

Abatement of heavy metal on the surface of newly prepared adsorbent.

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ABSTRACT

Chromium (VI) is one of the most strategic and critical material having wide range uses in various industries. Chromium and its compounds are widely used in electroplating leather tanning, dyeing, metal processing, wood preservatives etc. These industries produce large quantities of toxic waste water effluents. The maximum concentration limit for chromium discharge into inland surface water is 0.1mg/l and it should not exceed to 0.05mg/l in potable water. The present research article reports the characterization and use of activated carbon derived from the bark of *Tamarindus indica* (TIAC) as a potential adsorbent for removal of hexavalent chromium from aqueous solution. SEM analysis proved the mesoporous nature of the material under investigation. The batch experiment was carried out to study the effect of significant process parameters such as pH, contact time and adsorbent doses. The maximum adsorption efficacy for Cr(VI) removal by TIAC was found at pH 5.5, 5 gm/lit of adsorbent dose and 135 min contact time. The adsorption data were found to be well fitted for Freundlich isotherm. The kinetic data were analyzed using 1st order Lagergren kinetic. The Gibb's free energy was determined and found to be -2.746 KJ/mole for Cr(VI) removal from industrial waste. The negative value of ΔG° indicates the feasibility and spontaneous nature of adsorption. This investigation verifies that TIAC, a mesoporous material can be successfully used as an excellent sorbent material for removal of hexavalent chromium from contaminated water and thus can be applied in wastewater treatment.

Keywords: Adsorption, Hexavalent chromium, *Tamarindus indica* bark, Freundlich isotherm, Gibb's free energy.

INTRODUCTION

The use of bio-adsorbents derived from bio-materials for the removal of pollutants from industrial waste effluent during recent past has shown interesting results and generated the new concept in of pollution. Pollution of water has its origin mainly in urbanization, industrialization and increase in human population observed during the past one and half century. Several industries like sugar factories, dairies, paper and pulp, tanneries, metal plating, fertilizer industries etc. releases substantial quantities of toxic heavy metals in water. The removal of heavy metal contaminants from aqueous solution is one of the most important environmental concern because metals are bio-refractory and are toxic to many life forms[1]. Metals which are significantly toxic to human beings and ecological environment, include chromium, copper, lead, mercury, cadmium, nickel, iron etc[2]. Some of these are capable of being assimilated, stored and concentrated in organisms[3-4].

Chromium(VI) is one of the most toxic and carcinogenic form for bacteria, plants and animals. Chromium and its compound are widely used in the chromplating, leather tanning, metal processing, wood preservatives etc[5-6]. The maximum concentration limit for chromium discharge into inland surface water is 0.1mg/l and it should not exceed to 0.05mg/l in potable water. A number of treatment methods have been employed for the removal of chromium from aqueous solution. The usual methods include chemical reduction, Nanofiltration[7], ion exchange[8], precipitation and adsorption[9-10]. Amongst all of these, adsorption onto commercial activated carbon is well-established and effective technique. Several research workers used different low cost adsorbents from agriculture wastes such as coconut coir pith, sawdust, rice husk, banana pith, cotton seed hulls, apples waste, sugarcane bagasse, peanut hull etc. for the removal of Cr(VI) from water and waste water. In spite of several researches adopted for various low cost adsorbents, there is still a need to develop suitable & more economical adsorbents for the removal of Cr(VI) from polluted water. The present studies were carried out for the removal of Cr(VI) from aqueous solution

using activated carbon derived from bark of *Tamarindus indica* which one of the largest families of flowering plant belong to *Fabaceae* family. It is extensively used in Ayurveda, Unani and Haemeopathic medicine and has becomes a cynosure of modern medicine[11]. The self-prepared sorbent was characterized by FTIR and Scanning Electron Microscopy (SEM) studies. Batch isothermal equilibrium method was conducted at 303K to evaluate the efficiency of newly synthesized bio-sorbent for removal of Cr(VI) from the aqueous solution. Experiments were carried out to study the effect of pH, adsorbent dosage, contact time and initial Cr(VI) concentration. The newly synthesized composite have been proved to be very good adsorbent which can be successfully used for removal of carcinogenic hexavalent chromium from aqueous solution.

METHODOLOGY

Chemicals

The chemicals used in the investigation were of either analytical or chemically pure grade.

