



Adsorption of chromium from aqueous solutions by maple sawdust

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Abstract

This paper presents the data for the effect of adsorbent dose, initial sorbate concentration, contact time, and pH on the adsorption of chromium(VI) on maple sawdust. Batch adsorption studies have been carried out. An empirical relationship has been obtained to predict the percentage chromium(VI) removal at any time for known values of sorbent and initial sorbate concentration. Under observed test conditions, the equilibrium adsorption data fits the linear Langmuir and Freundlich isotherms. The experimental result inferred that chelation ion exchange is one of the major adsorption mechanisms for binding metal ions to the maple sawdust.

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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 [1–9]. 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 preliminary investigations on the removal of heavy metal ion with sawdust have been reported [8]. The present study undertakes the adsorption capacity of maple sawdust for the removal of Cr(VI) from aqueous systems.

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2. Experimental procedure

The maple sawdust, used as an adsorbent, was obtained from a local industry. In each experiment, initial concentrations of chromium(VI) 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 Cr. The mixture of the test solution and maple sawdust was stirred in a shaker at 80 rpm continuously for several hours. Aliquots were drawn after variable hours and suspensions were centrifuged in centrifuge tubes for 5 min at 3000 rpm. Then, the metal concentrations were analyzed by a Perkin-Elmer 2100 atomic absorption spectrophotometer.

For isotherm and the pH-effect experiment, 24 h time period 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. The adsorption experiments were carried out at room temperature. The effect of pH, effects of initial Cr concentration, the consumption of sawdust, kinetics, and isotherms were observed.

3. Results and discussion

Various mechanisms and steps in adsorption phenomena can control the kinetics. Four major rate-limiting steps are generally cited [10]: (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 very rapid and non-limiting in this kinetic analysis: sorption is a rapid phenomenon. 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 model used to calculate the external mass transfer rate is described by the following equation:

$$\frac{dC_t}{dt} = -\beta_L S(C_t - C_s) \quad (1)$$

where β_L is the external mass transfer coefficient, S the specific surface, C_t the metal ion concentration in solution, and C_s the surface concentration of solute on the adsorbent. According to complementary hypotheses such as a surface concentration of solute on the sorbent ($C_s \rightarrow 0$) negligible at time $t = 0$, and the intraparticle diffusion rate also negligible, Eq. (1) can be simplified to:

$$\frac{d(C_t/C_0)}{dt} = -\beta_L S \quad (2)$$

according to boundary conditions and the hypothesis formulated:

$$C_t \rightarrow C_0$$

when

$$t \rightarrow 0$$

So the external mass transfer rate, $-\beta_L S$, is approximated by the initial slope of the C_t/C_0 graph and is obtained by the derivative (at $t = 0$) of the polynomial linearization of $C_t/C_0 = f(t)$, where C_0 is the initial metal concentration in solution. Theoretical treatments of intraparticle diffusion rates yield rather complex equations differing in form for different shapes of particle. Fick's laws of diffusion through solids are expressed by:

$$J = -D \left(\frac{dC}{dX} \right) \quad (3)$$

$$\frac{dC}{dt} = D \left(\frac{d^2C}{dX^2} \right) \quad (4)$$

where J is the rate of transfer per unit area of the section, X the space co-ordinate and D the diffusion coefficient.

The sorption rate (q_t) is calculated according to the conversion:

$$q_t = \frac{(C_0 - C_t)V}{m} = \left(\frac{1 - C_t}{C_0} \right) \frac{VC_0}{m} \quad (5)$$

The adsorption 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 [11–13].

3.1. Effect of time

The removal of Cr(VI) increases with time and attains saturation in about 100–200 min, shown in Figs. 1–4. Basically, the removal of sorbate is rapid but it gradually decreases with time until it reaches equilibrium. The percentage uptake is highly dependent on the initial concentration of the sorbate and sorbent. High removals have been recorded at low surface loading. This is important in terms of likely industrial applications.

