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CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research
Vol. 10, Issue, 02(F), pp. 31045-31053, February, 2019

ISSN: 0976-3031

International Journal of Recent Scientific Research

DOI: 10.24327/IJRSR

Research Article

BIOSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING UNMODIFIED AND NITRILOTRIACETIC ACID MODIFIED LEAVES OF *FICUS BENGHALENSI SL*

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DOI: http://dx.doi.org/10.24327/ijrsr.2019.1002.3181

ARTICLE INFO

Article History:
Received 10th November, 2018
Received in revised form 2nd December, 2018
Accepted 26th January, 2019
Published online 28th February, 2019

Key Words:

Biosphere, Nitrilotriacetic acid, Chromium, Isotherm, Kinetics, Thermodynamic

ABSTRACT

Environmental pollution is a severe and challenging problem all over the world because of the rapid progress in science, technology and industries. The presence of metallic ions in water is of great concern because these pollutants are hazardous to ecosystem due to their high toxicity, non-biodegradability and their accumulation in the biosphere. In the present study the potential of unmodified leaves of Ficus benghalensis (Fb) and nitrilotriacetic acid modified leaves of Ficus benghalensis (FbNTA) as green adsorbent for removal of chromium [Cr (VI)] from aqueous solution was investigated. The equilibrium studies were systematically carried out in a batch process which covered various process parameters such as effect of pH, contact time, temperature, adsorbent dose, agitation rate and initial ion concentration of Cr (VI). The adsorption isotherm study showed that Langmuir model ($R^2 = 0.9802$) for unmodified green adsorbent and Freundlich model ($R^2 = 0.9997$) for NTA modified green adsorbent provides an appropriate description of metal ion sorption process. The adsorption kinetics was found to follow pseudo-second-order rate kinetic model for modified and unmodified green adsorbent. Thermodynamic study revealed that the biosorption process for removal of Cr (VI) by using Fb was endothermic, non-spontaneous and proceeded with increased randomness whereas by using FbNTA it was endothermic, spontaneous and proceeded with increased randomness. All the experimental results revealed that NTA modification enhanced the adsorption capacity of leaves of Ficus benghalensis due to the chelating ability of NTA thus suitable for Cr (VI) removal from aqueous condition.

INTRODUCTION

Water, a valuable resource sustains all forms of life on the earth. The availability of clean water to the human population is of primeimportance in the current world. One of the severe dangers to our fascinating and fragile environment is the discharge of untreated effluent into the soil and water bodies. Among the various contaminants, discharges of heavy metal ions into the environment are of supreme anxiety because of their persistent nature, toxicity and non-biodegradability leading to ecological problems (Sud *et al*, 2008).Wastewaters with numerous heavy metals are discharged annually by a number of industries. Heavy metals like lead, cadmium, chromium, zinc and copper contamination in wastewater is mainly come from anthropogenic sources like battery, electronics, paper and pulp industries, metal fabrication and mining activities, smelting, electrolysing, drug manufacturing, paint preparation, alloy manufacturing, galvanizing, printing, dyeing, paper making, ceramics manufacturing and inorganic dyestuff preparation (Liu *et al*, 2008; Sari *et al*, 2007). Metal cations in their soluble form pose aexcessive threat, as these are easily transported and taken up by living ecosystems. The removal of heavy metals from industrial wastewater is thus very essential.

Chromium is one of the heavy metal which is ranked amongst the most toxic trace elements in the environment (Gardea-Torresday *et al*, 2000). The hexavalent form is 500 times more toxic than the trivalent (Kowalski, 1994). The maximum permitted level of chromium for drinking water is 0.05 mg/lit (Gupta *et al*, 2001). The chromium enters the aquatic systems through discharge of concentrated effluents from various industries such as tanneries, electroplating, paint, textile, etc. (Korngolt, 2003). Chemical reduction, precipitation, solvent extraction and ion exchange are some of the conventional methods for Cr (VI) removal from aqueous solutions and industrial effluents (Sharma, 2003). These techniques, apart from being expensive, have disadvantages like incomplete

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metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products that require special disposal. Hence efficient and eco-friendly strategies are needed to be developed to reduce and eliminate heavy metal content from waste water. In this context, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous effluents (Ahluwalia and Goyal, 2007).

“Biosorption technology” aims at eliminating heavy metals from effluents/ waste water without creating harmful sludge and at costs much lowers than that of conventional treatment practices. Biosorption of heavy metals from aqueous solutions is a comparatively new process that has been confirmed as a very promising process suitable to treat dilute heavy metal wastewater (Fourest and Roux, 1992; Petersen*et al*, 2005).

The search for innovative green ways for removal of heavy metals has forced attention on the use of new natural materials for removal of metal ions. The research will emphasis on the removal of Cr (VI) from its aqueous solution by unmodified leaves of *Ficus benghalensis* (Fb) and nitrilotriacetic acid (NTA) modified leaves of *Ficus benghalensis* (FbNTA) as a biosorbents. The objective of this study was to optimize various process parameters affecting the biosorption of metal ions such as solution pH, contact time, temperature, adsorbent dose, agitation rate and initial Cr (VI) metal ion concentration. Adsorption isotherms, kinetics and thermodynamic studies were employed to understand the probable biosorption mechanism.

MATERIALS AND METHODS

Preparation of Chemicals and Reagents

All the chemicals and reagents used were of analytical reagent (AR) grade. Millipore water was used for all experimental work. The desired pH of the metal ion solution was adjusted with the help of 0.1 N HCl and 0.1 N NaOH solutions.

