

# Environmental Friendly Surface Modified Adsorbent for Abatement of Cr(VI) From Waste Water

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## ABSTRACT

The present year, heavy metals in the environment is of major concern because of their toxicity, bio-accumulating tendency and threat to human life and the environment. In view of their toxicity, non-biodegradability and persistent nature their removal becomes an absolute necessity. Hexavalent chromium metal is one of the carcinogenic pollutant in the environment and is frequently present in wastewater from various industrial units. The present research paper reports the characterization and use of chitosan-coated activated carbon derived from the bark of *Madhuca longifolia* (CCMLAC) as a great 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, adsorbent doses and initial Cr(VI) concentration. The maximum adsorption efficacy for Cr(VI) removal by CCMLAC was found at pH 5.5, 5 gm/lit of adsorbent dose and 120 min contact time. Under optimum condition, 96.5% Cr(VI) was removed from aqueous solution. This investigation verifies that CCMLAC, 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:** Activated Carbon; Adsorption, Bio-sorbent, Chitosan, Hexavalent chromium, *Madhuca longifolia* bark

## Abbreviation

**MLAC-** *Madhuca Longifolia* Activated Carbon

**CCMLAC-** Chitosan Coated *Madhuca Longifolia* Activated Carbon

**FTIR** - Fourier Transform Infrared Spectroscopy

**SEM-** Scanning Electron Microscopy

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## INTRODUCTION

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 industrial and agricultural process and mining activities have increases the concentration of toxic contamination in water and wastewater around the world[1]. The presence of toxic metals in aqueous streams arising from direct discharge of untreated heavy metals containing wastewater into water bodies gives rise to one of the most serious environmental issues [2,3]. The Several industries like paper and pulp, metal plating, leather tanning, fertilizers etc. and mining activities have increased the concentration of toxic metal contamination in water and waste water around the world [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 [7]. 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 etc [8]. These processes may be expensive especially when these heavy metal ions are present in the solution in low concentration. 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, cottonseed hulls, sugarcane bagasse, peanut hull etc. for the removal of Cr(VI) from contaminated water. In the present work, studies were carried out for the removal of Cr(VI) from aqueous solution using activated carbon derived from bark of *Madhucalongifolia* belong to *Sapotaceae* family. *Madhucalongifolia* is one of those multipurpose forest tree species that provided food, fodder a fuel [9].

The Mahua tree is having lots of nutritional value in it. The flowers are used as tonic, analgesic and diuretic. Flowers are traditionally used as a cooling agent, tonic, aphrodisiac and astringent. *Madhucalongifolia* is also use as medicinal herb [10] and alkaloid extract of mahua is used in the treatment of Ant inflammatory, anti-ulcer and hypoglycemic activities of ethamolic [11]. It is also useful for external application in treating skin diseases, headache, piles, emetic and galactagogue. Chitosan{2-acetamido-2-deoxy- $\beta$ -D-glucose-(N-acetyl glucosamine)} 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 [12,13]. The newly prepared sorbent was characterized by FTIR and Scanning Electron Microscopy (SEM) studies. Batch isothermal equilibrium method was conducted at 308K 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 bio-sorbent have been proved to be very good adsorbent for removal of carcinogenic hexavalent chromium from aqueous solution.

## MATERIAL AND METHOD

### Chemicals

All the chemicals used in the investigation were of analytical grade and procured from Merck (Mumbai, India).

### Preparation of Activated Carbon from the bark of *Madhucalongifolia* (MLAC)

The bark of *Madhucalongifolia* 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 release of any colour of bark into aqueous solution. It was then 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 700-900°C for 7 to 8 hrs so that volatile constituents were removed and residue was converted into achar. The char was then subjected to microwave activation in microwave oven at 360 W for 30 min [14]. 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°C for 3 hrs and stored in airtight bottle.

### Preparation of Chitosan Gel

Chitosan was purchased from Otto Chemical, Mumbai (India). 35 g of chitosan was added into 1000 ml of 15% oxalic acid with constant stirring. The mixture was warmed at 40– 45°C for proper mixing. The chitosan-oxalic acid mixture was formed as a whitish viscous gel.

