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Research Article

Modeling the Sorption of Ni^{2+} and Co^{2+} on Saprist Peat Using the Response Surface Methodology

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A detailed study of the sorption of Ni^{2+} and Co^{2+} from simulated wastewater on saprist peat is presented. The significantly decomposed peat possessed a strong sorptive capacity that was maintained over a wide range of pH. With a metal concentration range of 50 to 200 mg/L, pH range of 3 to 10, peat dose of 2 to 40 g/L, and contact time of 12 to 24 h, batch experiments were conducted based on a four-factor Box-Behnken response surface design. The percentage removals of Ni^{2+} and Co^{2+} were analyzed using analysis of variance. Second order response surface models were developed with the significant factors and their interactions to predict the percentage sorption of Ni^{2+} and Co^{2+} independently. The prediction equations were verified with additional data not used in developing the equations. The study showed that the saprist peat could be a potential industrial metal adsorbent and the percentage of uptake of Ni^{2+} and Co^{2+} could be accurately predicted using the second order response surface models developed. Ni^{2+} uptake was greater for the two metals and reached a maximum value at just below a neutral pH and Co^{2+} uptake continued to increase from pH > 5, with higher uptake percentage at pH 10.

1. Introduction

Wastes from urban and industrial growth remain a major source of ground and surface water contamination [1] despite known scientific efforts and treatment technologies employed in most industries. Where mining is a major industry, metal pollution of waters is unlikely to be eliminated. Apart from their ecotoxicity and unlike organic contaminants, it is significant to note that metal contaminants are not biodegradable [2].

Nickel is a toxic trace element widely distributed in the environment [3, 4] and released by volcanoes, windblown dusts, and nickel based manufacturing processes. Soils typically contain 2 to 50 mg/kg of nickel and it can be readily absorbed by plant roots and mobilized in the plants [4]. Nickel compounds are human carcinogens to the extent that they are capable of releasing ionic nickel, which may become highly localized at critical tissue sites [3]. Above the daily permissible intake levels of 0.02 mg/L serious health impacts such as anemia, diarrhea, encephalopathy, hepatitis, and dysfunction of the central nervous system have been reported [5].

Cobalt occurs with copper, nickel, manganese, and arsenic, and small amounts are found in rocks, soil, water, plants, and animals. Average soil concentrations from 8 to 6.450 mg/kg have been reported at mine sites in Ontario, Canada [6]. Cobalt and cobalt compounds are possible human carcinogens and high intakes can lead to thyroid damage, heart problems, vomiting and nausea, and vision problems [3]. One study recommended that the interim maximum total Co concentration in a freshwater environment should not exceed 110 μg/L to protect aquatic life from acute effects of Co [7] because Co is highly toxic to zooplanktonic species [8, 9].

Adsorption remains an attractive technology in metal contaminated wastewater treatment but activated carbon is an expensive adsorbent. Thus inexpensive and alternate metals sorbents for wastewater treatment, such as rice husks [10],

clays [11, 12], and chitosan [13], have been investigated [14, 15]. Peat, especially the poorly humified form, has been tested in the laboratory for the removal of mercury, cadmium, zinc, copper, iron, nickel, silver, lead, and antimony [16–19]. In central Estonia, an Oostriku peat bog was reported to contain 40% by weight of iron, lead, zinc, manganese, copper, and arsenic due to long exposure to metal-rich groundwater [20]. Since peat resources are often proximal to sites of effluent treatment this could ensure low cost treatment [21].

Peat provides a unique material for developing knowledge of the mechanisms and factors influencing trace metal binding onto natural organic constituents [16] and many reactions have been suggested as being responsible for the metal uptake in peat. These include ion exchange, surface adsorption (physical), chemisorption, complexation, and adsorption complexation [17, 18, 22, 23]. Multivalent cations may also form coordinate linkages with uptake dependent on the ionic radius of the metal [24]. The carboxylic and phenolic acid groups in peat are known to react with metals to release protons or at high pH their anion sites will attract available metals [18, 25], a form of ion exchange widely regarded as the main uptake mechanism. Limited knowledge of the uptake mechanisms could be one of the reasons for the scarcity of large-scale peat applications in the treatment of metal contaminated wastewaters.

Organic carbon content, pH, temperature, contact time, water holding capacity, particle size, peat texture, and quantity of peat used are some of the factors that may determine the metal removal efficiency. Interactions between these factors could also be significant in the understanding of the uptake chemistry. The main objective of this study was to establish the influential sorption parameters and, if significant, their interactions on the closely related Ni^{2+} and Co^{2+} ions. This paper presents the statistical analysis, establishes the optimum sorption conditions within the experimental range, and proposes an adjusted predictive regression model for uptake of the two metals.

The study employed batch sorption experiments and analyzed results using the Box-Behnken response surface design. The unique feature of the response surface design lies in its ability to locate the optimum region for the dependent response [26], in this case the % of metal removed. A saprist peat (obtained from a natural bog owned by Traverse Nurseries, near St. John's, NL, Canada), of a homogeneous nature and containing predominantly oxygenated (carboxylic and alcoholic) and amine/amide functional groups and some cations but with no significant inorganic materials such as clays [27], was used. A summary of the physicochemical parameters of the saprist peat is presented in Table 1. A detailed characterization study has been reported in another study [27] with the presence of functional groups such as phenol, N-substituted aromatic, amine carbon, alcohol, carboxyl, and esters. Thus with this peat the metal uptake mechanism could be explained with less ambiguity. With the current mining of Ni and the recovery of Co in Newfoundland, the proximal availability of peat, especially the saprist type, if employed as a sorbent, could reduce Ni and Co loading to receiving waters.

