Biosorption of Chromium (VI) on Ficus Racemosa Bark Powder

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Abstract

Industrialization, urbanization and development of human civilization in unplanned matter have resulted to disturbances in natural ecosystem. The new industries are being set up as well as migrated in new areas where no surface/ ground water pollution had been observed. Now the presence of toxic metal chromium (hexavalent) as pollutant in surface / ground water has been found at various locations due to the discharge of untreated chromium containing effluents or dumping of solid waste contaminated chromium salts followed by leaching into water bodies in different parts of India and other countries. The presence of this metal in hexavalent form is one of the most important environmental problems due to its health impacts on human. Adsorption is one of the effective techniques for chromium (VI) removal from wastewater. In the present study, adsorbent has been prepared from Ficus racemosa bark and studies are carried out for chromium (VI) removal. The parameters investigated in this study are contact time, adsorbent dosage, temperature, variable initial chromium (VI) concentration and pH. The adsorption process of chromium (VI) is tested with Linear, Langmuir and Freundlich isotherm models. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 25.9 mg/g at 30°C at a solution pH of 7. The adsorption of chromium (VI) was found to be maximum up to 83.78% at low values of pH in the range of 1-3.The contact time of 60 min resulted to the 36.82% adsorption of metal in 50mg/L solution using adsorbent dose of 1g/L and can used for removal of chromium (VI) from the polluted water as a very low cost biosorbent. The Fourier transform infrared spectroscopy (FT–IR)

technique was also carried out to correlate the adsorption sites of biosorbent and hexavalent chromium.

Key Words: Biosorption, Hexavalent Chromium, Ficus racemosa bark

Introduction

Presence of chromium (VI) in surface and ground water is hazardous to the environment because of its toxicity, pollution effect on our ecosystem, possible human health risk and due to its high potentiality to contaminate drinking water sources [1]. In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement. Among the different heavy metals, chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters [2]. The two major sources of contamination are tanneries (trivalent chromium) and electroplating, metal finishing industries (hexavalent chromium). Chromium occurs most frequently as Cr (VI) or Cr (III) in aqueous solutions [3]. Both valency of chromium are potentially harmful but hexavalent chromium poses a greater risk due to its carcinogenic properties, most water soluble and easily enters the living cells [3]. Hexavalent chromium, which is primarily present in the form of chromate CrO_4^{--} and dichromate $Cr_2O_7^{--}$, has significantly higher levels of toxicity than the other valence states [4].

In general, chromium (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, cementation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, and evaporation, etc. [5]. These methods are, however, cost intensive and are unaffordable for large scale treatment of wastewater that is rich in chromium (VI). Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular [6,7]. Other commercial adsorbents are recently reported to have been used in industries, although their versatility and adsorption capacity are generally less than those of activated carbon [8].

Conventional methods for removing Cr (VI) ions from industrial wastewater include reduction [9], reduction followed by chemical precipitation [10], adsorption on the activated carbon [11], solvent extraction [12], cementation, freeze separation, reverse osmosis [13], ion-exchange [14] and electrolytic methods [15]. These methods have found limited application because they often involve high capital and operational costs. Biosorption is an effective and versatile method for removing chromium. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Most of the low cost biosorbents have the limitation of low sorptive capacity and thereby for the same degree of treatment, it generates more solid waste (pollutant laden sorbent after treatment), which poses disposal problems. Therefore, there is need to explore low cost biosorbent having high contaminant sorption capacity. Several recent publications utilized locally available

adsorbents [16, 17] and agricultural byproducts [18] for heavy metal removal. However, the literature is still insufficient to cover this problem and more work and investigations are needed to deal with other locally available and cheap biosorbents to eliminate Cr (VI) from industrial compositions and characteristics.

Ficus racemosa is a common tree in tropical countries. It is grown mainly for its fruits and wood. The astringent nature of the bark has been employed as a mouth wash in spongy gum and also internally in dysentery, menorrhagia and haemoptysis [19]. The bark is antiseptic, antipyretic and vermicidal, and the decoction of bark is used in the treatment of various skin diseases, ulcers and diabetes. It is also used as a poultice in inflammatory swellings/boils and regarded to be effective in the treatment of piles, dysentery, asthma, gonorrhea, gleet, menorrhagia, leucorrhea, hemoptysis, urinary diseases and plant is a rich source of Glycosides, Phenols & Flavonoids [20].

