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Research Article

USE OF *TERMINALIA CATAPPA* L. LEAVES FOR EFFECTIVE REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS

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Abstract

The use of *Tarminalia catappa* L. leaves for effective removal of chromium (VI) from aqueous solutions in a batch system was studied. The FTIR study of acid treated biosorbent showed that the possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. The SEM represents a porous structure with large surface area. The effects of operational factors including solution pH, biosorbent dose, initial chromium (VI) concentration, contact time and temperature were studied. The optimum solution pH for chromium (VI) adsorption by biosorbent was 2.0 with the optimal removal 70.20 %. The biosorbent dose 5 mg/ml was enough for optimal removal of 69.23 %. The equilibrium was achieved after 150 minutes of contact. The equilibrium data were well described by typical Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin adsorption isotherms. bioorption equilibrium exhibited better fit to Langmuir isotherm ($R = 0.9972$) than Freundlich isotherm ($R = 0.9151$), Temkin isotherm ($R = 0.8782$) and Dubinin-Kaganer-Redushkevich (DKR) isotherm ($R = 0.6773$). The maximum adsorption capacity determined from Langmuir isotherm was found to be 44.0528 mg per g of biosorbent. Furthermore, to determine the adsorption mechanism, a detailed analysis has been conducted by testing kinetic models such as pseudo-first-order, pseudo-second-order, Elovich equation and Weber & Morris intraparticule diffusion rate equation. Results clearly indicates that the pseudo-second-order kinetic model was found to be correlate the experimental data strongest than other three kinetic models. Thermodynamic study revealed that the adsorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. *Tarminalia catappa* L. leaves used successfully for removal of chromium (VI) from aqueous solutions can have promising application in industrial wastewater treatment.

Keywords: Effective removal, Chromium (VI), *Tarminalia catappa* L. leaves, FTIR, SEM, Adsorption isotherms, Adsorption kinetics, Thermodynamic study.

Introduction

The serious problem of heavy metal pollution in the environment due to industrial activities needs to be solved. Heavy metals tend to persist indefinitely circulating and eventually accumulating throughout the food chain which results in ecological and health hazard. Heavy metals are non-biodegradable and toxic to all forms of life including humans. Chromium is listed among top pollutants and is ranked 16th harmful pollutant due to its

carcinogenic and teratogenic characteristics on the community (Selomulya et al., 1999) (Geleel et al., 2013). Chromium occurs frequently as chromium (VI) and chromium (III) in aqueous solutions (Dakiky et al., 2002). Hexavalent chromium, which is primary present in the form of chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) possesses significantly higher level of toxicity than the other valence states (Smith et al., 1972) (Sharma et al.,

1995). chromium (VI) discharge into the environment can be due to various large numbers of industrial functions like dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, etc (Patterson, 1985).

Major diseases caused by toxic hexavalent chromium ions are bronchial asthma and lung cancer. Due to the several toxicity of chromium (VI), the EU Directive, WHO and US EPA have set the maximum contaminant concentration level for chromium (VI) in domestic water supplies as 0.05 ppm (Directive 98/83/EC). Therefore, there is an urgent need to seek alternative treatment methods which is cost effective and environmental-friendly for removal of chromium (VI) from wastewater.

The conventional methods for removing heavy metal ions from industrial effluents include oxidation/reduction, filtration by membranes, chemical precipitation, coagulation, solvent extraction, cementation, freeze separation, reverse osmosis, ion-exchange, electro-dialysis, electro-winning and electro-coagulation (Ahluwalia et al., 2007). These methods have found limited application because they often involve high capital and operational cost. Treatment of industrial effluent with adsorbents of biological origin is simple, cleaner, sustainable, comparatively inexpensive and friendly to the environment. Biosorption of heavy metals is very effective, versatile, powerful, most efficient and cost effective technologies involved in the removal of heavy metals from industrial effluents. Biosorption is the process based on the principle of metal binding capacities of biological materials.

Several investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of heavy metals ions. Use of low cost adsorbent for biosorption study of heavy metals is very advantageous (Maind et al., 2013). Among the various resources in biological waste, both dead and live biomass, exhibit particularly interesting metal-binding capacities. The use of dead biomass eliminates the problem of toxicity and the economics aspects of nutrient supply and culture maintenance. A variety of adsorbents, including leaf mould (Sharma et al., 1994), pongamia leaf (Sivamani et al., 2008), algae (Gupta et al., 2001), bacteria (Loukidou et al., 2004), tamarindus indica seeds (Agarwal et al., 2006), activated carbon (Selvi et al., 2001) (Saran et al., 2013), rice husks (Srinivasan, et al., 1988), quarternised rise husk (Low et al., 1999), hazelnut shell (Koby, 2004), almond shell (Candela et al., 1995), corn cob (Bosico, et al., 1996), quaternised wood (Low et al., 2001), groundnut husk

(Periasamy et al., 1991), coconut husk and palm pressed fibers (Tan et al., 1993), coconut shell (Alaerts et al., 1989), coconut jute (Chand et al., 1994), coconut tree sawdust (Selvi and et al., 2001), native and immobilized sugarcane bagasse (Ullah et al., 2013), synthetic material (Yu et al., 2013), inorganic materials (Rosales-Landeros et al., 2013), have been used for chromium (VI) removal.

Natural materials that are available in large quantities or certain waste products from industrial and agricultural operations may have potential as inexpensive adsorbents. The *Tarminalia catappa* L. leaves being one of the inexpensive materials. The *Tarminalia catappa* L. leaves was selected because of a low cost, possibility of higher adsorption capacity and availability of various function groups such as hydroxyl, carbonyl, carboxylic etc, which favours biosorption of heavy metals.