Preparation of Chromium (VI) Synthetic waste water

1000 ppm of Chromium (VI) was prepared by dissolving 2.8289 gm of potassium dichromate ($K_2Cr_2O_7$) in millipore water and the volume was made to the mark in a 1000 cm^3 volumetric flask using millipore water. Further desired working solutions of Cr (VI) were prepared using appropriate subsequent dilutions of the stock solution**.**

Preparation of Unmodified and NTA Modified Biosorbent

Leaves of *Ficus benghalensis* L. (Family: Moraceae) were collected locally from Mumbai. It was washed with distilled water to eliminate the dust and other impurities. The washed green adsorbent was dried initially at room temperature for a week and then in an oven at 50 °C for 24 hrs and grounded in a mechanical grinder to form powder. The powder was sieved through 250 µm size sieve and stored in air tight container to protect it from moisture and used as an unmodified leaves of *Ficus benghalensis* (Fb) for biosorption study. The nitrilotriacetic acid modification of leaves of *Ficus benghalensis* was carried out by similar method described by Marshall *et al,* (1999). For the modification of green adsorbent by nitrilotriacetic acid, 100 gm of unmodified green adsorbent powder was added to 2 L of 0.1 N NaOH and was stirred at 200 rpm for 1 hr at 30 °C. The powder was rinsed with double distilled water to remove excess of NaOH and dried in an oven at 60 °C for 48 hrs. After NaOH treatment, 50 gm of dried green adsorbent powder was added in 200 mL of 1 % NTA and the slurry was dried over night at 50 °C and then heated to 120°C for 1.5 hr. This NTA modified green adsorbent was rinsed with double distilled water repeatedly to remove excess of NTA. Finally the modified green adsorbent was dried in hot air oven at 60 °C for 48 hrs. The nitrilotriacetic acid modified leaves of *Ficus benghalensis* (FbNTA) adsorbent powder was stored in air tight container to protect it from moisture.

Instrumentation studies

The pH of the solution was measured by using digital pH meter (Labline; Model: LSC-16). Rotary incubator shaker (Labtop; Model: LS1-125/R) was employed for the maintaining shaking condition along with temperature. The concentration of Cr(VI) in the solutions before and after equilibrium was determined by measuring absorbance using Atomic Absorption Spectrophotometer (Agilent; Model: AA 240 FS).

Batch biosorption studies

The batch adsorption method was employed at temperature (30 °C) to examine the biosorption of Cr(VI) by Fb and FbNTA as biosorbents. The method was used to determine the adsorption capacity, stability of adsorbent and optimum biosorption conditions. Different experimental conditions such as solution pH, contact time, temperature, adsorbent dose, agitation rate and initial Cr(VI) ion concentration were optimized. The following equation was used to compute the percent removal (% Adsorption) of Cr(VI) by the adsorbent,

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

Where, C_i and C_e are the initial concentration and equilibrium concentration of the chromium (VI) in mg/L.

The equilibrium adsorptive quantity (q_e) was determined by the following equation,

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

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

Adsorption isotherm studies were systematically carried out by considering Langmuir isotherm, Freundlich Isotherm, Dubinin–Radushkevich (DKR) Isotherm and Temkin Isotherm adsorption models. Determination of adsorption kinetics was studied with the help of Pseudo-first-order, Pseudo-second-order, Elovich and Weber and Morris intraparticle diffusion kinetics model. Thermodynamic parameters such as Gibbs free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) have also been estimated.

RESULTS AND DISCUSSION

Batch Biosorption study

Effect of pH

The adsorption of the Cr (VI) ions primarily depends on the pH of the adsorption medium, which influences the surface charge of the adsorbent and degree of ionization of the adsorbate. The optimization of pH was done by varying the pH in the range of 2-10. Fig. 1 showed that biosorption of Cr (VI) decreases with increase in pH. The optimum removal of Cr (VI) by using Fb and FbNTA biosorbents was found to be 46.315% and 88.054% respectively at pH 2. From this observation, it is clear that the efficiency of adsorption is very high at low pH. According to the solution pH, Cr(VI) mainly exists as: chromate (CrO_4^{2-}), chromic acid (H_2CrO_4), hydrogen chromate ($HCrO_4^-$) or dichromate ($Cr_2O_7^{2-}$) (Cotton and Wilkinson, 1972; Brito and Mateo, 1997). Change in Cr (VI) adsorption with changing pH might be due to the fact that at low pH of solution the adsorbent can easily protonate and generate positive net charge. Thus, increase adsorption of Cr (VI) attained with decreased pH of the solution.

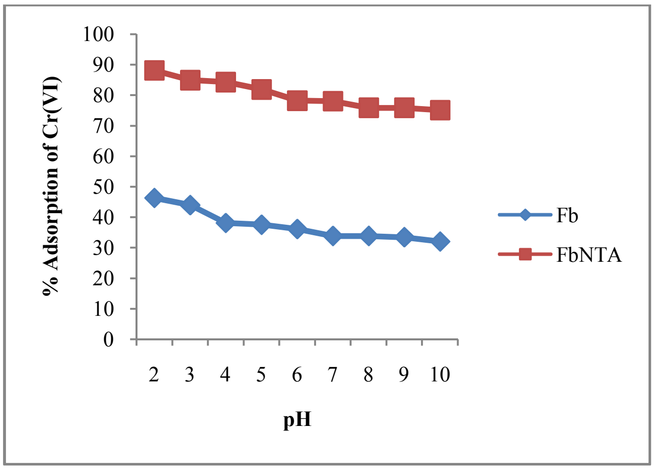


Fig. 1 Effect of pH on Cr (VI) biosorption by Fb and FbNTA (Adsorbent dose : 0.5 gm/50 ml, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

