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Removal of Cr(VI) onto *Turbinaria Vulgaris* sp. Equilibrium and Kinetic studies.

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ABSTRACT

This study focused on the biosorption of total chromium(VI) onto *turbinaria vulgaris* sp. biomass from aqueous solution. Experimental parameters affecting biosorption process such as pH, contact time, metal ion concentration, biomass dosage, biomass size and temperature were studied. Langmuir, Freundlich and Dubinin–Radushkevich (D–R), Temkin models were applied to describe the biosorption isotherms. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The biosorption capacity of *turbinaria vulgaris* sp. biomass for chromium(VI) was found to be 16.6 mg/g at pH 2 and 0.1g biomass dosage, 60 min equilibrium time and 303^o K. From the D–R isotherm model, the mean free energy was calculated as 8.02 kJ/mol, indicating that the biosorption of total chromium was taken place by chemisorption. Kinetic evaluation of experimental data showed that the biosorption processes of chromium(VI) followed well pseudo-second-order kinetics.

Keywords: Chromium(VI), *Turbinaria vulgaris* sp., Biosorption, Isotherm models, Kinetic models.

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INTRODUCTION

Water pollution is a major environmental problem faced by modern society that leads to ecological disequilibrium and health hazards. Heavy metal ions such as copper, cadmium, lead, nickel, arsenic and chromium, often found in industrial wastewater, present acute toxicity to aquatic and terrestrial life, including humans. Thus, the discharge of effluents into the environment is a chief concern [1]. Chromium(VI) is one such metal known to be carcinogenic and has an adverse potential to modify the DNA transcription process. It is also reported to cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage. It is reported that, chromate (CrO_4^{2-}) is the prevalent species of Cr (VI) in natural aqueous environments, and is the major pollutant from chromium related industries such as mining, iron sheet cleaning, chrome plating, leather tanning and wood preservation. Therefore, the reduction of amount of this metal from such effluents to a permissible limit before discharging them into streams and rivers is very important for human health and environment[2]. In this regard, several conventional wastewater treatment technologies such as chemical precipitation [3], ion exchange [4], membrane processes [5] and adsorption onto activated carbon [6] etc., have been used to remove heavy metal ions from various aqueous solutions. However, the application of such processes is often restricted because of technical or economic constraints [7,8]. Biosorption of heavy metals is one of the most promising technologies involved in the removal of toxic metal ions from wastewater. It is a potential alternative to conventional processes for the removal of metals due to the low cost, easily obtained, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents and no nutrient requirements [1]. A great interest has recently been directed to the biosorption of heavy metals from solutions using different biomaterials as adsorbents. Among the various resources in biological wastes, both dead and live biomass, exhibit particularly interesting metal-binding capacities [9, 10]. *Turbinaria* is a genus of brown algae (Phaeophyceae) found primarily in tropical marine waters. It generally grows on rocky substrates.[1] In tropical *Turbinaria* species that are often preferentially consumed by herbivorous fishes and echinoids, there is a relatively low level of phenolics and tannins. The genus has shown promise as a way of removing [lead](#) from aqueous solutions[11]. Various *Turbinaria* sp. are used as human food, fertilizer, pesticide and insect repellent.

The present work aimed to investigate the chromium biosorption capacity of *turbinaria vulgaris* sp. from aqueous solution. Experimental parameters affecting biosorption process such as contact time, pH, initial metal ion concentration, biomass dosage, biomass size and temperature were studied. The equilibrium biosorption data were evaluated by Langmuir, Freundlich, D-R and Temkin isotherm models and experimental data was fitted with pseudo first and second order rate models.

MATERIALS AND METHODS

Biosorbent collection and treatment

The *turbinaria vulgaris* sp. used in the present survey were gathered from the suryalanka beach, Bapatla, Andhra Pradesh, INDIA. The gathered algae were washed with deionized water several times to get rid of unwanted material. The washing procedure was kept till the wash water contains no malicious dirt. The washed algae were then totally dried in sunlight for 10 days. The dried leaves were then cut into little slices and powdered using domestic mixer. In the present study the powdered materials in the range of 75-212 μm average particle size were used.

Preparation of metal solution

A stock solution of chromium concentration 1000 mg/l was prepared by dissolving required amount of potassium dichromate in 1000 ml of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 20 to 100 mg/l and they were prepared by diluting the chromium stock solution, which were obtained by dissolving in deionized water.

Reagents utilized

Metal ion solutions were prepared by diluting stock metal ion solutions, which were obtained by dissolving weighed quantity of potassium dichromate of analytical reagent grade obtained from MERCK (India) in double distilled water.