The aim of this study is to characterize the biosorbent *Tarminalia catappa* L. leaves by FTIR and SEM, which helps to find out the functional groups which is responsible biosorption of chromium (VI) and to observe porosity of the biosorbent. The main objective of this work was to evaluate the adsorption capacity of *Tarminalia catappa* L. leaves for the effective removal of chromium (VI) from aqueous solutions by varying solution pH, biosorbent dose, initial chromium (VI) concentration, contact time and temperature. Equilibrium adsorption isotherms (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) for adsorption of chromium (VI) onto *Tarminalia catappa* L. leaves were described. Kinetic models (pseudo-first-order, pseudo-second-order, Elovich equation and Weber and Morris intraparticle diffusion rate equation) were employed to understand the probable adsorption mechanism. Thermodynamic studies were also carried out to estimate the standard free energy change (G^0), standard enthalpy change (H^0) and standard entropy change (S^0).

Materials and Methods

Chemicals and reagents

All the chemicals and reagents used were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of metal solutions. The desired pH of the metal ion solution was adjusted with the help of dilute sulphuric acid and dilute sodium hydroxide.

Preparation of chromium (VI) solution

The stock solution of 1000 ppm of chromium (VI) was prepared by dissolving 0.7072 g of potassium dichromate ($K_2Cr_2O_7$) (AR grade) (previously dried at 50°C for one hour) in 250 ml of double distilled water and further desired test solutions of chromium (VI) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent

The *Tarminalia catappa* L. leaves was collected and washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted material & water soluble impurities and water was squeezed out. The washed biosorbent was then dried at 50°C overnight and grounded in a mechanical grinder to form a powder. The powder was sieved and a size fraction in the range of 100-200 μm will be used in all the experiments. This powder was soaked (20 g/l) in 0.1 M sulphuric acid for 1 hour. The mixture was filtered and the powder residue was washed with distilled water, several times to remove any acid contents. This filtered biomass was first dried, at room temperature and then in an oven at 105°C for 1-2 hrs. For further use, the dried biomass was stored in air tighten plastic bottle to protect it from moisture.

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biosorbent. The biomass samples were examined using FTIR spectrometer (model:FT/IR-4100typeA) within range of 400-4000 cm^{-1} . All analysis was performed using KBr as back ground material. In order to form pellets, 0.02 g of biomass was mixed with 0.3 g KBr and pressed by applying pressure.

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The Scanning Electron Microscope (SEM) was used to see the porosity of the biosorbent. The samples were covered with a thin layer of gold and an electron acceleration voltage of 10 KV was applied and then Scanning Electron Micrograph was recorded.

Experimental procedure

The static (batch) method was employed at temperature (30°C) to examine the adsorption of chromium (VI) by biosorbents. The method was used to determine the adsorption capacity, stability of biosorbent and optimum adsorption

conditions. The parameters were studied by combining biosorbent with solution of chromium (VI) in 250 ml reagent bottle. The reagent bottles were placed on a shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals, centrifuged, the content was separated from the biosorbents by filtration, using Whatmann filter paper and amount of chromium (VI) in the supernatant/filtrate solutions was determined

Estimation of chromium (VI) concentration

A 0.2 % w/v solution of 1,5-Diphenylcarbazide was prepared in acetone containing 1 ml of H_2SO_4 (1:9). Known volume of sample solution containing chromium (VI), was pipetted out into 250 ml beaker and 3 to 4 drops of 0.02 % $KMnO_4$ solution added and covered the beaker with watch glass. The solution was heated without boiling for 15 minute. The acidity of the solution was made 0.05 M to 0.1 M by H_2SO_4 . If the pink color disappears in the course of heating, more $KMnO_4$ solution was added. The excess of oxidant was reduced by adding 1 % sodium azide solution dropwise. The solution was cooled and transferred in a 50 ml volumetric flask and 5 ml of 0.2 % w/v solution of 1,5-Diphenylcarbazide was added. The solution was diluted with water to 50 ml standard measuring flask. Chromium (VI) concentration was estimated by measuring absorbance of the pink color, chromium-diphenylcarbazide complex at 545-nm against water as a blank using a UV-visible spectrophotometer. A linear plot for standard chromium (VI) solution was obtained indicating adherence to the Beers Lamberts law in the concentration range studies and amount of chromium (VI) in the samples were estimated. The amount determined was a mean of triplicate sample analysis with standard deviation less than 5 %. The blank solution i.e. solution containing biosorbent without chromium (VI) was tested and results shows that no any appreciable signal of intensity at wavelength 545-nm obtained.

Instrumentation and data analysis

The concentration of chromium (VI) in the solutions before and after equilibrium was determined by measuring absorbance using digital UV-visible spectrophotometer (EQUIP-TRONICS, model no. Eq-820). The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode.

The data obtained in the batch adsorption studies were used to calculate the percentage adsorption of chromium (VI) by using the mass balance relationship. The chromium (VI) concentrations

adsorbed on the solid were calculated from the difference between initial chromium (VI) content (C_i) and chromium (VI) content after adsorption (C_e). The following equation was used to compute the percentage adsorption (% Ad) of chromium (VI) by the adsorbent,

$$\% \text{ Ad} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial concentrations and equilibrium concentrations of the chromium (VI) in mg/L.