Preparation of Activated Carbon from the bark of *Tamarindus indica* (TIAC):

The bark of *Tamarindus indica* tree was collected from the local area. The bark was cut into small pieces, washed with tap water to remove the sand particles and then treated with formaldehyde to avoid release of any colour of bark into aqueous solution. Then, it was washed several times with deionized water and sun dried for 6 days. After drying, the bark was subjected to pyrolysis process for carbonization using Muffle Furness at 800-900°C for 7 to 8 hrs so that volatile constituents were removed and residue was converted into a char. The char was then subjected to microwave activation in microwave oven. The input power of microwave equipment was set at 360 W for 30 min. The resulting activated carbon particles were ground and sieved in 120-200 mm size. This activated carbon was then washed with double distilled[12].

Characterization of TIAC

Characterization of TIAC was done by FTIR (Fig.1) and SEM (Fig.2)

Adsorption Studies

Standard working solution were prepared by progressive dilution of stock solution of Cr(VI). Removal of Cr(VI) using TIAC was carried out by batch equilibrium method. The effect of various parameters such as effect of pH, contact time, adsorbent dosage and initial Cr(VI) concentration were studied, taking 25 mg/l of initial Cr(VI) concentration and 5 g/l of adsorbent dose. The effect of adsorbent doses was studied by varying them from 0.5-10g/l. The effect of initial Cr(VI) concentration was studied by changing concentration from 10-100mg/l with adsorbent dose of 5g/l at 30°C. The residual concentrations were measured using atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Characterization of TIAC

FTIR spectrum of PPAC is shown in Fig.1. The band at 3445.27cm⁻¹ indicates presence of the free hydroxyl group. The band at 2662.41cm⁻¹ is due to the C-H bond stretching of aldehyde (C-H=O Group). The absorption at 1633.30cm⁻¹ is due to the C=O stretching mode of the amido (CONH) group. The two characteristic bands appeared at 1005.85cm⁻¹ and 911.73cm⁻¹ (skeletal vibration involved in C-O-C stretching) prove the presence of saccharide structure. The peaks at 532.07cm⁻¹ and 464.47cm⁻¹ corresponds to N-H bending.

Fig.2 represents SEM micrographs of TIAC. SEM image has been obtained using an accelerating voltage of 20kV at X1500, magnification. High magnification SEM micrographs clearly reveal that the wide varieties of pores are present on the surface of PPAC accompanied with fibrous structure. It can also be noticed that there are holes and cave type openings on the surface of the adsorbent, which would have created more surface area available for adsorption. The size of holes and caves was found to be in the range 1- 10µm.

Effect of pH

The effect of pH on the adsorption of Cr(VI) by TIAC was studied at pH 1 to 8. From fig.3 it is clear that the removal of Cr(VI) increases with increase in pH from 1.0 to 5.0 and it is optimum at 5. The percent of adsorption increases from 65 to 95 as pH was

increased from 1 to 5. The percentage of adsorption decreases steadily to 83% when pH increased above 5.0 and it was further decreased to 70% as pH was raised to 8.

Effect of Contact Time

Adsorption experiments were conducted as a function of contact time and results have shown in Fig.4. It can be observed that Cr(VI) removal ability of TIAC increased with increase in contact time before equilibrium was reached. Other parameters such as dose of TIAC, pH of solution and initial concentration were kept optimum. It can be seen from fig.4 that Cr(VI) removal efficiency increased from 25 to 96% when contact time was increased from 10 to 180 min. Optimum contact time for TIAC was found to be 135 min. Cr(VI) removal efficiency remained nearly constant after 135 min i.e. equilibrium time.

Effect of Adsorbent Dosage

Fig.5 shows the effect of dosage on the removal of Cr(VI) which was studied by varying the amount of TIAC from 0.5 to 10g/l while keeping other parameters (pH, contact time and initial concentration) constant. It is clear from the figure that percentage removal of Cr(VI) increased with the increase in TIAC doses and it was found to be maximum i.e. 95% at the dose of 5g/l. This is due to availability of more surface area. It indicates that by increasing the TIAC dosages, the adsorption efficiency for Cr(VI) removal increases. After 5g/l dose of TIAC, the adsorption efficiency remain constant because the maximum adsorption set in and amount of Cr(VI) present in the solution bounded to adsorbent remains nearly constant after this dose.

Adsorption Isotherm

Adsorption isotherm studies are very important for the designing of proper adsorbent. Isotherm represents the amount of solute adsorbed per unit mass of adsorbent as a function of equilibrium concentration in bulk solution at constant temp. The equilibrium data obtained were fitted to Langmuir & Freundlich isotherms. Linear form of Langmuir equation

$$\frac{1}{x} = \frac{1}{x_m} + \left(\frac{1}{C_e}\right) \left(\frac{1}{b x_m}\right)$$

Where X is the amount of solute adsorbed in mg, m is the mass of adsorbent, C_e is equilibrium concentration of solute (mg/lit), X_m is amount of solute adsorbed per unit wt. of adsorbent. b is constant related to heat of adsorption or Langmuir affinity constant (M^3/mole).

