



Full Length Research Article

BIOSORPTION OF Cr (VI) FROM AQUEOUS SOLUTION BY UNMODIFIED AND MODIFIED SUGARCANE BAGASSE

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ABSTRACT

Chromium has been widely used in various industries like textile, leather, paint industry and many other industries. Since hexavalent chromium is a priority toxic, mutagenic and carcinogenic chemical when present in excess, it is very much required to remove chromium from effluent before allowing it to enter any water system or on to land. In the present work the removal of Cr(VI) by adsorption on the sugarcane bagasse sodium hydroxide modified sugarcane bagasse were studied. The effect of pH and initial metal ion concentration on the biosorption of Cr(VI) ions were investigated. The experimental data obtained were analyzed with Langmuir and Freundlich isotherms models. The biosorbent was characterized by FT-IR analysis

INTRODUCTION

Metal ion contamination of drinking water and wastewater, with metal ions is a serious and ongoing problem. Heavy metals are toxic at high concentrations and are high frequency pollutants seen in municipalities and specific industries. Since contaminated wastewater can easily find its way into both surface and ground water, this problem should be of great concern to anyone who obtains their drinking water from these sources. The conventional methods used to remove heavy metals include chemical precipitation, ion exchange, electrochemical treatment and reverse osmosis (Matlock *et al.*, 2002; Feng *et al.*, 2000; Mohammadi *et al.*, 2005). However, most of these techniques have some disadvantages such as complicated treatment process and high cost. The search for new, effective and economical technologies involving the removal of toxic metals from wastewater has directed attention to biosorption based on metal binding capacities of various biological materials at little or no cost. In recent years, the searches for low cost agricultural by-products have been widely studied for metal ion removal from water and wastewater.

These include watermelon shell (Banerjee *et al.*, 2012), papaya peel (Abbaszadeh *et al.*, 2015), natural leaves (Mustaqeem *et al.*, 2013), maize stalks (El-Sayed *et al.*, 2011), coconut husk (Babarinde, 2002) and apple wastes (Maranon and Sastre, 1991). This paper presents the study of biosorption of Cr(VI) from aqueous solution by sugarcane bagasse.

MATERIALS AND METHODS

Preparation of adsorbent

The sugarcane bagasse was collected from a local juice shop and it was sun dried for four days. Then they were ground using a mechanical grinder, and the resultant powder was sieved in a 150 mm particle sized mesh. They were thoroughly washed with distilled water to remove dust, mud and other impurities and were heated in an oven at 80°C for 2 hours. About 10 g of oven dried sugarcane bagasse were poured into 250 ml flask containing 100 ml of 0.1 M NaOH solution, and then were shaken at 200 rpm for 4 hours at room temperature. The mixture was left over night, and then was washed several times with distilled water to provide neutral pH. The adsorbent was then oven dried at 85°C for 2 hours. The oven dried and sodium hydroxide modified sugarcane bagasse were labelled as SB and MSB and these adsorbents used for further adsorption studies.

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Preparation of stock solution

Stock solution of chromium was prepared by dissolving potassium dichromate in deionized water. All working solutions of varying concentrations were obtained by diluting the stock solution with deionized water. The pH of the effluent was adjusted by using 0.2 M acetic acid and 0.2 M sodium acetate solutions. The concentration of metal ions in effluent was analyzed by atomic absorption spectrophotometer (AAS).

Biosorption experiments

Biosorption experiments were carried out by shaking a stopper flask containing 25 ml of 100 mg/L metal ion solution and 0.2 g of adsorbent at 200 rpm for 60 min. The sample was allowed to settle and then it was filtered through a Whatmann filter paper. The filtrate of the sample was analyzed in an AAS for the final concentration of metal ions in aqueous solution. The amount of metal adsorbed per unit mass of the adsorbent was calculated using the following equation:

$$q = \frac{V(C_i - C_f)}{M} \quad \dots\dots\dots(1)$$

where, q is the metal uptake (mg/g), C_i and C_f are the initial and final or equilibrium metal concentration in the solution (mg/L), V is the volume of the metal solution in the flask (L) and M is the dry mass of biosorbent (g). The percentage removal (%R) of metal ions was calculated from the following equation:

$$\%R = \frac{(C_i - C_f)}{C_i} \times 100 \quad \dots\dots\dots(2)$$

RESULTS AND DISCUSSION

Effect of pH

The percentage removal of Cr(VI) ions was studied, using SB and MSB as adsorbents in the pH range of 3 to 6. The experimental results are shown in Figure 1. The percentage removal of Cr(VI) ions investigated was found to increase with an increase in the solution pH upto 5, and then it decreased with the increase in the solution pH. At a lower pH, the surface of the adsorbent was surrounded by H^+ ions. The adsorbent surface becomes more positively charged, so that the attraction between the adsorbent and metal ions get reduced. As the pH increases, the adsorbent surface becomes less positively charged and this facilitates higher metal ion removal. The maximum percentage removal of Cr(VI) was observed as 60.84% for SB and 78.27% for MSB at pH 5.

