



# Evacuation of Hexavalent Chromium from an Aqueous Solution by Application of Chitosan Based Activated Carbon Prepared from *Butea monosperma* Bark

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## Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

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## ABSTRACT

Industrial waste water may pollute the environment because of the presence of heavy metal ions bonded together. Heavy metal is a major source of pollution and harm to the environment across the world. Biological and environmental damage is caused by heavy metal contamination of drinking water and wastewater. Toxic, non-biodegradable, and long-lasting, they are an imperative must to remove. Environmental pollution is exacerbated by the presence of hexavalent chromium metal ion in waste water from numerous industrial facilities. Standard physical and chemical treatment procedures for removing hexavalent chromium are documented in the literature. In addition to being expensive and energy consuming, these processes appear to also result in the accumulation of hazardous byproducts. The current study used chitosan-coated *Butea monosperma* bark activated carbon to extract hexavalent chromium from an aqueous solution. The batch experiment was used to investigate pH effect, time of contact with adsorbent, adsorbent dose, and the starting concentration of Cr (VI) ions. The pH of the biosorbent was found to be optimum at three for Cr(VI) sorption. The elimination of Cr(VI) from the solution will be accelerated with rise of contact time. Up to 94% more Cr (VI) can be extracted for every unit increase in adsorbent dose. As the blood level of Cr (VI) increased, so did the clearance rate. In this study, researchers discovered that pre-treated biosorbent was an excellent material for eliminating of Cr(VI) ions from contaminated water.

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## 1. INTRODUCTION

People all across the world are dealing with the bad side of industrialisation, which is contamination of the environment. Environmental and human health might be seriously jeopardized if rapid industrialisation and an increase in global pollution result in significant metal contamination [1,2]. There are several companies that leak hazardous metals into the environment in amounts great enough to damage public health and environment. [3]. Contamination of organic materials, nutrients, microbes, and heavy metals [4] is the most common problem with surface and ground water supplies. Cadmium, arsenic, chrome, copper, lead, and mercury are common heavy metals [5]. Heavy metals may be found in the effluent of enterprises like as metal processing, lowland leachate, mining, pulp and paper, and pesticides, to name a few [6]. Heavy metal ions can cause a wide range of disorders that impact the nervous, digestive, respiratory, reproductive, and circulatory systems because they can harm the enzyme system in living organs [7]. Chromium, a heavy metal, is particularly hazardous to aquatic life [8]. According to some estimates, this element is the eighth most common on the Earth. These toxins will accumulate in plant cells and become harmful to animals and humans once they pass through the particle channels on the membrane. According to a series of studies, Chromium has been found to cause damage to a number of different organs. Because of this, the removal of Cr from contaminated water using proper agents is essential for global progress in heavy metal studies [9]. A wide range of industrial wastes, including electroplating, animal skin tanning, cement mining and textile dyeing and dye manufacture as well as paper ink and aluminium conversion coating activities, steel fabrication and facilities that create industrial inorganic chemicals, paints and pigments and metal improvement, fertiliser and photography all contain chromium. This poses a major health and environmental concern to people and other animals [10-13]. As far as environmental stability is concerned, the most stable forms of Cr are hexa- and trivalent chromium's. For this reason, Cr(VI) may be a strong oxidizer capable of penetrating biological cell membranes because of its resemblance in structure to sulphates. Despite the fact that Cr(III) is regarded a micronutrient at low levels, it may be harmful at high concentrations, thus it is best to avoid it.