Effect of adsorbent dose

Adsorbent dosage is a significant factor for the determination of biosorption potential of biosorbent at a given initial concentration. Fig. 2 shows the effect of adsorbent dose on the percentage removal of Cr (VI). The percentage of Cr(VI) ions adsorbed by Fb and FbNTA increased with an increase in the weight of adsorbent from 0.1 to 0.6 gm. The variation in adsorption capacities at different dosage of adsorbents could be mainly attributed to the available sites of adsorption. As the adsorbent dosage increased, more active sites and surface area of the adsorbent became available for the adsorption (Jadav *et al*, 2015; Rao*et al*, 2002).

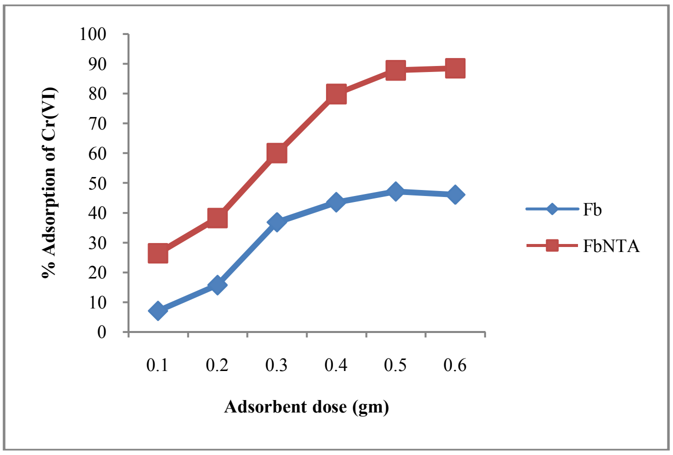


Fig. 2 Effect of adsorbent dose on Cr(VI) biosorption byFb andFbNTA (pH: 2, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

Effect of Initial Chromium (VI) ion Concentration

The experiment was conducted by maintaining the contact time at 90 minutes, pH 2, 0.5 gm of adsorbent dose (0.5 gm/50 ml), agitation rate 120 rpm and temperature at 30 °C. As can be seen in the Fig. 3 percentage removal of Cr(VI) ions to some extent decreased with the increase in initial Cr(VI) ions concentration by FbNTA whereas the percentage removal of Cr(VI) has shown significant decrease with the increase in the initial sorbate concentrations when Fb employed as biosorbent.

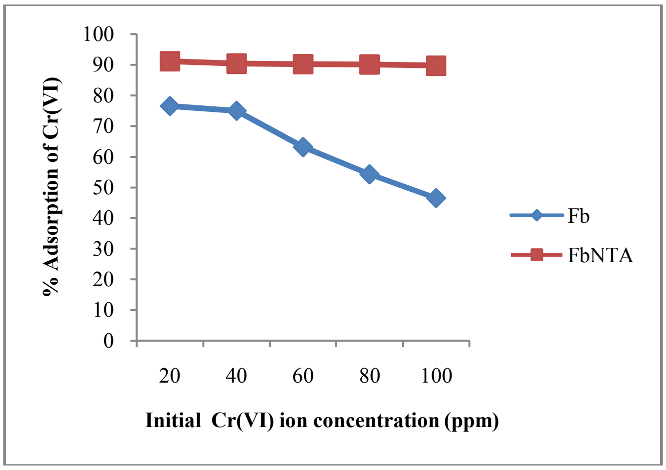


Fig 3 Effect of initial Cr (VI) ion concentration on biosorption by Fb and FbNTA (pH: 2, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

Effect of Contact time

In this experiment, all of the parameters except contact time were kept constant. The effect of contact time on Cr(VI) adsorption efficiency is shown in Fig.4. There is a significant increase in the biosorption efficiency with time by Fb and FbNTA. The maximum removal of Cr(VI) was found to be 47.048 % by Fb and 89.784 % by FbNTA after 90 minutes of contact time. The observed fast metal ions uptake is consistent with biosorption of metal involving non-energy mediated reactions, where metal removal from solutions is purely physico-chemical interaction between biomass and metal solution. This fast metal uptake from solution indicates that binding might have resulted from interaction with functional groups of the biosorbent rather than diffusion (Sanusi *et al*, 2018).

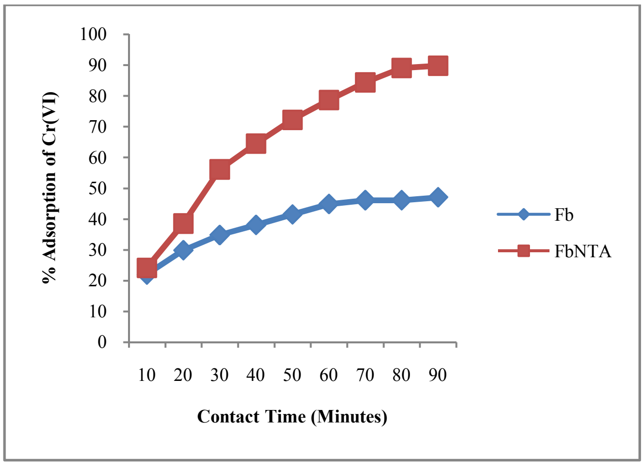


Fig 4 Effect of contact time on Cr(VI) biosorption by Fb and FbNTA (pH: 2, Adsorbent dose: 0.5 gm/50 ml, Cr(VI) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)

Effect of temperature

Experiment was performed at different temperatures 10 °C-60 °C. The biosorption of Cr (VI) increases with increase in temperature from 10 °C-40 °C i.e. from 35.491 % to 47.154 % when Fb as a green adsorbent employed in the process of biosorption. Further increase in temperature resulted in slight decrease in the Cr (VI) removal efficiency. However the sorption of Cr (VI) by FbNTA increases with increase in temperature from 10 °C- 50 °C i.e. from 75.686 % to 91.938 % as shown in the Fig. 5.

