Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2013, 4(3):79-87

ISSN: 0976-8505
CODEN (USA) CSHIA5

A study on adsorption of chromium (VI) ions from aqueous solution by *Ficus religiosa* leaves as adsorbent

R. Gayathri*, M. Thirumarimurugan and T. Kannadasan

Department of Chemical Engineering, Coimbatore Institute of Technology, Coimbatore, Tamil Nadu, India

---

ABSTRACT

Adsorption is one of the effective techniques for Cr (VI) removal from industrial wastewater. The present work deals with the determination of Cr (VI) removal capacity from aqueous solution using Ficus religiosa leaves. The effect of various parameters such as pH, contact time, adsorbent dose, initial metal concentration and temperature was investigated. The maximum adsorption of Cr (VI) on leaves was obtained at pH 2. Langmuir, Freundlich and Temkin models were used to explain the equilibrium data. The adsorption data were well fitted to Langmuir adsorption model. The maximum adsorption capacity obtained using the Langmuir isotherm model is 18.18 mg/g. Results indicate the following order to fit the isotherms: Langmuir > Temkin > Freundlich. Adsorption kinetic data were modeled using the Pseudo first order, Pseudo second order and Elovich models. The kinetics of adsorption process was well described by the Pseudo second order kinetic model.

Keywords: Adsorption, Chromium (VI), *Ficus religiosa* leaves, Isotherms, Kinetics

---

INTRODUCTION

Chromium is one of the contaminants which exist in hexavalent and trivalent forms. Trivalent chromium is an essential element in human nutrition and is much less toxic than the hexavalent one, which is recognized as a carcinogenic and mutagenic agent [1]. Sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication [2].

Due to environmental concern, discharge limits of both Cr(III) and Cr(VI) have been instituted by most industrial countries. Their concentration in industrial wastewaters ranges from 0.5 to 270 mg/L. The tolerance limit for Cr(VI) for discharge into inland surface water is 0.1 mg/L and in potable water is 0.05 mg/L. The Ministry of Environment and Forest (MOEE); Government of India has set minimal national standards (MINAS) of 0.1 mg/L for safe discharge of effluent containing Cr(VI) in surface water[3].

In general Chromium (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, and evaporation, etc. These methods have been found to be limited, since they often involve high capital and operational costs. Among these methods adsorption is the most efficient technique because of its convenience, easy operation and simplicity of design [4]. Adsorption which have proven to be effective for the removal of Cr(VI) from aqueous solutions and industrial effluents. Agricultural by-products have been widely studied for metal removal from waste water. These include peat, wood, pine bark, banana pith, soybean and cotton seed hulls, rice husk, saw dust, tamarind seeds, compost and leaves [5].

In the present study, activated *Ficus religiosa* leaves are used as low-cost adsorbent for the removal of Cr(VI) from aqueous solutions. Leaves of different trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. *Ficus religiosa* Linn commonly known as 'Peepal tree' is a large widely branched tree with leathery, heart-shaped, long-tipped leaves on long slender petioles and purple fruits growing in pairs. The tree is regarded as a sacred tree to both Hindus as well as Buddhists [12]. Cellulose, hemicelluloses, pectin and lignin present in the cell wall are the most important sorption sites. Leaves have chlorophyll, carotene, anthocyanin and tannin which contribute to metal biosorption. The important feature of these compounds is that they contain hydroxyl, carboxylic, carbonyl, amino and nitro groups which are important sites for metal sorption [2]. The influence of pH, contact time, metal ions concentration and adsorbent dose were investigated and experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms, and kinetic models.

MATERIALS AND METHODS

2.1. Materials

All chemicals used were of analytical reagent grade. Hexavalent chromium solution of 1000 mg/l concentration was prepared by dissolving 2.827 g potassium dichromate in one litre distilled water. These solutions were further diluted to get solutions of various known concentrations of chromium. For pH adjustments throughout the experiment hydrochloric acid and sodium hydroxide solutions were used. 1M Nitric acid was used for the treatment of leaves.

2.2. Adsorbent preparation

Ficus religiosa leaves were collected from local environment in Coimbatore city. These leaves were washed, many times with distilled water to remove dust and soluble impurities and were allowed to dry at room temperature for two days. The dried leaves were converted into fine powder by using mixer grinder. The powder was sieved to obtain particles of size range 0.01-0.1 mm. 40 g of powder sample was soaked in 400 ml of 1N HNO_3 for 24 h and then gently heated at 70^0C for 20 min. Treated biomass was washed with distilled water until maximum colour was removed and clear water obtained. It was first dried at room temperature and then in an oven at 105^0C. Finally, it was stored in air tight glass bottles to protect it from humidity.

