Original Research Article

Evacuation of Hexavalent Chromium from Aqueous Solution Using Chitosan Based Activated Carbon Derived from *Butea Monosperma* Bark

Abstract

Pollution of water because of the presence of bound heavy metals ions could be a severe socio-environmental issue caused by the discharge of industrial waste water. Heavy metal is one among the foremost environmental and ecological issues during this world. The presence of heavy metals in water and wastewater causes harmful effects to the living beings and the environment. In view of their toxicity, non-biodegradability and protracted 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. Many standard physical and chemical treatment techniques are reported in the literature for the removal of hexavalent chromium. But these process don't seem to be solely pricey and energy intensive, however conjointly cause the assembly of harmful by product. In the present study, activated carbon derived from the bark of *Butea monosperma* was used as a potential sorbent once coating it with chitosan, for removal of hexavalent chromium from aqueous solution was investigated. The batch experiment was dispensed to research the effect of significant process parameters such as effect of pH, contact time, adsorbent dose and initial Cr (VI) ion concentration. The utmost sorption of Cr(VI) on biosorbent was found at pH value of 3. The elimination of hexavalent chromium from aqueous solution will increases with rise in contact time. Any rise in adsorbent dose, there's increase of removal of Cr (VI) up to 94 %. The increase in initial concentration of Cr (VI) led to decrease in the percent 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

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Introduction:

People are facing the dark aspect of industrialization all round the world that is environmental pollution. Significant metal pollution as a result speedy industrialization and growth in world pollution could also be serious threat to environment and every one sorts of life [1,2] .The toxic metals are emitted to the environment from numerous industries in such an amount that cause risk to human health [3]. The most issues regarding surface and ground water resources square measure contamination of organic matters, nutrients, microorganisms and heavy metal [4]. The representative members of heavy metals include cadmium, arsenic, chromium, copper, lead, and mercury [5]. Heavy metals are contained with high concentration within the effluent of the many industries like metal process, lowland leachate, mining, pulp and paper; and pesticides [6]. It's been well-known that heavy metal ions will destroy the enzyme system in living organs, therefore causes several diseases associated with nervous, digestive, respiratory, reproductive, and circulatory systems [7]. Among the heavy metals, chromium has the harmful effects on the aquatic setting [8]. Chromium is reported to be the seventh most extensive component on earth. It will enter the plants cells by penetrating through the particle channels on the membrane, accumulate within the organic phenomenon and become poisons to animal and human. It's been recorded that Chromium will destroy several organs like excretory organ, lung, brain and immune system. Therefore, the study of heavy metals, particularly Chromium removal in water by applicable agents is extremely essential for the acceptable development of the world [9]. Chromium is present in industrial effluents created from electroplating, animal skin tanning, cement, mining, textile dyeing, dye producing, paper, ink, aluminium conversion coating operations, steel fabrication, plants manufacturing industrial inorganic chemicals, wood treatment units, paints and pigments, metal improvement, fertiliser and photography industries and cause severe environmental and public health issues (10,11).

