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Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*

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Abstract

This paper reports the research findings of a laboratory-based study on the removal of Cr(VI) from solution using the biomass (both roots and stems) of the non-living *Eichhornia Crassipes* as a biosorbent. The effect of physico-chemical parameters like pH, sorbent dose, contact time and initial concentrations were investigated. Although the Lagergren first order model was applicable to some of the data, the pseudo-second-order reaction model was applicable to all data. The Freundlich isotherm was found to represent the measured sorption data well. The Fourier transform infrared spectrometry showed that the hydroxyl group was the chromium-binding site within pH range (pH 1–5) where chromium does not precipitate. The results indicated that the biomass of *E. Crassipes* is suitable for development of efficient biosorbent for the removal of chromium from wastewater of chemical and allied process industries.

Keywords: Cr(VI) removal; Waste water treatment; Biosorption; Heavy metal removal; Water pollution control; Adsorbent

1. Introduction

Biosorption is currently gaining considerable importance as an alternative technology for the treatment of heavy metal waste. Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake [1]. A wide range of non-living biomass like bark [2], lignin [3], peanut hulls [4] as well as living biomass like fungi [5–7], bacteria [8,9], yeast [10,11], moss [12], aquatic plants [13] and algae [14,15] has been used as biosorbents. The major advantages of biosorption over other conventional treatment methods are: (1) low cost, (2) high efficiency of metal removal from dilute solutions, (3) no additional nutrient requirements, (4) regeneration of biosorbent, and (5) possibility of metal recovery.

Critical review of literature reveals that the uptake of metal ions by microorganisms can take place in numerous path ways. The mechanisms of biosorption have been discussed by Veglio and Beolchini [16] who reported that there are many ways for the metal to be captured by cells. Gadd [17] and Brierley [18] reviewed the known ways in which bacteria, fungi and algae can take up toxic metals. The uptake of heavy metal ions can take place by entrapment in the cellular structure and subsequent sorption onto the binding sites present in the cellular structure.

Chromium exists primarily as the soluble, highly toxic Cr(VI) anion and the less soluble, less toxic Cr(III) species. Many facultative and strictly anaerobic bacteria and plants biomass commonly found in soils sediments are capable of reducing Cr(VI) to Cr(III). This method of uptake is independent of the biological metabolic cycle and known as passive uptake. It is worthy to mention that metal uptake by dead cells takes place by the passive mode. The process includes the active participation of several anionic legends present on the biomass, like phosphoryl, carboxyl, carbonyl, sulfydryl and hydroxyl groups to immobilize metal ions [19]. The performance of any biosorbent also depends on biomass characteristics, physico-chemical characteristics of the target metals and the microenvironment of contact solution, i.e., the solution pH, temperature, and interaction with other ions, etc. [20].

Literature survey also reveals that the ability of aquatic plants, both living and dead to remove heavy metals has been studied extensively [21]. These plants are generally seen in aquatic environments like streams, littoral zones of the lakes, drainage systems and wetlands. Some fresh water macrophytes like *Myriophyllum spicatum*, *Potamogeton lucens*, *Salvinia herzogoi*, *Cabomba* sp., *Ceratophyllum demersum* [22] have been investigated for the removal of heavy metals.

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Heavy metal ions are used in various industries due to their technological importance. Chromium is one of them, which is used heavily in chromium leather tanning, chromium plating, metal cleaning and processing, wood preservation and alloy preparation industries. Chromium is present in these effluents chiefly as hexavalent chromium, which is toxic and mutagenic for most organisms. Strong exposure of Cr(VI) causes cancer in digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage [23]. Chromate is also hazardous to fauna and flora in natural aquatic ecosystems [24]. It is therefore, essential to remove Cr(VI) from wastewater before disposal.

Eichhornia crassipes (water hyacinth) is a submerged aquatic plant, found abundantly throughout the year in very large and drainage channel systems in and around the fields of irrigation, which are common in India. The usefulness of the biomass of non-living *E. crassipes* roots in removing metal ions from solution was investigated recently and it was shown that the roots have the potential of being used as a cheap source of biosorbent for metal ions [25–28]. This paper reports the detailed investigation of a laboratory study on the removal of Cr(VI) from solution using the biomass (whole plant) of the non-living *E. crassipes* as a biosorbent.