Table 1: Summary of physicochemical parameters of saprist peat.

Parameter	Value
Degree of decomposition*	7-8H
pH (in deionized water)	4.2
Moisture content (%)	86
Fiber content (%)	69
Ash content (%)	9
Organic matter (%)	91
Dry bulk density (g/cm^3)	0.28
pH 7.0 CEC** (meq/100 g)	70

*Degree of decomposition is based on the von Post scale in which the percentage of undecomposed fiber in peat is used in the classification of a sample from 1H (least decomposed to 10H (most decomposed) [28]).
**CEC (cation exchange capacity) based on the calcium acetate/chloride method [29].
Other parameters were determined using the American Society for Testing and Materials (ASTM) for soils methods.

2. Materials and Methods

Saprist peat samples (between 7H and 8H on the von Post humification scale) were air-dried and sieved. Peat fractions ≤ 850 μm (90% of the peat) were further separated into fractions <450 μm and >450 μm for use as Ni and Co sorbents. The peat samples did not undergo any other treatment.

Nickel (II) and cobalt (II) solutions were prepared from analytical grade nitrate hexahydrates supplied by Anachemia Chemicals, Canada, by dilution in distilled water. The natural pHs of the Ni(II) and Co(II) solutions (5.5 and 5.8, resp.) were adjusted by adding 0.25 M sulphuric acid or buffer solution pH 10 containing carbonate, borate, and hydroxide of potassium buffer 0.05 M (Fischer Scientific, Canada) for a selection of pHs as indicated below and pH was measured with an ATI Orion model 3000 VWR brand pH/mV/temperature meter (VWR Scientific, Canada).

Preliminary batch experiments employed a two-level fractional factorial design with six factors (initial metal concentration, solution pH, contact time, peat dose, peat particle size, and agitation level). Analysis of variance (ANOVA) showed that agitation level and peat particle size were statistically insignificant at the 5% level and so these two factors were eliminated from further experiments. The metal adsorption behavior was also found to be nonlinear; hence a three-level Box-Behnken response surface design was chosen for further experimentation, to obtain predictive equations and to determine the optimum response within the range of the factors investigated.

Initial metal concentration, solution pH, contact time, and peat dose were the four factors selected for investigation in triplicate batch experiments. Samples of the saprist peat (0.08, 0.84, and 1.6 g) of ≤450 μm in size were combined with Ni^{2+} or Co^{2+} stock solutions (concentrations of 50, 125, and 200 mg/L) to give peat doses of 2, 21, and 40 g/L. Stock solutions were adjusted to pHs of 3, 6.5, and 10 before being added to the peat in 50 mL serum bottles. The samples were taped to a 5900 Eberbach reciprocal shaker and shaken for 12, 18, and 24 h, filtered with 45 μm quantitative

Table 2: Values of design variables and percentages of metals removed that were used in the Box-Behnken analysis.

Run number	Actual factors				Metal removed, %	
	A	B	C	D	Co^{2+}	Ni^{2+}
	Conc. (mg/L)	Peat dose (g/L)	Time (h)	pH		
1	50	2	18	6.5	45.0	98.0
2	200	2	18	6.5	30.0	58.7
3	50	40	18	6.5	93.8	98.8
4	200	40	18	6.5	84.6	99.6
5	125	21	12	3	77.2	93.0
6	125	21	24	3	78.7	94.4
7	125	21	12	10	94.6	23.7
8	125	21	24	10	94.8	26.2
9	50	21	18	3	86.4	94.0
10	200	21	18	3	73.6	79.7
11	50	21	18	10	96.2	32.8
12	200	21	18	10	93.5	23.4
13	125	2	12	6.5	36.3	69.9
14	125	40	12	6.5	87.9	99.6
15	125	2	24	6.5	33.4	70.8
16	125	40	24	6.5	88.9	83.6
17	50	21	12	6.5	89.6	95.5
18	200	21	12	6.5	78.8	80.5
19	50	21	24	6.5	90.4	96.1
20	200	21	24	6.5	74.0	87.3
21	125	2	18	3	33.1	31.7
22	125	40	18	3	87.3	97.3
23	125	2	18	10	54.9	17.5
24	125	40	18	10	95.7	30.4
25	125	21	18	6.5	81.3	78.8
26	125	21	18	6.5	78.6	88.9
27	125	21	18	6.5	80.7	91.4
28	125	21	18	6.5	80.2	90.2
29	125	21	18	6.5	79.4	99.7

filter paper (Anachemia Chemicals, Canada), and acidified with 0.5 M sulphuric acid, and the Ni^{2+} or Co^{2+} contents were determined with a Varian SpectrAA-55 flame atomic absorption spectrometer in air-acetylene flame. The data from these batch experiments were analyzed and regression models fitted to the data while the data from additional batch tests with metal concentrations of 100 and 150 mg/L, peat doses of 5, 10, 15, and 20 g/L, and pHs of 6 and 8 were used to validate the regression models.

