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Review

Biosorption of Lead (II) and Chromium (VI) Onto *Tarminalia Catappa* L. Leaves: A Comparative Evaluation

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ABSTRACT

A comparative evaluation to test the ability of Tarminalia catappa L. leaves to biosorb lead (II) and chromium (VI) was investigated. The biosorbent was characterized by FTIR and SEM before and after biosorption. The batch experiments were performed in order to optimize the various parameters such as solution pH, biosorbent dose, initial metal concentration, contact time and temperature. Equilibrium data were well described by typical Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin adsorption isotherm models. Langmuir adsorption isotherm model provided a better fit with the experimental data for both lead (II) and chromium (VI). The maximum biosorption capacity of lead (II) and chromium (VI) which was determined from Langmuir adsorption isotherm was found to be 50.00 mg g^{-1} and 44.05 mg g^{1} respectively. Furthermore, a detailed analysis has been conducted by testing simple chemical reaction kinetic models such as pseudo-first-order, pseudo-second-order, Elovich and Weber & Morris intra-particle diffusion. Predictions based on the so-called pseudo-second-order kinetic model was found in satisfactory accordance with experimental data for both lead (II) and chromium (VI), which suggests that biosorption is chemical sorption controlled. Thermodynamic study revealed that the biosorption process was spontaneous, endothermic and increasing randomness of the solid solution interfaces. The Tarminalia catappa L. leaves was found to remove lead (II) and chromium (VI) effective from aqueous solutions with uptake and selectivity in the order of lead (II) > chromium (VI). The whole study showed that the Tarminalia catappa L. leaves tested can be very promising for the removal of lead (II) and chromium (VI) in industrial wastewater.

Keywords: Biosorption, Lead (II), Chromium (VI), Comparative evaluation, Tarminalia catappa L. leaves, FTIR, SEM, Adsorption isotherms, Adsorption kinetics, Thermodynamic study.

INTRODUCTION

Heavy metals present in wastewater are recognized as long-term hazardous contaminants because of their non-biodegradable behavior, high toxicity, accumulation and retention in human body and carcinogenic properties [1]. Heavy metals pollute drinking water resources and even at low concentration, they can

accumulate along the food chain which results in serious ecological and health hazard [2]. Lead is a toxic heavy metal of significant environmental and occupational concern which ranks 2nd in the list of prioritized hazardous materials. Lead enter into the water bodies through industries like metal production, phosphate fertilizers, electrical wiring, manufacture of batteries, pigments, electroplating, air conditioning tubing and plumbing. Chromium is listed among top pollutants and is ranked 16th harmful pollutant due to its carcinogenic and teratogenic characteristics on the community. Chromium 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. Severe lead poising can cause encephalopathy, with permanent damage, while moderate lead poising result in neurobehavioral and intelligent deficit [3]. Lead can cause anaemia, hepatitis and nephritic syndrome [4]. Lead poisoning causes damage of brain, kidney, and nervous system, reproductive system, liver and bone [5-6]. Major diseases caused by chromium are bronchial asthma and lung cancer. Strong exposure of chromium causes cancer in the digestive tract and may cause gastric pain, nausea, vomiting, several diarrhea, hemorrhage [7]. When heavy metals (lead and chromium) are present in the wastewater beyond the permissible limits of concentration, it can have severe toxicological effects on both human and aquatic ecosystems. United States Environmental Protection Agency (USEPA) has demarcated the maximum permissible limits in wastewater and potable water is 0.1 mg/L and 0.015 mg L^{-1} for lead (II) and 1.0 mg L^{-1} and 0.05 mg L^{-1} for chromium (VI) respectively [8]. Hence, the removal of heavy metals becomes mandatory before discharge of industrial effluents into main water stream.

The conventional methods for removing heavy metals 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[9]. These methods have found limited application because they often involve high capital and operational cost. Treatment of industrial effluents with sorbents of biological origin is simple, 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 [10]. Biosorption is the process based on the principle of metal binding capacities of biological materials. Biosorption is a process that utilizes low-cost biosorbents to sequester toxic heavy metals. Biosorption has distinct advantages over expensive clean up technologies which used in industrial sector. The major advantages of biosorption which include reusability of biomaterial, low operating cost, and high efficiency of metal removal from dilute solution, no additional nutrient requirement, short operation time, no chemical and/or biological sludge and the possibility of metal recovery [11-12].

In the recent years many low cost biosorbents materials have been utilized for heavy metal removal in waste water. We reported previously and investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of heavy metals [13-16]. 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 [17]. Several authors have been intensively examined, many low cost biosorbents for their abilities to be applied for removal of lead (II) and chromium (VI) from aqueous solutions.

Natural materials that are available in large quantities or certain waste products from industrial and agricultural operations may have potential as inexpensive biosorbents. *Terminalia catappa* L. is a large tropical tree in the Leadwood tree family, belongs to the Combretaceae. Leaves of *Terminalia catappa* L. contain several Flavonoids, tannins, saponins and phytosterols and can accumulate heavy metals from their external environments by means of physico-chemical and biological mechanism. *Terminalia catappa* L. leaves were selected because of a cost effective, higher adsorption capacity, possibility of availability of function groups such as hydroxyl, carbonyl, carboxylic etc.

The aim of the present research was to utilize the *Terminalia catappa* L. leaves for the biosorption of lead (II) and chromium (VI) from aqueous solutions in a batch system. The objective of this study was to characterize biosorbent befour and after biosorption using FTIR and SEM. The study was extended with the objective for estimation and calculation of various parameters affecting the biosorption of heavy metals such as solution pH, biosorbent dose, contact time, initial metal concentration and temperature. Adsorption isotherm models (Langmuir, Freundlich, Dubinin-kaganer-Redushkevich (DKR) and Temkin) and kinetics models (pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion) was employed to understand the probable biosorption mechanism. Thermodynamic studies was also carried out to estimate the standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^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. pH of the metal ion solution adjusted with dilute hydrochloric acid and dilute sodium hydroxide.