Adsorption isotherms

A series of solutions containing different initial concentrations of chromium (VI) were prepared and the batch biosorption studies were done at 30°C to check the applicability of the biosorption isotherms under the specified condition, the solution pH of 2.0, biosorbent dose of 5 mg/ml, an initial chromium (VI) concentration range 5 mg/L - 250 mg/L and contact time 150 min. Analysis of chromium (VI) content in various solutions were performed by UV-Visible spectrophotometer method. The data obtained in batch adsorption studies was used to calculate the equilibrium chromium (VI) biosorptive quantity by the following equation:

$$q_e = \frac{(C_i - C_e)}{w} \times V \quad (2)$$

where q_e (mg metal per g dry biosorbent) is the amount of chromium (VI) adsorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

Adsorption kinetics

The kinetic measurements were conducted by employing adsorption dose of 5 mg/ml of adsorbent contacted with 10 mg/L of a chromium

(VI) solution with optimum pH 2.0 and temperature 30°C in a rotary shaker. The concentration of chromium (VI) in the solution was determined at known time intervals. Analysis of chromium (VI) content in various solutions was performed by UV-visible spectrophotometer. The amount of chromium (VI) adsorbed q_t (mg/g) at time t was calculated by Equation. (2).

Results and Discussion

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis

To investigate the functional groups of biosorbent and metal loaded with biosorbent, a FTIR analysis was carried out and the spectra are shown in Figure.1. (a and b). As seen in the figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biomass. The broad peak at 3421 cm^{-1} is the indicator of -OH and -NH groups. The stretching of the -OH groups bound to methyl groups presented in the signal at 2922 cm^{-1} . The peaks at 2361 cm^{-1} and 2343 cm^{-1} are stretching peaks. The peaks located at 1734 cm^{-1} and 1637 cm^{-1} are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biomass. The peak at 1508 cm^{-1} is associated with the stretching in aromatic rings. The peaks observed at 1057 cm^{-1} are due to C-H and C-O bonds. The -OH, NH, carbonyl and carboxyl groups are important sorption sites (Volesky et al.2003). As compared to simple biosorbent, biosorbent loaded with chromium (VI) ions, the broadening of -OH peak at 3421 cm^{-1} and carbonyl group peak at 1637 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of chromium (VI).

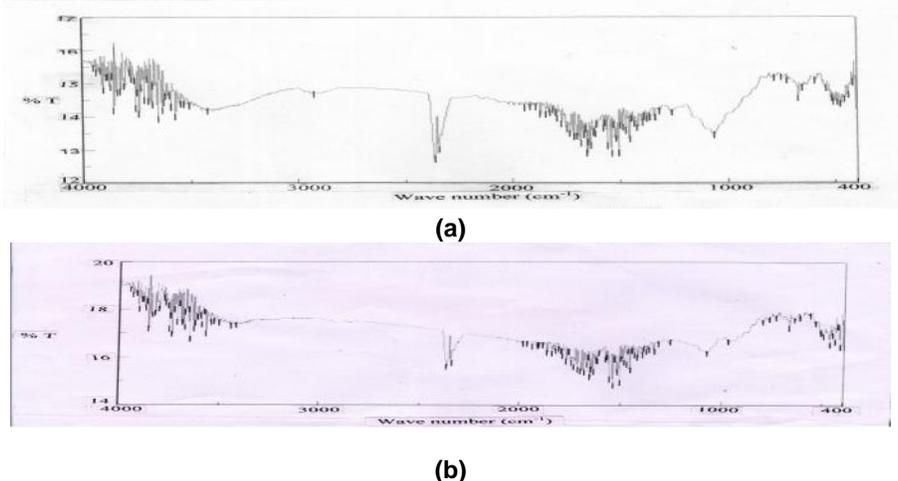


Figure.1. FTIR spectra (a) biosorbent *Terminalia catappa* L. leaves (b) biosorbent *Terminalia catappa* L. leaves loaded with Chromium (VI) ions

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The surface characteristics, structure and particle size distribution of biosorbent before and after biosorption was examined using Scanning Electron Microscope (SEM). The SEM micrographs are shown in Figure. 2. (a and b). These micrographs represent a porous structure with large surface area. The SEM clearly

demonstrated that there is more uniformity after biosorption on metal ions in comparison to before biosorption. It was evident from the micrographs that the biosorbent presents an unequal structure before metal adsorbed. The number of canals in the biosorbent was higher in the initial case. The metal ions adsorbed on the cell wall matrix and created stronger cross linking and uniformity on the surface of biosorbent.

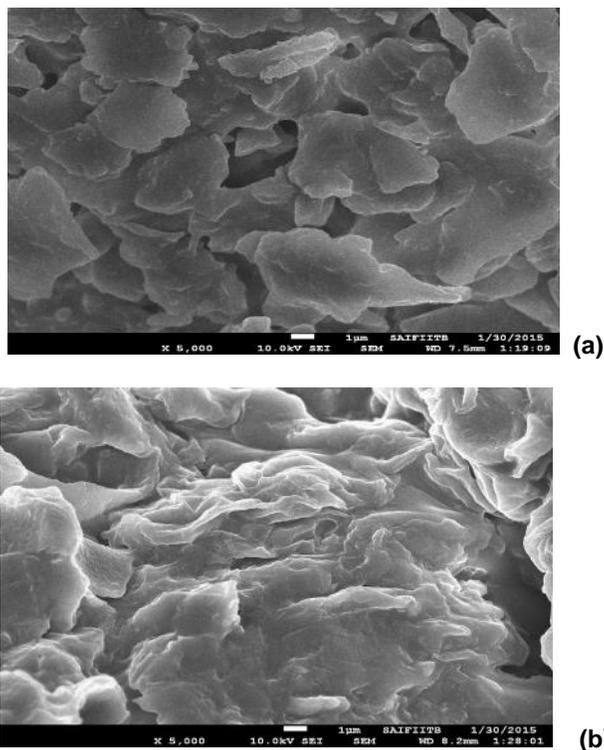


Figure. 2. SEM analysis (a) biosorbent *Terminalia catappa* L. leaves unloaded with Chromium (VI) ions (b) biosorbent *Terminalia catappa* L. leaves loaded with Chromium (VI) ions