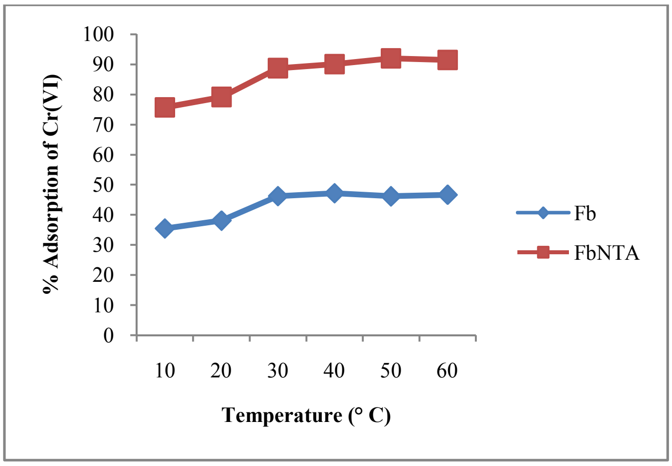


Fig 5 Effect of temperature on Cr (VI) biosorption by Fb and FbNTA(pH: 2, Adsorbent dose: 0.5 gm/50 ml, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

Effect of agitation rate

Experiment was carried out by taking Cr (VI) ion concentration 100 mg/L, adsorbent dose 0.5 gm/50 ml, pH 2, contact time of 90 minutes and temperature at 30 °C with varying agitation speed (0 – 200 rpm). The effect of agitation speed on the adsorption of Cr (VI) ions is shown in Fig. 6. As agitation speed increased up to 160 rpm, adsorption capacity for removal of Cr (VI) also increased from 22.902 % to 48.076 % by Fb and 41.461% to 89.914 % by FbNTA. Further increase in agitation speed resulted in slight decrease in removal efficiency of Cr (VI).

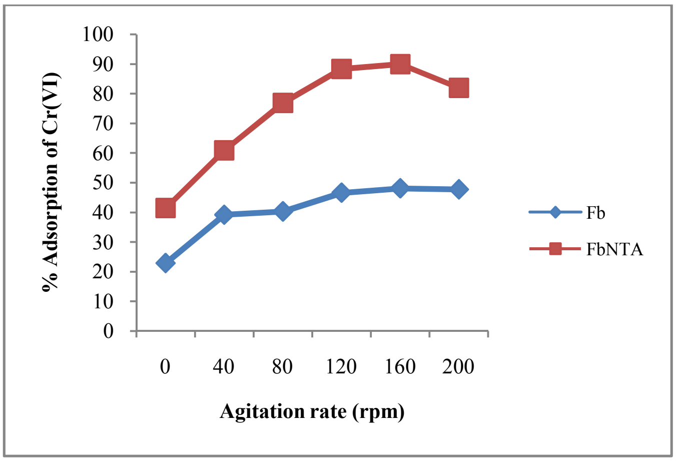


Fig 6 Effect of agitation rate on Cr (VI) biosorption by Fb and FbNTA (pH: 2, Adsorbent dose: 0.5 gm/50 ml, Cr (VI) concentration: 100 mg/L, Contact time: 90 minutes, Temperature: 30 °C)

Adsorption Isotherm study

The results obtained from the biosorption of Cr (VI) ions on Fb and FbNTA was investigated using adsorption isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Radushkevich (DKR) and Temkin to describe the equilibrium between the metal ions sorbed on the biomass as shown in Table 1 and Table 2.

Langmuir isotherm

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites (Langmuir, 1918), is given by;

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

Where q_m is the maximum biosorption capacity of adsorbent (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:

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

The linear plots of $1/q_e$vs$1/c_e$ is shown in Fig. 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) for removal of Cr (VI) by Fb and FbNTA are listed in Table 1 and Table 2 respectively.

Freundlich Adsorption Isotherm

The Freundlich isotherm is based on the assumption that the adsorption occurs on heterogeneous surface of an adsorbent with interaction between the adsorbate molecules. Freundlich equation is represented by;

$$q = KC_e^{1/n} \qquad (5)$$

Where K and n are empirical constants which incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively (Freundlich, 1906).

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

$$\log qe = \log K + \frac{1}{n}\log C_e \qquad (6)$$

Equilibrium data for the adsorption is plotted as log $q_e$vs log $C_{e,}$ as shown in Fig. 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) for removal of Cr (VI) by Fb and FbNTA are listed in Table 1 and Table 2 respectively.

