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Sorption of Heavy Metals by Untreated Red Fir Sawdust

PATRICK S. BRYANT,[1] JAMES N. PETERSEN,*[,1]
JAMES M. LEE,[1] AND THOMAS M. BROUNS[2]

[1] *Department of Chemical Engineering, Washington State University, Pullman, WA 99164-2710; and [2] Waste Treatment Department, Battelle Pacific Northwest Laboratories, Richland, WA 99352*

ABSTRACT

Equilibrium and rate relationships have been determined for the sorption of divalent copper (Cu^{2+}) and hexavalent chromium (Cr^{6+}) onto untreated Red Fir sawdust. For both ions, the equilibrium sorption levels were determined to be a function of the solution pH and temperature. The equilibrium adsorption capacity of the sawdust for Cu^{2+} was found to increase with increasing pH. However, for Cr^{6+} the sorption capacity increased with decreasing pH. For both ions, the rate of adsorption and the equilibrium adsorption capacity increased with temperature. The sorption capacity of α-cellulose was at least an order of magnitude less than the untreated sawdust.

Index Entries: Sawdust; wood; adsorption; heavy metals.

INTRODUCTION

Heavy metals, which are toxic to many living organisms, are present in the waste water streams of many industrial processes. Such processes include mining, electroplating and nuclear power operations, and semiconductor, aerospace, and battery manufacturing processes. A need exists for an economical process to remove low concentrations of these heavy metals from such large-volume waste streams. In addition, the restoration of previously contaminated ground water sites requires the removal and recovery of heavy metals on a massive scale if the sites are to be restored to drinking water standards.

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*Author to whom all correspondence and reprint requests should be addressed.

Many times, such heavy metal contaminated streams are in close proximity to lumber mills that produce large quantities of sawdust. If this sawdust could be used as an absorbent, then both the environment and wood agriculture would benefit: Contaminated streams would be cleaned, and a new market would be opened for the sawdust.

If, after it has absorbed the heavy metals, the sawdust were burned to produce useful energy, much of its cost could be recovered. In many regions of the US, the current prices of sawdust and oil favor displacement of fuel oil with sawdust, even without the benefits added when heavy metals are removed from aqueous streams. For example, if sawdust can be obtained for $30/dry t and burned in a wood-fired boiler with a 65% efficiency, then the break-even point, compared to an oil-fired boiler at 85% efficiency, is an oil price of $13.50/bbl. If the price of sawdust were lower or the price of oil higher, then the burning of sawdust in place of oil would be profitable, especially if it were used to lessen the costs associated with removing heavy metals from aqueous streams.

Disposal of the metal-rich ash that will be produced when the sawdust is burned could be accomplished in various ways. First, because the environment at the bottom of the furnace where the ash will fall is, in general, reducing in nature, the metal could be recovered in a useable form. Alternatively, a vitrification system could be used to immobilize the ash so that it could be stored indefinitely.

Current technology for the removal of heavy metals from waste water includes precipitation (*1–3*), ion exchange with synthetic resins (*3–5*), and adsorption with activated carbon (*5*). Precipitation of heavy metals as hydroxides from basic solutions has been used widely in industry. However, precipitation alone usually cannot reduce heavy metal concentrations far enough to meet current water-quality standards, such as those proposed for the State of Washington (*6*). Ion exchange with synthetic resins or adsorption with activated carbon can be highly efficient in heavy metal removal, but is relatively expensive when used on a large scale. In addition, to be economical, the adsorbent must be regenerated. Typically, this is accomplished by desorbing the metal ions to another liquid stream, producing a high-volume secondary waste stream that must also be treated and/or stored.

Previous investigations have shown that heavy metals will bind to sawdust and other agricultural byproducts (*7–11*). The adsorption of acid and basic dyes from textile mill effluent onto sawdust has been investigated (*12*), and a significant amount of work has been done on the adsorptive capacity of various tree barks (*13–15*). However, the ash content of bark is about 10× higher than that of sawdust for many species (*16*), which makes it less suitable for heavy metal recovery by combustion. Also, bark as processed from the lumber mill has a much larger average particle size than sawdust. It is likely that most of the bark would have to be processed through size-reduction equipment to make it suitable as an adsorbent, whereas only over-sized particles of sawdust, which could be separated by screening, would need to be processed through size-reduction equipment.