2.3. Batch experiments

Adsorption of Cr(VI) was studied in batch experiments. In all sets of experiments, fixed volume of Cr(VI) solution of 100mL was stirred with desired adsorbent dose 10 g/L at 30 ± 2^0C and 200 rpm for 4 hour. Different conditions of pH (2-10), initial metal concentration (100-600 mg/L) and contact time of 4h were evaluated during study. In order to regulate pH of the medium 0.1N NaOH and 0.1N HCl were used. After completion of each batch, the solution was filtered through filter paper and the filtrate was analyzed for remaining Cr(VI) concentration in the sample using UV visible spectrophotometer with 1, 5-diphenylcarbazide in acid medium by following APHA, AWWA standard methods for examination of water and wastewater [6]. The absorbance of purple-violet colored solution is measured at a wavelength of 540 nm. The amount of Cr(VI) adsorbed per unit mass of the adsorbent was evaluated by using the following mass balance equation,

$$q = [(C_i - C_e) \times V]/W \qquad (1)$$

where V is the volume of the solution (L) and W, the amount of adsorbent (g); C_i and C_e (mg/L), the initial and equilibrium metal concentrations.

The percent removal of Cr(VI) was calculated as follows:

$$\%\ \text{Removal of Cr(VI)} = [\ (\ C_{initial} - C_{final})\ /\ C_{initial}\ ] \times 100 \qquad (2)$$

Adsorption isotherm studies were carried out with six different initial concentrations of Cr(VI) from 100 mg/L to 600 mg/L at pH 2, contact time 4 h and adsorbent dosage level of 10g/L. The kinetic parameters for the adsorption process were studied on the batch adsorption of 100 mg/L of Cr(VI) at pH 2. The contact time was varied from 30 min to 240 min and the percent removal of Cr(VI) was monitored during the study.

RESULTS AND DISCUSSION

3.1. Effect of pH

The solution pH has been reported to be most important variable governing the adsorption of metal ions by adsorbents. In order to establish the effect of pH on the sorption of Cr(VI) ions onto *Ficus religiosa*, batch equilibrium studies at different pH values were carried in the range 2-10. It was found that maximum percent removal of chromium (VI) ions on the adsorbent was observed at pH 2 and significantly decreased at higher pH values. The dominant form of Cr(VI) at pH 2 is $HCrO_4^-$ which arises from the hydrolysis reaction of the dichromate ion ($Cr_2O_7^{2-}$) Increasing the pH will shift the concentration of $HCrO^{4-}$ to $Cr_2O_7^{2-}$ and other forms as CrO^{4-}.

Maximum adsorption at pH 2 and 3 indicates that it was the $HCrO^{4-}$ form of Cr (VI), which was the predominant species at this pH range and adsorbed preferentially on the adsorbents. Better adsorption capacity observed at low pH values with optimum range of pH between 2 and 3 may be attributed to the large number of H^+ ions present at these pH values, which in turn neutralize the negatively charged hydroxyl group on adsorbed surface thereby reducing the hindrance to the diffusion of dichromate ions. At higher pH values, the reduction in adsorption may be possible due to abundance of OH^- ions causing increased hindrance to diffusion of dichromate ions [3].

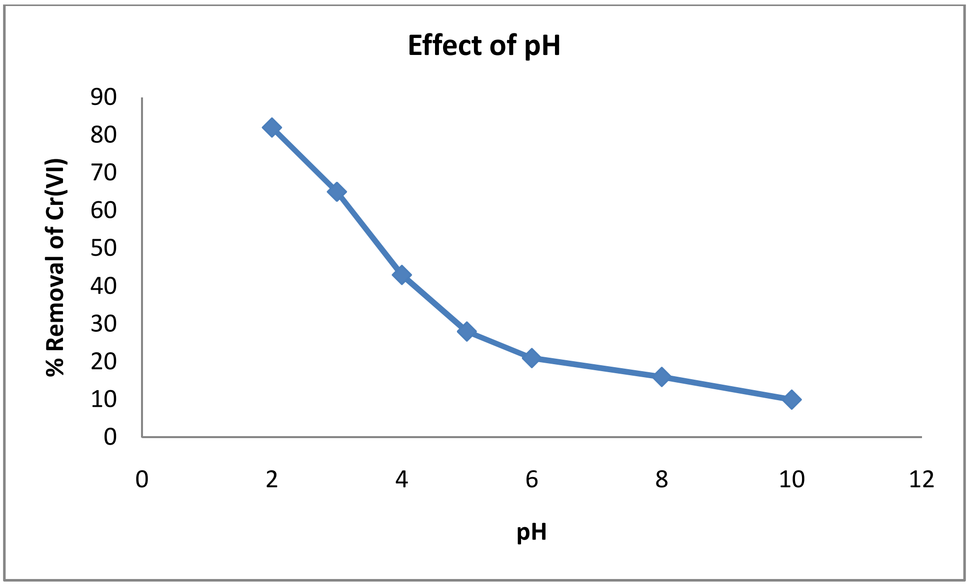


Fig.1. Effect of pH on the adsorption of Cr(VI) onto *Ficus religiosa* leaves. Initial concentration 100 mg/L, adsorbent dosage 10 g/L, contact time 4h.

