

Adsorption of Chromium (VI) by a Low-Cost Adsorbent Prepared from Tamarind Seeds

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ABSTRACT

The presence of toxic heavy metals such as chromium (VI) contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies, is one of the most important environmental problems. Adsorption is one of the effective techniques for chromium (VI) removal from wastewater. In the present study, adsorbent is prepared from tamarind seeds and studies are carried out for chromium (VI) removal. Tamarind seeds are activated with the use of concentrated sulfuric acid (98% w/w). Batch adsorption studies demonstrate that the adsorbent prepared from tamarind seeds has a significant capacity for adsorption of chromium (VI) from aqueous solution. The parameters investigated in this study include contact time, adsorbent dosage, initial chromium (VI) concentration and pH. The adsorption process of chromium (VI) is tested with Langmuir and Freundlich isotherm models. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 11.08 mg/g at a solution pH of 7. The adsorption of chromium (VI) was found to be maximum at low values of pH in the range of 1-3.

Keywords: Adsorption capacity; Chromium (VI); Tamarind seeds; Langmuir isotherm.

INTRODUCTION

Chromium is used in industries such as electroplating, leather tanning, paints, and pigments etc., and has the potential to contaminate drinking water sources [1,2]. Chromium exists in different oxidation states in nature, of which chromium (VI) is the most water soluble and easily enters the living cells. As determined by the National Toxicology Program (NTP), the International Agency for Research on Cancer (IARC), Chromium (VI) is a human carcinogen.

In general, chromium (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, cementation, ion-exchange, reverse osmosis, electrodialysis, solvent extraction, and evaporation, etc. [3]. These methods are, however, cost intensive and are unaffordable for large scale treatment of wastewater that is rich in chromium (VI). Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular [4,5]. Other commercial adsorbents are recently reported to have been used in industries, although their versatility and adsorption capacity are generally less than those of activated carbon [6].

In the present study, adsorbent is prepared from tamarind seeds and studies are carried out for chromium (VI) removal. Tamarind seeds are activated by giving heat treatment with the use of concentrated sulfuric acid (98% w/w). Batch experiments are carried out for kinetic studies on the removal of chromium (VI) from aqueous solution using the activated tamarind seeds adsorbent. The effect of various parameters such as contact time, adsorbent dosage, initial chromium (VI) concentration and pH has been studied.

EXPERIMENTAL WORK

Preparation of Adsorbent

Tamarind seeds are collected from the wastage of Cafeteria and Guest House (BITS - Pilani) of the institute. The seeds are washed with distilled water and dried at 110°C for 5 h. The dried seeds are crushed in small particles by using Jaw crusher. Then it is treated with concentrated sulphuric

acid (98% w/w) in 1:1 weight ratio and is kept in oven at 150°C for 24 h. The carbonized material is washed with distilled water to remove the free acid and dried again at 100°C for 5 h.

Batch Experiments

All the chemicals used are of analytical grade. A stock solution of chromium (VI) is prepared by dissolving 2.8287 g of 99.9% potassium dichromate ($K_2Cr_2O_7$) in 1000 ml of distilled water. This solution is diluted as required to obtain standard solutions containing 20, 40, 50, 60, 80, 100, and 200 mg/L of chromium (VI). 0.5 N HCl and 0.5 N NaOH solutions are used for pH adjustments.

The batch experiments are carried out in 100 mL borosil conical flasks by agitating a pre-weighed amount of the tamarind seeds adsorbent with 25 mL of the aqueous chromium (VI) solutions for a predetermined period at 30°C on a water bath-cum-mechanical shaker. The adsorbent is separated with filter paper. Adsorption isotherm study is carried out with different initial concentrations of chromium (VI) from 20 to 200 mg/L while maintaining the adsorbent dosage at 10 g/L. The effect of time and pH are studied at 30°C with a chromium (VI) concentration of 50 mg/L and an adsorbent dosage of 10 g/L. The effect of adsorbent dosage is studied by varying the adsorbent amount from 4 g/L to 24 g/L with a chromium (VI) concentration of 50 g/L.

The concentration of free chromium (VI) ions in the effluent was determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as an complexing agent. The absorbance of the purple-violet colored solution is read at 540 nm after 20 min.

RESULTS AND DISCUSSION

In the present study, tamarind seeds are activated and used for chromium (VI) removal from aqueous solutions. Table-1 shows the adsorbent capacity of various adsorbents. When compared with other non-conventional adsorbents, the results of the present study indicate that adsorbent prepared from tamarind seeds has better adsorption capacity in many cases (biomass residual slurry, Fe(III)/Cr(III) hydroxide, Waste tea, walnut shell), comparable adsorption capacity with (palm pressed-fibers, maize cob, sugar cane bagasse) and lower adsorption capacity with (activated carbon, saw dust) for chromium (VI) ions [3,7,8,9,10,11]. Based on the above results obtained, the effect of various parameters such as equilibrium time, pH, amount of adsorbent etc. has been studied.