Cancer, urinary organ damage, epigastric discomfort, nausea, vomiting, and mortality have all been related to Cr(VI) compounds [14,15]. If waste from the tanning and electroplating, textile dyeing, mining, and wood preservation sectors is not properly disposed of or managed, harmful Cr(VI) compounds may be released into the environment. It is defined by world Health Organization (WHO) that wastewater contain hexavalent chromium concentrations of less than 0.05 mg/L [16]. According to the US Environmental Protection Agency, the maximum concentration of Cr(VI) in drinking water is 0.05 mg/L, whereas the maximum concentration of Cr(VI) in inland surface waters is 0.1 mg/L [17]. Skin irritation, liver damage, and lung congestion may occur if the level of water containing hexavalent chromium exceeds the acceptable limit for that particular chemical [18]. As a result, enterprises must reduce their wastewater's Cr(VI) concentration to a safe level before dumping it into the water supply. Chromium can be extracted from industrial wastewater using a variety of techniques, including ion exchange [19,20], electro-dialysis [21], chemical coagulation [22], nanoparticles [23], membrane filtering [24], electrochemical technologies [25], and adsorption [26]. There are various drawbacks to these methods, including high capital costs, ineffective removal of metals, a big amount of hazardous sludge, and a high energy consumption [28]. Biomaterials such as bacteria, fungus, algae, industrial waste, and agricultural waste have lately gained attention in the removal of chromium from wastewater that includes chromium adsorbents/biosorbents [29-33]. Operational costs and inconsistencies in performance are some of the drawbacks of these methods. Because of its great potency, cost-effectiveness, reusability of adsorbent and convenience of operation, adsorption is the most effective approach for eliminating hazardous metals from waste water [34]. To remove the metal chromium (VI) from the contaminated water, there are several adsorbents available [35-39]. Commercial adsorbents, in addition to their high price and low absorption capacity, have trouble in the separation process. As a result, demand for less expensive activated carbon made from locally accessible garbage has increased. According to many research, agricultural waste and byproducts such as maize cob [40], sawdust [41], hazelnut shell [42], groundnut hull [43], sugarcane pulp [44], pea pod peel [45], avocado seed kernel [46], tea waste

[47] and olive pulp [48] as adsorbents to remove Cr(VI) from contaminated water. Despite multiple research on low-cost adsorbents, additional cost-effective adsorbents to extract Cr(VI) from waste water are still essential. The recent work implies the studies conducted to extract Cr (VI) in an aqueous solution using activated carbon from *Butea Monosperma* bark as Chitosan was covered. This ostentatiously named seed plant is actually part of a much larger seed family known as *Butea monosperma*. In Ayurveda, Unani, and Homeopathy as well as others, modern medicine has found a place. 2-acetamido-2-deoxy-D-glucose-(N-acetylglucosamine) polymer chitosan is produced by deacetylation of chitin with a strong alkaline solution. It has extraordinary qualities, both in terms of chemistry and physics. Biodegradable and kind to the environment, Chitosan, a biosorbent, may be dissolved at low pH levels due to its biocompatibility. As a bonus, it is extremely malleable and has a tendency to gel when exposed to water [49,50] An SEM, FTIR, XRD and TG analysis of the composite sorbent material were utilised to determine its characteristic properties. When the biosorbent was tested at 305K in batch isothermal equilibrium testing, its ability to remove Cr (VI) was determined. Researchers took into account the adsorbent dose, contact time, and starting Cr(VI) concentrations. So it has been concluded that the newly synthesised composites can be used to remove carcinogenic Cr(VI) from contaminated water.

## 2. MATERIALS AND METHODS

### 2.1 Chemicals

Merck supplied all of the analytical-grade compounds utilised in the experiment.

### 2.2 Preparation of Activated Carbon from the *Butea Monosperma* Bark (ACBMB)

*Butea monosperma* Bark was collected from the native forest area. Pieces of the tree's bark were hacked off. To prevent the release of any bark colour into the solution, the sand particles attached with the bark was rinsed under running water and then formaldehyde-treated. Deionized water should be used for a final rinse. After that, they were exposed to the sun for five days to dry. A pyrolysis method was used to carbonise the bark after it had been dried. In order to eliminate volatile products and regenerate residue into a char, the temperature of the furnace fluctuated between 800-900°C for around 7 to 8 hours at

this temperature. The char was then heated in a microwave oven to activate it. For 40 minutes, the microwave instrumentation's input power was set to 360W. We used 120-200 metric linear unit size to screen the activated carbon particles to ensure they were free of impurities. A double-distilled water wash followed by a four to five-hour drying period at 105°C finished off the setup process.

### 2.3 Preparation of Chitosan Gel

It was filtered after 1000 cc of 10% oxalic acid was added to 30gm Chitosan with steady stirring. The mixture was warmed between 40°C to 45°C in order to get the optimal intermixture. It was a white viscous gel made of chitosan with oxalic acid.