2. Materials and methods

2.1. Materials

All reagents used were of AR grade either from Merck, Germany or Std. Fine-CHEM Ltd., India.

2.2. Equipment

PH measurements were made using a pH meter (model CT No. CL46, Toshniwal, India). Electrode is immersed in the testing liquid and from the calibration pH is measured very accurately. The chromium was analyzed spectrophotometrically at 540 nm complexing with diphenyl carbazide using an UV absorption spectrophotometer (model SPEKOL 1200). The details about the standard method of measurement have been presented elsewhere [23].

2.3. Biosorbent

Fresh *E. crassipes* species was collected locally and then washed with water to remove dirt and was kept on a filter paper to reduce the water content. After this, the biomass was sun dried for 24 h and then oven dried at 60 °C for 2 h. After that it was reduced to powder form in a ball mill. The biomass was then passed through 52-mesh size screen for use.

2.4. Preparation of synthetic sample

A stock solution of hexavalent chromium (100 mg/l) was prepared in raw water (tap water) with potassium dichromate. All working solutions of varying concentrations were obtained by successive dilution.

2.5. Kinetic studies

Batch sorption studies were conducted in 500 ml conical flasks at pH 5.85 (at natural pH). Dry biomass (0.2, 0.4, 0.6 g) was thoroughly mixed individually with 200 ml of chromium solutions (10 mg/l) and the suspensions were shaken in an incubator-shaker at room temperature (25 °C). Samples of 5 ml were drawn from the conical flask at required time intervals and were filtered through Whattman No. 1 filter paper. The filtrates were then analyzed for residual chromium concentrations in the solution. The constant volume was maintained by keeping ten number of conical flasks at the beginning of the experiments and taking out one by one with a fixed time interval.

Similar procedure is repeated for 20 and 30 mg/l initial concentrations for different biomass doses at required time intervals.

The following numerical relation between contact time and percent removal has been used to find out adsorption kinetics constant for *E. crassipes*:

$$R = a(t)^b \tag{1}$$

where R is the percent removal of chromium, a and b are the constants and t is the contact time in minutes. The linearised form of Eq. (1) can be expressed as

$$\log R = \log a + b \log t \tag{2}$$

2.6. Adsorption isotherms

Batch isotherm experiments were carried out in 250 ml conical flask at 25 °C in an incubator-shaker for 450 min. The dry biomass (0.2 g) was thoroughly mixed with 100 ml of chromium solutions. The isotherm studies were performed by varying the initial chromium concentrations from 10 to 100 mg/l at a pH 1.0. The pH value was adjusted using H_2S0_4 or NaOH before addition of biomass and were maintained throughout the experiment. After shaking the flask for 450 min, the reaction mixture was analyzed for residual chromium concentration.

The biosorption equilibrium uptake capacity for each sample was calculated according to mass balance on the metal ion expressed as

$$q = \frac{V(C_0 - C_e)}{M} \tag{3}$$

where V is the sample volume (l), C_0 the initial metal ion concentration (mg/l), C_e the equilibrium or final metal concentration (mg/l), M the biomass dry weight (g), and q is the biomass biosorption equilibrium metal uptake capacity (mg/g).

3. Results and discussion

3.1. Kinetic studies

The results of percent chromium removal as a function of time at three different sorbent doses have been shown plotted in Fig. 1. This typical figure show that the sorption of Cr(VI) increases (at varying initial concentrations with various sorbent doses of 0.2–0.6 g/200 ml) with time (0–240 min for 10 mg/l ini-