Literature survey reveals that in most of the peer reviewed journals the adsorption study of Cr(VI) with Ficus racemosa bark as an biosorbent has not been investigated and this is the first such study undertaken by the authors. Based on their efficacy, Ficus racemosa bark was selected for further study. The effect of pH, contact time, temperature, initial hexavalent chromium concentration, variable adsorbent doses and adsorption equilibrium were investigated. FTIR of adsorbent and chromium adsorbed adsorbent was also carried out for spectral studies.

Methods & Material

All the chemicals used were of analytical reagent grade. The standard stock Cr(VI) solutions was prepared by weighing 2.8287 g of Potassium dichromate in one liter double distilled water and it was further diluted to desired concentrations containing 20, 40, 50, 60, 80, 100, and 200 mg/L of chromium (VI) in aqueous phase standard solutions. The estimation of hexavalent chromium was carried out by using Diphenyl carbazide method as per standard methods [21]. Shimadzu UV-VIS Spectrophotometer at 540 nm was used for measurement. The Cr (VI) loadings on sorbents were computed based on mass balance through loss of metal from aqueous solution. The pH of solution was maintained using 0.5 N HCl and 0.5 N NaOH solutions. The temperature of the solutions was maintained by using temp. regulatory oven. The FTIR of the sorbent (Ficus racemosa bark) and chromium loaded was carried out using Bruker FTIR Spectrophotometer for absorption peaks.

Preparation of Biosorbent (Ficus racemosa bark powder)

The sorbents used was Ficus racemosa bark powder. The materials were obtained from local area. Material was washed, dried and then pulverized in pulverizer and air-dried in the sun for five days. After drying, the materials were kept in air tight plastic bottles. The powdered material was used as such and no pretreatment was given to the materials. The particle size was maintained in the range of 212–300 µm (geometric mean size: 252.2 µm).

Screening of Biosorbent

The experiments were carried out in 150 mL borosil conical flasks by agitating a pre-

weighed amount of the Ficus racemosa bark powdered adsorbent with 10 - 100 mL of the aqueous chromium (VI) solutions for a predetermined period at 10-40°C in an ice bath / oven. The Biosorbent doses were maintained 1-5 g/L for different experiments. The adsorbent is separated with whatmann filter paper no 41. Adsorption isotherm study is carried out with different initial concentrations of chromium (VI) from 20 to 100 mg/L with the adsorbent dosage of 1-5 g/L. The effect of pH on Cr (VI) biosorption was studied at 30^0C with chromium (VI) concentration of 50 mg/L and an adsorbent dosage of 4 g/L. The effect of adsorbent dosage is studied by varying the adsorbent amount from 1 g/L to 5 g/L with chromium (VI) concentration of 50 mg/L. The effect of temperature varying from 10- 40°C was studied at Cr (VI) concentration of 50 mg/L and Biosorbent dose of 4 g/L. The time duration 60-300 min was studied at Cr (VI) concentration of 5 mg/L and Biosorbent dose of 4 g/L.

The concentration of free chromium (VI) ions in the solution was determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as complexing agent. The absorbance of the purple-violet colored solution was read at 540 nm after 20 min.

Results and Discussion

In the present study, Ficus racemosa bark has been used for chromium (VI) removal from aqueous solutions. Table-1 shows the adsorbent capacity of various adsorbents. When compared with other non-conventional adsorbents, the results of the present study indicate that adsorbent prepared from Ficus racemosa bark has better adsorption capacity in many cases (biomass residual slurry, Fe(III)/Cr(III) hydroxide, Waste tea, walnut shell), comparable adsorption capacity with(palm pressed-fibers, maize cob, sugar cane bagasse) and lower adsorption capacity with (activated carbon, saw dust) for chromium (VI) ions [15,22-27]. Based on the above results obtained, the effect of various parameters such as equilibrium time, pH, amount of adsorbent etc. has been studied.