Preparation of lead (II) chromium (VI) solution: The stock solution of 1000 ppm of lead (II) was prepared by dissolving 0.250 g lead metal in 1 ml concentrated nitric acid and diluted in 250 ml of double distilled water. 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 50^0C for one hour) in 250 ml of double distilled water. Further desired test solutions of lead (II) chromium (VI) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent: The *Terminalia catappa* L. leaves were collected and washed with several times with distilled water to remove the surface adhered particles, dirt, other unwanted materials, water soluble impurities and water was squeezed out. Biosorbent was then dried at 50^0C overnight and crushed. It was sieved to select particles 100 μm in size will be used in all the experiments. This powder was soaked (20 g L^{-1}) in 0.1 M nitric acid for 1 h. 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 105ºC for 1-2 h. 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) spectroscopy: 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): 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 (30^0C) to examine the biosorption of lead (II) and chromium (VI) by biosorbents. The method was used to determine the biosorption capacity, stability of biosorbent, and optimum biosorption conditions. The parameters were studied by combining biosorbent with solution of lead (II) and chromium (VI) in 250 mL separate reagent bottles. 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 Whatman filter paper and amount of lead (II) and chromium (VI) in the

supernatant/filtrate solutions was determined using digital UV-visible spectrophotometer (EQUIP-TRONICS, model no. Eq-820). The following equation was used to compute the percentage adsorption (% Ad) of lead (II) and chromium (VI) by the biosorbent,

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

Where C_i is the initial concentrations and C_e is equilibrium concentrations of the lead (II) and chromium (VI) in mg L^{-1}.

The equilibrium lead (II) and chromium (VI) adsorptive quantity (q_e) was determined by the following equation,

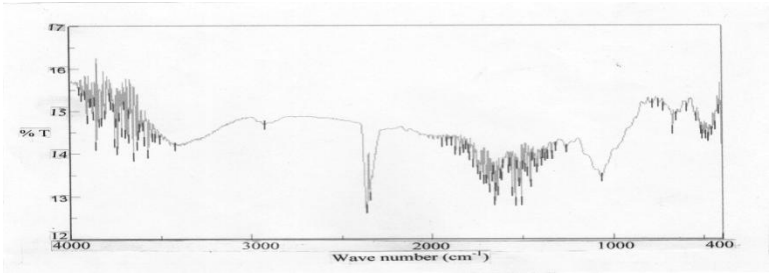
$$q_e = \frac{(C_i - C_e)}{w} \times V \qquad (2)$$

Where q_e (mg metal per g dry biosorbent) is the amount of lead (II) or chromium (VI) adsorbed, V (in L) is the solution volume and w (in g) is the amount of dry biosorbent used.

Estimations of lead (II) and chromium (VI) concentration: Quantitative estimations of lead (II) and chromium (VI) were carried out by UV-visible spectrophotometer using dithizone and 1,5-Diphenylcarbazide as a complex forming regent for lead (II) and chromium (VI) respectively.

RESULTS AND DISCUSSION

Characterization of biosorbent by Fourier Transform Infrared (FTIR) spectroscopy: To investigate the functional groups of biosorbent and metal loaded with biosorbent, a FTIR analysis was carried out and the spectra are shown in fig.1. (a, b and c). As seen in the figure unloaded biomass displays a number of absorption peaks, reflecting the complex nature of biomass. The spectrums clearly showed the broad peak of -OH and -NH groups. The stretching of the –OH groups bound to methyl groups are clearly indicated in the spectrum. The characteristics peak of carbonyl group is present. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biomass. The peak of stretching and the stretching in aromatic rings are present. The peaks of C-H and C-O bonds observed. The –OH, NH, carbonyl and carboxyl groups are important sorption sites[18]. As compared to simple biosorbent, biosorbent loaded with metal, the broadening of -OH group peak and carbonyl group peak was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of metal.



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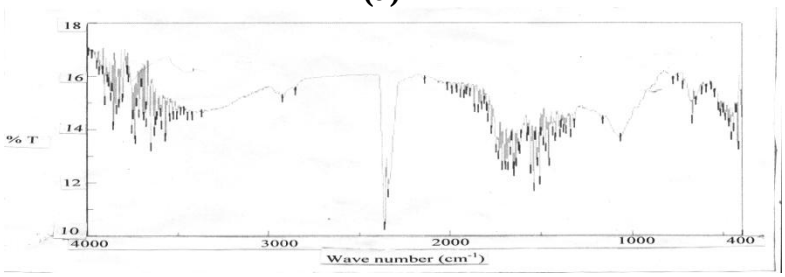

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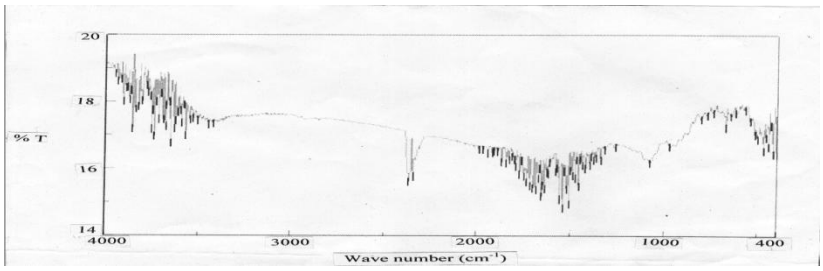