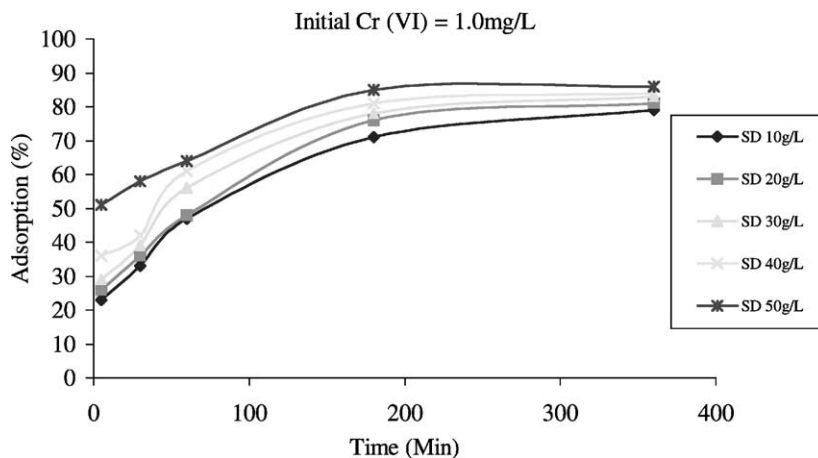


Fig. 1. Percent removal of chromium (1 ppm) vs. time.

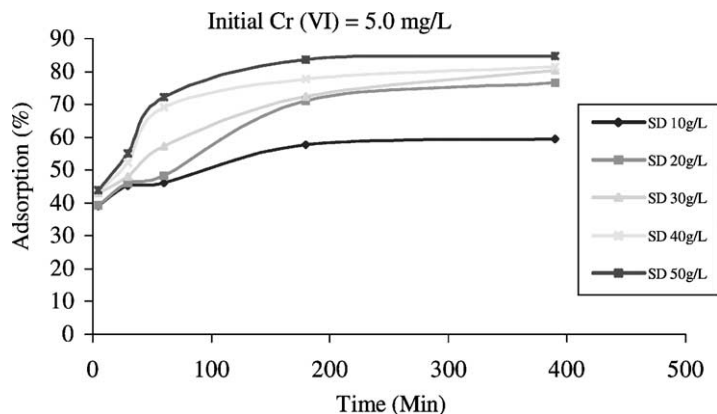


Fig. 2. Percent removal of chromium (5 ppm) vs. time.

3.2. Effect of chromium concentration

The results for 1.0, 5.0, and 10.0 mg/l concentrations of chromium are presented in Fig. 5. The plots represent the percentage removals of chromium versus the contact time for the initial metal concentrations. The plots reveal the maximum percent metal removal was attained after about 1 h of stirring time. There does not seem to be much benefit from a stirring time longer than these stir. 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. After the adsorbed material forms a one 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

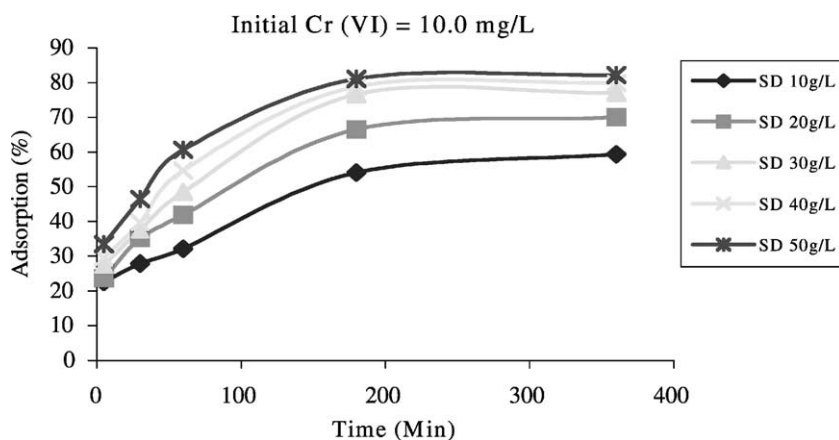


Fig. 3. Percent removal of chromium (10 ppm) vs. time.

