

Removal of high concentrations of chromium from aqueous solutions using leaves of *Tamarindus indica*: Kinetics and equilibrium studies

A. Muthulakshmi^{1,3*}, R. Baskaran² and N. Ashwin Karthick³

¹Sathyabama University, Chennai-600 119, India

²Department of Chemical Engineering, St. Joseph's Engineering College, Chennai-600 119, India

³Department of Biotechnology, Jeppiaar Engineering College, Chennai-600 119, India

*Corresponding Author E-mail: visitmuthu1980@gmail.com

Publication Info

Paper received:
20 September 2015

Revised received:
10 May 2016

Accepted:
20 August 2016

Abstract

The need for removal of heavy metal from the environment has been increasing. The present study was conducted to identify a potential ability of the plant leaf powder in removal of high concentrations of Cr (VI). *Tamarindus indica*, a widespread plant capable of growing under all climatic and soil conditions was evaluated for its potential to remove high concentration of Cr (VI) (1000 mg l⁻¹) using leaf. The effect of process parameters such as pH, contact time and adsorbent dosage for Cr (VI) adsorption was studied. The results showed that at pH 3.0, up to 560 mg l⁻¹ of Cr (VI) was adsorbed onto the surface of 1g of leaf within 30 min. However, desorption occurred with increase in contact time. While, stable adsorption of 260 mg l⁻¹ was observed at pH 6.0 using 1g of adsorbent after 2 hrs. Further, it was observed that the adsorption phenomenon followed Langmuir adsorption isotherm. The kinetics of the adsorption studies was studied, and it was observed that the adsorption followed second order kinetics with second order rate constant of 2.4x10⁻⁴ g mg⁻¹ min⁻¹.

Key words

Adsorption isotherm, Adsorption kinetics, Chromium (VI), *Tamarindus indica*

Introduction

Toxicity of heavy metals is imperative, making it a global concern (Singh *et al.*, 2010). As rapid global economic development results in release of large volumes of heavy metal containing effluents. Cr (VI) is widely used in leather tanning, cement, dye plating and electroplating industries (Mishra *et al.*, 2009) and is recognized as a priority pollutant by the US EPA (2014). Cr (VI) is estimated to be five hundred times more toxic than Cr (III) (Fahim *et al.*, 2006). It has been termed as carcinogen owing to its accumulation and persistent character in the environment (Pushan *et al.*, 2012). Cr (VI) can be a cause of liver damage, pulmonary congestion, edema, skin irritation (Raji and Anirudhan, 1998), and drinking water contaminated with Cr (VI) increases the risk of bladder, liver, kidney and skin cancers (Hsu *et al.*, 2007; Xing *et al.*, 2007). The tolerance limit for

discharge into inland surface waters is 0.1 mg l⁻¹ and 0.05 mg l⁻¹ in potable water. However, large volume of Cr (VI) is released in the effluents (Huang *et al.*, 2009; Nriagu *et al.*, 1988), where its concentration ranges from 0.5 to 270, 000 mg l⁻¹ (Patterson, 1985). Thus, an efficient method is necessary for the for removal of chromate from water.

Adsorption is a reliable and has served as an efficient technique for the removal of heavy metals from contaminated water (Malkoc *et al.*, 2006). In comparison with the traditional chemical sorbent materials, such as carbon materials, (Lo *et al.*, 2012), mesoporous alumina-silicate (Seprehian *et al.*, 2010) and granular titanium dioxide (Xie *et al.*, 2009), natural adsorbents such as powdered marine algae (Lee *et al.*, 2000), palm fiber (Isa *et al.*, 2008), coconut coir pith (Suksabye *et al.*, 2008), *Ocimum americanum* seed pods (Levankumar *et al.*, 2009), *Hydrilla verticillata* (Baralet *et al.*,

2009), wheat bran (Nameni *et al.*, 2008), *Azadirachta indica* leaf powder (Sharma and Bhattacharyya, 2005), *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* (Onyanha *et al.*, 2008), *Helianthus annuus* stem waste (Jain *et al.*, 2009), corn stalks (Chen *et al.*, 2011), sugarcane bagasse (Garget *et al.*, 2009; Cronje *et al.*, 2011), and *Borassu saethiopum* flower (Elangovan *et al.*, 2008) have gained attention. Adsorption of heavy metals using plant parts is reliable because of their low cost, reasonable adsorption capacity and eco-friendliness and thus, can serve as an efficient decontamination technique for heavy metal contaminated water. However, their efficiency at high concentration of metals is low.

Tamarindus indica, a widespread plant belonging to the family Fabaceae can grow in all climatic and soil conditions, and its seeds (Agarwalet *et al.*, 2006; Gupta and Babu, 2006, 2009), fruit shell and hull (Popuri *et al.*, 2007; Verma *et al.*, 2006) and wood bark (Sahu *et al.*, 2009, 2010; Acharya, 2009) have been reported as an excellent adsorbent. However, a detailed literature survey has shown that the adsorption using leaves of *Tamarindus indica* has not been studied, and further absorption of higher concentrations of metal contaminants has not been reported in adsorption using any natural adsorbents. Thus, the present study aimed to assess the adsorption capacity of leaves of *Tamarindus indica* at high concentrations of Cr (VI), as the leaves possess high surface area and functional bonds. Optimization of adsorption at various pH, an initial concentration of adsorbent and adsorbate and adsorption time was performed to achieve maximum adsorption. Further, the data obtained was subjected to kinetic studies to find out the adsorption kinetics by the leaves of *Tamarindus indica*.