Batch biosorption experiments conducted

Biosorption studies were carried out at 303K with an initial concentration range from 20 to 100 mg/l, biosorbent dosage range from 0.1 to 0.5g and size of the biosorbent ranges from 75-212 μm. Equilibrium was attained by shaking the flasks for 3 hours at 180 RPM in an orbital shaker. A known volume of the solution was removed and filtered for chromium analysis. Known amounts of biomass were contacted with each metal solution. The effects of following parameters such as pH, contact time, initial metal ion concentration, dosage, size and temperature were studied.

Metal Analysis

The final concentration of metal ions was analyzed by Atomic Absorption Spectrophotometer ((Shimadzu AA-6300)).

Calculation of biosorption capacity

In order to assess the amount of chromium ions held per unit mass of *turbinaria vulgaris sp.* , the biosorption capacity was computed using the following equation:

$$q_e = \frac{V(C_i - C_f)}{1000w} \dots\dots\dots (1)$$

where V is the volume of the solution in ml and w is the mass of the biosorbent in g. Preliminary trails had demonstrated that metal biosorption losses to the flask walls and to the filter paper were negligible. All the trails were rehashed five times and the average values have been recorded. Additionally, blank trails were run to guarantee that no biosorption was taking place on the walls of the apparatus used.

RESULTS AND DISCUSSION

Effect of pH

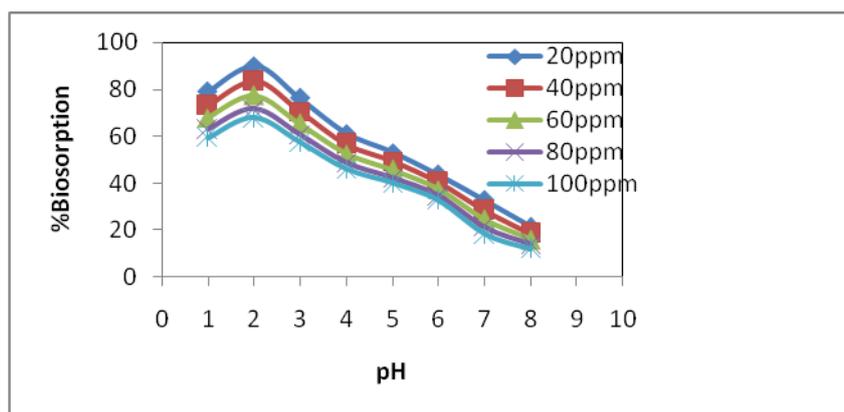


Fig 1: Effect of pH on Cr(VI) removal by *turbinaria vulgaris sp.* for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The pH of solution is one of the most critical parameters in the adsorption process, which affects the surface charge of the adsorbent material, the degree of ionization, and the specification of the adsorbate. Various authors [12,13] have shown that solution pH greatly influences metal biosorption by algae biomass. The effect of pH on the sorption efficiency of chromium onto *tubinaria vulgaris* was studied by varying pH of the metal solution of 20mg/l concentration in the range of 1–8 by keeping the adsorbent concentration at 0.1

g/30mL and the results were presented in Fig. 1. From this figure it is clear that the percent removal of chromium is maximum at pH 2 and thereafter decreases with increase in pH. At a lower pH value, the dominant form of Cr(VI) is HCrO_4^- while the surface of the adsorbent is charged positively. The stable forms of chromium such as H_2CrO_4 and CrO_3 exist as polynuclear species at higher chromium concentrations and hence the low pH value results in a higher percentage removal of Cr(VI). In addition, for the pH values above 2, the adsorption capacity decreases with increasing pH. Increasing the pH value will shift the concentration of HCrO_4^- to other forms (CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$). The decrease in adsorption of Cr(VI) with increase in the pH value may be due to the dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates [14]. The maximum % biosorption was found as 90.08% at pH 2.0.

Effect of contact time

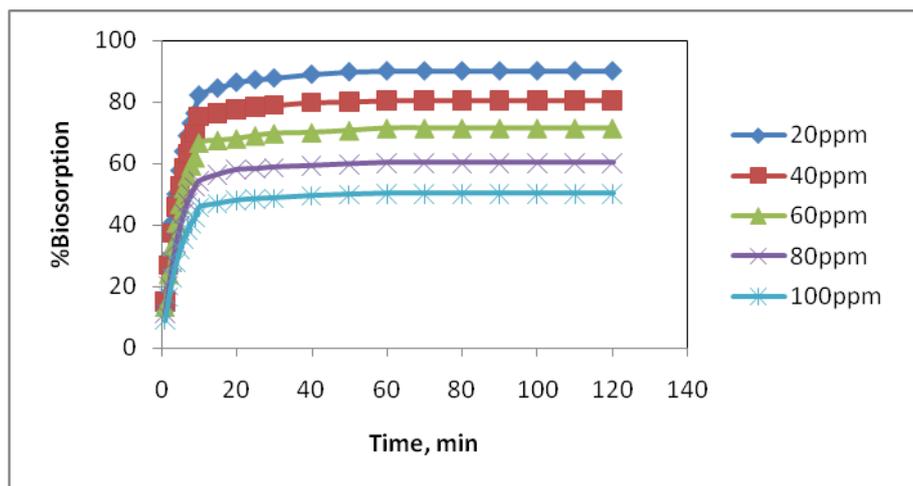


Fig 2: Effect of contact time on Cr(VI) removal by *turbinaria vulgaris sp.* for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