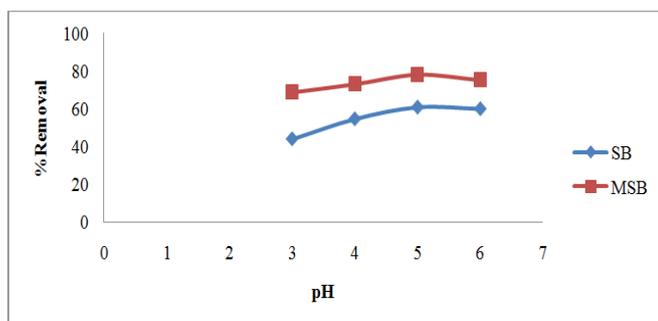


Figure 1. Effect of pH on the biosorption of Cr(VI) by SB and MSB

Effect of initial metal ion concentration

The effect of initial metal ion concentration on the biosorption of Cr(VI) ions by SB and MSB were investigated. The biosorption of metal ions decreases gradually with increase in the metal ion concentration.

Isotherm studies

Adsorption isotherm studies were conducted to determine the nature of the adsorption isotherm and the adsorption capacity of the adsorbent for the removal of metal ions. For the isotherm studies the initial metal concentrations were varied from 100 to 300 mg/L. The experimental data were applied to the two parameter isotherm models: Langmuir and Freundlich.

Langmuir isotherm

The Langmuir isotherm assumes that the uptake of metal ions on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions (Langmuir, 1918). The Langmuir isotherm can be expressed as

$$q = \frac{q_{max}bC_f}{1+bC_f} \quad \dots\dots\dots(3)$$

where, q is the metal uptake (mg of metal ion/g of adsorbent), q_{max} is the maximum metal uptake per unit mass of adsorbent (mg/g), b is Langmuir constant (L/mg) related to energy of sorption which reflects quantitatively the affinity between the adsorbent and metal ions. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is calculated by the following equation.

$$\frac{C_f}{q} = \frac{1}{q_{max}b} + \frac{C_f}{q_{max}} \quad \dots\dots\dots(4)$$

The values of q_{max} and b were calculated from slope and intercept of the linear plot of C_f/q versus C_f .

Freundlich Isotherm

The Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous species (Freundlich, 1939). The equation is commonly represented as:

$$q = KC_f^{1/n} \quad \dots\dots\dots(5)$$

where, K and n are Freundlich constants related to adsorption capacity and intensity of adsorption respectively. The above equation is rearranged in linear form to give:

$$\log q = \log K + \frac{1}{n} \log C_f \quad \dots\dots\dots(6)$$

K and n are, respectively, determined from the intercept and slope of plotting in q versus C_f . The linearised Langmuir and Freundlich isotherms of Cr(VI) are shown in Figure 2 and Figure 3. The Langmuir and Freundlich parameters and correlation coefficients (R^2) for the adsorption of Cu(II) and Zn(II) by SB and MSB are shown in Table 1. From the R^2 values the adsorption of Cr(VI) ions onto the SB and MSB is well represented by the Langmuir model, than the Freundlich isotherm model, which is based on monolayer adsorption of metal ions by the adsorbents.

Table 1. Langmuir and Freundlich isotherm constants for biosorption of Cr (VI) by SB and MSB

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{\max} (mg/g)	b (L/mg)	R^2	n	K	R^2
SB	21.7391	0.01415	0.991	2.0790	1.3152	0.955
MSB	45.4545	0.0098	1	1.5360	1.1220	0.995