Effect of pH

The adsorption capacity of the biosorbent and speciation of metals in the solution is pH dependent. The optimization of pH was done by varying the pH in the range of 1-8 for biosorption of chromium (VI) and pH trend observed in this case is shown in Figure. 3. It was found that at pH 2 the adsorption process was maximum with 70.20 % and after increasing pH, adsorption was decreases. According to the solubility equilibrium of chromium, HCrO_4^- is the dominant species of chromium (VI) at a pH 2. As the pH increases, the dominant form of chromium becomes CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Furthermore, the surface of biosorbent

may be positively charged at pH 2. Therefore, at this pH it is likely to be adsorbed chromium (VI) onto biosorbent through electrostatic attraction and /or by the binding of HCrO_4^- to acidic functional groups on the surface of biosorbent. Also at pH 2, the number of protons available on the surface of biosorbent increases, which increases the attraction between HCrO_4^- & biosorbent and increases the sorption capacity (Rao et al., 1992). As the pH of the solution increases, charges on the surface of biosorbent becomes negative, this leads to generation of repulsive forces between chromium (VI) & biosorbent and inhibits adsorption and resultantly percent chromium (VI) uptake may decrease.

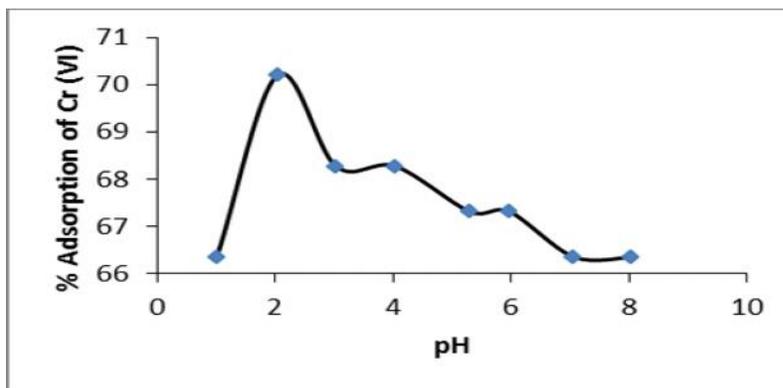


Figure. 3 . Effect of pH on chromium (VI) biosorption by *Tarminalia catappa* L. leaves (biosorbent dose concentration: 5 mg/ml, chromium (VI) concentration: 10 mg/L, contact time: 150 minute, temperature: 30°C)

Effect of biosorbent dose

Effect of biosorbent dose of metal ions biosorption onto biosorbent which is an important parameter was studied while conducting batch adsorption studies. The adsorption capacity of chromium (VI) on to the *Tarminalia catappa* L. leaves by varying biosorbent dose from 1.0 mg/ml to 15.00 mg/ml is as shown in Fig. 4. From the results it was found that adsorption of chromium (VI) increases with increase in adsorbent dosage and is highly dependent on biosorbent concentration. Increase in adsorption by increase in biosorbent dose is

because of increase of ion exchange site ability, surface areas and the number of available adsorption sites (Naiya et al., 2009). The point of saturation for *Tarminalia catappa* L. leaves was found at 5 mg/ml of biosorbent dose with 69.23 % of removal efficiency. The decrease in efficiency at higher biosorbent concentration could be explained as a consequence of partial aggregation of biosorbent which results in a decrease in effective surface area for metal uptake (Karthikeyan et al., 2007). The biosorbent dose 5 mg/ml was chosen for all further studies

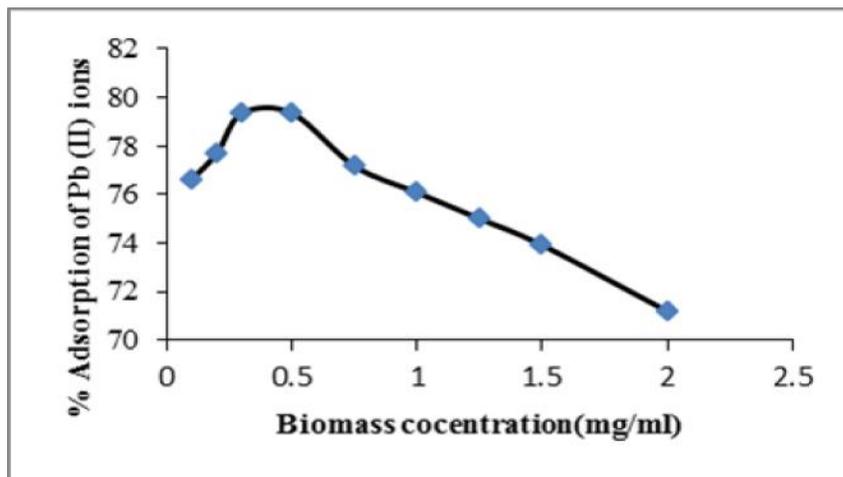


Figure. 4. Effect of biosorbent dose concentration on chromium (VI) biosorption by *Tarminalia catappa* L. leaves (pH: 2, chromium (VI) concentration: 10 mg/L, contact time: 150 minute, temperature: 30°C).

Effect of initial chromium (VI) concentration

The effect of initial chromium (VI) concentration from 5 mg/L - 250 mg/L on the removal of chromium (VI) from aqueous solutions at biosorbent dose 5 mg/ml and at optimum pH 2.0

at 30°C temperature was studied and shown in Figure. 5. On increasing the initial chromium (VI) concentration, the total chromium (VI) ions uptake decreased appreciably when chromium (VI) concentration increases from 5 mg/L - 250 mg/L.