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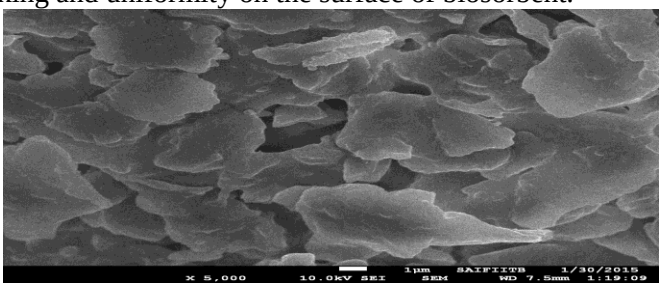
Fig. 1. FTIR spectra (a) biosorbent, *Tarminalia catappa* L. leaves (b) biosorbent, *Tarminalia catappa* L. leaves loaded with lead (II) (c) biosorbent, *Tarminalia catappa* L. leaves loaded with chromium (VI)

Characterization of biosorbent by Scanning Electron Microscope (SEM): 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 fig. 2. (a, b and c). 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.



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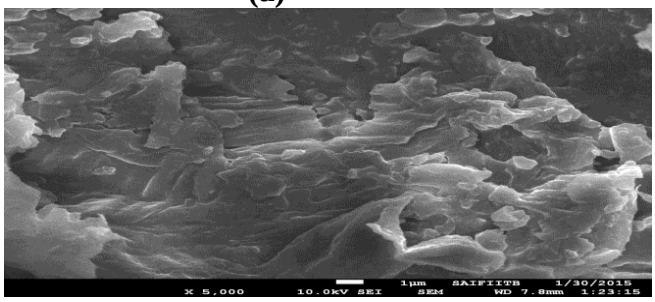

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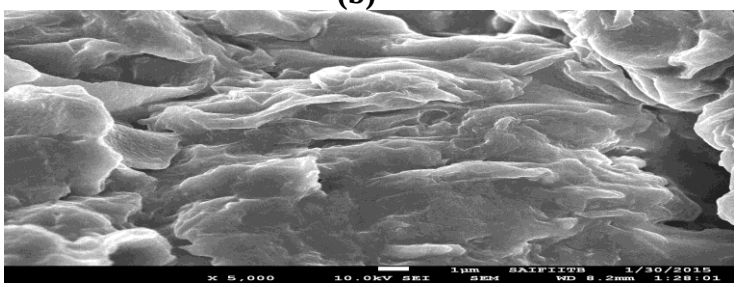

(c)

Fig. 2. Scanning Electron Microscope (SEM) image (a) biosorbent, *Tarminalia catappa* L. leaves (b) biosorbent, *Tarminalia catappa* L. leaves loaded with lead (II) (b) biosorbent, *Tarminalia catappa* L. leaves loaded with chromium (VI)

Effect of pH: pH is considered as a very important parameter in biosorption process. The functional groups are responsible for binding of metal ions in the biosorbent, affected by pH. It also affects the competition of metal ions that gets adsorb to active sites of biosorbent. The biosorption capacity of the biosorbent and speciation of metals in the solution is pH dependent (Table 1). pH influences the chemical structure of the lead (II) and chromium (VI) in aqueous solution, hence influencing its bioavailability. The biosorption capacity of the lead (II) and chromium (VI) depends on the pH of the biosorption medium, which influences electrostatic binding of lead (II) and chromium (VI) ions to corresponding functional groups. The optimization of pH was done by varying the pH in the range of 2 to 10 for lead (II) and 1 to 8 for chromium (VI) and pH trend observed in this case is shown in fig. 3. Percentage adsorption of lead (II) and chromium (VI) with respect to pH is shown in Table1. It was found that biosorption of lead (II) with biosorbent has increased by increasing pH and at pH 6 the biosorption process maximum with 82.06 % and then decreases till pH 10. The lesser biosorption at lower pH was due to lesser surface sites are available for biosorption. pH 6 was chosen for all further biosorption studies for lead (II). It was found that at pH 2, biosorption of chromium (VI) with biosorbent maximum with 70.20 % and after increasing pH, biosorption 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 $Cr_2O_7^{2-}$. Furthermore, the surface of biosorbent may be positively charged at pH 2. Therefore, at this pH it is likely to be chromium (VI) biosorbed 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 [19]. 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) and biosorbent and inhibits biosorption; resultantly percent chromium (VI) uptake may decrease.

Table 1. Percentage adsorption of lead (II) and chromium (VI) with respect to pH

pH	**Percentage adsorption (%Ad)**	
	Lead (II)	**Chromium (VI)**
1	--	66.35
2	77.17	70.20
3	78.80	68.27
4	80.43	68.27
5	82.06	67.31
6	82.06	67.31
7	81.52	66.35
8	78.80	66.35
9	78.26	--
10	78.26	--

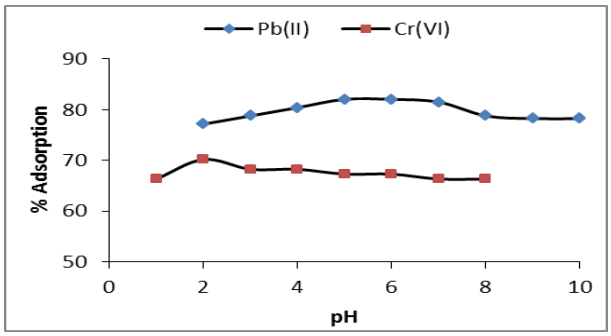

Fig. 3. Effect of pH on biosorption of lead (II) and chromium (VI) using *Tarminalia catappa* L. leaves