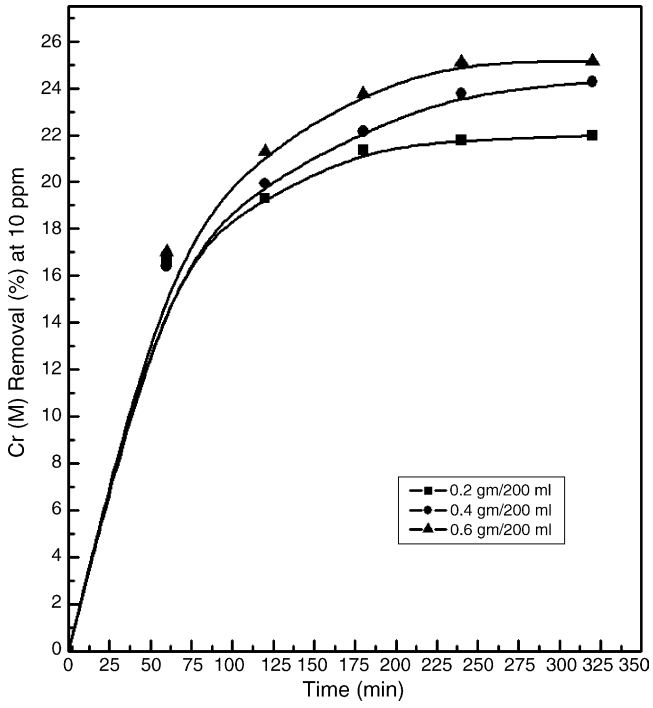

Fig. 1. Effect of percent removal of chromium with time. Initial Cr(VI) concentration = 10 ppm.

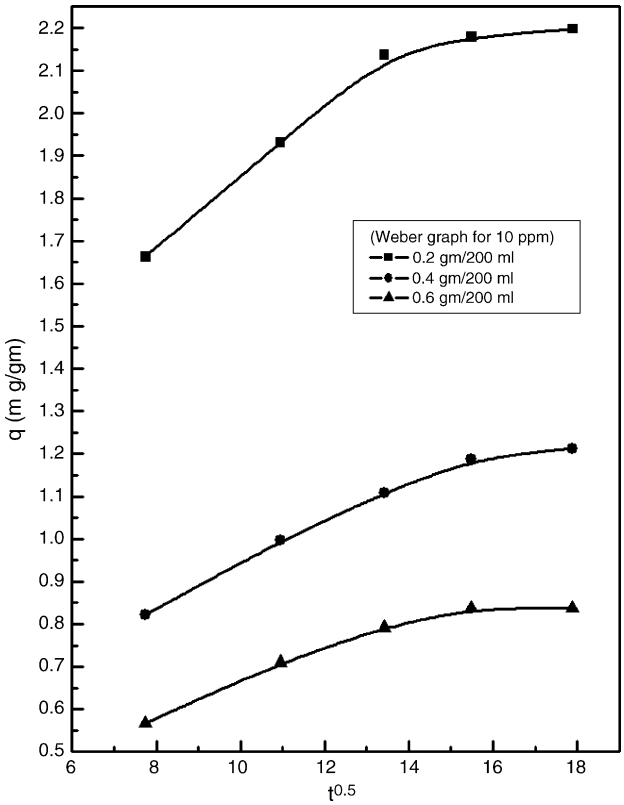

Fig. 2. Weber and Morris plot for 10 ppm initial Cr(VI) concentration

tial concentration) and after that becomes almost constant up to the end of the experiment (360 min for 10 mg/l initial concentration). The removal of Cr(VI) ranges from 15 to 22% with various sorbent doses. It can be concluded that the rate of Cr(VI) binding with the biomass is more at initial stages, which gradually decreases and remains almost constant after an optimum period of 240 min for 10 mg/l initial concentration. Similar plots for 20 mg/l and 30 mg/l initial Cr(VI) concentration as a function of time at three different sorbent doses were plotted, but are not shown in this paper.

From Fig. 1, it can be seen that a non-linear relationship exists in percent removal of Cr (VI) and contact time. Hence Eq. (1) was fitted in the experimental data and constants a and b were calculated and the values are shown in Table 1. The values of a ranges from 5.72 to 19.67. It is clear from the table that with increase in sorbent dose for same initial Cr(VI) concentration, value of a increases, which suggest that with increase in sorbent dose, adsorption capacity also increases. The value of a is highest at Cr(VI) concentration of 30 mg/l with a sorbent dose of 0.6 g/200 ml. The value of b ranges from 0.0219 to 0.252. The low values of b suggest that with increase in time, the rate of percentage removal of Cr(VI) decreases.

Table 1
Adsorption kinetic constants

Initial Cr(VI) concentration (mg/l)	Dose (g/200 ml)	a	b
10	0.2	5.721	0.2474
	0.4	6.16	0.2478
	0.6	6.265	0.252
20	0.2	13.249	0.0753
	0.4	16.12	0.0532
	0.6	18.731	0.0383
30	0.2	12.785	0.0708
	0.4	16.13	0.04374
	0.6	19.67	0.0219

If the movement of the solute from the bulk liquid film surrounding the adsorbent is ignored, the adsorption process for porous solids can be separated into three stages, viz. (1) mass transfer (boundary layer diffusion), (2) sorption of ions onto sites, (3) intra particle diffusion. In many cases there is a possibility that intra particle diffusion will be the rate limiting step and this normally determined by using the equation described by Weber and Morris:

$$K_p = \frac{q}{t^{0.5}} \quad (4)$$

where q (mg/g) is the amount adsorbed at time t and K_p is the intra particle rate constant (mg/g min$^{0.5}$).

