

Removal of hexavalent chromium from aqueous solution by lignocellulosic solid wastes

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ABSTRACT: The batch removal of Cr(VI) from aqueous solution using lignocellulosic solid wastes such as sawdust and pine leaves under different experimental conditions was investigated in this study. The influence of pH, temperature, contact time, initial concentration of Cr(VI) and particle size on the chromium removal was investigated. Adsorption of Cr(VI) is highly pH-dependent and the results indicate that the optimum pH for the removal is 2. The capacity of chromium adsorption at equilibrium by these natural wastes increased with absorbent concentration. Temperature in the range of 20-60 °C showed a restricted effect on the adsorption capacity of pine leaves, but had a considerable effect on the adsorption capacity of sawdust. The capacity of chromium adsorption at the equilibrium increased with the decrease in particle sizes. The suitability of adsorbents was tested with Langmuir and Freundlich isotherms and their constants were evaluated. Results indicated that the Freundlich model gave a better fit to the experimental data in comparison with the Langmuir equation. The study showed that lignocellulosic solid wastes such as sawdust and pine leaves can be used as effective adsorbents for removal of Cr(VI) from wastewater.

Key words: Lignocellulosic solid wastes, sawdust, pine leaves, adsorption, hexavalent chromium

INTRODUCTION

Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, and cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic (Cieslak-Golonka, 1996). Its concentrations in industrial wastewaters range from 0.5 to 270 mg/l (Patterson, 1985). The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/l (EPA, 1990). In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) to acceptable levels. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Juang and Shiau, 2000; Yan and Viraraghavan, 2001). These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly

methods are thus needed to be developed to reduce heavy metal content. In this context, considerable attention has been focused in recent years upon the field of sorption by lignocellulosic solid wastes such as straw, coconut husks, exhausted coffee (Dakiky *et al.*, 2002), waste tea (Amir *et al.*, 2005), walnut skin, coconut fibre (Espinola *et al.*, 1999), seeds of *Ocimum Basilicum* (Melo and Disouza, 2004), defatted rice bran, rice hulls, soybean hulls and cotton seed hulls (Marshall and Champagne, 1995; Teixeira and Zezzi, 2004), wheat bran, pea pod, cotton and mustard seed cakes, (Iqbal *et al.*, 2002; Saeed *et al.*, 2002). The aim for this research is to develop inexpensive and effective chromium ion adsorbents from plentiful sources of natural wastes, such as tree leaves and sawdust to offer these adsorbents as replacements for existing commercial materials. However, to our knowledge, few such studies have been performed previously to use the tree leaves to clean the wastewater.

MATERIALS AND METHODS

Preparation of Chromium solution

Standard stock solution was prepared from potassium dichromate. For each experimental run, a solution of Cr metal ion was added to exact amount of deionized water

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in a volumetric flask in order to obtain a known concentration of the metal. pH of the solution was adjusted using 0.1 N HCl or NaOH. Fresh dilutions were used for each study.

Biosorbent materials

Pine leaves were gathered from twigs into clean plastic bags, washed with deionized water and laid flat on clean table to dry. Dry leaves were grounded, sieved and stored into plastic bag by size, and ready for use.

Adsorption experiment

Batch adsorber tests were carried out by mechanical agitation (agitation speed: 300 rpm) at 25°C, unless stated otherwise. After agitation, all sample solutions were filtered through 0.45 µm membrane filter paper and the filtrate was analyzed. The amount of adsorbed Cr (VI) was calculated by the difference of the initial and residual amount in the solution divided by the weight of the adsorbent used. To check the repeatability of the experimental data, each experiment was conducted thrice.

Chromium detection

For all experiments, the method of detection is by colorimetric techniques. The chromium is first to be complexed with a solution of 1,5 diphenyl carbazide (DIPC) in acetone, acidified and then, tested in a spectrophotometer set at 540 nm.