Table No. 1: Summary of adsorbent capacity of various adsorbents

Adsorbent	Maximum Adsorbent Capacity, q_m (mg/g)	Reference
Activated Carbon (Filtrisorb-400)	57.7	[7]
Sawdust	39.7	[8]
Palm pressed-fibers	15.0	[9]
Maize cob	13.8	[8]
Sugar cane bagasse	13.4	[8]
Tamarind seeds	11.08	Present Study
Biomass residual slurry	5.87	[3]
Waste tea	1.55	[10]
Fe(III)/Cr(III) hydroxide	1.43	[11]
Walnut shell	1.33	[10]

Effect of Contact Time

Fig. 1 shows the effect of contact time for the adsorption of chromium (VI) on Tamarind seeds. It is evident that time has significant influence on the adsorption of chromium (VI). It is apparent from Fig. 1 that till 10 h, the percentage removal of chromium (VI) from aqueous solution increases rapidly and reaches upto 65%. After that, the percentage removal of chromium (VI) increases slowly till 50 h and reaches upto 71%. A further increase in contact time has a negligible effect on the percentage removal. Therefore, the contact time of 50 h could be considered for adsorption of chromium (VI) on Tamarind seeds for entire batch studies.

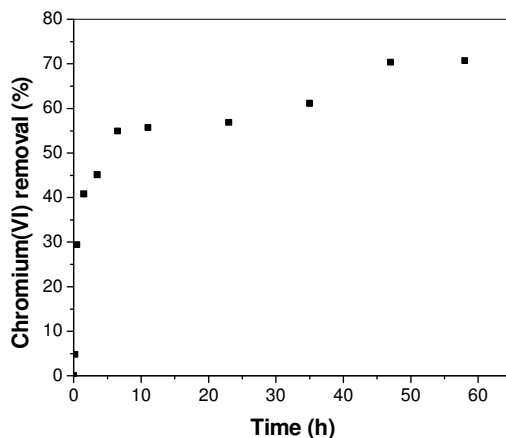


Fig. No. 1: Effect of contact time on chromium (VI) adsorption

Adsorption Isotherm

The equilibrium of sorption is one of the important physico-chemical aspects for the evaluation of the sorption process as a unit operation. The sorption isotherm studies are conducted by varying the initial concentration of chromium (VI) from 20 to 200 mg/L and maintaining the adsorbent dosage of 10 g/L. The adsorption isotherm (q_e versus C_e) shows the equilibrium between the concentration of chromium (VI) in the aqueous solution and its concentration on the solid (mass of chromium (VI) per unit mass of Tamarind seeds). It is evident that adsorption capacity increases with increasing equilibrium chromium (VI) concentrations. Fig. 2 shows that the adsorption capacity increases rapidly from 0 to 4.2 mg/g for the equilibrium concentration of 0 to 20 mg/L. Further a gradual increase in adsorption capacity is observed with the increase in equilibrium concentration and it reaches upto 10.5 mg/g for the equilibrium concentration of 102 mg/L. In order to model the sorption behavior, adsorption isotherms have been studied. The adsorption process of chromium (VI) are tested with Langmuir and Freundlich isotherm models. Langmuir and Freundlich equations are given in equation (1) and (2), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (1)$$

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (2)$$

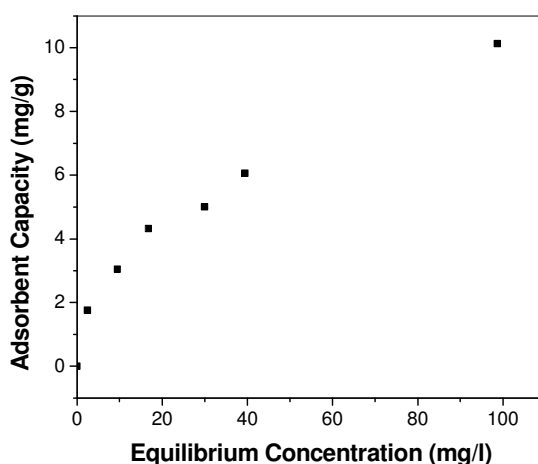


Fig. No. 2: Adsorption isotherm for chromium (VI) removal on Tamarind seeds.

