

African Journal of Biotechnology Vol. 11(39), pp. 9407-9415, 15 May, 2012
Available online at <http://www.academicjournals.org/AJB>
DOI: 10.5897/AJB11.2117
ISSN 1684-5315 © 2012 Academic Journals

Full Length Research Paper

Cobalt removal from wastewater using pine sawdust

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Accepted 27 September 2011

Agricultural wastes can cause environmental problems if not well managed, but there is a lot of potential to use these wastes as raw material in other processes. In this investigation, pine sawdust was evaluated as an adsorbent in the treatment of wastewater containing cobalt ions. A two-level three-factor full-factorial experimental design with centre points was used to study the interactive effect of the operating parameters in order to achieve the best conditions for the batch adsorption of cobalt ions. A response surface analysis was also conducted to further understand the interactions amongst the factors such as adsorbent dose, solution pH and initial concentration. In addition, adsorption isotherms, namely the Freundlich and Langmuir, were used to characterize the removal of cobalt from the wastewater. It was observed that the combined effect of low adsorbent dose, high pH and high initial concentration of wastewater resulted in the highest adsorption capacity. The Freundlich isotherm provided a better fit to the experimental data than the Langmuir isotherm. Moreover, pine sawdust showed adsorption capabilities for cobalt, and hence it could be an option in the quest to use waste to treat wastewater.

Key words: Adsorption, cobalt, isotherm, sawdust, wastewater.

INTRODUCTION

Agricultural activities such as the use of fertilizer, pesticide and herbicide contribute to environmental pollution. However, agricultural waste beneficiation is a concept that is rapidly gaining interest. Such beneficiation activities include energy production and wastewater treatment. Increased pollution of water bodies has resulted in strict government regulations on the discharge of toxic waste. In some instances, secondary wastewater treatment is inadequate and tertiary/advanced wastewater treatment methods are required. Advanced wastewater treatment methods include ion exchange (Cavaco et al., 2007), membrane separation (Mavrov et al., 2006),

electrolysis (Kurt et al., 2007) and adsorption (Onyango et al., 2004). Most of these methods are costly, require a high level of expertise and therefore limited in application by several end-users. For these reasons, adsorption technology has gained a wider application due to its inherent low cost, versatility and robustness. Thus, the use of agricultural waste-derived adsorbents for wastewater treatment constitutes the main focus of this study.

Recalcitrant organic compounds and non biodegradable inorganic compounds are removed using advanced methods together with secondary methods (Singh et al., 2007). Since industries are forced to comply with stringent effluent discharge regulations, there has been increased research regarding advanced methods of wastewater treatment to remove toxins in wastewater streams. Unfortunately, large capital and running costs are associated with advanced methods. As a measure to

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Table 1. Experimental variable levels and factors.

Factor	Coded symbol	Levels		
		-1	0	1
Adsorbent dose (g/L)	x_1	20.0	40.0	60.0
pH	x_2	1.3	2.6	3.9
[Co(II) and Ni(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

reduce costs, the concept of using an advanced method of wastewater treatment, such as adsorption with agricultural adsorbents has been applied. In doing so, solid wastes 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), among others, can be used to treat wastewater. These materials can be employed to treat wastewater streams such as acid mine drainage, and those from petrochemical industries and semiconductor fabrication plants.

It is important to remove cobalt from wastewater due to its known toxicity. The effects of acute cobalt poisoning in humans are very serious; among them are asthma-like allergy, damage to the heart, causing heart failure, damage to the thyroid and liver. Cobalt may also cause mutations (genetic changes) in living cells (Rangaraj and Moon, 2002). Furthermore, metallic cobalt or cobalt sulphate are the most plausible causes of cobalt asthma. Also, cobalt has a role in the development of diffuse interstitial lung disease (Linna et al., 2003). With a better awareness of the problems associated with cobalt, research studies related to the method of removing cobalt from wastewater have increasingly drawn attention. The objectives of this study are to determine the adsorption capacity of pine sawdust in terms of mass of cobalt ions adsorbed per unit mass of adsorbent and to investigate the interactive effects of adsorbent dose, pH and initial concentration on adsorption capacity.

MATERIALS AND METHODS

Adsorbent preparation and characterization

Pine sawdust collected from a local company was ground and sieved to a particle size range of 500 to 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 to provide additional carboxyl groups to those on pine sawdust surfaces in order to substantially increase its metal uptake. The mixture was stirred using the Rushton turbine impellers 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 to remove the moisture, after which the temperature was raised to 120°C and maintained for 90 min. The sawdust was allowed to cool and washed five times using hot distilled water (60 to 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 that could possibly emanate from pine sawdust, especially in cases where it had been previously treated with pesticides.