Fig. 2 shows that the relationships for *E. crassipes* and chromium system for different initial concentrations at a particular sorbent dose are not linear over the entire time range, indicating that more than one process is affecting the adsorption. This type of non-linearity has been reported previously by Mohanty et al. [23]. The slope of the initial linear portion can be used to derive the intra particle rate constant, K_p. The various values of K_p are shown in Table 2. The rate constant for intra particle diffusion increased with increasing chromium concentration.

Table 2
Weber and Morris equation constants

Initial Cr(VI) concentration (mg/l)	Dose (g/200 ml)	K_p
10	0.2	0.0093
	0.4	0.0109
	0.6	0.0053
20	0.2	0.0145
	0.4	0.0143
	0.6	0.00224
30	0.2	0.0231
	0.4	0.0103
	0.6	0.0042

In many cases, the kinetics of adsorption by any biological material has been tested for the first order expression given by Lagergren. However, it has also been shown that a pseudo-second-order approach can sometimes provide a better description of the adsorption kinetics. The first order Lagergren equation is

$$\log(q_e - q) = \log q_e - \left(\frac{K_d}{2.303}\right) t \quad (5)$$

The pseudo-second-order equation is

$$\frac{t}{q_t} = \left[\frac{1}{2} K' q_e^2\right] + \frac{t}{q_e} \quad (6)$$

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time t (min), K the first-order reaction rate constant of adsorption (per min), and K' the pseudo-second-order rate constant of adsorption (mg/g min).

It was found that although the first-order equation was suitable for some of the data; it was not applicable to all the results. Therefore, no further consideration was given to it. The pseudo-second-order reaction model, however, was applicable to all the data and the results are shown in Fig. 3. The values of the reaction rate constants and correlation coefficients are listed in Table 3. The pseudo-second-order kinetics found in this study is supported by the findings of many other researchers [28–31].

Table 3
Pseudo-second-order constants

Initial Cr(VI) concentration (mg/l)	Dose (g/200 ml)	q_e	K'
10	0.2	1.0	100.124
	0.4	1.3782	34.95
	0.6	2.533	5.7134
20	0.2	1.6942	15.193
	0.4	2.444	6.046
	0.6	4.739	1.266
30	0.2	2.3696	3.755
	0.4	3.612	3.06
	0.6	6.985	0.55

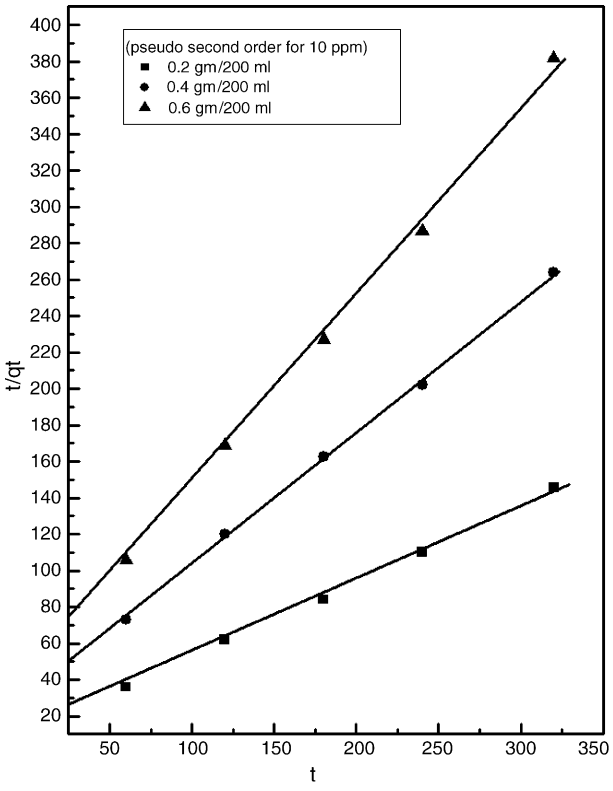

Fig. 3. Pseudo-second-order reaction model for initial Cr(VI) concentration = 10 ppm.