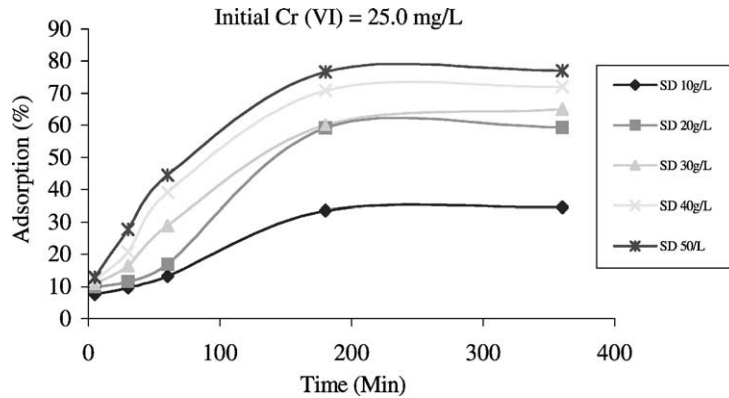


Fig. 4. Percent removal of chromium (25 ppm) vs. time.

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.

The effect of sorbate concentration is 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 sawdust concentrations

The effect of sawdust concentrations is presented in Figs. 6 and 7. It can easily be inferred that the percent removal of metal ions increases with increasing weight of the sawdust.

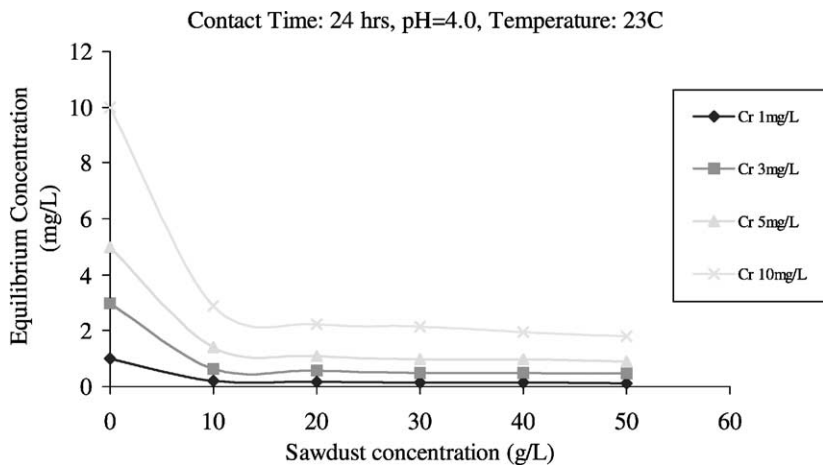


Fig. 5. Effect of sorbate concentration on removal of chromium(VI): initial concentration of Cr(VI) vs. percent removal of Cr(VI).

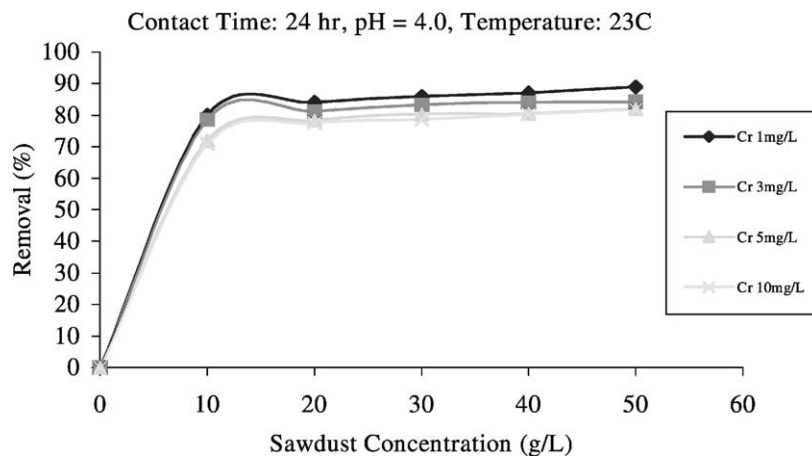


Fig. 6. Effect of concentration of sawdust on equilibrium concentration of chromium.

This is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent.