The isotherm data has linearized using the Langmuir equation and shown in Fig. 3. The regression constants are tabulated in Table-1. The high value of correlation coefficient ($R^2 = 0.93$) indicated a good agreement between the parameters. The constant q_m , which is a measure of the adsorption capacity to form a monolayer, can be as high as 11.08 mg/g at pH 7. The constant b , which denotes adsorption energy, is equal to 0.049 L/mg. The same data also fitted with the Freundlich equation and shown in Fig. 4. The regression constants are listed in Table-2. The value of correlation coefficient ($R^2 = 0.99$) showed that the data conform well to the Freundlich equation although the strength of the relationship between parameters is not as good as in the case of the Langmuir equation.

Table No. 2: Isotherm constants for adsorption of chromium (VI) on activated neem leaves.

Langmuir Isotherm			Freundlich Isotherm		
Constants		Correlation Coefficient (R^2)	Constants		Correlation Coefficient (R^2)
q_m (mg/g)	b (L/mg)		K_F	n	
11.08	0.049	0.93	1.051	2.06	0.99

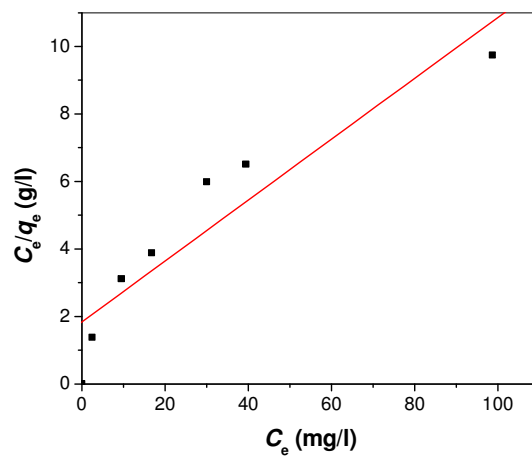


Fig. No. 3: Langmuir Isotherm for adsorption of chromium (VI)

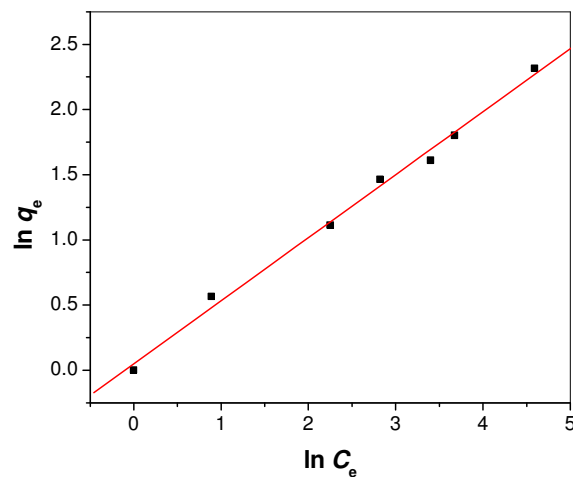


Fig. No. 4: Freundlich isotherm for adsorption of chromium (VI)

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of chromium (VI) process is shown in Fig. 5. Removal of chromium (VI) increases with increase of adsorbent dosage. The percentage removal increases from 49 to 95% by increasing the adsorbent dosage from 4 to 24 g/L. However, the adsorption capacity showed a decreasing trend with increasing resin dosage. The adsorption capacity dropped from 3.7 to 2 mg/g by increasing the adsorbent dosage from 4 to 24 g/L. The drop in adsorption capacity is basically due to sites remaining unsaturated during the adsorption process.

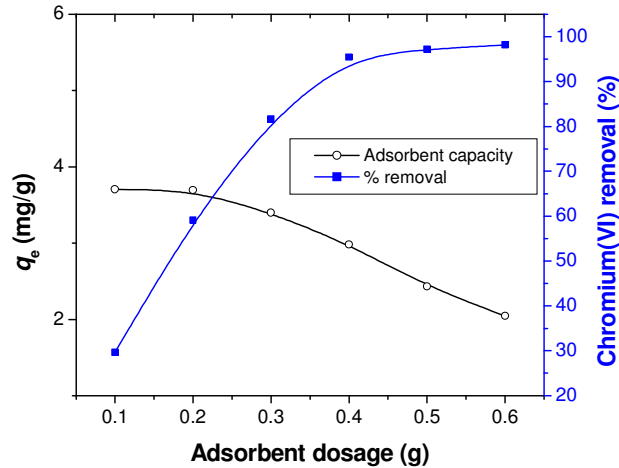


Fig. No. 5: Effect of adsorbent dosage on adsorption of chromium (VI).

