pb(II) adsorption using porous chitosan bead-supported MnFe2O4 nanoparticles'', *Int. J. MiningSci. Technology 2021,31, 1107–1115.*

[22] B. Chen, S. Bao, Y. Zhang, ''Synergetic strengthening mechanism of ultrasound combined with calcium fluoride towards vanadium extraction from low-grade vanadium-bearing shale'', *Int. J. Mining Sci. Technology 2021,31, 1095–1106, https://doi.org/10.1016/j.ijmst.2021.07.008.*

[23] S.Elfeghe, S.Anwar, Y. Zhang, ''Adsorption and removal studies of cadmium ion onto sulfonic/phosphonic acid functionalization resins''. *Canadian J. Chemical Eng. 2022, 100, 3006–3014. https://doi.org/10.1002/cjce.24400.*

[24] J.B. Foresman, AE. Frisch, ''Exploring Chemistry with Electronic Structure Methods'', *3rd ed., Gaussian Inc, Wallingford, CT, 2015.*

[25] D.R. Hartree, ''The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I.

Theory and Methods'', *Math. Proc. Cambridge Philos. Soc. 1928, 24 89–110, https://doi.org/10.1017/S0305004100011919*.

[26] V. Fock, Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems, *Zeitschrift für Physik (in German) 61 (1930) 126–148,https://doi.org/10.1007/BF01340294*.

[27] Z.Tang, Q. Zhang, Y. Sun, P.Gao, Y.Han, ''Pilot-scale extraction of iron from flotation tailings via suspension magnetization roasting in a mixture of CO and H2 followed by magnetic separation'', *Resour. Conserv. Recycl. 2021,172,105680*.

[28] K. Kim, K.D. Jordan, ''Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer'', *J. Phys. Chem. 1994,98, 10089–10094, https://doi.org/10.1021/j100091a024*.

[29] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, ''Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields'', *J. Phys. Chem. 1994,98, 11623–11627*.

[30] C.Knill, J.Kennedy. ''Essentials of Computational Chemistry:Theories and Models'', *C.J. Kramer, 2nd ed., Wiley, Chichester, UK; 2005.Carbohydrate Polymers.2006, 65, 218–219. https://doi.org/10.1016/j.carbpol.2006.01.002*

[31] R.D. Lins, E.R. Vorpagel, M. Guglielmi, T.P. Straatsma, ''Computer Simulation ofUranyl Uptake by the Rough Lipopolysaccharide Membrane of Pseudomonas aeruginosa'', *Biomacromolecules 2008,9, 29–35*.

[32] X. Peng, P. Yang, K. Dai, Y. Chen, X. Chen, W. Zhuang, H. Ying, J. Wu, ''Synthesis, adsorption and molecular simulation study of methylamine-modified hypercross-linked

resins for efficient removal of citric acid from aqueous solution'',Sci. Rep. 2020,10,9623. https://doi.org/10.1038/s41598-020-66592-8.

[33] K. Gupta, K. Zhang, J. Jiang, ''Glucose recovery from aqueous solutions by adsorption in metal–organic framework MIL-101: a molecular simulationstudy'', *Sci. Rep. 2015,5, 12821, https://doi.org/10.1038/srep12821.*

[34] L. Delahaye, J.T. Hobson, M.P. Rando, B. Sweeney, A.B. Brown, G.A. Tompsett, A.Ates, N.A. Deskins, M.T. Timko, ''Experimental and Computational Evaluation of Heavy Metal Cation Adsorption for Molecular Design of Hydrothermal Char'', *Energies 2020,13, 4203.*

[35] Z. Cheng, Y. Zhu, Y. Li, S. Butt, ''Experimental and MD simulation of 3-dodecyloxyprop anamine and 3-tetradecyloxypropylamine adsorbed ontoquartz (1 0 1) surface'', *Int. J. Mining Sci. Technology 2021,31, 1033–1042.*

[36] Singha Deb, A.K ; Sahu, P ; Boda, A ; Ali, Sk M ; Shenoy, K.T ; Upadhyay, D,Physical Chemistry Chemical Physics : *PCCP, 2020, 22 , 14682.*

[37] R. Mukherjee, B. Gebreslassie, U.M. Diwekar, ''Design of novel polymeric adsorbents for metal ion removal from water using computer-aided moleculardesign'', *Clean Techn Environ Policy 2017,19, 483–499, https://doi.org/10.1007/s10098-016-1236-6.*

[38] Z. Tang, Q. Zhang, Y. Sun, P. Gao, Y. Han, ''Prospects of green extraction of iron from waste dumped flotation tailings by H2: A pilot case study'', *J. Cleaner Prod.2022,330, 129853.*

[39] R.A. Silva, K. Hawboldt, Y. Zhang, ''Application of resins with functional groups in the separation of metal ions/species–a review'', Miner. Process. Extr. Metall.Rev. *2018,39,*

395413, https://doi.org/10.1080/08827508.2018.1459619.