### Surface coating of MLAC with Chitosan Gel

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

### Characterization of CCMLAC

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

### Adsorption Studies

Working standards solution were prepared by progressive dilution of stock solution of Cr(VI). Removal of Cr(VI) using CCMLAC 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 amount of adsorbent from 1-10g/l. The effect of initial Cr(VI) concentration was studied by changing concentration from 10-100mg/l with adsorbent dose of 5g/l at 35°C. The residual concentrations were measured using atomic absorption spectrophotometer.

## RESULT AND DISCUSSION

### Characterization of CCMLAC

FTIR spectrum of CCMLAC is shown in **Fig.1**. The band at  $3445.27\text{cm}^{-1}$  indicates presence of the free hydroxyl group stretching of chitosan molecules. The band at  $2662.41\text{cm}^{-1}$  is due to the C-H bond stretching of aldehyde (C-H=O Group). The shifting of band from its standard value ( $2889.21\text{cm}^{-1}$ ) due to the involvement of chitosan in composite formation. The absorption at  $1633.30\text{cm}^{-1}$  is due to the C=O stretching mode of the amido (CONH) group of chitosan. The two characteristic bands appeared at  $1005.85\text{cm}^{-1}$  and  $911.73\text{cm}^{-1}$  (skeletal vibration involved in C-O-C stretching) prove the presence of saccharide structure. The peaks at  $532.07\text{cm}^{-1}$  and  $464.47\text{cm}^{-1}$  corresponds to N-H bending.

**Fig.2** represents SEM image of CCMLAC. 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/holes are present on the surface of CCMLAC. 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 CCZMAC 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 5.5 and it is optimum at 5.5. The percent of adsorption increases from 60 to 94 as pH was increased from 1 to 5.5. The percentage of adsorption decreases steadily to 83% when pH increased above 5.5 and it was further decreased to 70% as pH was raised to 8.

### Effect of Contact Time

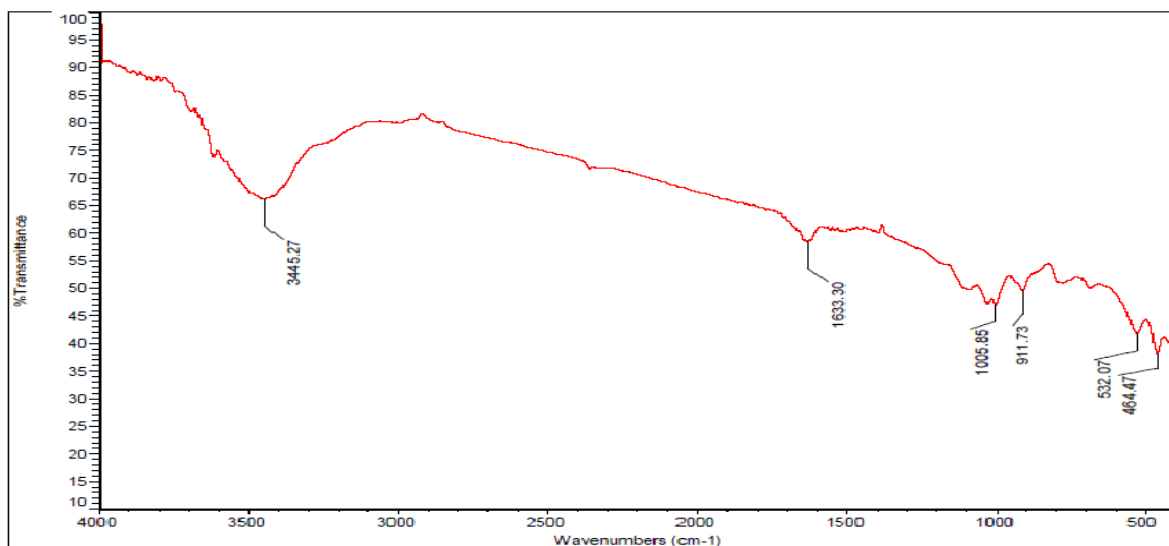
Adsorption experiments were carried out as a function of contact time and results have shown in **Fig.4**. It can be observed that Cr(VI) removal ability of CCMLAC increased with increase in contact time before equilibrium was reached. Other parameters like dose of CCMLAC, pH of solution and initial concentration were kept optimum. It can be seen from **fig.4** that Cr(VI) removal efficiency increased from 24 to 96.5% when contact time was increased from 10 to 180 min. Optimum contact time for CCMLAC was found to be 120 min. Cr(VI) removal efficiency remained nearly constant after 120 min i.e. equilibrium time.

