Removal of nickel from wastewater using an agricultural adsorbent

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Abstract

Chemical wastewater streams may contain toxic compounds which are non-biodegradable, and therefore require advanced treatment techniques such as adsorption. However, application of adsorption processes is often limited by the cost of adsorbents. In this study, the adsorption capacity of a low-cost adsorbent (pine sawdust) was investigated by treating wastewater containing nickel (II) and other heavy metal ions. Results were analysed using response surface methodology and a factorial design was employed to determine the interactive effects of the various factors on the adsorption capacity. Furthermore, Langmuir and Freundlich adsorption isotherms were fitted to experimental data to characterise the adsorption of the nickel ions by the pine sawdust. As a result, the highest adsorption capacity was attained at the combined effect of low adsorbent dose, high pH and high initial concentration. On the other hand, the Freundlich isotherm fitted the experimental data better than the Langmuir isotherm. Results of this study indicate that the use of pine sawdust could be a promising solution to the elimination of nickel ions from multi-component aqueous solutions.

Keywords: sawdust, adsorption, nickel ions, wastewater, isotherm

Nomenclature

β_i	dimensionless regression coefficients
C_o	Initial concentration (mg/ℓ)
C_e	Equilibrium concentration (mg/ℓ)
i	$= 0,1,2,\ldots.,k$
k	Number of variables
K_F	Freundlich constant related with adsorption capacity (mg/g)
K_L	Langmuir affinity constant (ℓ/mg)
m	Mass of dry adsorbent (g)
n	dimensionless Freundlich constant related with adsorption intensity
q_e	Equilibrium adsorption capacity (mg/g)
q_{max}	Maximum monolayer adsorption capacity (mg/g)
q_{Ni}	Predicted adsorption capacity for Nickel (mg/g)
R^2	dimensionless correlation coefficient
V	Volume of wastewater (ℓ)
x_1	dimensionless coded variable for dose
x_2	dimensionless coded variable for pH
x_3	dimensionless coded variable for initial concentration
Y	Predicted response

Introduction

A vast number of raw materials for industrial processes originate from agricultural activities, which result in the production of chemical and solid wastes. The chemical wastes arise from the use of pesticides, dyes and fertilisers while the solid wastes include bagasse, sawdust, rice husk, peanut shell and coffee husk, among others. Interestingly, the agricultural solid wastes can be converted to adsorption media and used to treat the chemical wastes; a concept of using waste to treat waste. By this concept, the cost of adsorption material for wastewater treatment, which is a major constraint in wastewater management, is generally reduced. Due to environmental concerns and the demand for high-quality water, there has been an increase in regulations controlling the discharge of heavy metals and non-biodegradable toxic compounds into water bodies. This has resulted in developing toxic waste removal techniques such that only minute quantities remain in the wastewater discharged into water bodies. Secondary wastewater treatment is not completely adequate in removing toxic material and thus advanced methods have become necessary. Secondary methods are employed in conjunction with advanced methods to separate the recalcitrant organic compounds and non-biodegradable inorganic compounds (Singh et al., 2007). Advanced methods of removing toxic compounds from wastewater include membrane separation (Mavrov et al., 2006), ion exchange (Cavaco et al., 2007), lime precipitation (Zhang et al., 2007), neutralisation, metal hydroxide precipitation (Ayyappan et al., 2003), electrolytic methods (Kurt et al., 2007) and adsorption (Dean et al., 1972). However, these processes are costly (Dae and Young, 2005); in particular, the use of activated carbon and ion exchange resins is not suitable for developing countries due to their high capital and operational costs (Raji and Anirudhan, 1997).

Adsorption has gained a relatively wide application due to the fact that there are several types of adsorbents that are commonly used, which includes clay, activated carbon, zeolite and silica gel and the agricultural adsorbents such as coffee husk (Kumar, 2006), peanut shells (Wafwoyo et al., 1999), bagasse (Azhar et al., 2005), rice husk (Kumar and Bandyopadhyay, 2006) and sawdust (Argun et al., 2007). Thus, by using natural, abundant, cheap agricultural wastes (Taty-Costodes et al.,

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2003), the adsorption of pollutants from aqueous solutions can be much more economical with regard to other similar physico-chemical processes (Mahvi, 2008). The concept of using waste has not been investigated in detail. To the best of our knowledge, no work has been reported on the use of pine sawdust in the removal of nickel (II) ions from multi-component aqueous solutions using the response surface methodological approach; many researchers use the one-factor-at-a-time (OFAT) method. However, this method is extremely time consuming and expensive since it requires a large number of experiments (Elibol, 2002). The aim of this study was to investigate the interactive effects of operating parameters such as adsorbent dose, pH and initial concentration on adsorption capacity of pine sawdust towards nickel (II) ions using the response surface methodology (RSM). Furthermore, the adsorption capacity of pine sawdust in the removal of nickel (II) ions from multi-component aqueous solutions was determined.

