

Removal of Hexavalent Chromium from Aqueous Solution using Pre-treated Bio-Sorbent

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ABSTRACT

Pollution of water due to the presence of certain heavy metals ions is a severe socio-environmental problems caused by the discharge of industrial waste water. In view of their toxicity, non-biodegradability and persistent nature their removal becomes an absolute necessity. Hexavalent chromium metal ion is the major pollutants in the environment and is frequently present in waste water from the 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. In the present study, activated carbon derived from the bark of *Butea monosperma* was used as a potential sorbent after coating it with chitosan, a deacetylated derivative from chitin for removal of hexavalent chromium from aqueous solution was investigated. The batch experiment was carried out to investigate the effect of significant process parameters such as effect of pH, contact time, adsorbent dosage and initial Cr (VI) ion concentration. The maximum adsorption of Cr(VI) on biosorbent was found at pH value of 3. The removal of hexavalent chromium from aqueous solution increases with increase in contact time. Further an increase in adsorbent dose, there is increase of removal of Cr (VI) up to 96 %. The increase in initial concentration of Cr (VI) led to decrease in the percentage of removal of Cr(VI). This investigation verifies that pre-treated bio-sorbent as a valuable material for removal of hexavalent chromium from aqueous solution.

Keywords: Adsorption, *Butea monosperma* bark (BMB), Chitosan, Hexavalent chromium, Biosorbent,

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INTRODUCTION

The pollution of water resources due to the indiscriminate disposal of heavy metal has been causing world wide concern for the last few decades. It is well known that some metals can have toxic or harmful effects on many forms of the life[1]. Metals which are significantly toxic to human beings and ecological environments ,includes chromium, copper, lead, mercury cadmium, nickel iron etc [2]. This problem has received considerable amount of attention in recent years. These heavy metals are toxic to aquatic flora and fauna even in relatively low concentration .Some of these are capable of being assimilated, store and concentrated by organism [3,4]. Generally, metals that form compounds with biological constituents can be toxic, carcinogenic or mutagenic even in a very low concentration[5]. Unlike organic pollutants; the majority of which are susceptible to biological degradation; metal ions do not degrade into harmless end products [6]. They are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Modernization, industrialization and urbanization has drastically changed the biogeochemical cycles and balance of some metals.

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 [7]. Chromium is a toxic metal of widespread use in many industries such as electroplating, leather tanning, metal finishing, texture industries and chromate preparation [8,9]. 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. Among all the methods adsorption is highly effective and economical. Though the use of commercial activated carbon is well known as adsorbent for

the removal of heavy metals from waste water, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, 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 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 [9]. 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 *Butea Monosperma* on which Chitosan was coated. *Butea monosperma* one of the largest families of flowering plant belong to *Fabaceae* family, popularly known as dhak or palas commonly known as 'Flame of Forest'. *Butea monosperma* is extensively used in Ayurveda, Unani and Homeopathic medicine and has become a cynosure of modern medicine [10]. Chitosan (2-acetamido-2-deoxy- β -D-glucose-(N-acetylglucosamine) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with strong alkaline solution. It has excellent physicochemical properties. It is environmentally friendly and bioactive. The biosorbent material, chitosan, is slightly soluble at low pHs. It is also soft and has tendency to form a gel in aqueous solution [11,12]. The composite sorbent was characterized by FTIR and scanning electron microscopy (SEM) studies. Batch isothermal equilibrium method was conducted at 305K to evaluate the efficiency of newly synthesized biosorbent for removal of Cr(VI) from the aqueous solution. Experiment were carried out as effect of pH, adsorbent dosage, contact time and initial Cr(VI) concentration. Thus 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 METHOD

Chemicals:

The entire chemicals used were procured from Merck of analytical grade.

Preparation of Activated Carbon from the bark of *Butea Monosperma* (ACBMB):

The bark of *Butea monosperma* tree species was collected from the local area. The bark was cut into small pieces. It was washed with tap water to remove the sand particles and then treated with formaldehyde to avoid release any colour of bark into aqueous solution. Again wash with several time of deionized water. Then they were sun dried for 6 days. After drying, the bark was subjected to pyrolysis process for carbonization using muffle Furnace at about 800-900°C temperature range for about 7 to 8 hr so that volatile products 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 grounded and sieved in 120-200 μ m size. This activated carbon was then washed with double distilled water and dried at 105°C for 3 hr.