### 2.4 Coating of Surface of ACBMB with Chitosan Gel

Using a water bath, we made 500 cc of Chitosan gel diluted with distilled water and warmed between the temperatures 40°C - 45°C. Using a rotator shaker, we added gradually 300 g of ACBMB to a diluted chitosan gel and continuous stirring for 24 hours. A deionized water wash and drying was then done on the chitosan coated ACBMB (CCACBMB). The technique was repeated three times to coat the ACBMB surface with a thick layer of chitosan. About 30 to 35 percent of the chitosan was covered. It was then cleansed with deionized water, dried in the sun, and neutralised with 0.5 percent sodium hydroxide.

### 2.5 Characterization of CCACBMB

CCACBMB was characterised using FTIR , SEM , XRD, and TGA

### 2.6 Adsorption Studies

Cr stock solution is gradually reduced to prepare working standards solution of Cr(VI). CCACBMB was employed in a batch equilibrium technique to remove Cr (VI). Several variables were assessed, including pH of the solution, time in contact with the adsorbent, dose of the adsorbent, and the initial concentration of Cr (VI) ion. The Cr(VI) ion concentration in a 50 ml solution was 20 mg/l, while the adsorbent concentration was 5 g/lit. In 20 mg/l concentrations of Cr(VI) at 32°C, the effect of adsorbent dose is studied by varying the quantity of adsorbent from 1gm to 9gm. Initial

concentration effect was studied by varying the concentration of Cr (VI) ions from 10mg/l to 50 mg/l with 5gm/l of adsorbent. An atomic absorption spectrophotometer was used to measure the residual concentration.

### 3. RESULT AND DISCUSSION

#### 3.1 Characterization of Composite (CCACBMB)

The functional groups on the sorbent material were studied using FTIR analysis. CCACBMB's FTIR spectrum (Fig. 3) shows a wide range of absorption peaks, demonstrating the compound's intricacy. FTIR study pointed to free amino groups as well as water and hydroxyl groups as the source of the broad absorption band at  $3438.57\text{cm}^{-1}$ . The broad nature of the band because of merging of bands due to  $-\text{OH}$  and  $-\text{NH}$  group. FTIR of CCACBMB shows the precise signal at  $1612.03\text{cm}^{-1}$  (strong absorption) and  $2284.47\text{cm}^{-1}$  (weak absorption), which can be assigned to the acyl amino group and S-H vibration respectively. C-H and O-H deformation vibrations may be found in the  $1314.26\text{cm}^{-1}$  band. The stretching of the C-OH bond may be responsible for an extra peak at  $1230\text{cm}^{-1}$ . At  $779.13\text{cm}^{-1}$ ,  $-\text{CH}_2$  rocking is fully evident.

Fig. 4 SEM picture of adsorbent implies that the distinct pore structure created on the surface of CCACBMB. On the surface, there is no sign of cellulose structure. However, the CCACBMB's surface is covered in a plethora of microscopic voids. The material's large surface area and excellent sorptive properties were a result of its cavity-like structure. The pore size of cavities on the surface of a material determines the amount of heavy metal that may be accumulated. Since heavy metals have an increased tendency to adhere to the surface of the CCACBMB, it is a good adsorbent.

Fig. 5 shows XRD analysis of chitosan film (a), activated carbon (b), and chitosan amalgamated film (c). Chitosan characteristic peak at  $2\theta = 25^\circ$  can be seen in Figure 5(a), which corroborated the diffractogram. This unsatisfactory outcome is consistent with the bioactivity of polyester as a result of the use of chitosan. The amorphous form was confirmed by the diffractogram of activated Carbon from *Butea Monosperma* bark (figure 5b). Amorphous chitosan amalgamated film is guaranteed by the addition of activated carbon to the chitosan film, as shown in figure (5c). To maximise adsorption, this amorphous segment has active regions that are more available to the adsorbate.

Fig. 6. Thermogravimetric analysis of CCACBMB : The TG curve for CCACBMB is shown in Fig. 6. From this figure, we can see that four consecutive weight loss steps had been observed with CCACBMB. The loss of water content at the adsorbent's surface (about 6.5 percent) at  $132.71\text{C}$  may indicate that the adsorbent's characteristics are hygroscopic. The scission of the ether linkage inside the chitosan skeleton results in a 26 percent weight loss of the adsorbent, according to the thermograph at  $342.89\text{C}$ . The 20% weight loss indicated by CCACBMB is determined at  $487.23^\circ\text{C}$ . This may be due to the loss of some volatile material from the adsorbent material. At  $698.69^\circ\text{C}$ , the weight loss of the adsorbent is approximately 20.0%, which corresponds to the thermal decomposition of the glucosamine moiety at some stage in the degradation of the chitosan. After  $700^\circ\text{C}$ , round 10% residue remain. This highly stable residue even at  $700^\circ\text{C}$  or higher seems to be an inorganic component contained in CCACBMB adsorbent consisting of minerals and ash that are non-degradable at high temperatures.