Materials and methods

Adsorbent preparation and wastewater synthesis

Pine sawdust collected from a local company was ground and sieved to a particle size range of 500-850 μm. It was then placed in stainless steel trays and dried in an oven (EcoTherm) at 50°C for 24 h. A mass of 100 g was placed in a 1 ℓ glass beaker and 660 mℓ of 0.6 M citric acid solution was added. The mixture was manually stirred for 30 min, and then separated by vacuum filtration. The wet sawdust was then spread in stainless steel trays and dried in an oven at 50°C for 24 h and then the temperature was raised to 120°C and maintained for 90 min. The sawdust was allowed to cool and washed 5 times using hot distilled water (60-80°C) and then dried at 50°C for 24 h (Wafwoyo et al., 1999). Finally, the temperature was raised to 250°C and maintained for 24 h, after which the sawdust particles were removed from the stainless steel trays and stored for adsorption tests. No leaching experiments were carried out to check for the presence of toxic soluble leachate, which could possibly emanate from pine sawdust especially when its source has been previously treated with pesticides. Fourier Transform Infrared (FT-IR) spectra of the pine sawdust before and after adsorption were recorded in the range 500 to 4 000 cm^{-1} on an FT-IR (Bruker, Tensor 27 TPR) system, to explore the number and positions of the functional groups responsible for adsorption.

The stock solutions (1 000 mg/ℓ) of Ni(II), Co(II) and Fe(III) prepared from the metal nitrates were diluted with distilled water to obtain the desired initial concentrations according to the levels specified in Table 1. The zero level concentration of heavy metals was 10 times that reported by Patel and Mudamwar (2002) for a particular petrochemical wastewater sample. Thus, the medium values in the reported ranges were multiplied by 10 and taken as the zero levels in the present study. Additionally, the composition and concentrations of the synthetic aqueous solutions prepared fall within the range of the typical petrochemical wastewater described in the Pollution Prevention and Abatement Handbook (World Bank Group, 2008), which specifies a heavy metal concentration range of 0.1 to 100 mg/ℓ. The pH of the solutions was adjusted using either dilute HNO$_3$ or NaOH. A high (+) pH level of 3.9, which is below the pH point of precipitation (pH$_{ppt}$) for each of the metal hydroxides, was chosen to prevent possible precipitation (Al-Degs et al., 2006). All the pH measurements were done using a pH meter (LabX Direct-SevenMulti, Mettler Toledo)

and all the chemicals used were of analytical grade, supplied by Merck Chemical Company (South Africa).

Experimental design and optimisation of parameters

The adsorbent dose, pH and initial concentration were chosen as independent variables and the adsorption capacity, q_e, as the dependent output response variable. A 2^3 full-factorial design with 4 centre points leading to 12 experimental runs was performed (Table 2). The centre point replicates were chosen to verify any change in the estimation procedure, as a measure of precision property (Ravikumar et al., 2007). For statistical calculations, the variables X_i were coded as x_i, according to the following relationship:

$$x_i = \frac{X_i - X_0}{\Delta X} \qquad (1)$$

where:
x_i is the independent variable coded value;
X_i, independent variable real value;
X_0, independent variable real value on the centre point; and
ΔX, step change value (Elibol, 2002) of which the values for dose, pH and initial concentration (C_0) in this case are 2.0, 1.3 and 0.88, respectively.

Table 1 gives the range and the levels of the variables (low and high) investigated in this study.

