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Detoxification of chromium(VI) contaminated water using natural adsorbents

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Abstract

In the present study, the removal of Cr(VI) from aqueous solution using natural adsorbents such as apricot and pistachio tree leaves was investigated. The equilibrium studies were systematically carried out in a batch process, covering various process parameters including contact time, initial concentration of metal ions, adsorbents dosage and pH of the solution. The optimum pH and contact time for maximum adsorption were 2.5 and about 30 min, respectively. The Langmuir, Freundlich and Temkin isotherms were used to describe the adsorption equilibrium data. The results indicated that the data fit better to the Freundlich equation than to the Langmuir and Temkin equations. Comparing to activated carbon, these natural absorbents are suitable alternative for the adsorption process.

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Introduction

Chromium is an essential micronutrient required for the growth of many organisms. However, at high concentration it is toxic and carcinogenic (Gardea-Torresdey et al., 2000). Chromium exists in two stable oxidation states Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent (Kowalski, 1994). It is toxic to microorganisms, plants, animals and humans. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage (Cieslak-Golonka, 1996).

Chromium compounds are widely used in electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood protection, chemical manufacturing, brass, electrical and electronic equipment, catalysis and so on (Kimbrough et al.,1999).

Several treatment technologies have been developed to remove chromium from water and wastewater. Common methods include chemical precipitation (Patterson, 1985), ion exchange (Rengaraj et al., 2001) membrane separation (Kozlowski and Walkowiak, 2002), ultrafiltration (Ghosh and Bhattacharya, 2006), flotation (Matis and Mavros, 1991), solvent extraction (Salazar et al., 1992), reduction (Chen and Hao, 1998), reverse osmosis (Ozaki et al., 2002), evaporation, cementation, dilution, air stripping, steam stripping, flocculation and adsorption on activated carbon. However, these methods are costly and can themselves produce other waste problems. Therefore, there is a need to develop new cost-effective methods that are more environmentally friendly. The most commonly used agricultural by-products include sawdust (Dakiky et al., 2002; Yu et al., 2003), sugar beet pulp (Altundogan, 2005), rice hulls (Teixeria et al.,2004), pine leaves (Aliabadi et al.,2006), waste tea and coconut fiber (Malkoc and Nuhoglu, 2006), soybean hulls and cotton seed hulls (Marshall, 1995) and so on.

The aim of this study was to evaluate the adsorption capacity of Cr(VI) from aqueous solutions by natural adsorbents such as apricot and pistachio tree leaves (ATL, PTL) and to compare them to activated carbon (AC). However, to our knowledge, few such studies have been performed previously to use the tree leaves to clean the wastewaters.

Materials and methods

Preparation of biosorbent

Tree 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 and sieved. The 20–30 mesh fraction was separated for the experiments. This fraction was preserved in plastic bags for use as an adsorbent.

Preparation of chromium solution

Stock solution of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (purchased from Merck, Darmstadt, Germany) in deionized water. For each experimental run, a solution of Cr(VI) metal ion was added to the deionized water in a volumetric flask in order to obtain a known concentration of the metal. The solution pH was adjusted using 0.1 N HCl or NaOH. Fresh dilutions were used for each study.

Adsorption experiment

Batch absorption tests were carried out by mechanical agitation (agitation speed: 400 rpm) at 25°C. A known quantity of the dried adsorbent was added into the metal bearing solution of a given concentration in volumetric flasks. 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 minimize the experimental errors, each experiment was conducted thrice.

Chromium detection

The colorimetric method was used to analyze the Cr(VI) concentrations in the filtrate. The unadsorbated Cr(VI) in the aqueous medium was determined with the spectrophotometer (JENWAY 6305 UV/Vis) at a wavelength of 540 nm, using 1,5-diphenyl carbazide as a complexing agent.