3.4. The effect of pH

The effect of pH is presented in Fig. 8. The effect of pH on adsorption of chromium(VI) 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 3–10, showing the maximum adsorption at pH 5. The greatest increase in the rate of adsorption of metal ions on sawdust was observed for pH changes from 2 to 5 for chromium(VI).

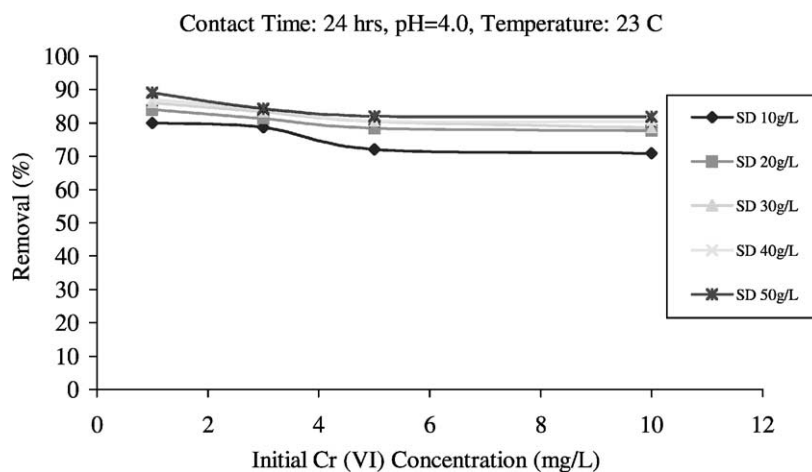


Fig. 7. Effect of concentration of sawdust on percentage removal of chromium.

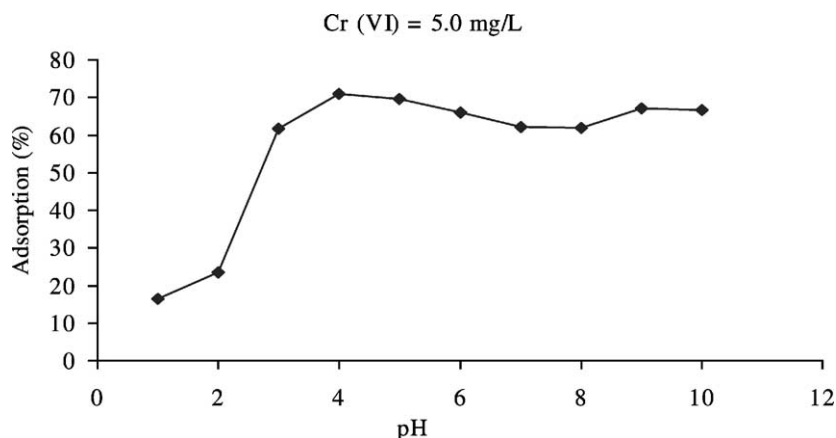
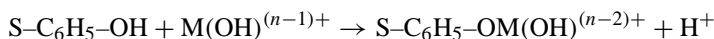
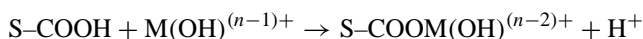
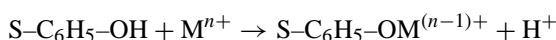
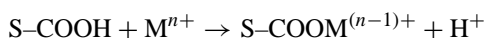


Fig. 8. Effect of pH on removal of chromium.

The effect of pH can be explained in terms of pH_{zpc} (zero point of charge) of the adsorbent. The pH_{zpc} of sawdust is at 6.0, and below this pH, the surface charge of the adsorbent is positive. On the other hand, at pH less than pH_{zpc} , the predominant metal species [M^{n+} and $\text{M}(\text{OH})^{(n-1)+}$] are positively charged, therefore, uptake of metals in the pH range of 2–6 is a $\text{H}^+ - \text{M}^{n+}$ exchange process. The possible sites on sawdust for specific adsorption includes H^+ ions in $-\text{C}_6\text{H}_5-\text{OH}$ and $-\text{COOH}$ functional groups in which H^+ ions can be exchanged for cations in solution:



where S denotes the polymerized surface.

