Full Length Research Paper

Adsorption of Cr(III) and speciation of chromium in aqueous solution using Ambrosia beetle-generated acacia polycantha frass

C. Mahamadi

Department of Chemistry, Bindura University of Science Education, P. Bag 1020, Bindura, Zimbabwe.

Acacia polycantha frass (APF) generated by boring activity of Ambrosia beetles was investigated using a batch technique for its potential to adsorb Cr(III) ions from aqueous solution. Studies were carried out to determine the effect of pH, adsorbent dose, and KBr concentration on the sorption behavior Cr(III) on the adsorbent. The adsorption process was found to be highly dependent on solution pH with maximum removal occurring at pH 11. Thermodynamic studies indicated that the sorption process was exothermic and spontaneous. Adsorption recoveries of up to 75 and 95% for a 5 mgL-1 solution were obtained for untreated and acid-treated APF respectively at room temperature. In all experiments the acid-treated adsorbent showed an apparently higher metal uptake than the untreated one. Reduction of Cr(VI) to Cr(III) in synthetic solution using hydroxylamine prior to adsorption preconcentration showed potential for studying chromium speciation.

Key words: Adsorption, entropy of activation, enthalpy of activation, chromium, speciation, acacia polycantha frass.

INTRODUCTION

The presence of heavy metals in the environment has become a major threat to plant, animal and human life due to their bioaccumulating tendency and toxicity and therefore must be removed from industrial effluents before discharge. Conventional physico-chemical methods for removing heavy metals from waste streams include electrochemical treatment, chemical reduction, ion-exchange, precipitation and evaporation recovery (Rengaraj et al., 2003; Ahluwalia and Goyal, 2007). Nevertheless, many of these approaches are marginally cost-effective or difficult to implement (Pipiska et al., 2007).

Biosorption, which utilizes inexpensive biological materials such as fungi, bacteria, algae, and agricultural waste products has increasingly been studied as

a possible alterative technique for metal removal from aquatic environments (Volesky and Holan, 1995; Volesky et al., 2000; Schmuhl et al., 2001; Vasudevan et al., 2001, 2002, 2003; Aksu, 2002; Chojnacka and Nowryta, 2004; Loukidou et al., 2004; Chojnacka et al., 2005; Horsfall and Spiff, 2004b; Singh et al., 2011; Sarkar and Majumdar, 2011; Benamer et al., 2011; Zhang et al., 2011; Kumar et al., 2011). Despite such volumes of work, industrial application of the biosorption technology is still to be developed for use in routine metal-detoxification of aqueous solutions. The present study investigated the sorption properties of acid-treated and untreated frass generated by the boring activity of Ambrosia beetles on acacia polycantha for the sorption of Cr(III) ions from a
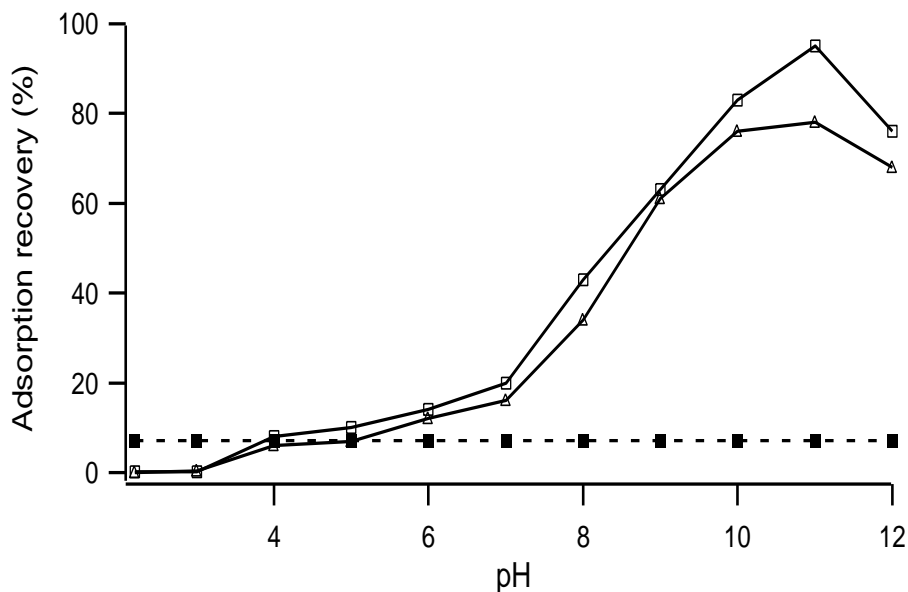
*Corresponding author. E-mail: cmahamadi@buse.ac.zw. Tel: +263 271 – 7531-6, Ext: 1007. Fax: +2632717534.