Effect of biosorbent dose: Effect of biosorbent dose of biosorption of metal ions onto biosorbent which is an important parameter was studied while conducting batch biosorption studies. The biosorption capacity of lead (II) and chromium (VI) onto the biosorbent by varying biosorbent dose from 1.0 mg mL^{-1} to 20 mg m L^{-1} for lead (II) and 1.0 mg m L^{-1} to 15 mg m L^{-1} for chromium (VI) is as shown in fig. 4. Percentage adsorption of lead (II) and chromium (VI) with respect to biosorbent dose concentration (mg m L^{-1}) is shown in table 2. From the results it was found that biosorption of lead (II) and chromium (VI) increases with increase in biosorbent dose and is highly dependent on biosorbent concentration. Increase in biosorption by increase in biosorbent dose is because of increase of ion exchange site ability, surface areas and the number of available biosorption sites [20]. The point of saturation for the biosorbent was found at 5 mg m L^{-1} of biosorbent dose with maximum removal efficiency for both lead (II) and chromium (VI). 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[21]. The biosorbent dose 5 mg mL^{-1} was chosen for all further studies.

Table 2. Percentage adsorption of lead (II) and chromium (VI) with respect to biosorbent dose concentration (mg mL^{-1})

Biosorbent dose concentration (mg/ml)	**Percentage adsorption (%Ad)**	
	Lead (II)	**Chromium (VI)**
1	76.63	66.34
2	77.71	67.31
3	79.35	67.31
5	79.35	69.23
7.5	77.17	68.27
10.0	76.08	68.27
1.25	75.00	68.27
1.50	73.91	68.27
20.0	71.19	--

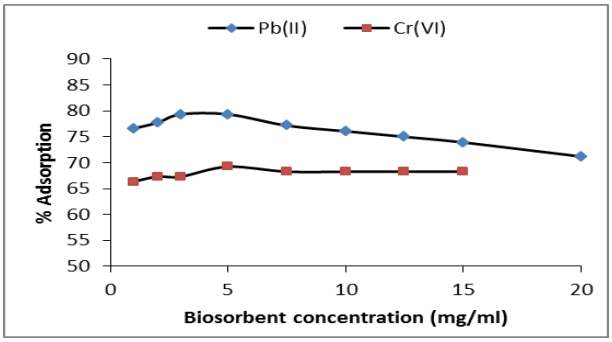

Fig. 4. Effect of biosorbent dose concentration on biosorption of lead (II) and chromium (VI) using *Tarminalia catappa* L. leaves

Effect of initial lead (II) and chromium (VI) concentration: The effect of initial lead (II) concentration from 5 mg L^{-1} -300 mg L^{-1} and chromium (VI) concentration from 5 mg L^{-1} - 250 mg L^{-1} on the removal of lead (II) and chromium (VI) from aqueous solutions at biosorbent dose 5 mg mL^{-1} and at optimum pH at 30^0C temperature was studied. On increasing the initial lead (II) concentration, the total lead (II) uptake increased appreciably and the total chromium (VI) uptake decreased appreciably.

Effect of contact time: Contact time plays an important role in affecting efficiency of biosorption. Contact time is the time needed for biosorption 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 lead (II), contact time was varied between 5 – 180 min and for chromium (VI), 10 – 180 min on the removal of metal ions from aqueous solutions in the concentration of metal ions 10 mg L^{-1}, biosorbent dose 5 mg mL^{-1}, at optimum pH and 30^0C temperature (Fig. 5). Percentage adsorption of lead (II) and chromium (VI) with respect to time (min) is shown in table 3. The results obtained from the biosorption capacity of lead (II) and chromium (VI) onto the biosorbent showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of lead (II) and chromium (VI) onto the biosorbent was 90 min and 150 min with maximum removal. The rapid uptake of lead (II) is due to the availability of ample active sites for sorption. A further increase in the contact time has a negligible effect on the biosorption capacity. So a contact time of 90 min and 150 min was fixed for lead (II) and chromium (VI) respectively for further experiments.

Table 3. Percentage adsorption of lead (II) and chromium (VI) with respect to time (min)

Time (min)	**Percentage adsorption (%Ad)**	
	Lead (II)	**Chromium (VI)**
5	64.67	-
10	66.31	61.53
20	67.39	61.53
30	69.02	61.53
60	69.02	64.42
90	74.45	66.34

120	74.45	67.31
150	74.45	70.19
180	74.45	70.19

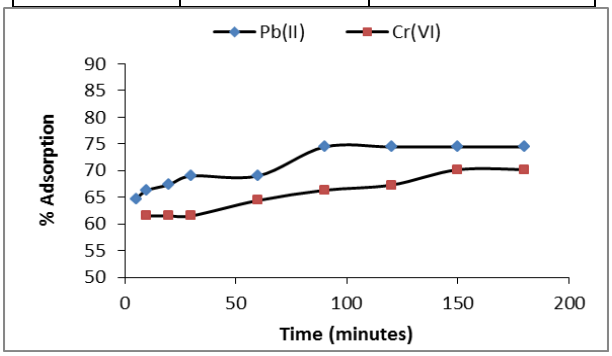

Fig. 5. Effect of time on biosorption of lead (II) and chromium (VI) using *Tarminalia catappa* L. leaves

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 was applied to the two-parameter isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

Langmuir adsorption isotherm [22]: The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by,

$$q_e = \frac{q_m\ b\ C_e}{1+bC_e} \qquad (3)$$

where q_m is the maximum biosorption capacity of biosorbent (mg g^{-1}). b is the Langmuir biosorption constant (L mg^{-1}) related to the affinity between the biosorbent and biosorbate.