Materials and Methods

Collection of plant leaves : The leaves of *Tamarindus indica* were collected from Chennai, Tamil Nadu, India. The collected leaves were repeatedly washed under tap water and dried under shade in room temperature for 6 days. Dried leaves were then crushed and powdered and passed through sieve to obtain a uniform size of 300 μ m. (ASTM-E11 No.50)

Batch studies on adsorption of chromium using *Tamarindus indica* leaves : A stock solution of 1000 mg l⁻¹ was prepared by dissolving 28.285 g of dried potassium dichromate of analytical reagent grade in deionized distilled water and diluted to 1 l. Stock solution was diluted to 1000 mg l⁻¹ Cr. Batch sorption experiments were carried out by using 200 ml of 1000 mg l⁻¹ Cr solution. One gram of adsorbent was used to study the impact of pH, adsorbate and adsorbent concentration and contact time on adsorption. The adsorption experiments were carried out at different pH (3, 4, 5 and 6), adsorbate concentration (0.5, 1, 1.5 and 2 g 250 ml⁻¹), adsorbent concentration (250, 500, 750 and 1000 mg l⁻¹).

After adsorption, the samples were digested using concentrated HCl, and Cr (VI) concentration was estimated by Atomic Absorption Spectroscopy (Shimadzu, AA 7000, Japan) at 353 nm.

Adsorption isotherm : Various isotherm equations have been used to describe the adsorption phenomenon with some providing a theoretical foundation, while some being of mere empirical nature. In the present study, Langmuir, Freundlich, and Temkin adsorption isotherm studies were tested.

Langmuir isotherm : To test if only one monolayer of the molecule (Chromium) was adsorbed onto the adsorbate, Langmuir isotherm was validated using the following formula

$$C_e/q_e = (1/bq_m) + (1/q_m)C_e$$

The plot is said to follow Langmuir, if the plot of (C_e/q_e) vs. C_e yield a straight line; q_m is the adsorbate quantity required to form a single monolayer on unit mass of adsorbent and q_e is the amount adsorbed on unit mass of the adsorbent when the equilibrium concentration is C_e. The slope and the intercept of this line give the values of q_m and b. The adsorption energy (b) was calculated by using the equation

$$b = k_d/k_a$$

Where, k_a and k_d are the respective constants for adsorption and desorption.

Further a dimensionless parameter R_L, also known as separation factor, was analyzed by the formula:

$$R_L = 1/(1+bC_e)$$

Freundlich isotherm model : The adsorption intensity of the adsorbate by leaves is represented by Freundlich model and is given by:

$$q_e = k_f C_e^{(1/n)}$$

Where, q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg g⁻¹); C_e is the amount of metal ion concentration at time t (mg l⁻¹); K_f and n are the Freundlich constants. The equation can be linearized as

$$\text{Log } q_e = \text{log } k_f + \text{log } C_e$$

and a plot of logq_e against logC_e was used to validate Freundlich adsorption isotherm. The slope and intercept of the plot gave the values of the constants 1/n and logk_f (Owamah, 2014).

Temkin isotherm : The Temkin isotherm model is given by:

$$q_e = RT/b \ln (A_r C_e)$$

The plot of q_e against $\ln C_e$ gives the derivation for uniform distribution of binding energies. The equation can be expanded as :

$$q_e = RT/b_T \ln(A_T) + RT/b_T \ln(C_e)$$

$$B = RT/b_T$$

Replacing the constant B, we can rewrite the formula as

$$q_e = B \ln(A_T) + B \ln(C_e)$$

Where, A_T = Temkin isotherm equilibrium binding constant ($l\ g^{-1}$); b_T = Temkin isotherm constant; R = Universal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$); T = Temperature at 298K; B = Constant related to heat of sorption ($J\ mol^{-1}$)

Adsorption kinetics : Elovich kinetic models were applied to data to find out the first and second order rate kinetics (Chien *et al.*, 1980). A simple pseudo first order equation due to Lagergren for the sorption is represented by:

$$dq_t/dt = k_1 (q_e - q_t)$$

Where, q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is the mass of metal adsorbed at time t ($mg\ g^{-1}$); k_1 is the first order reaction rate constant (min^{-1}). The integrated rate law at $q_t=0$ and $t=0$ is given as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

The pseudo first order constant was obtained by plotting t against $\ln (q_e - q_t)$, from which the first order rate constant k_1 was obtained.