Figure 1. pH dependency of adsorption recovery of 5 mg L^{-1} Cr(III) and Cr(VI): acid-treated APF: (□); untreated APF: (△); Cr(VI): (■).

Cr(III)-Cr(VI) mixture for the first time and assessed the applicability of the adsorbent for chromium speciation.

EXPERIMENTAL

Stock solutions of 500 mgL^{-1} of Chromium(III) and (VI) were prepared from Chromium(III) nitrate non-ahydrate and potassium dichromate (Saarchem Muldersdrift, RSA), respectively. Working solutions were prepared daily from the stock solution by serial dilutions with double distilled de-ionised water. All glassware was soaked in 5% (v/v) nitric acid for at least 24 h and washed with water. Samples of Acacia polycantha frass (APF) were generated through the boring activity of Ambrosia beetles on acacia polycantha at room temperature. The samples were oven-dried at 65°C for 12 h, and sieved through 2.5 mm. Acid-treatment was achieved by mixing 10 g of the adsorbent with 500 ml of HNO$_3$ and agitating at 150 rpm for 4 h at room temperature. The adsorbent was then collected by centrifugation at 4500 × g for 10 min and then washed several times with distilled water to remove excess acid. The collected biomass was further agitated in acetone (500 ml) for 4 h, centrifuged, air-dried and stored in polythene bottles until use.

The concentration of metal ions in samples was determined by a Unicam 701-Emission Inductively Coupled Argon Plasma Echelle Spectrophotometer with "crossed" dispersion. The instrument was optimised using a 100-mg/L solution of Mn. For adsorption, 0.1-4 g of adsorbent was weighed into individual centrifuge tubes. To the tubes were added 10 ml of 1-5 mgL^{-1} of Cr(III) and Cr(VI) pH-adjusted solutions (pH was adjusted using Na$_2$CO$_3$-NaHCO$_3$). The resulting mixture was agitated at 25°C for 30 min in a water bath shaking at 150 rpm and then centrifuged at 5000 × g for 10 min. 5 ml of the supernatant was extracted and diluted to 50 ml using deionised distilled water and analysed for Cr using ICP-AES. The adsorbent was re-suspended in metal-free buffer solution to wash out traces of metal not sorbed but present on the surface. The mixture was centrifuged 4500 × g for 10 min and the supernatant discarded. The chromium ions adsorbed were extracted twice by suspending the biomass in 20 ml aliquots of 0.1 molL^{-1} HNO$_3$ and repeating the centrifuging and metal analysis procedure.

RESULTS AND DISCUSSION

Effect of pH

The pH was the first critical parameter evaluated concerning its effect on the sorption of Cr(III) from aqueous solution by the acid-treated and untreated APF. Sorption experiments were performed at 5 mgL^{-1} of metal solution, at room temperature in the pH range 2-12. As can be seen in Figure 1, adsorption of Cr(III) is highly depended on solution pH. At pH 11, nearly all Cr(III) is retained on the acid-treated APF (about 95%) compared to about 75% by the untreated APF. At low pH, cell wall ligands were closely associated with the hydroxonium ions [H$_3$O$^+$] and restricted the approach of metal cations as a result of the repulsive force.

Effect of amount of adsorbent:

The results obtained for the effect of adsorbent dose on Cr(III) uptake showed that more than 87 and 97% of Cr(III) was adsorbed by untreated and acid-treated APF respectively in the 0.1-4.0 g mass range. Optimum adsorbent doses were found to be 1.0 and 1.25 g/L for adsorption onto untreated and acid-treated biomass, respectively.

Table 1. Results from determination of Cr(III) and total Chromium.

Adsorbent	Added (mg/L)		Determined (mg/L)		
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(total)
Acid-treated APF	0.5	0.5	0.5+0.1	0.5+0.2	1.0+0.1
	1.0	1.0	1.1+0.3	1.0+0.1	1.0+0.2
	5.0	5.0	4.8+0.3	5.2+0.2	10+0.2
Untreated APF	0.5	0.5	0.4+0.1	0.4+0.1	0.8+0.1
	1.0	1.0	0.7+0.3	0.8+0.1	1.5+0.2
	5.0	5.0	3.7+0.2	3.2+0.1	6.9+0.2