Freundlich equation indicate adsorptive capacity, x/m is function of equilibrium concentration of solute. The Freundlich equation is expressed as

$$\log \frac{x}{m} = \log k_f + \frac{1}{n} \log C_e$$

The thermodynamic equilibrium constant K_c was obtained at $32 \pm 1^\circ\text{C}$

$$K_c = \frac{C_a}{C_e}$$

C_a = concentration of Cr(VI) on adsorbent at equilibrium in mg/lit and C_e = equilibrium concentration of Cr(VI) in solution gm/lit.

Initial concentration of Cr(VI) tested was 100ppm for both, synthetic effluent as well as waste water, at an adsorbent dosage of 5 g/lit. The adsorption followed Freundlich isotherm. Freundlich plot is shown in Fig 6. The graph show that the process is followed 1st order mechanism. The K_f & n values as calculated from fig 6. For synthetic effluent having 100ppm of

Cr(VI) was found out to be as 4.365 mg/g. and 3.759mg/g respectively. Waste water having 100ppm of Cr(VI) at 5.5 pH has K_f & n values as 15.72 mg/g. and 7.580 respectively. The value of 'n' greater than 1 indicates that the adsorption on TIAC is favorable and though the capacity is slightly reduced at the lower equilibrium concentration. The higher value of adsorption capacity obtained with TIAC sorbent indicates that it can be used for the treatment of chromium waste.

The Gibbs free energy (ΔG°) for the adsorption process was obtained using equation.

$$\Delta G^\circ = -RT \ln K_c^\circ$$

Value of ΔG° & thermodynamic constant K_c° for various systems are show in table no. 2

The Gibbs free energy gives idea regarding the spontaneity of the adsorption process. Higher negative values indicate more favorable adsorption process. The -ve value of ΔG° for the system under investigation confirms feasibility of the adsorbent and spontaneity of adsorption. Lower pH is found suitable for better adsorption of Cr(VI). For waste water sample more than 89% of Cr(VI) removal was observed. It is noticed that there is negligible influence of presence of other metal ions on adsorption of Cr (IV). Thus TIAC is more selective for chromium adsorption.

Table 1: Adsorption rate constant for TIAC for various System.

Con. Of Cr(VI)	pH	Rate Constant K_{ads} (min^{-1})	R^2
100 ppm Cr(VI)	2.0	1.780×10^{-2}	0.9623
100 ppm Cr(VI)	3.0	1.091×10^{-2}	0.9554
100 ppm Cr(VI)	4.7	0.912×10^{-2}	0.9997
100 ppm Waste Water	4.5	4.12×10^{-3}	0.9510

Table 2: Thermodynamic parameter for the adsorption of Cr(VI) by TIAC

Effluent	Conc. Of Cr(VI)	pH	Equilibrium Constant K_c	Gibbs free Energy ΔG° KJ /mole
Pure solution	100 Cr(VI)	2	7.50	- 5.109
Pure solution	100 Cr(VI)	3	3.10	- 2.867
Pure solution	100 Cr(VI)	4	1.20	- 0.462
Waste Water	100 Cr(VI)	4.7	2.95	- 2.746