### Effect of Adsorbent Dosage

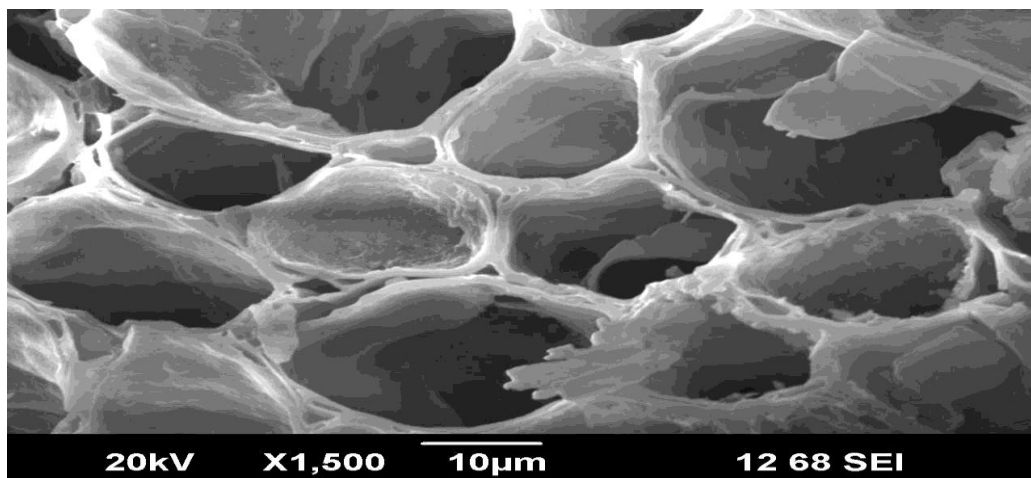
**Fig.5** shows the effect of dosage on the removal of Cr(VI) which was studied by varying the amount of CCMLAC from 0.5 to 10g/l while keeping other parameters (pH, contact time and initial concentration) constant. It is clear from the figure that percentage removal of Cr(VI) increased with the increase in CCMLAC doses and it was found to be maximum i.e. 97% at the dose of 5g/l. This is due to availability of more surface area. It indicates that by increasing the CCMLAC dosages, the adsorption efficiency for Cr(VI) removal increases.

