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Kinetic, Equilibrium and Thermodynamic Studies of Biosorption of Chromium (VI) from Aqueous Solutions using *Azolla filiculoidus*

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Biosorption of Cr(VI) by *Azolla Filiculoidus* was studied in the present study. The batch experiments were carried out to investigate the effect of the significant process parameters such as pH, contact time, initial Cr(VI) concentration, and biomass dosage. The results of this study showed that higher chromium removal was observed at lower pH points, and maximum chromium removal (83.341 %) was obtained at pH of 2. Adsorption of chromium by *Azolla Filiculoidus* reached to equilibrium after 100 min and after that a little change of chromium removal efficiency was observed. Biosorption of chromium by *Azolla Filiculoidus* was decreased with increasing in initial chromium concentration and increased with increasing in biomass dosage. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherms. The maximum adsorption capacity obtained was 10.638 mg g"1 at a pH value of 2. From the D–R isotherm model, the mean free energy was calculated as 8.494 kJ/mol, indicating that the biosorption of Cr(VI) the metal ions were taken place by chemisorptions. Biosorption process follows the second-order kinetics and the corresponding rate constants are obtained. The calculated thermodynamic parameters ("G^0, "H^0, and "S^0) showed that the biosorption of Cr(VI) ions onto *Azolla Filiculoidus* was feasible, spontaneous and exothermic at 293–323 K. The results indicate that *Azolla Filiculoidus* can be employed as a low cost alternative to commercial adsorbents in the removal of Cr(VI) from industrial wastewater.

Key words: Biosorption, Chromium(VI), *Azolla Filiculoidus*, Isotherm, Kinetics, Thermodynamics.

The progressive increase of Industrialization resulted indiscriminate processing of natural resources by discharging huge amounts of heavy metals into the water bodies. This discharge of heavy metals has caused serious problems of contamination of aquatic ecosystems and posing severe threat to aquatic life and through food chain to mankind. Many industrial activities such as metal plating, fertilizer industry, mining operations, and textile dispose heavy metals to environment through their waste effluents[1, 2]. Chromium is a metal particle that occurs naturally in rocks but is most commonly produced by industrial processes. The most common forms of chromium are trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] which are commonly used in various industrial processes. Cr(VI) is also used in various other industries such as

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electroplating, glass, ceramics, fungicides, rubber, fertilizers, tanning, mining, metallurgical, etc. [3–10]. Its ability to react with other elements makes hexavalent chromium a health hazard. Cr(VI) is highly mobile and is considered acutely toxic, carcinogenic and mutagenic to the living organisms, and hence more hazardous than other heavy metals. In addition, it also has an effect on human skin, liver, kidney, and respiratory organs. This results in a variety of diseases such as dermatitis, bronchitis, perforation of nasal septum, bronchogenic carcinoma, liver damage, ulcer formation, etc. [11–16]. Therefore, it is necessary to eliminate Cr(VI) from the environment, in order to prevent the deleterious impact of Cr(VI) on ecosystem and public health. Because of the stricter environmental regulations, a cost effective alternate technology for the treatment of Cr(VI) contaminated wastewater is highly desired by the industries[17]. Cr(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 [18]. It is reported that, chromate ($CrO4^{"2}$) is the prevalent species of Cr (VI) in natural aqueous environments. The usual methods for removal of heavy metal ions from aqueous solutions can be ordered as chemical precipitation, ion exchange, solvent extraction, phytoextraction, ultra filtration, reverse osmosis, electrodialysis, and adsorption[19, 20]. Application of such traditional treatment techniques needs enormous cost and continuous input of chemicals which becomes impracticable and uneconomical an causes further environment damage[21]. Biosorption is an emerging technology for removal of heavy metals from industrial wastewater[22]. The major advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time and no production of secondary compounds which might be toxic[23,24]. Along with afore mentioned advantages the presence of wide variety of functional groups in waste biomaterials such as hydroxyl, carboxyl, carbonyl, amine, amide, alcoholic, phenolic, thiol and phosphate have high affinity to form metal complexes and/or chelates with heavy metal ions [25]. *Azolla* is a small aquatic fern. In fact, it is a symbiotic pair of *Azolla filiculoides* and a heterocystous blue-green alga *Anabaena azollae*. Because of its nitrogen-fixing capability it has been using as fertilizer in botanical gardens[26]. *Azolla* has been used for several decades as green manure in rice fields. On the other hand, it has negative effects on the aquatic ecology due to its capable of colonizing rapidly to form dense mats over water surfaces. Controlling its reproduction has been deemed necessary in some *Azolla*-abundant areas like South Africa[27] and the north part of Iran. In this regard, the development of an *Azolla*-based biosorbent for wastewater treatment, especially in developing countries, may benefit environmental problems, by removing heavy metals from water using this weed[28]. *Azolla* has been shown to be able to effectively adsorb various metals like chromium, zinc (II) and nickel (II) from solutions and electroplating effluent[28, 29, 30] and gold (III) from aqueous solution[31]. The present work aimed to investigate the chromium biosorption capacity of *Azolla filiculoides* from aqueous solution. Experimental parameters affecting biosorption process such as contact time, pH, initial metal ion concentration and biomass dosage were studied. The equilibrium biosorption data were evaluated by Langmuir and Freundlich isotherm models and experimental data was fitted with pseudo first and second order rate models.