Table 1 The experimental range and levels of the independent variables				
Factor	Coded symbol	Levels		
		-1	0	1
Dose (g)	x_1	2.0	4.0	6.0
pH	x_2	1.3	2.6	3.9
[Ni(II) and Co (II)]$_o$ (mg/ℓ)	x_3	0.875	1.75	2.625
[Fe(III)]$_o$ (mg/ℓ)	x_3	2.125	4.25	6.375

The quadratic model for predicting the adsorption capacity for nickel was expressed according to Eq. (2):

$$Y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2$$
$$+ \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \qquad (2)$$

where:
Y is the response predicted by the model, whilst x_1, x_2, x_3 are the coded forms of dose, pH and initial concentration, respectively. The term β_o is the offset term, β_1, β_2 and β_3 are linear terms, β_{11}, β_{22} and β_{33} are the quadratic terms whilst β_{12}, β_{13} and β_{23} are the interaction terms (Bhatia et al., 2009).

The analysis of variance (ANOVA) for the quadratic model was carried out to establish its statistical significance at 5% level of significance (95% confidence level). Design Expert Version 6.0.6 (Stat Ease, Inc., Minneapolis, USA) and Matlab Version 7.0.1 software were used for regression and graphical analysis of the data obtained. The statistical significance of the regression coefficients was determined by the Student's t-test and p-values.

Adsorption procedure

All adsorption experiments conducted were of the batch type. A 100 mℓ wastewater solution was contacted with the desired

mass of pine sawdust in 250 mℓ Erlenmeyer flasks. Blank solutions (solution without the adsorbent) were also included. The flasks were covered with parafilm. The mixture was shaken at 250 r/min in an incubator with shaking platform (FSIM-SPO16, Labcon) at 25°C for a predetermined contact time of 45 h. The supernatant was separated by filtration. Initial and final heavy metal ion concentrations were determined using the Atomic Absorption Spectrometer (SpectroAA 55 B, Varian). The response, i.e., adsorption capacity, q_e, was calculated as:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (3)$$

where:

C_o and C_e are the initial and equilibrium adsorbate concentrations in solution (mg/ℓ), respectively
V is a known volume of synthetic wastewater (ℓ)
m is a known mass of adsorbent (g).

Adsorption isotherms

The adsorption isotherm data for nickel ions were generated by contacting a fixed amount of pine sawdust (4 g) with 100 mℓ of synthetic wastewater with the concentration of metal ions ranging from 2 to 20 mg/ℓ in 250 mℓ flasks. The flasks were shaken at 250 r/min in an incubator with shaking platform at 25°C for 45 h. At the end, the residual concentrations of the nickel ions were measured and the adsorption capacity, q_e, was determined. The results were fitted to the commonly-used Langmuir and Freundlich isotherms. Equation (4) is the linear form of the Langmuir isotherm:

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{Ce} + \frac{1}{q_{max}} \qquad (4)$$

where:

q_e is the adsorption capacity at equilibrium (mg/g)
q_{max} is the theoretical maximum adsorption capacity of the adsorbent (mg/g)
K_L is the Langmuir affinity constant (ℓ/mg)
C_e is the supernatant equilibrium concentration of the system (mg/ℓ) (Febrianto et al., 2009).

The Freundlich isotherm model can also be expressed in the linearised logarithmic form (Eq. (5)):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right)\log C_e \qquad (5)$$

where:

K_F is the Freundlich constant related with adsorption capacity (mg/g)
n is the heterogeneity coefficient (dimensionless).

Results and discussion

Surface functional groups

Citric acid provides additional carboxyl groups to those on pine sawdust surfaces and substantially increases its metal uptake (Mcsweeny et al., 2006). The spectra shown in Fig. 1 display a number of absorption peaks, indicating the complex nature of the surfaces of pine sawdust. The peak at 3381.2 cm⁻¹ before adsorption can be attributed to the hydrogen-bonded OH group of alcohols and phenols (Yang and Lua, 2003) and it shifted to 3217.2 cm⁻¹ after adsorption. Also, the peak at 1184.3 cm⁻¹ before sorption is associated with C—O stretching vibrations in carboxylic acids (Pavia et al., 1987), and it shifted to