**Effect of pH:** The pH was determined by looking at how much concentration of  $\text{H}^+$  ion in the solution. Aqueous pH impacts the solubility of metal ions in solution, making it essential for ion adsorption. The impact of pH on the elimination of hexavalent chromium by using composite material ie. CCACBMB tuned into result (Fig.7). From graph it clearly implies that from pH 1.0 to 3.0, the elimination of Cr(VI) rises, and reaches a maximum at 3.0. The elimination percentage increases from 55.0 to 95.8 percentage when the pH rises from 1.0 to 3.0. From pH 3 to 6, the elimination rate decreases gradually to 80%, then lowers an additional 65% as the pH climbs to 8.0.

**Effect of Contact Time:** Impact of contact time with percent removal of Cr(VI) by used of composite material was calculated and end outcomes shown in Fig. 8. Histogram indicate the elimination of Cr(VI) by the composite adsorbent accelerated with rise of contact time before reached to equilibrium. Various parameters which includes adsorbent dose, solution pH, initial Cr(VI) ion concentration was unbroken maximum. Fig. 8 represents that elimination potency of metal ion accelerated from 55 percent to 94 percent with rise in time of contact with adsorbent from 60 min to 120 min. For CCACBMB, a contact time of 120 minutes was shown to be optimum. Beyond that time, elimination of Cr(VI) metal ion was stable.



Fig. 1. Bark of *Butea Monosperma* Tree



Fig. 2. Chitosan Coated Activated Carbon (CCACBMB)

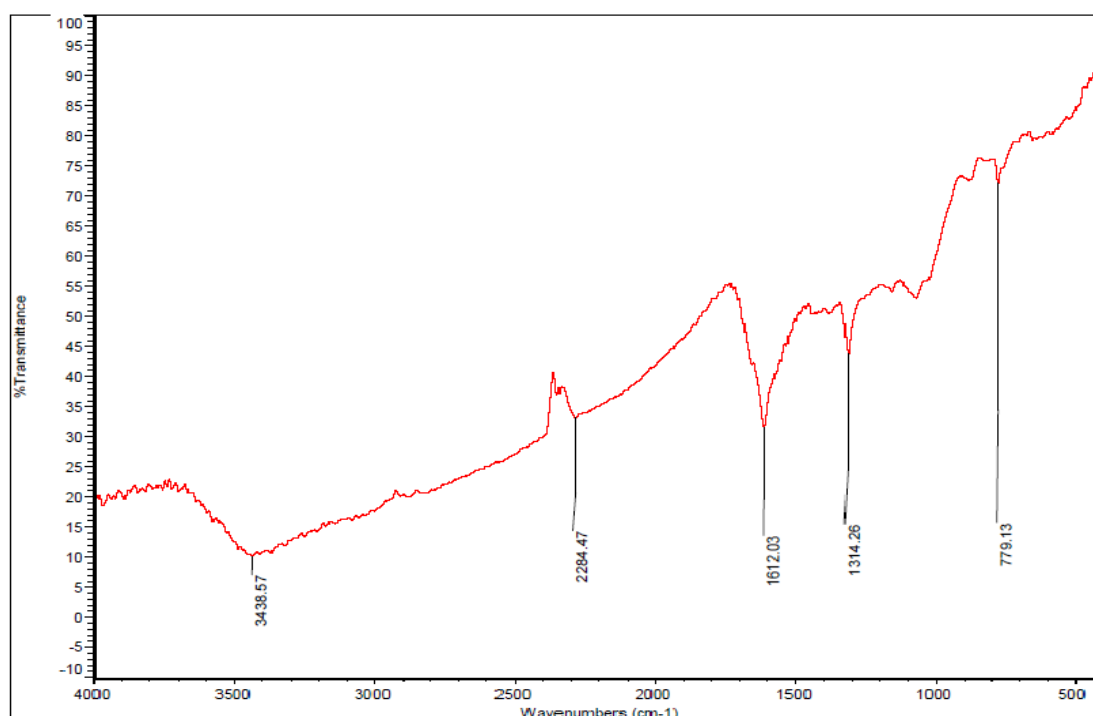


Fig. 3. FT-IR spectra of CCACBMB

**Effect of Adsorbent Dosage:** Other variables, such as pH, contact time, and beginning concentration, remained constant while the CCACBMB concentration rose from 1 to 9 g/l. Researchers were able to investigate the effect of dose on the removal of Cr (VI) from the contaminated water. As can be seen in the graph, 94.5 percent of the Cr(VI) was removed