MATERIALS AND METHODS

Preparation of biosorbent

Azolla Filiculoidus a fresh water macro alga was collected from Sangam Diary, Biofertilizer and Cattle field unit, Vadlamudi, of Guntur District**,** Where it is cultivated and used as biofertilizer. To remove mud and impurities it was washed first thoroughly with tap water and later with distilled water. Then it was dried in a hot air oven at 30^0C for two days. Then it is powdered by ball mill and the average particle size was maintained at 100 ìm. Then it was stored in air tight polythene covers for further use in biosorption experiments.

Chemicals

Analytical grades of $K_2Cr_2O_7$, HCl and NaOH were purchased from Merck, India. Chromium ions were prepared by dissolving its corresponding sulphate salt in distilled water. The pH of solutions was adjusted with 0.1 N HCl and

NaOH. All the experiments were repeated four times and the average values have been reported. Also, blank experiments were conducted to ensure that no biosorption was taking place on the walls of the apparatus used.

Biosorption experiments

Biosorption experiments were carried out in an orbital shaker at 180 rpm using 250 mL Erlenmeyer flasks with 30 mL of different chromium concentration solutions. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g *of Azolla Filiculoidus* biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The residual metal concentration in the supernatant was determined by di-phenyl carbazide method after filtering the biosorbent with whatman filter paper. The amount of metal adsorbed by *Azolla Filiculoidus* was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = (C_0 - C_f)X\frac{V}{M} \qquad ...(1)$$

Where Q is the metal uptake (mg/g); C_0 and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (mL); and M is the mass of biosorbent (g).

Estimation of chromium

Amount of chromium in a given sample solution was determined spectrophotometrically at 540 nm using 1, 5-diphenyl carbazide as the complexing agent [32]. The sample containing Cr(VI) ions was mixed with 1 ml of 3 N H_2SO_4 and 1 ml of 0.25% 1, 5-diphenyl carbazide solution and made up to known volume. The absorbance at 540 nm was measured for the purple coloured solution after 10 minutes incubation. A calibration curve was drawn in the range of 5 to 50 ppm by plotting absorbance against concentration of chromium.

RESULTS AND DISCUSSION

Effect of pH on Cr(VI) removal by *Azolla filiculoidus*

It is well known that the pH of solution is one of the important factors affecting adsorption of metal ions. It affects the cell wall metal binding sites and the metal ion chemistry in water. Various authors [33, 34] have shown that solution pH greatly influences metal biosorption by algae biomass. The effect of pH on the sorption efficiency of chromium onto *Azolla Filiculoidus* was studied by varying pH of the metal solution of 20mg/L concentration in the range of 1–6 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)[35]. 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 $Cr_2O_7^{2"}$). The decrease in adsorption of Cr(VI) with increase in the pH value may be due to the dual competition of both the anions(CrO4 2" and OH”) to be adsorbed on the surface of the adsorbent of which $OH^{"}$ predominates[36]. The maximum equilibrium uptake value was found as 83.341% at pH 2.0.

Effect of Contact Time on adsorption of Cr(VI) by *Azolla filiculoidus*

To establish an appropriate contact time between the biosorbent and metallic ion solution, adsorption 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 *Azolla Filiculoidus* being available at beginning for the adsorption of metal ions. As the surface adsorption sites become exhausted, the rate of adsorption decrease because the uptake rate is controlled by the rate at which the adsorbate is transported from the surface to the interior sites of the adsorbent particles. The rate of chromium removal was attained constant after approximately 100min of stirring. Stirring beyond 100min seems to be not useful because of any increase in rate of metal removal. Therefore, equilibrium contact time of 100min was selected for all further studies.