A number of investigators have shown that various chemical treatments of sawdust and other agriculture wastes can improve the heavy metal binding capacity of these materials by severalfold (*17–20*). However, because of the low costs of most agricultural wastes, it is unclear whether this increase in adsorption will pay for the added cost associated with the chemical treatment. The purpose of this research was to begin to gain a fundamental understanding of the chemical and physical phenomena associated with the binding of heavy metals to untreated sawdust.

MATERIALS AND METHODS

Heavy Metals

The heavy metals used in this investigation were Cu^{2+} and Cr^{6+}. Copper is representative of many of the divalent cations often found in many industrial waste water streams. It forms many moderately strong complexes and generally has rapid reaction kinetics. By contrast, chromium is found as mainly as +6 oxyanions, such as $HCr_2O_7^-$, $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and as the +3 cation. The +3 species is kinetically inert, although the oxyanions are labile. Of the two forms, the hexavalent form is of greater interest because it is highly toxic and is present in the waste streams from many processing operations. Because of these differences, simultaneous work on Cu^{2+} and Cr^{6+} provides an opportunity to develop a general methodology for waste reduction applicable to a variety of sludges and aqueous or mixed solvents. The Cu^{2+} stock solution was prepared from $CuNO_3 \cdot H_2O$ (Sigma Chemical Co., St. Louis, MO), and the Cr^{6+} was prepared from K_2CrO_4 (J. T. Baker Chemical Co., Phillipsburg, NJ).

Sawdust and α-Cellulose

Fresh Red Fir (*Abies magnifica*) sawdust was obtained from a local sawmill. The sawdust was allowed to air-dry for 1 wk at room temperature. It was then screened, and particles over 2.0 mm in size were removed. The particle size distribution of the sawdust as received from the sawmill is given in Table 1. Sawdust moisture content was determined by drying samples to constant weight in an oven at 105°C (4–8 h, depending on sample size).

The α-cellulose was obtained from FMC (Philadelphia, PA) as Avicel PH-102, which has an average particle size of 90 μm. Moisture content was determined in the same manner as described above for sawdust.

Equilibrium Adsorption Capacity

Equilibrium adsorption capacity experiments were carried out by placing 3–7 air-dry g of weighed biomass (sawdust or α-cellulose) in a

Table 1
Red Fir Particle Size Distribution

Particle size, mm	Distribution, %
>200	5.8
1.65–2.00	6.4
0.84–1.65	57.2
0.42–0.84	27.7
0.21–0.42	2.9
<0.21	Trace

150-mL Erlenmeyer flask containing 50 mL deionized water and a known initial metal ion concentration. Sample pHs were adjusted to the desired value with 1.0*N* HNO_3 and/or 1.0*N* NaOH. Covered samples were agitated by placing on a gyratory shaker at 180 rpm for 24 h at 27°C. The pH was checked and adjusted as needed periodically throughout the 24-h period. Blanks without biomass were prepared at each initial metal concentration, and pH studied. The initial ion concentrations within these blanks were used for the initial concentration value in adsorption calculations. These blanks were then processed following the same procedures employed for the samples to ensure that negligible metal ions were adsorbed by the glassware.

After 24 h, an aliquot of 1.5 mL was removed and centrifuged for 5 min at 15,000×*g* to remove suspended particles. The supernatant was removed and analyzed to determine the equilibrium metal concentration using a Perkin Elmer 2280 Atomic Absorption Spectrophotometer.

Adsorption Rate Studies

Adsorption rate studies were conducted by placing 240.0 air-dried g of sawdust and 4.0 L of deionized water in a stirred tank reactor with automatic temperature and pH control. Temperature control was accomplished with an indirect heat exchanger, and pH control was accomplished by the automatic addition of 1.0*N* HNO_3 or 1.0*N* NaOH. The slurry was agitated at 300 rpm with twin six flat-blade turbine impellers. Once the desired steady-state temperature and pH had been reached, the required quantity of heavy metal stock solution was added to bring the initial concentration to 200 ppm. Over the next 24–30 h, 1.5 mL samples were withdrawn periodically and centrifuged for 5 min at 15,000×*g* to remove suspended particles. The supernatant was removed and analyzed to determine the solution metal concentration using a Perkin Elmer 2280 Atomic Absorption Spectrophotometer.

