SORPTION OF CADMIUM AND NICKEL FROM SOLUTION BY PEAT AND MODIFIED PEAT

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Sorption of cadmium and nickel from solution by peat and modified peat

by

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Abstract

The performance of peat and modified peat in the remediation of wastewater containing cadmium (Cd) and nickel (Ni) was investigated in both batch and continuous process. Peat is an attractive natural sorbent because it is widespread and inexpensive. The sorption capacity can be determined using Langmuir and Freundlich isotherms. The batch sorption results showed that sulfuric acid treatment (STP) enhances the sorption capacity of the peat. Temperature, concentration of metals and time influences the sorption process. Breakthrough curves for cadmium and nickel were evaluated for several column characteristics: the height of the exchange zone, time taken by the exchange zone to travel its own height and rate of movement of the exchange zone. The column showed a better performance at lower concentration when compared to higher concentrations of cadmium and nickel. From the infrared (IR) measurements the difference in the antisymmetrical and symmetrical stretching of carboxylic group of peat confirms an unidentate complex with Ni and Cd.

Table of contents

CONTENT **PAGE**

List of tables

List of figures

List of Abbreviations

ASTM	: American Society for Testing Materials
EC	: Exchangeable cations
DBP	: Debituminized peat
IR	: Infrared spectroscopy
STP	: Sulfuric acid treated peat
UMP	: Unmodified peat
FCC	: Fluidized catalytic cracking
T_h	: Time required by exchange zone to move the length of its own height (h)
T_B	: Time required for exchange zone to move completely out of the bed (h)
R_z	: Rate of sorption zone movement (cm/h)
h_z	: Height of the exchange zone (cm)
f_w	: Metal solution flow rate
l_E	: Total volume of metal solution treated to the point of exhaustion

1.0 Introduction

1.1 Objectives

The toxicity of heavy metals has been a great concern in recent years due to their non-biodegradable nature and the tendency to accumulate in living organisms. Wastewater from industries such as metal plating facilities, mining operations and tanneries contains heavy metals that pollute the surrounding water bodies and soils. Metals that are associated with these industries are cadmium (Cd), nickel (Ni), lead (Pb) and mercury (Hg).

As many heavy metals are toxic in low concentrations, efficient treatment methods should be employed. Sorption is one of the reliable methods for the treatment of wastewaters containing metals. Various naturally-available adsorbents such as lignite (Allen *et al.*, 1989), clay (Viraraghavan and Konduru, 1997 and Weber, 1980), fly ash (Viraraghavan and Konduru, 1997), peat (Brown *et al.*, 2000) and commercial ion exchange resins have been used in the sorption process.

Peat has been recognized as a potential adsorbent for the treatment of wastewaters, due to its properties, availability and low cost. Several studies on peat have been reported in the literature for the treatment of wastewaters in batch (Thevenot *et al.*, 1986), fixed bed (MacCarthy and Ansted, 1984) and as a biofilter (Martin, 1991 and Talbot *et al.*, 1996). The present study is primarily aimed to optimize conditions for the sorption of cadmium and nickel from solution in batch or continuous system.

1.2 Industrial pollutants

1.2.1 General

The existence of pollution in the environment as a world problem was recognized in early 1960s (Tatsumoto and Patterson, 1963a). The increase in human population associated with industrial growth is mainly responsible for the pollution. Most industrial pollution is caused by the release of toxic waste in the form of solid, liquid and gases during industrial processes.

Many industries such as metal plating, food processing, pesticides, pharmaceuticals, chemical and thermal power plants, etc. consume large quantities of water. The major uses, steam generation, cooling and processing, are common to all industries (Rees, 1969). The processed water or wastewater from these industries contains numerous organic and inorganic pollutants which are harmful to animals and plants. Arsenic, cyanide and heavy metals such as cadmium, chromium, copper, nickel, mercury and zinc are the most common inorganic substances found in industrial wastewaters (Henry and Heinke, 1996). Some of the organic compounds widely used in industries and released with wastewaters are chlorophenols (Liu and Chang, 1997), dyes (Viraraghavan and Konduru, 1997) and petroleum hydrocarbons (Doerffer, 1992). Major industries have treatment facilities for effluents, but this is not the case for small-scale industries which cannot afford the cost of the pollution control equipment.

Water pollution has many other sources such as municipal sewage and agricultural run-off from fields (Henry and Heinke, 1996).

1.2.2 Inorganic pollutants

The main source of metal pollution in the environment originates from industrial processing of ores and metals, geological weathering, leaching of metals from solid dump sites and animal and human excretions.

The percentage of metals in a New York City effluent treatment plant can be seen in Table 1.2.1. Kneip *et al.* (1974) investigated the cadmium and nickel enrichment in an aquatic ecosystem along the eastern side of the Hudson River. The enrichment of metals was attributed to wastewaters from a battery plant. The average cadmium and nickel concentrations in industrial wastewater from the textile and dyeing industries were 115 and 740 μg/L, respectively (Wittmann, 1981). The main sources of mercury in Canada's aquatic environments include various mining and smelting processes (Anonymous, 1979). Mercury pollution also arose from residential sewage. It has been reported that raw urban sewage contains 2μg/L mercury, which occurs from washing, cosmetics and medical uses. The extensive use of boron compounds increased the concentration of this element in sewage plants (Duranceau and Itri, 1976). The main source of boron in sewage effluents was due to the use of detergents.

The largest current use of lead is in the production of automotive and industrial lead acid batteries (Atwood *et al.*, 2002). The recycling of lead batteries produces Pb and other metals such as Sb, As, Cd, Se and Sn. During the recycling process large volumes of heavy-metal-containing wastewaters are produced, which contaminate the surrounding soils and waters. The two major sources of silver are electroplating and photographic industries (Lasko and Hurst, 1999). The presence of silver in wastewater is of great

Table 1.2.1: Relative contributions of metals to the New York City wastewater treatment plants

Sources	Percentage of metals received in New York City treatment plant			
	Ni	Zn	Cd	Total metals (%)
Water Supply	0.0	7.0	0.0	2.3
Industrial effluent	65.0	20.0	39.0	41.0
Run off	10.0	31.0	12.0	17.6
Residential	25.0	42.0	49.0	38.6

(after Wittmann, 1981)

concern due to its harmful effect. The above mentioned studies illustrate that a wide spectrum of heavy metals are released into the environment by industries.

Henry and Heinke (1996) reported that human sewage is also a major source of inorganic constituents such as chlorides, sulfates, nitrogen, phosphorus, carbonates and bicarbonates in wastewater. Another important source of metals in the environment is geological weathering (Wittmann, 1981).

1.2.3 Effects of cadmium and nickel on health

The outbreak of a painful disease of a rheumatic nature in villages on the banks of the Jintsu River, Japan was recognized in late 1947. This disease became known as the itai-itai disease and after extensive investigation by the Japanese Ministry of Health and Welfare, it was revealed in 1961 that deaths were caused by cadmium poisoning (Wittmann, 1981). The disease was mainly due to the consumption of rice grown in the cadmium-contaminated irrigation water. Ingestion of the cadmium can cause gastrointestinal effects such as choking attacks, persistent vomiting, abdominal pain and loss of consciousness (Elinder, 1986). The low levels of exposure to cadmium has been shown to affect the kidney (Bernard and Lauwerts, 1991) which increases the occurrence of kidney stones (Adams, 1992). The exposure to cadmium was also reported to be carcinogenic (Elinder *et al.*, 1985).

One of the most common consequences of long-term nickel poisoning in humans are respiratory and dermal. The toxicity of nickel depends largely on the route by which it enters the body such as inhalation, skin contact, parenteral and oral intake (Sunderman, 1982). Venugopal and Luckey (1978) reported that oral toxicity of nickel causes growth retardation in mice. This was attributed to the reduced activities of liver cytochrome oxidase, kidney malic acid dehydrogenase and heart cytochrome oxidase. Nickel and its compounds are primary carcinogens. Nickel binds firmly to nucleic acid and inhibits DNA-dependent RNA synthesis, which causes the possible mechanism involved in nickel carcinogenesis (Heath and Webb, 1967).

1.2.4 Waste water technology

Methods of cadmium and nickel wastewater treatment currently in use are essentially those employed for most heavy metal wastes such as chemical precipitation and ion exchange.

1.2.4.1 Chemical precipitation

The formation and precipitation of the metal hydroxide is generally the basis for the destructive treatment of metal bearing wastes. Metals are converted to insoluble particles by raising the pH of wastewaters using caustic solutions such as sodium hydroxide. The precipitation is followed by coagulation which causes smaller suspended particles to gather to form larger aggregates (Amirtharajah and O'Mella, 1990). The insoluble metal particles are then separated by filtration or centrifugation from the wastewater (Techobanoglous and Burton, 1991). The chemical agents most commonly used for the precipitation are lime (calcium oxide), ferrous sulfate, alum $(Al_2(SO_4)_3.14$

H_2O), ferric chloride and polymers. The cost of chemical precipitation depends on many variables, including the characteristics of the wastewater, volume of the wastewater to be treated and the dosage of chemicals.

Chemical precipitation has several advantages and disadvantages (U.S. EPA, 2000)

Advantages:

1) Chemical precipitation is the most commonly-used technology with readily-available equipment and chemicals.
2) The cost of chemical precipitation is inexpensive when compared to other treatment technologies such as ion exchange.
3) It is a completely controlled treatment with less maintenance.

Disadvantages:

1) Chemical precipitation results in an increase of waste sludge to be disposed of.
2) Polymers which are used as coagulants in chemical precipitation are expensive.
3) Increases operators safety concerns.
4) Chemical precipitation does not remove metals completely.

1.2.4.2 Ion exchange

Recovery of metals can be accomplished by ion exchange and has been used for some time. Studies have shown the effectiveness of ion exchange resins in the recovery of cadmium (Gavaskar, 1993) and nickel (Patterson, 1975) from wastewaters. Recovery of nickel from waste streams is more attractive than other metals, due to the high value of nickel.

1.3 Sorption

1.3.1 Definition

The sorption process has been defined in many ways and one of the definitions given by Morrill *et al.* (1982) states "the condensation of gases on free surfaces or fixation of solutes from a solution on the surface of a solid". When ions or gas molecules come in contact with a solid surface it is collected on the surface of the solid. This phenomenon is called adsorption. Absorption on the other hand takes place when ion or gas molecules penetrate the solid structure.

The metal ions are attached to the adsorbent in two different ways 1) physical or van der Waals adsorption and 2) chemisorption. Physical sorption is a weak interaction between the adsorbent and the ion. The latter termed 'chemisorption' is the result of a chemical reaction. The ions are first bonded to the surface of the adsorbent by chemical forces followed by the attraction caused due to weak van der Waal forces.

1.3.2 Commercial adsorbents

Activated carbon is a common commercial adsorbent used for the treatment of wastewaters. It is mainly available in two forms, as carbon powder and granular carbon. Leyva-Ramos *et al.* (1997) reported that the sorption capacity of activated carbon for cadmium increases with a decrease in the temperature. Activated carbon has also been evaluated for its efficiency to adsorb trichloroethane (Chang and Tsai, 1994), dye (Girgis and Khalil, 1998) and metals (Reed and Arunachalam, 1994).

Many metal oxides such as TiO_2 (Hongxiang *et al.*, 1998) and MnO_2 (Lawrance *et al.*, 1998) have been used as adsorbents. They were efficient in adsorbing metals like chromium (VI), lead (II), copper (II), zinc (II) and thallium (I). A study by Rawat and Bharadwaj (1999) showed that Duolite ES 467 has some sorption capabilities for transition metal ions.

1.3.3 Natural adsorbents

In recent years, naturally-available materials or industrial waste products have been successfully used as adsorbents in the treatment of wastewaters. Baes *et al.* (1997) investigated the potential of coconut coir for removing nitrate, chromium (VI), arsenic (V) and selenium from ground water. The coconut coir was modified using amine to increase the sorption capacity. Although the exchange capacity was 10 times lower than the commercial ion exchange resin (Amberlite IRA-900) coconut coir was efficient in the treatment of metals at lower concentrations. Sorption of metal ions onto mineral particles was studied by Petrovic *et al.* (1999). The comparison between different minerals (sand, calcite and kaolin) and humic acids for lead, zinc and copper was investigated. They concluded that the three component system (heavy metals-humic acid- kaolin) can bind metal ions along with the metal-bound humic substances. This was mainly due to the large surface area of kaolin. But the sorption capacity of other minerals (sand and calcite) was affected due to the blocking of binding sites on minerals by humic molecules. A study by Afzal *et al.* (1998) reported that zeolite-3A (K_9Na_3 $(AlO_2)_{12}$ $(SiO_2).27H_2O$) demonstrated strong affinity for chromium ions from tannery waste. Isotherm studies showed that temperature, pH and the concentration of the adsorbent were important factors affecting chromium removal. Maximum sorption of chromium was reported at higher temperatures leading to an endothermic sorption process. Vasylechko *et al.* (1999) used the trancartathain climoptilolite another type of zeolite to adsorb copper (II) ion from solutions. This zeolite showed sorption capacity of 725 μg/g at pH 7.1. The adsorbed copper was entirely extracted using HNO_3 (1:1) and HNO_3 (1:2) solutions. There are numerous studies on the usage of peat and humic substances in wastewater treatment, and they will be discussed in detail in the next section (1.4.6).

Most industrial waste of cellulose origin has a high affinity to adsorb metals. Daifullah and Aly (1998) studied the sorptive capacities of bagasse pith, a waste product from the sugar cane industry. The sorption capacity of bagasse pith was tested in batch and continuous flow mode. They concluded that bagasse pith had a high affinity for cadmium and lead at pH 5-6. It also had the affinity to remove color from wastewater (Khattri and Singh, 1999).

Industrial waste is generally disposed by incineration, landfill and tollage. Some of the industrial waste is hazardous and requires expensive modes of disposal such as incineration. Yubin *et al.* (1998) investigated the capacity of fluidized catalytic cracking (FCC), a hazardous waste product from petrochemical industries, to adsorb heavy metals. FCC is mainly composed of zeolite (10%) and silica/alumina (90%). Due to its high cation exchange capacity it can be used as an adsorbent in wastewater treatment. The study indicates that 97.0%, 90.5% and 91.5% of lead, copper and zinc, respectively, were successfully removed from the wastewater. This new approach of the treatment of wastewaters also reduced the cost of disposing hazardous waste material.

In another study, Namasivayam and Senthilkumar (1995) successfully used Fe (III)/Cr (III) hydroxides (solid waste generated in the fertilizer industry) as an adsorbent. A preliminary result showed that the Fe (III)/Cr (III) hydroxides was efficient in the treatment of wastewaters containing arsenic (III), mercury (II), chromium (III) and dyes. Zarraa (1995) concluded that sawdust can adsorb chromium (VI) from wastewater in a forced batch reactor. He investigated the sorption as a factor of the initial concentration of chromium (VI), rotational speed of the impellers and the weight and diameter of the sawdust.

Several other studies have been reported on natural adsorbents in treatment of wastewater containing inorganic and organic impurities. The natural adsorbents include dead biomass (Niu *et al.*, 1993), ash (Daifullah *et al.*, 1998 b), lignite (Duggan and Allen, 1997), mineral suspension (Pickering and Aualiitia, 1987) and bagasse pith (McKay *et al.*, 1998c). Most of these adsorbents were efficient in the removal of the metals from wastewater in low concentrations. The toxicity of heavy metals and stringent laws on the lower level of metal disposal in wastewater has also encouraged the search for alternative methods of treatment. The use of natural adsorbents is cheaper than the current treatment technologies.

1.3.4 Types of adsorbent systems

1.3.4.1 Introduction

The sorption process is generally operated in six different ways depending on the wastewater and the volume of the effluent to be treated (McKay and Brady, 1996b):

1) Batch sorption

2) Continuous or fixed-bed sorption

3) Pulsed beds

4) Steady-state moving beds

5) Fluidized beds

6) Moving mat filters

Only the batch and continuous (or fixed-bed) processes will be discussed here.