Effect of Metal ion Concentration on boisorption of Cr(VI)

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 adsorbent 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”1 at an initial pH value of 2 while maintaining the *Azolla Filiculoidus* amount of 0.1 g L”1. This data is further utilized for developing Freundlich and Langmuir adsorption isotherms models for fitment from which the efficiency of the adsorbent 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”1, the percentage removal decreases from 86.34% to 48.48%. The decrease in the percentage removal of Cr(VI) can be explained with the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration

Effect of *Azolla Filiculoidus* dosage on biosorption of Cr(VI)

The effect of dosage of the adsorbent on the biosorption of the chromium was studied. The change of percentage adsorption due to increase in the dosage of the adsorbent were shown in the Fig.4. Due to increase in the dosage of the adsorbent there is an increase in the percentage adsorption but at a marginal rate. It was observed that the percentage adsorption had increased up to 96.76% for Chromium at the dose of adsorbent 0.5g/30ml. Even though the total metal uptake increase with the dose of adsorbent, the metal uptake per gram of adsorbent had been drastically decreased. 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 adsorbent

Biosorption Equilibrium for Cr(VI)

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[37]. In this study, three important sorption isotherm models were selected to fit experimental data, which are namely Langmuir, and Freundlich isotherm models. The Langmuir model assumes that the uptake of metal ions on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir isotherm can be defined according to the following formula[38]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad ...(2)$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), qm is the monolayer biosorption capacity of the adsorbent (mg/g) and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption. Fig. 5 indicates the linear relationship between the amount (mg) of total chromium sorbed per unit mass (g) of *Azolla Filiculoidus* biomass against the concentration

Table.1 Coefficients of the Langmuir, Freundlich and Dubinin–Radushkevich isotherm models for chromium biosorption by *Azolla Filiculoidus*

Metal	Langmuir isotherm model			Freundlich isotherm model			D–R isotherm model		
	q_{max} (mgg^{-1})	b (L mg^{-1})	r^2	n	K_f	r^2	q_{max} (mgg^{-1})	β	E kJ/mol
chromium	10.638	0.273	0.99	4.255	4.051	0.923	4.0×10^{-2}	-0.693×10^{-8}	8.494

Table.2 Comparison of rate constants and equilibrium metal uptake for Cr(VI) binding by *Azolla Filiculoidus* at pH 2 and initial metal ion concentration of 20 mg L^{-1} , adsorbent dose is 0.1 mg.

Metal	$q_{e\ exp}$ (mgg^{-1})	Pseudo first order model			Pseudo second order model		
		k_1(min^{-1})	$q_{e\ cal}$ (mgg^{-1})	r^2	k_1(min^{-1})	$q_{e\ cal}$ (mgg^{-1})	r^2
chromium	5.0	0.0253	.698	0.989	0.00862	5.88	0.998

of chromium remaining in solution (mg/L). The coefficients of determination (R^2) were found to be 0.980 for chromium biosorption, indicating that the biosorption of the metal ions onto *Azolla Filiculoidus* fitted well the Langmuir model. In other words, the sorption of metal ions onto *Azolla Filiculoidus* was taken place at the functional groups/binding sites on the surface of the biomass

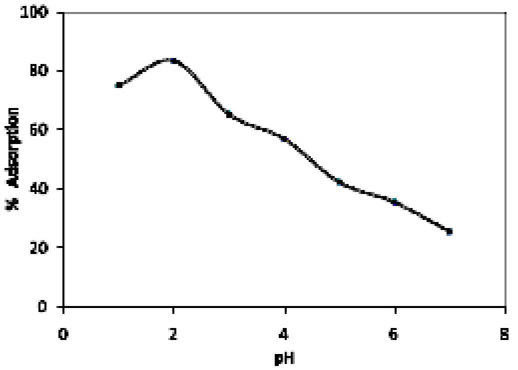

Fig. 1. Effect of pH on Cr(VI) removal by *Azolla Filiculoidus* for 20mg/L. metal and 0.1 g/30 mL. of adsorbent concentration.

