



Role of Newly Developed Adsorbent In The Control of Cr(VI) Pollution

Hunge S.S.¹; Rahangdale P.K.². and Lanjewar M.R.³.

¹Chintamani College of Science, Pombhurna (Gondwana University)-441224(India)

²Bhawabhuti College, Amgaon (Nagpur University) -441902 (India)

³PGTD of Chemistry, RTM Nagpur University, Nagpur-440033(India)
sudhirhunge@yahoo.com

Abstract

The adsorption ability of activated carbon derived from the bark of *Ziziphus mauritiana* for removal of Cr(VI) from polluted water has been studied with respect to various parameters such as effect of pH, adsorbent dosage, contact time and initial Cr(VI) concentration. The chromium(VI) uptake was dependent on equilibrium pH=5.5, being the optimum pH values. The removal of Cr(VI) from aqueous solution increases with increase in contact time and equilibrium was attained at 180 min. Further on increasing adsorbent dose, there was increase of Cr(VI) removal. The optimum adsorption (89%) was noticed at 5.0 g/l of adsorbent dose. The increase in initial concentration of Cr(VI) led to decrease in the percent removal of Cr(VI). This investigation verifies that the newly prepared activated carbon from the bark of *Ziziphus mauritiana*, can be used as a cost effective, valuable adsorbent for removal of Cr(VI) from aqueous solution and thus can be successfully applied for wastewater treatment.

Keywords: Adsorption, *Ziziphus mauritiana*(ZM), batch experiment, Activated carbon

Introduction

Water is one of the most important factors of living and non-living organisms. The pollution of water emerged as one of the most significant environmental problems of recent times. 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 metal in water. 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 forms¹. Metals, which are significantly toxic to human beings and ecological environments, include chromium, copper, lead, mercury, cadmium, nickel, iron etc².

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^{3,4}. 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. Several technologies have been developed to remove carcinogenic chromium(VI) from water and waste water. The most common methods include chemical precipitation, ion exchange, ultra filtration, solvent extraction, sedimentation, reverse osmosis, dialysis and adsorption etc⁵. However, these conventional methods have certain major disadvantages such as incomplete removal and high operating cost. Amongst all of these, adsorption onto commercial activated carbon is well-established and effective technique. However, it is highly expensive since most of the activated





carbon materials are obtained from non renewable sources like coal, lignite, peat etc. It is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several research workers used different low cost adsorbents from agriculture waste such as coconut coir pith, sawdust, rice husk, cotton seed hulls, sugarcane bagasse, peanut hull etc. for the removal of Cr(VI) from contaminated water. The present investigation, studies were carried out for the removal of Cr(VI) from aqueous solution using activated carbon derived from bark of *Ziziphus mauritiana* belong to *Rhamnaceae* family which is an extremely drought hardy and native fruit of India. It is useful as food, fodder, nutrient and medicine. *Ziziphus mauritiana* having tremendous medicinal properties, attributed by adverse group of secondary metabolites such as alkaloids, flavonoids, terpenoids, saponin, pectin, triterpenic acids and lipids. It is extensively used in Ayurveda, Unani and Haemeopathic medicine. The activated carbon derived from the bark of *Ziziphus mauritiana* was characterized by FTIR and scanning electron microscopy (SEM) studies. Batch isothermal equilibrium method was conducted at 303K to evaluate the efficiency of newly developed adsorbent for removal of Cr(VI) from the aqueous solution. Experiments were carried out to evaluate effect of pH, adsorbent dosage, contact time and initial Cr(VI) concentration. Thus, the newly synthesized activated carbon have been proved to be very good adsorbent which can be successfully used for removal of Cr(VI) from aqueous solution.

Material and Methods:

Chemicals

All 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 *Ziziphus mauritiana* (ZMAC)

The bark of *Ziziphus mauritiana* 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 Furnace 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 at 360 W for 30 min⁶. The resulting activated carbon particles were ground and sieved in 120-200 μm size. This activated carbon was then washed with double distilled water and dried at 105°C for 3 hrs and stored in air tight bottle.