Table No. 1: Summary of adsorbent capacity of various adsorbents

Adsorbent	Maximum Adsorbent Capacity, q_m (mg/g)	Reference
Walnut shell	1.33	[26]
Fe(III)/Cr(III) hydroxide	1.43	[27]
Waste tea	1.55	[26]
Biomass residual slurry	5.87	[15]
Tamarind seeds	11.08	[25]
Sugar cane bagasse	13.4	[23]
Maize cob	13.8	[23]
Palm pressed-fibers	15.0	[24]
Ficus racemosa bark	25.9	Present study
Sawdust	39.7	[23]
Activated Carbon (Filtrasorb-400)	57.7	[22]

Effect of Contact Time on Chromium (VI) Adsorption

The effect of contact time up to 300 min. on chromium VI adsorption was studied using Biosorbent dose of 1 g/L and hexavalent Chromium concentration of 50 mg/L.(Fig -1). The extraction process was carried out with standard Cr (VI) 100 mL solution of 50 mg/L in 150 mL conical flask with Biosorbent dose of 1g/L and the concentration of hexavalent chromium in the solution was recorded by filtration through whatmann filter paper followed by development of colour using Diphenyl carbazide at 540 nm in time interval of 10, 20, 30, 60, 120, 180, 240 and 300 minutes. Most of the adsorption takes place in first hour of contact and longer contact time has no effect on extraction of chromium (fig-1)

Fig-1 Effect of contact time on Cr(VI) biosorption

Fig-2 Effect of Increasing Concn of Cr (VI) on biosorption
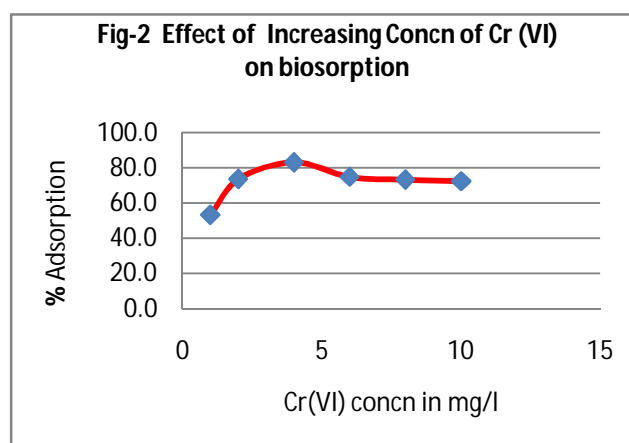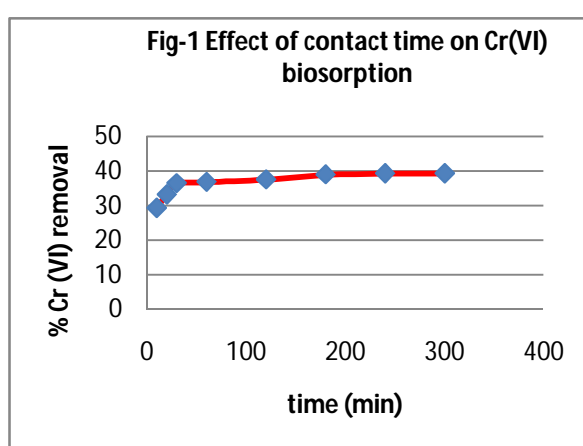
Effect of Increasing Concentration of Cr (VI) on Adsorption