1.3.4.2 Batch processes

In the batch sorption process the wastewater is mixed thoroughly with the adsorbent in a reaction vessel for a specific period. Batch sorption is effective in the treatment of small volumes of effluent. It is operated with a single reaction vessel or series of reaction vessels depending on the level of the treatment (McKay and Brady, 1996b). The efficiency of the batch sorption mainly depends on the type and amount of the adsorbent, contact time, mixing or agitation, temperature and concentration of the pollutant. McKay and Brady (1996b) reported that the batch sorption process commonly consists of a batch reactor, a filter press and a tank to store the treated effluent. After equilibrium, the adsorbent is separated from the treated effluent, following this the adsorbent is then regenerated or disposed of safely. A preliminary sorption experiment in the laboratory is useful for optimizing the conditions in the design of the batch sorption system.

1.3.4.3 Continuous processes

Continuous or fixed-bed sorption system is widely encountered for the treatment of wastewater. The adsorbent is in continuous contact with the effluent, which enables the treatment of large volumes of wastewater. The factors that determine the fixed-bed sorption process include total feed rate and length of the sorption zone (Harland, 1994). In general, most applications have two fixed beds in operation, one in the sorption mode and the other in the regeneration mode. A sorption zone is created when the effluent is passed through the column. In the initial stage most of the sorption takes place at the top of the bed. As the effluent is passed through the bed, the upper zone gets saturated with the solute, resulting in the downward movement of the sorption zone through the column. The time taken by the sorption zone to move through the column is expressed graphically by a breakthrough curve (Benefield *et al.*, 1982), obtained by plotting the effluent solute concentration vs. time. This is an important parameter in the design of a large scale fixed bed.

1.4 Peat

1.4.1 Definition

Peat is an organic soil formed by the decomposition of plant material in wet conditions. Water is the main constituent of peat, followed by organic material and small amounts of inorganic compounds commonly called "ash". The composition of the peat varies with the location and conditions. The sphagnum peat is slightly decomposed and has low levels of carbon and hydrogen than reed sedge peat. The elemental composition of different types of peat shown as w/w (%) can be seen from Table 1.4.1.

1.4.2 Peat resources and different uses

Peat which is the first stage of the coal formation, is estimated to be 0.3 x 10^{12} tonnes worldwide, much less then the coal reserves of 7.6 X 10^{12} tonnes (Spedding, 1998). The largest deposits are found in the Northern Hemisphere, particularly in Russia, U.S.A and Canada. Peat reserves are also found in tropical countries like Indonesia, Sri Lanka, and Brazil. Table 1.4.2 presents the world peat reserves. The large deposits of peat attract commercial interest in Northern Hemisphere. Peat is being extensively used in Germany and Finland for the production of peat coke which is used for the metallurgical industry. In the United States and Canada peat is mainly produced for horticultural purposes. Peat resources in U.S.A and Canada can be seen in Table 1.4.3. Peat is mainly used as soil amendment and as a growing medium in three forms: as a raw material, peat soil mixes

Table 1.4.1: Elemental composition of peat (%)

Organic elements	Sphagnum peat[a]	Low moor peat[a]	Reed sedge peat[b]
Carbon	48.0-53.0	59.0-63.0	56.8
Hydrogen	5.0-6.1	5.1-6.1	5.6
Oxygen	40.0-46.0	31.0-34.0	34.6
Nitrogen	0.5-1.0	0.9-1.9	2.7
Sulfur	0.1-0.2	0.2-0.5	0.3

a :Fuchsman, (1980a)
b: Punwani, (1980)

Table 1.4.2: World peat reserves

Country	Area (millions of hectares)	Resources (billions of tons)
Russia*	150.0[a, c]	302.0[d]
USA	21.3[d], 21.0[a]	70.0[d]
Canada	153.0[b], 112.0[a]	0.2[e]
Finland	10.4[c], 9.68[a]	30.0[e]
Sweden	7.0[c], 7.8[a]	8.0[e]
Germany	5.3[d], 5.2[a]	--
Indonesia	1.3[d]	--
New Zealand	0.2	--

a: Farnham, (1979)
b: Rubec and Pollet (1979)
c: Kivinen (1979)
d: Farnham (1978)
e: Mickelsen, (1975)
*: includes all former Soviet Union States

Table 1.4.3: Peat resources of Canada and United States

Country	Acres (millions)	Quantity (million tons)
Alaska [a]	27.5	617.0
Minnesota [a]	7.2	165.0
Michigan [a]	4.5	103.0
Florida[a]	3.0	69.0
Wisconsin [a]	2.8	64.0
New York [a*]	0.6	15.0
Nova Scotia[b*]	0.01	23.0
New Brunswick[b*]	0.1	103.0
Manitoba [b*]	0.2	103.0
Ontario [b*]	0.1	135.0

a :Farnham, (1979)

b*: Scott *et al.*, 1980, Calculations based on measured peat resources and as compost mixtures (Anderson, 1993). Components of peat are also produced for waxes, sugar and other chemicals. The peat waxes are used as an ingredient in shoe polish, candle production, electrical insulation, as a paint-waterproofing agent, inks, grease and leather dressings. Peat has been extensively used for the production of activated carbon in Holland and Ireland (Fuchsman, 1980b). In Poland, peat was studied for the production of peat-based fertilizers (Haber, 1992). Punwani (1980) reported peat as a source of energy in Germany, Denmark, Netherlands, USA, Ireland and Finland till 1960 but since then these countries have abandoned peat in favor of other fossil fuels. At present, peat is only used as a boiler-feed to produce steam for electric power generation.

1.4.3 Peat as an adsorbent

Peat is a soil with complex organic material such as lignin, humic acid, cellulose and bitumen. Peat organic substances are mainly derived by the decomposition of plants. These components are insoluble in water and are readily metabolized by microorganisms. Bitumens are mainly formed during the decomposition of lipids such as fats, waxes and vegetable oils which are soluble in organic solvents. The origin of humic acids is still not clear, although they form a major fraction of peat. Many theories (Stevenson, 1982) exist for the formation of humic substances. According to the lignin theory, lignin is partially decomposed by microorganisms to form humic substances. Humic substances are heterogeneous in structure and bear polar functional groups such as alcohols, aldehydes, ketones, ethers, carboxylic acids, phenols and a significant amount of nitrogen. These constituents, especially carboxylic groups, are mainly involved in the chemical bonding with metals (Chaney and Hundemann, 1979). These properties make peat a potential adsorbent for the treatment of wastewaters containing heavy metals.

Over the last 20 years peat has been mainly studied as a natural metal adsorbent in three areas (McKay and Allen, 1997):

1) Optimization of the conditions for maximum sorption.
2) The mechanism by which the metal ions are sorbed.
3) Studies of peat modification for achieving maximum metal sorption.

Prakash and Brown (1976) found peat to be efficient in recovering zirconium from solution. The zirconium was four times more adsorbed than titanium. These results suggest that peat can be used to separate zirconium from effluent containing both metals. As well, peat was more effective than coal or activated carbon in adsorbing zirconium and titanium. Sorption of metals at different concentrations ranging from 0.01 to 100 mM was reported by Thevenot *et al.* (1986). The metal binding equilibrium constant decreased in the following order: nickel > copper > cadmium = zinc. The metal removal rate was maximum for 10 mM solution and was greatly dependent on the peat origin, metal cation, concentration and pH of the solution. The removal of copper, nickel, cadmium and zinc was optimal at pH 4.0, 4.5, 5.6 and 6.7, respectively. All metal cations were completely released when the pH was fixed below 1.5, except for nickel, which was strongly bound to the peat. Forster and Sharma (1993) studied the sorption of chromium onto peat as a factor of pH and temperature. For chromium, the maximum sorption was in the pH range of 1.5- 3.0 and increased with an increase in temperature from 25 to 40^0 C. They concluded that chromium removal was mainly governed by chemical reduction of chromium (VI) to chromium (III). Wase *et al.* (1995) investigated the batch nickel removal from solution by peat. The efficiency of nickel removal is controlled by initial pH and concentration of the solution. The maximum sorption was obtained in the pH range of 4.0-7.0 and ceased with a decrease in the pH. Copper (II) ion fixation depends largely on the initial copper concentration, peat type and pH (Thevenot *et al.,* 1990). All authors agree that maximum sorption for metal cations onto peat is in the pH range of 4.0 - 7.0.

Various researchers have used isotherms to examine the importance of different factors on metal ion sorption by peat. The two most popular isotherm theories that have been used were Langmuir and Freundlich (Section 3.2). McKay *et al.* (1998d) investigated the equilibrium isotherms (Langmuir, Freundlich and Redlich–Peterson) for metals. This author concluded that the Langmuir isotherm is best suited for the sorption of cadmium, copper, nickel and zinc and the Freundlich isotherm was best suited for cobalt. The maximum sorption capacity for cadmium was 11.18 mg/g peat, 26.34 mg/g for cobalt, 12.60 mg/g for copper, 6.65 mg/g nickel and 9.28 mg/g for zinc, respectively. Forster and Sharma (1993) concluded that the Langmuir model is better suitable for the chromium removal from aqueous solution in the pH range 1.5-3.0.

Another important factor to consider is the temperature at which the sorption process takes place. Viraraghavan and Rao (1993) investigated cadmium and chromium sorption onto peat at 5, 10, 15 and 21^{0}C. They concluded that the sorption of cadmium onto peat may be an exothermic reaction because of the possible decrease in the sorption between the sorbent and sorbate at higher temperature. On the other hand, chromium sorption was endothermic. In another study, Forster and Sharma (1993) reported a two-fold increase in the sorption of chromium with an increase in temperature from 25 to 40^0C.

Several studies have shown that the mechanisms by which metal ions are sorbed onto peat are ion exchange, chemisorption and complexation. In a preliminary study, Zhu *et al.* (1984) reported calcium, magnesium, iron, sodium and potassium were the main exchangeable cations present in peat. The increase in the sorption of metal ions by peat was observed with an increase in Ca^{2+} content in the peat. In another study, Wolf *et al.* (1977) also reported that sorption of metals increased with an increase in the Ca^{2+} content in the peat and decreased with an increase in the Ca^{2+} concentration in the solution. The sorption of copper onto peat is due to both ion exchange and complexation (Thevenot *et al.*, 1990). A total of 185 and 1650 mequiv./Kg cations occupied ion exchange sites in eutrophic and oligitrophic peat, respectively. When the initial concentration of copper in the solution is low, ion exchange is predominant, but with an increase in the concentration the sorption is mainly due to complexation. Kadlec and Rathbun (1983) studied the intraparticle phenomena of batch copper sorption onto peat. The authors concluded that diffusion of copper ions into the individual particles of peat is a relatively slow process when compared to ion exchange. Dissanayake and Weerasooriya (1981) studied the effect of Na^+ on the sorption of Cu^{2+}. In the presence of monovalent ions the absorption maxima was lowered, indicating the buffer action of the sorption sites.

Peat showed selectivity towards the sorption of metals, with less nickel removal when compared to other metals (Wase *et al.*, 1995). The selectivity of peat towards the metals was due to the formation of covalent bonds (Zhu *et al.*, 1984). Some studies have also shown that more electronegative metal ions are strongly attracted towards the surface of peat (McKay *et al.*, 1998d).

Raw peat has a number of disadvantages, such as impermeability to water, making it unsuitable for column use, and leaching of organic compounds from it into water. Some research has been done to improve the sorption capacity by modifying the peat. Spigarelli and Patricia (1989) investigated modified peat to adsorb copper and chromium. The method of modification involved debituminization (extraction of bitumen) and wet carbonization. The authors concluded that wet carbonized peat, although having less sorption capacity than unmodified peat, was suitable for column use. Kertman *et al.* (1993) reported that chemically modified peat had a high affinity for heavy metals. Although the type of modification was not mentioned, it was reported to be simple and cheap with readily available chemicals.

Sulfuric acid-treated peat showed a significant cation exchange capacity (MacCarthy and Ansted, 1984 and Smith *et al.*, 1977). The modified peat was effective in removing a variety of metal ions from solution over a wide range of pH, ionic strength and flow rate. The authors concluded that sorption of metals decreased with a decrease in pH, increase in ionic strength and an increase in flow rate. Two main advantages of sulfuric acid-treated peat is its resistance to leaching of organics, and its suitability for column use. Viraraghavan and Rao (1993) studied the sorption of chromium and cadmium by peat and acid-treated peat. The modification was carried by shaking the peat with 1M HCl for 2hrs and washing with deionized water until the filtrate reached pH of

4.0. The results showed that acid-treated peat is a better adsorbent of cadmium and chromium from wastewater compared to raw peat.

Peat has been studied in the treatment of wastewater containing metals and organic pollutants in different sorption systems such as batch and column sorption. Talbot *et al.* (1996) developed a peat-based bio-filter for the onsite treatment of wastewater. The study was divided into three phases: an experimental phase to select the peat to be used for bio-filter, experiments in the field and a phase to demonstrate the adaptability of the system. The bio-filters showed high removal efficiencies for parameters usually considered in a secondary treatment plant. A compact and simple bio-filter was introduced into the market (Ecoflo®) based on results from the three phase program. According to Aldrich and Feng (2000) biosorptive flotation was effective in the solid-liquid separation process. Heavy metals in the wastewater were treated with the peat in the batch type and peat moss was separated from the wastewater by dispersed air flotation. In the study different surfactants were used to compare flotation performance. Peat moss adhered to the bubbles floated in the reactor. The biosorptive flotation decreased the costs of separation such as filtration, sedimentation and centrifugation.

Ghaly and Pyke (2001) studied the in-vessel bioremediation of hydrocarbon-contaminated peat. The results indicated that peat is an excellent adsorbent of oil from wastewater. Oil-adsorbed peat was then successfully treated using three microbial populations (psychrophilic, mesophilic and thermophilic). The bioremediation process achieved a 60% reduction in the oil content. These results showed an alternative and safe disposal of the treated peat and a lower cost compared to biopiling and land farming.

The present study is primarily aimed to optimize conditions for the sorption of cadmium and nickel from solution in batch or continuous system.

The objectives of the study are:

1) To investigate the physical and chemical properties of peat and modified peat.
2) Optimize conditions for the batch sorption of cadmium and nickel onto unmodified peat (UMP), debituminized peat (DBP) and sulfuric acid treated peat (STP) as a factor of concentration, temperature and time.
3) To study the equilibrium data using Langmuir and Freundlich isotherms.
4) Optimize the conditions for the sorption of cadmium and nickel onto sulfuric acid treated peat in a continuous system as a factor of concentration and time.
5) To identify the mode (unidentate, bidentate or bridging) by which peat complexes with cadmium and nickel.

2.0 Materials and methods

2.1 Chemicals and equipment

All chemicals used were analytical grade. Glassware was cleaned in the following sequence: detergent (Alconox laboratory detergent), tap water, 1:1 hydrochloric acid, followed by three washings with deionized water. Concentrations of the metal ions were measured using a Varian Spectr AA-50/55 flame atomic absorption spectrophotometer. Infrared spectra of peat were measured in KBr discs using a Mattson Polaris spectrometer. Peristaltic pumps (Masterflex pump controller, Cole Parmer Instrument Co.) were used for the column experiments. Reciprocal shakers (Model G76D New Brunswick Scientific Co. Inc., Edison, New Jersey, U.S.A.) were used for the batch experiments. A laboratory oven (Blue M Electric Company, Illinois, U.S.A) was used for drying the peat samples. A Waring commercial blender was used to ground the peat which was then sieved through an ASTME –11 no.100 (American Society for Testing Materials) mesh.

2.2 Metal solutions

Cadmium and nickel stock solutions (10 mM) were prepared by dissolving their corresponding chloride salts ($CdCl_2 .2.5H_2O$ and $NiCl_2 .6H_2O$) in deionized water. All working solutions were prepared by diluting the stock solution with deionized water. Nitric acid and sodium hydroxide solutions were used to adjust the pH of the metal solutions and buffered using pH 5.00 buffer solution. Metal concentrations were measured using flame atomic absorption spectrophotometry.

2.3 Chemical and physical properties

2.3.1 Ash content

The determination of ash content in peat, debituminized peat and sulfuric acid treated peat was performed as described by McKay and Brady (1996a). One gram of sample was taken in a pre-weighed porcelain crucible. The crucible was then placed in a muffle furnace and heated at 550^0C for 24 hrs. The sample was removed from the furnace and allowed to cool in a desiccator before the crucible and contents were weighed.

The ash content is expressed as:

$$\%\text{Ash} = \frac{(\text{wt. of ash})}{\text{wt. of the adsorbent}} \times 100$$

2.3.2 Moisture content

The moisture content of peat and modified peat was determined according to the Anonymous (1995) method.

