



Removal of Hexavalent Chromium from Aqueous Solution by Adsorption on Raw Powder and Chemically Activated Carbon of *Hibiscus rosa-sinensis* Flowers

Renny Mariam Mathew, M. Arthy, M. P. Saravanakumar and C. Balamurali Krishna
School of Mechanical and Building Sciences, VIT University, Vellore-632 014, T. N., India

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ABSTRACT

Adsorption using low cost adsorbents is one of the cheapest methods that can be used for removal of hexavalent chromium from water. In this study, a comparison has been carried out on adsorption using raw *Hibiscus rosa-sinensis* flowers and activated carbon prepared by impregnation of the *Hibiscus rosa-sinensis* flower. *Hibiscus rosa-sinensis* flowers are low cost adsorbents available throughout the year and easily biodegradable, and hence cost effective. Impregnation of the flower powder with different ratios of sulphuric acid was carried out. Adsorption using carbon is found to be more efficient as compared to the raw flowers. The optimum adsorbent dosage for the carbon was found to be 200mg/100mL, and for the raw flower 400mg/100mL. Both, Langmuir and Freundlich isotherms were studied and from the values of coefficient of determination obtained, it was concluded that the Langmuir isotherm fits well. Kinetic studies were also conducted. This included the pseudo first order and pseudo second order kinetics. The $q_{e,cal}$ values obtained for pseudo first order kinetics for the carbon and raw flower were 7.799 mg/g and 29.459mg/g respectively. This showed a large variation from the experimental value. But for the pseudo second order kinetics only a slight variation from the experimental value was observed. Hence, it was concluded that the adsorption process followed pseudo second order kinetics.

INTRODUCTION

Heavy metal contamination of water occurs due to a number of industries like tanneries, metal plating, alloy industries, storage battery industries, etc. (Vivek et al. 2009). The effluents coming from these industries have high concentrations of heavy metals which do not degrade easily, and hence pollute the waters. The various heavy metals present include chromium, cadmium, lead, nickel, etc. Chromium compounds are one of the most harmful water pollutants. The hardness value of chromium is very high. Chromium is released into the environment by a number of natural processes like weathering of rocks and by volcanic activity (Natale et al. 2007). Various industries like leather tanning, electroplating, metal finishing, etc. are also a major source of chromium (Umesh et al. 2009). A major release of chromium into the environment is from the tanning industry itself. With around 2161 tanneries in India, more than 5,00,000 tonnes of skins and hides are processed in a year (Dinesh et al. 2006). It is present as trivalent chromium and hexavalent chromium. Trivalent chromium is considered as a bioelement in lower concentrations whereas hexavalent chromium is highly toxic, carcinogenic and mutagenic and 500 times more toxic than trivalent chromium. Hexavalent chromium is also found to have higher mobility than trivalent chromium. The effects of chromium on humans include lung

cancer and damage to kidneys, liver, etc. (Vinod et al. 2010). Trivalent chromium is not toxic but when disposed from industries as liquid effluents these can be oxidised to hexavalent chromium. Hence, limiting values are set for both trivalent and hexavalent chromium. As per the Bureau of Indian Standards, 0.05mg/L is set as the maximum permissible limit for hexavalent chromium.

Various methods are used for removal of hexavalent chromium like ion exchange, reverse osmosis and precipitation. These methods have a lot of disadvantages like a large amount of toxic sludges, incomplete metal removal and high energy requirements. Adsorption is a cost effective method for removal of chromium from water (Albino et al. 2007). Adsorption using low cost adsorbents is highly effective. Various studies have been carried out using various naturally available materials for chromium removal. Low cost adsorbents like rice hull ash, used tyres, used tea leaves, fertilizer industry waste, agricultural industry waste, etc. have been used effectively for removal of chromium from aqueous solutions.

In this study flowers of *Hibiscus rosa-sinensis* have been used for adsorbing chromium from aqueous medium. The flowers are natural adsorbents available throughout the year and are easily biodegradable making them a suitable adsorbent. The stems and leaves of *Hibiscus rosa-sinensis* have been used earlier as adsorbent for heavy metal removal and found to be highly effective in this process (Krishnaveni et al. 2012).