Characterization of ZMAC

Characterization of ZMAC was done by FTIR (Figure.1) and SEM (Figure.2)

Adsorption Studies

Working standards were prepared by progressive dilution of stock solution of Cr(VI). Removal of Cr(VI) using ZMAC 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) 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.

Result and Discussion:

Characterization of ZMAC

FTIR spectrum of ZMAC is shown in **Fig1**. A band at 3442.21cm^{-1} is connected with -OH stretching band. The -OH groups are seem to be associated by means of hydrogen bonds, as the band for hydroxyl group not involved in hydrogen bonding usually appears as a sharp band located above 3500cm^{-1} . The band for -OH stretching in the range below 3700cm^{-1} was assigned by Zawadzki⁷. A band at 1633.75cm^{-1} is indicative of C=O stretching in aldehyde or ketone (carbonyl group). The sufficiently lowering in the band position suggest that C=O group may also involved hydrogen bonding. It is because of the reason that the intramolecular hydrogen bonded structure is stabilized by the phenomenon of resonance. The peak at 1084.14cm^{-1} is suggestive of ortho- substitution. Low band at 565.20cm^{-1} is evidence of C-I stretching vibration^{8,9}. **Figure.2** represents SEM micrographs of ZMAC. 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 *Ziziphus mauritiana* activated carbon (ZMAC) 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- 10 μm .

Effect of pH

The effect of pH on the adsorption of Cr(VI) by ZMAC was studied at pH 1 to 8. From **Figure.3** it is clear that the removal of Cr(VI) increases with an increase in pH from 1.0 to 5.5 and it is optimum at 5.5. The percent of adsorption increases from 60 to 90 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 **Figure.4**. It can be observed that Cr(VI) removal ability of ZMAC increased with increase in contact time before equilibrium was reached. Other parameters such as dose of ZMAC, pH of solution and initial concentration were kept optimum. It can be seen from Figure.4 that Cr(VI) removal efficiency increased from 25 to 90% when contact time was increased from 10 to 180 min. Optimum contact time for ZMAC was found to be 180 min. Cr(VI) removal efficiency remained nearly constant after 180 min i.e. equilibrium time.

Effect of Adsorbent Dosage



Figure.5 shows the effect of dosage on the removal of Cr(VI) which was studied by varying the amount of ZMAC 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 ZMAC doses and it was found to be maximum i.e. 89% at the dose of 5g/l. This is due to availability of more surface area. It indicates that by increasing the ZMAC dosages, the adsorption efficiency for Cr(VI) removal increases. After 5g/l dose of ZMAC, 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.

Effect of initial metal ion concentration

The effect of initial metal ion concentration on the percentage removal of hexavalent chromium by ZMAC has shown in Figure.6. It can be seen that the percent 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 89 to 49%. This can be justified by the fact that adsorbent have limited number of active sites which are saturated beyond certain concentration of adsorbate.

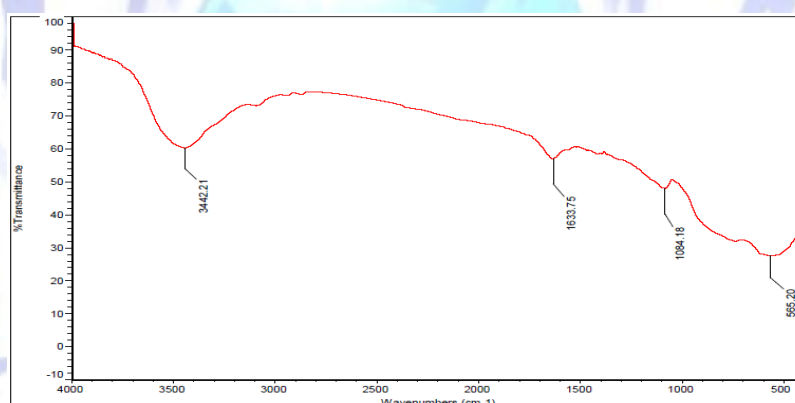


Figure.1- FTIR Spectrum of *Ziziphus mauritiana* Activated Carbon (ZMAC)