Calculation of moisture content is as follows:

$$\text{Moisture content,\%} = \left[(A - B)(100)\right] / B$$

Where

A= weight of peat, g

B = weight of oven–dried peat, g.

2.3.3 Exchangeable cations

The method described here was developed by Lavkulich and reported by Martin (1993). Forty mL of 1M ammonium acetate was added to a 125 mL Erlenmeyer flask containing 2 g of sample. The flask was shaken for 5 minutes on a reciprocal shaker (115 rpm) and allowed to stand overnight. The sample was again mixed for 15 minutes on the shaker and then filtered through Whatman filter paper (no. 42). Then the sample was washed with 1M ammonium acetate (four 30 mL portions, the washes combined with the filtrate) and diluted to 250 mL. Concentrations of exchangeable cations (calcium, sodium, magnesium and potassium) were determined using flame atomic absorption spectrophotometry. Concentrations of exchangeable cations for debitumized peat and sulfuric acid treated peat were determined using the same procedure.

Exchangeable cations were calculated as follows:

$$M^{+}\text{cmol}(+)\text{kg}^{-1} = C\text{cmol}(+)\,\text{L}^{-1} \times (0.25\text{L} / \text{wt.peat g}) \times 1000\text{g}\,\text{kg}^{-1}$$

Where:

M^{+}: Concentration of adsorbed cations cmol (+) kg $^{-1}$

C: Concentration of cation in the ammonium acetate extract (cmol (+) L $^{-1}$).

2.3.4 Organic matter

The organic matter content in peat and modified peat was determined by the Anonymous (1995) method. The amount of organic matter was calculated by difference as follows:

Organic matter % = 100 – a

Where:

a = ash content, %

2.4 Peat and modified peat

2.4.1 Peat

Sphagnum peat extracted from the bogs from the Province of Newfoundland and Labrador Canada, was used in this study. Its humification value on the von Post Scale corresponds to H2. The humification scale was first developed by Lennart von Post in 1926. The von Post scale ranges from 1 to 10 showing different stages in the formation of the peat. The calculation is based on the r-value introduced by von Keppler and reported by Pollett (1968).

Calculation of r-value was as follows:

$$r = \frac{(I - II) \times 100}{\frac{E.(I - W + a)}{100}}$$

Where

I = weight of the residue after drying

II = weight of the residue after burning

E = weight of the air-dried sample

W = moisture content of the air-dried sample

a = ash content of air-dried sample

2.4.2 Debituminized peat

Air-dried peat was extracted in a Soxhlet extractor for 7 hrs with toluene: ethanol (1:1) (Martin *et al.,* 1990). The debituminized peat was air-dried, ground in a blender and sieved through an ASTME-11 No. 100 mesh.

2.4.3 Sulfuric acid-treated peat

Air-dried peat was treated with concentrated sulfuric acid (H_2SO_4) in the ratio of 4.0 mL to 1.2 g of dried peat as reported by MacCarthy and Ansted (1984). The mixture was slowly heated to 150^0C in a fume hood for 2 hrs. The modified peat was then washed repeatedly with deionized water until the pH of the wash water was 4. The sample was then dried in an oven at 110^0C for 24 hrs, ground in a blender and sieved through an ASTME –11 NO. 100) mesh.

2.5 Batch sorption experiments

2.5.1 Batch sorption studies at various concentrations

The effect of concentration on the sorption of cadmium and nickel on peat and modified peat was studied at various concentrations ranging from 0.1 to 3 mM. The flow diagram of batch sorption experiments is shown in Figure 2.5.1. One gram of peat was mixed with 100 mL of solution for 24 hrs on a reciprocal shaker at 160 rpm. Peat was then separated by filtration and concentrations of metal ions were measured in the filtrate by atomic adsorption spectrophotometry.

2.5.2 Batch sorption studies at various temperatures

The sorption of cadmium and nickel from solution by peat and modified peat at various temperatures was studied by conducting batch experiments at 14^0C, 26^0C and 40^0C. One gram of peat was mixed with 100 mL of solution and treated as in section 2.5.1. The sorption of cadmium and nickel were determined as in earlier experiments (section 2.5.1).

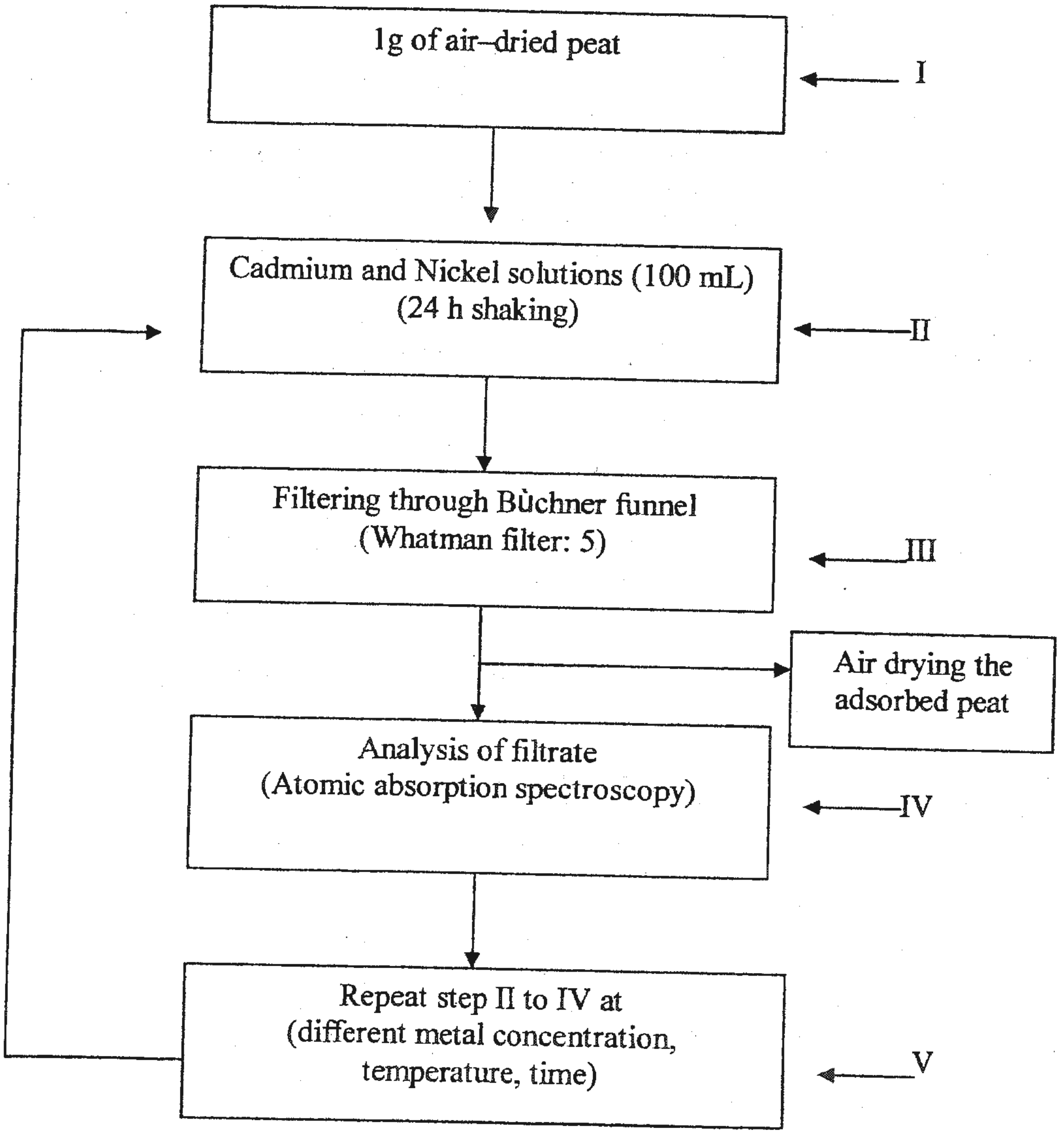


Fig 2.5.1: Flow diagram of batch sorption experiments

2.5.3 Batch sorption studies at various times

The effect of time on sorption of cadmium and nickel using sulfuric acid-treated peat was carried out at 26^0C. One gram of sulfuric acid-treated peat was mixed with 100 mL of 0.1 mM of metal solutions. The concentrations of cadmium and nickel in the metal solutions were determined as in earlier experiments (section 2.5.1). The samples were filtered every two-hours during the eight-hour study period to determine the equilibrium time necessary for the sorption of cadmium and nickel onto peat.

2.6 Column experiments

2.6.1 Continuous sorption at low concentration

An ion exchange column of 20 mm internal diameter and 380 mm length was made of pyrex glass with a narrow inlet and outlet as shown in the Figure 2.6.1. The column was filled with 25.0g sulfuric acid treated peat. The sulfuric acid treated peat had a moisture content of 10.8%, which was calculated by the method previously described (2.3.2). Glass wool was inserted at the base of the column as a supporting medium to retain the peat. Eight liters of a solution with a total metal ion concentration of 0.1mM was pumped through the column at a flow rate of 8.0 mL/min using peristaltic pumps. All connections were made with Tygon tubing. The column setup is shown in Figure 2.6.1. Samples were collected at regular intervals during the 16.5 hours period of study. The concentrations of cadmium and nickel in the eluates were determined by flame atomic absorption spectrophotometry. All the experiments were done in triplicate.

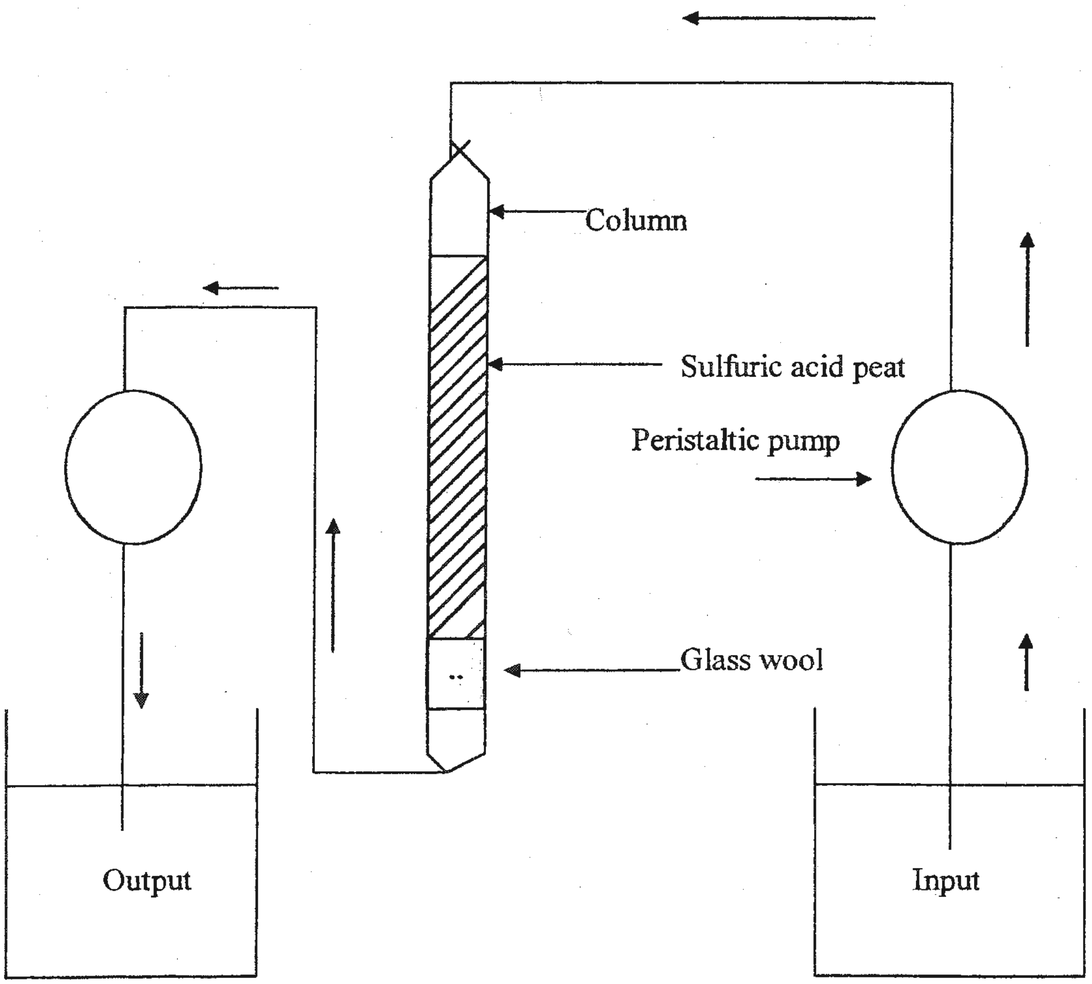


Fig 2.6.1: Flow diagram of the column set up

2.6.2 Continuous sorption at high concentration

All experiments were performed with the same column as described above (section 2.6.1). The column was filled with 12.5 g of sulfuric acid treated peat. In these experiments 4 L of metal solution with a total concentration of 3 mM was passed through the column at a flow rate of 8.8 mL/min. Samples were collected at regular intervals during the 7.5 hours period of study. The concentrations of cadmium or nickel in the eluates were determined by flame atomic absorption spectrophotometry.

2.6.3 Column regeneration

The column containing the bound metal ions were eluted using two successive 100 mL portion of 3M hydrochloric acid. All Tygon tubing was washed thoroughly by passing 3 L of deionized water using a peristaltic pump. The concentrations of cadmium or nickel in the eluates were determined by flame atomic absorption spectrophotometry. The regenerated column was then thoroughly washed with deionized water.

2.7 Peat characterization

The complexation of the carboxylic group in peat with metals was studied using infrared spectroscopy. Approximately 160 mg of potassium bromide and 0.2 mg of peat were mixed in a mortar and pestle. The mixture was then made into a disc using a KBr disc press under a pressure of 7.5 metric tons. Infrared spectra were recorded between 400 and 2000 cm^{-1}.

3.0 Results and discussion

3.1 Physical and chemical properties

Physical and chemical properties of peat vary from treatment to treatment. In the present study analyses of unmodified peat (UMP), debituminized peat (DBP) and sulfuric acid-treated peat (STP) were conducted for ash content, moisture content, organic matter content and exchangeable cations. Table 3.1.1 shows the physical and chemical properties of UMP, DBP and STP.

3.2 Batch experiments

3.2.1 Effect of temperature on removal efficiency

The experimental sorption measurements were analyzed using Langmuir and Freundlich isotherms.

The Langmuir sorption isotherm (Langmuir, 1918) is a commonly used isotherm for the sorption of solutes from liquids.

$$C/q = 1/ba + c/a$$

Where

q: Sorption capacity at equilibrium,

C: Concentration of the solute in the solution (mg/L)

a and b: constants related to maximum capacity and binding energy

The Langmuir isotherm is constructed by plotting C/q vs. C. The constants a and b can be obtained from the intercept and slope respectively.

Table: 3.1.1: Physical and chemical properties of Unmodifed and modified peat

Name	UMP	DBP	STP
Ash (%)	1.31±0.10	1.38±0.04	1.84±0.03
Moisture (%)	9.60±0.21	9.88±0.24	10.80±0.28
Organic Matter (%)	91.49±0.10	91.22±0.04	89.26±0.03
EC (mequiv/kg)	1120.56±0.73	1178.00±1.05	129.86±0.41

UMP: Unmodified peat
DBP : Debitumized peat
STP : Sulfuric acid-treated peat
EC : Exchangeable cations

The Freundlich isotherm (Benefield *et al.*, 1982) is expressed as

$$\log q = \log K + b \log C$$

Where

q: Sorption capacity at equilibrium,

C: Concentration of solute in the solution (mg/L),

K and b: constants related to sorption capacity and heterogeneity factor, respectively.

The Freundlich model is constructed by plotting log q vs. log C. The constant K can be obtained from the intercept. These two isotherm models are used to calculate the maximum sorption, binding energy, sorption capacity and intensity of the sorption which can then be used in mathematical modeling.