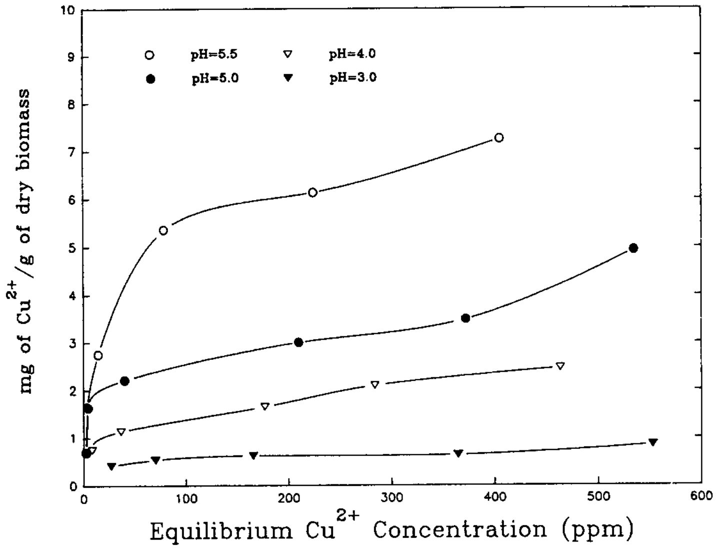

Fig. 1. Adsorption of Cu^{2+} on Red Fir sawdust at 27°C.

RESULTS AND DISCUSSION

Equilibrium Adsorption

Equilibrium adsorption of Cu^{2+} on sawdust was determined using 3 g of air-dried Red Fir sawdust in 50 mL of deionized water following the procedure given in the previous section. The results of these equilibrium experiments are shown in Fig. 1. These data demonstrate that adsorption capacity of Cu^{2+} on sawdust increases with increasing pH. Adsorption also increases with increasing equilibrium concentration.

To ascertain whether the metal ions are sorbed to the cellulose backbone of the sawdust, the equilibrium adsorption of Cu^{2+} on α-cellulose was determined as above, except that 7 g of α-cellulose was used. Figure 2 shows that an order of magnitude less Cu^{2+} will sorb to a unit mass of α-cellulose than will sorb to a unit mass of sawdust. This suggests that Cu^{2+} is not adsorbed primarily onto the cellulose contained within the sawdust, but is sorbed to other wood components, possibly the lignin contained in the wood.

In a like manner, equilibrium experiments were performed to ascertain the adsorption capacity of Cr^{6+} on Red Fir sawdust. These results are shown in Fig. 3. In contrast to the results obtained for Cu^{2+}, these data indicate that adsorption capacity of Cr^{6+} on sawdust increases with decreasing pH. Adsorption also increases with increasing equilibrium concentration and then levels off to a maximum adsorption capacity of the sawdust for a given pH. The experimental method for the adsorption of

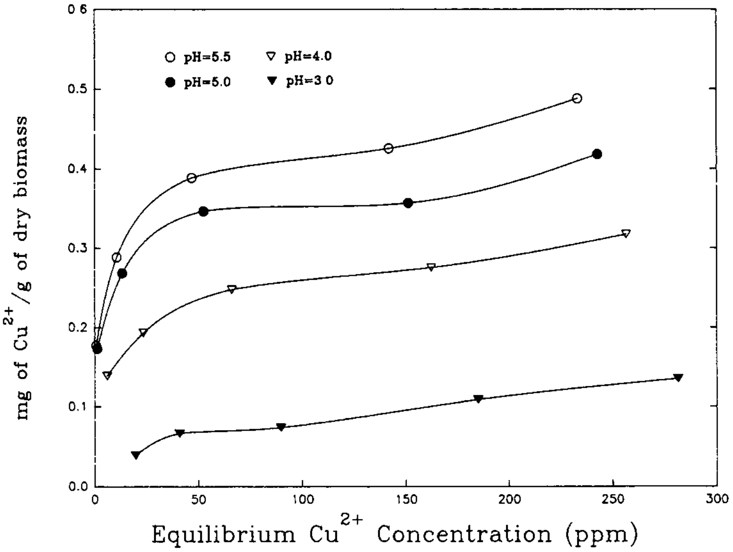

Fig. 2. Adsorption of Cu^{2+} on α-cellulose at 27°C.