The x-ray diffraction (XRD) spectra of the pine sawdust was obtained using an x-ray diffractometer (PANalytical, Philips PW 1710, EA Almelo, the Netherlands) with Cu K α radiation at 40 kV and 50 mA to determine the present phases (amorphous or crystalline). The spectra were recorded from 10 to 65° at a scan rate of 1.2° min⁻¹. In addition, Fourier Transform Infrared (FT-IR) spectra of the pine sawdust before and after adsorption were recorded in the range 500 to 4000 cm⁻¹ on an FT-IR (Bruker, Tensor 27 TPR, Ettlingen, Germany) system to explore the number and positions of the functional groups responsible for adsorption. Also, the surface morphology of the adsorbents was visualized via a scanning electron microscope (SEM, Joel JSM-840, Tokyo, Japan) operated at the accelerating voltage of 20 keV.

Synthesis of wastewater

The stock solutions (1000 mg/L) of Co(II), Ni(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 (centre point) was ten 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 ten and taken as the zero levels in the present study. This was to raise the concentrations to the levels that were less susceptible errors compared to the low values reported. Further, 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 that heavy metal concentration range is 0.1 to 100 mg/L. The pH of the solutions was adjusted using either dilute HNO₃ or NaOH. A high pH level (+1) 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, Columbus, OH, USA) and all the chemicals used were of analytical grade supplied by Merck Chemical Company (Johannesburg, South Africa).

Statistical design of experiments

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 2³ full-factorial design with four centre point runs leading to 12 experimental runs were performed (Table 2). The centre point replicates were chosen to verify any change in the estimation procedure and as a measure of the precision property (Ravikumar et al., 2007). For statistical

Table 2. The two-level three factor full-factorial design with four centre points.

Standard Order	Coded levels			Actual levels			$q_e \times 10^{-3}$ (mg/g)	
	x_1	x_2	x_3	Dose (g/L)	pH	C_o (mg/L)	Observed	Predicted
1	-1	-1	-1	20.0	1.3	0.875	11.50	8.01
2	+1	-1	-1	60.0	1.3	0.875	1.96	5.45
3	-1	+1	-1	20.0	3.9	0.875	24.50	28.00
4	+1	+1	-1	60.0	3.9	0.875	5.38	1.89
5	-1	-1	+1	20.0	1.3	2.625	13.50	17.00
6	+1	-1	+1	60.0	1.3	2.625	15.40	12.00
7	-1	+1	+1	20.0	3.9	2.625	56.00	53.00
8	+1	+1	+1	60.0	3.9	2.625	20.40	24.00
9	0	0	0	40.0	2.6	1.750	7.92	7.96
10	0	0	0	40.0	2.6	1.750	8.08	7.96
11	0	0	0	40.0	2.6	1.750	7.95	7.96
12	0	0	0	40.0	2.6	1.750	8.00	7.96

calculations, the variables X_i were coded as x_i according to the following relationship:

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

Where x_i is the independent variable coded value; X_i is the 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 adsorbent dose, pH and initial concentration 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.

The quadratic model for predicting the adsorption capacity for cobalt was expressed according to Equation 2:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (2)$$

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_0 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 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 (MathWorks, Natick, Massachusetts) 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.

Batch adsorption procedure

A 100 ml wastewater solution was contacted with the desired mass of sawdust in 250 ml Erlenmeyer flasks. Blank solutions (solution without the adsorbent) were also included and the flasks were covered with parafilm. The mixture was shaken at 250 rpm in an incubator with shaking platform (FSIM-SPO16, Labcon, Johannesburg, South Africa) 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, Victoria, Australia). The response (adsorption capacity, q_e) was calculated as:

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

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), and m is a known mass of adsorbent (g).