when the concentration of CCACBMB was raised upto 6gm. As a result, a bigger percentage of the pores and surface area were revealed. Cr (VI) adsorption was increased by increasing the concentration of CCACBMB. Cr(VI) ions stay virtually constant in the solution after 6gm dose of adsorbent has been used, therefore adsorption is constant.

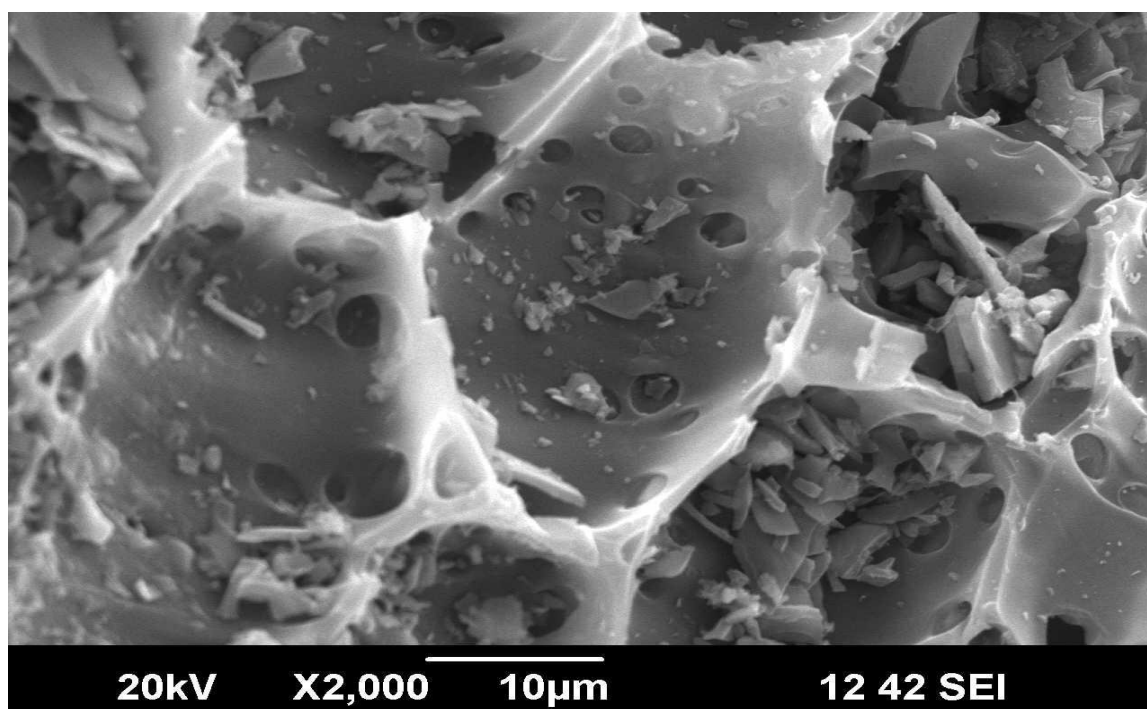


Fig. 4. SEM picture of Composite at 2000 x

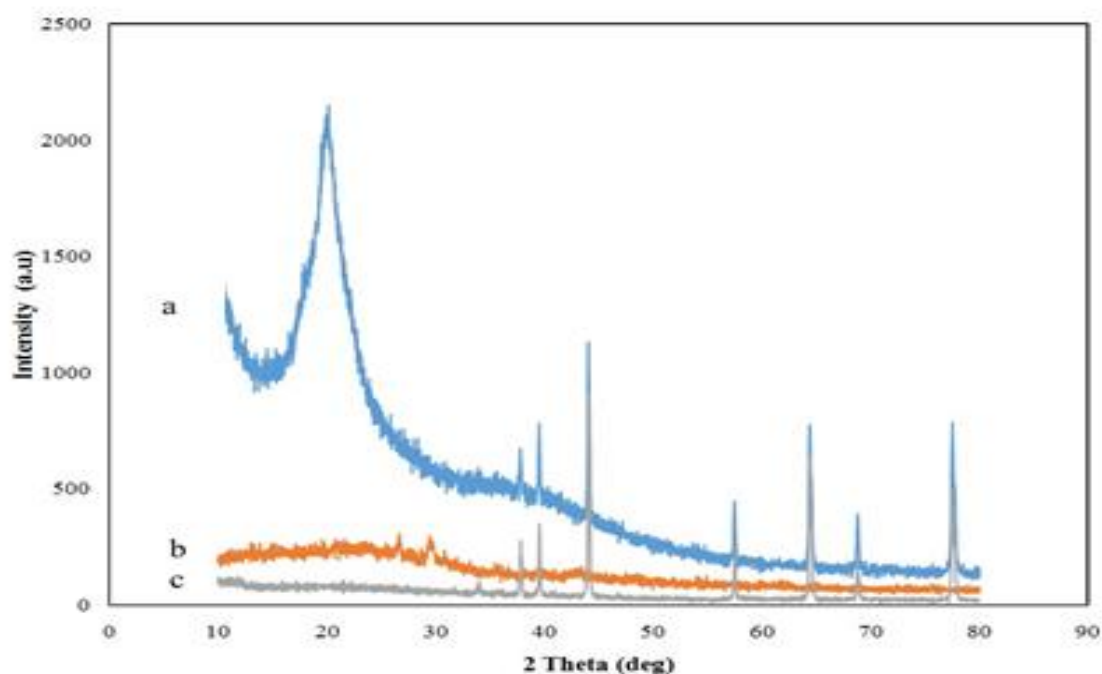


Fig. 5. XRD spectra of chitosan film (a) activated carbon (b) and chitosan amalgamated film (c).