Results and discussion

Effect of pH

Determination of optimum pH is very important since the pH value affects not only the surface charge of adsorbent, but also the degree of ionization and speciation of adsorbate during reaction. Adsorption experiments were carried out in the pH range of 2-7 for ATL and PTL and AC by keeping all other parameters constant (chromium concentration = 5mg/l; stirring speed = 400 rpm; contact time = 30 min, adsorbent dose = 4g/l, temp. = 25°C). The maximum adsorption of chromium (VI) was 97.1, 90.1 and 95.0% for PTL, ATL and AC, respectively at pH 2 (Fig. 1). In the pH range of 2–6 chromium ions co-exists in different forms, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ of which $HCrO_4^-$ predominates. As the pH of the solution increases, the predominant species are CrO_4^{2-} and $Cr_2O_7^{2-}$. More adsorption at acidic pH indicates that the lower pH results in an increase in H^+ ions on the adsorbent surface that results is significantly strong electrostatic attraction between positively charged adsorbent surface and chromate ions. Lesser adsorption of Cr(VI) at pH values greater than 6.0 may be due the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates. This is in accordance with the earlier studies that have reported the removal of Cr(VI) by different adsorbents (Karthikeyan et al., 2005; Huang and Wu, 1977).

Effect of adsorbent dose

The effect of adsorbent dose was studied by varying the amount of adsorbents (0.1-4gr) while keeping other parameters (initial Cr(IV) concentration, solution pH and agitation speed) constant. From Fig. 2, it can be observed that removal efficiency of adsorbents generally improved with increasing dose up to a certain value and then, there is no further increase of adsorption. At 4 mg/l of Cr(VI) concentration, the Cr(VI) removal efficiency significantly increased from 9% to 85% for ATL, 12% to 94% for PTL and 8% to 79% for AC and when the dose of adsorbents was increased from 0.1 to 2.0 gr. It may be due to the fact that the higher the dose of adsorbent in the solution, the greater availability of exchangeable sites for metal ions.

Table 1. Langmuir isotherm parameters.

Adsorbent	Langmuir constants		
	b	Q_e	R^2
PTL	18.247	0.2111	0.6986
ATL	22.736	0.1449	0.8912

Table 2. Freundlich isotherm parameters.

Adsorbent	Freundlich constants		
	1/n	K_f	R^2
PTL	0.7575	1.0167	0.9968
ATL	0.6804	0.58264	0.9983

Table 3. Temkin isotherm parameters.

Adsorbent	Temkin constants		
	A	B	R^2
PTL	489.303	0.0228	0.9657
ATL	382.744	0.0247	0.9074

Effect of initial chromium(VI) concentration

The adsorption of Cr(VI) with different adsorbents was studied by varying chromium concentration (0.5, 1, 2, 4 mg/l) keeping other parameters (adsorbent dose, stirring speed, solution pH, temperature and contact time) constant. As illustrated in Fig. 3, Cr(VI) uptake reduced from 93.7% to 85.7% for ATL, from 94.9% to 90.7% for PTL, and from 93.6% to 89.3% for AC, as the chromium concentration increased from 0.5 to 4 mg/l. The equilibrium data revealed that the percentage of removal decreased with increase in Cr(VI) concentration but the actual amount of Cr(VI) adsorbed per unit mass of the adsorbent increased with increase in metal concentration.

Effect of contact time

The effect of contact time was studied at optimum condition of dose, pH, and agitation speed. From Fig. 4, it is observed that removal efficiency increased with an increase in contact time and then, it tends to become constant with a longer period of agitation time. The metal adsorption increased rapidly during the first 40 min for ATL and AC, and 20 min for PTL. After this equilibrium period, the amount of adsorbed metal ions did not significantly change with time.

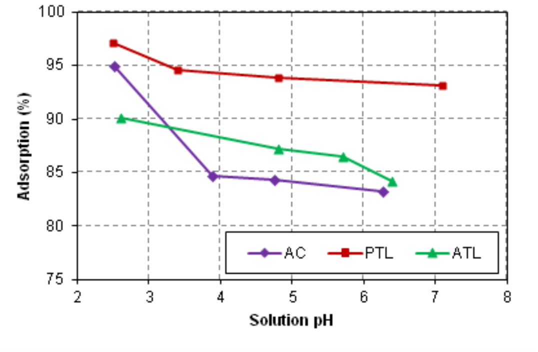

Fig. 1. Effect of pH on the chromium adsorption.