To establish an appropriate contact time between the biosorbent and metallic ion solution, biosorption capacities of metal ions were measured as a function of time at optimum pH (Fig.2). From the plot it is evident that the rate of the percentage of chromium removal is higher at the beginning. That is probably due to the larger surface area of the *turbinaria vulgaris sp.* being available at beginning for the biosorption of metal ions. As the surface biosorption sites become exhausted, the rate of biosorption decrease because the uptake rate is controlled by the rate at which the biosorbate is transported from the surface to the interior sites of the biosorbent particles [15]. The rate of chromium removal was attained constant after approximately 60 min of stirring. Stirring beyond 60 min seems to be not useful because of any increase in rate of metal removal. Therefore, equilibrium contact time of 60 min was selected for all further studies.

Effect of initial metal ion concentration

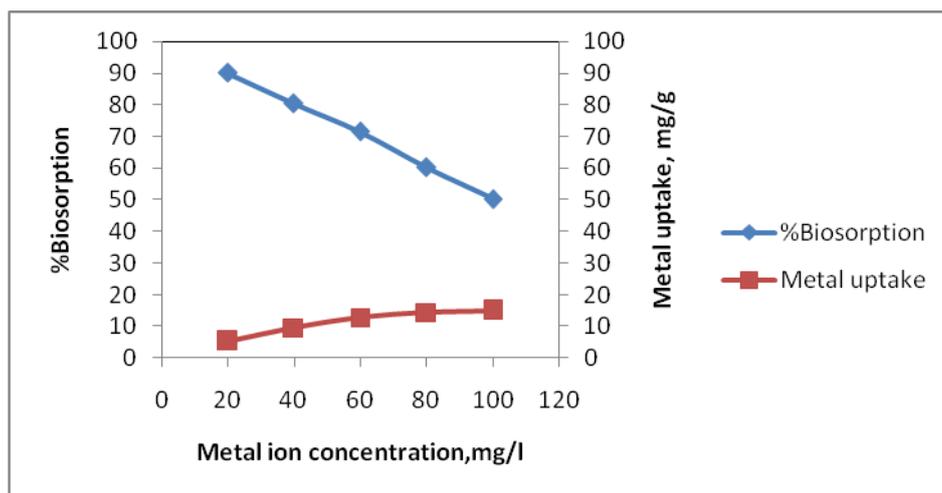


Fig 3: Effect of metal ion concentration on biosorption capacity of Cr(VI) by *turbinaria vulgaris sp.* of 0.1g/30ml of biosorbent concentration.

Initial metal ion concentration strongly influences the metal uptake in the biosorption of aqueous solutions. Metals ions are adsorbed on active sites of the surface of the biosorbent while with the increase of metal ion concentration all active sites are saturated and the vacant sites are filled. In the present study, the adsorption experiments are performed to study the effect of initial Cr(VI) concentration by varying it from 20 to 100mg/l at an initial pH value of 2 while maintaining the *turbinaria vulgaris* amount of 0.1g/l. This data is further utilized for developing Freundlich and Langmuir biosorption isotherm models for fitment from which the efficiency of the biosorbent can be calculated. The results were presented in Fig.3. It shows that with an increase in the Cr(VI) concentration from 20 to 100mg/l, the percentage removal decreases from 90.08% to 50.24%. The decrease in the percentage removal of Cr(VI) can be explained with the fact that all the biosorbents had a limited number of active sites, which would have become saturated above a certain concentration.

Effect of biosorbent dosage

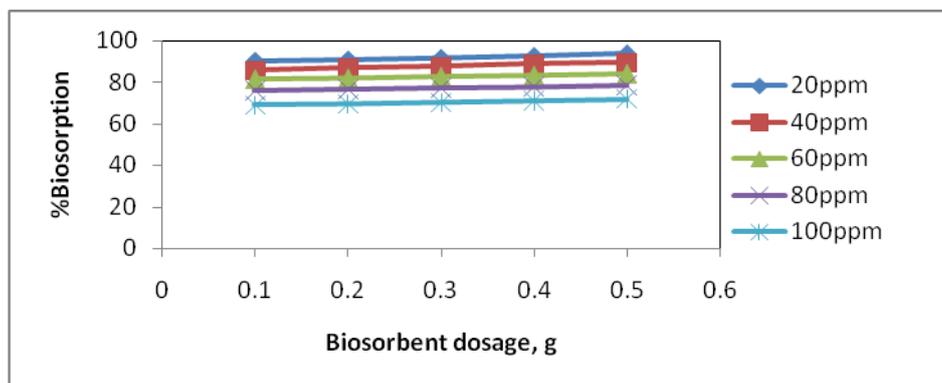


Fig 4: Effect of biosorbent dosage on Cr(VI) removal by *turbinaria vulgaris sp.* for 20, 40, 60, 80, 100mg/l metal and 0.1 to 0.5g/30ml of biosorbent concentration.