Figures 3.2.2, 3.2.3, 3.2.4, 3.2.5, 3.2.6, 3.2.7, 3.2.8, 3.2.9, 3.2.10, 3.2.11, 3.2.12, and 3.2.13 illustrate the Langmuir and Freundlich isotherms for cadmium and nickel on UMP, DBP and STP. The isotherms for the sorption have been divided into five types (Brunauer *et al.*, 1940) as shown in Figure 3.2.1. The adsorbents with a definite saturation limit are normally of type A. The saturation limit exists because the pores are so narrow and the adsorbent cannot accommodate more than a single layer on their walls (Gregg and Sing, 1967). Type B and type C isotherms represent adsorbents with a wide range of pore size. Isotherms of type D and E depend on the diameter of the pore and intermolecular attraction. The shape of the isotherms in the present study represents type B isotherm which suggests that peat and modified peat have a wide range of pore sizes.

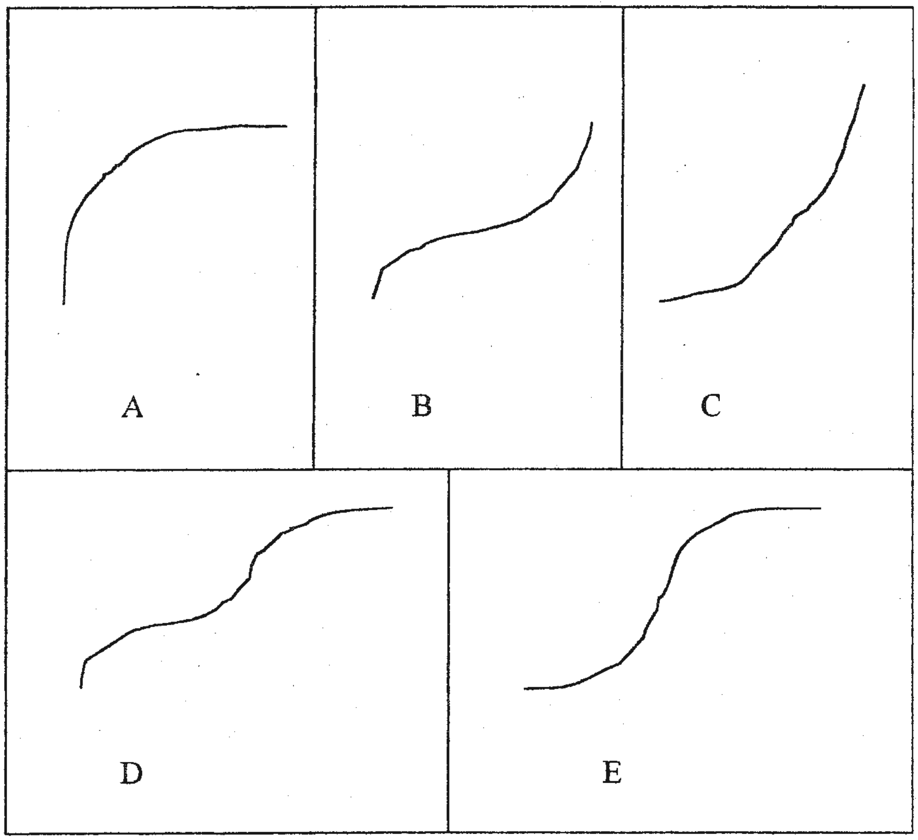


Fig. 3.2.1: Classification of isotherms

(after Brunauer *et al.*, 1940)

A, B, C, D and E: Different types of sorption isotherms.

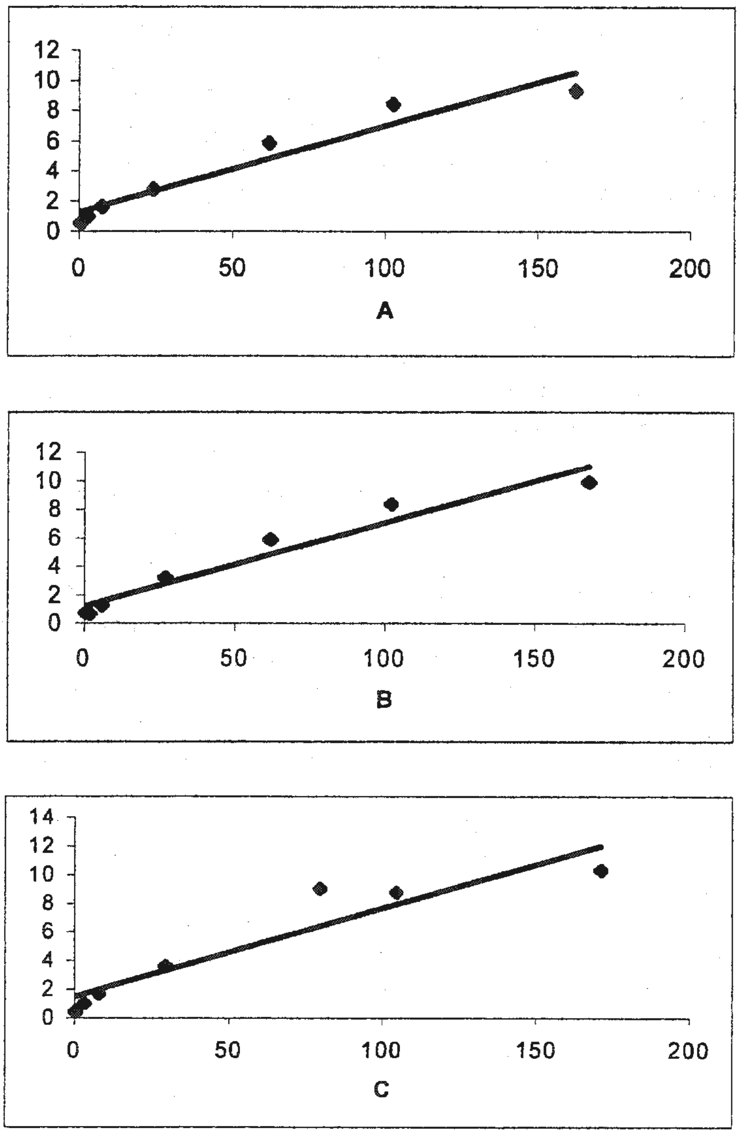


Fig 3.2.2: Langmuir isotherms for cadmium on unmodified peat at different temperatures

A, B, C: Langmuir isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of cadmium solution, Y axis: cadmium sorbed (mg/L) / g peat.

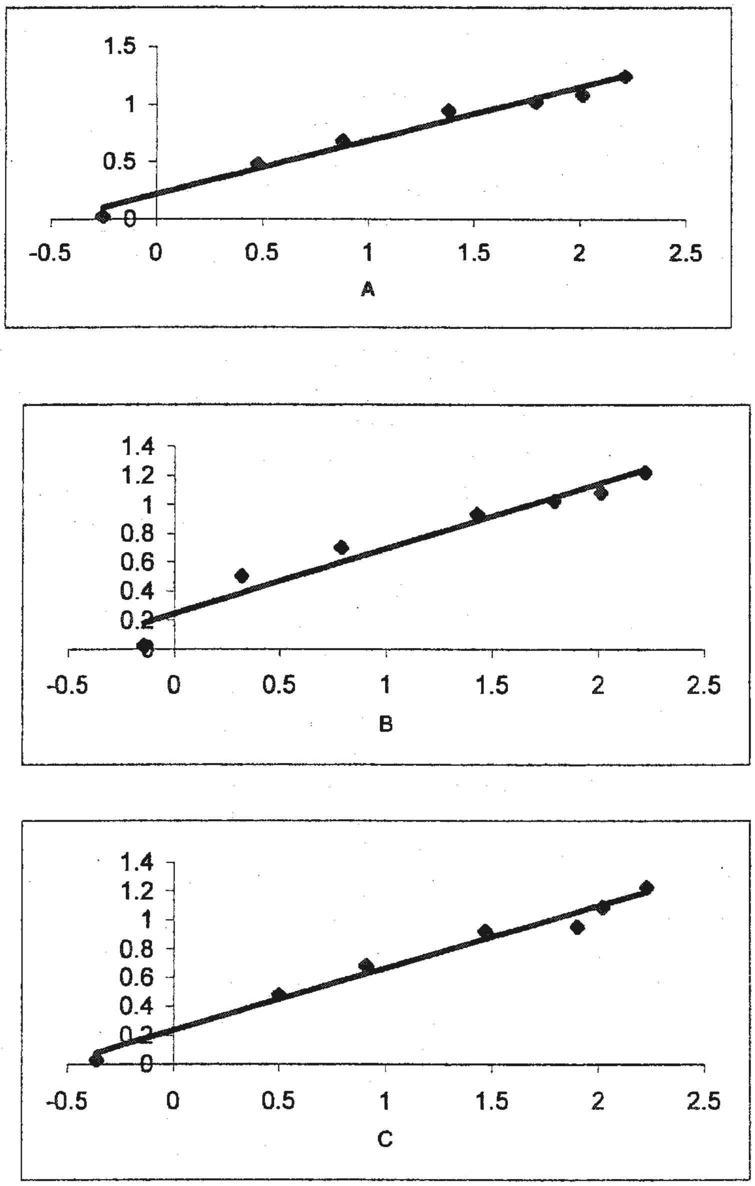
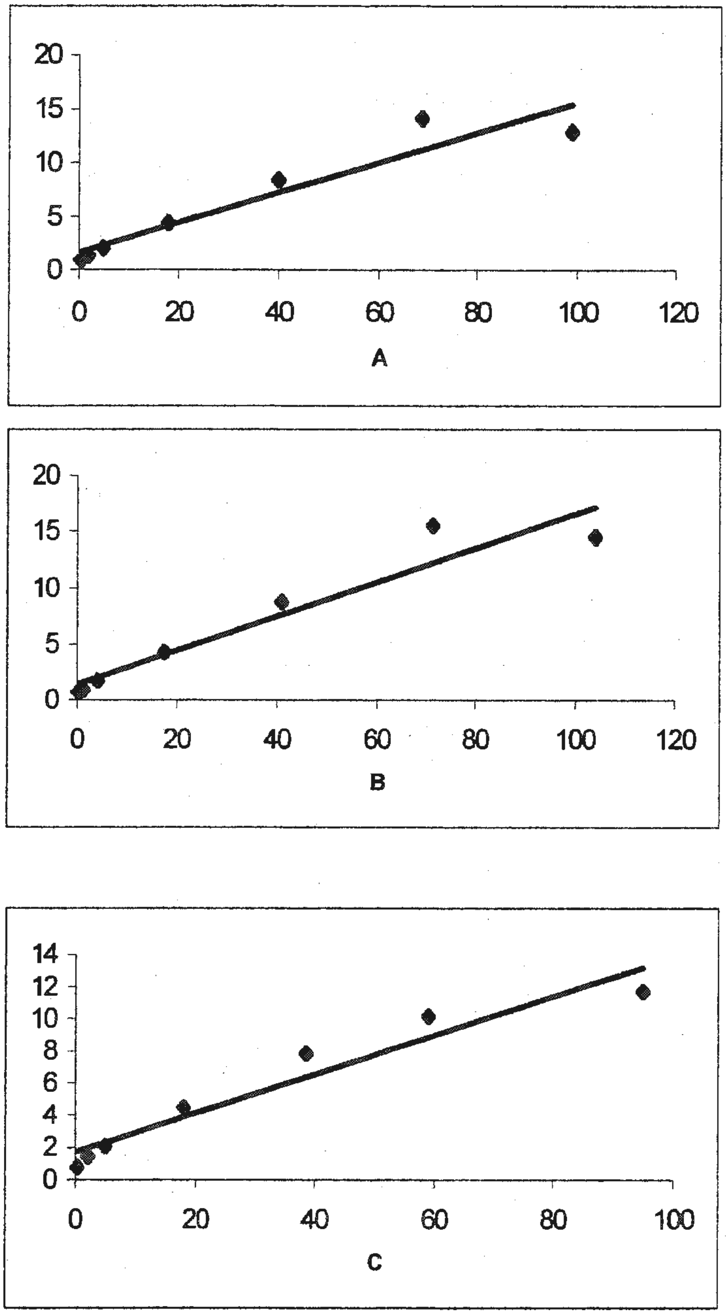


Fig 3.2.3: Freundlich isotherms for cadmium on unmodified peat at different temperatures

A, B, and C: Freundlich isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of cadmium solution, Y axis: cadmium sorbed (mg/L) / g peat.



<u>Fig 3.2.4: Langmuir isotherms for nickel on unmodified peat at different temperatures</u>

A, B, C: Langmuir isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of nickel solution, Y axis: nickel sorbed (mg/L) / g peat.

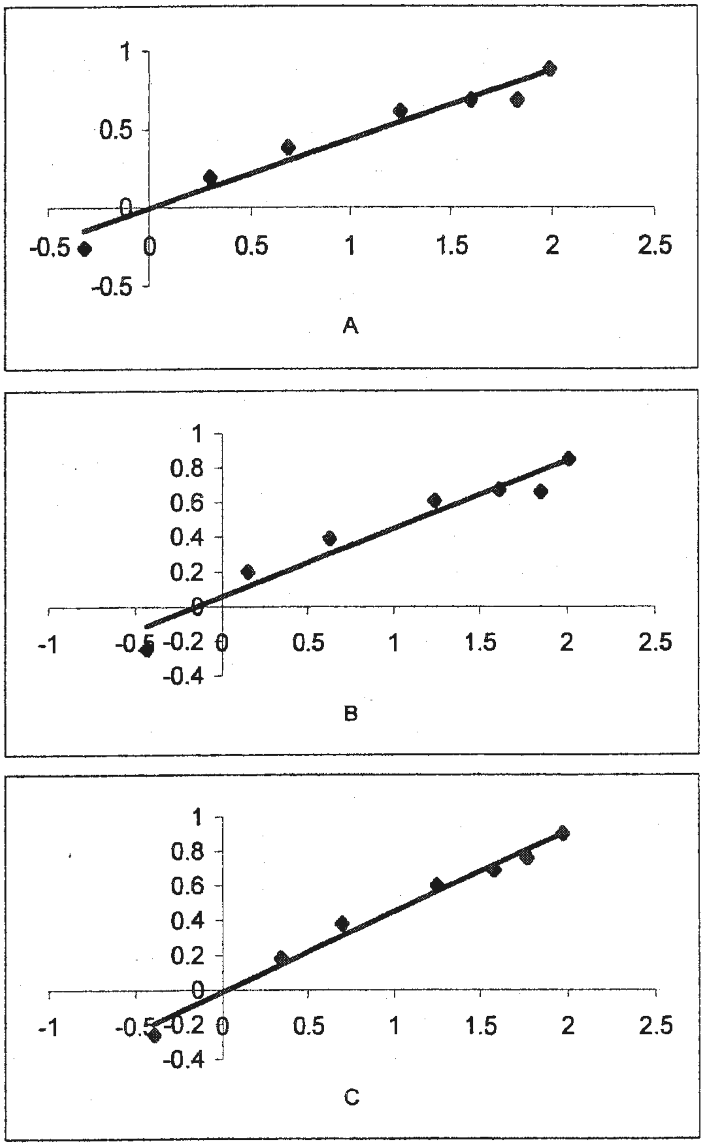


Fig 3.2.5: Freundlich isotherms for nickel on unmodified peat at different temperatures

A, B, C: Freundlich isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of nickel solution, Y axis: nickel sorbed (mg/L) / g peat.