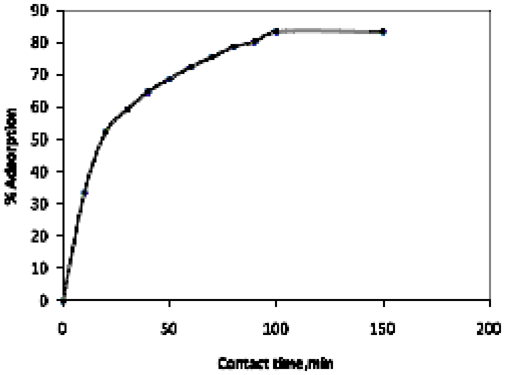

Fig. 2. Effect of contact time on adsorption of Cr(VI) by *Azolla Filiculoidus* for 20mg/L of metal concentration and 0.1/30mL of adsorbent concentration at pH of 2.

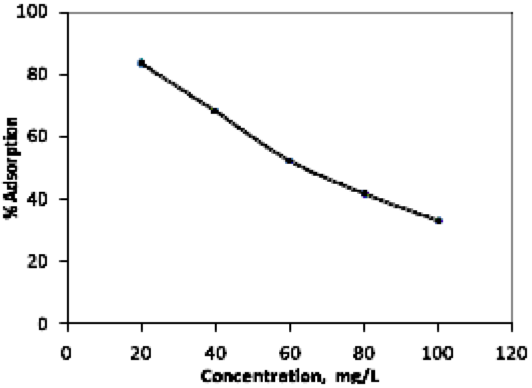

Fig. 3. Effect of metal ion concentration on boisorption of Cr(VI) by *Azolla Filiculoidus* at 0.1 g/30mL of adsorbent concentration, pH 2 and contact time 100 min.

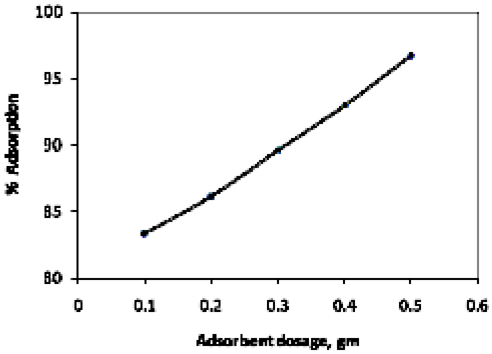

Fig. 4. Effect of *Azolla Filiculoidus* dosage on biosorption of Cr(VI) for 20mg/L of metal solution concentration at pH 2 and 100 min of contact time.

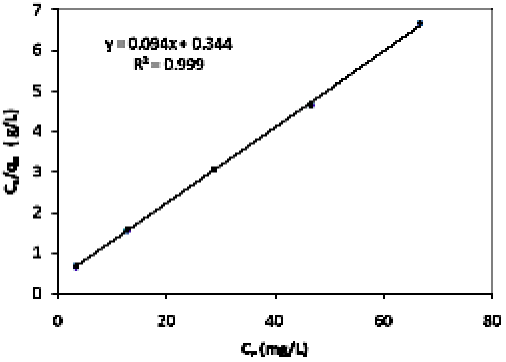

Fig. 5. Langmuir adsorption isotherm for Cr(VI) at 0.1 g/ 30 ml of biomass concentration

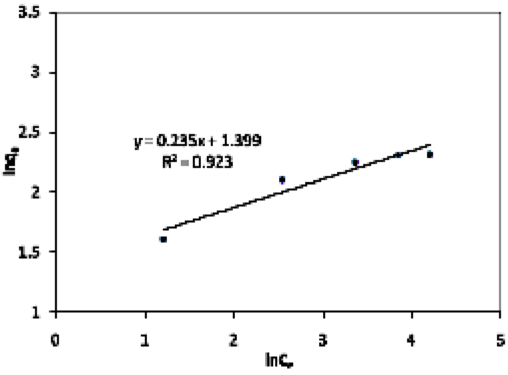

Fig. 6. Freundlich adsorption isotherm for Cr(VI) at 0.1 g/ 30 ml of biomass concentration

which is regarded as monolayer biosorption. The K_L value was found as 4.4×10"2 L/mg and the maximum biosorption capacity (q_m) was found to be 15.55 mg/g as seen in Table 1. Therefore, it can be noteworthy that the *Azolla Filiculoidus* has considerable potential for the removal of total chromium from aqueous solution.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained as follows[39]:

Table 3. Thermodynamic parameters for the adsorption of Cr(VI) ions on *Azolla Filiculoidus* at different temperatures