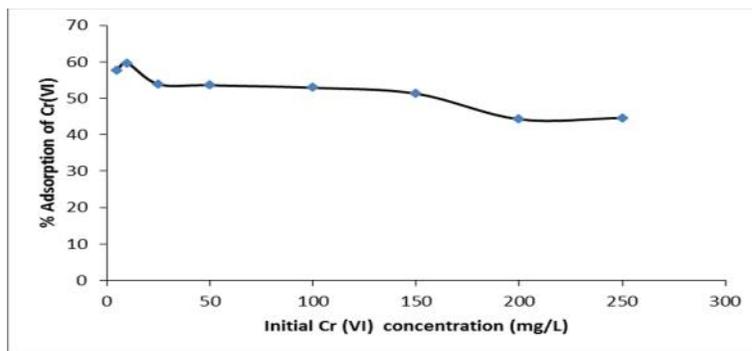


Figure.5. Effect of chromium (VI) concentration on chromium (VI) biosorption by *Tarminalia catappa* L. leaves (pH: 2, biosorbent dose concentration: 5 mg/L, contact time: 150 minute, temperature: 30°C)

Effect of contact time

Contact time plays an important role in affecting efficiency of adsorption. Contact time is the time needed for adsorption process to achieve equilibrium when no more changes in adsorptive concentration were observed after a certain period of time. The contact time which is required to achieve equilibrium depends on the differences in the characteristics properties of the biosorbents. In order to optimize the contact time for the maximum uptake of chromium (VI), contact time was varied between 10 minutes – 180 minutes on the removal of chromium (VI) from aqueous solutions in the concentration of

chromium (VI) 10 mg/L, biosorbent dose 5 mg/ml, optimum pH 2.0 and 30°C temperature (Figure. 6). The results obtained from the biosorption capacity of chromium (VI) onto rind of *Tarminalia catappa* L. leaves showed that the adsorption increases with increase in contact time until it reached equilibrium. The optimum contact time for adsorption of chromium (VI) onto the *Tarminalia catappa* L. leaves was 150 minutes with maximum adsorption. The rapid uptake of chromium (VI) is due to the availability of ample active sites for adsorption. A further increase in the contact time has a negligible effect on the adsorption capacity of chromium (VI) biosorption. So a contact time of 150 minutes was fixed for further experiments.

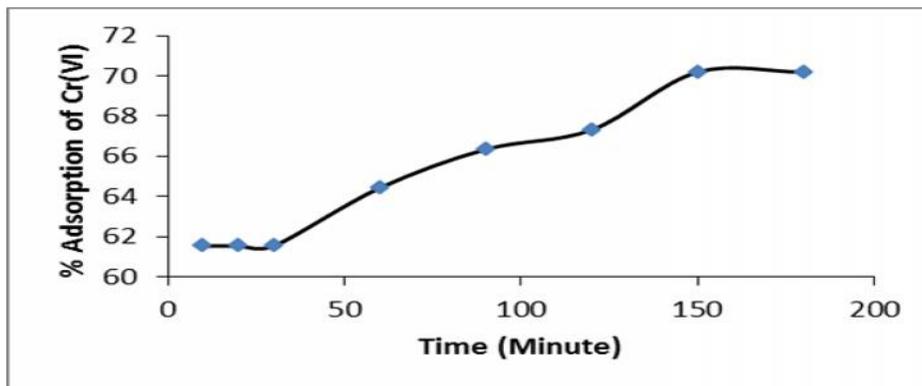


Figure.6. Effect of contact time on chromium (VI) biosorption by *Tarminalia catappa* L. leaves (pH:2, biosorbent dose concentration: 5 mg/L, initial chromium (VI) concentration: 10 mg/ml, temperature: 30°C)

Adsorption isotherms

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm

models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

Langmuir adsorption isotherm (I. Langmuir 1918):

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

where q_m is the maximum adsorption capacity of biosorbent (mg g^{-1}). b is the Langmuir adsorption constant (L mg^{-1}) related to the affinity between the biosorbent and biosorbate. Linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constants and is represented as:

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{4}$$

The linear plots of $1/q_e$ vs $1/C_e$ is shown in Fig. 7 (a). The two constants b and q_m are calculated from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line. The values of q_m , b and regression coefficient (R^2) are listed in Table 1. Maximum adsorption capacity of biosorbent (q_m) is found to be 44.0528 mg per g of biosorbent which is higher than the other adsorbents used by many authors. The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent using separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation:

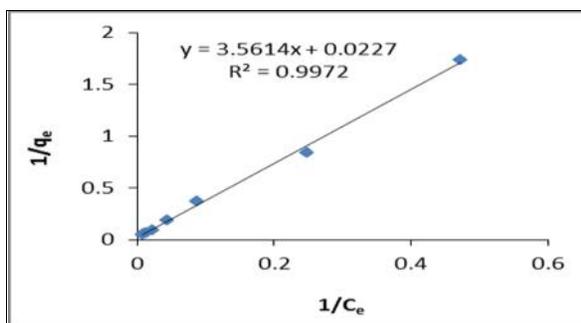
$$R_L = \frac{1}{1 + b C_i} \tag{5}$$

Where b is the Langmuir constant and C_i is the maximum initial concentration of chromium (VI). The value of separation parameters R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). The R_L was found to be 0.3883-0.9694 for concentration of 5 mg/L -250 mg/L of chromium (VI). They are in the range of 0-1 which indicates favorable biosorption (E. Malkoc et al., 2005).