**Effect of initial metal ion concentration:** The percentage elimination of Cr(VI) with concentration is represented in Fig.10 It is observed that an increasing the metal ion concentration through the composite, reduced the elimination percentage. In this experiment, the effect of starting concentration was studied

between 10mg/l to 50mg/l. Concentration of adsorbent was kept constant to 5g/L. The final results revealed up to a 73% reduction in percentage elimination of Cr(VI). Adsorbents have confined a wide variety of active sites to saturate at a certain concentration, which justifies this result.

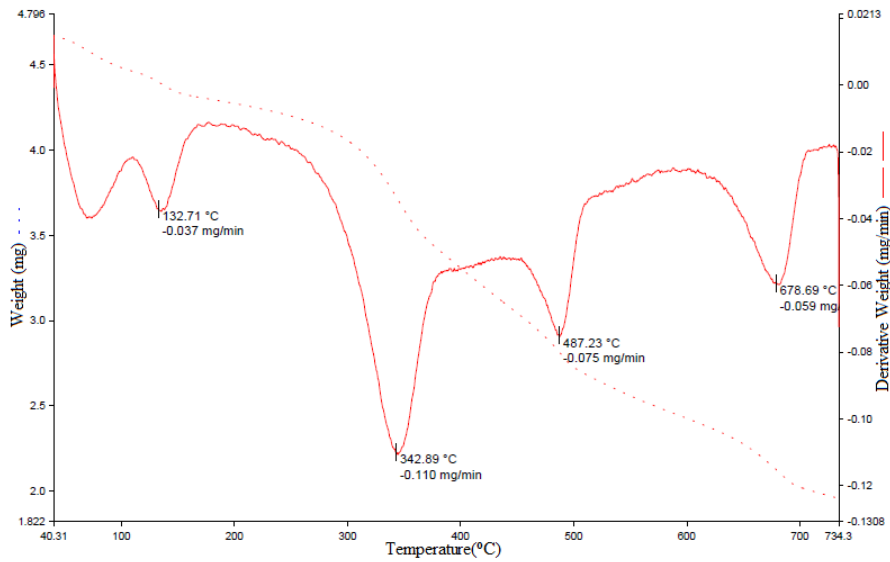


Fig. 6. TG curve of composite (CCACBMB)