Standard order	Coded levels			Actual levels			$q_e \times 10^{-3}$ (mg/g)	
	x_1	x_2	x_3	Dose (g)	pH	C_o (mg/ℓ)	Observed	Predicted
1	-1	-1	-1	2.0	1.3	0.875	5.00	1.93
2	+1	-1	-1	6.0	1.3	0.875	1.79	4.87
3	-1	+1	-1	2.0	3.9	0.875	28.83	32.0
4	+1	+1	-1	6.0	3.9	0.875	6.29	3.22
5	-1	-1	+1	2.0	1.3	2.625	7.50	11.0
6	+1	-1	+1	6.0	1.3	2.625	3.21	0.13
7	-1	+1	+1	2.0	3.9	2.625	65.90	63.00
8	+1	+1	+1	6.0	3.9	2.625	17.68	21.00
9	0	0	0	4.0	2.6	1.750	5.92	5.71
10	0	0	0	4.0	2.6	1.750	5.83	5.71
11	0	0	0	4.0	2.6	1.750	5.33	5.71
12	0	0	0	4.0	2.6	1.750	5.75	5.71

Table 2
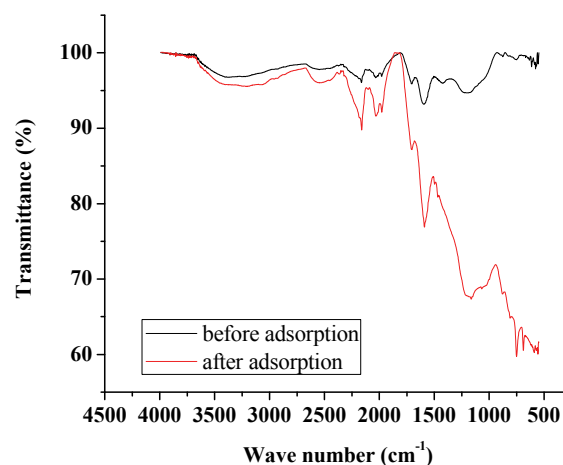**The 2³ full-factorial design with 4 centre points**

Figure 1
FT-IR spectra of pine sawdust before and after adsorption

1163.1 cm⁻¹ after adsorption. These major shifts in band suggest that the alcohols/phenols and carboxylic acid groups were involved in metal binding. Agricultural biomasses mainly consist of lignin, cellulose, hemicelluloses and some proteins which make them effective adsorbents for heavy metal cations (Garg et al., 2008). In addition, the band at 1 597.0 cm⁻¹ represents the C=C skeletal stretch in condensed aromatic system and a peak at 754.2.3 cm⁻¹ can be assigned to the out-of-plane C—H bending modes of an aromatic compound (Al-Qodah and Shawabkah, 2009).

Fitting of a quadratic model

By applying multiple regression analysis methods, the predicted adsorption capacities can be obtained and given as:

$$q_{Ni} = 0.123 - 0.0098x_1 + 0.0127x_2 - 0.0079x_1x_2 - 0.112x_3^2 \qquad (6)$$

where:

q_{Ni} is the predicted adsorption capacity for nickel ions
x_1, x_2, x_3 are the coded values of the test variables, dose (g), pH and initial concentration (mg/ℓ), respectively.

The statistical significance of the second-order model equation was evaluated by the F-test and the analysis of variance

(ANOVA), which is summarised in Table 4. In this work, the model acceptance was based on the 95% confidence level. In order for a term to be significant at this confidence level, the calculated probability should be lower than 0.05 (Bhatia et al., 2009). The ANOVA revealed that this regression model is statistically significant, as is evident from the Fisher's F-test with a very low probability value (<0.0033) i.e the associated Prob.> F value for the model is lower than 0.05. The lack-of-fit measures the failure of the model to represent data in the experimental domain at points which are not included in the regression. The associated Prob.> F for the lack-of-fit is 0.0515 which is greater than 0.05 and this indicates that the lack-of fit is not significant. Thus, the non-significant value of lack of fit (>0.05) reveals that the quadratic model is statistically significant (Sharma et al., 2009). A standard deviation of 4.35×10^{-3} and a relatively lower value of the coefficient of variation (CV=32.9%) indicates a better precision and reliability of the experiments carried out. The model presented a relatively high R^2 value (0.9792) explaining 97.9% of the variables; dose, pH and initial concentration in the response and it indicates that 2.1% of the total variation is not explained by the model.

