Full Paper

Biosorption of Cr(VI) from Aqueous Solution Using *Murraya koenigii* (Curry tree) Stems

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Abstract: In the present work, the sorption capacity of *Murraya Koenigii* Stems (MKST), an agricultural waste, is identified for the removal of Cr(VI) from aqueous solution and the effect of different process parameters likes pH and adsorbent dosage were studied. pH 1 is observed to be the optimum pH for Cr(VI) sorption onto the biosorbent. The equilibrium data of Cr(VI) sorption fit well with the Langmuir model with a monolayer sorption capacity of 12.25 mg/g. The results show that the metal ion interacts strongly with the biosorbent and can be effectively used in the removal of Cr(VI) from aqueous solution.

Keywords: Cr(VI); equilibrium; Murraya koenigii stems; sorption

1. INTRODUCTION

The presence of Cr(VI) in surface and ground water even in low concentrations is toxic and leads to carcinogenic and mutagenic effects [1]. Chromium is a highly toxic metal compared to other toxic heavy metals discharged into water bodies through industrial effluents. Cr(VI) is present in an undesirable quantity in the effluent from metal cleaning, plating, leather and mining industries [2]. The toxic Cr (VI) mixed water damage the aquatic biota by their toxic effects and hence removal of Cr(VI) is important. Some of the methods involved in the removal of Cr(VI) include ion exchange, electrochemical precipitation [3, 4], biological method [5], reverse osmosis [6] etc. However, these methods have considerable disadvantages like high cost and incomplete Cr (VI) removal, hence biosorption is widely used for the removal of Cr(VI) from wastewater.

Biosorption with low cost materials is effective for Chromium removal from wastewater. Some of the biosorbents studied in biosorption of chromium includes, sugarcane bagasse [7], catla catla scales [8], Sawdust [9], *Tamarindus indica* seeds [10], walnut, hazelnut and almond shell [11], wheat bran [12], pistanchio hull waste [13], soy hull [14] etc. Still there is continuously search for biosorbents in removal of Cr(VI) from aqueous solution due to the importance associated with the sorption of Cr(VI) from industrial waste water.

Murraya koenigii which is commonly known as curry tree [15] is widely available in the southern part of India. The stems were a solid agricultural waste discarded in market places in India and is available free of cost. The material has gained attention in using this as an absorbent in sorption of Cr(VI) from aqueous solution. The objective of the present work is to examine the biosorption and access the feasibility of using curry tree stem (an abundant material in south India) as an biosorbent for the removal of Cr(VI) from aqueous solution.

2. MATERIAL AND METHODS

2.1 Chemicals

The Cr(VI) stock solution (1000mg/L) using $K_2Cr_2O_7$ (HiMedia Laboratories Pvt. Limited, Mumbai) was prepared by dissolving 2.828 of potassium dichromate in 1000 mL of deionised water. From the stock solution, different concentrations of Cr(VI) were prepared by appropriate dilution and used in sorption studies.

2.2 Preparation of biosorbent

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The stems of *Murraya koenigii* used in the present investigation were collected from the local Market in Chennai, Tamilnadu. The collected materials were cut into small pieces, washed with double distilled water to remove the dirt particles and it is then dried in a hot air oven at 60 °C for 24 hours. The material is then ground using a domestic mixer. The ground material is then sieved to particle size of 80-100 mesh (BSS). The material is then stored in plastic bottles for adsorption studies [16].