Linearized Langmuir isotherm allows the calculation of biosorption capacities and Langmuir constants and is represented as,

$$\frac{1}{q_e} = \frac{1}{q_m\ b\ C_e} + \frac{1}{q_m} \qquad (4)$$

The linear plots of $1/q_e$ vs $1/c_e$ is shown in Fig. 6 (a). The 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 4. Maximum biosorption capacity (q_m) of lead (II) and chromium (VI) is found to be 50.00 mg per g and 44.05 mg per g, respectively. 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:

$$R_L = \frac{1}{1+bC_i} \qquad (5)$$

where b is the Langmuir constant and C_i is the maximum initial concentration of metal ions.

The value of separation parameters R_L provides important information about the nature of biosorption. 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 0.2904-0.9608 for concentration of 5 mg L^{-1} -300 mg L^{-1} with respect to lead (II) and 0.3883-0.9694 for concentration of 5 mg L^{-1} -250 mg L^{-1} with respect to chromium (VI). They are in the range of 0-1 which indicates favorable biosorption [23].

Biosorption 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:

$$bC_i = \frac{\Theta}{1-\Theta} \qquad (6)$$

where θ is the suface area coverage. The θ was found to be 0.0391-0.7095 for concentration of 5 mg L^{-1} - 300 mg L^{-1} with respect to lead (II) and 0.0305-0.5365 for concentration of 5 mg L^{-1} - 250 mg L^{-1} with respect to chromium (VI).

Freundlic adsorption isotherm [24]: Freundlich equation is represented by,

$$q = KC_e^{1/n} \qquad (7)$$

Where *K* and *n* are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively.

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

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad (8)$$

Equilibrium data for the biosorption is plotted as log q_e vs log C_e, as shown in fig. 6 (b). The 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 4.

The *n* value indicates the degree of non-linearity between solution concentration and biosorption as follows: if n = 1, then biosorption is linear; if $n < 1$, then biosorption is chemical process; if $n > 1$, then biosorption 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 0.7897 and 1.1494 with respect to lead (II) and chromium (VI). Since $n < 1$, this indicates the chemical biosorption for lead (II) and $n > 1$, this indicates the physical biosorption for chromium (VI) onto the biosorbent. The higher value of *K* (3.4458) for lead (II) and *K* (3.0192) for chromium (VI), indicates the higher biosorption capacity of the biosorbent.

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm [25]: Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as,

$$lnq_e = \ln q_m - \beta\,\varepsilon^2 \qquad (9)$$

where q_m is the maximum biosorption capacity, β is the activity coefficient related to mean biosorption energy and ε is the polanyi potential, which is calculated from the following relation,

$$\varepsilon = RTln\,(1 + \frac{1}{C_e}) \qquad (10)$$

Equilibrium data for the biosorption is plotted as ln q_e vs ε^2, as shown in Fig. 6 (c). The constants β and q_m are calculated from the slope (β) and intercept ($ln\ q_m$) of the line, respectively. The values of adsorption energy *E* was obtained by the following relationship.

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

The values of q_m, β, *E* and regression coefficient (R^2) are listed in Table 4.

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[26]. In the present work, *E* value is 0.408 KJ mol^{-1} for both lead (II) and chromium (VI) which is less than 8 KJ mol^{-1}, the biosorption of lead (II) and chromium (VI) onto biosorbent, is of physical in nature [27].

Temkin adsorption isotherm [28]: Linearized Temkin adsorption isotherm is given by the equation,

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

where b_T is the Temkin constant related to heat of biosorption (J/mol) and A_T is the Temkin isotherm constant (L/g). Equilibrium data for the biosorption is plotted as q_e vs ln C_e, as shown in Fig. 6 (d). The constants b_T and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot lnA_T$) of the line, respectively. The values of A_T, b_T and regression coefficient (R^2) are listed in table 4.

Table 4. Adsorption isotherm constants for biosorption of lead (II) and chromium (VI) by *Tarminalia catappa* L. leaves

Metal	Langmuir constants			Freundlich constants			DKR constants				Temkin constants		
	q_m	b	R^2	K	$1/n$	R^2	q_m	β	E	R^2	A_T	b_T	R^2
Lead (II)	50.00	0.0081	0.9978	3.4458	1.2662	0.9360	16.243	-3E-6	0.4082	0.6114	3.0413	208.021	0.5705
Chromium (VI)	44.05	0.0063	0.9972	3.0192	0.8700	0.9951	9.189	-3E-6	0.4082	0.6773	3.6722	502.47	0.8782

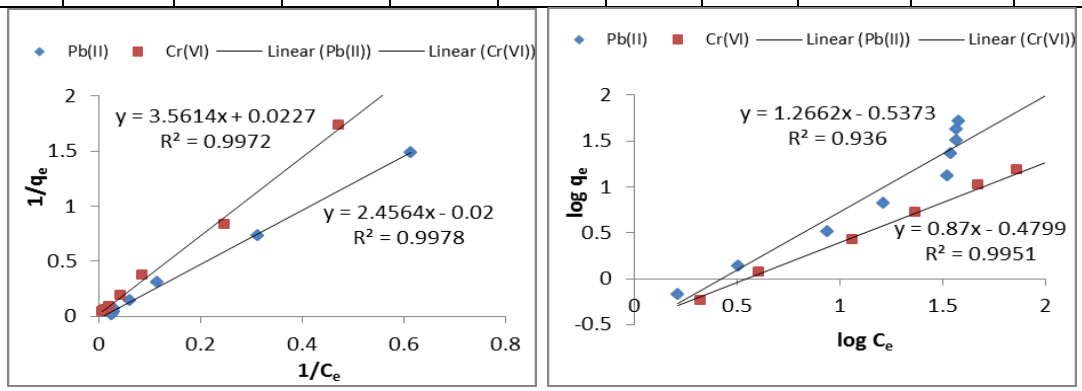

Fig. 6. Adsorption isotherm models (a) Langmuir (b) Freundlich (c) DKR and (d) Temkin, for biosorption of lead (II) and chromium (VI) using *Tarminalia catappa* L. leaves