[40] S.F. Lincoln, D.T. Richens, A.G. Sykes, ‘‘Metal Aqua Ions’’. in J. A. McCleverty and T. J. Meyer (eds.) Comprehensive Coordination Chemistry II, Vol. 1, pp. 515-555.

[41] Wiley Richard H., Devenuto Giovanni. ‘‘Kinetics of the polymerization and styrene copolymerization of m- and p-divinylbenzene’’. *Journal of Polymer Science Part A General Papers, 1965,3, 1959-1967.https://doi.org/10.1002/pol.1965.100030525*.

Chapter 8

Summary, Conclusions and Recommendations

8.1 Summary

This research work investigates the application of resin adsorption process for the removal and separation of heavy metals, i.e., copper, lead, and cadmium, from water solutions for environment protection /remediation and recovery/recylcation of metals. Removal and separation of lead, copper, and cadmium from industrial effluents helps to solve serious challenges in wastewater treatment management and environment protection. The presented study of resin adsorption technologies addresses these challenges and led to an invention in this research, which relates to the removal of cadmium ions using low dimensional resins bearing sulfonic acid group from aqueous systems, including but not limited to industrial wastewater, contaminated water streams in commercial and agricultural production, and polluted rivers and lakes. A novel adsorption process using low dimensional styrene-divinylbenzene (SDVB) resins (i.e., resin fibers) bearing sulfonic acid group fabricated through electrospinning and sulfonation method demonstrated excellent efficiency for Cd(II) ion removal from aqueous systems under desired conditions. The loaded resin could be recycled with a customized elution process using hydrochloric acid solution, sodium citrate solution, or a mixture of them.

In order to find the efficient resins for the removal of single heavy metals such as lead, copper, and cadmium as well as for the separation of these metals in a binary solution, Tweny-seven commercial resins with different functional groups have been investigated.

To test the performance of the selected resins, the influences of different operational conditions such as solution pH, resin dosage, adsorption time, shaking speed, initial metal concentrations, and temperature have been assessed.

Three common adsorption isotherms, i.e., Langmuir, Freundlich, and Temkin isotherms, have been applied to provide information on adsorption mechanisms, as well as the adsorption capacity of the resins, which is one of the most important parameters in the design of an adsorption system.

Kinetics and thermodynamics studies on the selected resins have been done to explain the rate of chemical reactions and nature of sorption process.

Resin desorption process is very important for the economic advantage of the sorption processes, in which resins can be recycled by elution/regeneration processes.

The ion exchange resins G-26 and MTS9570 studied in this work for the removal of single Cu^{2+}, Cd^{2+} and Pb^{2+} metals as well as the resins MTS9140 used for the separation of binary metals solutions (Cu^{2+}& Pb^{2+}) have higher adsorption capacities than those of the adsorbents reported in the literature. Although these ion exchangers are manufactured for specific application as recommended by their suppliers, however, they can be used efficiently in the removal and separation of lead, copper and cadmium ions in water sysetms.

8.2 Conclusions

The following conclusions can be drawn from the conducted studies:

1. Dowex G-26 resin with a sulphonic functional group and Puromet™ MTS9570 resin with both sulphonic and phosphonic functional groups efficiently removed cadmium ions from

aqueous solutions by systemic batch approach. Hence, they are good candidates for cadmium ions removal from wastewater.

2. The use of G-26 and MTS9570 commercial resins achieved efficient uptake of copper from acidic solutions. The adsorption/desorption studies demonstrated that the performance of G-26 resin is better than that of MTS9570 resin.
3. Exchange resins G-26 and MTS9570 have the potency to efficiently remove lead ions from wastewater system. The results show that both resins have higher adsorption capacities than those of the adsorbents reported in literatures.
4. Chelating resin Puromet MTS 9140 with a thiourea group is an efficient absorbent for the separation of copper and lead from acidic water solution. The absorbent has adsorption preference for Cu(II) ions over Pb(II) ions with a higher adsorption capacity than those of the adsorbents reported.
5. The mechanism study of Cd(II) ion adsorption onto Dowex G-26 and Puromet™ MTS9570 resins using B3LYP and HF molecular simulation methods demonstrates that the adsorption of Cd(II) ions onto the resins via bonding with sulfonic acid groups are thermodynamically favorable. The results show that simulating electronic structure properties with HF method is more efficient than B3LYP DFT method in this case.

8.3 Recommendation for future study

1. To understand the influence of coexisting ions, for example, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, Fe^{3+}, Al^{2+}, Cu^{2+}, and SO_4^{2-}, it is recommended that the effect of such ions on the adsorption rate of interested metals should be studied.

2. Column adsorption tests are recommended for removing high wastewater volume as well as pollution load. The advantage of this technique is that it is very similar to practical adsorption processes.

3. More studies on resin elution and metal recovery from eluted metal solutions are also recommended.

4. A complete process for metal separation through resin adsorption, resin elution and recycling, and metal recovery from eluted solutions should be inverstigated.