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm

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

$$lnq_e = \ln q_m - \beta\, \varepsilon^2 \qquad (7)$$

Where q_m is the maximum biosorption capacity, β is the activity coefficient related to mean biosorption energy and ε is the polanyi potential (Dubinin, 1947), which is calculated from the following relation;

$$\varepsilon = RTln\,(1 + \frac{1}{C_e}) \qquad (8)$$

Equilibrium data for the adsorption is plotted as ln$q_e$vs ε^2, as shown in Fig. 7 (c). The two constants β and q_m are calculated from the slope (β) and intercept (lnq_m) of the line, respectively. The values of adsorption energy E was obtained by the following relationship,

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (9)$$

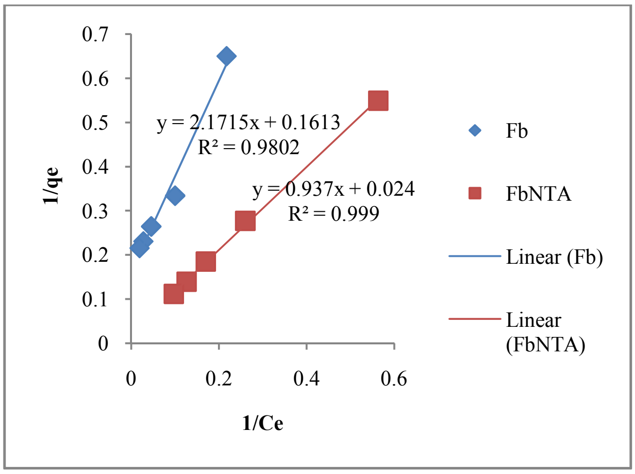
The E value was found to be 0.35 KJ mol^{-1}for Fb and 0.7071 KJ mol^{-1} for FbNTA. The mean free energy gives evidence about biosorption mechanism whether it is physical or chemical biosorption. If the value of E is less than 8 KJ mol^{-1}, then the biosorption process can be explained by physisorption mechanism, if E is between 8 and 16 KJ mol^{-1}, the process is dominated by ion exchange mechanism, and if $E > 16$ KJ mol^{-1}, the biosorption process is dominated by chemisorption (Olivieri and Brittenham, 1997). In the present work, E value is less than 8 KJ mol^{-1}, the biosorption of Cr(VI) ions onto Fb and FbNTA is of physical in nature.

Temkin Adsorption Isotherm

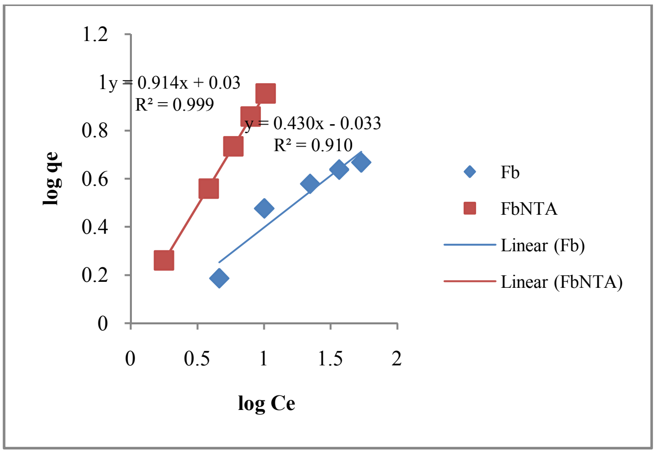
Linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{b_T}\, ln\, A_T + \frac{RT}{b_T} ln\, C_e \qquad (10)$$

Where b_T is the Temkin constant related to heat of biosorption (J/mol) and A_T is the Temkin isotherm constant (L/g) (Temkin, 1940). Equilibrium data for the adsorption is plotted as $q_e$vsln $C_{e,}$ as shown in Fig. 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. The values of A_T, b_T and regression coefficient (R^2) for removal of Cr(VI) by Fb and FbNTA are listed in Table 1 and Table 2 respectively.



(a)



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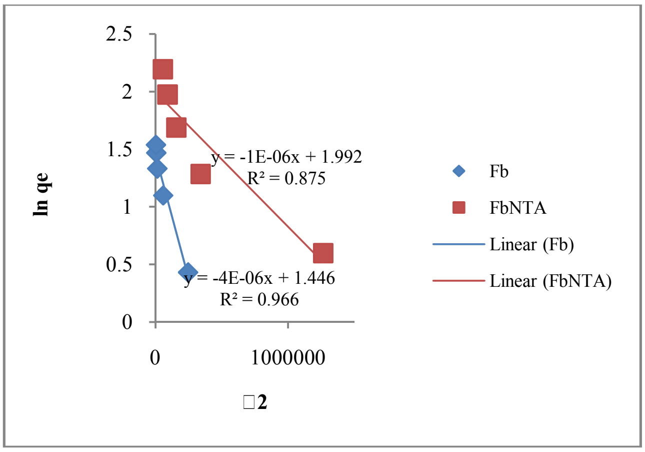

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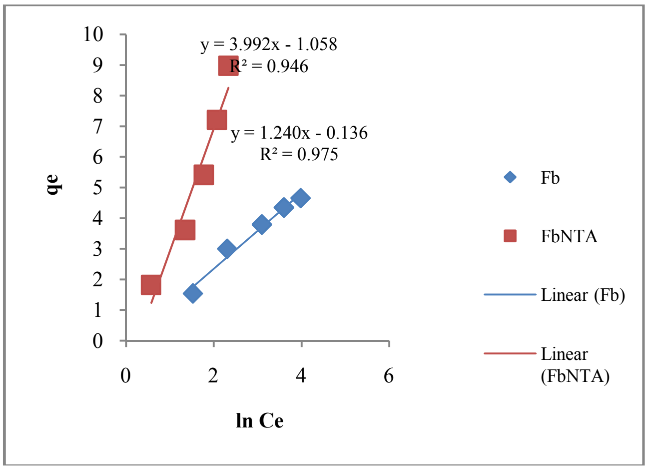