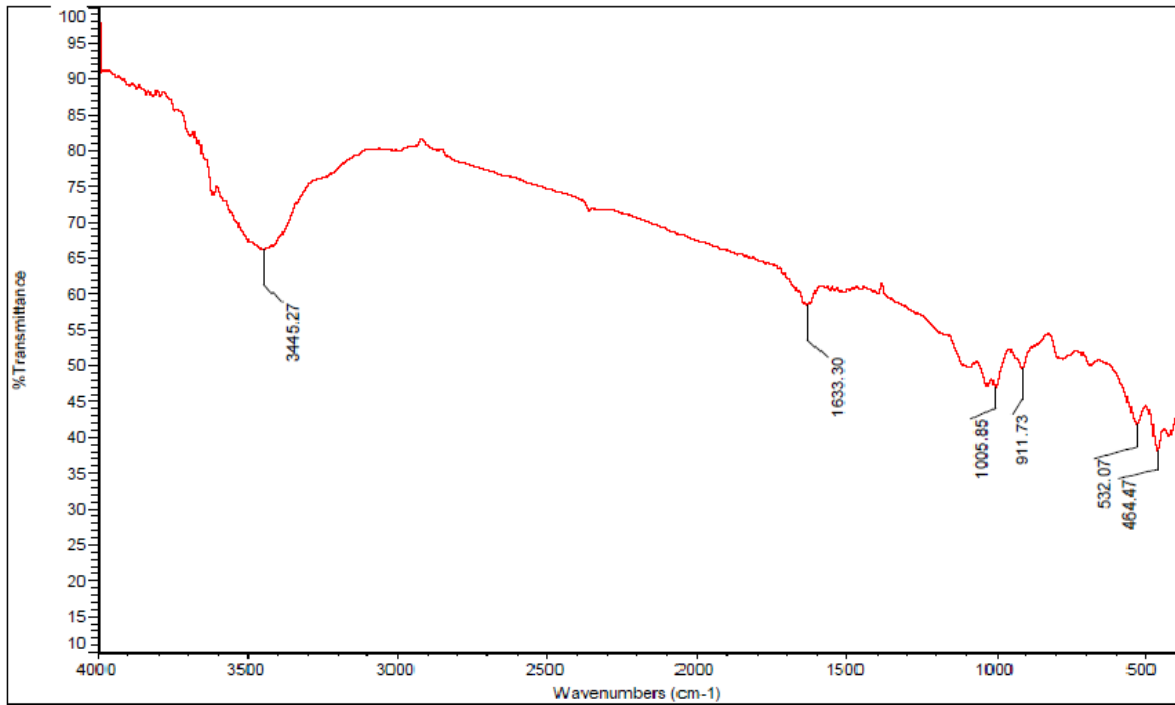


Fig.1 FTIR Spectrum of *Tamarindus indica* Activated Carbon (TIAC)

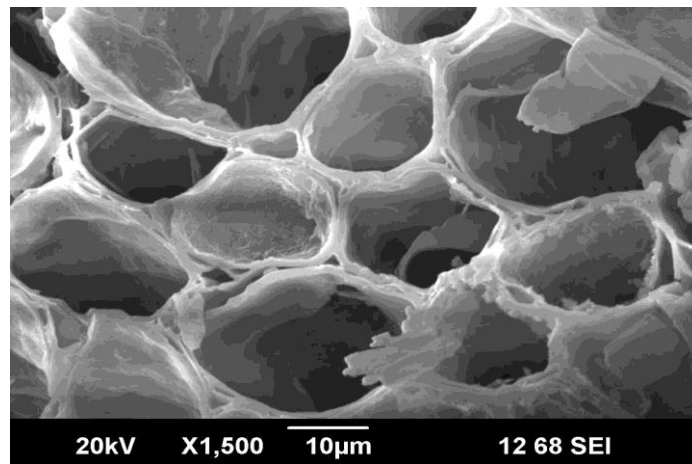
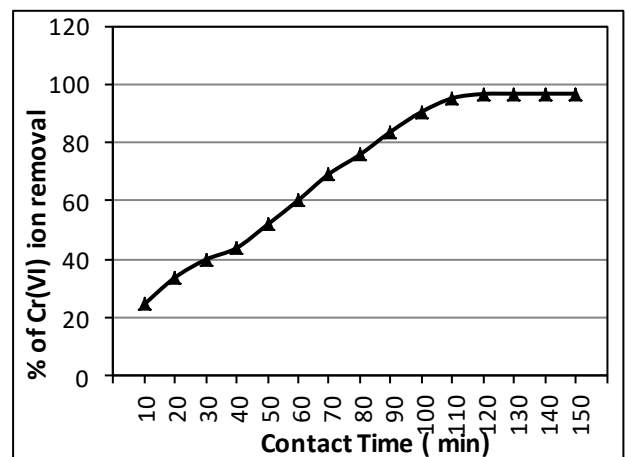
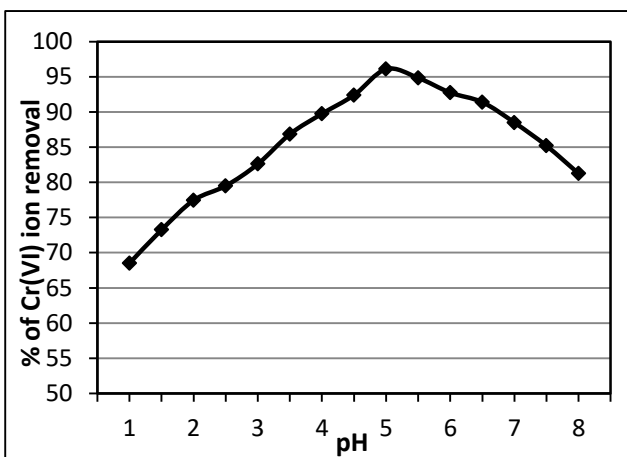


Fig.2 SEM image of *Tamarindus indica* Activated Carbon (TIAC)