Preparation of Chitosan:

Chitin was purchased from Global Chemical, Nagpur (Maharashtra). A modified deacetylation method was used [13]. The commercially obtained chitin particles were soaked in 5% hydrochloric acid solution for about 1 hr at room temperature to remove any calcium salt. Wash it with several time of distilled water then transfer to 50% sodium hydroxide solution for 30 min. The solution was irradiated in microwave oven for 15 min for deacetylation. After rinsing with distilled water, dried deacetylated chitin (Chitosan) at 50°C in oven.

Preparation of Chitosan Gel:

30 g of chitosan was added into 1000 ml of 10% oxalic acid with constant stirring. The mixture was warm at a temperature range 40°C – 45°C for proper mixing. The chitosan-oxalic acid mixture was formed a whitish viscous gel.

Surface coating of ACBMB with Chitosan Gel:

About 500 ml of Chitosan gel was diluted with distilled water nearly of 500 ml and warmed to 40°C -45°C. 300 g of ACBMB was slowly added to diluted chitosan gel and shake mechanically using rotator shaker for 24 hr. The chitosan coated ACBMB (CCACBMB) was then wash with deionized water and dried. The process was repeated for 3 times to form thick coating of chitosan on the ACBMB surface. The chitosan coated was about 30 to 35% by weight. CCACBMB neutralized with 0.5% sodium Hydroxide solution and then extensively rinsed with deionized water and dried [14].

Characterization of CCACBMB:

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

Adsorption Studies:

Working standard were prepared by progressive dilution of stock solution of Cr(VI). Removal of Cr(VI) using CCACBMB was carried out by batch equilibrium method. Batch study was carried out in 250ml conical flask. The influence of various parameters such as effect of pH, contact time, adsorbent dosage and initial Cr (VI) ion concentration were studied. The effect of pH and contact time is studied at 32°C with initial Cr (VI) concentration 20 mg/l and adsorbent amount 5g/lit by taking 50 ml of aqueous Cr(VI) solution. The effect of adsorbent dosage is studied by varying adsorbent amount from 1g to 9g with Cr (VI) concentration 20mg/l while effect of initial Cr (VI) concentration is studied by changing concentration from 10mg/l to 50mg/l with adsorbent amount 5g/l at 32°C. The residual concentrations were measured using atomic absorption spectrophotometer using an air acetylene flame.

RESULT AND DISCUSSION

Characterization of CCACBMB

FTIR (fig.1) analysis was performed to examine the functional groups present on adsorbent material. FTIR spectrum of CCACBMB displays number of absorption peaks, indicating the complex nature of CCACBMB. The FTIR analysis indicated broad band at 3420 cm^{-1} representing -OH and -NH stretching. The band observed at 2960 cm^{-1} could be assigned to the aliphatic C-H group. The band present at 1740 cm^{-1} corresponds to -C=O (band from carboxylic group or ester group). The peak around 1620 cm^{-1} indicating to -C=O (amide band primarily a stretching band). The band at 1520 cm^{-1} corresponds to -C=O (carbonyl stretching band).

Fig.2 The scanning electron microscopy (SEM) of CCACBMB indicates that it has clear pore structure developed. There is no cellulosic structure form on the surface but there are very small and many cavities over the surface of the CCACBMB. Due to this cavity like structure of the surface of the material possessed high surface area and high adsorptive properties. Adsorption of any heavy metal depends upon the pore size of the activated carbon. So CCACBMB has high tendency to adsorb any heavy metals on his surface and has excellent adsorbent.