Desorption of Ni^{2+} and Co^{2+} from the peat samples was investigated by the addition of 0.5, 1.0, and 2 M HCl to the peat-metal materials. The mixture was agitated for 2 h on a 5900 Eberbach reciprocal shaker and filtered using quantitative filter paper with 45 μm openings (Anachemia Chemicals, Canada). The filtrates were analyzed using flame atomic absorption spectrometry to determine the amounts of metals desorbed.

The combination of the four factors in the three-level design required 29 experimental runs for each metal and Design-Expert 8.0.4 (Stat-Ease, Inc.) was used for both experimental design and data analysis. The measured percentages of Ni^{2+} or Co^{2+} uptakes (the responses) are summarized in Table 2.

The data were fitted to a second order polynomial function represented by the following equation for z factors:

$$Y_{z,t} = \beta_0 + \sum_i \beta_i Z_i + \sum_i \beta_{ii} Z_{ii}^2 + \sum_{i<j} \beta_{ij} Z_i Z_j + \varepsilon_{zt}, \quad (1)$$

where β_i is the linear effect of the ith factor, β_{ii} is the quadratic effect, β_{ij} is the interaction or cross product effect between ith and jth factors, and ε is the random error term.

3. Results and Discussion

Before the addition of metals only 4 mg/kg Ni and no Co were detected to be naturally occurring in the peat [30]. Table 3 is the summary of the ANOVA for the response surface reduced quadratic model for the batch experiment results. For Ni^{2+} and Co^{2+} the R^2 values were 0.9431 and

Table 3: ANOVA for response surface reduced* quadratic model for Ni^{2+} and Co^{2+}.

Source	Sum of squares	Degrees of freedom	Mean square	F value	P value prob. > F	Comments
A-Ni^{2+} conc.	616	1	617	10	0.0050	
B-peat dose	2204	1	2205	35	<0.0001	
D-pH	9413	1	9414	150	<0.0001	
AB	402	1	403	6	0.0194	
BD	694	1	694	11	0.0032	
B^2	499	1	500	8	0.0102	
D^2	8449	1	8450	134	<0.0001	
Residual	1319	21	63			
Lack of fit	1096	17	65	1	0.4939	Not significant
Pure error	222	4	56			
Cor. total	23198	28				
A-Co^{2+} conc.	372	1	373	97	<0.0050	
B-peat dose	7777	1	7778	2030	<0.0001	
D-pH	726	1	727	190	<0.0001	
AD	26	1	26	7	<0.0194	
BD	45	1	45	12	<0.0032	
A^2	24	1	24	6	<0.0102	
B^2	2357	1	2357	615	<0.0001	
D^2	216	1	216	56	<0.0001	
Residual	77	20	4			
Lack of fit	72	16	4	4	0.0955	Not significant
Pure error	4	4	1			
Cor. total	11994	28				

*Reduced means factors and interactions were eliminated when their P values were > 0.05.

0.9936, respectively, and the predicted R^2 values were 0.8215 and 0.9812, respectively, suggesting that the model for the two cations could be better at predicting responses for new conditions.

The ANOVA (Table 3) eliminated statistically insignificant effects (contact time) and interactions. Contact time may have been insignificant in removing metals because of the rapidity of the reactions once the metals were exposed to the peat. The largest sum of squares values showed that pH had the strongest influence on Ni^{2+} sorption, peat dose moderately influenced Ni^{2+} uptake, and peat dose had the strongest influence on Co^{2+} uptake. The other factors and all interactions were of lesser importance.

The following equations are the initial second order quadratic models of the actual factors for Ni^{2+} and Co^{2+} sorption on the saprist peat, respectively:

$$\begin{aligned}\%\,Ni^{2+} &= 0.83 - 0.24\text{Conc.} + 2.11\text{Peat dose} \\ &\quad + 33.29\text{pH} + 7.04\times10^{-3}\text{Conc.}\times\text{Peat dose} \\ &\quad - 0.20\text{Peat dose}\times\text{pH} \\ &\quad - 0.02\text{Peat dose}^2 - 2.86\text{pH}^2,\end{aligned} \tag{2}$$

$$\begin{aligned}\%\,Co^{2+} &= 50.05 - 0.22\text{Conc.} + 3.85\text{Peat dose} - 3.94\text{pH} \\ &\quad + 9.62\times10^{-3}\text{Conc.}\times\text{pH} \\ &\quad - 0.05\text{Peat dose}\times\text{pH} \\ &\quad + 3.39\times10^{-4}\text{Conc.}^2 - 0.05\text{Peat dose}^2 \\ &\quad + 0.46\text{pH}^2.\end{aligned} \tag{3}$$

After regression diagnostic checks on the regression models, the models were used to predict the uptake of Ni^{2+} and Co^{2+} at metal concentrations, peat doses, and solution pHs within the range of experimental values, with data not used in developing the models (50 to 200 mg/L of metal, pH 3 to 10, and peat doses of 2 to 40 g/L). The experimental and predicted values were compared for the two models ((2) and (3)) to determine the mean absolute percent errors (MAPEs), referred to as the original MAPEs.