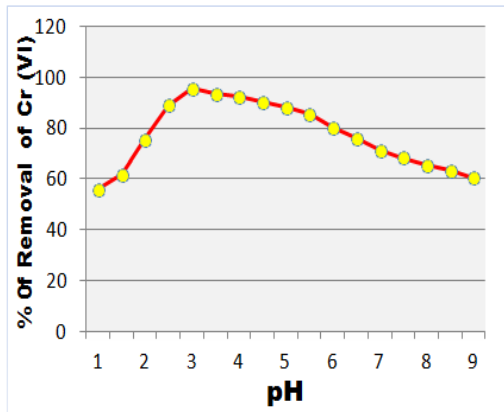


Fig. 7. Impact of pH on Cr(VI) adsorption

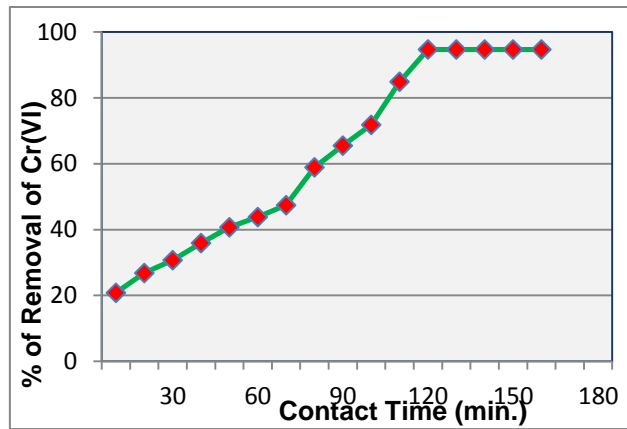


Fig. 8. Impact of Contact time on Cr(VI) adsorption

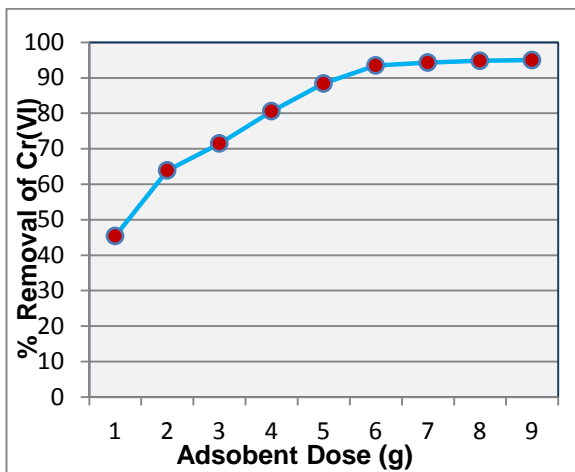


Fig. 9. Impact of Adsorbent dose on Cr(VI) adsorption

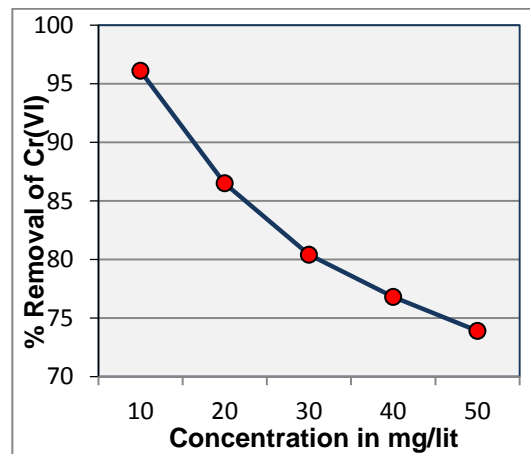


Fig. 10. Impact of concentration on Cr(VI) adsorption

#### 4. CONCLUSION

- Chitosan coated activated carbon successfully prepared from *Butea Monosperma* tree bark and characterized using SEM, XRD, FT-IR and TG analysis.
- CCACBMB was successfully utilized as an adsorbent for elimination of Hexavalent Chromium.
- At pH=3, CCACBMB achieved a 96% removal efficiency for Cr (VI). Adsorption is extremely sensitive to pH changes. As pH increased, so did the efficacy of eliminating Cr(VI).
- Additional dosage and contact time were shown to promote Cr(VI) elimination by up to 94% to 96% if further increases were made.
- The Percentage elimination of Cr(VI) reduced with rise of concentration of Cr(VI) ion keeping adsorbent concentration was constant.
- The composite biosorbent CCACBMB material is a cost-effective and environmentally friendly utilised to remove Cr(VI) from aqueous solutions.

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#### COMPETING INTERESTS

Author has declared that no competing interests exist.

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