RESULTS

Effect of contact time

Preliminary experiments showed that the adsorption of chromium ions by sawdust and pine leaves reached equilibrium in less than 15 minutes. Fig. 1 shows the experimental results of adsorption of containing 5 mg/l Cr(VI). The experiments were carried out under the conditions of 25 °C, particle size of 20-30 mesh, with 4 g of adsorbent in 100 mL of chromium solution with pH=5. All sample solutions were filtered through 0.45 µm membrane filter paper and, the filtrate was analyzed. The experiments showed that the removal rate occurs quickly, seemingly reaching equilibrium within the first fifteen minutes of adsorption.

Effect of adsorbent mass

As illustrated in Fig. 2, capacity of chromium adsorption at equilibrium increases with the quantity of adsorbent either sawdust or pine leaves introduced

(1-10 g/100L); this can be explained by the fact that more the mass increases, more the contact surface offered to the adsorption of chromium becomes important. Beyond 6 g of pine leaves, this capacity of chromium did not nearly rise and the maximal quantity at the equilibrium of chromium removal by pine leaves was about 0.12 mg/g.

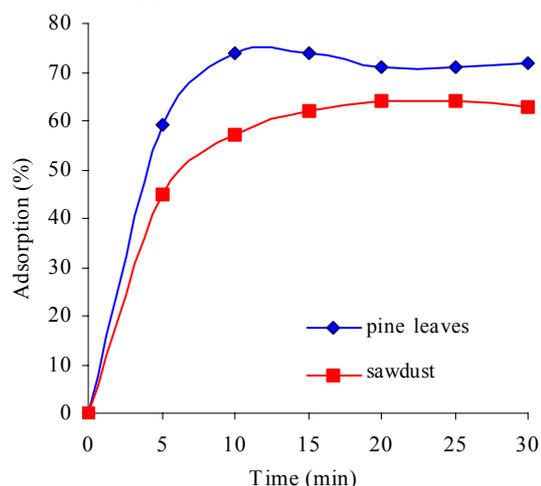


Fig. 1: Effect of contact time on the chromium adsorption

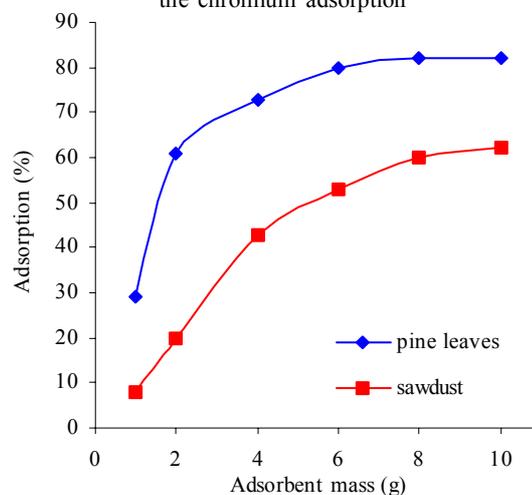


Fig. 2: Effect of adsorbent mass on the chromium adsorption capacity

Effect of pH

Chromium exhibits different types of pH dependent equilibria in aqueous solutions. As the pH is shifted, the equilibrium will also shift; in the pH range 2-6, HCrO₄⁻ and Cr₂O₇²⁻ ions are in equilibrium. At lower pH (pH <2.0) values, Cr₃O₁₀⁻ and Cr₄O₁₃²⁻ species are formed. The removal of Cr(VI) by sawdust and pine

leaves at different pHs at an initial Cr(VI) concentration of 5 mg/L, a temperature of 25 °C, particle size of 20-30 mesh was investigated. As illustrated in Fig. 3, The optimum initial pH was observed at pH 2.0. This observation may be attributed to the fact that by decreasing pH, hydroxyl groups in lignocellulosic wastes, tend to diffuse into the solution, so, it would be more probable for $\text{Cr}_2\text{O}_7^{2-}$ ions to be adsorbed on available adsorption sites. Using a Fourier transform infrared spectrometer (FTIR) analysis showed a wide peak at about 3400 cm^{-1} that confirm the existence of hydroxyl groups in either sawdust and pine leaves. As illustrated in Fig. 3, for pine leaves, 99% of Cr(VI) was adsorbed from a solution of 5 mg/L at pH 2.0, whereas a 15% reduction in biosorption was determined as the pH shifted from 2.0 to 6.0. In the case of sawdust, this decrease was about 22%.