When the experimental and predicted values were compared it was discovered that the equations could be improved by including the additional data to the model. This involved only a small change in the intercept term of the models obtained by adding (Ni^{2+}) and taking (Co^{2+}) the average of the absolute values of the deviations (actual minus experimental values) from the intercept term. Equations (4) and (5)

Table 4: Corrected predicted and actual % metals retained after 18 h contact/shaking time.

	Metal conc. (mg/L)	Peat dose (g/L)	Predicted pH 3	Actual pH 3	Predicted pH 6	Actual pH 6	Predicted pH 8	Actual pH 8	Predicted pH 10	Actual pH 10
Ni^{2+}	50	5	82.4	66.9	102.9*	86.5	86.6	72.4	48.2	32.6
	50	10	86.7	74.5	103.4*	91.0	85.9	76.0	45.5	40.0
	50	15	90.2	83.7	103.7*	96.4	84.2	77.1	41.8	40.5
	50	20	92.3	91.5	103.0*	98.5	81.5	78.0	37.1	44.0
	100	5	68.7	56.2	88.3	73.5	72.8	57.2	34.5	22.0
	100	10	71.2	62.5	87.9	84.0	70.4	64.7	30.0	32.4
	100	15	72.7	64.0	86.4	88.2	66.9	69.5	24.5	34.3
	100	20	73.3	76.2	83.9	97.5	62.4	72.8	18.0	33.5
	150	5	54.9	42.5	74.6	58.6	59.1	49.0	20.7	15.9
	150	10	55.7	57.3	72.3	71.5	54.8	62.0	14.5	18.6
	150	15	55.5	72.5	69.1	83.8	49.6	66.1	07.2	21.1
	150	20	54.2	80.0	64.9	91.6	43.4	68.0	–1.0**	22.8
Co^{2+}	50	5	46.5	46.0	47.8	50.0	53.3	54.0	62.4	62.6
	50	10	61.3	62.5	61.8	61.5	66.8	69.0	75.4	74.8
	50	15	73.5	73.1	73.3	76.0	77.8	80.1	85.9	91.0
	50	20	83.3	80.5	82.3	83.0	86.3	86.4	93.9	94.0
	100	5	39.5	40.2	42.3	43.2	48.7	57.2	58.8	60.0
	100	10	54.3	56.5	56.3	54.0	62.2	61.7	71.8	72.5
	100	15	66.5	67.3	67.8	58.0	73.2	71.5	82.3	80.8
	100	20	76.3	76.2	76.8	74.0	81.7	82.0	90.3	96.5
	150	5	34.2	42.5	38.4	38.5	45.8	47.0	56.8	59.5
	150	10	48.9	57.3	52.4	53.2	59.3	60.0	69.8	68.6
	150	15	61.2	72.5	63.9	63.5	70.3	71.1	80.3	75.5
	150	20	70.9	80.0	72.9	71.5	78.8	80.0	88.3	88.0
	MAPE for Ni^{2+}, original			0.16		0.15		0.21		0.65
	MAPE for Ni^{2+}, corrected			0.16		0.13		0.16		0.36
	MAPE for Co^{2+}, original			0.07		0.09		0.06		0.06
	MAPE for Co^{2+}, corrected			0.06		0.002		0.03		0.03

*The model predicted >100% Ni^{2+} uptake.
**The model predicted negative Ni^{2+} uptake.

show the corrected prediction equations and Table 4 presents the predicted values obtained from (4) and (5) and the actual values:

$$\begin{aligned} \%\,Ni^{2+} &= 15.02 - 0.24\text{Conc.} + 2.11\text{Peat dose} \\ &\quad + 33.29\text{pH} + 7.04 \times 10^{-3}\text{Conc.} \times \text{Peat dose} \\ &\quad - 0.02\text{Peat dose} \times \text{pH} \\ &\quad - 0.02\text{Peat dose}^2 - 2.86\text{pH}^2, \end{aligned} \tag{4}$$

$$\begin{aligned} \%\,Co^{2+} &= 45.67 - 0.22\text{Conc.} + 3.84\text{Peat dose} \\ &\quad - 3.94\text{pH} + 9.62 \times 10^{-3}\text{Conc.} \times \text{pH} \\ &\quad - 0.05\text{Peat dose} \times \text{pH} + 3.39 \times 10^{-4}\text{Conc.}^2 \\ &\quad - 0.05\text{Peat dose}^2 + 0.46\text{pH}^2. \end{aligned} \tag{5}$$

The metal bonding capacity of the saprist peat is represented by the percentage of metal removed from solution. How the three noneliminated factors (pH, peat dose, and metal concentration) and their interactions affected the two metals uptakes is shown in Figures 1(a), 1(b), 2(a), and 2(b). On the x-axis of the plots in the figures, the Design-Expert 8.0 generated two mid points in addition to the experimental mid points (125 mg/L for concentration and 21 g/L for peat dose). These additional mid points are at concentrations 162.5 mg/L (for points 125 and 200 mg/L) and 87.5 mg/L (for points 125 and 50 mg/L). For peat dose, the mid points are 30.5 g/L (for points 21 and 40 g/L) and 11.5 g/L (for points 21 and 2 g/L). Five design points representing the mid points used at various combinations of concentration, pH, and peat dose and their corresponding uptakes depicted by the green circles are also included in the plots.