Table 3
Analysis of variance (ANOVA) for the quadratic model

Source of variation	Sum of squares	Degree of freedom	Mean square	F-value	Probability > F
Model	3.57E-03	7	5.10E-04	26.9	0.0033
Residual	7.58E-05	4	1.90E-05		
Lack of fit	7.56E-05	1	7.56E-05	5.01	0.0515
Pure error	2.02E-07	3	6.72E-08		
Total	3.64E-03	11			

The model Eq. (6) has dimensionless input values, i.e, it consists of coded variables only. However, in practical cases a model equation with the real variables must be used. Thus, the relationship between each coded and real variable was deduced from Eq. (1) and substituted into the model Eq. (6); upon rearrangement, Eq. (7) was obtained:

$$q_{Ni} = 0.192 + 0.00105\,Dose + 0.0125\,pH \\ - 0.00127\,Dose.pH - 0.0602C_o^2 \tag{7}$$

Equation (7) was then used to plot the 3-dimensional surfaces of dose – pH at constant C_o, (Fig. 2a), dose – C_o at constant pH (Fig. 2b) and pH – C_o at constant dose (figure not shown) as a function of adsorption capacity. No curvature is displayed in Fig. 2a since C_o was kept constant, and as a result there were no second-order terms in Eq. (7).

Interactive effect of parameters

Low doses resulted in high adsorption capacities (q_e), whilst high doses resulted in low q_e values (Fig. 2a). At the same time, the adsorption capacity slightly increased with increase in solution pH. Thus, the removal of nickel increases with increasing pH and decreasing dose. This trend predicted by the model is consistent with the experimental results shown in Table 2, in which the highest adsorption capacity of 65.9×10^{-3} mg/g was observed at low dose and high pH. It can be assumed from these results and
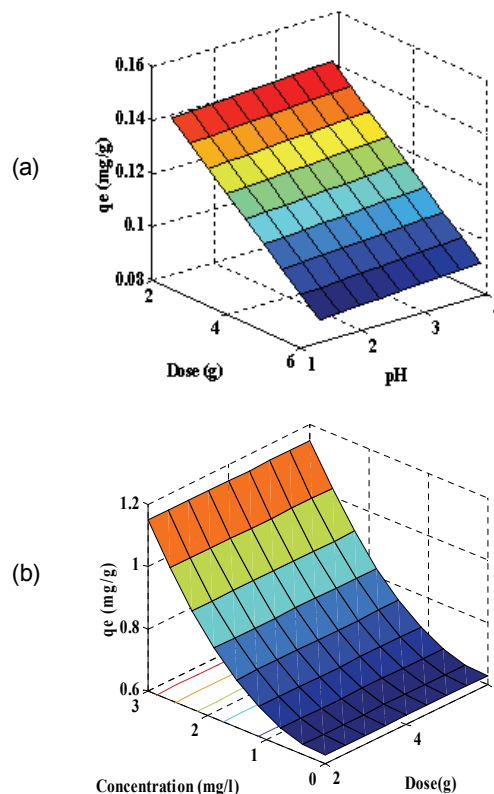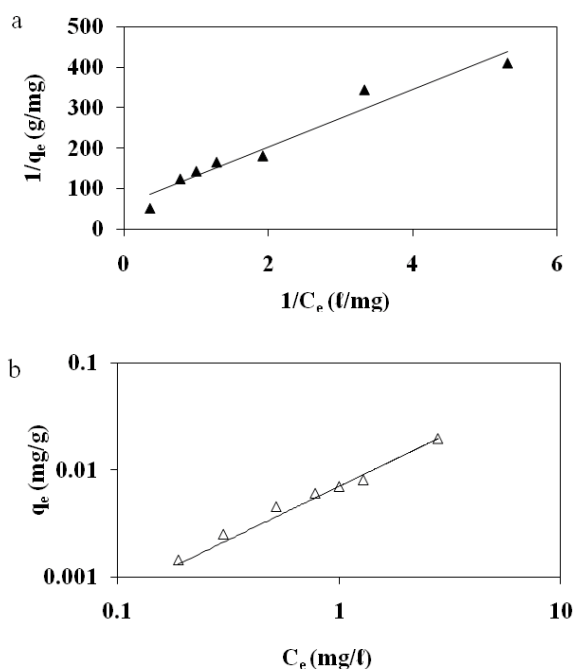

Figure 2
Adsorption capacity as a function of:
(a) dose and pH at constant initial concentration and
(b) initial concentration and dose at constant pH

the FT-IR spectra that the possible adsorption mechanism is probably due to ion exchange. High concentrations of H^+ ions at low pH of 1.3 may change the direction of reversible ion exchange equilibrium back to starting materials to give low q_e values (Yu et al., 2001). At a high pH of 3.9, relatively low concentration of H^+ ions means less competition for the adsorption site on sawdust particles, which results in high q_e values for nickel ions. The FT-IR spectra showed that the —OH and —COOH groups took part in the sorption process. However the sites responsible for the sorption process might not be exclusively due to the —OH and —COOH groups; other sites on the adsorbent may also contribute to the sorption process and physical adsorption is quite probable (Yu et al., 2001).