The second order rate equation is represented by:

$$dq_t/dt = k_2(q_e - q_t)$$

which can be expressed in the form:

$$t/q_t = [1/(k_2 q_e^2)] + (t/q_e)$$

where, k_2 is the second order reaction rate equilibrium constant ($g\ mg^{-1}\ min$). A plot of t/q_t against t indicates the second order kinetics. The value $k_2 q_e^2$ can be replaced by h , which is regarded as the initial sorption rate (at $t=0$). Plot of t/q_t vs t can be used to compute the values of k , h and q_e if the plot was linear.

Finally, the simple Elovich was expressed in the form of:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$$

A plot of q_t versus $\ln t$ gives a linear relationship for the applicability, and yields the value of α and β .

Results and Discussion

Effect of pH : At basic pH, most of the heavy metals precipitate as hydroxides (Kaouaha *et al.*, 2014) and Cr (VI) was found to be in equilibrium in the pH range of less than 6.0 (Cotton and Wilkinson, 1980; Greenwood and Earnshaw, 1984; Swietlik, 1998; Darko *et al.*, 2011), while it is found as Cr^{3+} at $pH < 7.0$. Hence, the experiments were carried out only in acidic pH (3.0-6.0) to avoid the influence of precipitation on sorption. The results for the adsorption studies revealed that highest adsorption capacity was at pH 3.0 with $560\ mg\ l^{-1}$ of chromium adsorbed within 30 min. Srinivasan *et al.* (1988), also reported that maximum adsorption was at pH 3. As the pH increased, the adsorption capacity was found to be reduced. In aqueous solution, hydrolysis of Cr_2O_3 formed $HCrO_4^-$. Thus, the predominant form of Cr (VI) in aqueous solution is $HCrO_4^-$ (Isa *et al.*, 2008) which gets adsorbed onto the adsorbent. At pH 3.0, protonation of the surface of adsorbent by H^+ ions occurs and promotes the adsorption of negatively charged $HCrO_4^-$ ions, thus, explaining high sorption of Cr (VI) at pH 3.0. While at high pH, the adsorbent is protonated with low charges, thus causing the electrostatic force of attraction between the adsorbent and adsorbate ions to decrease (Abdullah and Prasad, 2009).

Effect of contact time : The effect of contact time was studied on all the hydrogen ion concentrations to establish a plot on the effect of contact time, hydrogen ion concentration and adsorbent concentration. The results showed that at pH 6 the adsorption was stable. Babu and Gupta (2008) and Owamah (2014) reported that adsorption was stable at pH 6. However, at low hydrogen ion concentration such as pH 3, 4 and 5, the adsorption decreased with time. The rate of Cr (VI) adsorption by *T. indica* increased rapidly till 30 min at low pH. However, on further increasing the contact time negative effect on the adsorption was observed. Initially, the biosorption was high as Cr (VI) was available as metal ions at acidic pH which was rapidly adsorbed onto the surface of sorbent which had vacant sites for the uptake of chromium (Wang *et al.*, 2008 and Mezenner, 2009). However, with increase in contact time, the binding energy between Cr and adsorbent was found to be less than equilibrium constant and hence, desorption was observed resulting in negative adsorption.

Effect on adsorbent dosage : The effect on adsorbent concentration was studied on different pH and contact time. An increase in adsorbent dosage increased the amount of adsorption due to increase in the surface area of the biosorbent (Abdullah and Prasad, 2009). However, in the present study, the adsorption was found to increase initially, but decreased with increase in concentration of the adsorbent. This might be due to overcrowding of the adsorbent particles resulting in overlapping of the adsorption sites (Kumar and

Table 1 : Percentage adsorption of Cr(VI) by *T. indica* with respect to various adsorbent mass and contact times at different pH

Adsorbent concentration/Time		30 min	60 min	90 min	120 min
pH 3.0	0.5g	56.08	44.53	1.27	0.98
	1g	18.43	17.59	1.01	0.28
	1.5g	22.12	17.23	1.07	0.83
	2g	22.57	2.2	1.16	0.86
pH 4.0	0.5g	44.24	27.86	20.45	14.06
	1g	14.04	12.88	11.06	8.61
	1.5g	16.03	13.62	10.45	6.12
	2g	18.23	17.41	10.08	4.87
pH 5.0	0.5g	30.41	22.68	18.4	13.54
	1g	26.26	13.85	9.62	4.58
	1.5g	23.23	12.68	8.91	6.22
	2g	21.63	13.29	11.46	5.67
pH 6.0	0.5g	17.24	17.4	18.38	21.24
	1g	4.58	13.32	23.35	26.34
	1.5g	6.92	13.31	18.28	23.93
	2g	8.37	14.36	15.69	20.69

Table 2 : Parameters for plotting Langmuir, Freundlich and Temkin Adsorption Isotherms of Cr(VI) ion into *T. indica*