Adsorption kinetics: As aforementioned, a lumped analysis of biosorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) pseudo-first-order [29] (b) pseudo-second-order [30] (c) Elovich [31] (d) Weber & Morris intra-particle diffusion [32] are presented below,

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

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

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

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

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 α (mg g^{-1} min^{-1}) and β (g mg^{-1}) are Elovich coefficients representing initial biosorption rate and desorption constants, respectively. k_i (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant, c is intercept.

If the biosorption 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 biosorption process obeys the pseudo-second order rate equation. If the biosorption 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 biosorption process obeys the Weber & Morris intra-particle diffusion rate equation.

Biosorption of metal ions on to biosorbent was monitored at different specific time interval. The metal ions uptake was calculated from the data obtained. From the metal ions uptake was plotted against time to determine a suitable kinetic model, the biosorption data was fitted into pseudo-first-order rate equation, pseudo-second-order rate equation, Elovich rate equation and the Weber & Morris intra-particle diffusion rate equation. The pseudo-first-order equation was plotted for ln (q_e-q_t) against t (Fig. 7 (a)). The values of $k_1$and q_e values were calculated from the slope (k_1) and intercept (ln q_e) of this plot. The values of q_e, k_1 and regression coefficient (R^2) are listed in Table 5. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the metal ions biosorbed onto it [33]. The pseudo-second-order equation was plotted for t/q_t against t (Fig. 7 (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. The values of q_e, k_2 and regression coefficient (R^2) are listed in table 5. This suggests that metal ions biosorption occurs in a monolayer fashion and which relies on the assumption that chemisorption or chemical biosorption is the rate-limiting step. Metal ions react chemically with the specific binding sites on the surface of biosorbent. The Elovich equation was plotted for q_t against ln t (Fig. 7 (c)). The values of β and α are calculated from the slope ($1/\beta$) and the intercept (ln $(\alpha\ \beta)/\beta$) of the plot. The values of β, α, and regression coefficient (R^2) are listed in table 5. The Elovich equation has been used to further explain the pseudo-second-order equation with the assumption that the actual adsorption surface is energetically heterogeneous. Therefore, this could be used to explain that the biosorption surface is energetically heterogeneous [34]. The intra-particle diffusion rate equation was plotted for q_t against $t^{0.5}$ (Fig. 7 (d)). The value of k_i and c are calculated from the slope (k_i) and intercept (c) of the plot. The values of k_i, c and regression coefficient (R^2) are listed in table 5. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intra-particle pore diffusion is not only rate-limiting step [32]. The plot of intra-particle diffusion rate equation showed multi linearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of biosorbate through the solution to the external surface of biosorbent 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 biosorption [35].

Table 5. Adsorption kinetic data for biosorption of lead (II) and chromium (VI) by *Tarminalia catappa* L. leaves

Metal	**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	a	β	R^2	ki	c	R^2
Lead (II)	5.5594	0.0101	0.7325	1.5078	0.3033	0.9995	1.8356 E7	16.528	0.9116	0.0188	1.265	0.9120
Chromium (VI)	4.6678	0.0109	0.9762	1.4236	0.1661	0.9988	3.9514 E5	15.015	0.8729	0.0192	1.1466	0.9572