The decrease in adsorption capacity with increase in dose (Fig. 2a) could be due to the aggregation or overlapping of adsorption sites caused by overcrowding of the sawdust particles). Such aggregation would lead to decrease in total surface area of the sorbent and an increase in diffusional path length (Shukla et al., 2002). This trend is comparable to that reported by Ayyappan et al. (2003) for the removal of Pb(II) from aqueous solution using a low-cost adsorbent. Figure 2b shows that the sorption capacity of sawdust for nickel ions increased with increasing initial concentration. This trend can be explained by the fact that initial concentration provides a significant driving force of the concentration gradient to overcome all the mass transfer resistance between the solid and aqueous phase. This is in agreement with the findings of Ghorbani et al. (2008). The highest adsorption capacity obtained for nickel was 65.9×10^{-3} mg/g at low dose, high initial concentration and high pH.

Figure 3
Plot of (a) Langmuir and (b) Freundlich adsorption isotherm
(pH = 2.6, dose = 4.0 g, temperature = 25°C).

Adsorption isotherms

The adsorption data was correlated with commonly-used adsorption isotherms, namely; Langmuir and Freundlich models. The Langmuir isotherm was obtained by plotting $1/q_e$ versus $1/C_e$ (Fig. 3a) whilst the Freundlich isotherm was obtained by plotting q_e versus C_e on a logarithmic scale (Fig. 3b) and the constants obtained along with the correlation coefficients; R^2 values are shown in Table 4.

Table 4
Adsorption isotherm constants

Metal ion	Freundlich			Langmuir		
	$1/n$	K_F (mg/g)	R^2	q_{max} (mg/g)	K_L (ℓ/mg)	R^2
Nickel (II)	0.2105	0.005	0.9844	0.0100	0.8800	0.9110

The Freundlich model presented a high correlation coefficient ($R^2 = 0.9844$) as compared to that obtained for the Langmuir model (0.9110). Thus, it is evident that the equilibrium data conforms to the Freundlich model, which assumes heterogeneity in the surface binding process. This observation is consistent with the heterogeneous nature of pine sawdust which consists of different active sites such as —OH and —COOH groups as revealed by the FT-IR spectra (Fig. 1). The Langmuir model assumes homogeneity (i.e., all the active sites possess equal affinity) in the surface binding process and that is why it could not fit well to the experimental data. Agricultural adsorbents display heterogeneity (Gupta and Ali, 2004). This observation was also reported by Fritz and Schlünder (1981). The intensity of adsorption, $1/n$, lies between 0 and 1, which implies stronger interaction between the pine sawdust and the nickel (II) ions (Site, 2001). Disposal of pine sawdust after use can be accomplished by either composting or incineration (Marshall and Johns, 1996) and the metal residues could be recovered by subsequent treatment of the post-combustion ash (Wase and Forster, 1997).

Conclusions

Pine sawdust has been successfully used to remove nickel (II) ions from multi-component aqueous solutions. Assessment of the interactive effects of process variables (dose, pH and initial concentration) revealed that the system was sensitive to the tested process variables and the process was technically feasible. A combination of low adsorbent dose (2 g), high initial concentration (2.625 mg/ℓ) and high pH (3.9) resulted in the highest adsorption capacity of 65.9×10^{-3} mg/g. Fitting the experimental data to a second-order response surface model resulted in the model slightly over-predicting the adsorption capacities. Moreover, the adsorption process was better described by the Freundlich isotherm than the Langmuir model. Thus, the Freundlich isotherm can be used as a predictive tool. Further studies need to be carried out to investigate the effects of metal ion interaction during adsorption. In this study pine sawdust, a natural, abundant and low-cost adsorbent has shown adsorption capabilities for nickel (II) ions; hence, it could be an option in the quest to use waste to treat wastewater.

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