Standard Cr (VI) solutions of 100 mL having initial concentration of 1, 2, 4, 6, 8 and 10 mg/L were treated with Biosorbent 0.1 g dose in each solution. The concentration of Cr (VI) in the solution was determined using the standard methods. The percentage adsorption increases up to 82.9 for 4 mg/L Cr (VI) concentration there after it decreases (figure-2).
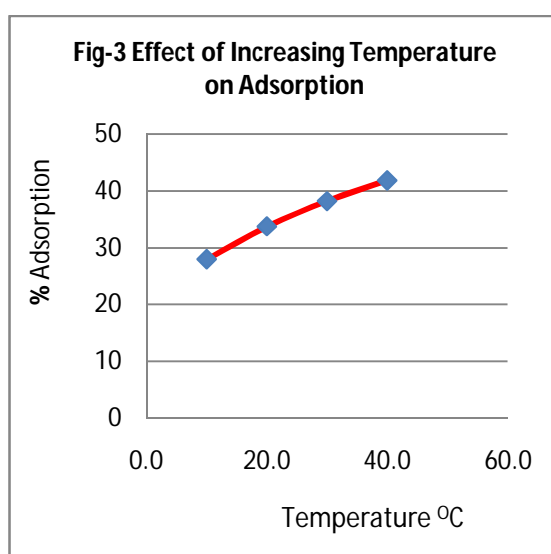
Effect of Temperature on Cr (VI) biosorption
The 100 mL samples of 50 mg/L hexavalent chromium concentration in 150 mL conical flasks were treated with 0.1 g of Biosorbent (Ficus racemosa bark powder) maintained at 10, 20, 30 & 40°C. The solutions were kept for 120 min. with gentle shaking at periodical intervals and the concentration of Cr (VI) was measured in the solution after filtering through Whatmann filter paper and developing the colour using Diphenyl carbazide at 540 nm spectrophotometrically. The percentage biosorption of Cr (VI) was found maximum at 40°C and minimum at 10°C showing an increasing trend with temperature. (Figure-3)
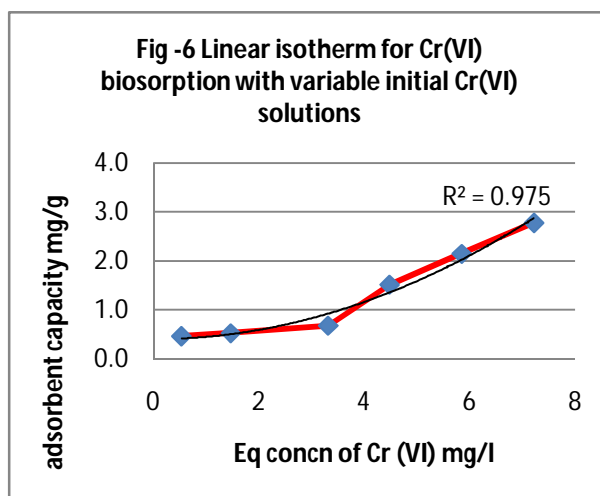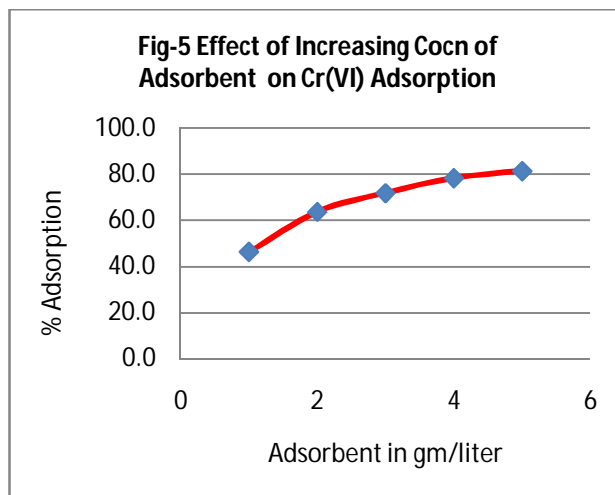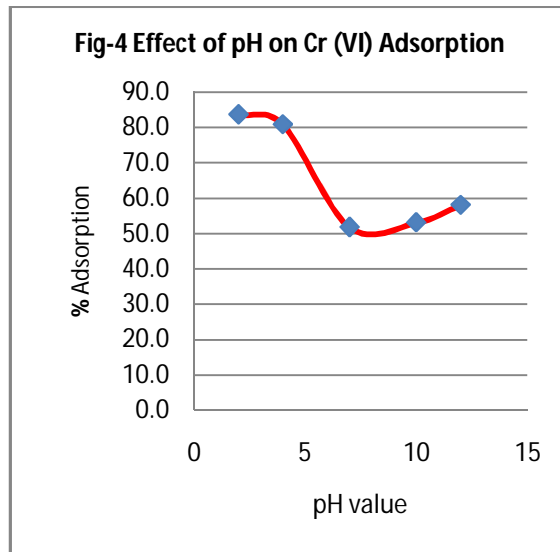
Effect of pH on Cr (VI) biosorption
The experiments using 100 mL of 50 mg/L Cr (VI) solutions for 120 min time and adsorbent dose of 0.1 g were carried out at pH 2, 4, 7, 10 and 12 and the biosorption of Cr (VI) is depicted in figure-4. The acidic medium (pH-2) has been found to show maximum biosorption up to 83.78% of initial chromium (VI) which decreases to 51.8% at neutral (pH-7) and further increases to 58.1% in basic medium (pH-12).(Figure-4)