3.2. Effect of contact time

The effect of contact time on the batch adsorption of Cr(VI) at pH 2 and initial Cr(VI) concentration of 100 mg/L is shown in Fig. 2. The removal of chromium ions increases with time and attains equilibrium in 240 min, basically the removal of sorbate is rapid, but it gradually decreases with time until it reaches equilibrium. The rate of percent metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of metal. The two stage sorption mechanism with the first rapid and quantitatively predominant and the slower and the quantitatively insignificant [7].

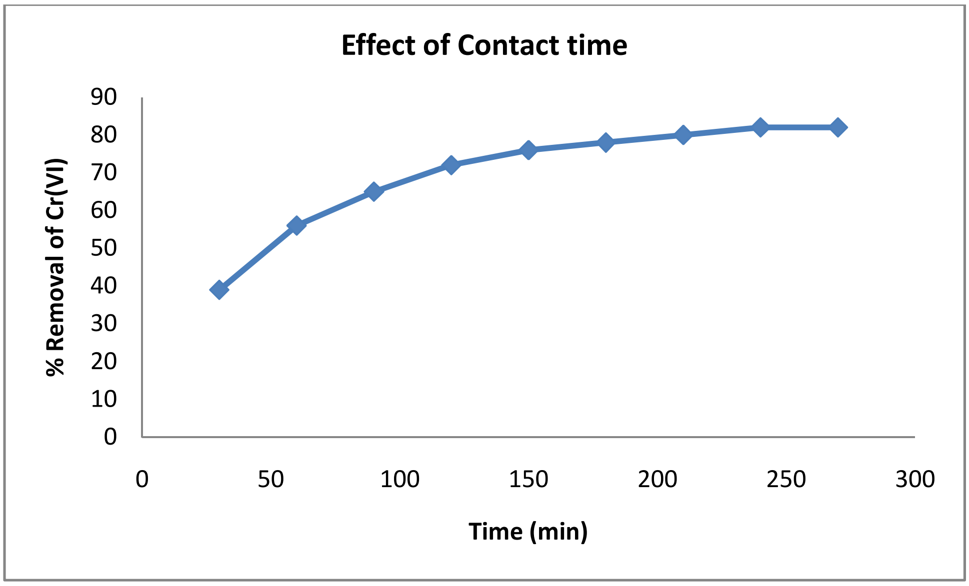
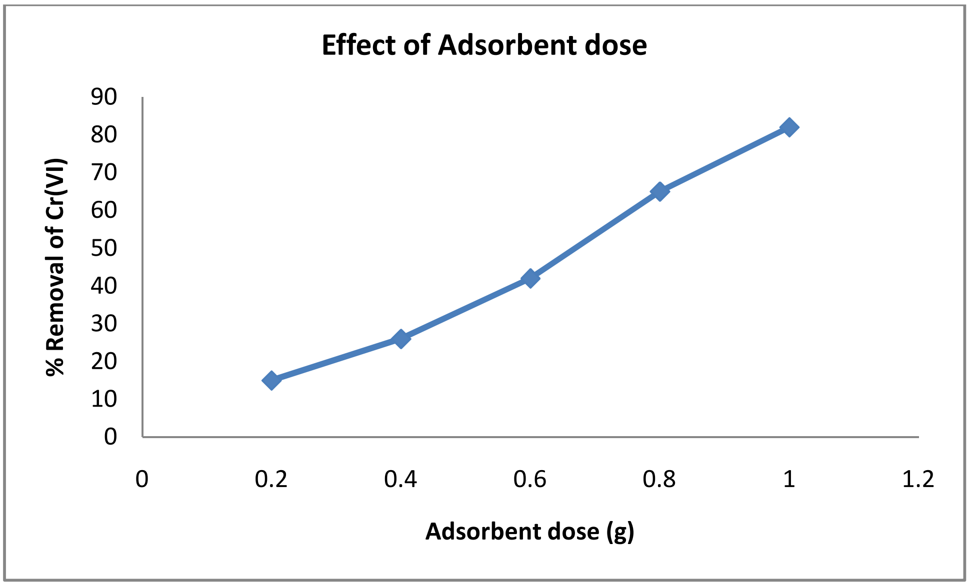


Fig. 2.Effect of contact time on the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, initial concentration 100 mg/L, adsorbent dosage 10 g/L.

3.3. Effect of adsorbent concentration

Keeping all other parameters constant adsorbent dose was varied from 2 to 10 gm/L. It can be seen from Figure 3 that an adsorbent dose of 10 gm/L is sufficient for optimal removal of metal. After certain adsorbent dosage the removal efficiency is not increased so significantly. The removal capacity was low at high dose rate and vice versa. This was due to metal concentration shortage in solution at high dose rates.