Hexavalent chromium and trivalent chromium are the foremost stable forms of Chromium within the environment. Cr(VI) may be a hepatotoxic sturdy oxidiser capable of penetrating the biological cell membranes because of its similarity to sulphates in structure[12]. On the opposite hand, Cr(III) is a smaller amount hepatotoxic and is considered as a micronutrient at minute concentrations however may be toxic if concentrations are high [13]. Exposure to Cr(VI) compounds could cause health prejudicious effects like carcinoma, urinary organ harm, epigastric pain, nausea, vomiting, and even death[14,15]. Careless disposal and improper treatment of effluents from animal skin tanning, electroplating, textile dyeing, mining, and wood preservation industries cause contamination of the environment by Cr(VI) compounds. According to the World Health Organization (WHO), the most acceptable limit of hexavalent chromium concentration is 0.05 mg/L in wastewater (16). US Environmental Protection Agency (US EPA) has suggested the acceptable level of Cr(VI) is 0.05 mg/L for potable water and is 0.1 mg/L for inland surface waters (17). If hexavalent chromium is present in water on the far side the suitable limit that causes skin irritation leading to lesion formation, liver damage and pulmonary congestion (18). Hence it is necessary for industries to decrease the Cr(VI) concentration from their wastewater to acceptable limit before discharging into the aquatic environment. There are varied processes enforced to get rid of chromium from industrial wastewater including ion exchange (19, 20), electro-dialysis (21), chemical coagulation (22), nanoparticles (23), membrane filtration (24), electrochemical technologies (25), and adsorption (26,27). These processes have several disadvantages like high cost of capital, incomplete metal removal, large quantity of harmful sludge, high energy demand (28). Increasing attention has been paid recently to the employment of eco-friendly and low cost biomaterials as adsorbents/bio-sorption for chromium removal from wastewater like microorganism, fungi, and algae, industrial and agricultural wastes (29-33). Most of those strategies suffer various drawbacks such as from high operational costs, unreliable nature of operation, etc. Among all the strategies, adsorption method has been found to be appropriate process to get rid of toxic metals from wastewater victimization low cost adsorbents due to its high potency, economical and simple to operate, low cost, reusability of adsorbent (34). Activated carbon, biological materials, chitosan, fly ash etc. are some of the usually used adsorbents for Cr(VI) removal (35-39). The disadvantages of commercial available adsorbents are high cost, low adsorption capacity, difficulty of separation after adsorption. Hence, it's a growing have to be compelled to derive the activated carbon from cheaper and locally available waste materials. Many literatures have reportable the employment of low cost adsorbent from numerous agricultural waste and byproducts like 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 for the removal of Cr(VI) from aqueous solution. In spite of many researches adopted for numerous low cost adsorbents, there's still a desire to develop appropriate & more economical adsorbents for the removal of Cr(VI) from waste water. The current 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 that Chitosan was coated. *Butea monosperma* one in every of the biggest families of seed plant belong to *Fabaceae* family, popularly known as "dhak" or "palas" unremarkably called 'Flame of Forest'. *Butea monosperma* is extensively used in Ayurveda, Unani and Homeopathic medication and has becomes a cynosure of contemporary medication [49]. Chitosan (2-acetamido-2-deoxy-β-D-glucose-(N-acetylglucosamine) could be a part deacetylated compound of polymer of chitin and is typically prepared from chitin by deacetylation with strong alkaline solution. It has excellent physicochemical properties. It's environmentally friendly and bioactive. The biosorbent material,

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chitosan, is slightly soluble at low pH. It's additionally soft and has tendency to create a gel in aqueous solution (49,50) The composite sorbent material was characterized by FTIR and scanning microscopy (SEM) and XRD studies. Batch isothermal equilibrium technique was conducted at 305K to judge the potency of newly synthesized biosorbent for removal of Cr (VI) from the aqueous solution. Experiment were dispensed as effect of pH, adsorbent dosage, contact time and initial Cr(VI) ion concentration. Therefore the newly synthesized composite are well tried to be superb adsorbent which may 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 native area. The bark was cuts into little pieces. It has been washed with tap water to get rid of the sand particles and so treated with formaldehyde to avoid unleash any colour of bark into solution. Once more wash with many time of deionized water. Then they were sun dried for five days. Once drying, the bark was subjected to pyrolysis process for carbonization using muffle Furness at concerning 800-900^{0}C temperature vary for about 7 to 8 hr in order that volatile product were removed and residue was regenerate into a char. The char was then subjected to microwave activation in microwave. The input power of microwave instrumentation was set at 360W for 40 min. The ensuring activated carbon particles were grounded and sieved in 120-200 metric linear unit size. This activated carbon was then washed with double distilled water and dried at 105^{o}C for four to five hr.

Preparation of Chitosan Gel:

30 g of chitosan was accessorial into 1000 ml of 10% oxalic acid with constant stirring. The mixture was heat at a temperature vary 40^{0}C – 45^{0}C for correct intermixture. The chitosan-oxalic acid mixture was shaped a whitish viscous gel.