The effect of dosage of the biosorbent on the biosorption of the chromium was studied. The change of percentage biosorption due to increase in the dosage of the biosorbent were shown in the Fig.4. Due to increase in the dosage of the biosorbent there is an increase in the percentage biosorption but at a marginal rate. It was observed that the percentage biosorption had increased up to 93.68% for chromium at the dose of biosorbent 0.5g/30ml. This is due to the fact that the interference of inter particle cohesive forces, interference of binding sites, desorption due to abrasion, turbulence and reduced mixing due to large mass of the biosorbent.

Effect of biosorbent size

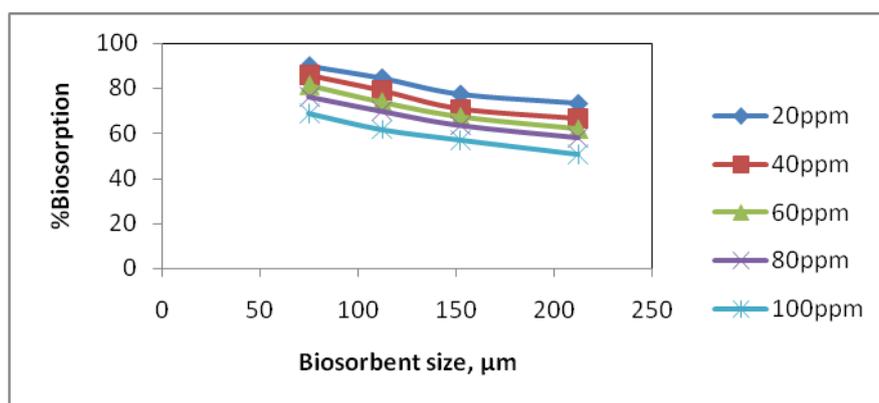


Fig 5: Effect of biosorbent size on Cr(VI) removal by *turbinaria vulgaris* sp. for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The effect of different biosorbent particle sizes (75-212 µm) on the percentage removal of chromium onto *turbinaria vulgaris* was investigated and showed in Fig.5. It reveals that the biosorption of chromium onto *turbinaria vulgaris* sp. decreases with an increase in particle size from 75 to 212 µm with different chromium concentrations. It is well known that decreasing the average particle size of the biosorbent increases the surface area, which in turn increases the biosorption capacity.

Effect of Temperature

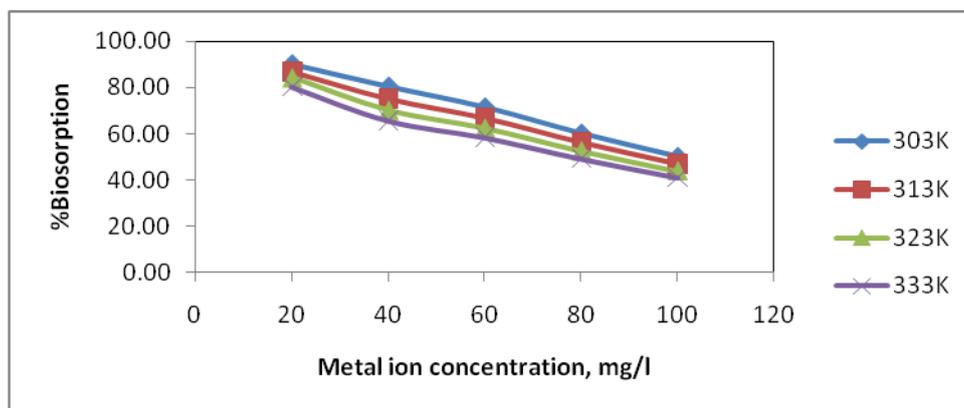


Fig 6: Effect of temperature on Cr(VI) removal by *turbinaria vulgaris* for 20,40,60,80,100mg/l metal and 0.1g/30ml of biosorbent concentration.

The rate of biosorption is a function of initial metal ion concentration as well as its temperature. The percent biosorption of chromium onto *turbinaria vulgaris* is shown in Fig.6 as a function of the initial metal ion concentration at 303, 313, 323 and 333 K. The percentage biosorption of chromium ions onto *turbinaria vulgaris* sp. decreased from 90.08 to 80.34% as the temperature increased from 303 to 333 K at 20 mg/l. The percentage biosorption at higher temperature levels shows a decreasing trend because at lower temperatures, all chromium ions present in solution could interact with the binding sites and thus the percentage biosorption was higher than those at higher temperatures. This happens because of more interaction of the ions in solution due to convection. At higher temperatures, lower biosorption yield is due to the mobilization of ions in solution because of highly energized ions. As a result, the purification yield can be increased by reducing the temperature. The decrease of the percentage biosorption at increased temperature indicated that the biosorption of chromium ions onto *turbinaria vulgaris* sp. is exothermic in nature.