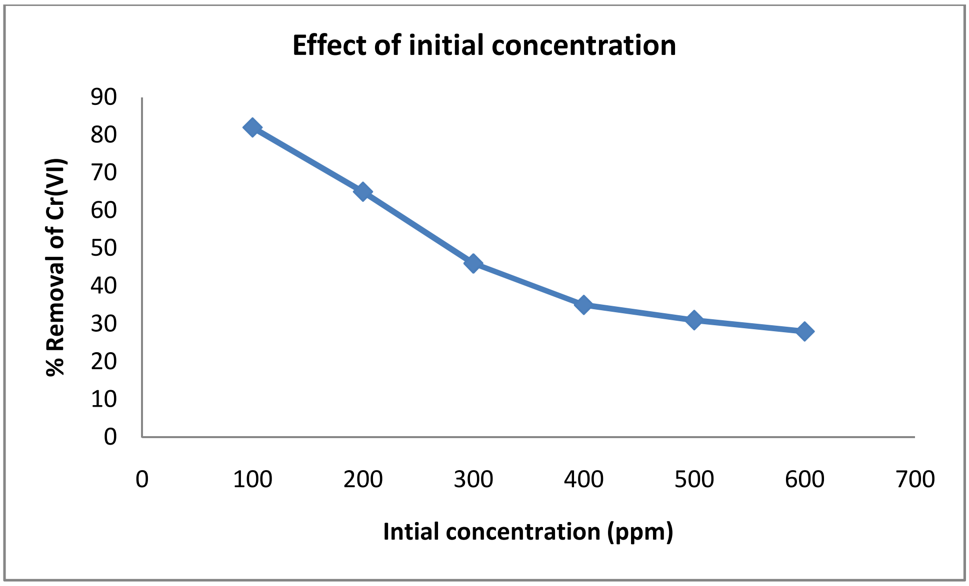


.

Fig. 3.Effect of adsorbent dosage on the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, contact time 4h, initial concentration 100 mg/L.

3.4. Effect of initial metal ion concentration

Initial concentration of metal was varied from 100 to 600 mg/L and quantity of adsorbent was kept constant at 10 gm/L. It was observed that percentage removal decreased with increase in metal concentration as shown in Fig. 4. At low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled [7].



.

Fig. 4.Effect of initial concentration on the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, contact time 4h, adsorbent dosage 10 g/L.

3.5. Effect of temperature

Keeping all other parameters constant temperature was varied from 30ºC to 50ºC. The sorption of chromium increased slightly with the increase in temperature up to 40ºC and then started decreased Fig. 5. The temperature higher than 40°C caused a change in the texture of the biomass and thus reduced its sorption capacity. Biomass contains more than one type of sites for metal binding.

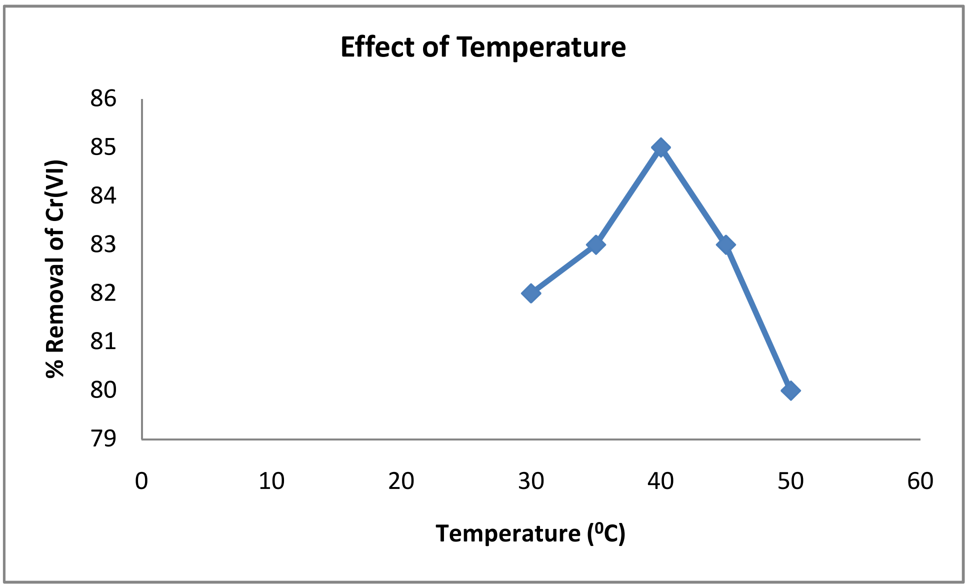


Fig. 5.Effect of temperature on the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, contact time 4h, initial concentration 100 mg/L, adsorbent dosage 10 g/L.

3.6. Adsorption isotherms

Modeling the equilibrium data is a fundamental for the industrial application of adsorption since it gives information for designing and optimizing operating procedure. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e.

In order to successively represent the equilibrium adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Three kinds of several isotherms equations were tested to fit the experimental data [8].