Adsorption isotherms

In order to optimize the design of an adsorption system for the removal of adsorbate, it is important to obtain the equilibrium adsorption data. Thus, the equilibrium adsorption isotherm data for cobalt was generated by contacting a fixed amount of 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 rpm in an incubator with shaking platform at 25°C for 45 h. At the end, the residual concentrations of the cobalt 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:

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

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) and 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 linearized logarithmic form (Equation 5):

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

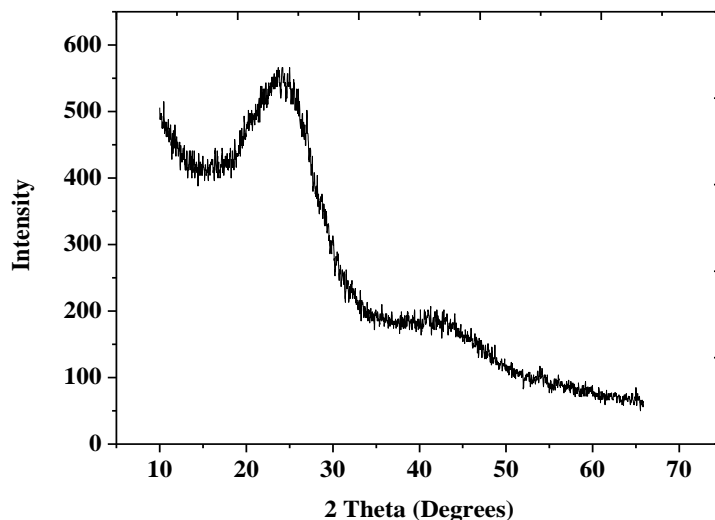


Figure 1. The X-ray diffraction profile (diffractogram) of pine sawdust.

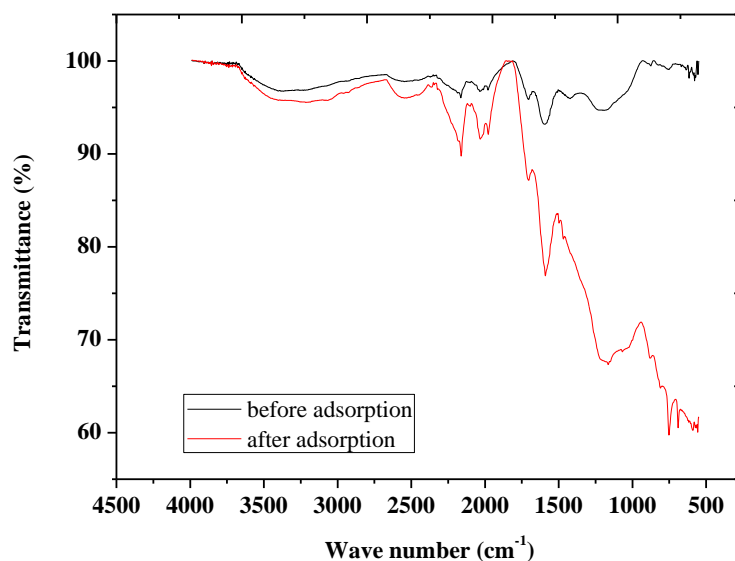


Figure 2. FT-IR spectra of pine sawdust before and after adsorption of cobalt ions.

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

RESULTS

Characterization of the adsorbent

The X-ray diffraction (XRD) technique is a powerful tool to analyze the crystalline nature of the materials. The X-ray diffraction pattern of pine sawdust presented in Figure 1 shows two very broad diffraction peaks; a major peak appears at 25 and a minor one at 40 degrees. The

spectra shown in Figure 2 display a number of absorption peaks, indicating the complex nature of the surfaces of pine sawdust. Between the wave number of 2250 and 4000 cm^{-1} , the transmittance for sawdust before and after adsorption did not change much. However, between 1750 and 750 cm^{-1} the transmittance after adsorption was significantly lower than that for the sawdust before adsorption. The SEM image analysis of pine sawdust presented in Figure 3 reveals that the surfaces are rough and protrusions can be seen throughout the micrographs.

It is clear that the modified pine sawdust (Figure 3b), has a considerable number of pores and there is good possibility for cobalt to be adsorbed into these pores as