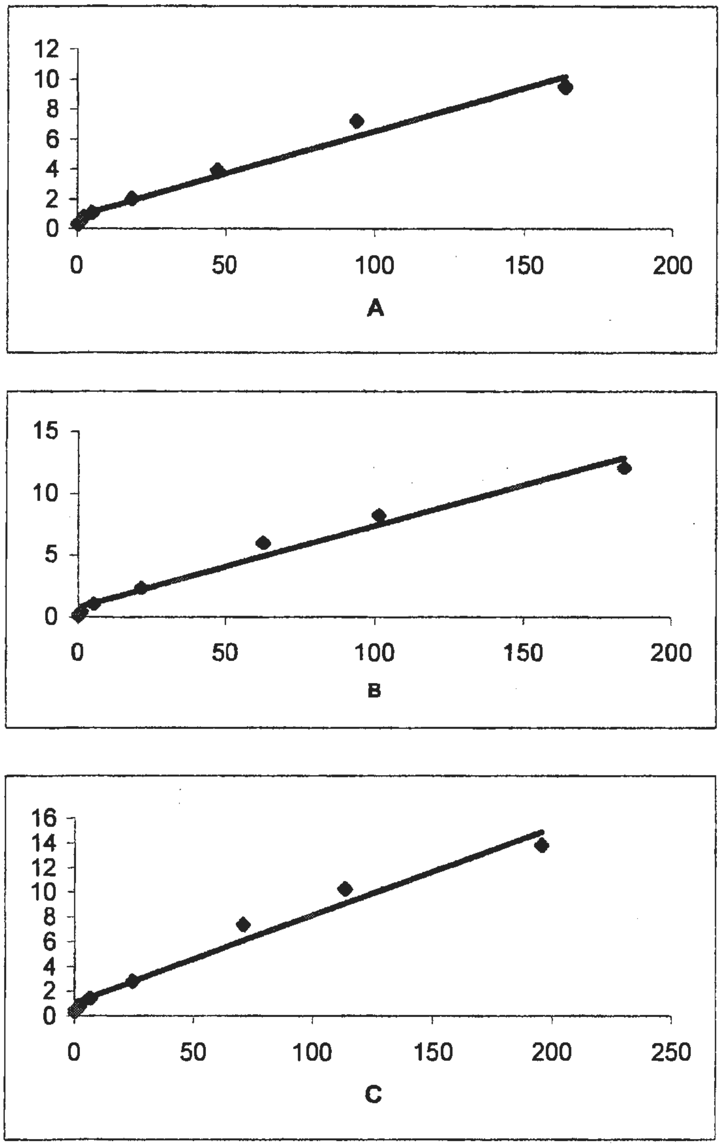


Fig 3.2.6: Langmuir isotherms for cadmium on debituminized peat at different temperatures

A, B, C: Langmuir isotherms at 14^0C, 26^0C and 40^0C, respectively.
X axis: Concentration of cadmium solution, Y axis: cadmium sorbed (mg/L) /g peat.

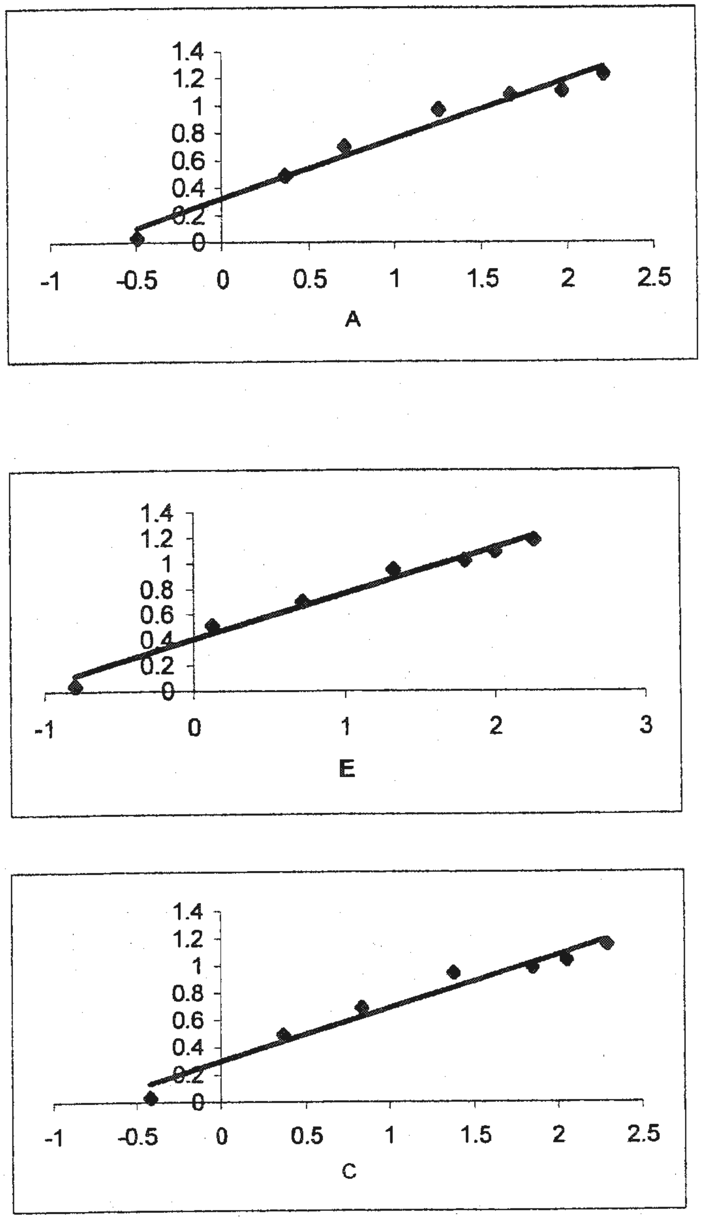


Fig 3.2.7: Freundlich isotherms for cadmium on debituminized peat at different temperatures

A, B and C: Freundlich isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of cadmium solution, Y axis: cadmium sorbed (mg/L) / g peat.

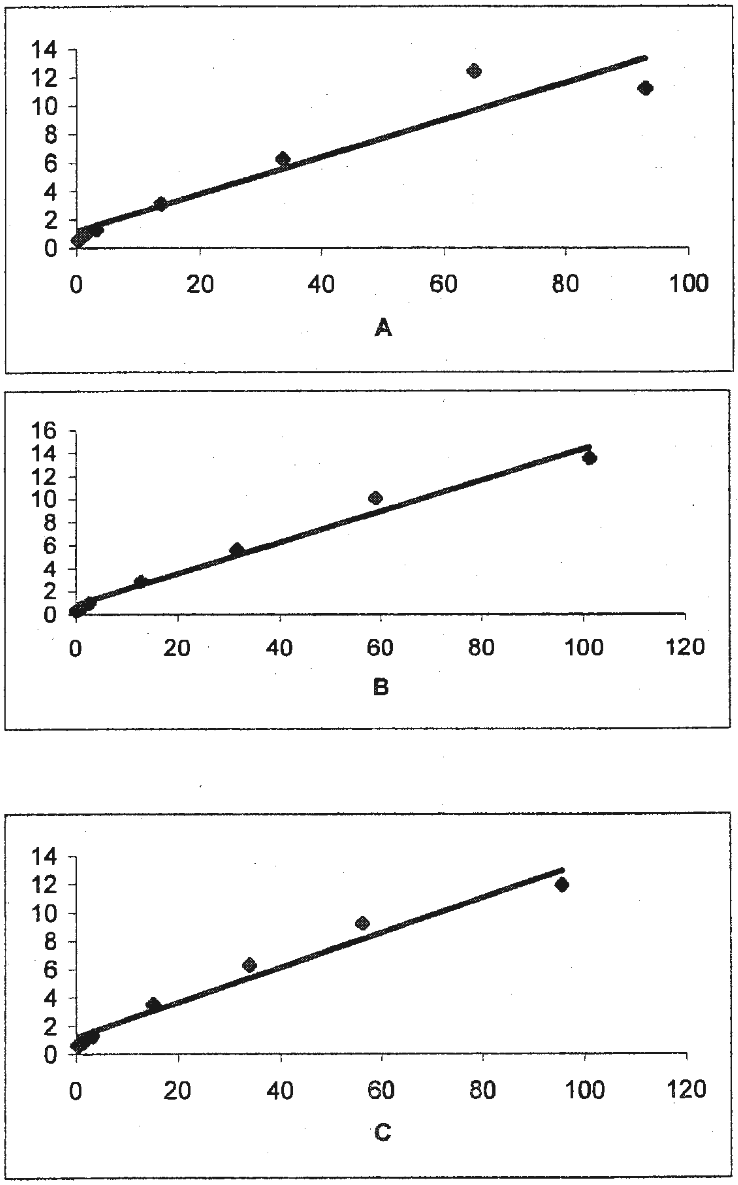


Fig 3.2.8: Langmuir isotherms for nickel on debituminized peat at different temperatures

A, B, C: Langmuir isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of nickel solution, Y axis: nickel sorbed (mg/L) / g peat.

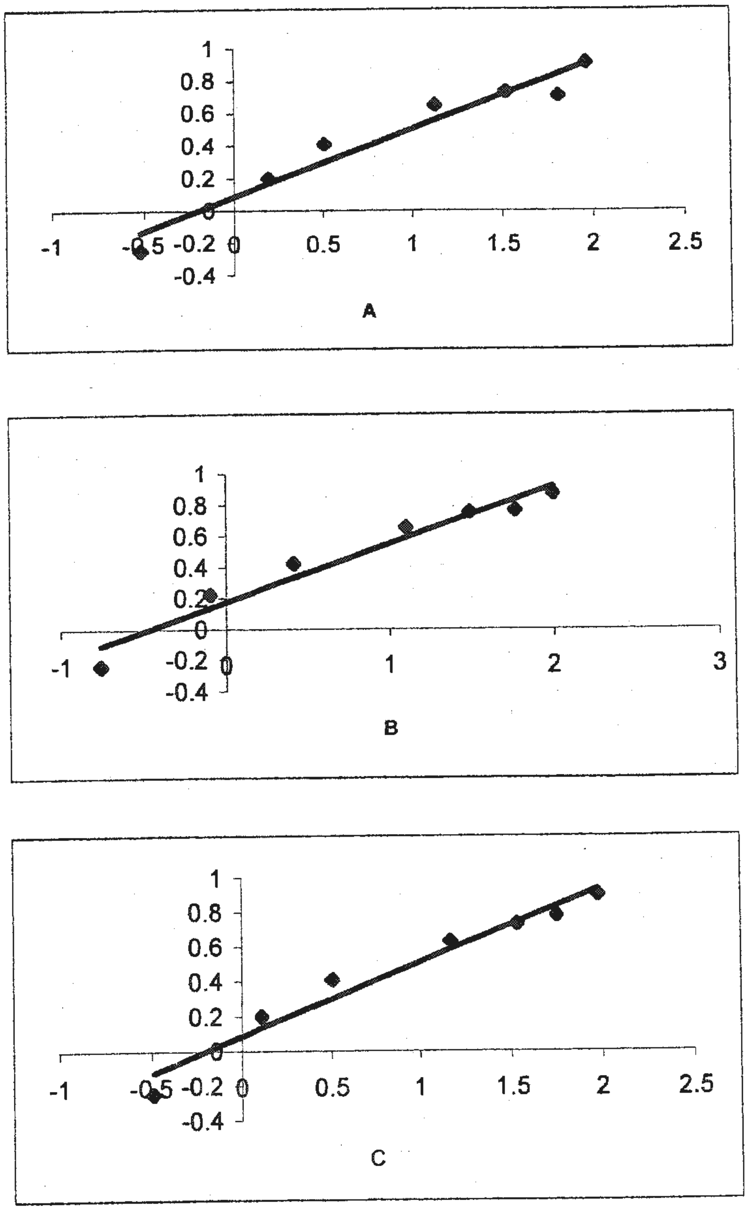
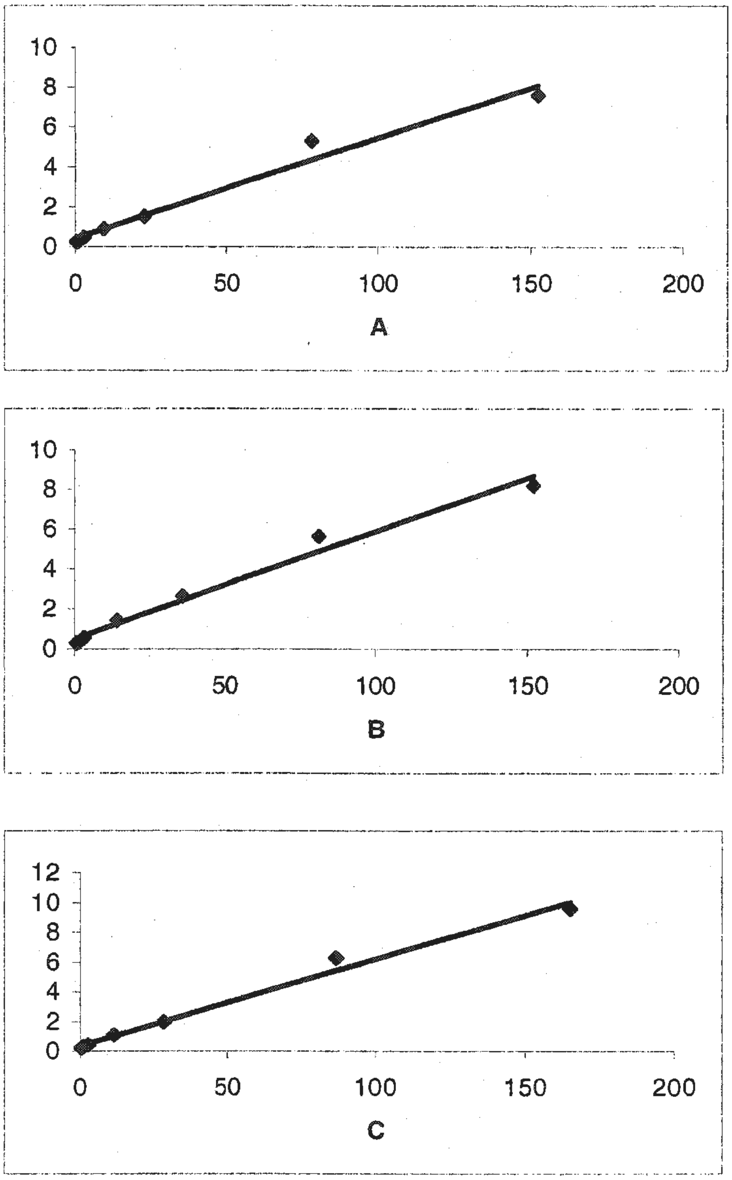


Fig 3.2.9: Freundlich isotherms for nickel on debituminized peat at different temperatures

A, B and C: Freundlich isotherm at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of nickel solution, Y axis: nickel sorbed (mg/L) / g peat.



<u>Fig 3.2.10: Langmuir isotherms for cadmium on sulfuric acid-treated peat at different temperatures</u>

A, B, C: Langmuir isotherms at 14^0C, 26^0C and 40^0C, respectively.
X axis: Concentration of cadmium solution, Y axis: cadmium sorbed (mg/L) / g peat.

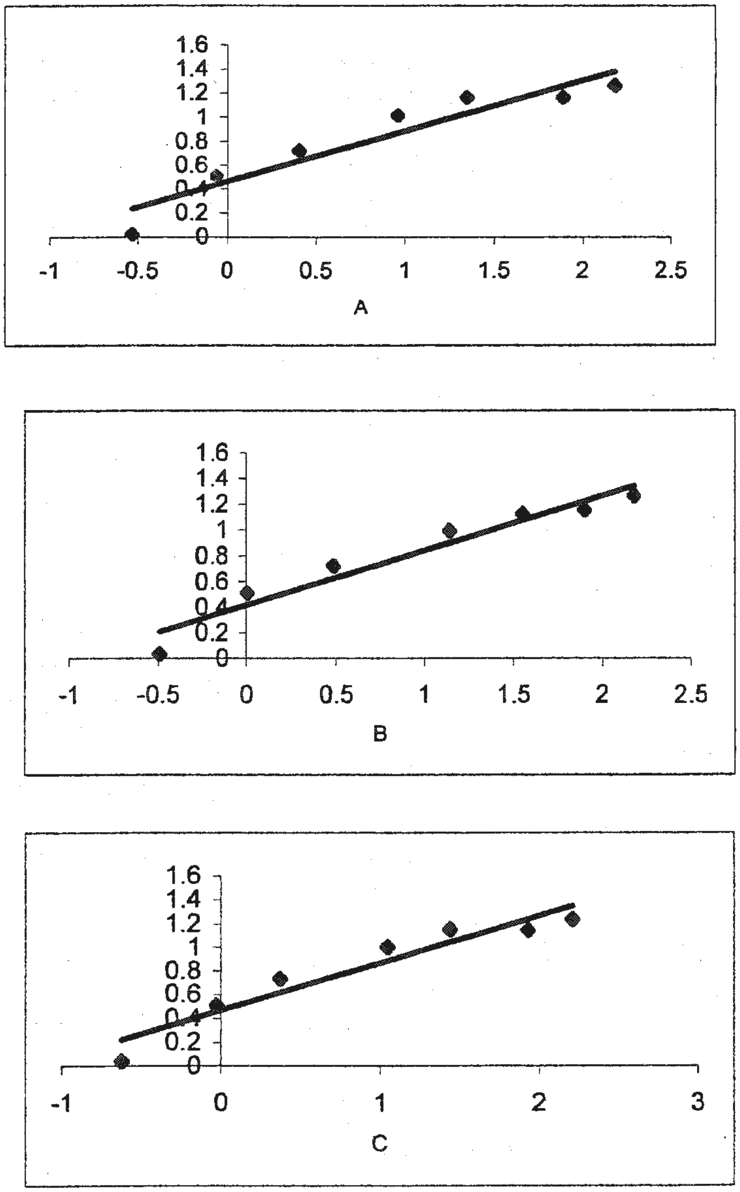


Fig 3.2.11: Freundlich isotherms for cadmium on sulfuric acid-treated peat at different temperatures

A, B, C: Freundlich isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of cadmium solution, Y axis: cadmium sorbed (mg/L) / g peat.