### Effect of initial metal ion concentration

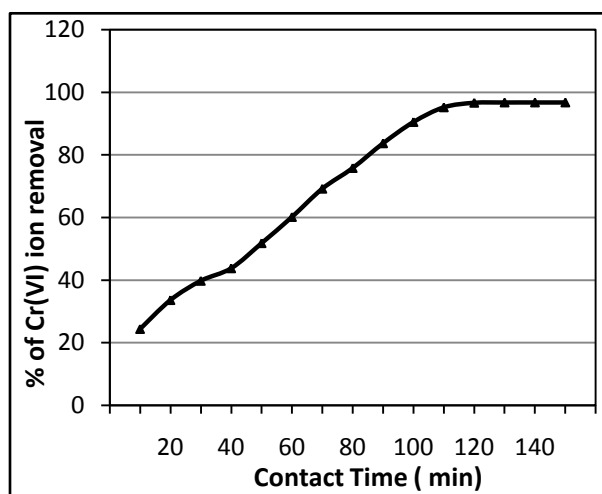
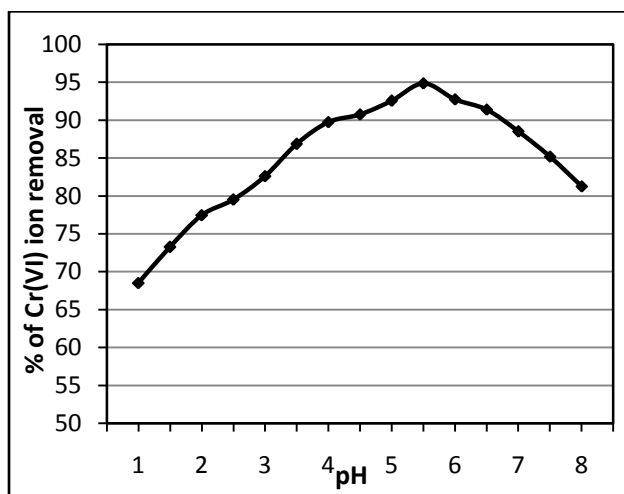
The effect of initial metal ion concentration on the percentage removal of hexavalent chromium by CCMLAC has shown in **fig.6**. It can be seen that the percent removal of Cr(VI) decreases with the increase in initial Cr(VI) concentration. In this study, the experiment was performed to study the initial concentration effect in the range 10-100mg/l. The adsorbent dose was maintained 5g/l. The result shows the decrease in removal from 96 to 47%. This can be justified by the fact that adsorbent has limited number of active sites which are saturated beyond certain concentration of adsorbate.



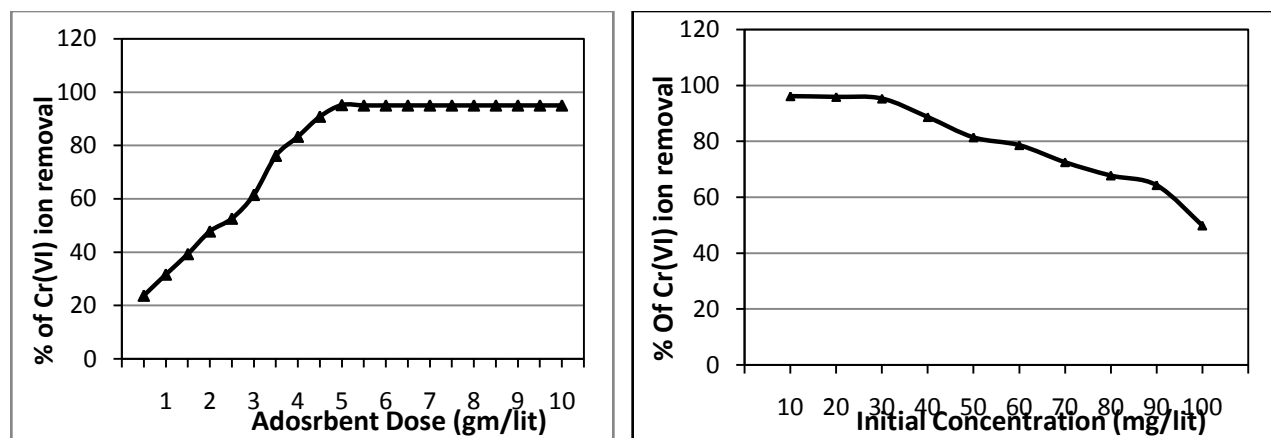
**Fig.1 FTIR Spectrum of Chitosan Coated *Madhucalongifolia* Activated Carbon (CCMLAC)**



**Fig.2 SEM image of Chitosan Coated *Madhucalongifolia* Activated Carbon (CCMLAC)**



**Fig.3 Effect of pH on Cr(VI) removal by CCMLAC Fig.4 Effect of Contact time on Cr(VI) removal by CCMLAC**



**Fig.5 Effect of Adsorbent dose on Cr(VI) removal Fig.6 Effect of initial concentration of Cr(VI) removal**

### CONCLUSION

- The activated carbon derived from the bark of *Madhucalongifolia* tree and surface was successfully coated with chitosan and characterized employing FTIR and SEM studies.
- The newly prepared CCMLAC high porous structure and excellent surface area.
- CCMLAC was most efficient for Cr(VI) removal. At pH 5.5, 94.5% 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 120 min. of contact time.
- The Chitosan coated 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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