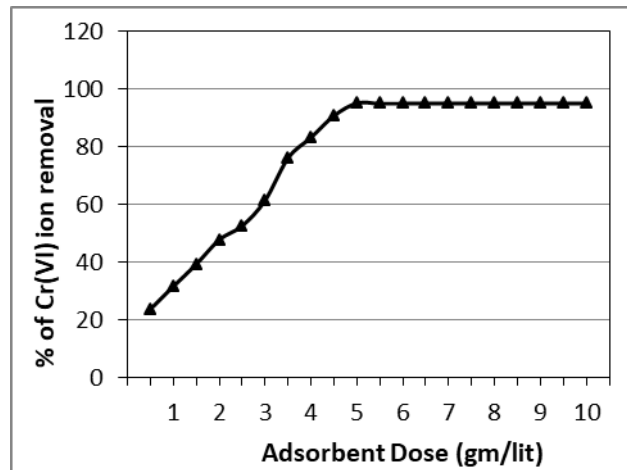


Fig.5 Effect of Adsorbent dose on Cr(VI) removal

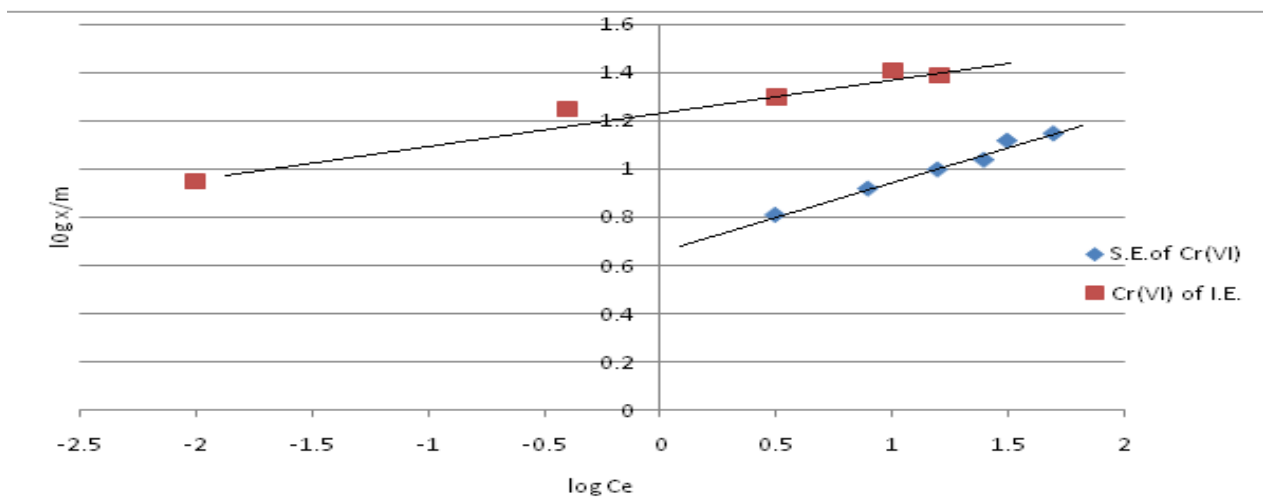


Fig.6: Freundlich plot for the adsorption of Cr(VI) from synthetic effluent (S.E.) having Cr(VI) 100 ppm and waste water (I.E.) having Cr(VI) 100 ppm at 32°C

CONCLUSION

- Text must be type in Book Antiqua font size 10. Text must be type in Book Antiqua font size 10. Text must The activated carbon derived from the bark of *Tamarindus indica* and characterized employing FTIR and SEM studies.
- The newly developed TIAC show high porous structure and excellent surface area.
- TIAC was most effective for Cr(VI) removal. At pH 5.5, 96% of Cr(VI) was removed from aqueous solution. Adsorption was found to pH dependent. Above pH 5.5, decline in Cr(VI) removal was noticed.
- The increase in percent removal capacity for Cr(VI) was observed with increase of adsorbent dose and contact time. Maximum removal is 95% for 5.0 g/l dose and 135 min. of contact time.
- The kinetic of Cr(VI) adsorption of TIAC was found to follow first order mechanics. The Gibbs free energy for the system was found to - 2.746 KJ/mole for Cr(VI) for removal from waste water
- The adsorption data satisfactory explained by Freundlich isotherm. High sorption capacity of TIAC proves the practical applicability of the sorbent under investigation for control of Cr(VI) pollution.
- The activated carbon under present investigation can be successfully employed for Cr(VI) abatement from contaminated water and thus can be used for water/ wastewater treatment.

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Conflicts of interest: The authors stated that no conflicts of interest.

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