Effect of pH

The effect of pH on the process is presented in Fig. 6. The percentage adsorption of chromium (VI) is decreasing from 98% to 45% with increasing pH from 1 to 11. The percentage removal of chromium (VI) is maximum and remains constant in the pH range 1-3.

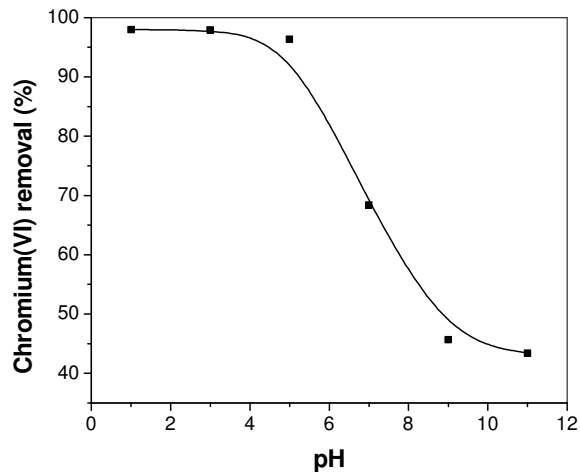


Fig. No. 6: Effect of pH on chromium (VI) removal.

CONCLUSIONS

Following conclusions are drawn from the above discussed results:

- Adsorbent prepared from tamarind seeds could be used for the removal of chromium (VI) from aqueous solutions.
- The equilibrium time for the adsorption of chromium (VI) on the adsorbate prepared from tamarind seeds in the present study from aqueous solutions is found to be 50 h.
- The adsorption process of chromium (VI) can be described by Langmuir isotherm and Freundlich isotherm models. However, Freundlich isotherm model shows a good agreement with the equilibrium data.
- Adsorption of chromium (VI) on Tamarind seeds yielded maximum adsorption capacity of 11.08 mg/g at solution pH of 7.
- Removal of chromium (VI) increases with increase of adsorbent dosage.
- The maximum adsorption of chromium (VI) took place in the pH range 1-3.

NOMENCLATURE

b	Langmuir constant (L/mg)
C_e	Concentration of Cr(VI) at equilibrium (mg/L)
q_e	Amount of Cr(VI) adsorbed by the adsorbent (mg/g)
q_m	Maximum adsorption capacity (mg/g)
K_F	Freundlich constant (mg/g)
n	Freundlich constant (L/mg)

REFERENCES

1. Sharma, Y. C. (2001). "Adsorption of Cr(VI) onto Wollastonite: Effect of pH", *Indian Journal of Chemical Technology*, **8**, pp. 186.
2. Hu, Z., Lei, L., Li, Y. and Ni, Y. (2003). "Chromium adsorption on high-performance activated carbons from aqueous solution", *Separation and Purification Technology*, **31**, pp. 13-18.
3. Namasivayam, C. and Yamuna, R. T. (1995). "Adsorption of Chromium (VI) by a Low-Cost Adsorbent: Biogas Residual Slurry", *Chemosphere*, **30** (3), pp. 561-578.
4. Sharma, A. and Bhattacharyya, K. G. (2004). "Adsorption of Chromium (VI) on *Azadirachta Indica* (Neem) Leaf Powder", *Adsorption*, **10**, pp. 327-338.
5. Jianlong, W., Xinmin, Z. and Yi, Q. (2000). "Removal of Cr(VI) from Aqueous Solution by Macroporous Resion Adsorption", *Journal of Environmental Science Health*, **35** (7), pp. 1211-1230.
6. Gupta, S. and Babu, B. V. (2006). "Adsorption of Cr(VI) by a Low-Cost Adsorbent Prepared from Neem Leaves", *Proceedings of National Conference on Environmental Conservation (NCEC-2006)*, BITS-Pilani, September 1-3, 2006, pp. 175-180.
7. Huang, C. P. and Wu, M. H. (1977). "The removal of chromium (VI) from dilute aqueous solution by activated carbon", *Water Research*, **11**, pp. 673-679.
8. Sharma, D. C. and Forster, C. F. (1994). "A Preliminary examination into the adsorption of hexavalent chromium using Low-cost adsorbents", *Bioresource Technology*, **47**, pp. 257-264.
9. Tan, W. T., Ooi, S. T. and Lee, C. K. (1993). "Removal of chromium (VI) from solution by coconut husk and palm pressed fibres", *Environmental Technology*, **14**, pp. 277-282.
10. Orhan Y. and Buyukgungur, H. (1993). "The removal of heavy metals by using agricultural wastes", *Water Science Technology*, **28** (2), pp. 247-255.
11. Namasivayam, C. and Ranganathan, K. (1993). "Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater", *Environmental Pollution*, **82**, pp. 255-261.