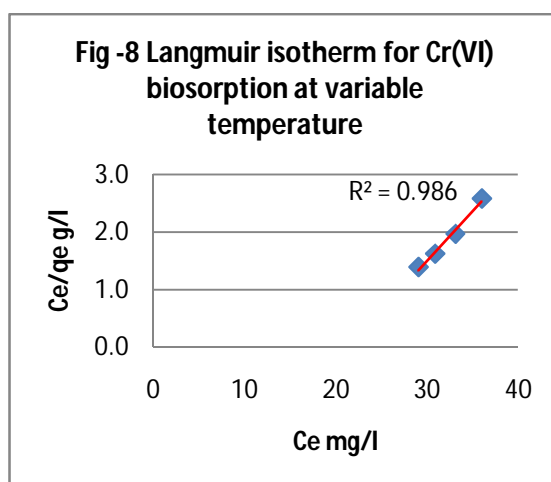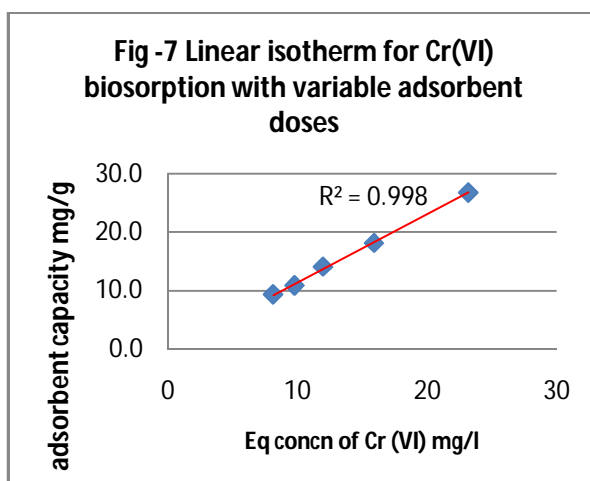**Effect of Biosorbent Concentration on Cr (VI) Adsorption**
The 100 mL samples of 50 mg/L hexavalent chromium concentration in 150 mL conical flasks were treated with 0.1, 0.2, 0.3, 0.4, 0.5 g of Biosorbent (Ficus racemosa bark powder) maintained at room temperature 25 ^{o}C. The solutions were kept for 120 min. with gentle shaking at periodical intervals and the concentration of Cr (VI) was measured in the solution after filtering through Whatmann filter paper and developing the colour using Diphenyl carbazide at 540 nm spectrophotometrically. The percentage biosorption of Cr (VI) was found maximum with Biosorbent dose of 0.5g and minimum at 0.1g showing an increasing trend with increasing Biosorbent. (Figure-5)

Fig-3 Effect of Increasing Temperature on Adsorption

Fig-4 Effect of pH on Cr (VI) Adsorption

Fig-5 Effect of Increasing Cocn of Adsorbent on Cr(VI) Adsorption

Fig -6 Linear isotherm for Cr(VI) biosorption with variable initial Cr(VI) solutions

Adsorption Isotherms

The equilibrium of sorption is one of the important physico-chemical aspects for the evaluation of the sorption process as a unit operation. The sorption isotherm studies are conducted by varying initial concentration of chromium (VI) from 1-10 mg/L , constant adsorbent dosage of 1 g/L ; constant initial concentration of 50 mg/L with varying biosorbent doses of 1-5 g/L and maintaining the temp.(Fig-6 &7). The adsorption isotherm (*q*e versus *C*e) shows the equilibrium between the concentration of chromium (VI) in the aqueous solution and its concentration on the solid (mass of chromium (VI) per unit mass of Ficus racemosa bark). It is evident that adsorption capacity increases with increasing equilibrium chromium (VI) concentrations. Fig. - 6 show that the adsorption capacity increases slowly from 0 to 1.5 mg/g for the equilibrium concentration of 0 to 0.5 mg/L. Further a gradual increase in adsorption Capacity is observed with the increase in equilibrium concentration and it reaches up to 7.2 mg/g for the equilibrium concentration of 2.8 mg/L. The linear isotherm with variable biosorbent (Fig-7) shows a linear increase in adsorption capacity up to 23.2 mg/g for the equilibrium concentration of 26.8 mg/L. In order to model the sorption behavior,