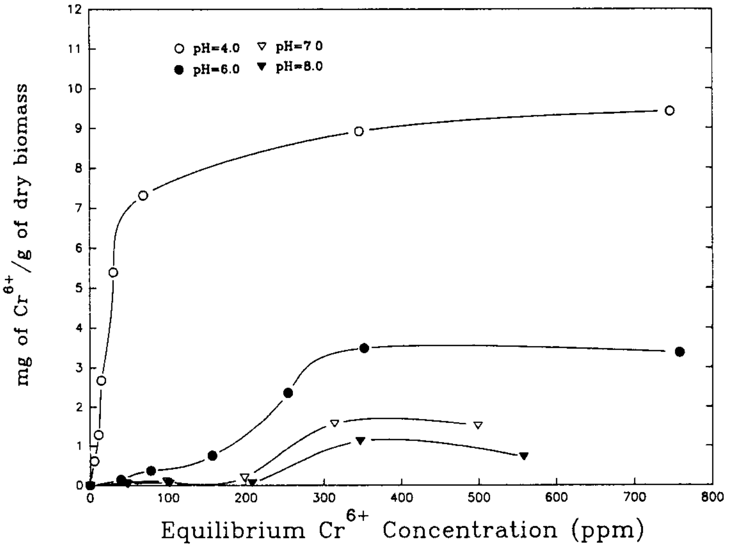

Fig. 3. Adsorption of Cr^{6+} on Red Fir sawdust at 27°C.

Cr^{6+} was identical to that used for Cu^{2+} adsorption, except that 4.0 g of sawdust was used rather than 3.0 g.

The adsorption capacity of Cr^{6+} on α-cellulose is approx two orders of magnitude less than that observed for sawdust. These data suggest that, like Cu^{2+}, Cr^{6+} is not adsorbed primarily onto the cellulose, but rather to other components contained within the sawdust. Like the sawdust, α-cellulose showed increasing adsorption capacity for Cr^{6+} as the pH was dropped. At an equilibrium concentration of approx 200 ppm,

Cr^{6+} adsorption values of 0.056, 0.035, 0.033, and 0.011 for pHs of 4.0, 6.0, 7.0, and 8.0, respectively, were measured. The very low adsorption capacity of α-cellulose for Cr^{6+} resulted in small changes from the initial to the final equilibrium concentration, which limited the accuracy of adsorption measurements.

The influence of pH upon the sorption isotherms is as one would expect. As a cation, Cu^{2+} is less soluble at higher pH values, so it will be more easily sorbed as the pH increases. On the other hand, Cr^{6+} is found as anions in solution, which will be less soluble at lower pH values, causing the sorption capacity of the sawdust to increase as the pH is lowered.

Adsorption Isotherms

To describe observed sorption phenomena, adsorption isotherms are often employed. One of the most common isotherms is the Langmuir adsorption isotherm. The Langmuir isotherm applies to adsorption on completely homogeneous surfaces, with negligible interaction between adsorbed molecules. For a single solute, it is given by

$$\frac{X}{M} = \frac{X_m b C_e}{1 + bC_e} \tag{1}$$

where C_e is the equilibrium solution concentration, X is the mass of solute adsorbed, M is the mass of the sorbent, X_m is the asymptotic maximum solid-phase concentration corresponding to the amount of adsorbate/U weight of adsorbent that forms a complete monolayer on the surface and represents the adsorption capacity of the sorbent for the solute, and b is a equilibrium constant that is related to the heat of adsorption. An empirical model that is often used to describe adsorption in aqueous systems is the Freundlich isotherm, which is given by

$$\frac{X}{M} = K_f C_e^{1/n} \tag{2}$$

where K_f and $1/n$ are constants characteristic of the system, and other parameters are defined as in Eq. 1.