Figure 1(a) indicates that percentage Ni^{2+} removal is always lesser at large initial Ni^{2+} concentration and low peat dose (point 1), while at low peat dose and low concentration (point 2) the Ni^{2+} uptake is slightly less than the observed uptake at low concentration and large peat dose (point 3) and at large concentration and large peat dose (point 4)

where greater uptake is observed (represented by the red line). Interaction is pronounced at low peat dose and low concentration (point 2) and at large peat dose and low concentration (point 3) combinations. As seen in Figure 1(a), the red and black lines nearly converge at points 2 and 3 while significantly diverging as the concentration is increased from 50 to 200 mg/L at low (point 1) and high peat doses (point 4).

Figure 1(b) shows the interaction between peat dose and pH for Ni^{2+} uptake. Larger Ni^{2+} uptake is observed at low pH and large peat dose (point 4). The uptake observed at low pH and low peat dose (point 3) is also larger than the uptakes at large pH and low peat dose (point 2) and large pH and large peat dose (point 1). The uptakes at the combinations of large pH and low peat dose and large pH and large peat dose are nearly the same.

The interactions effect requires the establishment of appropriate conditions depending on the desired uptakes. The percentage Ni^{2+} removal is greater at the larger peat dose except when combined with high pH and low Ni^{2+} concentration as shown in Table 3 with the pH having a greater influence than peat dose on Ni^{2+} removal.

For Co^{2+} uptake as seen in Figures 2(a) and 2(b) where the lines are almost parallel, the concentration-pH and peat dose-pH interactions are negligible (as also indicated in Table 3). Figure 2(a), however, shows greater Co^{2+} removal at the higher pH (represented by the red line) and at low Co^{2+} concentration (point 3). Figure 2(b) shows greater Co^{2+} removal at the higher pH (red line) and at high peat dose (point 3). Peat dose was seen to be the most significant factor in Co^{2+} removal (Table 3). When the Co^{2+} concentration increases, there are always small decreases in the percentage of Co^{2+} removal. The pH and metal concentration were seen to be less important than peat dose for their effect on Co^{2+} removal (Table 3). To summarize, Co^{2+} removal was seen to be greater with increase in peat dose, with increase in pH, and with decrease in Co^{2+} concentration.

Comparing uptake of the two metals by the saprist peat, it was the pH followed by the peat dose that was the most significant factor for Ni^{2+} uptake, and peat dose was the most significant factor for Co^{2+} uptake. In addition, greater percentage metal removal corresponded to lower pH for Ni^{2+} and higher pH for Co^{2+}.

The second order polynomial equations (4) and (5) were good at predicting experimental results for parameter values within the range of experimental values, but not actually used in the model development for Ni^{2+} and Co^{2+} (Table 4) and this is depicted by the scatterplots (Figures 3 and 4).

The dominant factor affecting Ni^{2+} uptake by the saprist peat was the solution pH. The highest Ni^{2+} uptake is calculated to occur in the range of pH 4.4 to 5.8 using (4). Table 5 also shows the best Ni^{2+} removal occurring at pH ~ 6. As pH increases from pH 3 to 5.5 deprotonation of the peat surface occurs and the H^+ ions released from the peat could compete with Ni^{2+} ions for sorption sites and the cations could be sorbed by complexation. At pH > 5.5 a high concentration of hydroxyl groups will exist and will permit the formation of the reactive carboxylic anions (RCO_2^-) and amine groups (RNH_2). These two groups are better reactive agents at higher pHs via the displacement of protons than Ni^{2+}. As solution pH is increased above pH 5.5, more Ni^{2+} complexes are formed due to the involvement of more O^- containing groups capable of donating electrons to the vacant orbital of the Ni^{2+} ions, thus replacing two displaced H^+ ions (ion exchange). For Ni^{2+} it appears that complexation is favored at pHs < 5.5 and ion exchange is favored at pHs > 5.5.

Since the dominant factor affecting Co^{2+} uptake was peat dose, higher peat doses may have provided more available active bonding sites due to a decreased sorption density and unsaturation of sorption sites. Thus the Co^{2+} uptake appears to have been governed by a different reaction mechanism compared to the Ni^{2+} uptake. Particle aggregation could also have been experienced as peat dose was increased, leading to hindered uptake and the need for greater space. At pH > 8, precipitation of the Co^{2+} complexes with available and active ligands could contribute to particle aggregation as well.

Metal concentration was the third significant factor affecting metal uptake and an increase in metal concentration resulted in a decrease in % Ni^{2+} and Co^{2+} removed. Comparing (4) and (5), however, the quadratic effect of concentration in (5) might also suggest a different uptake mechanism for Co^{2+} compared to Ni^{2+}.

A multiple response optimization technique based on desirability functions using Design-Expert 8.0.4, for minimal use of peat as the goal (Table 5), was tested but not experimentally verified for two scenarios. This technique allows for the best combinations of responses and the choice of desirability is from zero (worst) to one (best). A desirability of one implies that a small increase or decrease in the factors will not render the quality of the response unacceptable [31]. This optimization approach suggested that more Ni^{2+} was retained under more acidic conditions and lower peat doses compared to Co^{2+}.