3.2. Sorption as a function of dosage

The effect of sorbent dosages on the percentage removal of chromium has been shown in Fig. 4. It followed the predicted pattern of increasing percentage sorption as the dosage was increased and reaches a saturation level at high doses. This is probably because of the resistance to mass transfer of Cr(VI) from bulk liquid to the surface of the solid, which becomes important at high adsorbent loading in the conical flask in which the experiment was conducted. The removal of chromium increased from 73 to 89% (for initial concentration of 10 mg/l), 70–88% (for initial concentration of 20 mg/l), 67–87% (for initial concentration of 30 mg/l), when the dosage was changed from 0.05 to 0.2 g/100 ml. The increase in removal efficiency is quite obvious, as the doses of adsorbent increases, the surface area available is more to adsorb the Cr(VI).

3.3. Effect of pH

Earlier studies have indicated that solution pH is an important parameter affecting biosorption of heavy metals. Fig. 5 shows the removal of Cr(VI) as a function of pH at various sorbent doses. From this figure it is clear that the percent removal of Cr(VI) is maximum for all the concentrations at pH 1.0 and thereafter decreases with further increase in pH.

This behavior can be attributed to the presence of a large number of surface functional groups on the cell wall of the

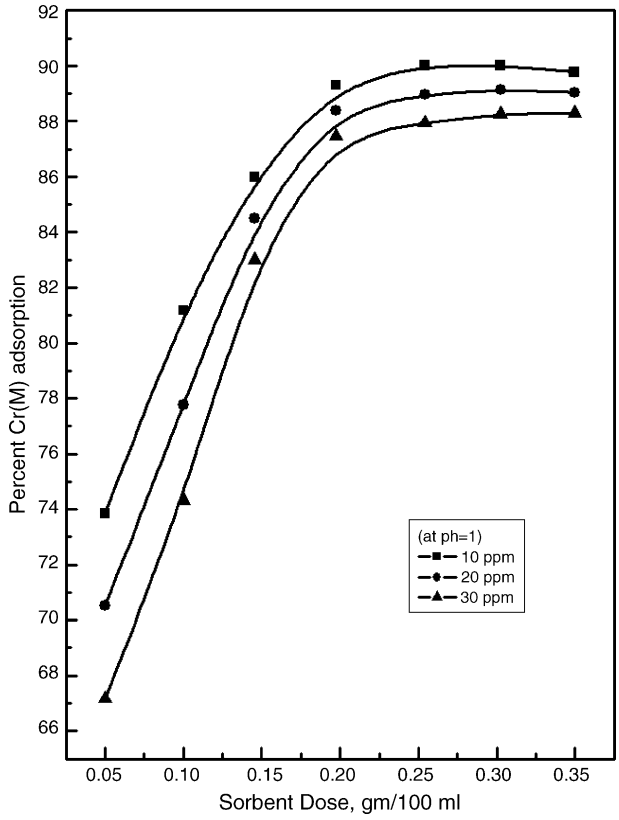

Fig. 4. Effect of sorbent dosages on the percentage removal of chromium.

biomass. The pH dependence of metal adsorption can largely be related to type and ionic state of these functional groups and also on the metal chemistry in solution [27]. At pH 1.0 (maximum adsorption) the negatively charged chromium species (chromate/dichromate) bind through electrostatic attraction to positively charged functional groups on the surface of biomass cell wall because at this pH more functional groups carrying positive charges would be exposed. But at lower pH values, it seems that, the number of functional groups carrying a net negative charge is more, which tends to repulse the anions. However, from the figure, it is clear that there is removal at lower pH values, but the rate of the removal is quite slow. Hence, it can be concluded that at lower pH values, other mechanisms like physical adsorption could have taken an important role and ion exchange mechanism might have reduced [32].