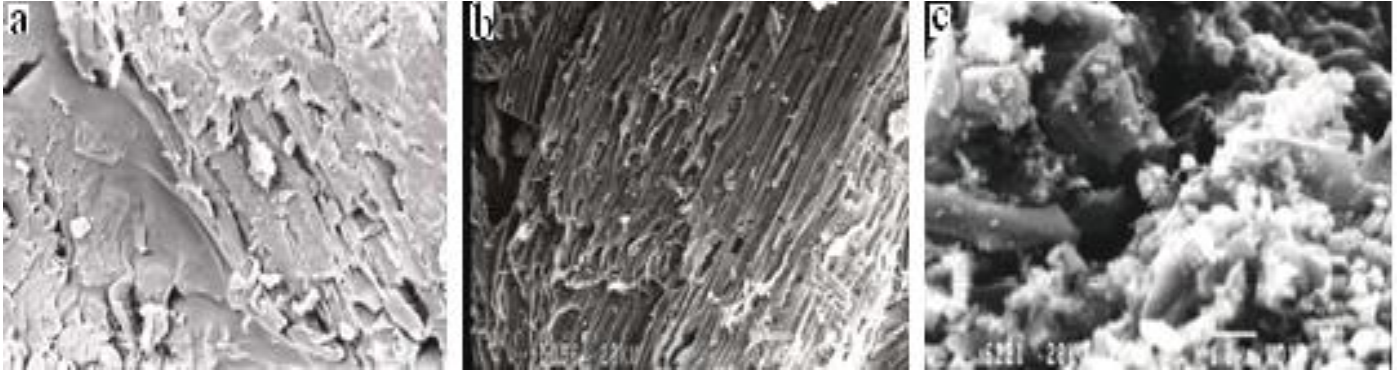


Figure 3. SEM images of pine sawdust (a) before surface modification (b) after surface modification and (c) after adsorption at 400 times magnification.

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	2.17E-03	7	3.11E-004	12.77	0.0134
Residual	9.75E-05	4	2.44E-005		
Lack of fit	9.75E-05	1	9.74E-005	5.01	0.0503
Pure error	2.97E-08	3	9.89E-009		
Total	2.28E-03	11			

$$R^2 = 0.9572.$$

compared to the raw material (Figure 3a). Surface coverage in the form of flakes indicates the presence of inorganic elements that could be heavy metals especially after adsorption (Figure 3c).

Fitting of a quadratic model

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

$$q_{Co} = 0.993 + 0.0157x_2 - 0.0008x_1x_3 - 0.0279x_2x_3 + 1.04x_3^2 \quad (6)$$

where q_{Co} is the predicted adsorption capacity for cobalt ions and x_1 , x_2 , x_3 are the coded values of the test variables, adsorbent dose (g/L), 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 summarized in Table 3. In this work, the model acceptance was made on the basis of 95% confidence level. A low standard deviation of 4.94×10^{-3} indicates a better precision and reliability of the experiments carried out. The model presented a relatively high R^2 value (0.9572) explaining 95.72% of the variables; dose, pH and initial concentration in the response and it indicates that 4.28% of the total variation is not explained by the

model.

The model equation (6) has dimensionless input values that is, it consist 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 were deduced from equation 1 and substituted into the model equation (6) upon rearrangement, from which equation 7 was obtained:

$$q_{Co} = 1.76 + 0.0299pH - 0.000201Dose.C_o - 0.0101pH.C_o + 0.59C_o^2 \quad (7)$$

Equation 7 was then used to plot the three dimensional surfaces depicting the interactive effects of adsorbent dose and pH at constant C_o (Figure 4), adsorbent dose and C_o at constant pH (Figure 5a), pH and C_o at constant adsorbent dose (Figure 5b), on the adsorption capacity of pine sawdust for cobalt.

Table 2 lists the experimental adsorption capacities obtained for different combinations of the three factors namely: adsorbent dose, pH and initial concentration. Runs 8 to 12 refer to centre points corresponding to the zero level of each factor. The highest adsorption capacity obtained was 56×10^{-3} mg/g, which occurred at low adsorbent dose and high initial concentration and pH. Figure 4 shows that low adsorbent doses resulted in high adsorption capacities (q_e), while high doses resulted in low q_e values. At the same time, the adsorption capacity