Speciation of Chromium

Total Chromium in solution was determined after reduction of Cr(VI) to Cr(III) with hydroxylamine. Two milliliters of 2 mol L^{-1} HCl was added to 20 ml of the Cr(III)-Cr(VI) mixture followed by addition of 2 ml of 0.5 mol L^{-1} hydroxylamine. The solution was left at room temperature for at least 30 min before 10 ml of 1 mol L^{-1} acetate was added, pH adjusted to 4 and the volume made up to 100 ml with distilled water. The analysis of Cr(III) was performed after adsorption using acid-treated and untreated APF using the above outlined procedure. The results shown in Table 1 indicate that generally the acid treated APF was more effective in adsorption of Cr(III) and hence more suitable for the speciation study of chromium than the untreated adsorbent at metal concentrations of 0.5-5 mg L^{-1}.

Effect of KBr concentration on Cr(III) adsorption at various temperatures

To study the effects of ionic strength and temperature on the adsorption of Cr(III) from aqueous solution by the adsorbents, the uptake of Cr(III) was investigated in the presence of 0, 0.08 and 0.2 mol L^{-1} KBr at a temperature range 60-80°C. The initial rates method was used to determine the rate constants for adsorption process and the results are shown in Table 2. The results indicate that the apparent adsorption rate constant, k_{ads}, was raised in the presence of KBr, but decreases as the salt concentration is increased from 0.08 to 0.2 mol L^{-1} for the acid-treated APF. However, for the untreated APF, the apparent k_{ads} values increased as the KBr concentration was raised from 0.00 to 0.2 mol L^{-1}. It has been observed that the mechanism of metal removal from aqueous metal solution involved four steps: (i) migration of metal ions from the bulk solution to the surface of the adsorbent; (ii) diffusion through boundary layer to the biomass surface; (iii) adsorption at a binding site and (iv) intra-particle diffusion into the interior of the biomass (Horsfall Jnr and Spiff, 2004b). The boundary layer resistance will be affected by the rate of sorption and increasing the agitation time will reduce this resistance and increase mobility of the ions.

Addition of divalent ions such as Mg^{2+} and Ca^{2+} may reduce metal adsorption through competitive adsorption (Benaissa and Benguella, 2004). Addition of KBr salt to the Cr(III) solution increases the overall ionic strength of the solution. Since adsorption is mainly electrostatic in nature due to presence of polar functional groups on the adsorbent cell wall, then addition of the monovalent ions is expected to affect the rate of adsorption of metal ions by adsorbents. It is proposed in this study that adsorption at a binding site may involve formation of an intermediate, with associated activation parameters. From Transition State Theory, the thermodynamic parameters relating to the activated complex can be calculated using Equations (1) and (2).

$$k_{ads} = k_B T exp(-\Delta G^0/RT) \tag{1}$$

$$ln(k_{ads}/T) = lnk_B + \Delta S^0/R - \Delta H^0/RT \tag{2}$$

where ΔG^0, ΔS^0, ΔH^0 are the Gibbs free energy, change in entropy, change in enthalpy; k_B and R are the Boltzman constant and the molar gas constant respectively.

Therefore plots of $ln(k_{ads}/T)$ against $1/T$ should enable evaluation of the activation parameters relating to the adsorption activated complex. Figures 2 and 3 show plots of $ln(k_{ads}/T)$ against $1/T$ used to evaluate both ΔS^0 and ΔH^0 and the values obtained are shown in Table 3. A negative ΔG^0 value confirms the feasibility of the process and spontaneous nature of adsorption of Cr(III) onto the biosorbent. Negative values of ΔH^0 showed that the uptake of Cr(III) decreased with increasing temperature suggesting that the adsorption process was exothermic whereas the negative values of ΔS^0 indicated a decrease in the degree of freedom of the adsorbed species.

Conclusion

The adsorption of Cr(III) onto acacia polycantha frass

Table 2. Apparent rate constants, k_{ads}, for the adsorption of Cr(III) onto acid-treated and untreated APF at various temperatures as a function of added KBr electrolyte concentrations.