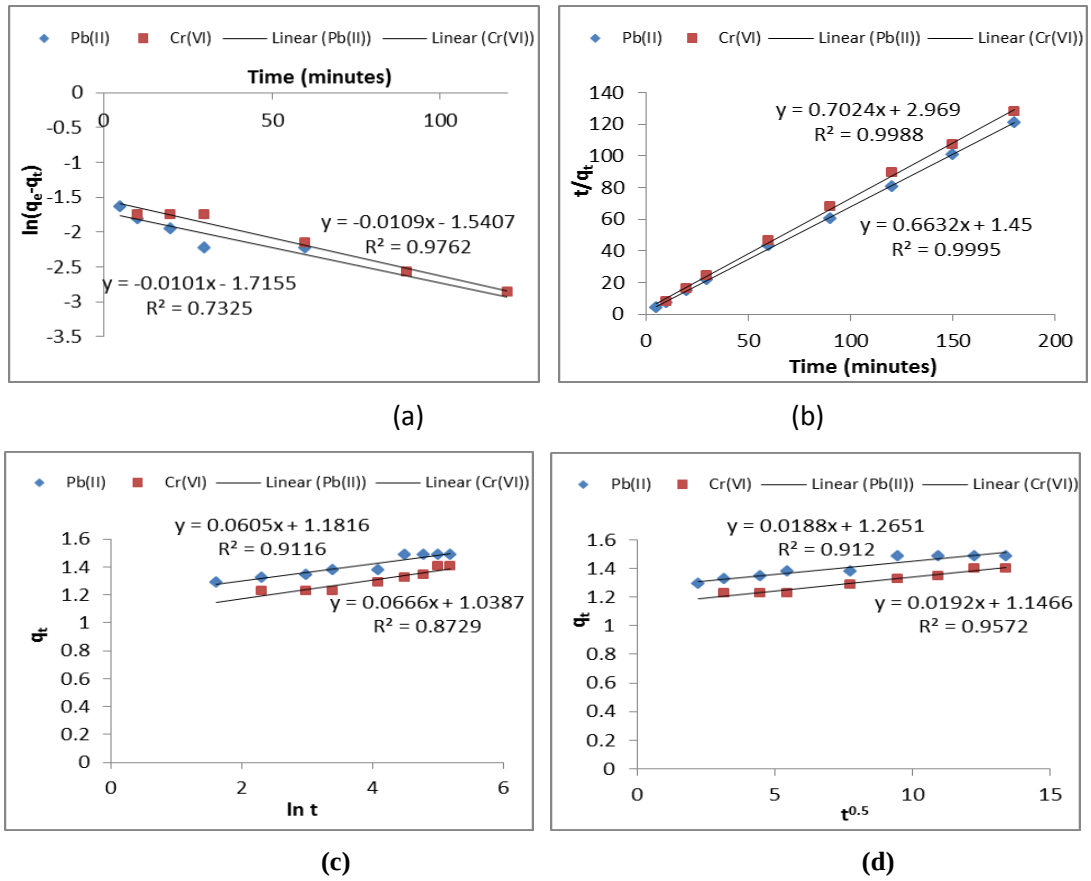

Fig. 7. Adsorption kinetic models (a) pseudo-first-order (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion, for biosorption of lead (II) and chromium (VI) using *Tarminalia catappa* L. leaves

Thermodynamic study: The effect of temperature on removal of metal ions from aqueous solutions in the metal ions concentration 10 mg L^{-1} and biosorbent dose 5 mg mL^{-1} with optimized pH was studied. Experiments were carried out at different temperatures from 20^0C-70^0C. The samples were allowed to attain equilibrium. Sorption slightly increases from 30^0C-50^0C for lead (II) and 20^0C-50^0C for chromium (VI). The equilibrium constant [36] at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations,

$$K_c = \frac{C_{Ae}}{C_e} \qquad (17)$$

$$\Delta G^0 = -RT \ln K_c \qquad (18)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (19)$$

$$lnK_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (20)$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration of metal ions in solution (mg L^{-1}) and C_{Ae} is the metal ions concentration biosorbed on the biosorbent per liter of solution at equilibrium (mg L^{-1}). ΔG^0, ΔH^0 and ΔS^0 are changes in standard, Gibbs free energy (kJ mol^{-1}), enthalpy (kJ mol^{-1}) and entropy (J mol^{-1} K), respectively. R is the gas constant (8.314 J mol^{-1} K), T is the temperature (Kelvin). The values of ΔH^0 and ΔS^0 were determined from the slope ($\Delta H^0/R$) and the intercept ($\Delta S^0/R$) from the plot of ln *Kc* versus *1/T* (Fig. 8.). The values of standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and the standard entropy change (ΔS^0) calculated in this work were presented in table 6. The equilibrium constant *Kc*, increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intra-particle diffusion. The standard Gibbs free energy change (ΔG^0) is

small and negative and indicates the spontaneous nature of the biosorption. The values of standard Gibbs free energy change (ΔG^0) were found to decreases as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The value of standard enthalpy change (ΔH^0) was positive, indicating the endothermic nature of the biosorption of metal ions onto the biosorbent. The positive values of standard entropy change (ΔS^0) shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

Table 6. Thermodynamic parameters of biosorption of lead (II) and chromium (VI) by *Tarminalia catappa* L. leaves

Metal	**$-\Delta G^0$ (kJ/mol)**				**ΔH^0 (KJ/mol)**	**ΔS^0 (J/mol K)**
	293 (Kelvin)	303 (Kelvin)	313 (Kelvin)	323 (Kelvin)		
Lead (II)		2.414	2.783	3.108	8.268	34.287
Chromium (VI)	1.596	1.766	1.939	1.999	3.670	17.752

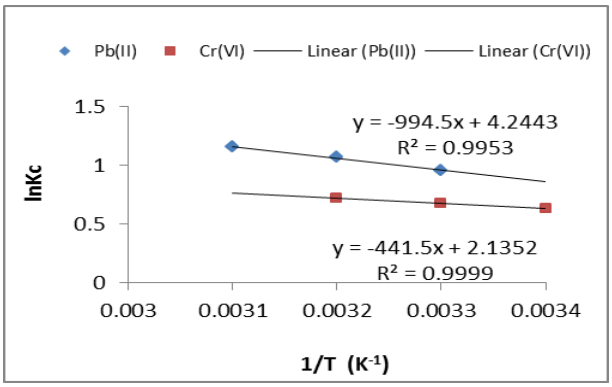

Fig. 8. Determination of thermodynamic parameters for biosorption of lead (II) and chromium (VI) using *Tarminalia catappa* L. leaves

APPLICATIONS

The leaves of *Tarminalia Catappa* L. are an inexpensive, excellent biosorbent for the removal of lead (II) and chromium (VI) from aqueous solutions.

CONCLUSIONS

The present investigation revealed that the *Tarminalia Catappa* L. leaves can be an inexpensive, excellent biosorbent for the removal of lead (II) and chromium (VI) from aqueous solutions. FTIR analysis of biosorbent confirmed that hydroxyl, carbonyl and carboxyl group, so that the cell wall surface of the biosorbent that may interact with the lead (II) and chromium (VI). The SEM represents a porous structure with large surface area. The optimal parameters such as solution pH, biosorbent dose, initial metal ions concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of lead (II) and chromium (VI) onto the *Tarminalia Catappa* L. leaves. Langmuir adsorption isotherm model provided a better fit with the experimental data for both lead (II) and chromium (VI). The maximum biosorption capacity of lead (II) and chromium (VI) which was determined from Langmuir isotherm was found to be 50.00 mg g^{1} and 44.05 mg g^{-1} respectively. Kinetics results clearly indicated that the pseudo-second-order kinetic model was found to be correlating the experimental data strongest for both lead (II) and chromium (VI). The thermodynamic study confirmed that reaction of biosorption of lead (II)

and chromium (VI) onto the *Tarminalia Catappa* L. leaves is spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that the *Tarminalia Catappa* L. leaves has considerable biosorption capacity, available in abundant, non-hazardous material could be used as an effective indigenous material for treatment of wastewater stream containing lead (II) and chromium (VI).