Fig -7 Linear isotherm for Cr(VI) biosorption with variable adsorbent doses

$R^2 = 0.998$

adsorbent capacity mg/g

Eq concn of Cr (VI) mg/l

Fig -8 Langmuir isotherm for Cr(VI) biosorption at variable temperature

$R^2 = 0.986$

Ce/qe g/l

Ce mg/l

adsorption isotherms have been studied. The adsorption process of chromium (VI) is tested with Langmuir and Freundlich isotherm models. Langmuir and Freundlich equations are given in equation (1) and (2), respectively.

$$\frac{Ce}{Qe} = \frac{1}{qmb} + \frac{1}{qm}Ce \tag{1}$$

[where b- Langmuir constant (L/mg), Ce - Concentration of Cr (VI) at equilibrium (mg/L) qe - Amount of Cr(VI) adsorbed by the adsorbent (mg/g) and qm - Maximum adsorption capacity (mg/g)]
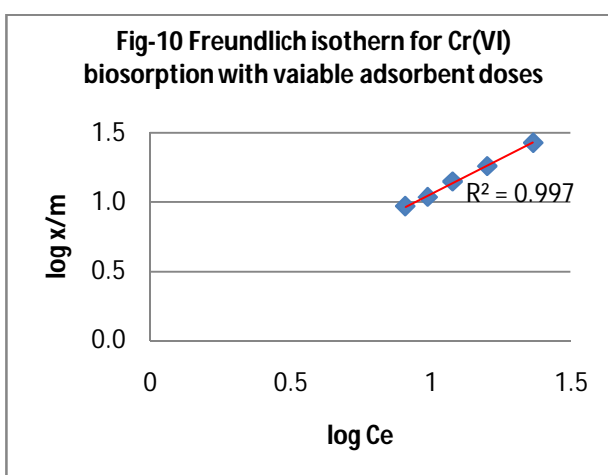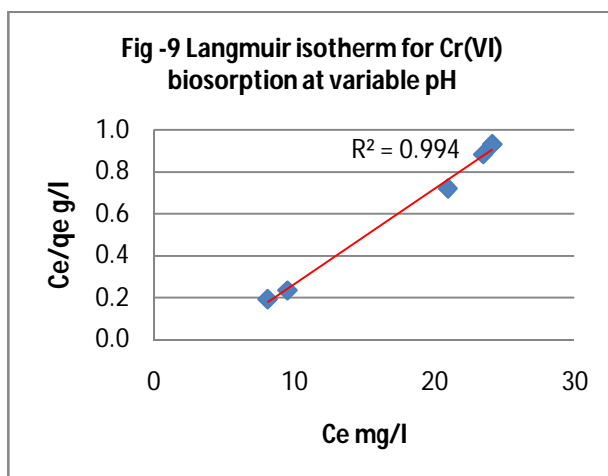
$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{2}$$

[where K_F - Freundlich constant (mg/g) and n - Freundlich constant (L/mg)]

The isotherm data has linearized using the Langmuir equation and shown in Fig.-8 & 9. The regression constants are tabulated in Table-2. The high value of correlation coefficient (R^2 = 0.9864) indicated a good agreement between the parameters. The constant qm, which is a measure of the adsorption capacity to form a monolayer, can be as high as 25.9 mg/g at pH 7. The constant b, which denotes adsorption energy, is equal to 0.1715 L/mg. The same data also fitted with the Freundlich equation and shown in Fig. 10. The regression constants are listed in Table-2. The value of correlation coefficient (R^2 = 0.9978) showed that the data conform well to the Freundlich equation also. The higher values (>1) of 1/n indicates the favorable condition of biosorption by the Ficus racemosa bark powder by hexa valent chromium in aqueous medium.

**Table No. 2:** Isotherm constants for adsorption of chromium (VI) on Ficus racemosa bark.

Langmuir Isotherm			Freundlich Isotherm		
Constants		Correlation	Constants		Correlation
Constants qm (mg/g)	b (L/mg)	Coefficient (R^2)	K_F	1/n	Coefficient (R^2)
25.9	0.1715	0.9864	1.096	1.0165	0.9978
25.9	0.0454	0.9947			

Fig -9 Langmuir isotherm for Cr(VI) biosorption at variable pH

$R^2 = 0.994$

Ce/qe g/l (y-axis)

Ce mg/l (x-axis)

Fig-10 Freundlich isothern for Cr(VI) biosorption with vaiable adsorbent doses

$R^2 = 0.997$

log x/m (y-axis)

log Ce (x-axis)