Adsorption using activated carbon is found to be highly effective due to the higher surface area of the carbon which enhances the adsorption capacity (Mojdeh et al. 2010). Removal efficiency depends on surface area and will be higher for higher surface area (Nadhem et al. 2001). The adsorption capacity on activated carbon also depends on the solution pH. Activated carbon is found effective in eliminating odour and taste from contaminated water. Acid treated *Hibiscus rosa-sinensis* leaf powder is an efficient adsorbent for removal of Cu(II), Ni(II) and Fe(III) from solutions (Shelke et al. 2010).

The effect of the various parameters like contact time, pH, initial ion concentration and adsorbent dosage have been studied. Chromium adsorption is found to increase with an increase in the adsorbent dosage due to the greater availability of the adsorption sites (Anandkumar et al. 2009). Maximum adsorption is found to occur at an acidic pH. The adsorption capacity is found to decrease with an increase in the initial ion concentration. This may be due to the limited number of active sites available for adsorption for a higher metal ion concentration.

MATERIALS AND METHODS

Preparation of biosorbent: *Hibiscus rosa-sinensis* flowers were collected and dried in a hot air oven at 150°C and powdered. A part of this powdered flowers was used as one adsorbent. The other adsorbent was prepared by chemically modifying the flower powder. This is done by impregnating the flower powder with concentrated sulphuric acid in a 1:1 ratio, i.e. one part of the dried powder is mixed with one part of sulphuric acid. This impregnated flower powder was kept in hot air oven at 150°C for 24 hours and further in muffle furnace at 450°C for 4 hours. The carbon obtained was then washed with distilled water until the pH of the water remains in the range of 6.5-7. The washed carbon was again dried and made to fine powder and used as an adsorbent.

Preparation of chromium solution: Chromium stock solution was prepared by dissolving 2.828 g of potassium dichromate in 1000mL distilled water. This gives a 1000ppm solution of chromium. All the solutions required for the experiment were prepared by diluting this stock solution. The standard solutions required for the analysis were also prepared from this stock solution by diluting it in suitable proportions.

Adsorption experiments: Adsorption experiments were carried out to optimize the contact time, initial ion concentration, adsorbent dosage and pH. In order to optimize the contact time, chromium solution of a known initial ion concentration and pH are taken and a known amount of adsorbent is added to it. This solution is then mixed in a rotary shaker at 150 rpm and the samples are collected every 30 minutes.

The samples were then filtered and analysed by atomic absorption spectroscopy (Make: VARIAN). Once the contact time is optimized, experiments were performed to optimize the other parameters. In order to optimize the initial ion concentration, the other parameters were kept constant and the initial ion concentrations were varied from 50mg/L to 300mg/L. The samples collected were analysed and the concentration with maximum removal efficiency was found out. Once the initial ion concentration is optimized, the pH and adsorbent dosage can be optimized in a similar way by varying the pH and adsorbent dosage respectively, and hence the effect of the parameters on the adsorption process can be found out. pH variation can be carried out using sodium hydroxide and concentrated hydrochloric acid.

Adsorption isotherms: Isotherms give the concentration of the adsorbate in the solution C_e (mg/L) to the amount adsorbed on the adsorbent q_e (mg/L). In this work, two types of isotherms were studied with the experimental data. The Langmuir isotherm shows that the metal ion adsorption takes place on a homogeneous surface by monolayer adsorption. The Langmuir isotherm is based on the following equation :

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot K_L} + \frac{C_e}{q_{max}} \quad \dots(1)$$

A graph is plotted with C_e/q_e vs. C_e and the values of q_e and K_L can be obtained from the graph. Here,

- C_e - equilibrium concentration (mg/L)
- q_e - amount adsorbed at equilibrium (mg/g)
- K_L - Langmuir isotherm constant (L/mg)

Freudlich isotherm gives the adsorption on a heterogeneous layer. The amount of adsorbate adsorbed onto a given mass of adsorbent to the amount of adsorbate in the solution is not constant at different concentrations. This is given by the Freundlich isotherm. The equation for Freundlich isotherm is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots(2)$$

A graph is drawn with $\log q_e$ vs $\log C_e$. The values of K_F and n are obtained from the graph.

Here, K_F is the Freundlich constant (mg/g) (L/g) $1/n$.