$C_e(\text{mg l}^{-1})$	$Q_e(\text{mg l}^{-1})$	$C_e(\text{mg l}^{-1})$	$1/C_e(\text{lmg}^{-1})$	$1/Q_e(\text{lmg}^{-1})$	$\text{Log } Q_e$	$\text{Ln } Q_e$	$1/C_e(\text{lmg}^{-1})$	$\text{Log } C_e$	$\text{Ln } C_e$	C_e/Q_e
0	0	0	0	0	0	0	0	0	0	0
250	198.79	51.21	0.004	0.005	2.2983	5.2922	0.01952	1.70935	3.93593	0.2576
500	316.14	183.86	0.002	0.0031	2.4998	5.7561	0.00543	2.26448	5.21417	0.5815
750	237.79	512.21	0.0013	0.0042	2.3761	5.4713	0.00195	2.70944	6.23873	2.1540
1000	263.21	736.79	0.001	0.0037	2.4203	5.5729	0.00135	2.86734	6.60230	2.7992

Table 3 : Langmuir, Freundlich and Temkin Isotherm Constants for the adsorption of Cr(VI) ion into *T. indica*

	Langmuir	Freundlich	Temkin
$b(\text{lmg}^{-1})$	4.454	$1/n$	$A_r(\text{l g}^{-1})$
$q_m(\text{mg g}^{-1})$	50.75	N	b_r
R_L	0.003	$k_f(\text{mg g}^{-1})$	B
R^2	0.9884	R^2	R^2

Kirithika, 2009). Similar observations have earlier been reported from the adsorbents prepared from pine needles powder (Hadjmohammadi *et al.*, 2011) and volcanic ash soil (Babel and Opiso, 2007) for adsorption of chromium. The maximum adsorption of 112.02 mg l^{-1} at pH 3 (30 min) was found with adsorbent concentration of 2 g l^{-1} , while stable adsorption of 52.68 mg l^{-1} at pH 6 (120 min) was observed with adsorbent concentration of 4 g l^{-1} .

The effect of pH, adsorbate mass and contact time are tabulated in Table 1. Fig. 1 represents standard concentration graph of Cr(VI).

Adsorption isotherms : The adsorption isotherms were plotted from the values obtained during the adsorption studies on different initial concentrations of adsorbate at pH 6 and adsorbent concentration of 4 g l^{-1} . The values are shown in the Table 2 and 3.

Adsorption isotherms : All the adsorption isotherms were performed by using the data from optimum pH concentration of pH 6 by varying the contact time, adsorbent concentration and adsorbate concentration, since stable adsorption was observed at pH 6. Table 2 illustrates the parameters for plotting Langmuir, Freundlich and Temkin adsorption Isotherms of Cr(VI) ion for *T. Indica* and Table 3 gives the Langmuir, Freundlich and Temkin Isotherm constants for the adsorption of Cr(VI) ion for *T. indica*.

Langmuir isotherm : If chromium is adsorbed as one monocular layer onto the adsorbent then Langmuir adsorption isotherm is applicable. The isotherm is based on the equilibrium between the chromium adsorbed and the liquid phase in which it is present, where the adsorption is described as formation of an ionic or covalent bond between adsorbent and adsorbate. The adsorption is said to follow