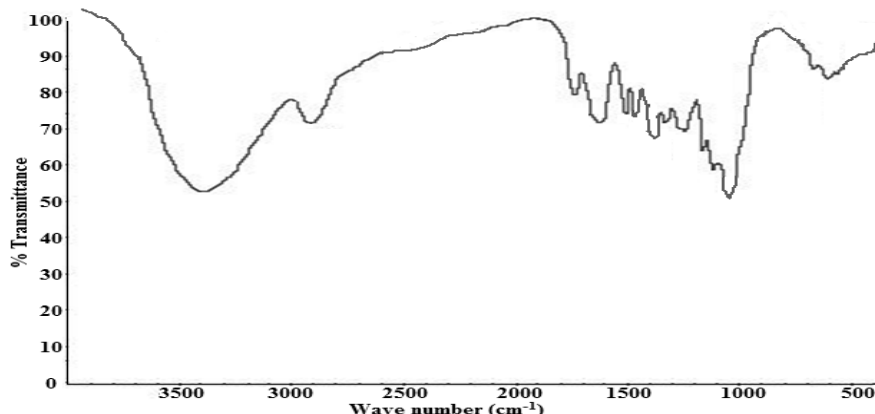


Fig. 1: FT-IR Spectrum of Chitosan coated activated carbon of Butea Monosperma bark (CCACBMB)

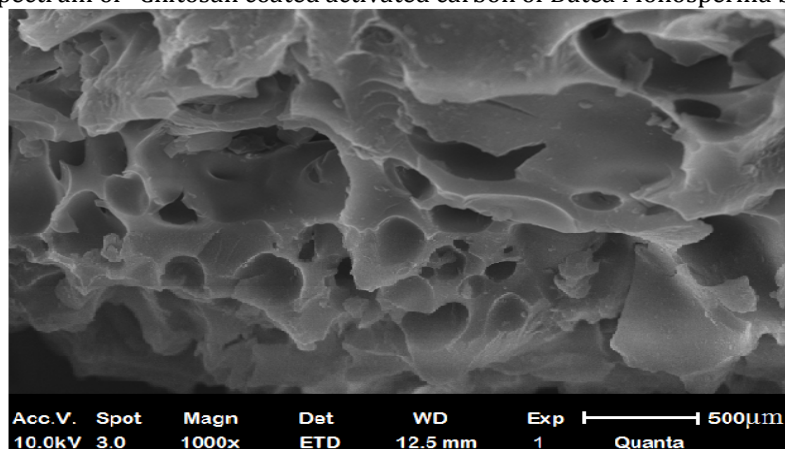


Fig. 2 : Scanning electron micrographs of the CCACBMB at 1000 x

Effect of pH: The role of H^+ ion concentration was examined in the solution at different pH. pH is an important parameter for adsorption of metal ions from the aqueous solution because it affects the solubility of the metal ions. The effect of initial pH on the removal of Cr(VI) using CCACBMB was studied (Fig.3) It is clear that removal of Cr(VI) increases with an increase in pH from 1.0 to 3.0 and it is optimum about 3.0 was observed. The percentage of adsorption increases from 55.0 to 95.8 as pH increased from 1 to 3. The percentage of adsorption decreases steadily to 80% when pH is increased from 3 to 6 and decrease further to 65 % as pH increase to 8.

Effect of Contact Time: Efficient uptake of Cr(VI) ion with effect of contact time by CCACBMB was studied and result are shown in fig.4. indicate that the Cr(VI) removal ability of CCACBMB increased with increasing in contact time before equilibrium is reached. Other parameters such as dose of CCACBMB, pH of solution and initial concentration was kept optimum. It can be seen from Fig.4 that Cr(VI) removal efficiency increased from 50% to 95% when contact time was increased from 60 to 120 min. Optimum contact time for CCACBMB was found to be 120 min. But after that time, removal efficiency of Cr(VI) was nearly constant.

