

Short communication

Removal of nickel from aqueous solutions by sawdust

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Abstract

The main parameters influencing Nickel (II) metal sorption on maple sawdust were: initial metal ion concentration, amount of adsorbent, and pH value of solution. The maximum percent metal removal was attained after about 1 h. The greatest increase in the rate of adsorption of metal ions on sawdust was observed for pH changes from 2 to 5. An empirical relationship has been obtained to predict the percentage Nickel (II) removal at any time for known values of sorbent and initial sorbate concentration. The experimental results provided evidence for chelation ion exchange as the major adsorption mechanisms for binding metal ions to the sawdust. The adsorbent can be effectively regenerated using 0.1 M strong acid and reused.

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1. Introduction

In recent years considerable attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural materials such as waste wool, nut wastes, tree barks, modified cotton and sawdust [1–6]. Many agricultural byproducts such as bark and sawdust are low cost (or of no economic value) materials. Sawdust from timber industry is often considered as waste material and widely available. Iron impregnated sawdust has been used as an adsorbent for phenolic compounds. Some previous investigations on the removal of heavy metal ion with sawdust have been reported [7–9]. The present study undertakes the adsorption capacity of maple sawdust for the removal of Ni (II) from aqueous systems.

2. Experimental procedure

The maple sawdust used as an adsorbent was obtained from a local industry. In each experiment, initial concentra-

tions of Nickel (II) of 1.0, 3.0, 5.0, and 10.0 mg/L were used. The untreated maple sawdust was used as an adsorbent in the bench-scale studies. Typically, 1.0–5.0 g sawdust was added in separate flasks each containing 100 mL of the test solution of Ni. The mixture of the test solution and maple sawdust was stirred in a shaker at 80 rpm. Aliquots were taken after 5, 30, 60, 180 and 360 min. The suspensions were centrifuged and the Ni concentrations were analyzed using a Perkin-Elmer 2100 Atomic Absorption Spectrophotometer.

The adsorption experiments were carried out at room temperature. Twenty-four hours was judged to be sufficient to reach equilibrium. The pH of the suspension in one set of experiments was adjusted with 0.1 M NaOH and 0.2 M HNO₃.

3. Results and discussion

Various mechanisms control the kinetics in the sorption phenomena [10]. Four major rate-limiting steps are generally cited: (1) mass transfer of solute from solution to the boundary film, (2) mass transfer of metal ions from boundary film to surface, (3) sorption of ions onto sites and (4) internal diffusion of solute. The third step is assumed to be

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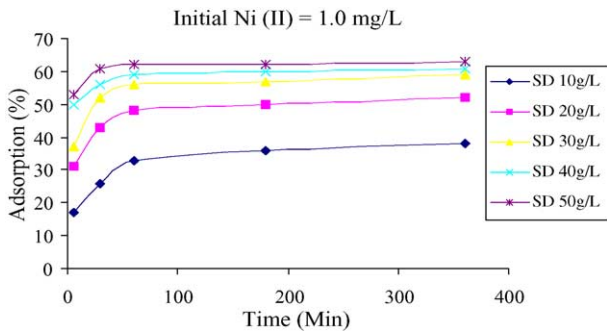


Fig. 1. Percent removal of nickel (1 ppm) vs. time.

very rapid and non-limiting in this kinetic analysis. The first and the second steps are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. The fourth one is an intraparticle diffusion resistance step.

The sorption rate (q_t) is calculated according to the con-
version:

$$q_t = (C_0 - C_t)V/m = (1 - C_t/C_0)VC_0/m \quad (1)$$

The sorption kinetics of the experiment is influenced by various factors. The main parameters influencing metal sorption were investigated: initial metal ion concentration, amount of adsorbent and pH value of solution.

3.1. Effect of time and nickel concentration

The removal of Ni (II) increases with time and attains saturation in about 100–200 min. Basically, the removal of sorbate is rapid but it gradually decreases with time until it reaches equilibrium. The results for 1.0, 5.0, 10.0, and 25.0 mg/L concentrations of nickel are presented in Figs. 1–4. The plots represent the percentage removal of nickel versus the contact time for the initial metal concentrations. The plots reveal that maximum percent metal removal was attained after about 1 h of stirring time. The rate of percent removal becomes almost insignificant due to a quick exhaustion of the adsorption sites. The rate of percent metal removal is higher in the beginning due to a larger surface area of the sawdust being available for the adsorption of the metals. Af-

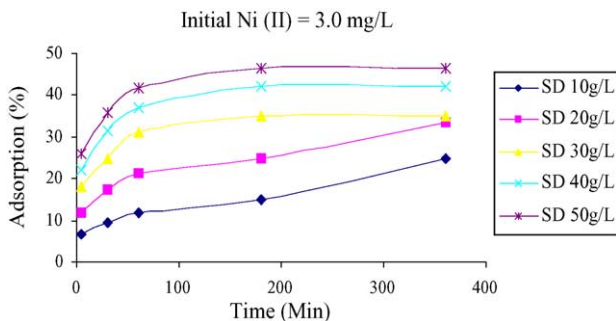


Fig. 2. Percent removal of nickel (3 ppm) vs. time.