(d)

Fig 7 Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for Cr(VI) biosorption by Fb and FbNTA (pH: 2.0, Adsorbent dose: 0.5 gm/50 ml, Contact time: 90 minutes, Temperature: 30 °C, Agitation rate: 120 rpm)

Table 1 Adsorption Isotherm constants for Cr (VI) biosorption by Fb

Langmuir parameters			Freundlich parameters			DKR parameters				Temkin parameters		
q_m	***b***	R^2	***K***	***1/n***	R^2	β	q_m	***E***	R^2	A_T	b_T	R^2
6.1996	0.0743	0.9802	2.6959	-0.0332	0.9107	-4×10^{-6}	4.25	0.3536	0.9663	0.8957	2030.42	0.9752

Table 2 Adsorption Isotherm constants for Cr (VI) biosorption by FbNTA

Langmuir parameters			Freundlich parameters			DKR parameters				Temkin parameters		
q_m	***b***	R^2	***K***	***1/n***	R^2	β	q_m	***E***	R^2	A_T	b_T	R^2
41.67	0.0256	0.9991	8.2035	0.03	0.9997	-1×10^{-6}	7.33	0.7071	0.8759	0.7672	630.95	0.946

Adsorption Kinetics Studies

Kinetic parameters of an adsorption process are crucial for the estimation of adsorption parameters, which in turn control the entire process of sorption, which are thus vital for designing sorption systems. The sorption kinetics of a system are controlled by different steps, including transfer of solute to the sorbent particle surface, transfer from the sorbent surface to the intra-particle active sites and retention on these active sites via sorption, complexation or intra-particle precipitation phenomena (Shroff and Vaidya, 2011). To determine the controlling mechanism of the biosorption process, experimental data were scrutinized for pseudo-first-order equation (Lagergren, 1898), pseudo-second-order equation (McKay *et al*, 1999), Elovich equation (Chien and Layton, 1980) and Weber & Morris intra-particle diffusion equation (Weber and Morris, 1963) which is presented below;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (12)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (13)$$

$$q_t = k_i t^{0.5} + c \qquad (14)$$

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 intra-particle diffusion rate constant, *c* is intercept.

If the adsorption follows the pseudo-first-order model, 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 model. If the adsorption process obeys Elovich model, 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 and Morris intra-particle diffusion model (Septhum *et al*, 2007).

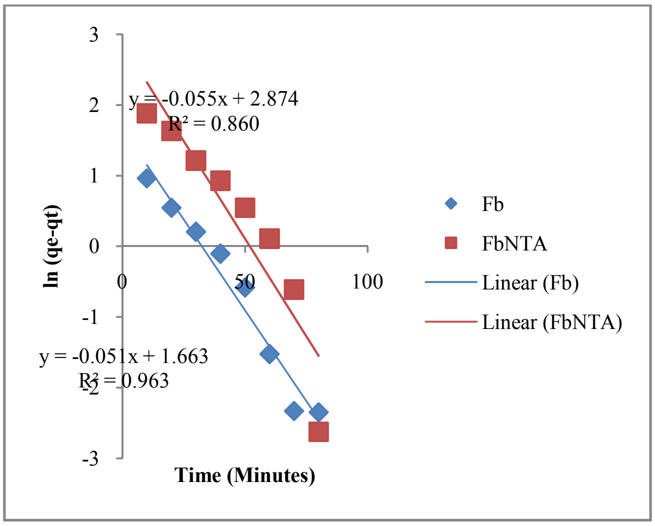
Biosorption of Cr (VI) onto Fb and FbNTAwas monitored at different specific time interval. The Cr (VI) uptake was calculated from the data obtained.

The pseudo-first-order model was plotted for $ln\ (q_e-q_t)$ against t as shown in the Fig.8 (a). The values of k_1 and q_e were estimated from the slope (k_1) and intercept (lnq_e) of the plot for removal of Cr (VI) by Fb and FbNTA are shown in Table 3 and Table 4 respectively.

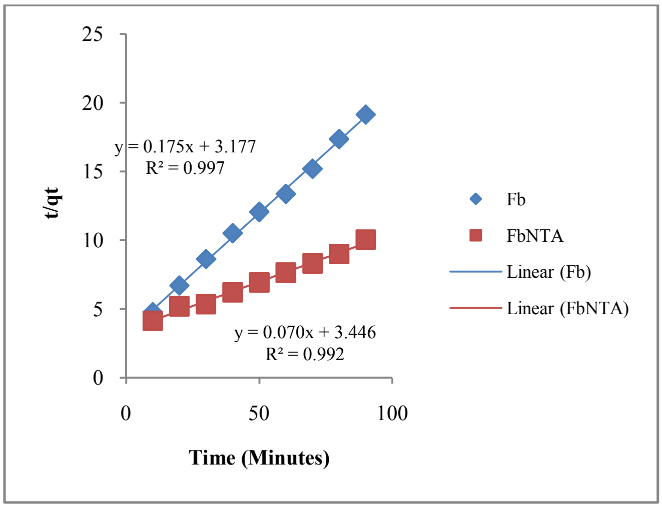
Pseudo-first-order model exhibited the correlation value being lower than the correlation coefficient for the pseudo-second-order model for both the adsorbent. Kinetic biosorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions adsorbed onto it (Septhum *et al*, 2007; Jadav*et al*, 2015).