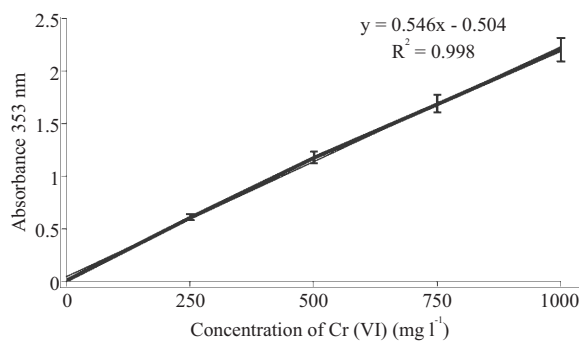


Fig. 1 : Standard graph between concentration of Cr(VI) and absorbance

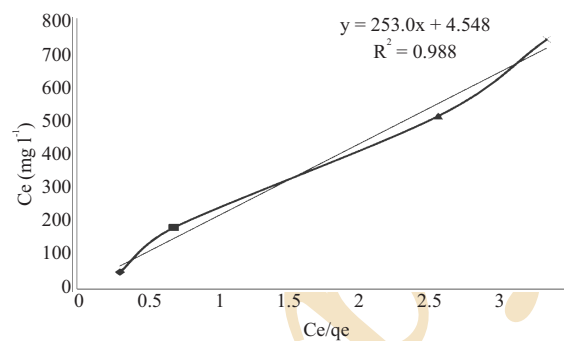


Fig. 2 : Langmuir plot between C_e/q_e and C_e

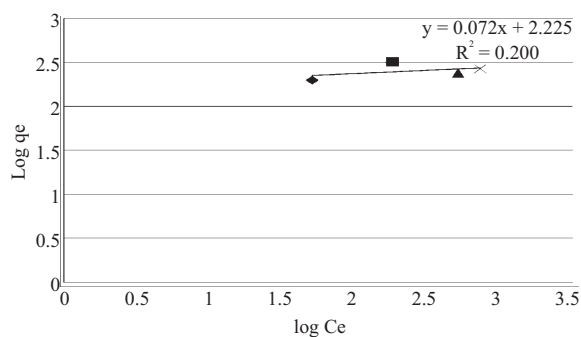


Fig. 3 : Freundlich plot between $\log q_e$ and $\log C_e$

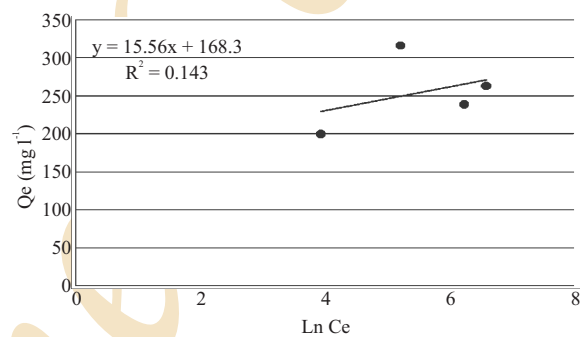


Fig. 4 : Temkin isotherm model between $\ln C_e$ and q_e

Langmuir, if the plot of (C_e/q_e) vs. C_e yield a straight line.

In the present study, the isotherm plot was linear and is shown in Fig. 2, thus indicating that monolayer adsorption had taken place. A high value of correlation coefficient ($R^2 = 0.9884$) validates the monolayer adsorption of Cr(VI) onto the adsorbent surface. The measure of the adsorption capacity to form monolayer represented by the constant (q_m) was as high as $253.07 \text{ mg } 4 \text{ g}^{-1}$ of the adsorbent, thus $50.75 \text{ mg } \text{g}^{-1}$ of the adsorbent. The adsorption energy denoted by b was equal to $4.454 \text{ L } \text{mg}^{-1}$. If the value of separation factor R_L lies between 0 and 1, the adsorption is said to be favorable. The adsorption is said to be linear if $R_L = 1$, and irreversible if $R_L = 0$. For R_L values > 1 , the adsorption is said to be unfavourable. The value of R_L was near to 0 in the present study which indicates that the adsorption was favourable and almost irreversible.

Freundlich isotherm model: The R^2 value was found to be 0.2002, which indicates that the data followed the isotherm with poor validity. The value of $1/n$ as obtained from the slope in Fig. 3 was 1 (0.0726), indicating that the adsorption was favourable (Mohan and Karthikeyan, 1997). The

constant k_f value was found to be as high as 168.05 mg per 4 g of adsorbent, hence $33.6 \text{ mg } \text{g}^{-1}$ of the adsorbent. The constant k_f gives the adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process (Voudrias *et al.*, 2002). It could be inferred that the adsorption did not follow Freundlich isotherm.

Temkin isotherm : The interactions between adsorbate and the adsorbent are related through the Temkin isotherm. The isotherm assumes that the heat of adsorption of all the molecules in the monolayer will decrease linearly rather than logarithmic coverage (Temkin *et al.*, 1940). From the plot showing in Fig. 4, it was observed that the R^2 value was 0.1432 which indicates that the data had a low fit and hence the temkin isotherm was not followed. The constant B value was found to be 15.568, which indicates the heat of sorption to the surface of the adsorbent. The Temkin isotherm constant calculated from b_T was 0.6022, and the Temkin isotherm equilibrium constant A , the equilibrium binding constant ($\text{L } \text{min}^{-1}$) corresponding to the maximum binding energy was $182.387 \text{ L } \text{g}^{-1}$. However, due to low fit it could be inferred that the adsorption did not follow the Temkin isotherm.

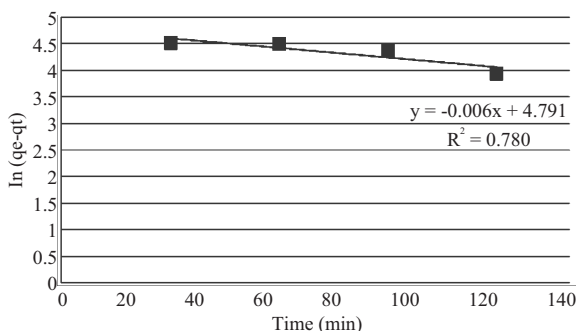


Fig. 5 : Pseudo first order plot between time (min) and ln (qe-qt)