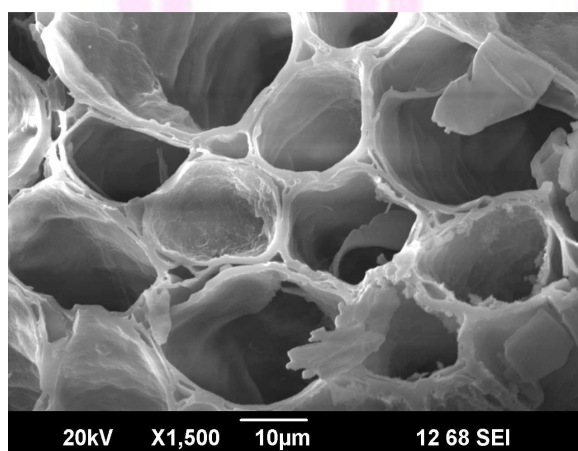


Figure.2- SEM image of *Ziziphus mauritiana* Activated Carbon (ZMAC)

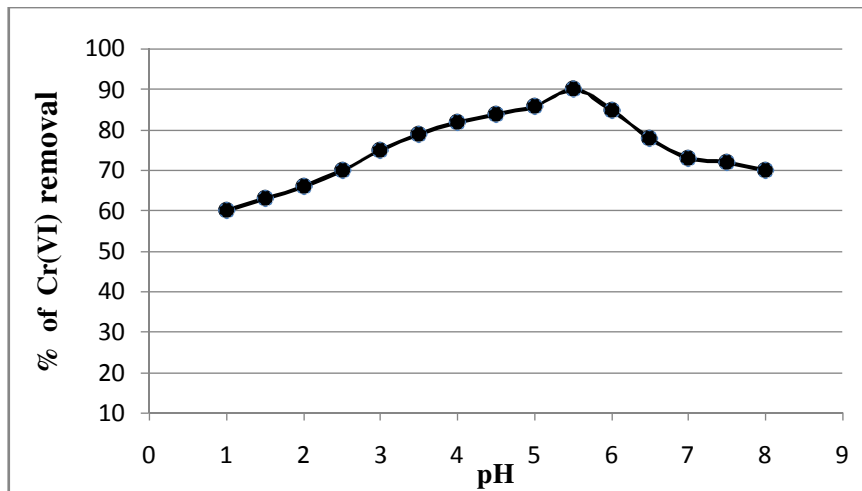


Figure. 3- Effect of pH on Cr(VI) removal by ZMAC

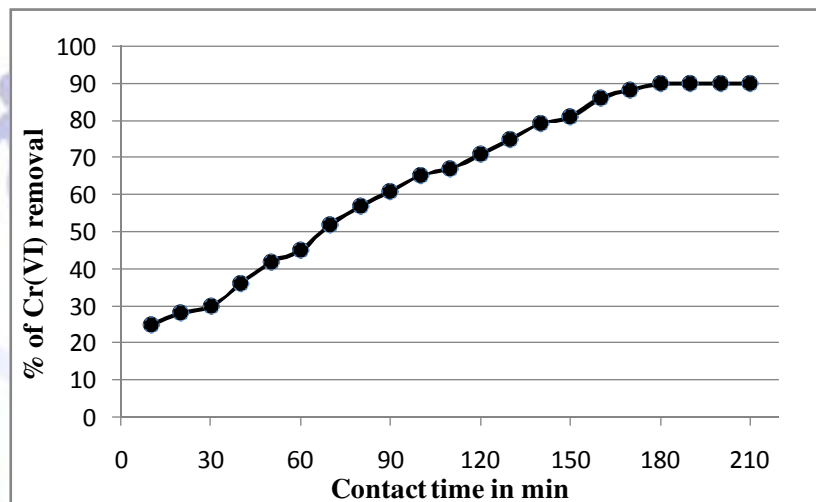


Figure.4- Effect of Contact time on Cr(VI) removal by ZMAC

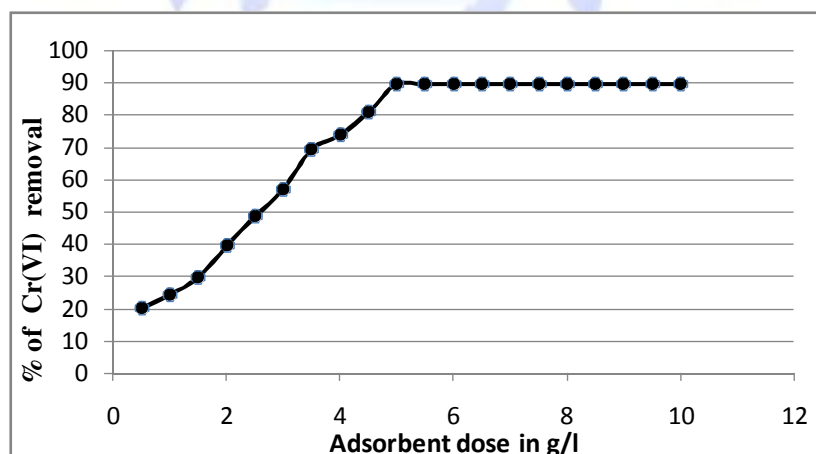


Figure.5- Effect of adsorbent dose on Cr(VI) removal by ZMAC



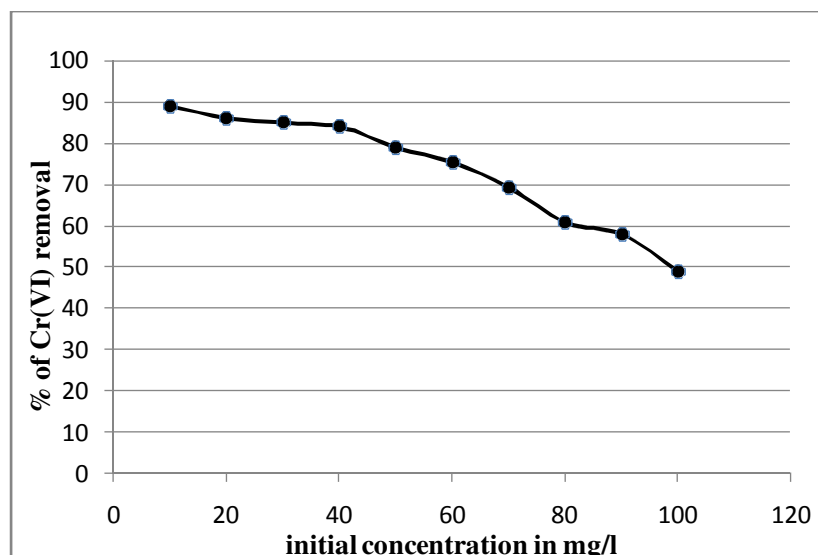


Figure.6- Effect of initial concentration of Cr(VI) removal by ZMAC

Conclusion:

- The activated carbon derived from the bark of *Ziziphus mauritiana* tree was successfully prepared and characterized employing FTIR and SEM studies.
- The newly developed activated carbon has high porous structure and excellent surface area.
- ZMAC was most effective for Cr(VI) removal. At pH 5.5, 90% of Cr (VI) was removed from aqueous solution. Adsorption was found to be 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 89% for 5.0 g/l dose and 180 min. of contact time.
- 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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