Langmuir equation: $C_e/q_e = (C_e/q_{max}) + [1/(q_{max}\ b)]$ (3)

Freundlich equation: $\log q_e = \log K_F + (1/n) \log C_e$ (4)

Temkin equation: $q_e = a + b \ln C_e$ (5)

Where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of metal ions in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation, q_{max} (mg/g) is the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on a sorbate surface, ‘b’ which reflects quantitatively the affinity between the adsorbent and adsorbate. Freundlich treatment gives the parameters, n, indicative of bond energies between metal ion and the adsorbent and K_F, related to bond strength.

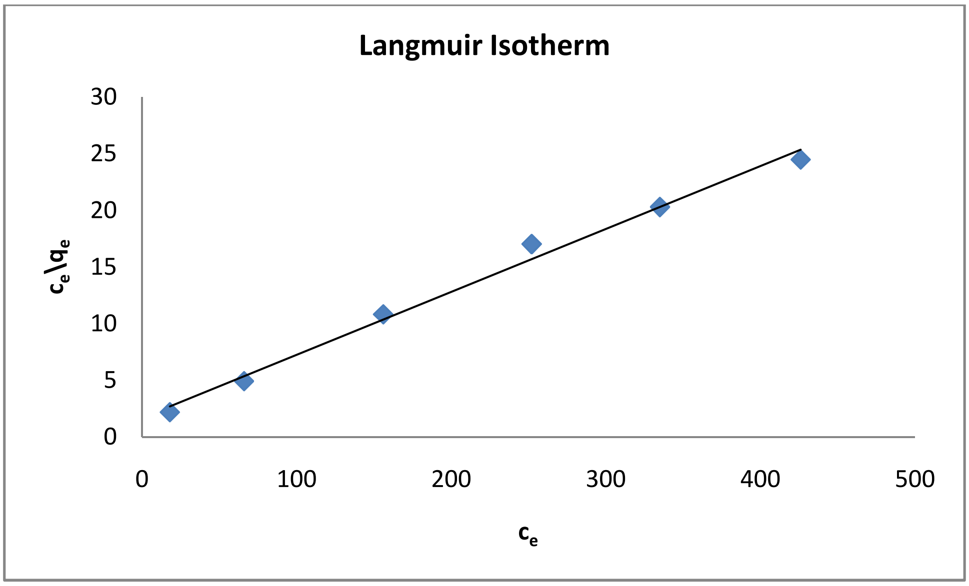


Fig. 6.Langmuir isotherm plot for the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, adsorbent dosage 10 g/L.

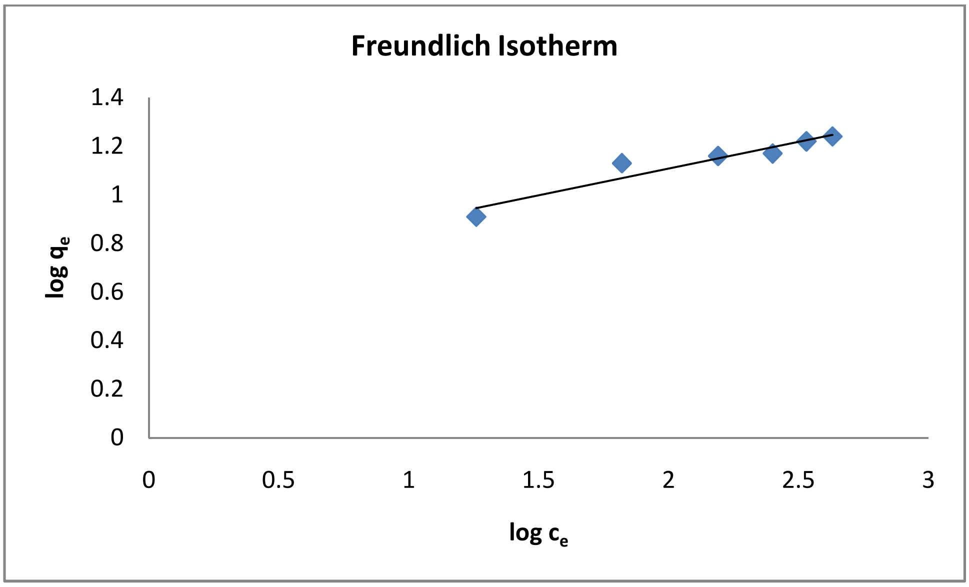


Fig. 7.Freundlich isotherm plot for the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, adsorbent dosage 10 g/L.