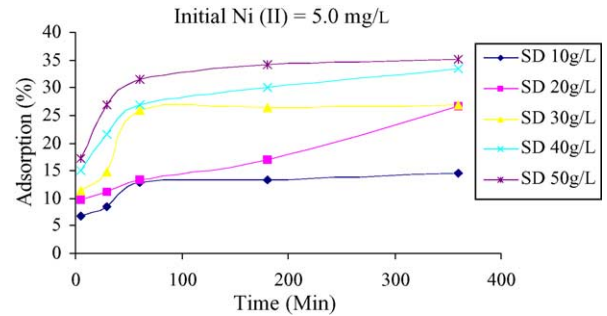


Fig. 3. Percent removal of nickel (5 ppm) vs. time.

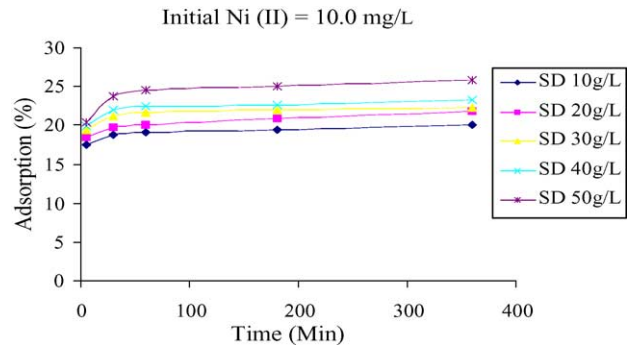


Fig. 4. Percent removal of nickel (10 ppm) vs. time.

ter the adsorbed material forms a 1 molecule (actually ion) thick layer, the capacity of the adsorbent gets exhausted and then the uptake rate is controlled by the rate at which the sorbate is transported from the exterior to the interior sites of the adsorbent particles. The data indicates that the initial metal concentration determines the equilibrium concentration, and also determines the uptake rate of metal ion and the kinetic character.

3.2. The effect of sawdust and sorbate concentrations

The effect of sawdust concentrations is presented in Fig. 5. It can easily be inferred that the percent removal of metal ions increases with increasing weight of the sawdust. This is due to the greater availability of the exchangeable sites or

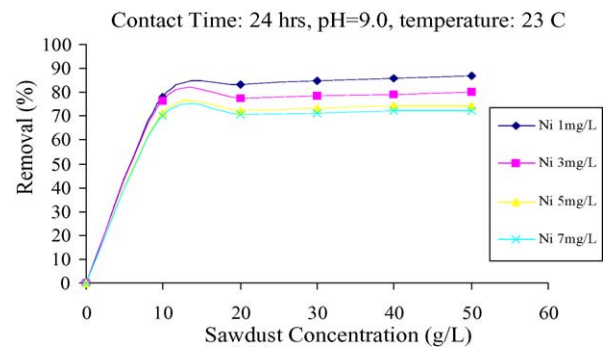


Fig. 5. Effect of sawdust concentration on removal of nickel (II) concentration of sawdust vs. percent removal of Ni (II).

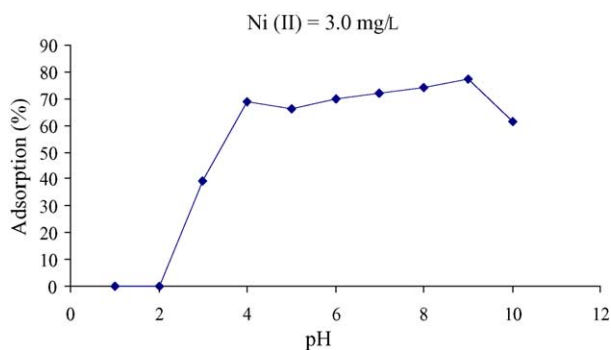


Fig. 6. Effect of pH variation on nickel removal through adsorption on sawdust.

surface area at higher concentration of the adsorbent. The effect of sorbate concentration is also shown in Fig. 5. In the case of low concentrations, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional adsorption becomes independent of initial concentrations. However, at higher concentrations the available sites of adsorption become fewer, and hence the percentage removal of metal ions depend upon the initial concentration.

3.3. The effect of pH

The effect of pH is presented in Fig. 6. The effect of pH on adsorption of nickel (II) was studied at room temperature by varying the pH of metal solution–sawdust suspension from 1 to 10. In pH range of 1–2, there is little or no adsorption. The percent adsorption increases in the pH range of 3–9, showing the maximum adsorption at pH 9, then the percent adsorption decreases in pH range of 9–10. The greatest increase in the rate of adsorption of metal ions on sawdust was observed for pH changes from 2 to 5 for nickel (II).