Kinetic studies: The pseudo first order and pseudo second order kinetics were studied. The kinetics with higher r^2 value indicated that the adsorption followed the particular kinetics. The pseudo first order kinetics is given by the following equation.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(3)$$

A graph is plotted between $\ln(q_e - q_t)$ vs. t from which q_e and k_1 can be calculated.

Pseudo second order kinetics follows the equation:

$$\frac{1}{q_e} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \quad \dots(4)$$

A graph is plotted with t/q_t vs. t . The value of q_e and K_2 can be calculated from the graph. From these equations,

K_{1p} is pseudo-first order kinetic model constant (h⁻¹)

K_2 is pseudo-second order kinetic model constant (g mg⁻¹ h⁻¹)

RESULTS AND DISCUSSION

Fig. 1 portrays that when the raw flowers were used as an adsorbent, 400mg/100mL was found suitable for the removal of hexavalent chromium. From the Fig. 2 it is observed that 200mg/100mL of adsorbent dosage (flowers made into carbon) was optimum when the experiments were carried out in the range of 100-500mg/100mL.

As discussed earlier, the biosorption equilibrium of Cr⁶⁺ by raw flower and carbon was modelled by using conventional isotherms, i.e., Langmuir and Freundlich. These models were applied to the experimental data of both raw and carbon adsorbents. Fig. 3 shows the Langmuir isotherms for the raw and carbon adsorbents. The Langmuir constants and coefficient of determination were calculated from the plots and given in Table 1.

The q_{max} values for the raw and carbon adsorbents were 11.904 and 16.94 mg/g respectively. The values show that the impregnation of *Hibiscus rosa-sinensis* flower petals in sulphuric acid increases the active sites which results in increase in maximum adsorption capacity. The R^2 values for raw and carbon adsorbents were 0.993 and 0.994 respectively.

The Freundlich isotherm is given in Fig. 4 and the constants are presented in Table 1. Although, Freundlich model presents a good adjustment to the experimental data in case of both raw flower and carbon, the determinant of coefficient supports the Langmuir isotherm than Freundlich isotherm. The application of both Langmuir and Freundlich models for the adsorption of Cr⁶⁺ on raw and carbon

adsorbents expresses the existence of monolayer adsorption and heterogeneous energetic distribution of active sites on the surface of the adsorbent.

For both raw and carbon adsorbents for the sorption of Cr⁶⁺, pseudo first order and second order kinetic were also plotted to find the rate kinetic constants and $q_{e,cal}$. In the pseudo first order, significant deviation between experimental and calculated q_e values was observed. But, the calculated and experimental values of q_e were similar in pseudo second order kinetics. Hence, it is concluded that pseudo second order kinetic model suits very well than the first order model. Also, the coefficient of determination supports this conclusion. Pseudo first order and second order are shown in Fig. 5 and Fig. 6 respectively. The kinetic constants and coefficient of determination are given in Table 2.

CONCLUSION

In this study conducted with both carbon and raw flowers, it was observed that the carbon showed a high removal efficiency as compared to the raw flower. The optimum dosage obtained for carbon was 200mg/100mL, whereas for the raw flower it was 400mg/100mL. From the coefficient of determination obtained, it was concluded that the Langmuir isotherm fits well for the adsorption process. This indicated adsorption on a monolayer. From the $q_{e,cal}$ values obtained from the graph and the coefficient of determination, it was found that the adsorption process followed the pseudo second order kinetics.

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Table 1: Langmuir and Freundlich parameters.

S.No	Biomass type	Langmuir parameters			Freundlich parameters		
		q_{max} (mg/g)	K_L	R^2	n	K_f	R^2
1.	Carbon	16.94	1.0727	0.9932	-6.134	4.233	0.9692
2.	Raw flower	11.904	2.21	0.9944	2.358	5.667	0.9823

Table 2: Pseudo first order and second order parameters.