2.3 Batch Chromium (VI) sorption Experiments

The amount of Cr(VI) sorbed onto the biosorbent was determined by using a sorbate concentration of 2 mg/L with different amount of the biosorbent (0.025, 0.050, 0.075, 0.1, 0.125, 0.150 g) in orbital shaker at room temperature for an equilibrium time of 8 h. The Cr(VI) samples were taken out after attaining equilibrium and the solid is separated from the liquid using whattman filter paper. To the above 15 mL solution is added 3 M sufficient H_2SO_4 in a 25 mL standard flask and to this is added 1mL of 1,5 diphenyl carbazide reagent and made up to 25 mL using deionized water to get a pink coloured complex. The solution concentration is then determined spectrophotometrically at a wavelength of 540 nm [17]. The percentage removal of metal ion and the amount of metal ion sorbed on to the unit weight of the sorbent mass was calculated using the equations:

$$\text{Percentage removal} = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

The amount of metal ion sorption at equilibrium q_e (mg/g) was calculated by

$$\text{Amount adsorbed } (q_e) = C_i - C_f \times \frac{V}{M} \qquad (2)$$

where C_i and C_e are the liquid phase concentrations of the metal ion at initial and equilibrium concentrations (mg/L) respectively. *M* is the mass (g) of biosorbent and *V* is the volume of metal ion solution (mL).

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The percentage sorption of Cr(VI) increases with decrease in pH (Figure 1) from 6.5 to 1 and reaches a limit in biosorption at pH 7 and after that no sorption is observed. It is observed that maximum sorption takes place at pH 1. This is because in acidic medium the biosorbent is protonated on the surface and a large number of positive surface functional groups binding with the negatively charged chromate ion at lower pH. Hence, the oxyanions of Cr(VI) attracts the biosorbent to a greater extent. As the pH is increased above 4, the biosorbent surface carries a negative charge and hence, reducing the sorption of Cr(VI).
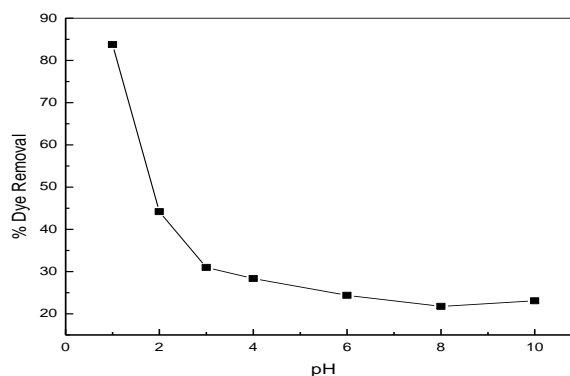

Figure 1. Effect of pH in sorption of Cr onto MKST (C_0 = 2 mg/L; m= 100 mg; V=0.05 L)

3.2 Effect of Adsorbent Dosage

The percentage Cr(VI) sorbed (mg/g) with an increase in sorbent dosage is observed to increase drastically and beyond a dosage of 150 mg reaches saturation as shown in Figure 2. The sorbent dosage was varied in the range of 25 to 150 mg and the sorption of Cr(VI) for a metal ion concentration of 2 mg/L was studied.

The percentage Cr(VI) removal at the optimum pH 1 was observed to increase from 62.6% to 98.31% for an biosorbent dosage of 25 to 150 mg and reaches saturation. This is due to the availability of sorption sites and surface area [18]. A sorbent dosage of 150 mg was required to attain maximum dye removal. It is evident that, the sorption of Cr(VI) onto the sorbent is low when the sorbent to the metal ion concentration is low. On the other hand, when the sorbent to the Cr(VI) concentration is high, then the sorption is more onto the sorbent surface and hence there is a decrease in the Cr(VI) concentration in the solution. Hence, more the sorbent dosage the greater is the volume of Cr(VI) that a particular biomass dosage can purify and the Cr(VI) concentration in the solution decreases.

3.3 Adsorption Isotherm

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The equilibrium sorption data for Cr(VI) onto the biosorbent is described by using various equilibrium isotherms Langmuir [19], Freundlich [20] and Temkin [21]. The Langmuir model assumes that the sorption occurs as a monolayer of Cr(VI) onto the biosorbent and the metal ion occupies a specific site on the sorbent and no further adsorption can take place at that site. The sorption of Cr(VI) were studied with the linear form of the isotherm equations 3, 4 and 5.

