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RESEARCH ARTICLE

ADSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTION USING BIO-SORBENT

***[1]Hunge, S. S., [2]Rahangdale, P. K. and [3]Lanjewar, M. R.**

[1]Chintamani College of Science, Pombhurna, Gondwana University - 441224, India
[2]Bhawabhuti College, Amgaon, Nagpur University - 441902, India
[3]PGTD of Chemistry, RTM Nagpur University, Nagpur - 440033, India

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ABSTRACT

Environment is deteriorating day to day due to the industrial pollution, toxic chemicals etc. which lead to the accumulation of contaminants inclusive of heavy metals in waste water. The water polluted by industrial effluents disturbs its normal use for agriculture and aquatic/terrestrial life. In view of toxicity, non-biodegradability and persistent nature their removal becomes an absolute necessity. Hexavalent chromium metal ion is one of the major pollutants in the environment and is frequently present in waste water released from various industrial units. Several conventional physical and chemical treatment techniques are reported in the literature for the removal of hexavalent chromium. However these processes are not only expensive and energy intensive, but also lead to the production of harmful by products. The present research article reports, the potential application of self prepared activated carbon derived from the bark of *Tamarindus indica* followed by chitosan (deacetylated derivative of chitin) coating as an adsorbent for removal of hexavalent chromium from aqueous solution. The batch experiments were carried out to investigate the effect of significant process parameters such as pH, contact time, adsorbent dosage and initial Cr(VI) ion concentration. The maximum adsorption of Cr(VI) on bio-sorbent was found at pH 4.5. The removal of hexavalent chromium from aqueous solution increases with increase in contact time and adsorbents dose. The maximum removal capacity for Cr(VI) have been noticed to be 96.50%. This investigation verifies that the chitosan coated activated carbon derived from *Tamarindus indica bark (a* bio-sorbent) can be used as a valuable adsorbent material for removal of hexavalent chromium from contaminated water and may contribute in pollution control.

INTRODUCTION

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing world wise concern for the last few decades. The removal of heavy metal contaminants from aqueous solutions is one of the most important environmental concerns because metals are biorefractory and are toxic to many life forms. Shanmugapriya *et al.* (2011); KaYrabulut *et al.* (2000) Metals which are significantly toxic to human beings and ecological environments, include chromium, copper, lead, mercury, cadmium, nickel, iron etc. Bowen (1979) This problem has received considerable attention in recent years. These heavy metals are toxic to aquatics flora and fauna even in relatively low concentrations. Some of these are capable of being assimilated, stored and concentrated by organisms. Zhang *et al.* (2000); Murley *et al.* (1992) Generally, metals that form compounds with biological constituents can be toxic, carcinogenic or mutagenic even in a very low concentration. Picardo *et al.* (2009) Unlike organic pollutants; the majority of which are susceptible to biological degradation; metal ions do not degrade into harmless end products. Gupta *et al.* (2001) They are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Modernization, industrialization and urbanization has drastically changed the biogeochemical cycle and balance of some metals in the ecosystem. Chromium(VI) is one of the most strategic and critical material having wide range uses in various industries. 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. US Department of Health and Human Services (1991) Chromium is a toxic metal of widespread use in many industries such as electroplating, leather tanning, metal finishing, textile industries and chromate preparation. Fiol *et al.* (2003); Vinod Gupta *et al.* (2003) Various treatment technologies have been developed for the purification of water and waste water contaminated by heavy metals. The most commonly used methods for the removal of metals ions from waste water are chemical precipitation, solvents extraction, oxidation, reduction, electrolytic extraction, reverse osmosis, ion-exchange, adsorption etc. Amongst all these methods adsorption is highly effective and economical. It is a growing need to derive activated carbons from cheaper and locally available waste terials. Several

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****Corresponding author: Hunge, S. S.***
Chintamani College of Science, Pombhurna, Gondwana University - 441224, India.

research workers used different low cost adsorbents from agriculture wastes such as coconut coir pith, sawdust, rice husk, banana pith, cottonseed hulls, apples wastes, 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 waste water. The present work reports the studies carried out for the removal of Cr(VI) from aqueous solution using activated carbon derived from bark of *Tamarindus indica* on which chitosan was coated. It is one of the largest families of flowering plant belong to *Fabaceae* family and extensively used in Ayurveda, Unani and Haemeopathic medicine and has becomes a cynosure of modern medicine. Kumar and Bhattacharya (2008) Chitosan {2-acetamido-2-deoxy-β-D-glucose-(N acetylglucosamine)} is a deacetylated polymer of chitin and is usually prepared by its deacetylation with strong alkaline solution. It has excellent physicochemical properties. It is environmental friendly and bioactive material which is slightly soluble at low pH. It is soft and has tendency to form a gel in aqueous solution. Govindarajan *et al.* (2011); Nomanbhay and Palanisamy (2005)

The composite 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.