Biosorption isotherm models

The capacity of a biomass can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the biomass. In this study, three important sorption isotherm models were selected to fit experimental data, which are namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models.

Langmuir Isotherm

The Langmuir model assumes that the uptake of metal ions on a homogenous surface by monolayer biosorption without any interaction between biosorbed ions. Langmuir isotherm can be defined according to the following formula[16]

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/l), q_m is the monolayer biosorption capacity of the biosorbent (mg/g) and K_L is the Langmuir biosorption constant (l/mg) relating the free energy of biosorption.

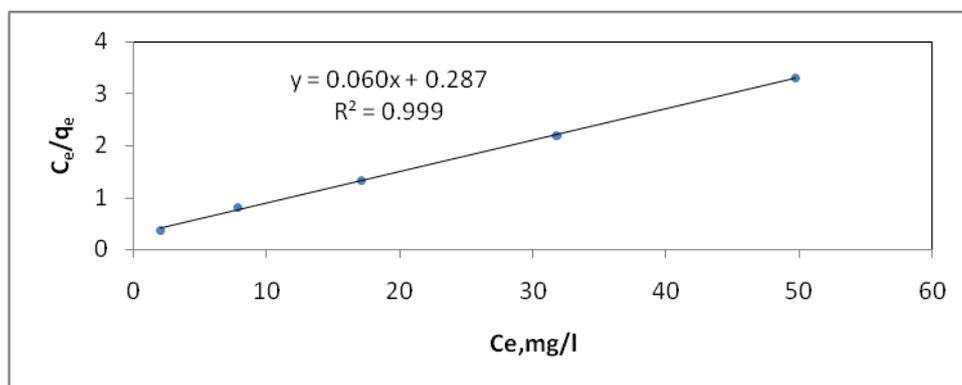


Fig 7: Langmuir biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Fig. 7 indicates the non-linear relationship between the amount (mg) of chromium sorbed per unit mass (g) of turbinaria vulgaris sp. biomass against the concentration of chromium remaining in solution (mg/l). The coefficient of determination (R^2) were found to be 0.999 for chromium biosorption, indicating that the biosorption of the metal ions onto turbinaria vulgaris sp. fitted well the Langmuir model. In other words, the sorption of metal ions onto turbinaria vulgaris sp. was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption.

The K_L value was found as 20.98×10^{-2} l/mg and the maximum biosorption capacity (q_m) was found to be 16.6 mg/g. As also seen in Table 1, in order to indicate the biosorption potential of turbinaria vulgaris sp. for chromium, q_m value is compared with other biosorbents reported in the literature [2]. The biosorption capacity of turbinaria vulgaris sp. biomass for chromium is higher than that of the majority of the biomasses. Therefore, it can be noteworthy that the turbinaria vulgaris sp. has considerable potential for the removal of chromium from aqueous solution.

Freundlich Isotherm

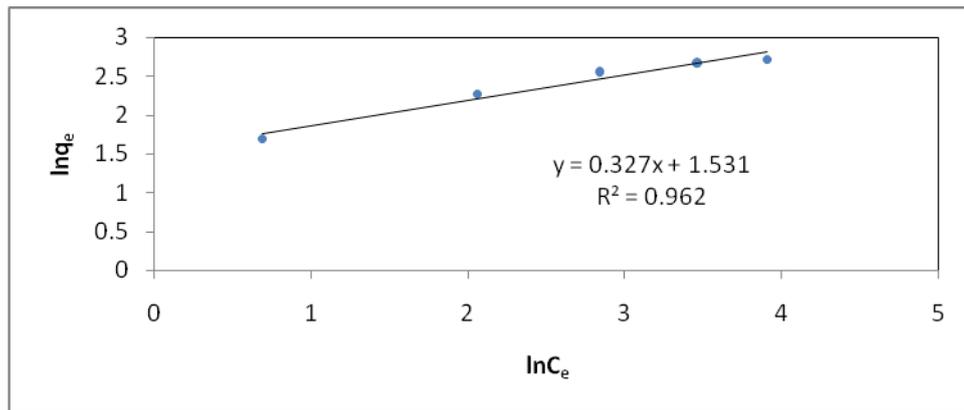


Fig 8: Freundlich biosorption isotherm at 0.1g/30ml of biosorbent concentration.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained as follows [2]

$$q_e = K_f C_e^{1/n} \tag{3}$$

where K_f is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material.