Table 2 contains Langmuir and Freundlich parameters for the adsorption of Cu^{2+} and Cr^{6+} on sawdust, which were fit by a nonlinear curve fitting algorithm. The algorithm searches the fitted parameters to minimize the norm (square root of the sum of squared residuals for the dependent variable). The coefficient of variation, CV, is a measure of the variability of a parameter as fit to the data. As such, each parameter will have an associated CV value. A small CV represents a relatively good fit, whereas a large CV represents a relatively poor fit.

Both models fit the Cu^{2+} adsorption data with CVs of 5–75% for the Langmuir fits and CVs of 7–31% for the Freundlich fits. As seen in Fig. 1, the general shape of the adsorption curves for Cu^{2+} is characterized by a

Table 2
Analysis of Langmuir and Freundlich Isotherm Parameters at Different pH Values

		Langmuir parameters				Freundlich parameters			
		X_m		$1/b$		K_f		n	
Ion	pH	Value, mg/g	CV, %	Value, mg/L	CV, %	Value, mg/g	CV, %	Value	CV, %
Cu^{2+}	5.5	7.09	4.99	21.0	23.4	1.16	20.8	3.21	12.5
	5.0	3.91	12.7	15.9	75.2	0.731	30.8	3.52	19.1
	4.0	2.35	9.96	34.5	47.0	0.366	12.5	3.26	7.34
	3.0	0.776	8.14	28.5	41.1	0.209	22.4	4.75	19.3
Cr^{6+}	8.0	3.85	426	1861	525	0.00196	413	1.039	70.0
	7.0	2.60	129	482	217	0.00109	305	0.845	43.0
	6.0	6.41	46.1	531	82.7	0.0490	129	1.52	31.7
	4.0	10.1	5.90	35.7	20.6	1.45	39.1	3.34	23.0

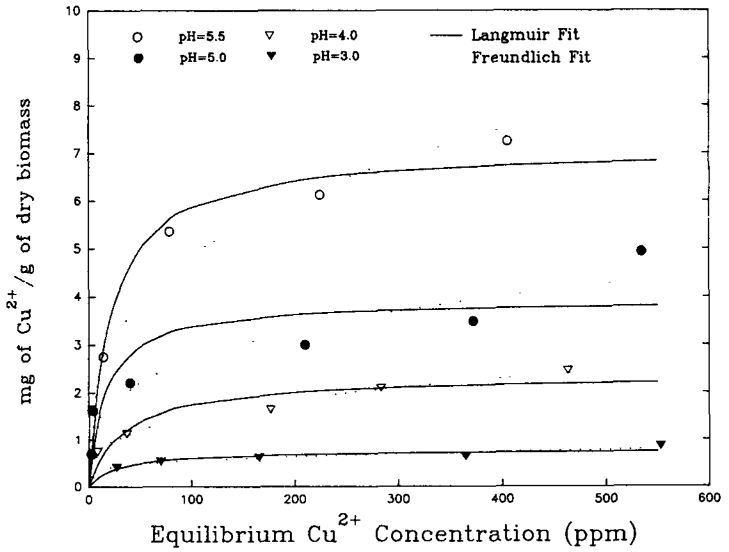

Fig. 4. Langmuir and Freundlich isotherm model fits for the adsorption of Cu^{2+} on Red Fir sawdust at 27°C.

decreasing positive slope without inflection points; these isotherms are commonly referred to as a Brunauer Type I isotherms (*21*). Langmuir and Freundlich models are expected to give fairly good fits to Type I isotherms. Plots of the Langmuir and Freundlich model predictions for Cu^{2+} adsorption on sawdust are shown in Fig. 4.

The general shape of the adsorption curves for Cr^{6+} is approx Type I at a pH of 4.0 and approx Type V or "s" shaped (*21*) at pHs 6.0, 7.0, and 8.0. Neither the Langmuir nor Freundlich model gives a good fit for these