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REFERENCES

[1] G.Cimino, C.Caristi, *Biol. Waste,* **1990**, 33, 201.
[2] J. M. Tobin, J. C. Roux, *Water Res,* **1998**, 32, 1407.
[3] J.P. Chen, L. Wang, S.W. Zou, *Chem. Eng. J.*, **2007,** 131 (1-3), 209.
[4] M.M.D Zulkali, A. L. Ahmad, N.H. Norulakmal, *Bioresour. Technol.*, **2006**, 97(1), 21.
[5] J. Wang, C. Chen, *Biotechnol. Adv.* **2009,** 27, 195.
[6] A. Ozer, *J. hazard. Materials,* **2007**, 141(3), 753.
[7] K. Mohanty, M. Jha, M.N.Biswas, B.C. Meikap, *Chemical Engineering Science*, **2005**, 60(11), 3049.
[8] D. Park, Y.S. Yun, J.M Park, *Chemoshere*, **2005**, 60(10), 1356.
[9] S. S. Ahluwalia, D. Goyal, *Bioresour. Technol.,* **2007**, 98, 2243.
[10] S. A. Bhalerao, *Bionano frontier, special issue,* **2011**, 219.
[11] D. Kratochvil, Volesky, *Trends in Biotechnology*, **1998**, 16(7), 291.
[12] D. P. Mungasavalli, T. Viraraghavan, JINYee-Chung, *Colloids and Surfaces A: Physicochemical Engineering Aspects*, **2007,** 301(1-3), 214.
[13] S. D. Maind, S. V. Rathod, S. Gajbhiye, V. K. Hile, S. A. Bhalerao, *Int. J. Environmental Sciences,* **2012,** 1(4), 402.
[14] S. D. Maind, S. V. Rathod, S. A Bhalerao, *Int. J. Chem.*, **2013**, 2, 136.
[15] S. D. Maind, S. V. Rathod, S. A Bhalerao, *Biological & Physical Sciences, special issue*, **2012**, 1, 111.
[16] S. D. Maind, S. A Bhalerao, *Int. J. Biotech. Chem. & Environ. Eng*, **2013**, 2(2), 26.
[17] G. H. Pino, L. M. Souza de Messquita, M. L. Torem, G. A. Pinto, *J. Minerals Eng.* **2006**, 19, 380.
[18] B.Volesky, Sorption and biosorption. Montreal-St. Lambert, *Quebec, Canada, BV Sorbex Inc.*, **2003**, 316.
[19] P. S. Rao, R. S. Mise, G. S. Munjunatha, *J. Environ. Sci. Health A,* **1992,** 27, 2227.
[20] T. K. Naiya , S. K. Das, A. K. Bhattacharya, *J. Coll. Inter. Sci.*, **2009,** 21, 434.
[21] S. Karthikeyan, R. Balasubramanian, C. S. P. Iyer, *Bioresour. Technol.*, **2007**, 98 (2), 452.
[22] I. Langmuir, *J. Am. Chem. Soc.*, **1918**, 40, 1361.
[23] E. Malkoc, Y. J. Nuhoglu, *J. Hazard. Mater. B,* **2005**, 127, 120.
[24] H. M. F. Freundlich, *Zeitschrift fue Physikalische Chemie (Leipzig)*, **1906**, A57, 385.
[25] M.M. Dubinin, L.V. Radushkevich, *Proc. Academy of Sci. Phy. Chem. Section, U.S.S.R.*, **1947,** 55, 331.
[26] N. F. Olivieri, G. M. Brittenham, *Blood*, **1997**, 89,739.
[27] M. F. Sawalha, J. R. Peralta-Videa, J. Romero-Gonzalez, J. L. Gardea-Torresdey *J. Colloid Interface Sci.*, **2006**, 300, 100.
[28] M. J. Temkin, V. Pyzhev, *Acta Physiochim. Urrs,* **1940**, 12, 217.
[29] S. Lagergren, *Kungliga Svenska Vetenskapsakademiens Handlingar*, **1898**, 24, 1.
[30] G. McKay, Y. S. Ho, J.C.Y. Ng, *Sep. Purif. Methi*, **1999,** 28, 87.

[31] S. H. Chien, W. R. Layton, *Soil Sci. Soc. Am. J.*, **1980**, 44, 265.
[32] W. J. Weber, J. C. Morris, *J. Sanit Eng. Div. Am. Soc. Civ. Engg.*, **1963**, 89, 31.
[33] C. Septhum, S. Rattanaphani, J. B. Bremner, V. Rattanaphani, *J. Hazardous Materials,* **2007,** 148, 185.
[34] J. M. Thomas, W. J. Thomas, Principle and Practice of heterogeneous catalysis, *weinheim, VCH.* **1997**.
[35] K. K. Panday, G. Prasad, V. N. Singh, *Environ. Technol. Lett.*, **1986**, 50 (7), 547.
[36] G. C. Catena, F. V. Bright, *Anal. Chem.*, **1989**, 61,905.

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