The mechanisms of adsorption of Ni^{2+} and Co^{2+} are considered in terms of the functional groups present in the saprist peat. The phenolic OH, COOH, and C=O (oxygenated) functional groups originating in the humic and/or fulvic acids of saprist peat are good complexing agents. The binding of Co^{2+} and Ni^{2+} by these surface functional groups in the peat begins effectively at pH 3 and rises to an optimum value within the pH 4.4 to 5.8 range for Ni^{2+} and pH 10 for Co^{2+}. These different values suggest different uptake reactions.

For Ni^{2+}, complexes formed by oxygenated, amino, and imino functional groups [27] and ion exchange reactions following deprotonation of the carboxylic component in the saprist peat could have led to higher overall Ni^{2+} uptakes. At low pH electronic cleavages and rearrangement due to the influence of the acidic environment may have aided the incorporation of Ni^{2+} cations onto the peat surface by complexation. At pH < 5.0, more ligands with negative charge are exposed leading to an increase attack by the Ni^{2+} ions in solution [32]. As the pH is increased and the peat surface becomes more negatively charged, complexes formation via an exchange of deprotonated sites of the hydroxides of Ni^{2+} ($Ni(OH)_2$) may have dominated. At the optimum uptake

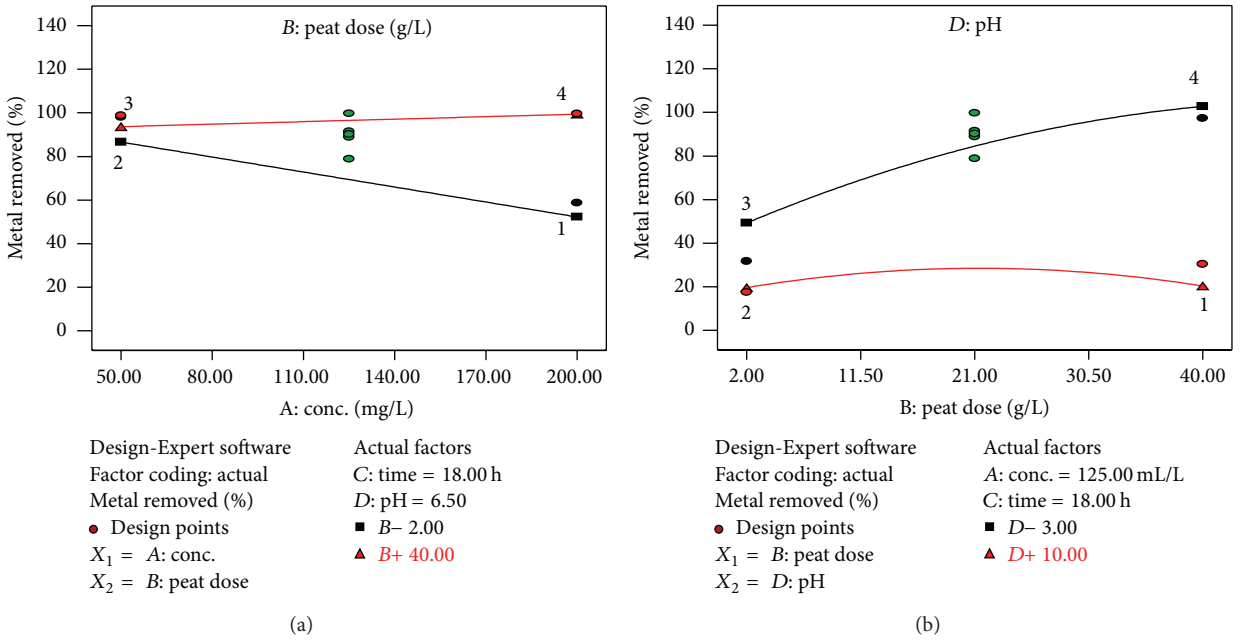

FIGURE 1: (a) Ni^{2+} concentration-peat dose interaction plot for % Ni^{2+} removed. (b) Peat dose-pH interaction plot for % Ni^{2+} removed.