3.4. Adsorption isotherms

The chromium sorption isotherm followed the linearized Freundlich model. The relation between the metal uptake capacity q_e (mg/g) of biomass and the residual metal ion concentration C_e (mg/l) at equilibrium is given by

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \quad (7)$$

where the intercept $\ln k$ is a measure of adsorbent capacity, and the slope $1/n$ is the sorption intensity. The values of the constants k and $1/n$ for different adsorbent doses were calculated from Fig. 6 and are presented in Table 4. Since the

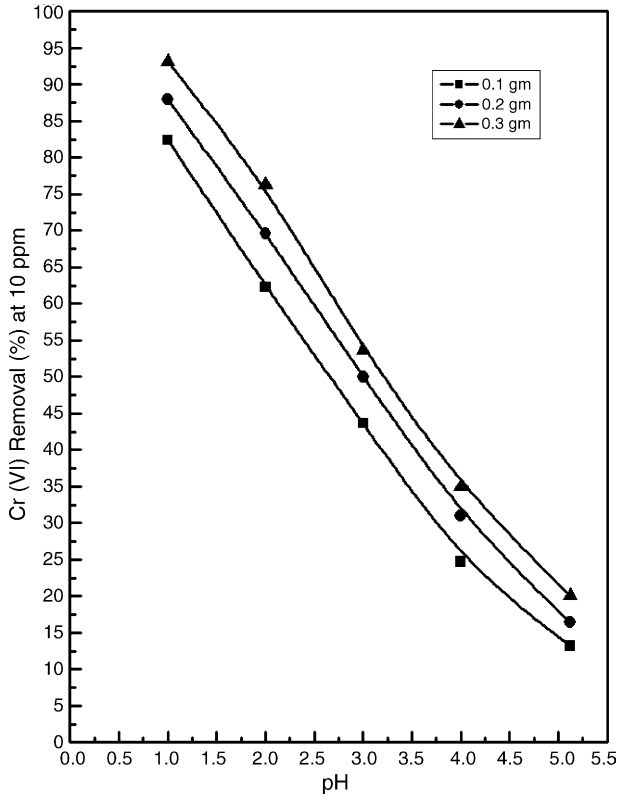

Fig. 5. Effect of pH for initial Cr(VI) concentration = 10 ppm.

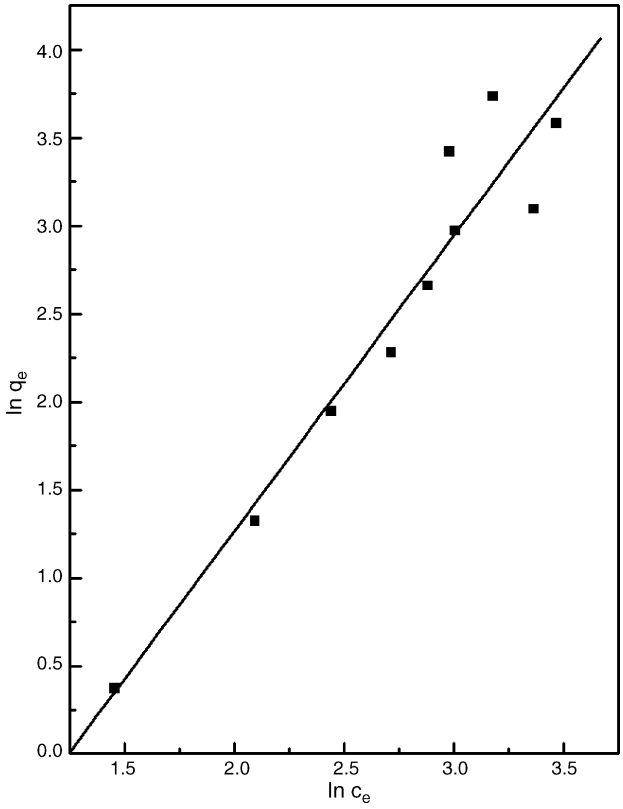

Fig. 6. Freundlich adsorption isotherm.

Table 4
Freundlich isotherm constants

Sorbent dose (g/100 ml)	K	$1/n$
0.1	9.0226	0.438
0.2	6.292	0.363
0.3	5.3942	0.313

values of $1/n$ are less than 1, it indicates a favorable adsorption.