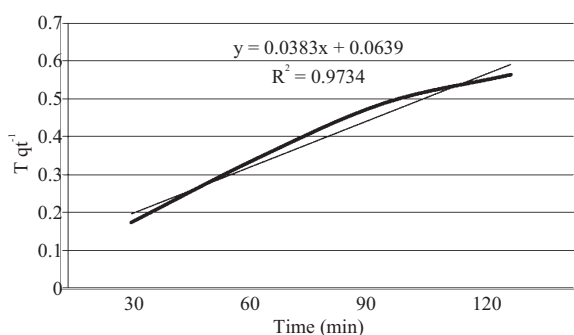


Fig. 6 : Pseudo second order reaction between time (min) and T/qt

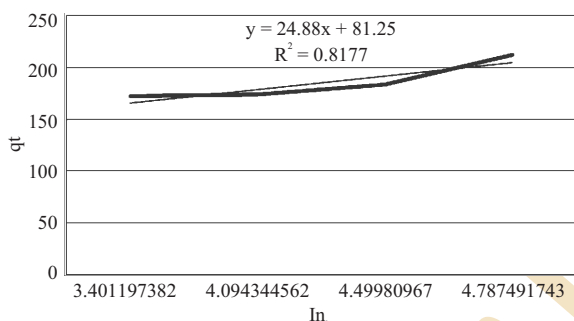


Fig. 7 : Elovich plot between qt and ln t

Adsorption kinetics : The pseudo first order indicates that the rate of adsorption of adsorbate onto the adsorbent sites is proportional to the number of unoccupied sites (Ho and McKay, 1998, 1999) as shown in Fig. 5. The pseudo first order curve between t vs $\ln (q_e - q_t)$ was used to compute the value of first order rate constant k_1 . The value of k_1 was found to be $6.2 \times 10^{-3} \text{ min}^{-1}$ and the q_e value was 120.48 mg l^{-1} much lower than the true q_e value of 263.21 mg l^{-1} . This indicates that the first order kinetics was inadequate to explain the kinetics of adsorption. Also, the R^2 value was also low indicating that the fit was not valid. In such cases where the first order rate equation is not sufficient to explain the kinetics since the $\ln q_e$ value was not found to be equal to the intercept of the plot, second order kinetics is to be tested

(Sharma and Bhattacharyya, 2004).

A plot of t/q_t against t as shown in Fig. 6 gives a linear relationship for the applicability of the second order kinetics. The value of q_e calculated from second order kinetics was $257.069 \text{ mg l}^{-1}$ of the adsorbent, which was much close to the true value of 263.21 mg l^{-1} . The second order rate constant was found to be $2.4 \times 10^{-4} \text{ g mg}^{-1} \text{ min}$. This indicates that the adsorption followed second order rate kinetics.

Elovich kinetics as shown in Fig. 7 should have a linear plot for its applicability. α and β values calculated from the plot were $65.2 \text{ mg g}^{-1} \cdot \text{min}^{-1}$ and 0.0401 g mg^{-1} respectively. The Elovich plot had a fitting value of 0.81. The α and β values indicate the initial chromium adsorption rate and desorption constant. The results of the present study indicate that the adsorption was initially rapid and desorption was calculated to be low.

The present study evaluates the adsorption of Cr (VI) onto leaves of *Tamarindus indica* at much higher concentration of 1000 mg l^{-1} . The adsorption of Cr (VI) was seen to follow the Langmuir adsorption isotherm explaining that monolayer of chromium was adsorbed onto the surface of the leaves. The optimization studies showed that at pH 3.0, 560 mg l^{-1} of Cr (VI) was adsorbed onto the surface in 30 min. However, desorption was found to occur with the increase in contact time. At pH 6.0, the adsorption was found to be increase with contact time and a maximum of 263 mg l^{-1} was adsorbed with second order kinetics and had low desorption constant value of 0.0401 g mg^{-1} . The present study reports the adsorption of Cr (VI) at high concentrations and the results indicate that *T. indica* removed 56% of Cr from 1000 mg l^{-1} within 30 min as adsorbent. Further, studies are required in order to implement this technique in decontaminating waste water.

References:

- Abdullah, M.A. and A.G.D. Prasad: Kinetic and equilibrium studies for the biosorption of Cr(VI) from aqueous solutions by potato peel waste. *Int. J. Chem. Eng. Res.*, **1**, 51–62 (2009).
- Acharya, J., J.N. Sahu, B.K. Sahoo, C.R. Mohanty and B.C. Meikap: Removal of Chromium(VI) from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride. *Chem. Eng. J.*, **150**, 25–39 (2009).
- Agarwal, G.S., H.K. Bhuptawat and S. Chaudhari: Biosorption of aqueous chromium (VI) by *Tamarindus indica* seeds. *Biores. Technol.*, **97**, 949–956 (2006).
- Babel, S. and E.M. Opiso: Removal of chromium from synthetic waste water by sorption into volcanic ash soil. *Int. J. Environ. Sci. Technol.*, **4**, 99–107 (2007).
- Babu, B.V. and S. Gupta: Adsorption of Cr (VI) using activated neem leaves: kinetic studies. *Adsorption*, **14**, 85–92 (2008).
- Baral, S.S., N. Das, G.R. Chaudhury and S.N. Das: A preliminary study on the adsorptive removal of Cr (VI) using seaweed, *Hydrilla*