FTIR spectra of Ficus racemosa bark and Biosorbent with Cr (VI)

The FTIR spectra of Biosorbent and Cr (VI) loaded was carried out using Bruker FTIR Spectrophotometer. The peaks at 618, 633,644, 682, 778, 1030, 1313, 1456, 1508, 1541, 1617, 3222,3618, 3735,3822, 3858 cm^{-1} wave numbers were observed in Ficus racemosa bark while after biosorption with Cr (VI) the peaks become less prominent at 614, 641, 667, 753, 1066, 1457, 1507, 1540, 1698, 2983,3610, 3688, 3828, 3852 cm^{-1} wave numbers (Fig-11) probably due to weak bonding with chromium (VI) atoms. The different functional groups after adsorption of Cr (VI) have shown less prominent absorption in IR spectrum.
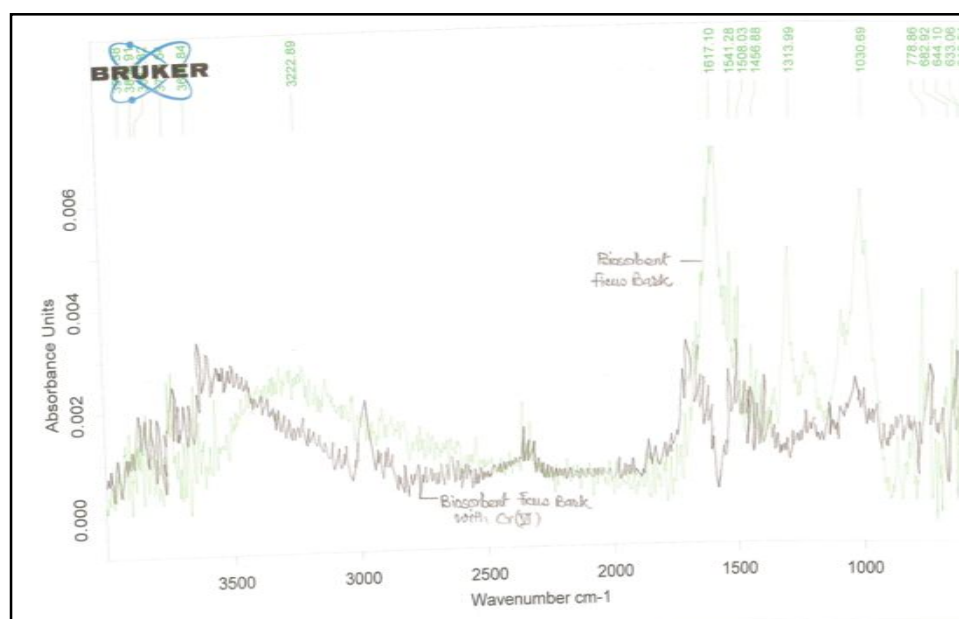
Figure 11 FTIR Spectra of Ficus racemosa bark and adsorbed with Hexavalent Chromium

Conclusions

Following conclusions are made based on present study and scientific information derived from literature-

- Adsorbent prepared from Ficus racemosa bark can be used for removal of chromium (VI) from aqueous solutions due to its remarkable higher biosorption capacity of 25.9 mg/g at pH=7.
- The equilibrium time for the adsorption of chromium (VI) on the adsorbate prepared from Ficus racemosa bark in the present study from aqueous solutions is found to be 30 m.
- The adsorption process of chromium (VI) can be described by Langmuir isotherm as well as Freundlich isotherm models and both isotherm models show a good agreement with the equilibrium data.
- Adsorption of chromium (VI) on Ficus racemosa bark yielded maximum adsorption capacity of 25.9 mg/g at solution pH of 7 and temperature 30 °C.
- Removal of chromium (VI) increases with increase of adsorbent dosage.
- The maximum adsorption of chromium (VI) took place in the pH range 1-3.
- The increase in temperature increases the biosorption up to 40 °C, showing the chemisorptions behavior.
- The maximum adsorption takes place in 30 minutes and further increase in duration of contact time has negligible effect.
- The higher values of Freundlich constant (>1) for 1/n indicates the favorable condition of biosorption by the Ficus racemosa bark by hexa valent chromium in aqueous medium.

Acknowledgement

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