The pseudo-second-order model was plotted for t/q_t against *t* as shown in the 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 for removal of Cr (VI) by Fb and FbNTA are shown in Table 3 and Table 4 respectively. Pseudo-second-order kinetic model revealed the strongest correlation for Fb (R^2= 0.9979) and FbNTA (R^2= 0.9921). This finding indicates that Cr (VI) biosorption follows in a monolayer fashion and which relies on the assumption that chemisorption or chemical adsorption is the rate-limiting step. Cr (VI) reacts chemically with the specific binding sites on the surface of biosorbent (Jadav *et al*, 2015). The Elovich model was plotted for q_t against *ln t* as shown in the Fig. 8 (c). The values of β and α are calculated from the slope ($1/\beta$) and the intercept ($\ln(\alpha\beta)/\beta$) of the plotfor removal of Cr (VI) by Fb and FbNTA are shown in Table 3 and Table 4 respectively. The Elovich model has been used with the assumption that the actual adsorption surface is energetically heterogeneous (Thomas and Thomas, 1947; Poojari and Bhalerao, 2018).

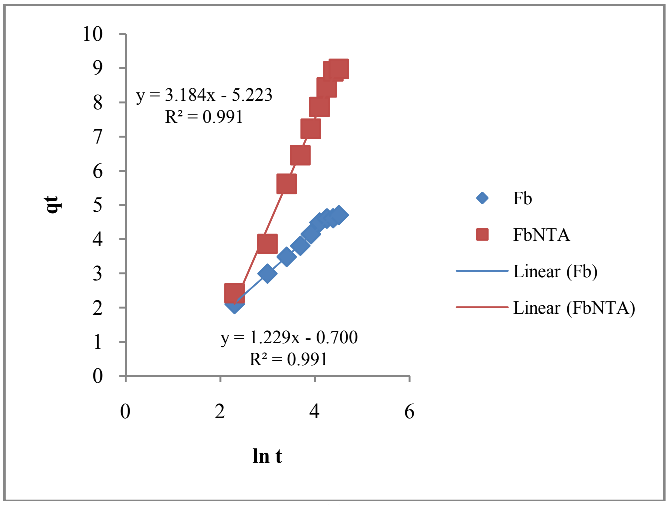
The Weber & Morris intra-particle diffusion model was plotted for q_t against $t^{0.5}$ as shown in the Fig. 8 (d). The value of k_i and *c* are calculated from the slope (k_i) and intercept (*c*) of the plot for removal of Cr (VI) by Fb and FbNTA are shown in Table 3 and Table 4 respectively. The intercept 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 (Weber and Morris, 1963; Poojari and Bhalerao, 2018).



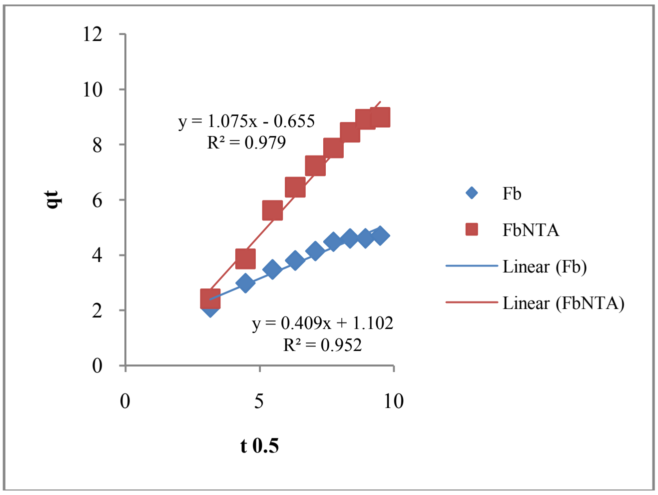
(a)



(b)



(c)



(d)

Figure 8 Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion for Cr(VI) biosorption by Fb and FbNTA (pH: 2.0, Adsorbent dose: 0.5 gm/50 ml, Initial Cr(VI) concentration: 100 mg/L, Temperature: 30 °C, Agitation rate: 120 rpm)

Thermodynamic Studies

Thermodynamic parameters are imperative factors that determine the feasibility and spontaneity of an adsorption process. The equilibrium constant at various temperatures and thermodynamic parameters of adsorption can be estimated from the following equations;

$$K_c = \frac{C_{Ae}}{C_e} \qquad (15)$$

$$\Delta G^0 = -RT\,\ln K_c \qquad (16)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (17)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (18)$$

Where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the amount of Cr (VI) biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). $\Delta G°$, ΔH °and $\Delta S°$ are changes in standard Gibbs free energy (kJ/mol), standard enthalpy (kJ/mol) and standard entropy (J/mol K) respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K) (Catena and Bright, 1989).

The values of ΔH °and $\Delta S°$ were determined from the slope and the intercept from the plot of *lnKc* versus *1/T* (Fig. 9). The values of equilibrium constant (*Kc*), Gibbs free energy ($\Delta G°$), the standard change in entropy ($\Delta S°$) and the standard change in enthalpy (ΔH °) were represented in Table 5. The value of standard Gibbs free energy change ($\Delta G°$) is small and negative and indicates the spontaneous nature of the biosorption when FbNTA employed as an adsorbent. The adsorption process were found to be non-spontaneous when Fb used as biosorbent for removal of Cr (VI). The values of $\Delta G°$ were found to decreases as the temperature increases for FbNTA, indicating more driving force and hence resulting in higher biosorption capacity. The value of $\Delta H°$ was positive, indicating the endothermic nature of the biosorption of Cr (VI) onto Fb and FbNTA. The positive value of $\Delta S°$ shows an affinity of biosorbent and the increasing randomness at the solid-solution interface during the biosorption process (Sharma and Bhalerao, 2018).