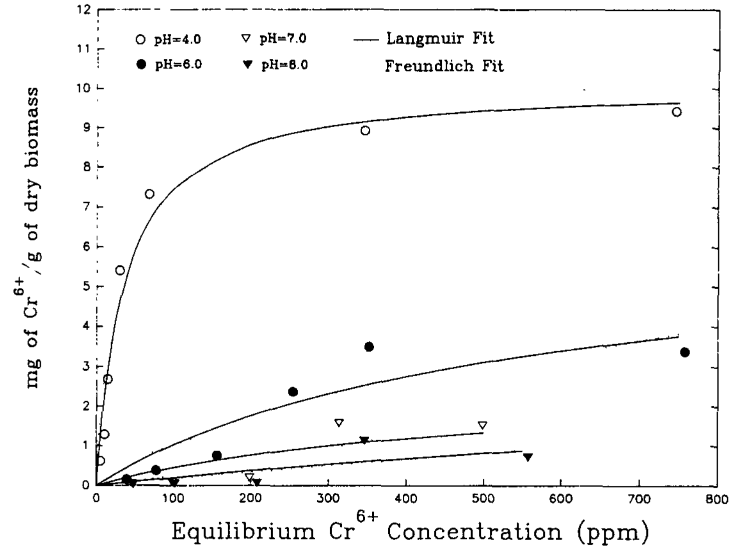

Fig. 5. Langmuir and Freundlich isotherm model fits for the adsorption of Cr^{6+} on Red Fir sawdust at 27°C.

Type V isotherms as indicated by the high CV values given in Table 2. The Langmuir model gives the best fit for adsorption at a pH of 4.0 with relatively low CV values. Plots of the Langmuir and Freundlich model predictions for Cr^{6+} adsorption on sawdust are shown in Fig. 5.

A change in the general shape of the adsorption isotherm for Cr^{6+} on sawdust and a significant increase in adsorption of Cr^{6+} are seen when the pH is decreased from 8.0 to 4.0. These changes correspond with an equilibrium shift of the predominate oxyanion species. The two predominate oxyanion species at the concentrations and pHs investigated are CrO_4^{2-} and $HCrO_4^-$. The reduction potential of $HCrO_4$ is > CrO_4^{2-} and is therefore more reactive. From equilibrium data (22), the relative percentage of $HCrO_4^-$ at pHs of 4.0, 6.0, 7.0, and 8.0 is 99.7, 73.8, 22, and 2.7%, respectively. It is reasonable to assume that the shift in equilibrium from CrO_4^{2-} to $HCrO_4^-$ contributes to the increase in equilibrium adsorption and to the change in the isotherm shape. Changes to the binding sites within the sawdust at different pH may also contribute to these changes with pH. Further studies are needed to determine the actual mechanism of adsorption for both divalent cations and oxyanions.

Adsorption Rate Studies

The adsorption of Cu^{2+} as a function of time and temperature is plotted in Fig. 6. The initial concentration was 220 ppm Cu^{2+}, and the pH was maintained at 5.0 with an automatic pH controller. In general, the adsorption rate and equilibrium adsorption level increase with increasing temperature. However, at 60°C, the adsorption level of Cu^{2+} increases to a

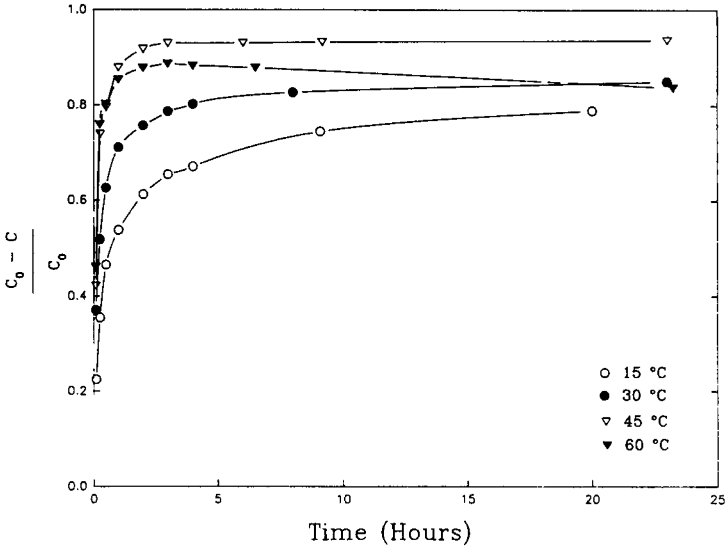

Fig. 6. Adsorption of Cu^{2+} on Red Fir sawdust at pH=5.0, C_0=200 ppm, and 60 g/L air-dry sawdust.

maximum and then decreases with time, resulting in an equilibrium adsorption level below that of both 30 and 45°C. This is likely a result of solubilization of wood extractives with bound Cu^{2+}. Wood extractives are a broad class of low-mol-wt organic compounds that are soluble in polar or nonpolar solvents (*16*). The solubilization of these extractives were not significant in the 15–45°C temperature range, but became significant at 60°C. These results indicate that the optimum temperature for equilibrium adsorption of Cu^{2+} on Red Fir sawdust lies between 30–60°C.