MATERIALS AND METHODS

Chemicals

The chemicals used in the investigation were of either analytical or chemically pure grade and procured from Merck (Mumbai, India).

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

The bark of *Tamarindus indica* 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 its colour 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^{0}C for 7-8 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 water and dried at 105^{o}C for 3 hrs and stored in air tight bottle.

Preparation of Chitosan Gel

Chitosan was procured from Otto Chemical, Mumbai (India). 30 g of chitosan was added into 1000 ml of 10% oxalic acid with constant stirring. The mixture was warmed at 40 – 45^{0}C for proper mixing. The chitosan-oxalic acid mixture was formed as a whitish viscous gel.

Surface coating of TIAC with Chitosan Gel

500 ml of Chitosan gel was double diluted with distilled water and warmed to 40 -45^{0}C. 300 g of TIAC was slowly added into diluted chitosan gel and shake mechanically using rotary shaker for 24 hr. The chitosan coated TIAC (CCTIAC) was then washed with deionized water and dried. The process was repeated 3 times to form thick coating of chitosan on the TIAC surface. The coated chitosan was 30 to 35% by weight. Oxalic acid was quantitatively neutralized Caiesoughlin *et al.* (1990) by 0.5% sodium Hydroxide solution. The solid CCTIAC was filtered, washed with deionized water, dried and stored in air tight container.

Characterization of CCTIAC

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

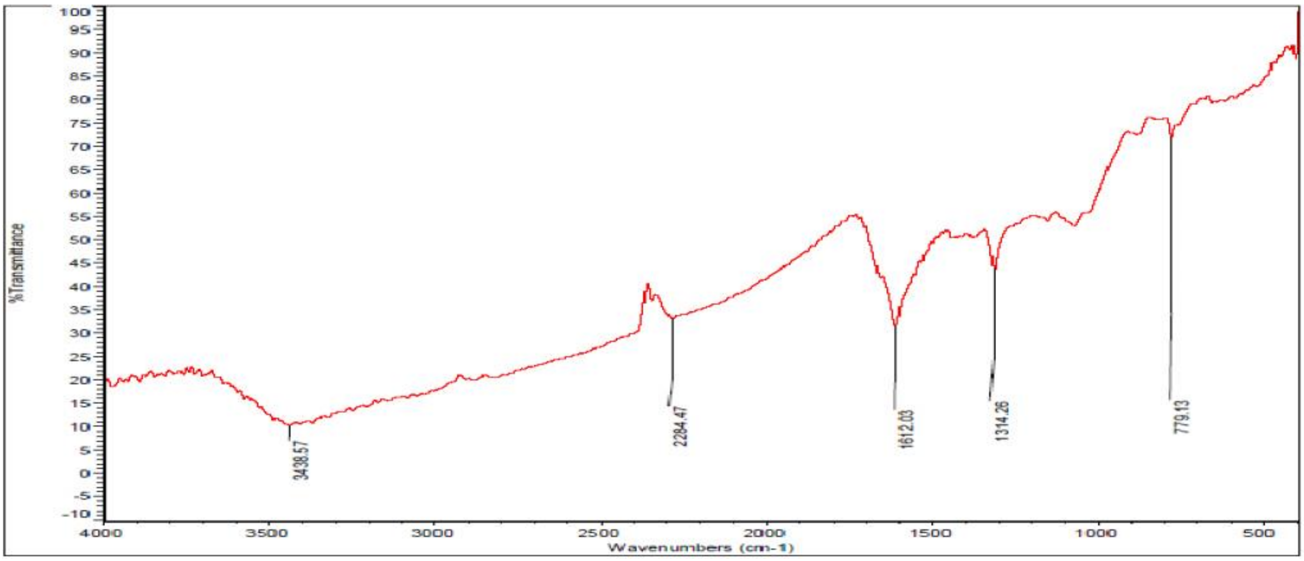

Fig. 1. FT-IR Spectrum of Chitosan coated activated carbon of *Tamarindus Indica* (CCTIAC)