However, the sites responsible for the adsorption process are not exclusively due to the $-\text{COOH}$ and $-\text{C}_6\text{H}_5-\text{OH}$ groups. Other sites on the modified sawdust can also contribute to the adsorption 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 species and adsorbent particles would lead to increase adsorption of metal ions. This is in accordance with the earlier observations. 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.

3.5. 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:

$$\frac{C_e}{x/m} = \frac{1}{KV_m} + \frac{C_e}{V_m} \quad (6)$$

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 is an equilibrium constant related to the heat of adsorption by equation:

$$K = K_0 \exp\left(\frac{q}{RT}\right) \quad (7)$$

where q is the heat of adsorption. The linear Langmuir equation for chromium on sawdust in distilled water system was determined to be (correlation coefficient, $R^2 = 0.8822$):

$$\frac{C_e}{x/m} = 5.1223C_e + 1.5614 \quad (8)$$

The results are shown in Fig. 9. Notice the fit of data to linearity is not very good.

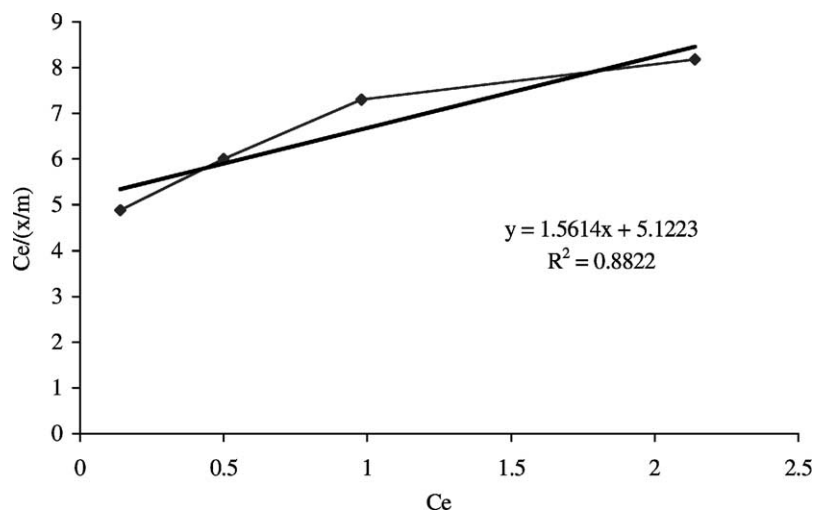


Fig. 9. Langmuir adsorption isotherms of chromium(VI) on sawdust.

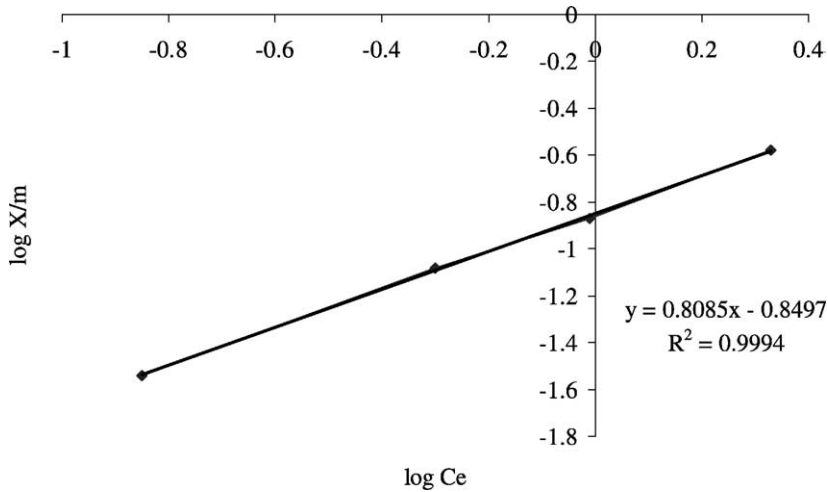


Fig. 10. Linear Freundlich isotherm of chromium sorption on sawdust.