- verticillata*. *J. Hazard. Mater.*, **171**, 358–369 (2009).
- Chen, S., Q. Yue, B. Gao, Q. Li and X. Xu: Removal of Cr(VI) from aqueous solution using modified cornstalks: Characteristic, equilibrium, kinetic and thermodynamic study. *Chem. Eng. J.*, **168**, 909–917 (2011).
- Chien, S. H. and W. R. Clayton: Application of Elovich equation to the kinetics of phosphate release and sorption on soils. *Soil Sci. Soc. Am.*, **44**, 265–268 (1980).
- Cotton, F.A. and G. Wilkinson: Chromium. In: Advanced inorganic chemistry: a comprehensive text. 4th Edn. Wiley, New York, p 719–736 (1980).
- Cronje, K.J., K. Chetty, M. Carsky, J.N. Sahu and B.C. Meikap: Optimization of Chromium(VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride. *Desalination*, **275**, 276–284 (2011).
- Darko, H.A., D.A. Tatjana, S.N. Ruzica, M.P. Milovan, D.B. Srdjan, L.B. Aleksandar, M.R. Milica: Leaching of chromium from chromium contaminated soil: a speciation study and geochemical modeling. *J. Serb. Chem. Soc.*, **76**, 1–20 (2011).
- Elangovan, R., L. Philip and K. Chandraraj: Biosorption of hexavalent and trivalent chromium by palm flower (*Borassus aethiopicum*). *Chem. Eng. J.*, **141**, 99–111 (2008).
- Fahim, N.F., B.N. Barsoum, A.E. Eid and M.S. Khalil: Removal of Chromium(III) from tannery waste water using activated carbon from sugar industrial waste. *J. Hazard. Mater.*, **136**, 303–309 (2006).
- Garg, U.K., M.P. Kaur, D. Sud and V.K. Garg: Removal of hexavalent chromium from aqueous solution by adsorption on treated sugarcane bagasse using response surface methodological approach. *Desalination*, **249**, 475–479 (2009).
- Greenwood, N.N. and A. Earnshaw: Chemistry of the elements. Pergamon Press, Oxford, pp 1187–1200 (1984).
- Gupta, S. and B.V. Babu: Adsorption of chromium (VI) by a low-cost adsorbent prepared from tamarind seeds. In: Proceedings of International Symposium & 59th Annual Session of IChE in association with International Partners (CHEMCON-2006), GNFC Complex, Bharuch, December 27–30, (2006).
- Gupta, S. and B.V. Babu: Utilization of waste product (tamarind seeds) for the removal of Cr(VI) from aqueous solutions: Equilibrium, kinetics, and regeneration studies. *J. Environ. Manage.*, **90**, 3013–32 (2009).
- Hadjmohammadi, M.R., M. Salary and P. Biparva: Removal of Cr(VI) from aqueous solution using pine needle powder as a Biosorbent. *J. Appl. Sci. Environ. Sanit.*, **6**, 1–13 (2011).
- Ho, Y.S. and G. Mckay: Kinetic model for lead (II) sorption on to peat. *Adsorp. Sci. Technol.*, **16**, 243–255 (1998).
- Ho, Y.S. and G. Mckay: A kinetic study of dye sorption by Biosorbent waste product pith. *Reso. Conser. Recy.*, **25**, 171–193 (1999).
- Hsu, C.L., S.L. Wang and Y.M. Tzou: Photocatalytic reduction of Cr(VI) in the presence of NO_3^- and Cl^- electrolytes as influenced by Fe(III). *Environ. Sci. Technol.*, **41**, 7907–7914 (2007).
- Huang, G.L., H.Y. Zhang and X. Jeffrey: Adsorption of Chromium(VI) from aqueous solutions using cross-linked magnetic chitosan beads. *Ind. Eng. Chem. Res.*, **48**, 2646–2651 (2009).
- Isa, M.H., N. Ibrahim, H.A. Aziz, M.N. Adlan, N.H.M. Sabiani, A.A.L. Zinatizadeh and S.R.M. Kutty: Removal of chromium (VI) from aqueous solution using treated oil palm fibre. *J. Hazard. Mater.*, **152**, 662–668 (2008).
- Jain, M., V.K. Garg and K. Kadirvelu: Chromium(VI) removal from aqueous system using *Helianthus annuus* (sunflower) stem waste. *J. Hazard. Mater.*, **162**, 365–372 (2009).
- Kaouaha, F., T. Berramaa, L. Brahmia, S. Boumazaa and Z. Bendjamaa: Removal of cadmium from aqueous solution by *Posidonia oceanica* (L.) leaf sheaths fibres using discontinuous stirring tank reactor. *Desal. Water Treat.*, **52**, 2272–2281 (2014).
- Kumar, P.S. and K. Kirthika: Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto Bael tree leaf powder. *J. Eng. Sci. Technol.*, **4**, 351–363 (2009).
- Lee, D.C., C.J. Park, J.E. Yang, Y.H. Jeong and H.I. Rhee: Screening of hexavalent chromium Biosorbent from marine algae. *Appl. Microbiol. Biotechnol.*, **54**, 445–448 (2000).
- Levankumar, L., V. Muthukumaran and M.B. Gobinath: Batch adsorption and kinetics of chromium (VI) removal from aqueous solutions by *Ocimum americanum* L. seed pods. *J. Hazard. Mater.*, **161**, 709–713 (2009).
- Lo, S.F., S.Y. Wang, M.J. Tsai and L.D. Lin: Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons. *Chem. Eng. Res. Des.*, **90**, 1397–1406 (2012).
- Malkoc, E., Y. Nuhoglu and M. Dundar: Adsorption of chromium(VI) on pomace—An olive oil industry waste: Batch and column studies. *J. Hazard. Mater.*, **138**, 142–151 (2006).
- Mezener, Y.N. and A. Bensmaili: Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. *Chem. Eng. J.*, **147**, 87–96 (2009).
- Mishra, K., K. Gupta and U.N. Rai: Bioconcentration and phytotoxicity of chromium in *Eichhornia crassipes*. *J. Environ. Biol.*, **30**, 521–26 (2009).
- Mohan, S. and J. Karthikeyan: Removal of lignin and tannin color from aqueous solution by adsorption on to activated carbon solution by adsorption on to activated charcoal. *Environ. Pollut.*, **97**, 183–187 (1997).
- Nameni, M., M.R.A. Moghadam and M. Arami: Adsorption of hexavalent chromium from aqueous solutions by wheat bran. *Int. J. Environ. Sci. Tech.*, **5**, 161–168 (2008).
- Nriagu, J.O. and J.M. Pacyna: Quantitative assessment of world wide contamination of air, water and soils by trace metals. *Nature*, **333**, 134–139 (1988).
- Onyancha, D., W. Mavura, J.C. Ngila, P. Ongoma and J. Chacha: Studies of chromium removal from tannery waste waters by algae biosorbents, *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*. *J. Hazard. Mater.*, **158**, 605–614 (2008).
- Owamah, H.I.: Biosorptive removal of Pb(II) and Cu(II) from waste water using activated carbon from cassava peels. *J. Mater. Cycles. Waste. Manag.*, **16**, 347–358 (2014).
- Patterson, J.W.: Industrial Wastewater Treatment Technology, second ed., Butterworth-Heinemann, London (1985).
- Popuri, R.S., A. Jammala, K.V.N.S. Reddy and K. Abburi: Biosorption of hexavalent chromium using tamarind (*Tamarindus indica*) fruit shell—a comparative study. *Electr. J. Biotechnol.*, **10**, (2007).
- Pushan, S., S. Vladimir and F.N. Peter: Speciation of chromium in Australian coals and combustion products. *Fuel*, **102**, 1–8 (2012).
- Raji, C. and T.S. Anirudhan: Batch Cr (VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics. *Water Research*, **32**, 3772–3780 (1998).
- Sahu, J.N., J. Acharya and B.C. Meikap: Response surface modeling and optimization of chromium(VI) removal from aqueous solution using Tamarind wood activated carbon in batch process. *J. Hazard.*