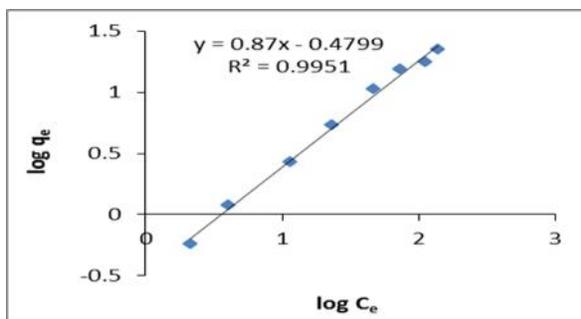
Adsorption can also be interpreted in terms of surface area coverage against initial metal ion concentration and separation factor. Langmuir model for surface area of biosorbent surface has been represented in the following equation:

$$b C_i = \frac{\theta}{1 - \theta} \tag{6}$$

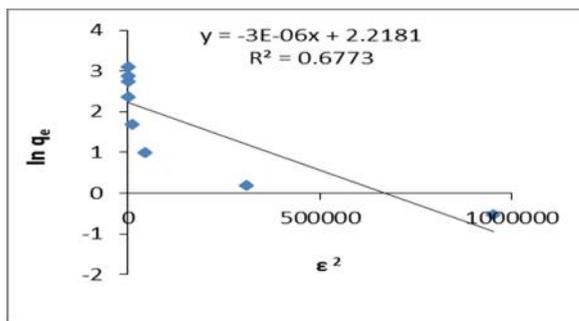
Where θ is the surface area coverage. The θ was found to be 0.0305-0.5365 for concentration of 5 mg/L -250 mg/L of chromium (VI).



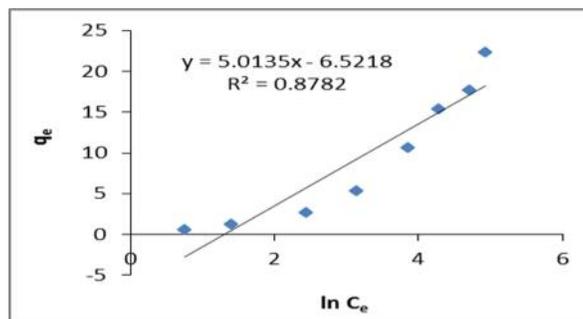
(a)



(b)



(c)



(d)

Figure. 7. Adsorption isotherm models (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for biosorption of chromium (VI) by *Tarminalia catappa* L. leaves (pH: 2.0, biosorbent dose concentration: 5 mg/ml, contact time: 150 minute, temperature: 30⁰C

Freundlich adsorption isotherm (H. M. F. Freundlich, 1906):

Freundlich equation is represented by;

$$q = KC_e^{1/n} \tag{7}$$

where K and n are empirical constants incorporating all parameters affecting the adsorption process such as, sorption capacity and sorption intensity respectively.

Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\log q_e = \log K + \frac{1}{n} \log C_e \tag{8}$$

Equilibrium data for the adsorption is plotted as $\log q_e$ vs $\log C_e$, as shown in Figure. 7 (b). The two constants n and K are calculated from the slope ($1/n$) and intercept ($\log K$) of the line, respectively. The values of K , $1/n$ and regression coefficient (R^2) are listed in Table 1.

The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is chemical process; if $n > 1$, then adsorption is a physical process. A relatively slight

slope and a small value of $1/n$ indicate that, the biosorption is good over entire range of concentration. The n value in Freundlich equation was found to be 2.0837. Since $n > 1$, this indicates the physical biosorption of chromium (VI) onto *Tarminalia catappa* L. leaves. The higher value of K (7.4131) indicates the higher adsorption capacity of the adsorbent.

Dubinin-Kaganer-Radushkevich(DKR) adsorption isotherm (M. M. Dubinin et al., 1947):

Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as:

$$\ln q_e = \ln q_m - \frac{\epsilon^2}{2} \tag{9}$$

Where q_m is the maximum adsorption capacity, ϵ is the activity coefficient related to mean adsorption energy and $\ln q_e$ is the Polanyi potential, which is calculated from the following relation;

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{10}$$

Equilibrium data for the adsorption is plotted as $\ln q_e$ vs ϵ^2 , as shown in Fig. 7 (c). The two constants q_m and $\ln q_m$ are calculated from the slope ($-1/2$) and intercept ($\ln q_m$) of the line, respectively.

The values of adsorption energy E was obtained by the following relationship.

$$E = \frac{1}{\sqrt{-2\beta}} \quad (11)$$

The values of q_m , E and regression coefficient (R^2) are listed in Table 1.

The mean free energy gives information about biosorption mechanism, whether it is physical or chemical biosorption. If E value lies between 8 KJ mol⁻¹ and 16 KJ mol⁻¹, the biosorption process take place chemically and $E < 8$ KJ mol⁻¹, the biosorption process of the physical in nature (N. F. Olivieri et al., 1997). In the present work, E value (0.4082 KJ mol⁻¹) which is less than 8 KJ mol⁻¹, the biosorption of chromium (VI) onto biosorbent is of physical in nature (Sawalha et al., 2006).