The effect of pH can be explained in terms of pH_{zpc} (zero point of charge) of the adsorbent [11–13]. The pH_{zpc} of sawdust is at 6.0, and below this pH surface charge of the adsorbent is positive. On the other hand, at pH less than pH_{zpc} the predominant metal species [M^{n+} and $M(OH)^{(n-1)+}$] are positively charged, therefore, uptake of metals in the pH range of 2–6 is a $H^+ - M^{n+}$ exchange process. The possible sites on sawdust for sorption are due to the $-COOH$ and $-C_6H_5-OH$ groups. Other sites on the modified sawdust can also contribute to the sorption process. In acidic medium the electromeric effect of the amide group in sawdust leads to surface protonation and possesses net positive charge on the surface. These H^+ ions from the surface are also exchanged with positively charged sorbate species with subsequent coordination of a metal ion.

An increase in pH above pH_{zpc} shows a slight increase in adsorption in which the surface of the adsorbent is negatively charged and the sorbate species are still positively charged. As the adsorbent surface is negatively charged as well, the increasing electrostatic attraction between positive sorbate

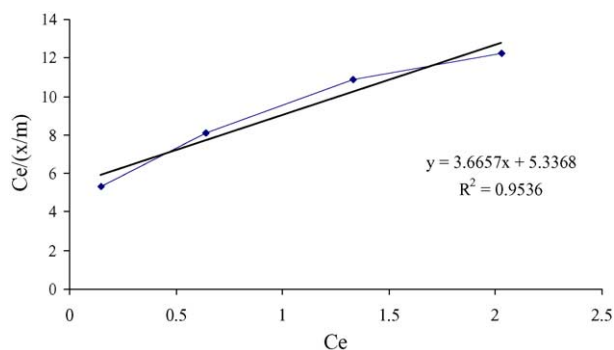


Fig. 7. Langmuir adsorption isotherms of nickel on sawdust.

species and adsorbent particles would lead to increase adsorption of metal ions. This is in accordance with the earlier observations [14]. Decrease in removal of metal ions at lower pH is apparently due to the higher concentration of H^+ ions present in the reaction mixture, which compete with the M^{2+} ions for the adsorption sites of sawdust. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes.

3.4. Adsorption isotherms

The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. The data for the uptake of metal ions by sawdust has been processed in accordance with a linearized form of the Langmuir isotherm equation:

$$C_e/(x/m) = 1/KV_m + C_e/V_m \quad (2)$$

where C_e is the equilibrium solution concentration, x/m the amount adsorbed per unit mass of adsorbent, m the mass of the adsorbent, V_m the monolayer capacity, and K an equilibrium constant that is related to the heat of adsorption by equation:

$$K = K_0 \exp(q/RT) \quad (3)$$

where q is the heat of adsorption. The linear Langmuir equation for nickel on sawdust in distilled water system was determined to be:

$$C_e/(x/m) = 3.6657C_e + 5.3368 \quad (4)$$

and the Langmuir plot is shown in Fig. 7. The data for the uptake of metal ions by sawdust was also processed in accordance with a linearized form of the Freundlich isotherm equation:

$$\log x/m = \log K_c + 1/n \log C_e \quad (5)$$

where K_c and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, and other parameters is the same as in the Langmuir isotherm. $\log x/m$ can be plotted against $\log C_e$ with slope $1/n$ and intercept $\log K_c$.

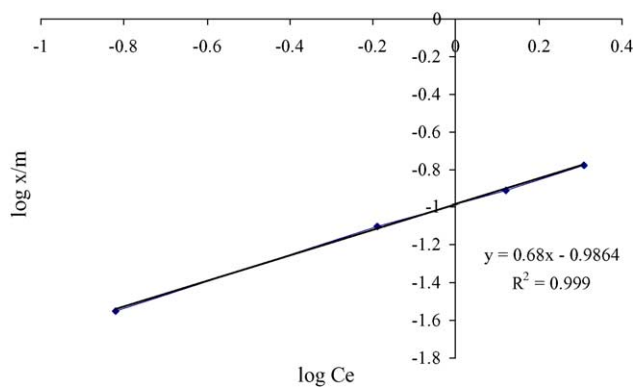


Fig. 8. Linear Freundlich isotherm of nickel sorption on sawdust.

This is shown in Fig. 8. The linear Freundlich equation for nickel from experimental result is determined to be:

$$x/m = 0.1032C_e^{0.6800} \quad (6)$$

The experimental data is best represented by the Freundlich equation as can be seen in Figs. 7 and 8.

4. Conclusions

Maple sawdust is found to be a promising adsorbent for the removal of nickel from untreated industrial wastewater. The percentage uptake is highly dependent on the initial concentration of the sorbate and sorbent. High removal have been recorded at low surface loading. This is important in terms of likely industrial applications. The maple sawdust can be regenerated and reused. Adsorption of the nickel is dependent on the initial concentrations of adsorbent, sorbate, time of contact and pH. Maximum percent removal of nickel (II) is at pH 9.0, while the minimum removal is at pH 2.0.

Acknowledgement

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