Fig. 8 shows the Freundlich isotherms obtained by fitting equilibrium data to Eq. (3). The values of K_f and $1/n$ were found to be 4.6 and 0.3, respectively. The $1/n$ values were between 0 and 1, indicating that the biosorption of total chromium onto *turbinaria vulgaris* sp. was favorable at studied conditions. However, compared to the R^2 values, 0.962 with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model is better fitted the equilibrium data.

D-R isotherm

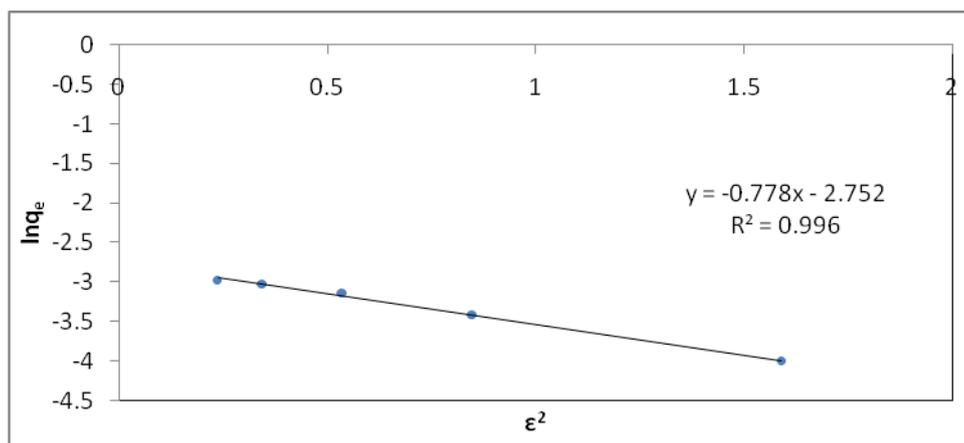


Fig 9: D-R biosorption isotherm at 0.1g/30ml of biosorbent concentration.

The equilibrium data were also applied to the D-R isotherm model to determine the nature of biosorption processes as physical or chemical. The linear form of the D-R isotherm equation [14] shown in the following equation

$$\ln q_e = \ln q_m - \beta \epsilon^2 \tag{4}$$

where q_e is the amount of metal ions biosorbed on per unit weight of biomass (mol/l), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to mean biosorption energy (mol^2/J^2) and ϵ is the Polanyi potential ($\epsilon = RT \ln(1+1/C_e)$).

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to 0.996 (Fig. 9). From the intercept of the plots, the q_m value was found to be 6.3×10^{-2} mol/g. The mean biosorption energy (E ; kJ/mol) is as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If E value lies between 8 and 16 kJ/mol, the biosorption process takes place chemically and while $E < 8$ kJ/mol the biosorption process is physically [14]. The mean biosorption energy was calculated as 8.02 kJ/mol and indicated that the biosorption of chromium onto *turbinaria vulgaris* sp. may be proceeded by binding surface functional groups.

Temkin Isotherm

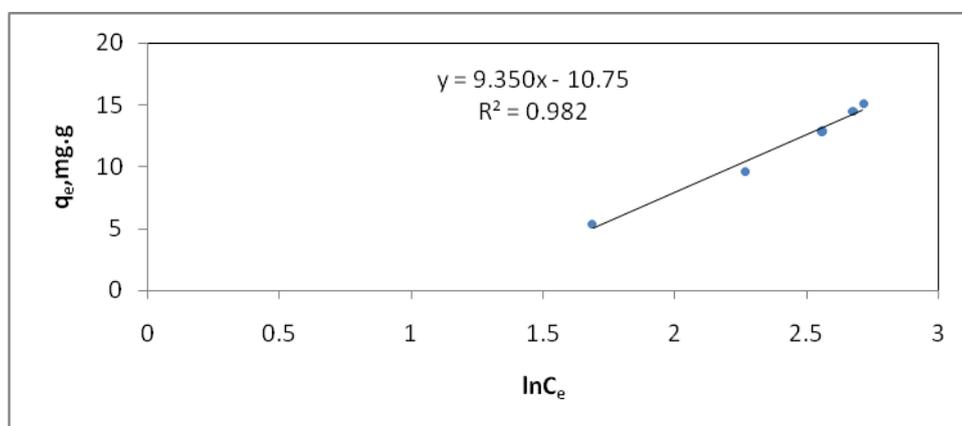


Fig 10: Temkin biosorption isotherm at 0.1g/30ml of biosorbent concentration.

The Temkin isotherm [15] has been used in the following form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \tag{6}$$

$$q_e = B \ln K_T + B \ln C_e \tag{7}$$

where, constant $B=RT/b$, which is related to the heat of sorption, R is the universal gas constant (KJ/mol K), T is the temperature (K), b is the variation of sorption energy (J/mol) and K_T is the equilibrium binding constant (l/mg) corresponding to the maximum binding energy. Fig. shows the plot of q_e versus $\ln C_e$, the isotherm constants were found and given in Table 1. The correlation factors show that the Langmuir model approximations to the experimental results are better than that of the Temkin model. Consequently, among the four isotherm models used, the Langmuir model offers the best correlation factors.