Temkin adsorption isotherm (M. J. Temkin et al., 1940):

Linearized Temkin adsorption isotherm is given by the equation:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (12)$$

Where b_T is the Temkin constant related to heat of sorption (J/mol) and A_T is the Temkin isotherm constant (L/g). Equilibrium data for the adsorption is plotted as q_e vs $\ln C_e$, as shown in Figure. 7 (d). The two constants b_T and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot \ln A_T$) of the line, respectively. The values of A_T , b_T and regression coefficient (R^2) are listed in Table 1

TABLE 1 Adsorption isotherm for adsorption of chromium (VI) by *Terminalia catappa* L. leaves

Langmuir constants			Freundlich constants			DKR constants				Temkin constants		
q_m	b	R^2	K	$1/n$	R^2	q_m		E	R^2	A_T	b_T	R^2
44.052	0.006	0.997	7.413	0.479	0.995	-3E-6	9.1898	0.408	0.677	3.672	502.4	0.878
8	3	2	1	9	1			2	3	2	7	2

Adsorption kinetics

As aforementioned, a lumped analysis of adsorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the pseudo-first-order equation (S. Lagergren et al., 1898), (b) the pseudo-second-order equation (G. McKay et al., 1999) (c) Elovich equation (S. H. Chien et al., 1980) (d) Weber and Morris intraparticle diffusion rate equation (W. J. Weber et al., 1963) are presented below,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (15)$$

$$q_t = k_i t^{0.5} + c \quad (16)$$

Where q_e (mg g⁻¹) is the solid phase concentration at equilibrium, q_t (mg g⁻¹) is the average solid phase concentration at time t (min), k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

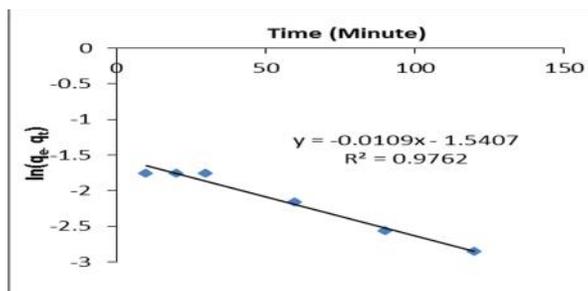
The symbols of (mg g⁻¹ min⁻¹) and (g mg⁻¹) are Elovich coefficients representing initial adsorption rate and desorption constants, respectively. k_i (mg g⁻¹ min^{-1/2}) is the intraparticle diffusion rate constant, c is intercept.

If the adsorption follows the pseudo-first-order rate equation, a plot of $\ln(q_e - q_t)$ against time t should be a straight line. Similarly, t/q_t should change lineally with time t if the adsorption process obeys the pseudo-second order rate equation. If the adsorption process obeys Elovich rate equation, a plot of q_t against $\ln t$ should be a straight line. Also a plot of q_t against $t^{0.5}$ changes lineally the adsorption process obeys the Weber & Morris intraparticle diffusion rate equation.

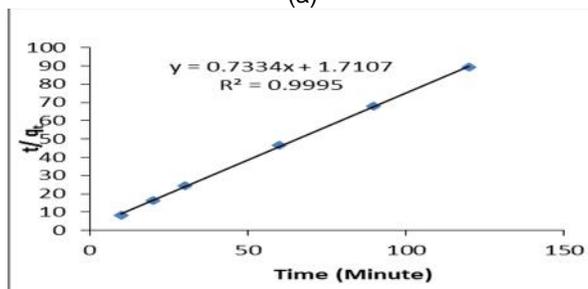
Adsorption of chromium (VI) onto biosorbent was monitored at different specific time interval. The chromium (VI) uptake was calculated from the data obtained. From the chromium (VI) uptake was plotted against time to determine a suitable kinetic model, the adsorption data was fitted into pseudo-first-order rate equation, pseudo-second-order rate equation, Elovich equation and the Weber & Morris intraparticle diffusion rate equation. The pseudo-first-order equation was plotted for $\ln(q_e - q_t)$ against t (Figure. 8 (a)).

The values of q_e and k_1 values were calculated from the slope (k_1) and intercept ($\ln q_e$) of the plot and shown in Table 2. Kinetic adsorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the adsorbent and the ions adsorbed onto it (Sephthum et al., 2007). The pseudo-second-order equation was plotted for t/q_t against t (Fig. 8 (b)). The values of q_e and k_2 are calculated from the slope ($1/q_e$) and intercept ($1/k_2 q_e^2$) of the plot and values are shown in Table 2. The Elovich equation was plotted for q_t against $\ln t$ (Figure. 8 (c)). The values of q_e and k_1 are calculated from the slope ($1/q_e$) and the intercept ($\ln () / ()$) of the plot and values are shown in Table 2. The Elovich equation has been used with the assumption that the actual adsorption surface is energetically heterogeneous (Thomas et al., 1997). The Weber & Morris intraparticle diffusion equation was plotted for q_t against $t^{0.5}$ (Figure. 8 (d)). The value of k_i and c are calculated from the slope (k_i) and intercept (c) of the plot and values are shown in Table 2. The

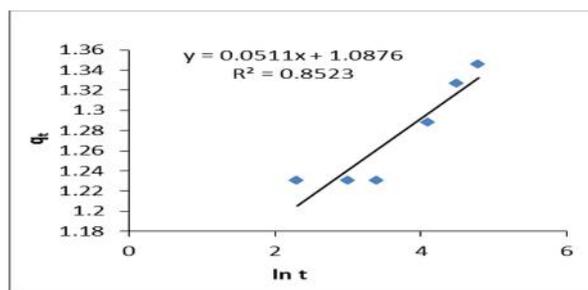
intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intraparticle pore diffusion is not only rate-limiting step (Weber et al., 1963). The plot of intraparticle diffusion equation showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of adsorption (Panday et al., 1986). The pseudo-second-order equation showed a strongest correlation value ($R^2 = 0.9995$) being higher than the correlation coefficient for the pseudo-first-order, Weber and Morris intra particle diffusion rate equation and Elovich equation.