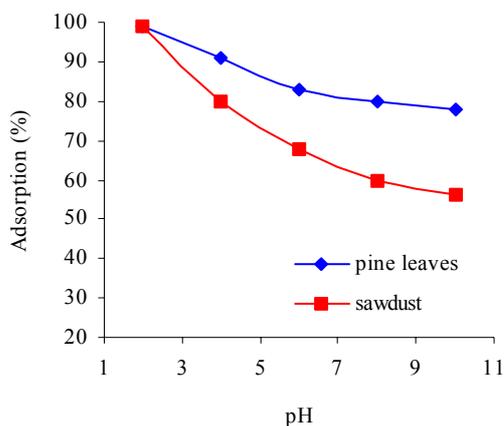


Fig. 3: Effect of pH on the chromium adsorption

Effect of temperature

The results obtained and presented in Fig. 4 indicate that an increase of the temperature in the range of 20-60 °C had considerable effect on chromium adsorption by sawdust but had a restricted effect on chromium adsorption by pine leaves. As shown, at the temperature below 40°C, pine leaves have higher chromium adsorption capacity. The necessary time to reach adsorption equilibrium for the different temperatures was practically the same (15 min). If adsorption is governed only by physical phenomena, an increase in temperature will result a decrease in adsorption capacity. Therefore, experimental results show that predominant mechanism is chemical adsorption.

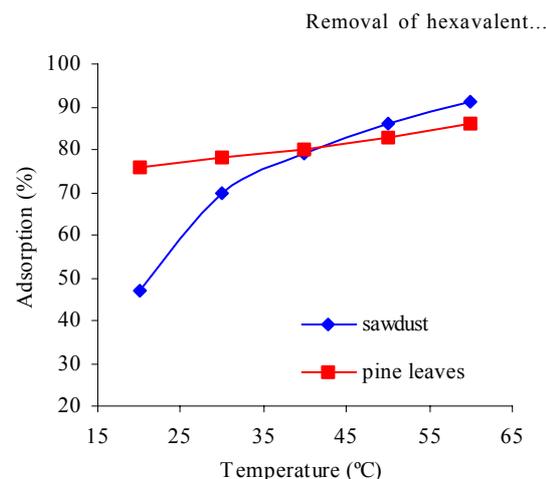


Fig. 4: Effect of temperature on the adsorption of chromium

Effect of initial chromium ion concentrations

As illustrated in Fig. 5, in the case of sawdust, by changing the initial concentration of Cr(VI) solution from 1 to 10 mg/l, chromium removal reduced from 62% to 45% at 25 °C, pH 5.0 and particle size of 20-30 mesh. But for pine leaves, initial concentration of Cr(VI) solution (in the range of 1-10 mg/l) had a restricted effect on chromium adsorption capacity. It was also noticed that amount of Cr ions on the solid phase with lower initial concentration of Cr(VI) was smaller than the amount when higher initial concentrations were used.

Effect of particle size

The batch adsorption experiments were carried out by using various particle sizes of the adsorbent (20-30 mesh and 30-50 mesh) at pH 5, 25°C, 300 rpm and initial concentration of 5 mg/l.

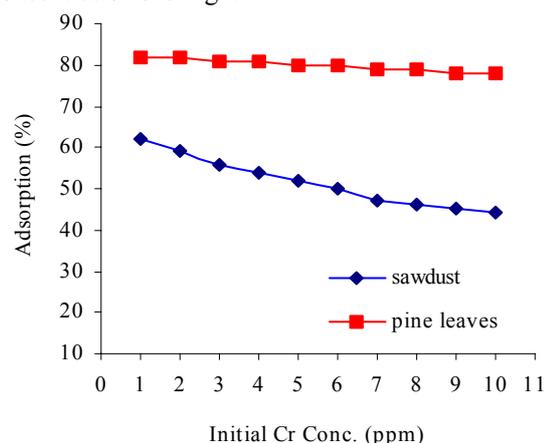


Fig. 5: Effect of initial chromium ion concentrations on the chromium adsorption

The removal of Cr(VI) ions at different particle sizes showed that the capacity of chromium adsorption at the equilibrium increased with the decrease in particle sizes. The relatively higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface areas and indicating that chromium ion adsorption occurs through a surface mechanism. It was also noticed that, there is a tendency that a smaller particle produces shorter time to equilibration. Thus, for particle size of 20-30 mesh, the time required was about 15 min, while for particle sizes of 30-50 mesh, the necessary time was about 10 min. These observations suggest that the chromium adsorption kinetic is largely affected by the particle size. Results are shown in Fig. 6.