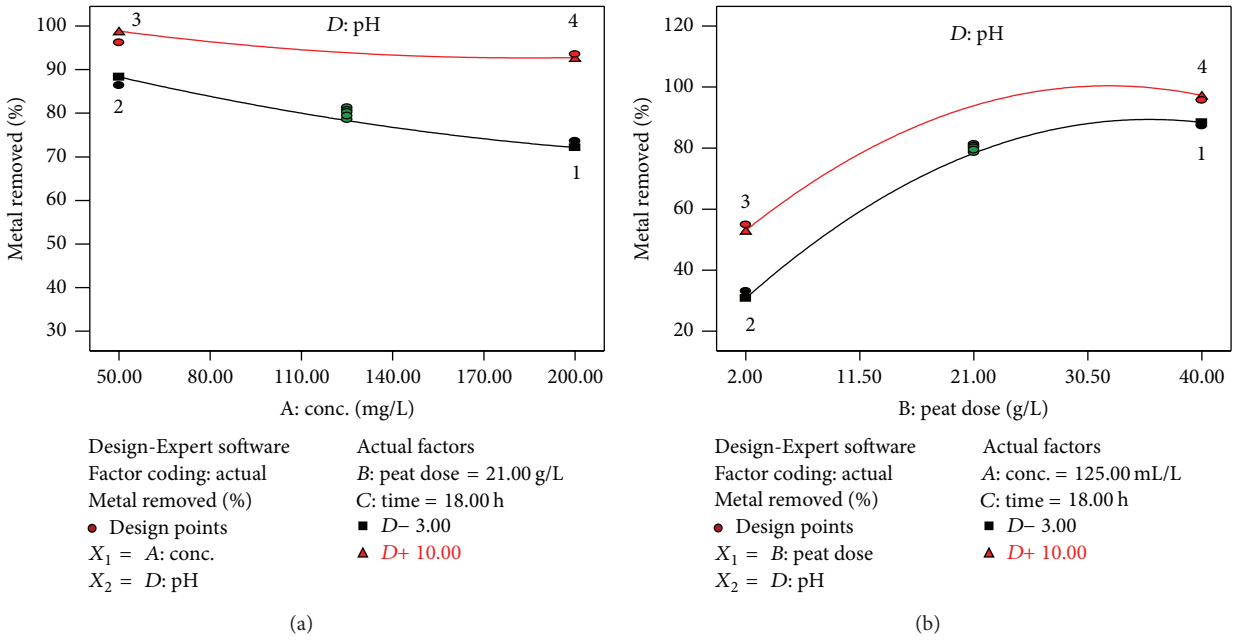

FIGURE 2: (a) Concentration-pH interaction plot for % Co^{2+} removed. (b) Peat dose-pH interaction plot for % Co^{2+} removed.

pH, complexation and ion exchange reactions may have combined to give the large observed Ni^{2+} uptake.

The surface charge of peat is negative and, at alkaline solution pHs, humic and fulvic acids in the peat would be dissolved and could react with Co^{2+} to form soluble Co^{2+} complexes. Co^{2+} is known to strongly complex with these acids [33]. Unlike Ni^{2+}, less Co^{2+} uptake by vacant sorption sites on the peat surface was experienced at low pHs when humic acid would have precipitated because access to the peat surface closely associated with H_3O^+ could have been repelled [32]. As pH increases towards pH 10, complexation leading to the precipitation of the Co^{2+} complexes formed with the ligands in the peat dominated leading to the uptake of the ion.

Desorption experiments have identified ion exchange as an uptake mechanism in peat-metal chemistry [22, 34]. To assess ion exchange of Ni^{2+} and Co^{2+} with the saprist peat, desorption tests with 0.5, 1.0, and 2.0 M HCl were conducted.

Table 5: Two solutions for Ni^{2+} and Co^{2+} uptake by multiple response optimization.

Constraints and limits	Goal	Solutions
Conc., 50–200 mg/L	In range	~100% Ni uptake at 50 mg/L conc.
Peat dose, 2–40 g/L	Minimize	14 g/L peat dose and pH 5.3
pH 4.5–pH 6.5	In range	~94% Co removed at 50 mg/L, 27 g/L peat dose and pH 6.5
Conc., 50–200 mg/L	In range	~100% Ni uptake at 200 mg/L conc.
Peat dose, 2–40 g/L	Minimize	28 g/L peat dose and pH 4.9
pH 4.5–pH 6.5	In range	~90% Co uptake at 104 mg/L conc., 30 g/L peat and pH 6.5

Table 6: % desorption of Ni^{2+} and Co^{2+} at a peat dose of 40 g/L and solution pH of 10.

Initial cation conc. (mg/L)	Ni^{2+}		Co^{2+}	
	12.5	200	12.5	200
% desorption with 0.5 M HCl	78.5	93.5	50.6	69.1
% desorption with 1.0 M HCl	82.4	96.9	61.7	72.5
% desorption with 2.0 M HCl	92.0	97.5	67.1	83.5

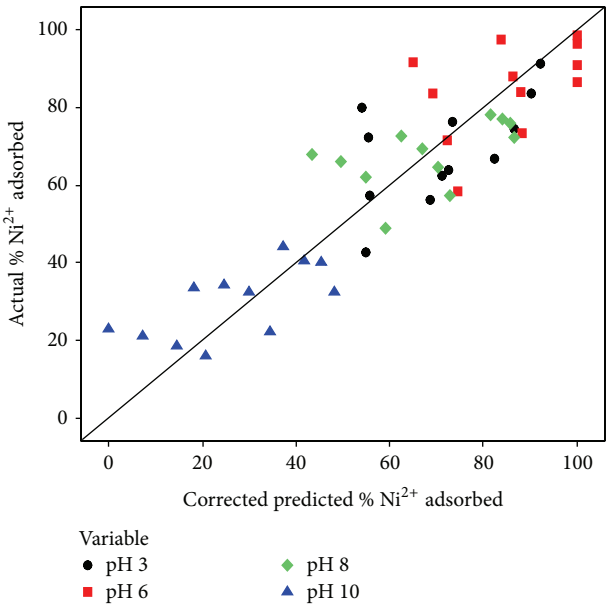

Figure 3: Scatter plots for % actual and % corrected predicted Ni^{2+} adsorbed.