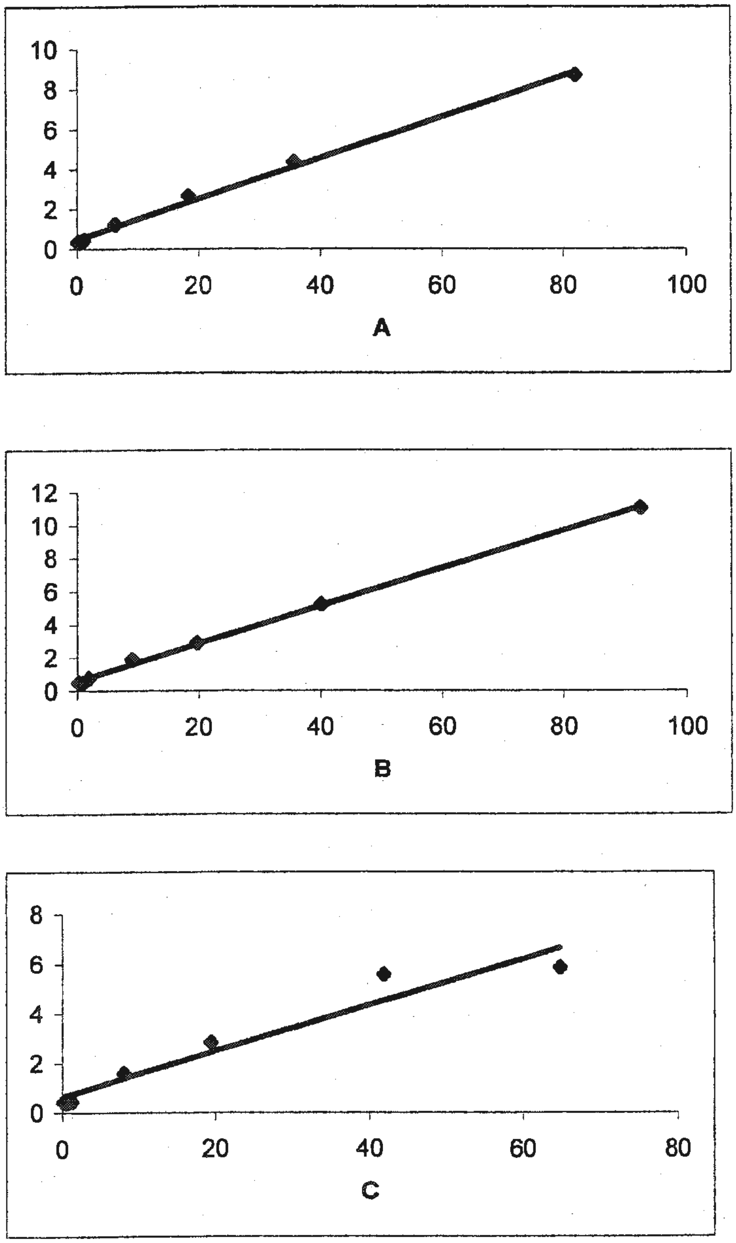


Fig 3.2.12:Langmuir isotherms for nickel on sulfuric acid-treated peat at different temperatures

A, B, C: Langmuir isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of nickel solution, Y axis: nickel sorbed (mg/L) / g peat.

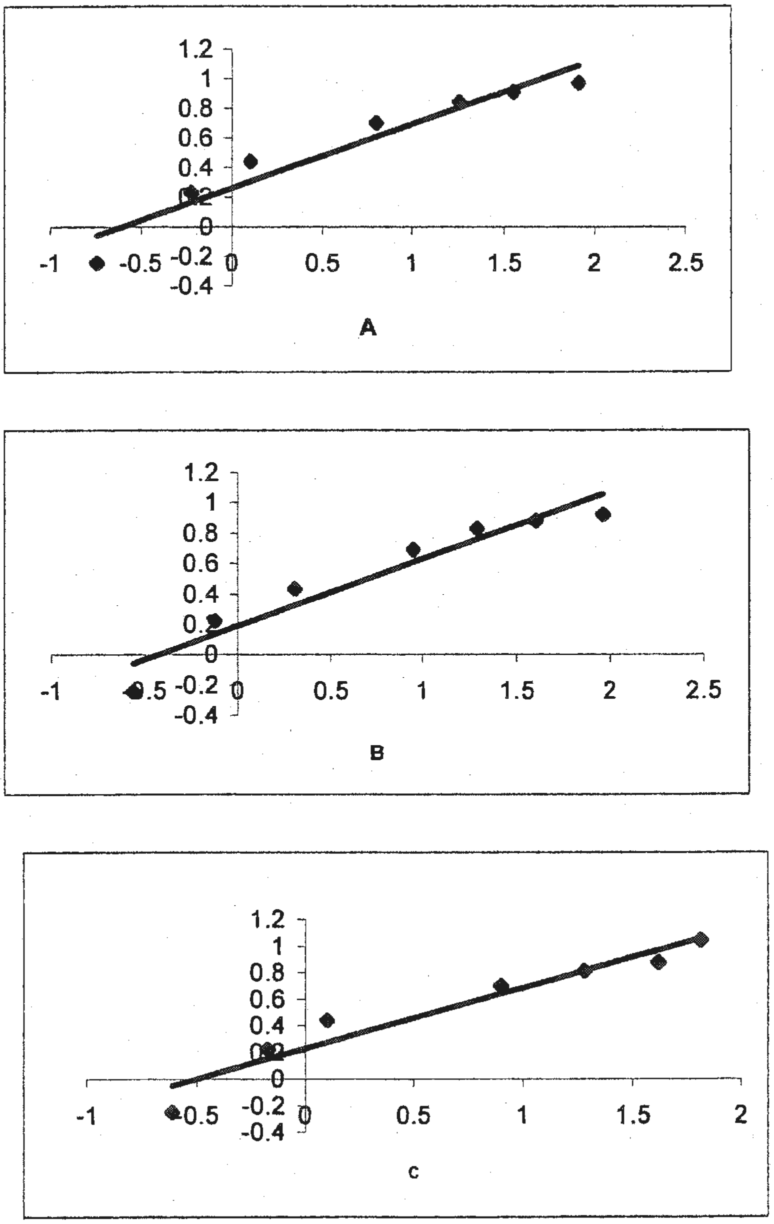


Fig 3.2.13: Freundlich isotherms for nickel on sulfuric acid-treated peat at different temperatures

A, B, C: Freundlich isotherms at 14^{0}C, 26^{0}C and 40^{0}C, respectively.
X axis: Concentration of nickel solution, Y axis: nickel sorbed (mg/L) / g peat.

According to the Langmuir isotherm metals are sorbed to the adsorbent in the single layer thickness and a linear isotherm is observed when the number of complexing sites remain constant throughout the range of metal concentration (Allen *et al.*, 1989). But the metals are forced into the pores of the adsorbate during the sorption process creating additional surfaces for the sorption which causes deviation from linearity of the isotherms.

The effect of the temperature on the sorption was evaluated using Langmuir and Freundlich isotherms at 14^0C, 26^0C and 40^0C. The correlation coefficient or R^2 values for the experiments were above 0.90 for all the isotherm data indicating peat to be a good adsorbent of cadmium and nickel.

The sorption data obtained at different temperatures with UMP, DBP and STP are summarized in Tables 3.2.1, 3.2.2, 3.2.3, 3.2.4, 3.2.5 and 3.2.6, respectively. The sorption capacity (Langmuir constant) of peat and modified peat for cadmium is higher at lower temperatures. The decrease in the sorption of cadmium with an increase in temperature indicates that the sorption process is exothermic. Earlier studies by Viraraghavan and Rao (1993) also indicated that cadmium sorption onto peat was exothermic. In another study, Leyva-Ramos *et al.* (1997) showed that activated carbon was efficient in adsorbing cadmium at 10^0C and the sorption capacity decreased with an increase in the temperature. Most sorption process are endothermic (Benefield *et al.*, 1982). The decrease in the sorption of cadmium with a increase in the temperature is due to the weakening of adsorptive forces between the sites of the peat and the cadmium ions (Viraraghavan and

Table 3.2.1: Comparison of Langmuir constants for cadmium and nickel sorption on unmodified peat at different temperatures

Conditions	Langmuir constants		
	a (mg /g)	b	R^2
Cadmium			
14° C ±1.0°C	17.48 ± 0.17	0.05	0.93
26° C ±0.5° C	17.00 ± 1.06	0.05	0.94
40° C ± 0.5°C	16.20 ± 0.09	0.04	0.90
Nickel			
14° C± 1.0°C	7.20 ± 0.03	0.08	0.90
26° C ± 0.5°C	6.61 ± 0.70	0.10	0.91
40° C ± 0.5° C	8.30 ± 0.06	0.07	0.93

a : Maximum sorption capacity (mg/g)
b : Binding energy
R^2: Correlation coefficient

Table 3.2.2: Comparison of Freundlich constants for cadmium and nickel sorption on unmodified peat at different temperatures

Conditions	Freundlich constants		
	K	n	R^2
Cadmium			
14°C ± 1.0°C	1.28± 0.02	0.42	0.97
26°C± 0.5° C	1.27 ± 0.08	0.44	0.94
40°C±0.5°C	1.25 ± 0.01	0.42	0.97
Nickel			
14°C ± 1.0°C	0.99 ± 0.00	0.43	0.95
26°C ± 0.5°C	1.05 ± 0.02	0.39	0.93
40°C± 0.5°C	0.99 ± 0.01	0.46	0.98

K : Sorption capacity
n : Heterogeneity factor
R^2: Correlation coefficient

Table 3.2.3: Comparison of Langmuir constants for cadmium and nickel sorption on debituminized peat at different temperatures

Conditions	Langmuir constants		
	a (mg /g)	b	R^2
Cadmium			
14°C ±1.0°C	17.54± 0.13	0.07	0.97
26°C ± 0.5°C	15.20 ± 0.72	0.08	0.97
40°C± 0.5°C	14.10 ± 0.99	0.06	0.97
Nickel			
14°C ±1.0°C	7.63± 0.33	0.11	0.91
26°C± 0.5°C	7.40± 0.45	0.16	0.97
40°C ± 0.5°C	8.10 ± 0.20	0.10	0.96

a : Maximum sorption capacity (mg/g)
b : Binding energy
R^2: Correlation coefficient

Table 3.2.4: Comparison of Freundlich constants for cadmium and nickel sorption on debituminized peat at different temperatures

Conditions	Freundlich constants		
	K	n	R^2
Cadmium			
14°C ±1.0°C	1.37 ± 0.08	0.43	0.97
26°C ± 0.5°C	1.49 ± 0.01	0.35	0.97
40°C ±0.5°C	1.33 ± 0.01	0.39	0.96
Nickel			
14°C ± 1.0°C	1.08 ± 0.02	0.42	0.94
26°C ± 0.5°C	1.18 ± 0.02	0.37	0.95
40°C ± 0.5°C	1.08 ± 0.01	0.42	0.96

K : Sorption capacity
n : Heterogeneity factor
R^2: Correlation coefficient

Table 3.2.5: Comparison of Langmuir constants for cadmium and nickel sorption on sulfuric acid-treated peat at different temperatures

Conditions	Langmuir constants		
	a (mg /g)	b	R^2
Cadmium			
14°C ±1.0°C	19.88 ± 0.20	0.11	0.97
26°C ± 0.5°C	18.69± 0.07	0.10	0.98
40°C ± 0.5°C	17.15± 0.06	0.15	0.98
Nickel			
14°C ± 1.0°C	9.73± 0.43	0.22	0.99
26°C± 0.5°C	8.74 ±0.02	0.20	0.99
40°C± 0.5°C	10.78 ± 0.19	0.15	0.93

a : Maximum sorption capacity (mg/g)
b : Binding energy
R^2: Correlation coefficient

Table 3.2.6: Comparison of Freundlich constants for cadmium and nickel sorption on sulfuric acid peat at different temperatures

Conditions	Freundlich constants		
	K	n	R^2
Cadmium			
14°C ±1.0°C	1.58 ± 0.21	0.45	0.90
26°C±0.5°C	1.51 ± 0.03	0.42	0.93
40°C± 0.5°C	1.58 ± 0.17	0.39	0.91
Nickel			
14°C ±1.0°C	1.29 ± 0.08	0.43	0.93
26°C ± 0.5°C	1.19 ± 0.08	0.44	0.92
40°C ± 0.5°C	1.24 ± 0.01	0.45	0.92

K : Sorption capacity
n : Heterogeneity factor
R^2: Correlation coefficient

Rao, 1993). The sorption of nickel onto peat and modified peat increased with the increase in the temperature indicating the sorption process is endothermic. The 't' test (Miller and Miller, 1983) for most of the isotherm data at a 95% confidence level showed a significant difference in the sorption of cadmium and nickel at extreme temperature (i.e. 14^0C and 40^0C), but no significant difference was observed at immediate temperature difference (i.e. 14^0C and 26^0C or 26^0C and 40^0C).

Various studies have used isotherms to examine the importance of temperature on metal ion sorption onto peat. Kapoor and Viraraghavan (1995) reported mercury sorption onto peat to be endothermic. The sorption capacity of peat for chromium is also reported to increase at higher temperatures (Forster and Sharma, 1993). All authors found temperature to be an important factor and indicated a slight increase or decrease in the sorption of metals with temperature. In the present study sorption of cadmium and nickel is explained well using the Langmuir equation. The Freundlich equation, although having higher correlation coefficients, showed no specific pattern of the sorption. The STP has higher sorption capacity (Langmuir constant) when compared to UMP and DBP. Table 3.2.5 shows the sorption capacity (Langmuir constants) of STP for cadmium and nickel. The "t" test (for Langmuir consants at 26^0C) showed that the sorption capacity of STP is significantly different then UMP at 95% confidence level.

The main constituent of peat is humic acids and the complexing ability of humic substances is mainly due to oxygen-containing functional groups such as carboxylic (COOH) and phenolic groups (Stevenson, 1982). The infrared spectrum of STP showed an increase in the carbonyl bands at 1730 cm^{-1} and 1620 cm^{-1} (Rubin, 1978). The increase in the sorption capacity of the STP in the present study is mainly due to the chemical changes occurring in the peat during the modification. The other main advantage of the STP modification is its stability and resistance to leaching (MacCarthy and Ansted, 1984). The method of modification has been a matter of considerable debate. Different studies have reached different conclusions. Smith *et al.* (1977), after an extensive study to optimize conditions for the sulfuric acid treatment of peat, concluded that treatment was cheap and enhanced the sorption capacities. Viraraghavan and Rao (1993) also showed acid-treated peat to have a higher sorption capacity for metals. On the other hand Zhu *et al.*, (1984) found that the efficiency of removing metals by acid washed peat was lower than raw peat without any treatment.