Table 1.Langmuir, Freundlich and Temkin adsorption isotherm constants for adsorption of Cr(VI) by *Ficus religiosa* leaves

Langmuir Isotherm			Freundlich Isotherm			Temkin Isotherm		
q_{max}(mg/g)	b(L/mg)	R^2	K_F	n	R^2	a	b	R^2
18.18	0.032	0.991	4.645	4.55	0.916	1.097	2.646	0.948

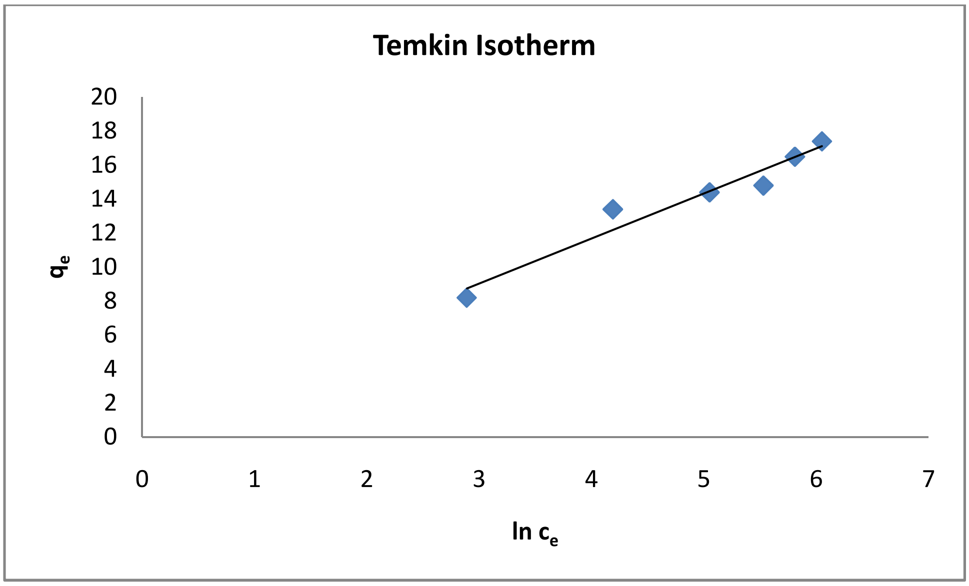


Fig. 8.Temkin isotherm plot for the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, adsorbent dosage 10 g/L.

The linearized Langmuir, Freundlich and Temkin isotherms of chromium (VI) are shown in Fig. 6-8. The estimated model parameters with correlation coefficient (R^2) for different models are shown in Table. 1. The values of R^2 are regarded as a measure of the goodness of fit of experimental data on the isotherm models. Applicability of the three isotherm models for the present data approximately follows the order: Langmuir> Temkin> Freundlich.

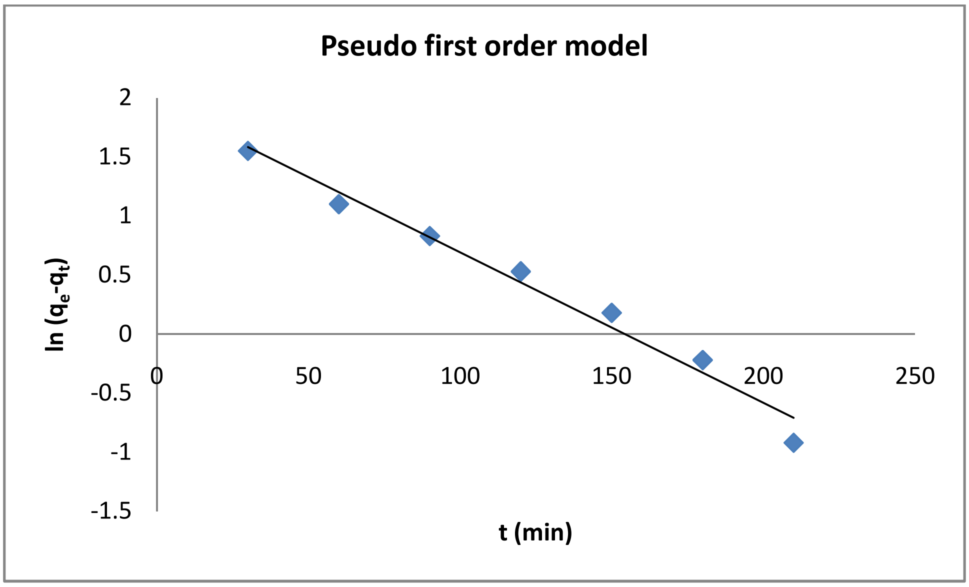


Fig. 9.Pseudo first order plot for the adsorption of Cr(VI) onto *Ficus religiosa* leaves. pH 2, initial concentration 100 mg/L, adsorbent dose 10 g/L.