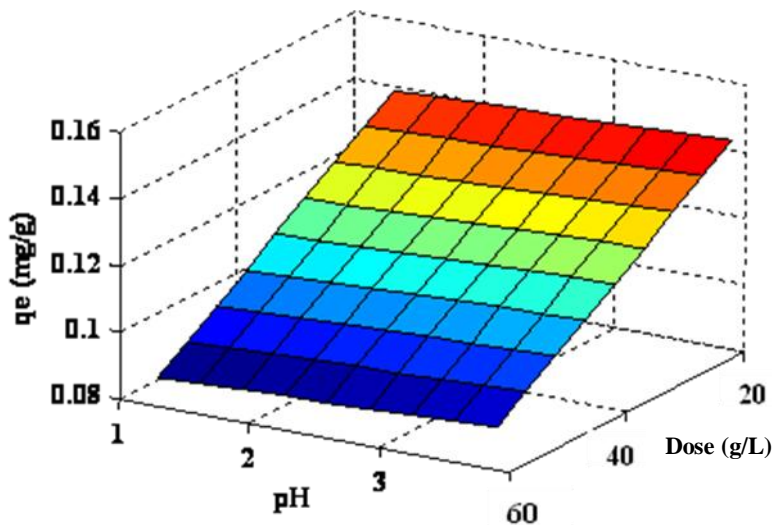


Figure 4. The response surface plot showing the interactive effects of pH and adsorbent dose on adsorption capacity at constant initial concentration.

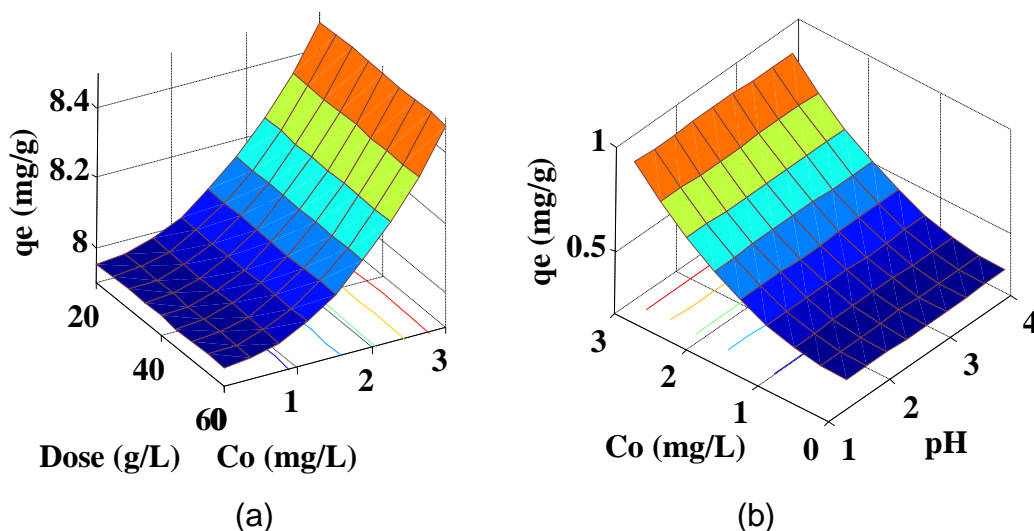


Figure 5. The response surface plot showing the interactive effects of (a) adsorbent dose and initial concentration at constant pH and (b) initial concentration and pH at constant adsorbent dose.

increased with increasing solution pH. Thus, the removal of cobalt increases with increasing pH and decreasing adsorbent dose. This trend predicted by the model is consistent with the experimental results shown in Table 2, in which the highest adsorption capacity of 56×10^{-3} mg/g was observed at low adsorbent dose and high pH.

Equilibrium modelling

The adsorption data was correlated with commonly used adsorption isotherms namely; Freundlich and Langmuir models. Freundlich isotherm was obtained by plotting q_e

versus C_e on a logarithmic scale (Figure 6a), whereas the Langmuir isotherm was obtained by plotting $1/q_e$ versus $1/C_e$ (Figure 6b). Furthermore, all the isotherm constants (model parameters) together with the R^2 values (goodness of fit criterion) computed by linear regression for the two types of isotherms were summarized in Table 4.

DISCUSSION

The absence of a sharp peak for the XRD analysis of pine sawdust in Figure 1 shows that the major part of the