3.5. Fourier transform infrared analysis (FT-IR)

To confirm the type of functional groups, infrared spectra of the native and chromium-loaded biomass were obtained using a Fourier transform infrared spectrometer (FT-IR 1600, Perkin-Elmer). For the FT-IR study, 5 mg of finely ground biomass was encapsulated in 400 mg of KBr in order to prepare the translucent sample disks. As shown in Fig. 7, the FT-IR spectra of the native biomass displays a number of absorption peaks, indicating the complex nature of the biomass examined. The broad absorption peak around 3419 cm^{-1} is indicative of the existence of bonded hydroxyl group. The peak observed at 1646 cm^{-1} can be assigned to the C=C group. The absorbance spectrum of the chromium-loaded biomass as shown in Fig. 8 was compared with that of native biomass. A significant shift of absorption peaks can be seen when comparing the FT-IR spectra of native and chromium-loaded biomass. This reflects chromium binding to the hydroxyl group.

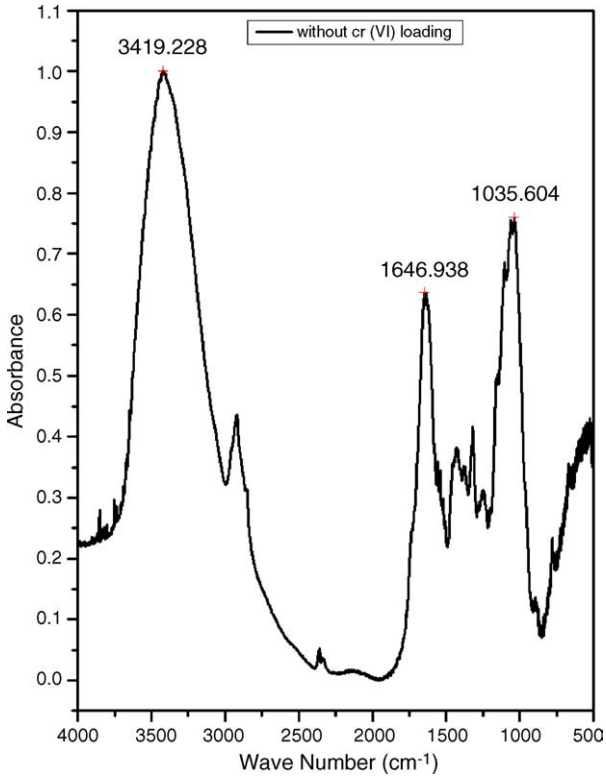

Fig. 7. FT-IR spectra of native biomass.

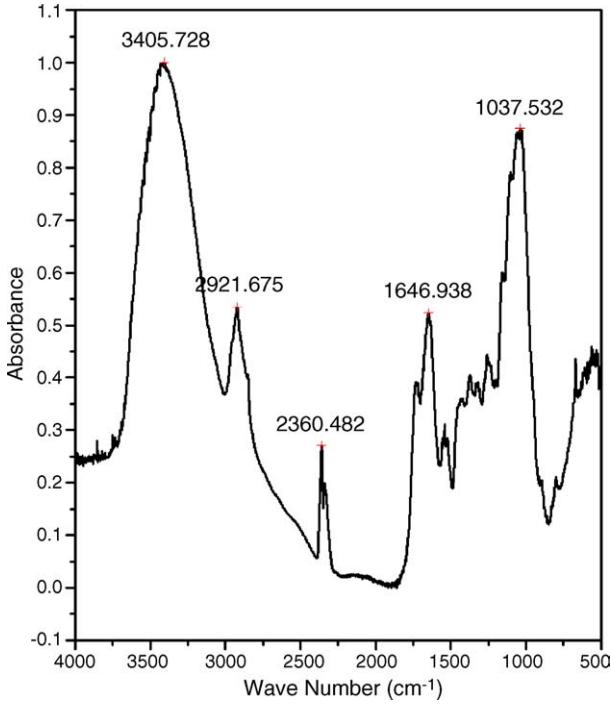

Fig. 8. FT-IR spectra of chromium loaded biomass.

4. Conclusions

A detailed study have been carried out by using the aquatic submerged plant *E. crassipes* as an effective biosorbent for the removal of chromium. Physico-chemical characteristics of the developed biosorbent were characterized. Results showed that the initial part of the adsorption of metal was governed by the diffusion process. The pseudo-second-order reaction model best described the overall adsorption rate. The Freundlich isotherm was found to represent the measured sorption data well. The Fourier transform infrared spectrometry showed that the hydroxyl group was the chromium binding site within pH range (pH 1–5) where chromium does not precipitate. The results indicated that the biomass of *E. crassipes* is suitable for development of efficient biosorbent for the removal of chromium from waste water.

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