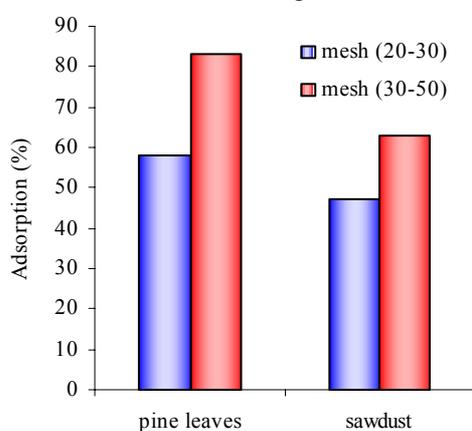


Fig. 6: Effect of particle size on the chromium adsorption

Adsorption isotherms

Two isotherms, as described below in Eqs. (1) and (2), were used for fitting the experimental data obtained at 25(±2)°C and at pH 5.0.

Langmuir equation:

$$1/q_e = 1/(\theta \cdot b \cdot C_e) + 1/\theta \quad (1)$$

Freundlich equation:

$$\log q_e = \log K + 1/n \log C_e \quad (2)$$

where:

q_e is the amount adsorbed at equilibrium (mg/g)

C_e is the equilibrium Cr(VI) concentration in solution (mg/L).

The other parameters are different isotherm constants, which can be determined by regression of the experimental data. Due to inconvenience of evaluating three isotherm parameters, the two-isotherm-parameter equations (Langmuir, Freundlich) are more widely used than the three-isotherm-parameter

equation (Redlich-Peterson equation). Though, the three-isotherm- parameters equations mostly provide a better fit of the isotherm data than a two-isotherm-parameters one. The estimated model parameters with correlation coefficient (R^2) for the different models are shown in Tables 1 and 2.

Table 1: Estimated isotherm parameters for Cr (VI) adsorption by sawdust

Isotherm models	Estimated isotherm parameters at 25 °C and pH=5.0		
	Langmuir equation $1/q_e=1/\theta \cdot b \cdot c_e+1/\theta$	R^2	θ (mg/g)
	0.975	0.198	0.219
Freundlich equation $\log q_e=\log K+1/n \log C_e$	R^2	K	n
	0.993	0.229	1.298

Table 2: Estimated isotherm parameters for Cr (VI) adsorption by pine leaves

Isotherm models	Estimated isotherm parameters at 25 °C and pH=5.0		
	Langmuir equation $1/q_e=1/\theta \cdot b \cdot c_e+1/\theta$	R^2	θ (mg/g)
	0.828	0.470	0.708
Freundlich equation $\log q_e=\log K +1/n \log C_e$	R^2	K	n
	0.952	0.277	0.342

DISCUSSION AND CONCLUSION

The present study showed that lignocellulosic solid wastes such as sawdust and pine leaves can be used as effective adsorbents for removal of Cr(VI) from wastewater. These natural wastes are available in large quantity and can be used as an alternative to existing commercial adsorbents for removal of Cr(VI). The removal of this carcinogenic toxicant was found to depend on materials, dosage, pH, Temperature, initial concentration of Cr(VI) and time. The contact time for the maximum adsorption required is nearly 15 min and optimum pH for highest Cr(VI) sorption is 2.0. The equilibrium sorption data are satisfactorily fitted with Freundlich and Langmuir equations. The calculated values of the dimensionless separation factor from the Langmuir constant confirm favourable sorption of Cr(VI) onto sawdust and pine leaves.

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