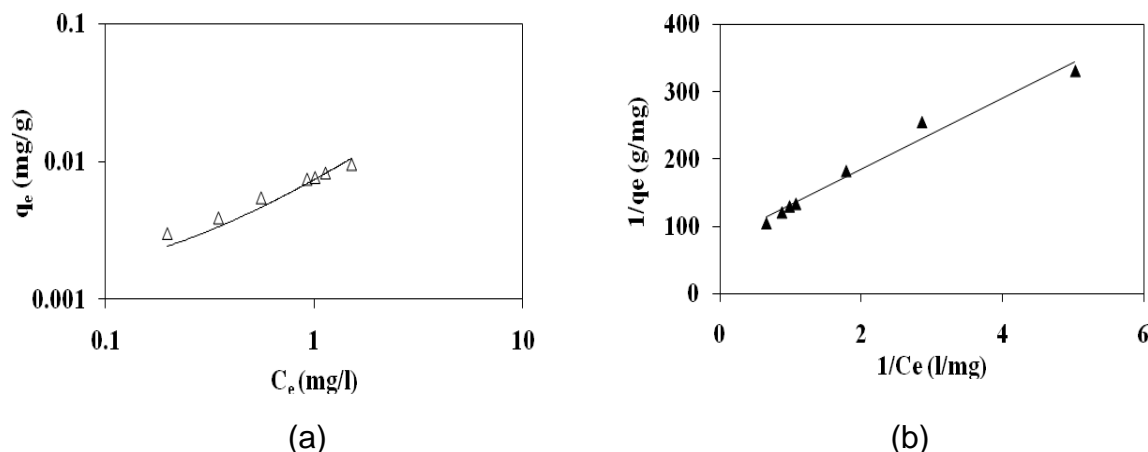


Figure 6. Linear regression analysis for: (a) Freundlich and (b) Langmuir adsorption isotherm.

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
Cobalt (II)	0.2151	0.0054	0.9860	0.0111	0.8810	0.9764

adsorbent is amorphous. This is an advantageous property for a good adsorbent (Madhava et al., 2008). The only two broad peaks at around 24.4 and 42.3° could be attributed to the presence of carbon and graphite (Bouchelta et al., 2008). If the material under investigation is crystalline, well-defined peaks are observed while non-crystalline or amorphous systems show a hollow instead of well-defined peak (Namasivayam and Kavitha, 2006). It has been proved that pine sawdust is amorphous. On the other hand, it has been shown that citric acid provides additional carboxyl groups to those on pine sawdust surfaces and substantially increases its metal uptake capacity (Mcsweeney et al., 2006). Also, from the particle morphology, it is apparent that pine sawdust is suitable to be used as an adsorbent.

The peak at 3381.2 cm^{-1} before adsorption (Figure 2) 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. Further, the peak at 1184.3 cm^{-1} before adsorption is associated with C—O stretching vibrations in carboxylic acids (Pavia and Lampman, 1987) and it shifted to 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). Additionally, the band at 1597.0 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).

It can be assumed from the results presented in Table 2, Figure 4 and the FT-IR spectra that the possible adsorption mechanism is probably due to ion exchange. High concentration 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 result in high q_e values for cobalt 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).

In order for a term to be significant at the 95% confidence level (Table 3), the calculated probability should be lower than 0.05 (Bhatia et al., 2009). The ANOVA test revealed that this regression model is statistically significant, as is evident from the Fisher's F -test with a very low probability value (<0.0134); 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 0.0503 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). The decrease in adsorption capacity with increase in adsorbent dose (Figure 4) 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 adsorbent 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. Figures 5a and b shows that the adsorption capacity of pine sawdust for cobalt 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 Freundlich model presented a high correlation coefficient ($R^2 = 0.9860$) as compared to (0.9764) for the Langmuir model. 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. The Langmuir model assumes homogeneity (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. Moreover, agricultural adsorbents display heterogeneity (Gupta and Ali, 2004). Such 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 cobalt (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).

Conclusion

Agricultural waste has been employed to treat synthetic industrial wastewater in a batch system. Following the batch adsorption experiments, the data obtained was used to calculate the adsorption capacity, model adsorption isotherms and conduct a response surface analysis. It was found that adsorbent dose, pH and initial concentration have a notable effect on the uptake of cobalt by the pine sawdust. Low adsorbent doses and high initial concentrations resulted in high adsorption capacities. Furthermore, a high pH in combination with the above factors resulted in the highest adsorption capacity of 56×10^{-3} mg/g. Hence, the area of high initial concentration and pH and low adsorbent dose, should be the focus of future research.

Fitting the experimental data to a second order response surface model resulted in the model slightly over-predicting the adsorption capacities. However, surface plots revealed that the general trend shown by the experimental data was evident in the model; that is, adsorption capacity increased with increasing initial concentration and pH and decreasing adsorbent dose. The second order response surface model was also found to be statistically significant. On the other hand, the experimental data was better described by the Freundlich isotherm than the Langmuir isotherm since pine sawdust conformed to the assumption of heterogeneity in the surface binding process. Moreover, pine sawdust has shown adsorption capabilities for cobalt, and hence it could be an option in the quest to use waste to treat wastewater. However, the adsorption capacity of the saw dust needs to be improved for its application to be economical.

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