Table1: Constant values of Langmuir, Freundlich, D-R, Temkin isotherm constants

| Isotherm | Isotherm constants and coefficients | |
|----------|-------------------------------------|--------|
| Langmuir | q_{max} (mg / g) | 16.6 |
| | k_l (l / mg) | 0.2098 |
| | R^2 | 0.999 |

| | | |
|------------------------|--------------------|------------------------|
| Freundlich | $K_f (mg / g)$ | 4.6 |
| | $1/n(g/l)$ | 0.3 |
| | R^2 | 0.962 |
| Dubinin – Radushkevich | β | 0.778×10^{-8} |
| | E(KJ/mol) | 8.02 |
| | $q_{max} (mg / g)$ | 6.3×10^{-2} |
| | R^2 | 0.996 |
| Temkin | $K_T (l / mg)$ | 0.316 |
| | $b (J/mg)$ | 269.42 |
| | R^2 | 0.982 |

Biosorption Kinetics

Kinetics is one of the major parameters to evaluate biosorption dynamics and the kinetic constants can be used to optimize the residence time of a biosorption process. In order to examine the controlling mechanism of the biosorption process, kinetic models are used to test the experimental data. In this study, the equilibrium data were analyzed using five kinetic models, pseudo first- order, pseudo-secondorder, intra particle, boyd, elovich model.

Pseudo first- order model

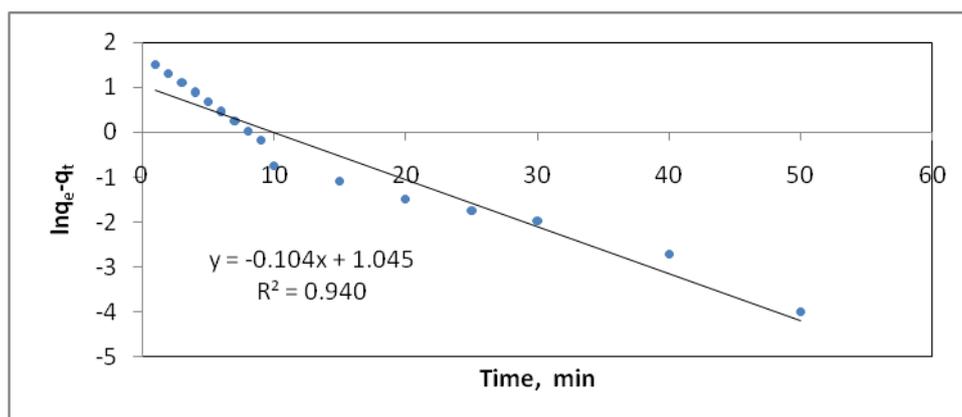


Fig 11: pseudo first order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

The linear form of the pseudo-first order rate equation is given as [14]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

Where q_t and q_e (mg/g) are the amounts of the metal ions adsorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t . The plot of $\ln(q_e - q_t)$ versus t for the pseudo-first-order model was shown in figure11. The R^2 value was found to be low ($R^2 = 0.94$, as seen in Table 2).Based on these results it can be concluded that the biosorption of Cr(VI) onto turbinaria vulgaris sp. does not fit a pseudo-first-order kinetic model. Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of chromium onto turbinaria vulgaris sp.

Pseudo second- order model

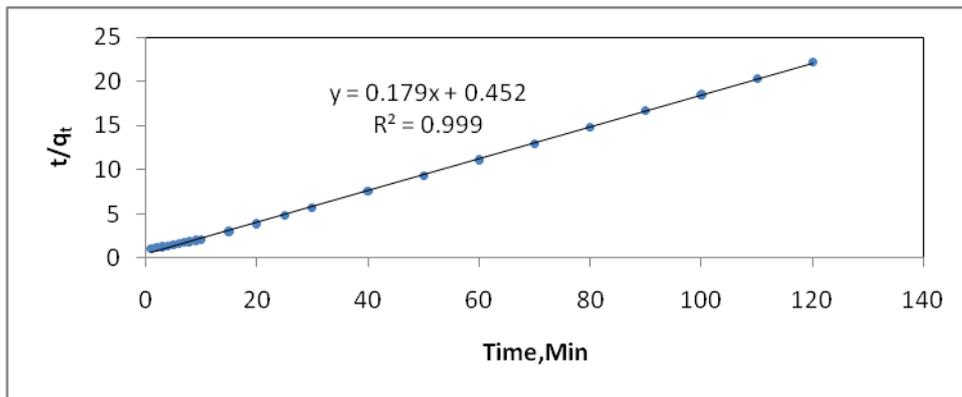


Fig 12: pseudo second order for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [2]

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e} \tag{9}$$

where k_2 (g/mgmin) is the rate constant of the second-order equation, q_t (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g). This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate controlling step [2]. The linear plot of t/q_t versus t for the pseudo-second-order model for the biosorption of Cr(VI) ions onto the alga biomass was shown in Fig.12 . The R^2 value is 0.999 as seen in Table 2. Therefore it can be said that the pseudosecond-order kinetic model provided a good correlation for the biosorption of chromium onto turbinaria vulgaris sp. in contrast to the pseudo-first order model.