The increase in extractive solubilization with temperature was visually evident by an increased darkening of both the sawdust and the slurry solution with increasing temperature. An important group of wood extractives are referred to as tannins, which is an indication of their tanning action on the proteins of hides (*16*). Young et al. (*23*) have suggested that tannins serve as the primary site for divalent cations binding to wood.

The adsorption of Cr^{6+} as a function of time and temperature is plotted in Fig. 7. The initial concentration was 200 ppm Cr^{2+}, and the pH was maintained at 4.0. As with Cu^{2+}, the adsorption rate and equilibrium adsorption level increase with increasing temperature. However, Cr^{6+} did not show the same decrease in adsorption at 60°C that Cu^{2+} demonstrated. This suggests that the Cr^{6+} is either binding to sites that are not solubilized at 60°C or that it forms insoluble complexes with the sawdust.

CONCLUSIONS

The ash content in temperate zone softwoods is typically 0.5% (*16*). Thus, this study demonstrates that untreated Red Fir sawdust can be used to adsorb both Cu^{2+} and Cr^{6+} at levels in excess of the natural ash content

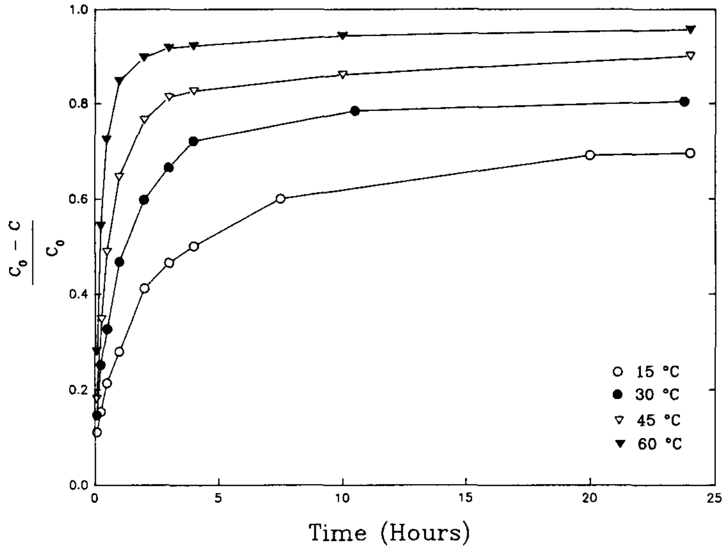

Fig. 7. Adsorption of Cr^{6+} on Red Fir sawdust at pH = 4.0, C$_0$ = 200 ppm, and 60 g/L air-dry sawdust.

of the wood. At these adsorption levels, a process using sawdust for the removal and recovery of heavy metals is potentially more economical than current process technology.

The adsorption of Cu^{2+} increases with increasing pH, whereas the adsorption of Cr^{6+} increases with decreasing pH. Both Langmuir and Freundlich isotherm models give reasonably good fits for Cu^{2+} adsorption, but neither the Langmuir model nor the Freundlich model describes Cr^{6+} adsorption at pHs of 6.0, 7.0, and 8.0 adequately. Nonetheless, either can be used to describe the data at pH 4.0. At these conditions, complex reactions that cannot be described by the simple isotherms are occurring to bind the ions to the wood.

In general, the adsorption rates and equilibrium adsorption levels of Cu^{2+} and Cr^{6+} increase with increasing temperature. However, the equilibrium adsorption level of Cu^{2+} decreases when the temperature is increased from 45 to 60°C, indicating an optimum temperature for maximum equilibrium adsorption of Cu^{2+} lies beween 30 and 60°C.

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