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \text{ or } C_e/q_e = 1/Q_m K_L + C_e/Q_m \quad (3)$$

$$q_e = K_F C_e^{1/n} \text{ or } \log q_e = 1/n \log C_e + \log K_F \quad (4)$$

$$q_e = RT/b \ln(K_T C_e) \text{ or } q_e = B_1 \ln K_T + B_1 \ln C_e \quad (5)$$

C_e is the concentration of the Cr(VI) solution (mg/L) at equilibrium, q_e the amount of Cr(VI) sorbed *per* unit weight of sorbent (mg/g) and K_L is the constant related to the free energy of adsorption (L/mg). The isotherm constants Q_0 and b for the biosorption of Cr(VI) was calculated from the slope and intercept of the linear plot Ce/qe vs Ce (Figure 3) and the results are shown in Table 1. K_F is a Freundlich constant indicative of the relative adsorption capacity of the sorbent (mg/g) and $1/n$ is the sorption intensity. The constant B=RT/b is related to the free energy of sorption and K_T is the temkin isotherm constant(L/g) where these constants can be calculated from a plot of q_e vs $\ln C_e$.
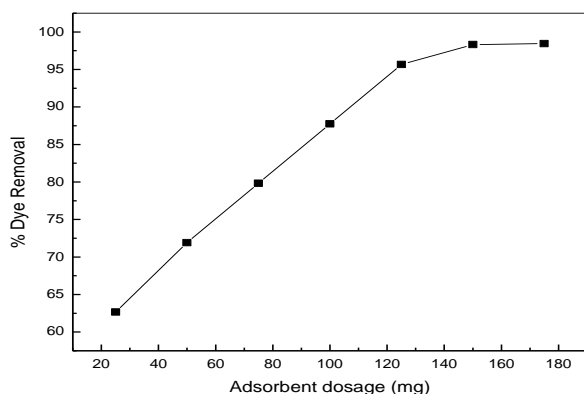

Figure 2. Effect of sorbent dosage in sorption of Cr onto MKST (C_0 = 2 mg/L; V=0.05 L).

The results of Cr(VI) removal by MKST using Langmuir, Freundlich and Temkin isotherm constants are shown in Table 1. The results of the Langmuir isotherm from Table 1 proves high R^2 value (>0.99) and hence proves that this isotherm provides the best fit for the sorption process in monolayer coverage of Cr(VI) onto the biosorbent.

The equilibrium parameter R_L is given by the

expression [22]:

$$R_L = 1/1 + K_L \times C_0 \quad (6)$$

The value of R_L in 0-1 range (0.7843-0.3773) for all the metal ion concentrations suggests that the sorption of Cr(VI) is a favorable process. A similar result in the biosorption of Cr(VI) onto the biosorbent was reported in the literature [22].

Table. 1. Langmuir, Freundlich and Temkin constants for sorption of Cr onto MKST.

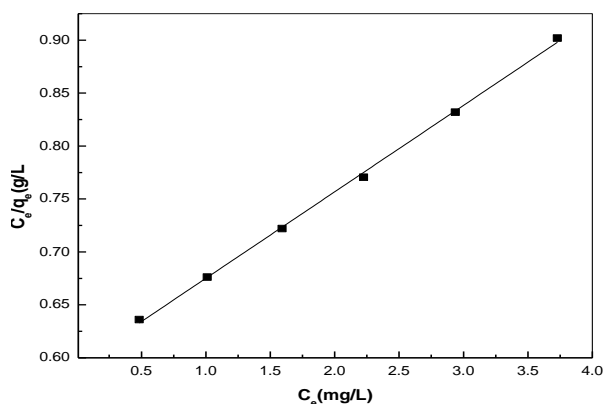| Langmuir constants	Freundlich constants	Temkin constants
Q_m (mg/g) = 12.25	K_F (mg/g) = 1.44	K_T (L/mg) = 2.78
K_L (L/mg) = 0.1375	n = 1.20	B_1 = 1.65
R^2 = 0.9987	R^2 = 0.9962	R^2 = 0.957
R_L = 0.7843–0.3773		

Figure 3. Langmuir Sorption Isotherm for Cr removal by MKST.