Intra particle diffusion

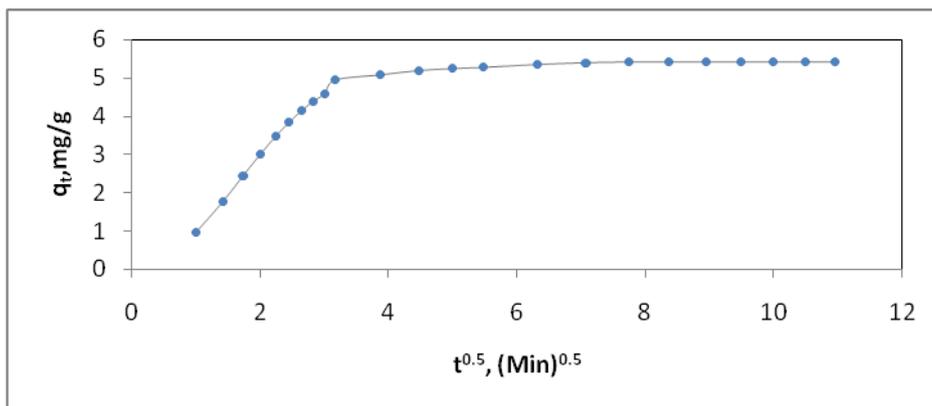


Fig 13: Intra particle diffusion model for 20 mg/l of metal and 0.1 g/ 30 ml of biomass concentration.

Weber’s intra particle diffusion model [2] is defined by the following equation:

$$q_t = k_{id} t^{0.5} + C \tag{10}$$

where K_{id} is the intraparticle diffusion rate constant (mg/(g min^{-0.5})) and C is the intercept. It was concluded that the sorption process of Cr(VI) onto turbinaria vulgaris sp. is comprised of three phases,

suggesting that the intraparticle diffusion is not the rate-limiting step for the whole reaction. The uptake rate was initially very fast, then medium, finally giving way to slow uptake. The rate constants of intraparticle diffusion were calculated from Fig.13. Pseudo-second-order model has higher correlation coefficient values, indicating that the sorption of Cr(VI) on the sorbent follows second-order kinetic model. Higher values of R^2 show a better fitness of the sorption data[16,17].

Table 2: Biosorption rate constants, q_e estimated and coefficient of correlation associated to the pseudo-first and second-order biosorption for the *turbinaria vulgaris sp.* Biomass

| Metal | q_e Exp (mg/g) | Pseudo first order | | | Pseudo second order | | |
|----------|------------------|----------------------------|-----------------|-------|---------------------|-----------------|-------|
| | | K_1 (min ⁻¹) | q_e cal(mg/g) | R^2 | K_2 ((g/mg) min) | q_e cal(mg/g) | R^2 |
| Chromium | 5.404 | 0.104 | 2.84 | 0.94 | 0.07 | 5.58 | 0.999 |

CONCLUSION

Utilization of naturally available and waste material such as *turbinaria vulgaris sp.* for the removal of Cr(VI) from aqueous solutions was investigated. *Turbinaria vulgaris sp.* was found to be a better biosorbent for the removal of Cr(VI) from industrial effluents. The maximum percentage removal of Cr(VI) was obtained at pH 2. The dominant form of Cr(VI) is $HCrO_4^-$ and the surface of biosorbent was charged positively at a lower pH values. It was found from the kinetic studies that the biosorption rate of Cr(VI) was faster for the initial 60 min and then it was constant in the later part of biosorption. With an increase of biosorbent amount, the percentage removal of Cr(VI) increases. The percentage removal decreases with an increase in the initial Cr(VI) concentration. The equilibrium biosorption data were tested with various isotherm models such as Langmuir, Freundlich, D-R, Temkin. The equilibrium data were best fitted with Langmuir, Dubinin–Radushkevich, Temkin and Freundlich isotherm models. The maximum biosorption capacity was obtained with the application of Langmuir isotherm model as 16.6 mg/g, which is comparatively good biosorption capacity. The kinetics of Cr(VI) biosorption using *turbinaria vulgaris sp.* as an biosorbent was explained by the second-order kinetic model. Based on the results, it can be concluded that the *turbinaria vulgaris sp.* is an effective biosorbent for the removal of Cr(VI) from aqueous medium.

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