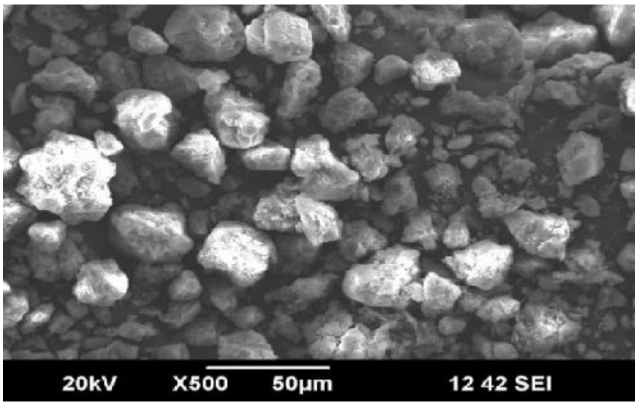

Fig. 2. Scanning electron micrographs (SEM) of the CCTIAC at 500 x

Adsorption Studies

Working standards were prepared by progressive dilution of stock solution of Cr(VI). Removal of Cr(VI) using CCTIAC was carried out by batch equilibrium method. The influence of various parameters such as effect of pH, contact time, adsorbent dosage and initial Cr(VI) ion concentration were studied at 30^{0}C, taking 25mg/l of initial Cr(VI) concentration and 5g/l of adsorbent dose. The effect of adsorbent dosage was studied by varying them from 1 to10g/l. The effect of initial Cr(VI) concentration was studied by changing concentration from 10 to100mg/l with fixed adsorbent dose of 5g/l at 30^{0}C. The residual concentration of Cr(VI) were measured by Atomic Absorption Spectrophotometer (AAS) using a air acetylene flame.

RESULTS AND DISCUSSION

Characterization of CCTIAC

Fig.1 represents FTIR of CCTIAC. The absorption band at 3438.57cm^{-1} correspond to –OH stretching vibration of water, hydroxyl group and -NH stretching of free amino groups. The signals at 1612.03 and 2284.47cm^{-1}(weak) are assigned to acylamino group and S-H vibrations respectively. The band at 1314.26cm^{-1} corresponds to C-H and O-H deformation vibrations. Absorption band at 1230cm^{-1} could be attributed to C-OH stretching. A peak at 779.13cm^{-1} is indicative of -CH_2 rocking. The surface morphology of CCTIAC has been characterized by SEM (Fig.2) which indicates porous and fibrous structure of the material under investigation. The shapes of the CCTIAC particle were nearly spherical and their size ranges from 5 to 50 µm. The surface was rough, uneven, gaped and folded due to the drying procedure. This is requisite for an effective adsorbent.

Effect of pH

Th**e** effect of pH on the adsorption of chromium(VI) by CCTIAC was studied at pH 1 to 8. From Fig.3, it is clear that the removal of Cr(VI) increases with an increase in pH from 1.0 to 4.5 and it is optimum at 4.5. The percentage of adsorption increases from 60 to 97.45% as pH was increased from 1 to 4.5. The percentage of adsorption decreases steadily to 93% when pH was increased above 4.5 and it was further decrease to 75% as pH was raised to 8.