T(⁰C)	Δ⁰(kJ/mol)	ΔH⁰(kJ/mol)	ΔS⁰(kJ/mol K)	r²
20	-0.98906	-92.119	-28.126	0.994
30	-0.69581			
40	-0.37317			
50	-0.16254			

$$q_e = K_f c_e^{1/n} \qquad ...(3)$$

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. 6 shows the Freundlich isotherms obtained by fitting equilibrium data to Eq. (3). The values of K_f and $1/n$ were found to be 3.828 and 0.329, respectively as seen in Table 1. The $1/n$ values were between 0 and 1, indicating that the biosorption of chromium onto *Azolla Filiculoidus* was favorable at studied conditions. The coefficients of determination (R^2) were found to be 0.986 for chromium biosorption, indicating that the biosorption of the metal ions onto *Azolla Filiculoidus* is also fitted well the

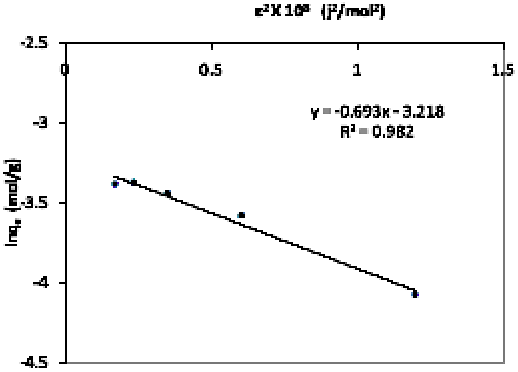

Fig. 7. Dubinin– Radushkevich isotherm adsorption isotherm for Cr(VI) at 0.1 g/ 30 ml of biomass concentration

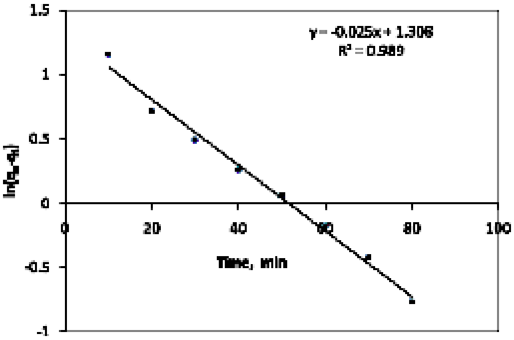

Fig. 8. **P**seudo first order biosorption of Cr(VI) by *Azolla Filiculoidus* test for 20 mg/L of metal and 0.1 g/ 30 ml of biomass concentration.

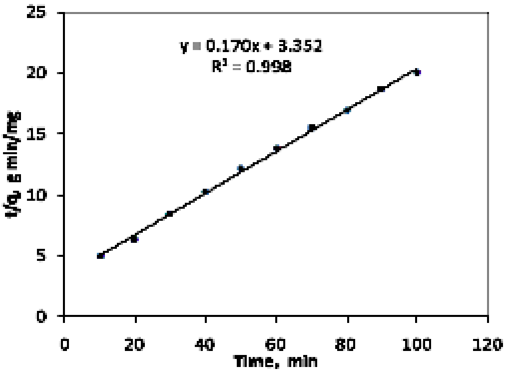

Fig. 9. **P**seudo second order biosorption of Cr(VI) by sea urchin test for 20 mg/L of metal and 0.1 g/ 30 ml of biomass concentration.

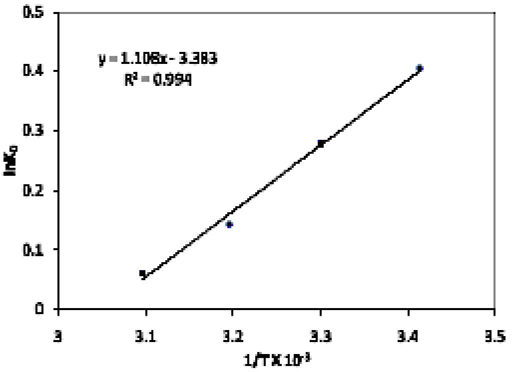

Fig. 10. Plot of $\ln(K_D)$ vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of Cr(VI) onto *Azolla Filiculoidus* biomass

Freundlich model.