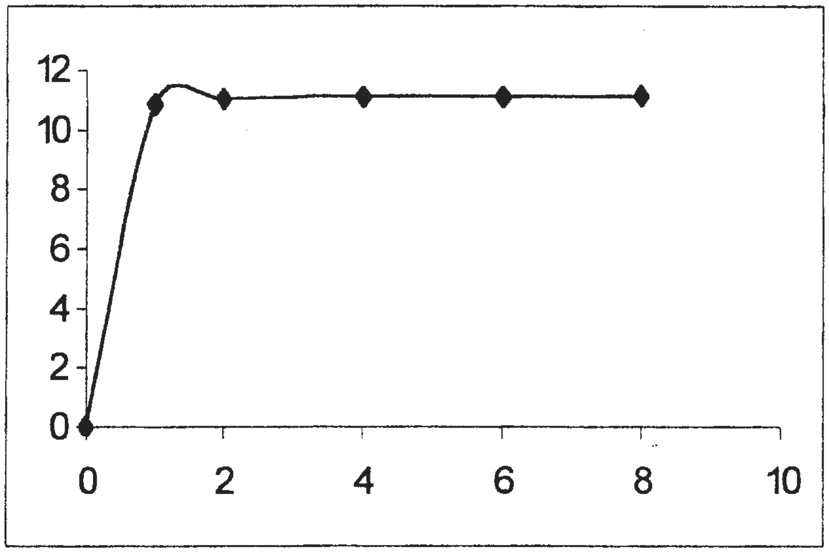
The sorption capacity of DBP was the same as for UMP for cadmium and nickel. The "t" tests (for Langmuir constant at 26^0C) showed that there was no significant different in the sorption capacity of DBP and UMP at 95% confidence interval. Debituminization is a process in which peat components are removed by organic solvent (Fuchsman, 1980a). Martin *et al.* (1990) reported sugar content to be the major composition of peat hydrolysate (bitumen). Fuchsman (1980a) concluded that bitumen mainly consists of monoacids and esters. The composition of the bitumen depends on the type of organic solvent used for the extraction. In an earlier study, Spigarelli and Patricia (1989) showed that debituminized peat to have the same sorption capacity as unmodified peat for Cu (II) and Cr (III). A conclusion can be drawn from the present study that the organic components present on the peat after debitumization have high ability to complex metals.

3.2.1 Batch kinetic studies

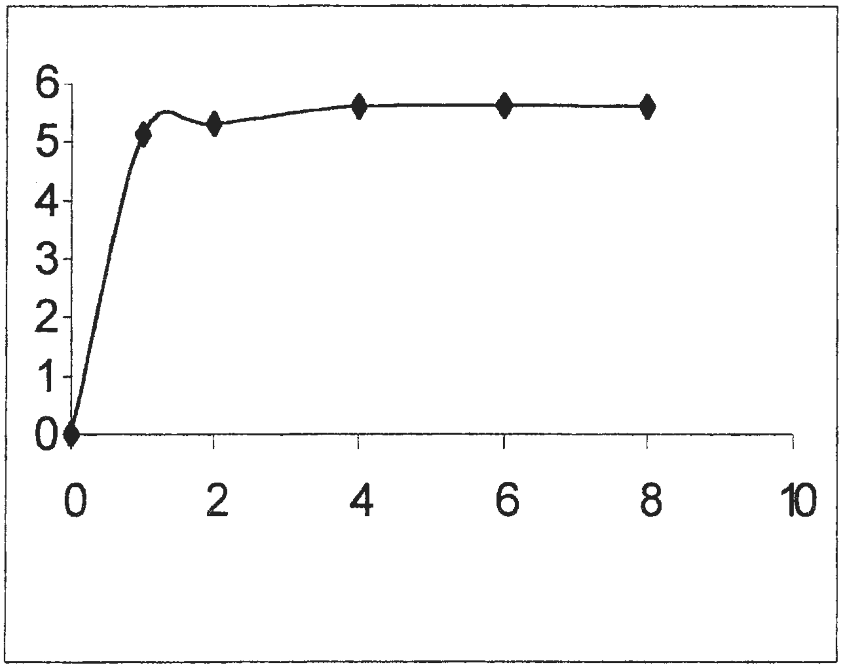
The effect of contact time on cadmium and nickel removal using STP can be seen in Figure 3.2.14. The result shows that removal of cadmium and nickel reached equilibrium within 60 minutes. The equilibrium time reported by Viraraghavan and Rao (1993) for cadmium was 120 minutes but an earlier study by Thevenot *et al.* (1986) reported a 60 minutes equilibrium time, the same as in the present study. The difference in the equilibrium time may be due to the use of municipal wastewater by Viraraghavan and Rao (1993) and the presence of organic or inorganic interferences increased the equilibrium time. These results confirm that an equilibrium time of 60 minutes is sufficient if the wastewater has a low concentration of metal ions. The equilibration time should be increased during the design of batch reactors when the wastewater is heterogeneous in nature.

3.2.2 Effect of concentration on removal efficiency

The effect of initial concentration of cadmium and nickel sorption on UMP can be seen from Table 3.2.7 and 3.2.8, respectively. The maximum sorption (%) was at lower concentration and decreased with the increase in the concentration of metal ions. The rapid or maximum sorption (%) at the lower concentration is due to ion exchange with surface cations on the peat and as the concentration is increased there is a decrease in the uptake of metal cations due to exchange which takes place in the inner surface of the peat (McKay and Ho, 1998). The same pattern was observed for STP and DBP i.e. the sorption of cadmium and nickel decreased with an increase in the concentration of metals in solution.



A



B

Fig 3.2.14: Removal of cadmium (A) and nickel (B) as a factor of time on sulfuric acid-treated peat

X axis: Time (h), Y axis: cadmium and nickel sorption (mg/g).

Table 3.2.7: Effect of concentration on cadmium sorption (%) on unmodified peat at different temperatures

Initial cadmium	Cd sorption (%)		
Conc. (ppm)	14°C	26°C	40°C
11.24	95.1±0.04	93.6±0.57	96.1±0.08
33.72	90.8±0.27	93.8±1.03	90.4±0.62
56.20	86.4±0.07	90.0±0.12	85.5±0.44
112.40	78.3±0.33	75.8±0.61	73.5±0.92
168.60	63.1±0.01	62.8±1.15	52.6±2.88
224.80	54.3±1.76	54.5±2.58	53.4±0.32
337.20	51.8±0.91	50.2±2.01	49.2±1.52

Table 3.2.8: Effect of concentration on nickel sorption (%) on unmodified peat at different temperatures

Initial nickel	Ni sorption (%)		
Conc. (ppm)	14°C	26° C	40°C
5.87	91.9±0.00	96.6±0.26	93.2±0.05
17.60	88.4±0.08	93.2± 0.42	87.5±0.07
29.34	83.1±0.19	87.4± 0.58	82.8±0.10
58.69	69.6±0.26	73.6±1.13	69.1±0.20
88.03	54.3±0.18	60.8± 1.59	56.1±0.19
117.38	41.5±0.10	54.2± 1.07	49.7±0.57
176.07	43.7±0.70	48.1± 0.90	46.0±0.54

3.3 Column studies

3.3.1 Continuous sorption as a factor of time and concentration

The column experiments to determine the effect of the concentration on the removal of cadmium and nickel were carried out at pH 5.0, a flow rate of 8.0 mL /min and total metal ion concentration values of 0.1mM and 3.0 mM. The results show a decrease in the removal of cadmium and nickel with an increase in the time and concentration of solution passed through the column.

Table 3.3.1 presents the sorption efficiencies (%) of the column using a total metal ion concentration 0.1mM. Saturation of the column was observed at 3.0 mM concentration as the metal solution was passed through the column. The results of the study (Table 3.3.2) showed a gradual decrease in the removal of cadmium and nickel metal ions after 3.5 and 4.5 h, respectively. Column saturation is due to greater competition for binding sites at higher concentrations compared to lower concentrations, which can be seen from Tables 3.3.1 and 3.3.2.

The operating capacity of the column is dependent on many factors (Harland, 1994) such as:

a) Bed-depth (height of the column)

b) Adsorbent characteristics (such as particle size, physical form, etc.)

c) Flow rates

d) Kinetics

e) Selectivity towards influent ions

Table 3.3.1 Removal (%) of cadmium and nickel at lower concentrations (0.1mM) as function of time

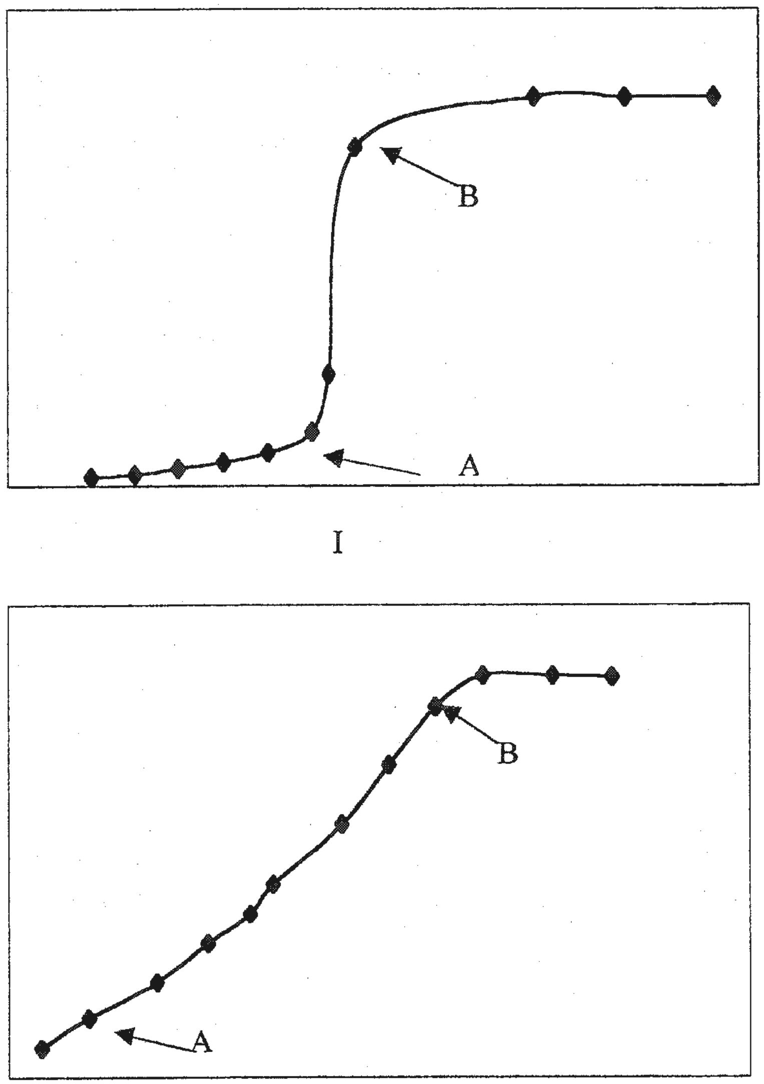
Time (h)	Cadmium Sorbed (%)	Nickel sorbed (%)
0.5	99.6±0.00	99.8±0.02
1.0	99.6±0.02	99.9±0.00
1.5	99.6±0.04	99.9±0.03
2.0	99.6±0.00	99.8±0.01
2.5	99.6±0.03	99.8±0.01
3.0	99.6±0.01	99.8±0.01
3.5	99.5±0.01	99.8±0.02
4.5	99.5±0.00	99.9±0.03
5.5	99.6±0.03	99.8±0.03
7.5	99.5±0.01	99.8±0.01
9.5	99.5±0.01	99.9±0.03
11.5	99.5±0.01	99.9±0.01
13.5	99.5±0.01	99.9±0.01
15.5	99.5±0.00	99.9±0.00
16.5	99.5±0.01	99.9±0.03

Table 3.3.2: Removal (%) of cadmium and nickel at higher concentrations (3.0 mM) as function of time

Time (h)	Cadmium Sorbed (%)	Nickel sorbed (%)
0.5	99.6±0.21	99.5±0.31
1.0	99.5±0.07	99.7±0.05
1.5	99.5±0.14	99.6±0.08
2.0	99.8±0.03	99.6±0.02
2.5	99.5±0.26	99.4±0.37
3.0	98.0±0.56	99.5±0.42
3.5	74.2±2.82	90.2±1.48
4.5	26.8±1.06	59.2±0.90
5.5	15.8±2.22	18.7±2.54
6.5	18.1±2.89	14.9±0.84
7.5	12.5±2.33	12.9±2.96

In earlier study, MacCarthy and Ansted (1984) concluded that sorption of metals decreased with a decrease in pH and an increase in flow rates. Girgis and Khalil (1998) investigated the removal capacity of activated carbon with different pore sizes to adsorb two dyestuffs, *i.e.* Direct red 99 and Reactive orange 11. The authors concluded that column capacity was greatly influenced by the adsorbent characteristics. The activated carbon with wider pores was more efficient in sorption of dyes. The present study to optimize the conditions for maximum sorption of cadmium and nickel reveals that concentration and time are important factors which affect the sorption process in the continuous flow system. The contact time between the metal solution and the fixed bed again greatly depends on the other factors such as diameter of the column, height of the column and flow rate of the solution through the column.

The breakthrough curves obtained for the two metals, cadmium and nickel, are shown in Figures 3.3.2 and 3.3.3. As discussed in section 1.3.4.3 breakthrough curves were obtained by plotting the concentration of the effluent vs. time. When the concentration of the effluent starts to increase on the breakthrough curve (point A, Figure 3.3.1), it is referred to as breaking point of the column. The point on the breakthrough curve (point B, Figure 3.3.1) where the concentration of the effluent reaches 95% of the influent concentration is termed the point of column exhaustion. Figure 3.3.1 shows the typical breakthrough curves (steep (I) and deep (II) curves).



I

II

Fig 3.3.1: Types of breakthrough curves (after Benefield *et al.* (1982))

I: Steep curve; II: Deep curve
A: Break point
B: Point of column exhaustion (effluent concentration is equal to 95% influent concentration
X axis: Time; Y axis: Effluent concentration