For a peat dose of 40 g/L and at pH 10, >50% of initially sorbed metal was desorbed (Table 6). At peat doses of 2 and 21 g/L and at pH 3, Ni^{2+} and Co^{2+} were not significantly desorbed, while, at pH 5.5 and 8, Co^{2+} was not significantly desorbed but >50% of Ni^{2+} was desorbed. Within the acid range of pH of desorption, the metal ions sorbed in a peat matrix are exchanged for the hydroxonium ion. Thus, where desorption was observed, ion exchange is suggested as an initial route through which the metal ion was sorbed. Ion exchange appears to have been more important for Ni^{2+} uptake than for Co^{2+} uptake.

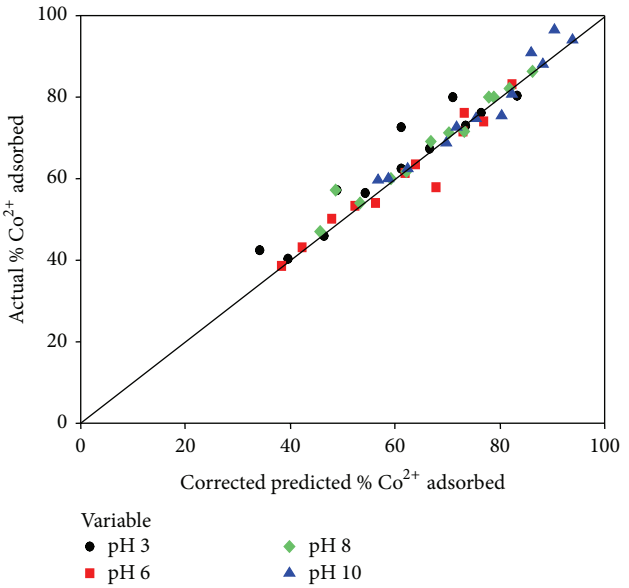

Figure 4: Scatter plots for % actual and % corrected predicted Co^{2+} adsorbed.

4. Conclusion

The conventional experimental approach of investigating reaction factors is to change one variable at a time but that does not allow an optimized formulation to be developed as interactions among the variables are neglected. This study employed the Box-Behnken design in the optimization of the saprist peat sorbent for the uptake of Ni^{2+} and Co^{2+}. The second order polynomial equations obtained were good at predicting experimental results that were not used in the model development but were within the range of tested values as shown in Table 3 for Ni^{2+} and Co^{2+} and depicted by the scatterplots in Figures 3 and 4. The models showed better results for Co^{2+} compared to Ni^{2+}. Peat being a nonrenewable material should be economically used if employed as a metal sorbent. This study utilized peat at a dose far less than the usual 20 : 1 solution to soil ratio employed in soil sorption studies; thus minimal use was achieved.

Statistical analyses indicated that it is unlikely that Ni^{2+} and Co^{2+} uptake are explained by a single reaction mechanism as the effect of each factor and interactions among

the factors differed for Ni^{2+} and Co^{2+}. However, metal concentration, peat dose, and pH were the same three main factors affecting sorption for each metal. Time of contact was statistically insignificant as reactions were initiated as soon as sufficient contact between the peat and the metal was established. The saprist peat could be a potential industrial metal sorbent.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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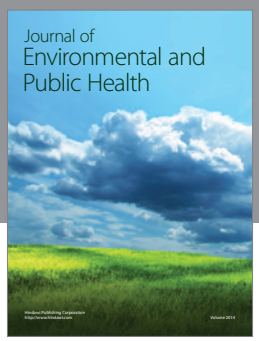

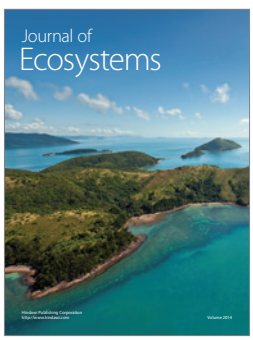

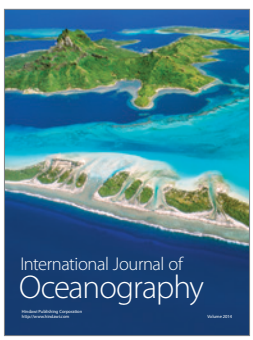

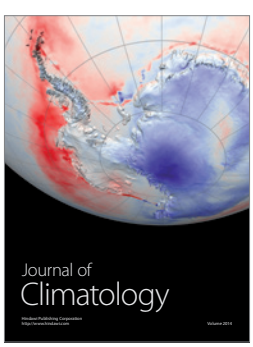

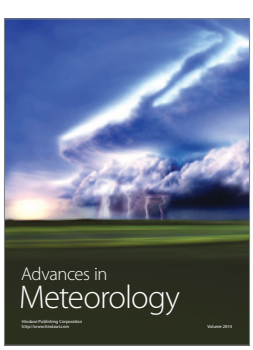

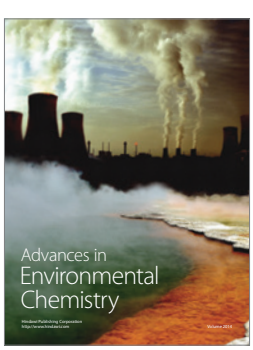

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