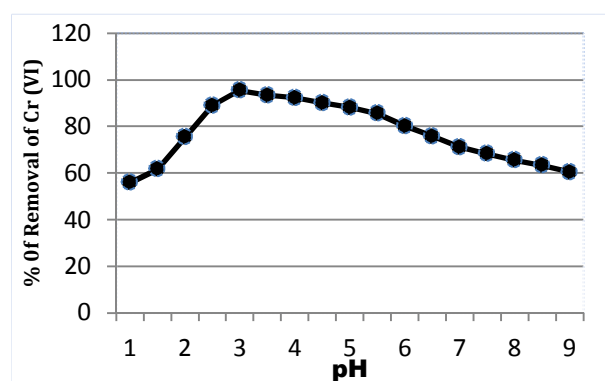


Fig.3. Effect of pH on Cr(VI) adsorption

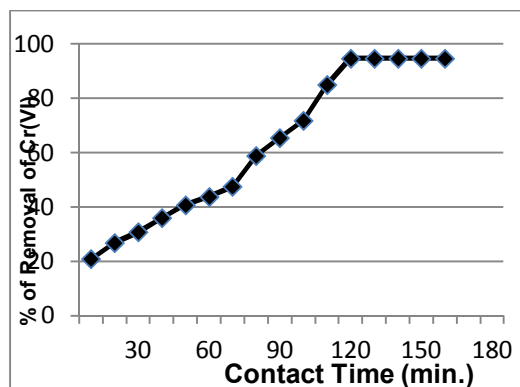


Fig.4. Effect of Contact time on Cr(VI) adsorption

Effect of Adsorbent Dosage: The effect of dosage on the removal of Cr(VI) was studied by varying the amount of CCACBMB from 1 to 9 g/l while keeping other parameters (pH, contact time and initial concentration) constant as shown in fig.5. From the figure, it was observed that percentage of removal of Cr(VI) increased with the increase in the amount of CCACBMB and it was found to 94.5%. This was due to availability of more biosorbents as well as more availability of surface area. It is indicate that by increasing the CCACBMB dosages, the adsorption efficiency of Cr(VI) increases. But after certain amount of adsorbent, the adsorption efficiency remains constant because the maximum adsorption set in and amount of Cr(VI) ion present in the solution bounded to adsorbent nearly constant

Effect of initial metal ion concentration: The effect of initial metal ion concentration on the percentage removal of hexavalent chromium by CCACBMB as 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 10mg/l to 50mg/l. The adsorbent amount was maintain 5g/l. The result shown the decrease in removal from 96% to 73%. This can be justified by the fact that adsorbent have limited number of active sites which are saturated beyond certain concentration.

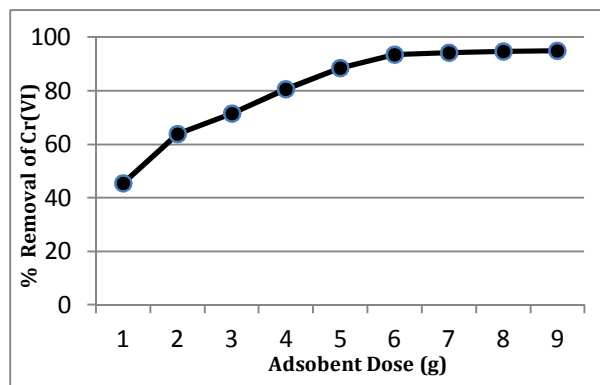


Fig.5. Effect of Adsorbent doses on Cr(VI) adsorption

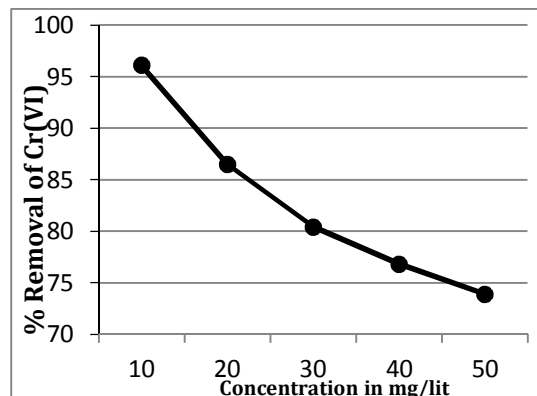


Fig.6. Effect of concentration on Cr(VI) adsorption

CONCLUSION

- The study show that the batch removal of toxic hexavalent chromium in from aqueous solution using CCACBMB was investigated
- CCACBMB was most effective for which removal reached 96% of Cr(VI) at pH= 3 .Show that adsorption was highly pH dependent. Above pH 3 , there was decreased in Cr(VI) removal capacity. The material is used effectively at pH 3for removal of Cr(VI) from aqueous solution.
- Further increase of amount of dosage and contact time were found to increase the percentage removal of Cr(VI) upto 94% to 96%.
- Adsorption of Cr(VI) decreases with the increase in the initial Cr(VI) concentration as amount of CCACBMB was fixed.
- The CCACBMB being suitable biosorbent can be used for the removal of Cr(VI) from aqueous solution through cost effective and environment friendly process.

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