Adsorbent	Temperature (°C)	K_{ads} (x10^{-8})		
		0.00 mol L^{-1} (KBr)	0.08 mol L^{-1} (KBr)	0.2 mol L^{-1} (KBr)
Acid-treated APF	60	1.02	21.2	18.2
	70	2.55	34.5	29.3
	75	3.82	55.2	36.4
	80	9.90	63.4	52.6
Untreated APF	60	0.87	2.80	1.51
	70	1.12	4.51	8.92
	75	2.21	6.29	12.3
	80	2.32	7.91	12.5
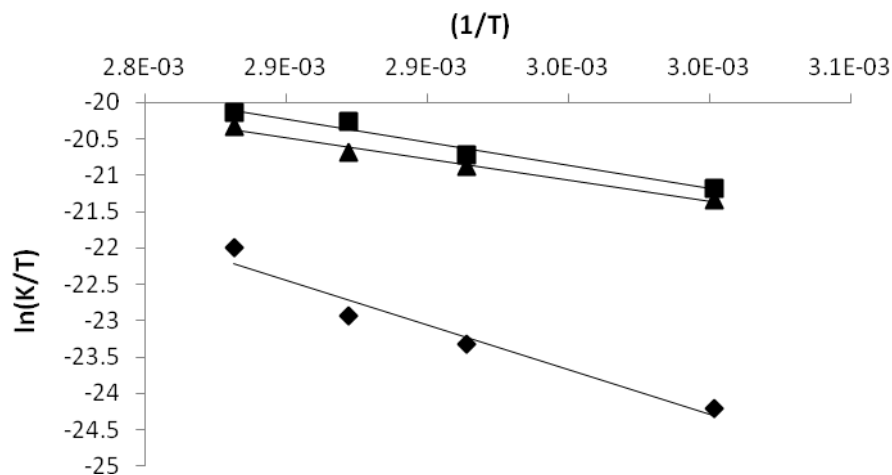
Figure 2. Effect of KBr on Cr(III) adsorption. 0.00 mol L^{-1}: (◆); 0.08 mol L^{-1}: (■); 0.2 mol L^{-1}: (▲), acid-treated APF.
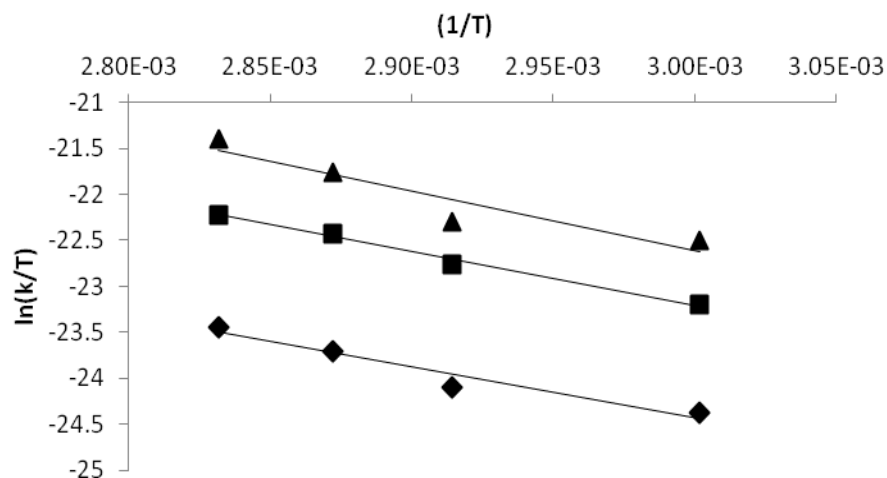
Figure 3. Effect of KBr on Cr(III) adsorption. 0.00 mol L^{-1}: (▲); 0.08 mol L^{-1}: (◆; 0.2 mol L^{-1}: (■), untreated APF.

Table 3. Thermodynamic parameters relating to the transition state for the effect of KBr on adsorption of Cr(III) by acid-treated and untreated APF.

Adsorbent	[KBr] (mol L^{-1})	ΔG^U (kJ mol^{-1})	ΔH^U (kJ mol^{-1})	ΔS^U (J mol^{-1} K^{-1})	R^2
Acid-treated APF	0.00	-32.38	-47.56	-42.10	0.8624
	0.08	-37.60	-53.60	-46.51	0.9629
	0.20	-33.69	-49.12	-44.68	0.9841
Untreated APF	0.00	-35.56	-45.56	-37.23	0.9422
	0.08	-26.82	-40.28	-39.24	0.9935
	0.20	-29.86	-44.73	-41.21	0.9821

generated by Ambrosia beetles was studied in a batch system with respect to the initial pH, temperature, adsorbent dose, and KBr concentration. Adsorption recovery for Cr(III) using acid-treated adsorbent was higher than for the untreated adsorbent showing that acid treatment enhanced the metal sorption capacity of the adsorbent. Thermodynamic parameters observed indicated that the sorption process was highly feasible. In the end it was possible to study the speciation of chromium after reduction of the hexavalent state to Cr(III) in hydroxylamine solution.

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