The equilibrium data were also applied to the Dubinin–Radushkevich isotherm model to determine the nature of biosorption process as physical or chemical.The linear form of the D–R isotherm equation[40] can be written as:

$$lnq_e = lnq_m - \beta \mathcal{E}^2 \qquad ...(4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/L), q_m is the maximum biosorption capacity(mol/g), â is the activity coefficient related to mean biosorption energy (mol^2/J^2) and å is the Polanyi potential (å = RT ln(1 + 1/Ce)). The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to 0.982 (Fig. 7). From the intercept of the plot, the q_m value was found to be $4.0x10^{-2}$ mol/g. The mean biosorption energy (E, kJ/mol) is as follows,

$$E = \frac{1}{\sqrt{-2\beta}} \qquad ...(5)$$

The mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If E value is between 8 and 16 kJ/mol, the biosorption process follows chemically and if $E < 8$ kJ/mol, the biosorption process is of a physically [41]. The mean biosorption energy was calculated as 8.494 kJ/mol for the biosorption of Cr(VI) ions. These results indicated that the biosorption process of Cr(VI) onto *Azolla Filiculoidus* may be carried out chemically via involving valence forces through sharing or exchange of electrons between sorbent and sorbate[42].

Adsorption 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 two simplest kinetic models, pseudo first- order and pseudo-second-order model. The linear form of the pseudo-first-order rate equation[43] is given as

$$\ln(q_e - q_t) = lnq_e - k_1 t \qquad ...(6)$$

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 were not shown as figure because the R^2 values are found to be low ($R^2 = 0.989$, as seen in Table 2). Based on these results it can be concluded that the biosorption of Cr(VI) onto *Azolla Filiculoidus* 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 *Azolla Filiculoidus*.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form[44]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \qquad ...(7)$$

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 [44]. 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. 9. The R^2 value is 0.998 as seen in Table 2. Therefore it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of chromium onto *Azolla Filiculoidus* in contrast to the pseudo-first-order model.

Biosorption Thermodynamics

Thermodynamic parameters including the change in free energy “G^0, enthalpy “H^0 and entropy “S^0 were used to describe thermodynamic behavior of the biosorption of Cr(VI) ions onto *Azolla Filiculoidus* powder. These parameters were calculated from the following equations:

$$\Delta G^0 = -RTlnK_D \qquad ...(8)$$

Where, R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_D (q_e/c_e) is the distribution coefficient. By considering the Van’t Hoff equation,

$$lnK_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad ...(9)$$

The enthalpy change “H^0 and entropy

change “S^0 of biosorption were estimated from the slope and intercept of the plot of ln K_D versus $1/T$ (Fig.10) yields, respectively and the results were given Table 3. The negative “G^0 values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in “G^0 values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The enthalpy of biosorption “H^0 was found to be -92.119 kJ/mol. The negative “H^0 is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. The enthalpy value (“92.119 kJ/mol) indicated that the biosorption process of Cr(VI) ions onto *Azolla Filiculoidus* biomass proceeded chemically because it falls into the 20.9–418.4 kJ/mol [45]. The “S^0 parameter was found to be -0.28.126 kJ/mol K for Cr(VI) biosorption. The negative “S^0 value suggests a decrease in the randomness at the solid/solution interface during the biosorption process.

CONCLUSIONS

Utilization of naturally available and waste material such as *Azolla Filiculoidus* for the removal of Cr(VI) from aqueous solutions is investigated. *Azolla Filiculoidus* is found to be a better adsorbent for the removal of Cr(VI) from industrial effluents. The maximum percentage removal of Cr(VI) is obtained at pH 2. The dominant form of Cr(VI) is HCrO4 “ and the surface of adsorbent is charged positively at a lower pH values. It is found from the kinetic studies that the adsorption rate of Cr(VI) is faster for the initial 100 min and then it is constant in the later part of adsorption. With the increase of adsorbent amount, the percentage removal of Cr(VI) increases. The percentage removal decreases with an increase in the initial Cr(VI) concentration. The equilibrium adsorption data are tested with various isotherm models such as Langmuir, Freundlich. The equilibrium data are best fitted with Langmuir Freundlich and Dubinin–Radushkevich isotherm models. The maximum adsorption capacity is obtained with the application of Langmuir isotherm model as 10.638 mgg”1, which is comparatively good adsorption capacity. The kinetics of Cr(VI) biosorption using *Azolla Filiculoidus* as an adsorbent is explained by the second-order kinetic model. The thermodynamic results show the feasibility, spontaneous and exothermic nature of biosorption of chromium(IV) onto *Azolla Filiculoidus*. Based on the results, it can be concluded that the *Azolla Filiculoidus* is an effective biosorbent for the removal of Cr(VI) from aqueous medium.

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