3.7. Adsorption kinetics

Adsorption kinetics, which describes the solute adsorption rate, is an important characteristic in evaluating the efficiency of the adsorption. In order to analyze the adsorption kinetics of heavy metal ions the Pseudo-first, Pseudo-second order and Elovich kinetic models were applied to data. The first order rate equation of Lagergren is most widely used for the sorption of a solute from liquid solution [9] and is represented as:

$$\ln (q_e - q_t) = \ln q_e - K_1 t \qquad (6)$$

where q_e and q_t are the amounts of metal ion sorbed (mg/g) at equilibrium and at time t, respectively. K_1 is the Lagergren rate constant of the biosorbents (1/min). Pseudo second order equation based on adsorption equilibrium capacity may be expressed in the form:

$t/q_t = [1/(K_2\, q_e^{2})] + (t/q_e)$ (7)

where the equilibrium biosorption capacity, q_e and the pseudo second order rate constant K_2 (g/mg min) were determined experimentally from graph. Finally, the simple Elovich may be expressed in form:

$q_t = \alpha + \beta \ln t$ (8)

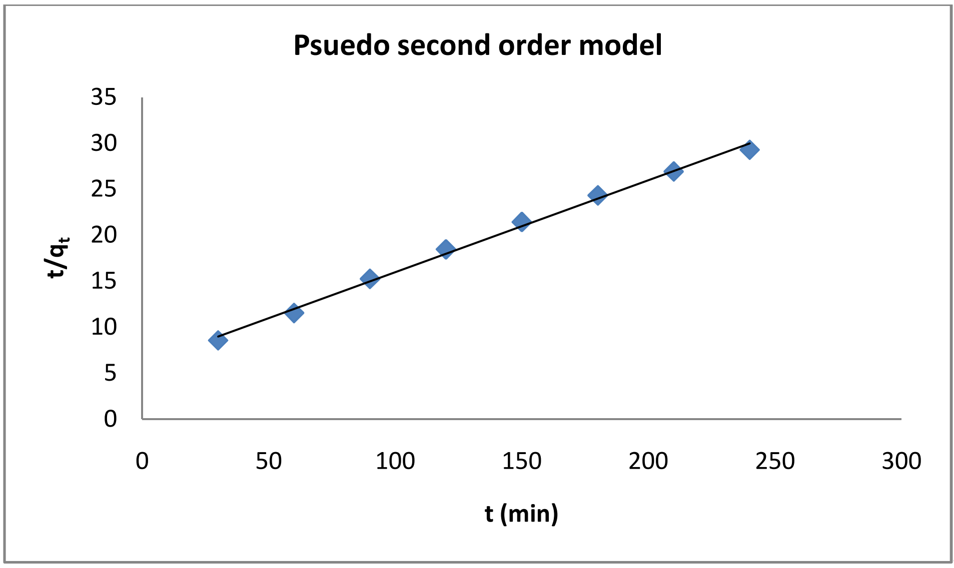


Fig. 10.Pseudo second order plot for the adsorption of Cr(VI) *Ficus religiosa* leaves. pH 2, initial concentration 100 mg/L, adsorbent dose 10 g/L

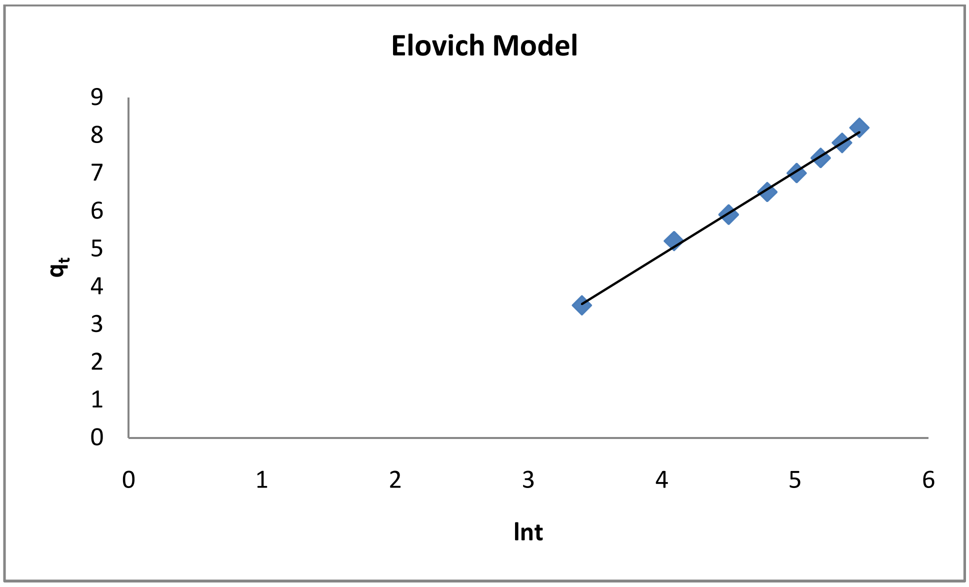


Fig. 11.Elovich plot for the adsorption of (VI) *Ficus religiosa* leaves. pH 2, initial concentration 100 mg/L, adsorbent dose 10 g/L.

Table 2.Calculated kinetic parameters for pseudo first-order, second order and Elovich kinetic models for the adsorption of Cr(VI) by *Ficus religiosa* leaves.

Pseudo first order			Pseudo second order			Elovich model		
K_1 (min^{-1})	q_e (mg/g)	R^2	$K_2 \times 10^{-3}$ (g mg^{-1} min^{-1})	q_e (mg/g)	R^2	α	β	R^2
0.012	7.13	0.978	1.675	10	0.996	-3.743	2.147	0.992

During the present study, the three different kinetic models were applied and showed in Fig. 9-11. The estimated model and the related statistic parameters are reported in Table. 1. The values of correlation coefficients indicated a better fit of Pseudo-second order model with the experimental data.