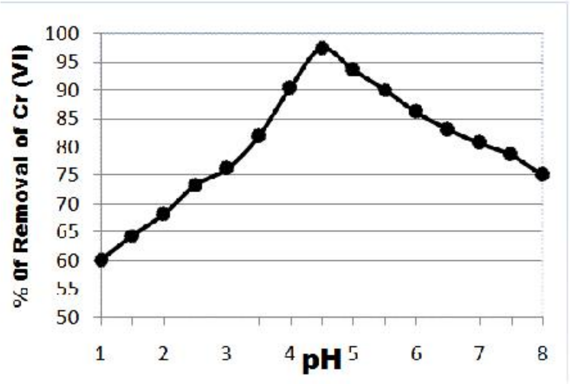

Fig.3. Effect of pH on Cr(VI) adsorption

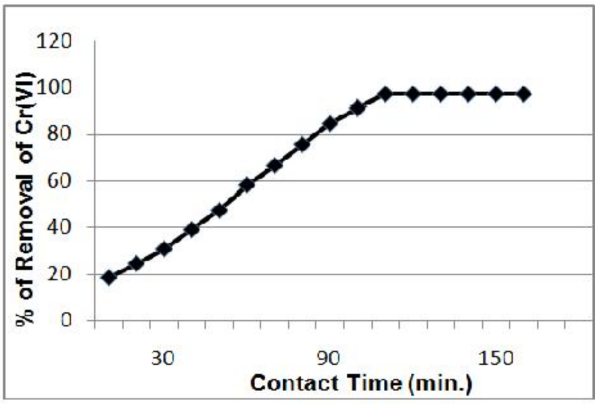

Fig.4. Effect of Contact time on Cr(VI) adsorption

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 CCTIAC increased with increase in contact time before equilibrium was reached. Other parameters such as dose of CCTIAC, pH of solution and initial concentration were kept optimum. It can be seen from fig.4 that Cr(VI) removal efficiency increased from 58 to 97% when contact time was increased from 60 to 110 min. Optimum contact time for CCTIAC was found to be 110 min. Cr(VI) removal efficiency remained nearly constant after 110 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 CCTIAC 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 CCTIAC doses and it was found to be maximum i.e. 96.5% at the dose of 4.0g/l. This is due to availability of more adsorbent (more surface area). It indicates that by increasing the CCTIAC dosages, the adsorption efficiency for Cr(VI) removal increases. After 4g/l dose of CCTIAC, the adsorption efficiency remained constant because the maximum adsorption set in and amount of Cr(VI) ion present in the solution bounded to adsorbent remains nearly constant after this dose.

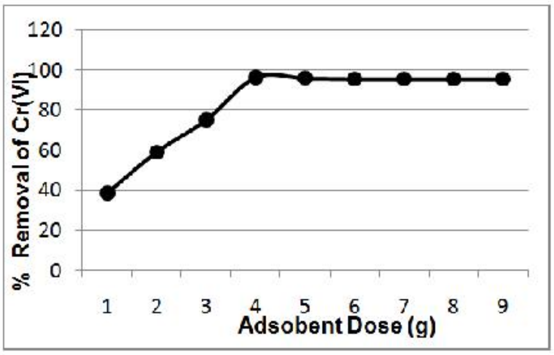

Fig.5. Effect of Adsorbent doses on Cr (VI) adsorption

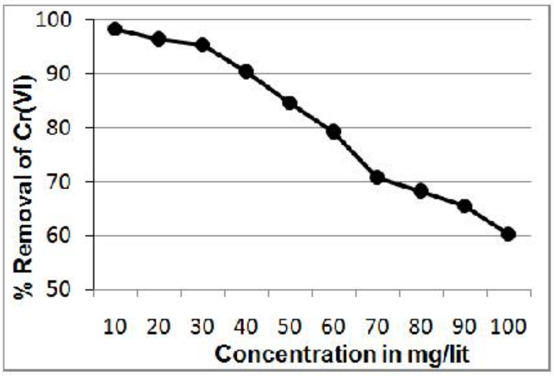

Fig.6. Effect of concentration on Cr(VI) adsorption

Effect of initial metal ion concentration

The effect of initial metal ion concentration on the percentage removal of hexavalent chromium by CCTIAC has shown in fig.6. It can be seen that the percentage removal of Cr(VI) decreases with the increase in initial Cr(VI) concentration. In this study, the experiment was performed to study the initial concentration effect in the range 10-100mg/l .The adsorbent dose was maintained 5g/l. The result shows the decrease in removal from 98 to 60%. This can be justified by the fact that adsorbent have limited number of active sites which are saturated beyond certain concentration of adsorbate.

Conclusion

- The activated carbon derived from the bark of *Tamarindus indica* and surface was successfully coated with chitosan and characterized employing FTIR and SEM studies.
- The newly developed modified activated carbon has high porous structure and excellent surface area.
- CCTIAC was most effective for Cr(VI) removal. At pH 4.5, 97% of Cr(VI) was removed from aqueous solution. Adsorption was found to pH dependent. Above pH 4.5, decrease in Cr(VI) removal was noticed.
- The increase in percent removal capacity for Cr(VI) was observed with increased of adsorbent doses and contact time. Maximum removal is 96% for 4.0 g/l dose and 110 min. of contact time.
- The newly obtained surface modified 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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