S.No	Biomass type	Pseudo first order			Pseudo second order		
		q_e (mg/g)	K_{1p}	R^2	q_e	K_2	R^2
1.	Carbon	7.799	0.037	0.9822	18.18	0.00927	1
2.	Raw flower	29.459	0.059	0.7605	16.12	0.00486	0.9907

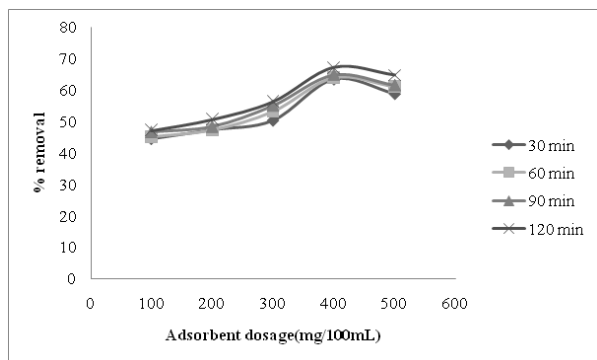


Fig. 1: Efficiency of Cr⁶⁺ removal with different adsorbent dosage (raw flowers).

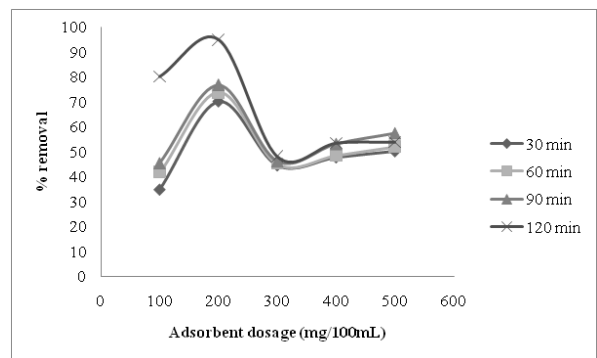


Fig. 2: Efficiency of Cr⁶⁺ removal with different adsorbent dosage (carbon).

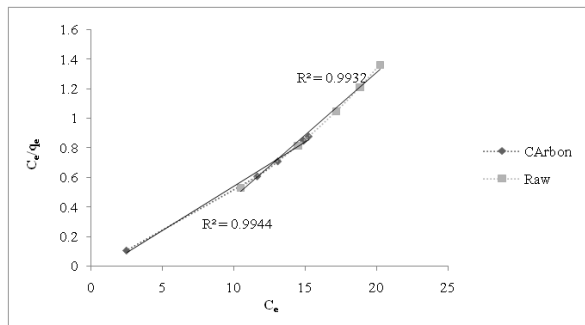


Fig. 3: Langmuir adsorption isotherm for carbon and raw flower.

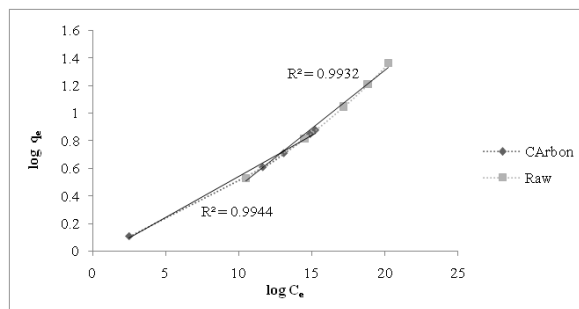


Fig. 4: Freundlich adsorption isotherm for carbon and raw flowers.

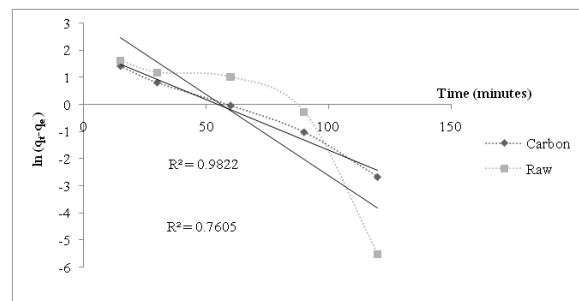


Fig. 5: Pseudo first order kinetics.

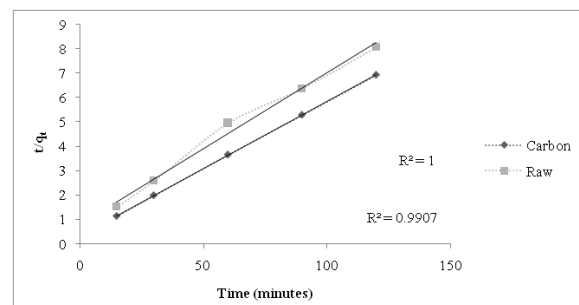


Fig. 6: Pseudo second order kinetics.

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