CONCLUSION

The following major conclusions can be drawn based on the above study:

- The removal of Cr (VI) from aqueous solutions strongly depends on the pH of the solution, adsorbent dosage, contact time, initial Cr (VI) concentration and temperature. The optimum pH for the removal was found to be 2. Increase in the dose of the adsorbent and decrease in the initial concentration of Cr (VI) leads to increase in Cr (VI) adsorption and increase in temperature and contact time increases the Cr (VI) removal.
- The experimental results have been analyzed by Langmuir, Freundlich and Temkin adsorption isotherms. The equilibrium data are best fitted with Langmuir Isotherm model thus, indicating the applicability of monolayer coverage of the Cr (VI) on the surface of adsorbent. Results indicate the following order to fit the isotherms: Langmuir > Temkin >Freundlich.
- The adsorption kinetics data were modeled using the Pseudo-first, Pseudo-second order and Elovich kinetics equations. It was shown that the Pseudo-second order kinetics described best the sorption kinetics.
- Finally, this works shows that activated *Ficus religiosa* leaves can be used as efficient adsorbent for Cr(VI) removal from waste water. However, further research should attempt to improve the adsorption capacity of *Ficus religiosa* leaves and apply this method to the removal of metals in large scale.

REFERENCES

[1] Mina Gholipour, Hassan Hashemipour and Maryam Mollashahi, *ARPN Journal of Engineering and Applied Sciences*, **2011**, Vol. 6, No. 9.
[2] Suleman Qaiser, Anwar R. Saleemi, Muhammad Mahmood Ahmad, *Electronic Journal of Biotechnology*, **2007,** Vol.10 No.3.
[3] Bhattacharya A.K, Naiya T.K, Mandal S.N, Dasa S.K, *Chemical Engineering Journal*, **2008,** 137, 529.
[4] Emine Malkoc, Yasar Nuhoglu, *Separation and Purification Technology*, **2007,** 54, 291.
[5] Ashtoukhya E.-S.Z. El, Amina N.K, Abdelwahabb O, *Desalination* **2008**, 223, 162.
[6] APHA, 16th ed., APHA, AWWA, WPCF, Washington, D.C, **1985**.
[7] Dhiraj Sud, Garima Mahajan, Kaur M.P, *Bioresource Technology*, **2008,** 99, 6017.
[8] Muhammad Zaheer Aslam, Naveed Ramzan ,Shahid Naveed, Nadeem Feroze, *J. Chil. Chem. Soc.*, **2010,** 55, 8.
[9] Jianlong W, Xinmin Z, Decai D and Ding Z, *J. Biotechnol.*, **2001,** 87, 273.
[10] Rifaqat A.K. Rao, Fouzia Rehman, *Journal of Hazardous Materials*, **2010,** 181, 405.
[11] Amna Shoaib, Nabila Aslam and Nida Aslam, *The Online Journal of Science and Technology*, **2012**, Volume 2, Issue 3.
[12] Inder Kumar Makhija, Indra Prakash Sharma, Devang Khamar, *Annals of Biological Research*, **2010**, 1, 171.
[13] Paresh Chakravarty, Sen Sarma N, Sarma H.P, *Desalination*, **2010,** 256, 16.
[14] Divya Jyothi M, Rohini Kiran K and Ravindhranath K, *International Journal of Water Resources and Environmental Engineering*, **2012,** Vol. 4(4), pp. 73.
[15] Moonis Ali Khan, Rifaqat Ali Khan Rao and Mohammad Ajmal, *J. Int. Environmental Application & Science*, **2008**, Vol. 3 (2), 101.
[16] Isah U. A and Lawal M, *Advances in Applied Science Research*, **2012**, 3 (6):4033.
[17] Dhiraj Sud, Garima Mahajan, Kaur M.P, *Bioresource Technology*, **2008**, 99, 6017.
[18] Ekta Khosla, Satindar Kaur and Pragnesh N. Dave, *Der Chemica Sinica*, **2011**, 2(5): 87.
[19] Upendra Kumar, *Scientific Research and Essay*, **2006**, Vol. 1 (2), pp. 033.
[20] Shashikant R. Kuchekar, Vishwas B. Gaikwad, Dadasaheb V. Sonawane and Shamarao P. Lawande, *Der Chemica Sinica*, **2011**, 2(6):281.
[21] Miretzky P, Fernandez Cirelli A, *Journal of Hazardous Materials*, **2010**, 180,1–19
[22] Saravanan D, Hemalatha R and Sudha P. N, *Der Pharma Chemica*, **2011**, 3 (6), 406.
[23] Jadhava H.V, Khetre S.M and Bamane S.R, *Der Chemica Sinica*, **2011**, 2(6):68.