- Mater.*, **172**, 818–825 (2009).
- Sahu, J.N., J. Acharya and B.C. Meikap: Optimization of production conditions for activated carbons from Tamarind wood by zinc chloride using response surface methodology. *Biores. Technol.*, **101**, 1974–1982 (2010).
- Sepehrian, H., S.J. Ahmadi and S. Waqif-Husain: Adsorption studies of heavy metal ions on mesoporousaluminosilicate, novel cation exchanger. *J. Hazard. Mater.*, **176**, 252–256 (2010).
- Sharma, A. and K.G. Bhattacharyya: Adsorption of Chromium (VI) on *Azadirachta indica* (Neem) leaf powder. *Adsorption.*, **10**, 327-338 (2005).
- Singh, R., D.P. Singh, N. Kumar, S.K. Bhargava and S.C. Barma: Accumulation and translocation of heavy metals in soil and plants from fly ash contaminated area. *J. Environ. Biol.*, **31**, 421-430 (2010).
- Srinivasan, K., N. Balasubramanian and T.V. Ramakrishna: Studies on chromium removal by rice husk carbon. *Indian J. Environ. Hlth.*, **30**, 376–387 (1988).
- Suksabye, P., P. Thiravetyan and W. Nakbanpote: Column study of chromium (VI) adsorption from electro-plating industry by coconut coir pith. *J. Hazard. Mater.*, **160**, 56–62 (2008).
- Swietlik, R.: Speciation analysis of chromium in waters. *Pol. J. Environ. Stud.*, **7**, 257-266 (1998).
- Temkin, M.I. and V. Pyzhev: Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Phys. Chim.*, **12**, 327–356 (1940).
- US EPA: Priority Pollutant List, 40 CFR Part 423, Appendix A (2014).
- Verma, A., S. Chakraborty and J.K. Basu: Adsorption study of hexavalent chromium using tamarind-hull based adsorbents. *Sep. Purif. Technol.*, **50**, 336–341 (2006).
- Voudrias, E., F. Fytianos and E. Bozani: Sorption description isotherms of dyes from aqueous solutions and waste waters with different sorbent materials. *Global Nest, The Int. J.*, **4**, 75-83 (2002).
- Wang, S., X. Jin, H. Zhao and F. Wu: Phosphate biosorption characteristics of a submerged macrophyte *Hydrilla verticillata*. *Aquat. Bot.*, **89**, 23–26 (2008).
- Xie, X.F. and L. Gao: Effect of crystal structure on adsorption behaviors of nanosized TiO₂ for heavy-metal cations. *Curr. Appl. Phys.*, **9**, S185–S188 (2009).
- Xing, Y., X. Chen and D. Wang: Electrically regenerated ion exchange for removal and recovery of Cr(VI) from wastewater. *Environ. Sci. Technol.*, **41**, 1439–1443 (2007).