The data for the uptake of metal ions by sawdust was processed in accordance with a linearized form of the Freundlich isotherm equation to be:

$$\log \frac{x}{m} = \log K_c + \frac{1}{n} \log C_e \quad (9)$$

where K_c and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, and other parameters are the same as in the Langmuir isotherm. The term $\log(x/m)$ can be plotted against $\log C_e$ with slope $1/n$ and intercept $\log K_c$. The linear Freundlich equation shown in Fig. 10 for chromium from experimental result is determined to be (correlation coefficient, $R^2 = 0.9994$):

$$\frac{x}{m} = 0.1414C_e^{0.8085} \quad (10)$$

3.6. Adsorption mechanism

The interactions of metals with sawdust surface molecules are complex, probably simultaneously dominated by adsorption, ion exchange and chelation. The pH dependence of adsorption may suggest that metal ions are adsorbed according to the ion-exchange mechanism, and deacetylation dependence of adsorption may indicate the chelation mechanism.

There are two major types of metal–organic interactions to be considered in an aquatic system. The first of these is complexation, usually chelation when organic ligands are involved. A reasonable definition of complexation by organics applicable to wastewater systems is a system in which a species is present that reversibly dissociates to a metal ion and an organic complexing species as a function of hydrogen ion concentration:



In this equation, M^{2+} is a metal ion and H_2L is the acidic form of a complexing—frequently chelating—ligand, L^{2-} , illustrated here as a compound that has two ionizable hydrogens.

Organometallic compounds, on the other hand, contain metals bound to organic entities by way of a carbon atom and do not dissociate reversibly at lower pH or greater dilution. Furthermore, the organic component, and sometimes the particular oxidation state of the metal involved, may not be stable apart from the organometallic compound. A simple way to classify organometallic compounds for the purpose of discussing their toxicology is given as follows.

1. Those in which the organic group is an alkyl group such as ethyl in tetraethyllead, $Pb(C_2H_5)_4$: C_2H_5- .
2. Carbonyls, some of which are quite volatile and toxic, having carbon monoxide bonded to metals: $C\equiv O$.
3. Those in which the organic group is a π electron donor, such as ethylene or benzene. $CH_2=CH_2$ (ethylene) C_6H_6 (benzene). Combinations exist of the three general types of compounds outlined above, the most prominent of which are arene carbonyl species in which a metal atom is bonded to both an aromatic entity such as benzene and to several carbon monoxide molecules.

Based on the structure of these phenolic compounds, a possible mechanism of ion exchange could be considered as an n -valent heavy metal ion (M^{n+}) attaching itself to adjacent hydroxyl groups and oxyl groups which could donate two pairs of electrons to metal ions, forming chelated compounds and releasing hydrogen ions into solution. A divalent heavy metal ion (M^{2+}) attaches two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution.

Generally, IR is an excellent way to study molecular interactions. In order to study the binding of metal ions to the sawdust, the IR spectra of sawdust and the metal sawdust were recorded. It was hoped that there would be a large number of metal ions bonded strongly to sites on the sawdust. The IR spectra show broad peak at 3400 cm^{-1} and weaker but more highly separated peak systems in $500\text{--}1500\text{ cm}^{-1}$ region. It can be seen that there is little or no change in the IR spectra of metal sawdust compared to that of untreated sawdust. Therefore, the IR is not capable of giving useful information about interaction of the metal with sites on the sawdust. It is probable that there may not be enough metal ions on the sawdust to cause any significant change in IR. Since there was no large change in the spectra, no effort was made to interpret IR spectra in any detail. If wood is considered to be 50% lignin, and assuming 2 oxygen atoms coordinated to each metal ion, then is estimated that about 1/700th of the possible metal binding sites in the sawdust have a bound metal when initial metal concentration of 1 mg/l and 10 g/l sawdust were employed.

4. Conclusions

Solute removal is built up, equilibrium conditions are attained after nearly 1 h. Adsorption of the chromium is dependent on the initial concentrations of adsorbent and sorbate and time of contact, and pH. Maximum percent removal of chromium(VI) is at pH 9.0. On the

other hand, the minimum percent removal of chromium(VI) is at pH 2.0. Maple sawdust is found to be a promising adsorbent for the removal of chromium from untreated industrial wastewater.

Acknowledgements

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