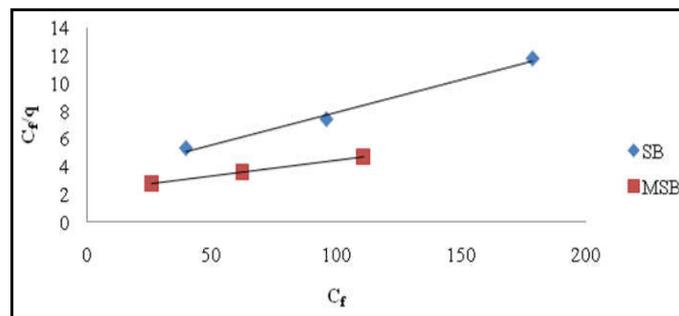


Figure 2. Langmuir isotherm plots for the biosorption of Cr(VI) by SB and MSB

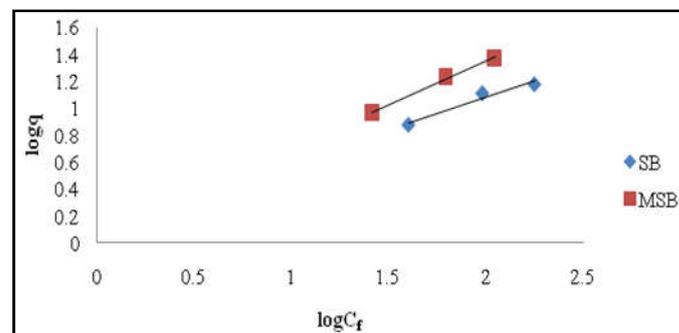


Figure 3. Freundlich isotherm plots for the biosorption of Cr(VI) by SB and MSB

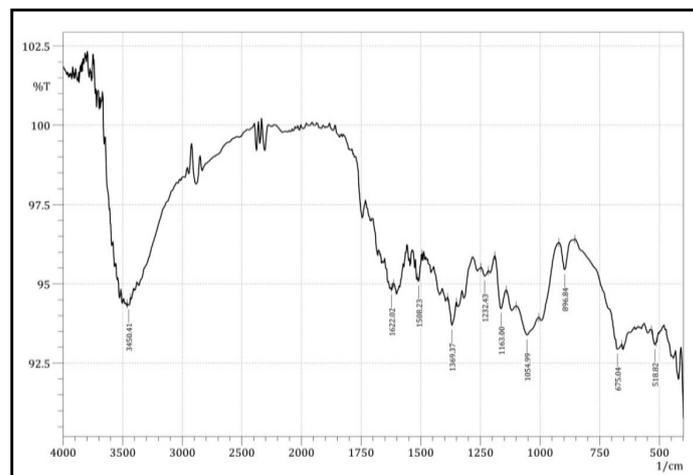


Figure 4(a). FT-IR spectrum of MSB

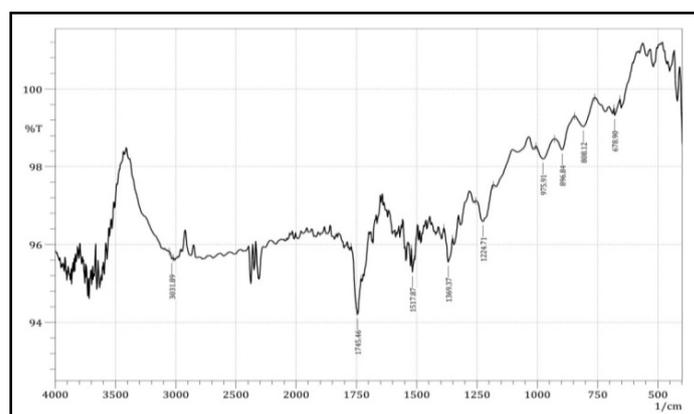


Figure 4(b). FT-IR spectrum of Cr(VI) loaded MSB

FT-IR analysis

Fourier transform infrared (FT-IR) spectral analysis was carried out in order to identify the different functional groups present in given samples. The FT-IR spectra of the MSB and metal loaded MSB adsorbent measured within the range of 500 - 4000 cm^{-1} are presented in Figure 4(a) and (b). From Figure 4(a) (MSB) the band formed at 3450.41 cm^{-1} indicates the presence of O-H stretching frequency of the H-bonded alcohols and phenols. The peak at 1622.02 cm^{-1} indicates the presence of -C=C- stretching frequency of alkenes. The peak at 1508.23 cm^{-1} indicates the presence of N=O stretching frequency of the nitro compounds (Pednekar and Raman, 2013). The FT-IR spectra of the MSB after biosorption of Cr(VI) is shown in Figure 4(b). After sorption, several functional groups which were initially present disappear, while some other had their position altered. This shows that the major functional groups involved in efficient removal of Cr(VI) are attributed to the presence of O-H, -C=C- and N=O bonds which can coordinate with Cr(VI).

Conclusion

The experimental investigation concluded that SB and MSB could be used as potential biosorbent for removal of Cr(VI) ions from aqueous solutions. The effect of pH of solution and initial metal concentration were found to be effective on the biosorption process. The Langmuir isotherm model showed the best fit for the experimental data. The interaction between Cr(VI) ions and functional groups on the surface of the biosorbent are confirmed by FT-IR analysis.

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