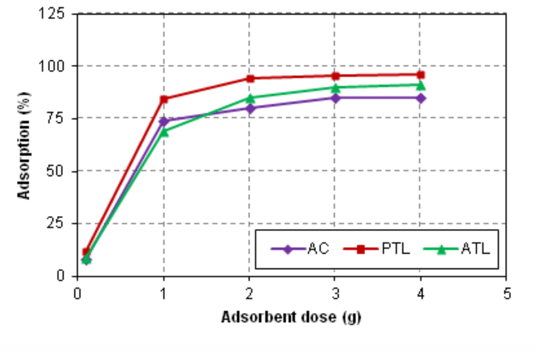

Fig. 2. Effect of adsorbent dose on the chromium adsorption.

Adsorption isotherms

Langmuir isotherm

The Langmuir model assumes that the uptakes of metal ions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir isotherm constants were calculated from the following linearized form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (1)$$

where C_e is the equilibrium concentration (mg/l), q_e the adsorbed amount at equilibrium time (mg/g) and Q_o and b are the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface (mg/g), whereas b is a constant related to the affinity of binding sites with the metal ions (Goel et al., 2005). The plots of C_e/ q_e versus C_e for ATL and PTL are not completely linear which shows that the adsorption of Cr(VI) cannot follows Langmuir isotherm model very well in the present adsorption study. Isotherm constants and correlation coefficient (R^2) are shown in the Table 1.

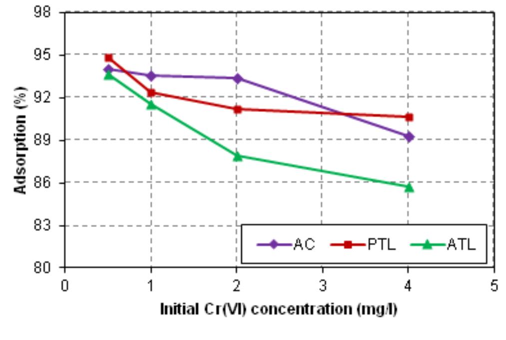

Fig. 3. Effect of initial chromium ion concentrations on the chromium adsorption.

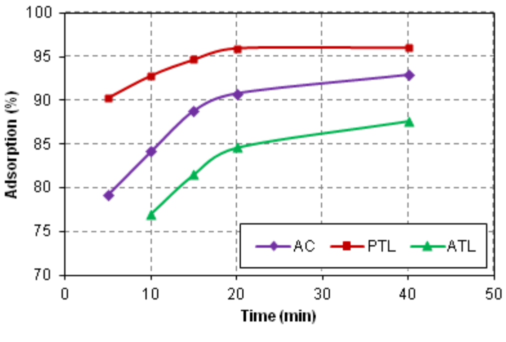

Fig. 4. Effect of contact time on the chromium adsorption.

Freundlich isotherm

Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and its constants were calculated from the following linearized form:

$$\log\frac{x}{m} = \log k_f + \frac{1}{n}\log C_e \qquad (2)$$

where K_f is an indicator of adsorption capacity and n indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity (Karthikeyan *et al.*, 2005). The plot of $\log(x/m)$ versus $\log Ce$ for various initial concentrations was linear. The adsorption capacities (K_f) and Freundlich constant (n) are given in Table 2. It was found that Freundlich isotherm is more applicable for adsorbents than Langmuir.

Temkin isotherm

Temkin isotherm based on the heat of adsorption of the ions, which is due to the adsorbate and adsorbent interactions taken in linear form, is given by (Hamadi *et al.*, 2001):

$$\frac{x}{m}=(\frac{RT}{b})\ln A+(\frac{RT}{b})\ln Ce\ , \qquad \frac{RT}{b}=B \qquad (3)$$

where A (l/g) and B are Temkin constants and given in Table 3.

The results of experiments showed that isotherm equilibrium data could not fitted reasonably well to the Temkin isotherm in the present adsorption study.

Conclusions

The present study showed that apricot and pistachio tree leaves can be used as effective adsorbents for the removal of Cr(VI) from aqueous solutions. PTL was the most effective even in comparison with activated carbon for which the removal of Cr(VI) reached more than 97% for Cr(VI) at pH 2. Increase in the dose of adsorbent, initial concentration of Cr(VI) and at contact time up to 40 min are favorable for the adsorption of Cr(VI). The adsorption data can be satisfactorily explained by Freundlich isotherm. Additionally, the study showed that these natural adsorbents (especially PTL) are useful and low-cost adsorbents for chromium ion removal from aqueous solution. These natural wastes are available in large quantity and can be used as an alternative to existing commercial adsorbents.

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