The Freuendlich isotherm constants n and K_f for the sorption of Cr(VI) onto MKST was calculated from the plot of log Ce vs log q_e (Figure 4) iand the results are given in Table 1. Then value was found to be 1.20 for MKST sorption indicating favorable sorption. The R^2 value (>0.99) for the sorption of Cr(VI) proves that the freundlich model is comparable to to the Langmuir model and is low compared to Langmuir and hence this proves that the Langmuir model proves to be the best fit for the sorption of Cr(VI) from aqueous solution.

Temkin isotherm suggests the heat of Cr(VI) sorption and the interactions of the molecules to decrease linearly with coverage [21]. and the sorption is characterized by uniform distribution of binding energy. The temkin isotherm constants B_1 and K_T are calculated from the plot of q_e vs $\ln C_e$ (Figure 5) and the

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results are shown in Table 1. The R^2 value 0.9570 is low compared to Langmuir model and Freundlich model and this proves that this model provides poor fit for the sorption of Cr(VI) onto the biosorbent.
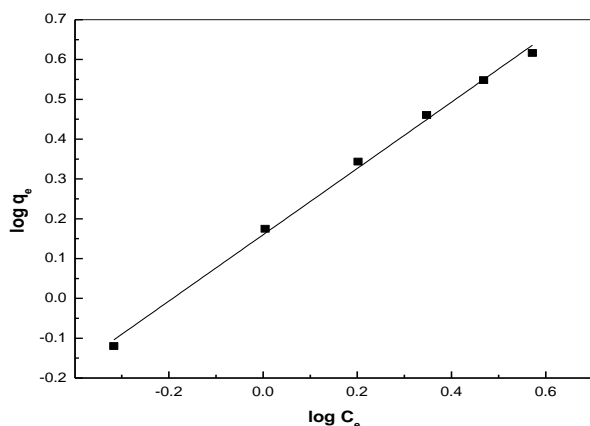

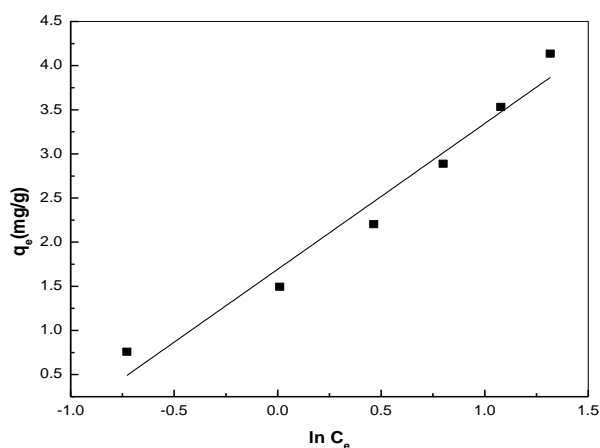**Figure 4.** Freundlich Sorption Isotherm for Cr removal by MKST.

Figure 5. Temkin Sorption Isotherm for Cr removal by MKST.

It is observed that the R^2 for Langmuir > Freuendlich > Temkin. This proves that Langmuir model is comparable to Freundlich model and it can be concluded that the coverage of Cr(VI) onto MKST follows both the isotherms in the present study.

4. CONCLUSION

The biosorption of Cr(VI) onto MKST reveals that it can be used for the removal of heavy metal ions from aqueous solution. The MKST sorption equilibrium data fitted well with the Langmuir isotherm, confirming the monolayer coverage of Cr(VI) onto MKST with a monolayer adsorption capacity of 12.25 mg/g. The dimensionless separation factor (R_L) value between 0 and 1 shows favorable sorption. The biosorbent used in this study is an agricultural waste product, freely and abundantly available and hence it can be used for the removal of heavy metal in industrial wastewater treatment processes.

5. REFERENCES AND NOTES

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