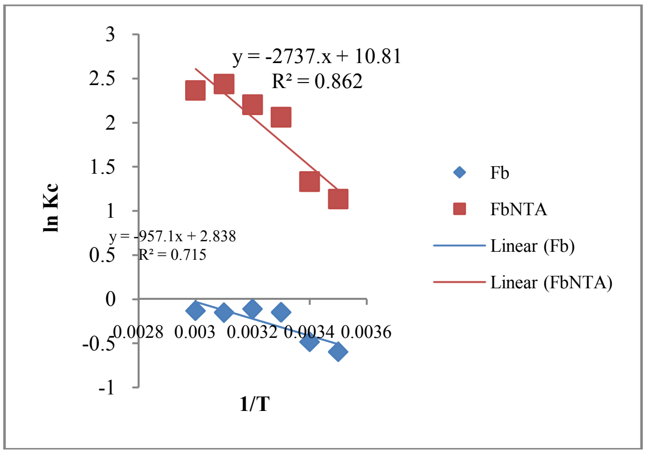


Fig 9 Plot of *lnKc* against *1/T* for determination of thermodynamic parameters for Cr (VI) biosorption by Fb and FbNTA (pH: 2.0, Adsorbent dose: 0.5 g/50 mL, Cr(VI) concentration: 100 mg/L, Contact time: 90 minutes, Agitation rate: 120 rpm)

Table 3 Adsorption kinetics data for Cr (VI) biosorption by Fb

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	α	β	R^2	K_i	C	R^2
5.2762	0.1184	0.9639	5.6883	0.0097	0. 9979	0.6960	0.8131	0.9911	0.4095	1.1029	0.9523

Table 4 Adsorption kinetics data for Cr (VI) biosorption by FbNTA

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	α	β	R^2	K_i	C	R^2
17.7077	0.1274	0.8607	14.2045	0.0144	0. 9921	0.6176	0.3140	0.991	1.0752	-0.6557	0.9793

Table 5 Thermodynamic parameters of Cr (VI) biosorption by Fb

Sr. No.	Temperature (^{0}C)	Temperature (K)	*Kc*	$-\Delta G^0$ (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	10 °C	283	0.55	-1.41	7.96	23.60
2	20 °C	293	0.62	-1.18		
3	30 °C	303	0.86	-0.38		
4	40 °C	313	0.89	-0.30		
5	50 °C	323	0.86	-0.41		
6	60 °C	333	0.88	-0.37		

Table 6 Thermodynamic parameters of Cr (VI) biosorption by FbNTA

Sr. No.	Temperature (^{0}C)	Temperature (K)	*Kc*	$-\Delta G^0$ (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	10 °C	283	3.11	2.67	22.76	89.92
2	20 °C	293	3.79	3.25		
3	30 °C	303	7.85	5.19		
4	40 °C	313	9.04	5.73		
5	50 °C	323	11.40	6.54		
6	60 °C	333	10.61	6.54		

CONCLUSION

The present study evaluates the efficacy of unmodified leaves of *Ficus benghalensis* (Fb) and nitrilotriacetic acid modified leaves of *Ficus benghalensis* (FbNTA) as low-cost adsorbent for effective removal of Cr (VI) ions from aqueous solution. The removal efficiency of Fb and FbNTA was found to be dependent on the pH, adsorbent dose, initial Cr (VI) ions concentration, temperature, contact time and agitation rate. Langmuir, Freundlich, DKR and Temkin isotherm models were applied to the experimental adsorption data and it was revealed that Langmuir model (R^2 = 0.9802) for unmodified green adsorbent and Freundlich model (R^2 = 0.9997) for NTA modified green adsorbent provides an appropriate description of metal ion sorption process as compared to the other studied adsorption isotherm models. The maximum monolayer coverage adsorption capacity from the Langmuir isotherm model was obtained as 6.1996 mg/g and 41.67 mg/g by Fb and FbNTA respectively. The kinetic data followed the pseudo-second-order kinetic model for Fb (R^2 = 0.9979) as well as for FbNTA (R^2 = 0.9921) as compared to the other kinetic models. Thermodynamic study revealed that the biosorption process for removal of Cr (VI) by using Fb was endothermic, non-spontaneous and proceeded with increased randomness whereas by using FbNTA it was endothermic, spontaneous and proceeded with increased randomness. It was observed that NTA modification enhanced the adsorption capacity of leaves of *Ficus benghalensis* due to the chelating ability of NTA. The obtained results are indication that the nitrilotriacetic acid modified leaves of *Ficus benghalensis* (FbNTA) can be efficiently used as biosorbent for the removal of Cr (VI) from aqueous solutions and can therefore be employed as an effective substitute method for the economic treatment of wastewater.

Acknowledgment

The authors are thankful to the Principal, Wilson College, Mumbai, for the administrative support, cooperation and help.

Also, special thanks to VIVA College, Virar, for the AAS analysis.

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How to cite this article:

Nikhil C. Teli and Satish A. Bhalerao.2019, Biosorption of Chromium (Vi) from Aqueous Solution Using Unmodified and Nitrilotriacetic Acid Modified Leaves of Ficus Benghalensi Sl. *Int J Recent Sci Res.* 10(02), pp. 31045-31053.
DOI: http://dx.doi.org/10.24327/ijrsr.2019.1002.3181

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