(a)



(b)



(c)

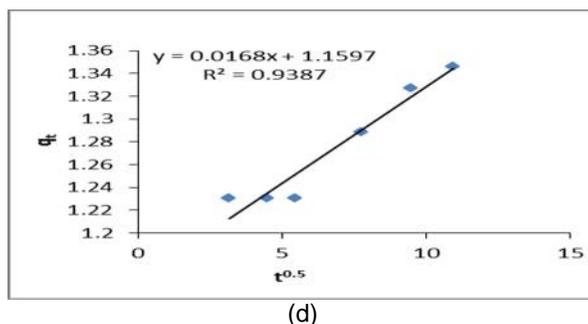


Figure. 8. Adsorption kinetic models (a) pseudo-first-order equation, (b) pseudo-second-order equation, (c) Elovich equation and (d) Weber and Morris intraparticle mixing equation, for biosorption of chromium (VI) by *Tarminalia catappa* L. leaves (pH: 2.0, biosorbent dose concentration: 5 mg/ml, chromium (VI) concentration: 10 mg/L, temperature: 30°C)

TABLE 2 Adsorption kinetic data for biosorption of chromium (VI) by *Tarminalia catappa* L. leaves

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra particle diffusion model		
q_e	K_1	R^2	q_e	K_2	R^2			R^2	K_i	c	R^2
4.6678	0.0109	0.9762	1.3635	0.3144	0.9995	8.9450 E-7	19.569	0.8523	0.0168	1.1597	0.9387

Thermodynamic study

The effect of temperature on removal of chromium (VI) from aqueous solutions in the chromium (VI) concentration 10 mg/L and adsorbent dose 5 mg/ml with optimum pH 2.0 was studied. Experiments were carried out at different temperatures from 20°C-50°C. The samples were allowed to attain equilibrium. adsorption slightly increases from 20°C-50°C. The equilibrium constant (Catena et al., 1989) at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \tag{17}$$

$$\Delta G^\circ = -RT \ln K_c \tag{18}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{19}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{20}$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the chromium (VI) concentration adsorbed on the adsorbent per liter of solution at equilibrium (mg/L). G° , H° and S° are changes in standard, Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K), T is the temperature (K). The values of H° and S° were determined from the slope (H°/R) and the intercept (S°/R) from the plot of $\ln K_c$ versus $1/T$ (Fig. 9.). The values of equilibrium constant (K_c),

standard Gibbs free energy change (G°), standard enthalpy change (H°) and standard entropy change (S°) calculated in this work were presented in Table 3. The equilibrium constant (K_c) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intraparticle diffusion. The standard Gibbs free energy change (G°) is small and negative and indicates the spontaneous nature of the adsorption. The values of G° were found to decrease as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The positive values of H° , indicating the endothermic nature of the adsorption of chromium (VI) onto *Tarminalia Catappa* L. leaves. The positive values of S° , shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

TABLE 3 Thermodynamic parameters of biosorption of chromium (VI) ions by *Tarminalia catappa* L. leaves

T (K)	Kc	- G ⁰ (kJ/mol)	H ⁰ (kJ/mo l)	S ⁰ (J/mol K)
293	1.885 1	1.5968	3.6706	17.384
303	1.971 7	1.7664		
313	2.059 0	1.9394		
323	2.059 0	1.9994		

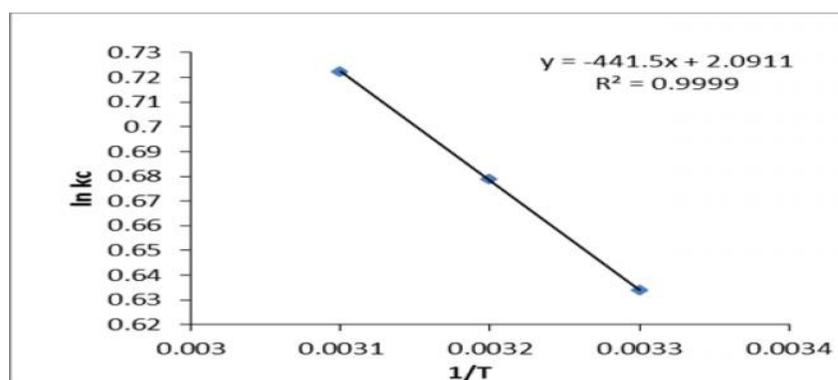


Figure. 9. Plot of $\ln K_c$ against $1/T$ for determination of thermodynamic parameters for biosorption of chromium (VI) by *Tarminalia catappa* L. leaves (pH: 2.0, biosorbent dose concentration: 5 mg/ml, Cr (VI) concentration: 10 mg/L, contact time: 150 minute)

Conclusion

The present investigation revealed that *Tarminalia catappa* L. leaves used as inexpensive, excellent biosorbent for the removal of chromium (VI) from aqueous solutions. The FTIR study of acid treated biosorbent showed that the possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc. The SEM represents a porous structure with large surface area. The optimal parameters such as solution pH, biosorbent dose, initial chromium (VI) concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of chromium (VI) onto *Tarminalia Catappa* L. leaves. adsorption equilibrium exhibited better fit to Langmuir isotherm than Freundlich isotherm, Temkin isotherm and Dubinin-Kaganer-Redushkevich (DKR) isotherm. The maximum chromium (VI) loading capacity (q_e) of *Tarminalia Catappa* L. leaves determined from Langmuir adsorption isotherm was found to be

44.0528 mg g⁻¹. The pseudo-second-order kinetic model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of adsorption of chromium (VI) onto *Tarminalia Catappa* L. leaves is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that *Tarminalia catappa* L. leaves has considerable adsorption capacity, available in abundant, non-hazardous material can be used as an effective indigenous material for treatment of wastewater stream containing chromium (VI).

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