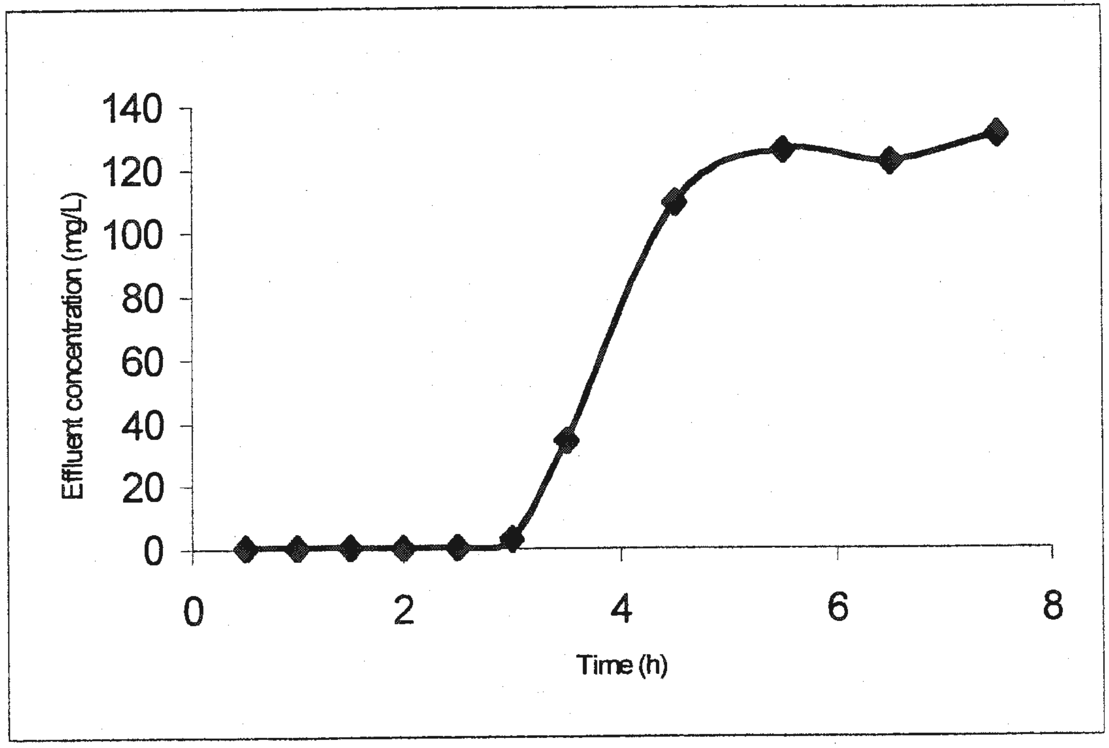


Fig 3.3.2: Breakthrough curve for cadmium ions on sulfuric acid-treated peat

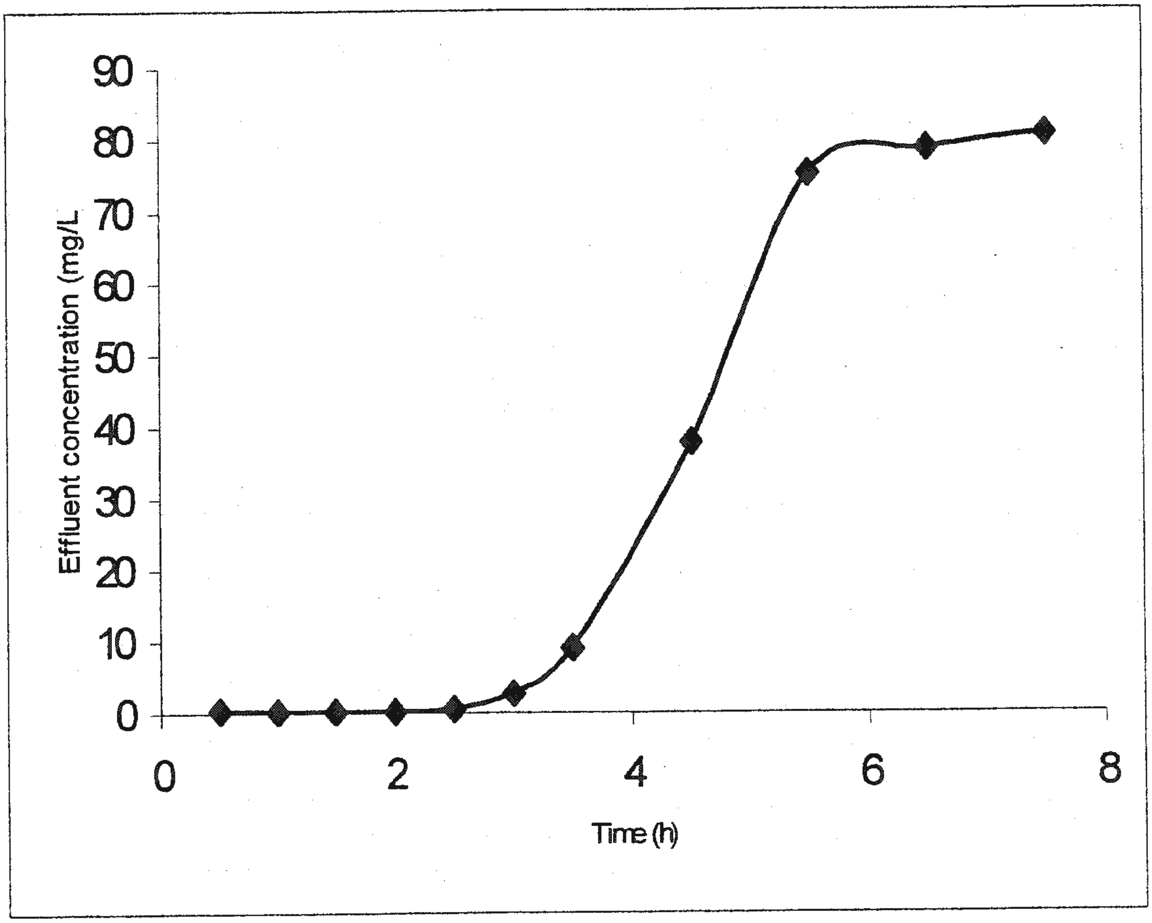


Fig 3.3.3: Breakthrough curve for nickel ions on sulfuric acid-treated peat

The values of T_h, T_B, R_z and h_Z have been calculated according to the equations (I) to (IV) and given in Table 3.3.3. The time required by the exchange zone to move the length of its own height once it has been established, T_h, is obtained by the following equation (Benefield *et al.*, 1982)

$$T_h = \frac{l}{f_W} \qquad \text{(I)}$$

Where

l = total volume of metal solution treated between breakthrough and point of exhaustion

f_W = metal solution flow rate

The time required for exchange zone to move completely out of the bed once it is established, T_B, was calculated from

$$T_B = \frac{l_E}{f_W} \qquad \text{(II)}$$

Where

l_E = total volume of metal solution treated to the point of exhaustion

The rate of sorption zone movement, R_z, was calculated from,

$$R_Z = \frac{h_Z}{T_h} = \frac{h}{T_b - t_f} \qquad \text{(III)}$$

Table 3.3.3: Breakthrough curve data for column uptake of cadmium and nickel onto sulfuric acid-treated peat

Metal	T_h	T_B	R_Z	h_Z
Cadmium	2.66	5.84	3.81	22.25
Nickel	4.76	7.90	4.01	32.31

T_h : Time required by the exchange zone to move its own height (h)
T_B : Time required by the exchange zone to move out completely from bed (h)
R_Z : The rate of movement of sorption zone (cm/h)
h_Z : Height of exchange zone (cm)

If the concentration in the breakthrough curve is characterized by an S-shaped curve, then

$$t_f = (1 - F)t_h$$

In a breakthrough curve if the sorption capacity of the sorbent gets saturated at the breakthrough point then the value of F is zero. But in an S-shaped curve the sorption zone still possesses some ability to sorb even after the breakthrough point and is approximately 0.5.

So equation can be written as

$$t_f = (0.5)t_h$$

Where

h_z = height of the exchange zone

h = total column height

F= capacity of the adsorbent to sorb the solute after the breakthrough point

t_f= time required for the exchange zone to form

The height of the exchange zone was calculated by rearranging the equation III

$$h_Z = \frac{h_Z(T_h)}{T_b - t_f} \qquad \text{(IV)}$$

The breakthrough point where the effluent solution concentration starts to raise usually increases with an increase in the exchange zone, a decrease in the particle size and a decrease in the flow rates (Sundstrom and Klei, 1979). As shown in Table 3.3.3, the height of the exchange zone h_Z (cm), had the lowest value in the case of cadmium and its greatest value in the case of nickel. The greater breakthrough point time for STP shows that better performance was achieved in removing cadmium from wastewater in continuous flow mode.

Fornwalt and Hutchins (1966a, 1966b) reported that, for a steep breakthrough curve, single column operation is feasible. This is mainly because the breaking point is very close to the point of exhaustion which enables the treatment of large volumes of the wastewater. But if the breaking point is reached in the early stages of the breakthrough curve the efficiency of the column is less, and a multiple column is installed for the treatment of the metals. In the present study, the breakthrough for cadmium and nickel occurred close to the point of exhaustion, indicating a steep curve (Figures 3.3.2 and 3.3.3). The breakthrough curves of cadmium and nickel indicate that the STP is efficient in the treatment of metal-containing wastewater in the continuous process. A single column operation is sufficient in the treatment of wastewater containing cadmium and nickel.

The design of a large scale fixed–bed sorption system is time-consuming and generally involves a four step process: studying the adsorbent sorption isotherms, running laboratory column tests, pilot-scale tests and finally designing a commercial unit. Hutchins (1973) developed a new calculation called bed-depth/ service-time (BDST) which can predict the effect of feed concentration, flow rates or effluent compositions. The BDST equation can be used to calculate the new rates which can be used to design the fixed bed on a large scale.

3.3.2 Column regeneration

The percentage of cadmium and nickel desorbed during the regeneration of the column is summarized in Table 3.3.4. These studies show that the efficiency of column regeneration was 64.2% and 77.9% for cadmium and nickel respectively, when metals were adsorbed at lower concentration (0.1mM). In the second set of experiments when cadmium and nickel were adsorbed at higher concentrations (3 mM), desorption was less, between 50.0% and 70.0% as can be seen in the Table 3.3.4. Maximum desorption of the metals occurred during the first successive addition of hydrochloric acid. MacCarthy and Ansted (1984) reported a 100% removal of bound metal ions using 3M HCl. In their experiments, a column containing bound metal ions on peat was allowed to stand for a few days in contact with metal ions before elution. Gardea-Torresdey *et al.* (1996) reported a 95% recovery of metals with 0.1 M HCl. In the present study, the lower recovery of metals is most likely due to the higher concentrations of metals used during sorption and then the acid was only in contact with the peat for few hours before elution. Although 100% removal of bound metals was achieved by MacCarthy and Ansted, (1984), it is not practical to use such an extended time in the treatment of wastewater. Most of the studies noted the effect of low pH but did not examine the possibility of regeneration. This is due to the fact that the regeneration was not economical due to low cost, availability and high sorption capacity of peat for metals. According to Forster and Sharma (1993), bound peat requires incineration and could not be regenerated due to the strong bond between the peat and Cr (IV). In another study, Coupal and Lalancette (1976) reported peat could be disposed of by incineration or landfill.

Table 3.3.4: Cadmium and nickel desorbed (%) with HCl in the column regeneration

Steps	Cadmium desorbed (%)		Nickel desorbed (%)	
	A	B	A	B
1st step	51.1±0.40	56.2±0.93	71.6±0.09	68.8±1.32
2nd step	13.1±0.12	0.1±0.27	6.3±0.68	0.1±0.20
Total	64.2	56.3	77.9	68.9

A: 0.1mM of the total metal ion concentration was passed through the column in sorption experiments
B: 3 mM of the total metal ion concentration was passed through the column in sorption experiments

Trujillo *et al., (*1991) concluded that use of the sulfuric acid followed by the 0.1M sodium carbonate solution was effective in the column and also improved the sorption capacity. This was mainly due to the increase in the porosity of the adsorbent. The present study clearly indicates that peat can be regenerated and reused in the treatment of wastewater containing cadmium and in low concentration. Also consideration to the cost of regeneration should be given in the treatment of wastewater with higher metal concentration.

3.4 Cadmium and nickel complexation by unmodified peat

This study mainly focused on characterizing the peat by infrared spectroscopy in the region of 1000-2000 cm $^{-1}$. The major functional groups in this region are protonated carboxylic groups, COOH with wave numbers around 1700 cm^{-1} and carboxylate ions COO^- with wave numbers around 1600 and 1400 cm^{-1}. During the complexation with metals the characteristic COOH carbonyl absorption vanishes and is replaced by two bands at 1600 and 1400 cm^{-1}, which correspond to the anti-symmetrical and symmetrical vibrations of the COO^- structure respectively. Boyd *et al.* (1980) reported that in complexed humic acids (Na-humate) the absorption band at 1718 cm^{-1} had been entirely replaced by carboxylate absorptions at 1600 and 1385 cm^{-1}.

The antisymmetrical υ_a (COO^-) and symmetrical stretching υ_S (COO^-) vibrations of the carboxylate complex can be related to the mode of complexation (Nakamoto, 1978). The carboxylate group may complex metal ions in any of the following ways which can be seen in Figure 3.4.1:

1) Unidentate; the difference between $\upsilon_a(COO^-)$ and υ_s (COO^-) is larger than for the uncomplexed carboxylate ion.
2) Bidentate; the difference is smaller than for the uncomplexed carboxylate ion.
3) Bridging complexes; the difference is close to the uncomplexed carboxylate ion value.

Boyd *et al.*, 1981 reported that complexation between the carboxylate group of humic acid with copper (II) and iron (III) is unidentate. Benzoate and salicylate values were used as a reference for the uncomplexed carboxylate ions. The values of antisymmetrical and symmetrical stretching vibrations of reference and Ni-peat and Cd-peat can be seen in Table 3.3.5. The difference in the values for Ni- and Cd-complexes were greater than the reference values. The results confirmed an unidentate complexation between Ni-and Cd–and the carboxylate group of peat.

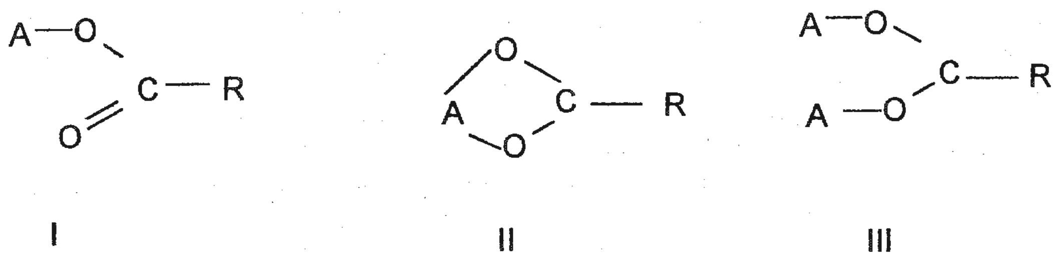


Figure 3.4.1: Different types of cadmium and nickel-peat carboxylic group complexes

A: Cadmium or nickel
I : Unidentate complex
II: Bidentate complex
III: Bridging complex

Table 3.3.5: Carboxylate stretching frequencies of reference and Ni- and Cd–unmodified peat complex

Compound	$\upsilon_a(COO^-)^*$	$\upsilon_S(COO^-)^{**}$	Difference***	Structure
Benzoate$^+$	1548	1391	157	Uncomplexed ion
Salicylate$^+$	1546	1377	169	Uncomplexed ion
Ni-UMP	1615	1375	240	Unidentate
Cd- UMP	1625	1373	252	Unidentate

* =Antisymmetrical stretching frequency of carboxylate ion
** =Symmetrical stretching frequency of carboxylate ion
*** = $\upsilon_a(COO^-) - \upsilon_s(COO^-)$
\+ = Data from Dunn and Mc Donald reported by Boyd *et al.* (1981)

4.0 Conclusion

The data show that peat has considerable potential for the removal of cadmium and nickel from water in both batch and continuous flow system. Modifying peat with sulfuric acid is inexpensive and quite simple. This modification increases the sorption capacity of the peat. The following conclusions can be drawn based on the present study:

1) Sorption of cadmium and nickel is highly dependent on the concentration of the solution and high sorption is obtained for low concentrations. At high concentrations, the sorption of cadmium and nickel decreases due to saturation of the peat.
2) Isotherm data show that the sorption of cadmium onto peat is exothermic *i.e.* sorption capacity of peat increases with a decrease in the temperature, while sorption of nickel is endothermic.
3) The kinetic studies indicated that batch sorption of cadmium and nickel onto sulfuric acid treated peat reaches equilibrium in one hour.
4) Sulfuric acid treated peat is suitable for a continuous sorption process of wastewater treatment. At lower concentrations the cadmium and nickel removal from solution remained high even after 16.5 hrs. The shape of the breakthrough curve is steep for high metal concentrations, which suggests that a single column is sufficient to treat large quantities of wastewater.

5) Hydrochloric acid (3.0 M) was efficient in regenerating the column. It was found to desorb a maximum of 64.2% and 77.9% of cadmium and nickel, respectively.

6) A unidentate complexation of nickel and cadmium by the carboxylate groups of peat was confirmed by IR spectroscopy.

This study indicates that peat is especially good for the treatment of wastewaters containing cadmium and nickel in low concentration (0.1 mM). In the treatment of wastewaters containing high concentrations, peat can be used as a filtering medium in the second or third stages. A series of columns or batch reactors can increase the contact time between the peat and the metals, which can efficiently treat wastewaters in high concentration. Suitable conditions for the maximum sorption of cadmium and nickel, obtained from the present and other studies are summarized in Tables 4.0 and 4.1

Table 4.0: Batch sorption conditions for maximum sorption of cadmium and nickel

Conditions	Batch sorption			
	1		2	3
	Cd	Ni		
Adsorbent	STP	STP	STP	UMP
Concentration	11.24 mg / L	5.87 mg / L	0.30	10.00
Temperature	14^{0}C	40^{0}C	5^{0}C	25^{0}C
pH	5.0	5.0	4.0-4.5	4.0-7.0
Time	60 min	60 min	120 min	25-90 min
Dose	1.0 g / 100 mL	1.0 g / 100 mL	2.5 g / 500 mL	----

Reference:

1) Present study (Cadmium and nickel)
2) Viraraghavan and Rao, 1992 (Cadmium)
3) Wase et al., 1995 (Nickel)

STP : Sulfuric acid-treated peat
UMP : Unmodified peat

Table 4.1: Continuous flow sorption conditions for maximum sorption of cadmium and nickel

Conditions	1	2
Adsorbent	STP	STP
Concentration	0.1 mM - 1.0 mM	10^{-3} mM
Flow rate	8.0 mL / min	49.0 mL / min
Temperature	26^0C	26^0C
pH	5.0	4.0-6.0
Time	16.5 h	5.1 h
Dose	3.1 g / L	3.3 g / L

Reference:

1) Present study

2) MacCarthy and Ansted, 1984

STP: Sulfuric acid-treated peat

5.0 References

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