Surface coating of ACBMB with Chitosan Gel:

500 ml of chitosan gel was diluted with distilled water nearly of 500 ml and warm to 40^{0}C -45^{0}C. 300 g of ACBMB was slowly additional to diluted chitosan gel and shake automatically victimization rotator shaker for 24 hr. The chitosan coated ACBMB (CCACBMB) was then wash with deionized water and dried. The method was perennial for 3 times to create thick coating of chitosan on the ACBMB surface. The chitosan coated was concerning 30 to 35% by weight. CCACBMB neutralized with 0.5% sodium hydroxide solution and then extensively rinsed with deionized water and dried in sunlight.

Characterization of CCACBMB:

Characterization of CCACBMB was done by, FTIR (Fig.3), SEM (Fig.4),XRD (Fig.5),TGA(Fig.6)

Adsorption Studies:

Working standard were ready by progressive dilution of stock solution of Cr(VI).Removal of Cr(VI) using CCACBMB was dispensed by batch equilibrium technique. The influence of varied parameters like 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^{0}C with initial Cr (VI) concentration 20 mg/l and adsorbent quantity 5g/lit by taking 50 ml Cr(VI) solution. The result of adsorbent dose is studied by varied adsorbent quantity from 1g to 9g with Cr (VI) ion concentration 20mg/l whereas result of initial Cr(VI) ion concentration is studied by ever changing concentration from 10mg/l to 50mg/l with adsorbent

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quantity 5g/l at 32^{0}C. The residual concentrations were measured in atomic absorption spectrophotometer.

Result and Discussion:

Characterization of CCACBMB

FTIR(fig.3) analysis was performed to examine the functional groups present on the sorbent material. FTIR spectrum of CCACBMB displays variety of absorption peaks, indicating the complex nature of CCACBMB. FTIR analysis indicated broad absorption band at 3438.57cm^{-1} correspond to –OH stretching vibration of water and hydroxyl group and –NH stretching vibration of free amino groups. The broad nature of the band because of merging of bands due to –OH and –NH group. FTIR of CCACBMB shows the precise signal at1612.03cm^{-1}(strong absorption) and 2284.47cm^{-1} (weak absorption), which can be assigned to the acyl amino group and S-H vibration respectively. The band at 1314.26cm^{-1} corresponds to C-H and O-H deformation vibrations. Another absorption peak at 1230cm^{-1} may well be attributed to C-OH stretching. A peak at 779.13cm^{-1} represent -CH_2 rocking.

Fig.4. The scanning electron microscopy (SEM) of CCACBMB indicates that it's clear pore structure developed. There is no cellulosic structure form on the surface. However but there spare measure terribly tiny and lots of cavities over the surface of the CCACBMB. Because of cavity like structure of the material possessed high extent surface area and high sorptive properties. Sorption of any heavy metal depends upon the pore size of cavities present on the surface of the material. Therefore CCACBMB has high tendency to adsorb heavy metals on his surface and has excellent adsorbent.

Fig.5 XRD assessment grow to be became completed on chitosan film (a), activated carbon (b) and chitosan amalgamated film (c). Figure 5(a) confirmed diffractogram of chitosan and it displayed typical peak of chitosan at $2\theta= 25^0$. This quit end result is in settlement to chitosan used as a bioactivity of polyester. The diffractogram of activated carbon of *Butea Monosperma* bark (figure 5b) confirmed the amorphous structure. Addition of activated carbon on chitosan film ensuring an amorphous chitosan film as proven in figure (5c). This amorphous segment is favorable for adsorption because of the active spots are greater handy for 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 preliminary weight loss (approximately 6.5%) of the material at 132.71^{0}C, may be due to the loss of water content at the surface of the adsorbent suggesting that the properties of adsorbent are hygroscopic. The thermograph at 342.89^{0}C suggest 26% weight loss of the adsorbent due to the scission of the ether linkage with inside the chitosan skeleton. The 20% weight loss indicated by CCACBMB is determined at 487.23^{0}C. This may be due to the loss of some volatile material from the adsorbent material. At 698.69^{0}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^{0}C, round 10% residue remain. This highly stable residue even at 700^{0}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.

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Fig.1 Bark of ***Butea Monosperma***

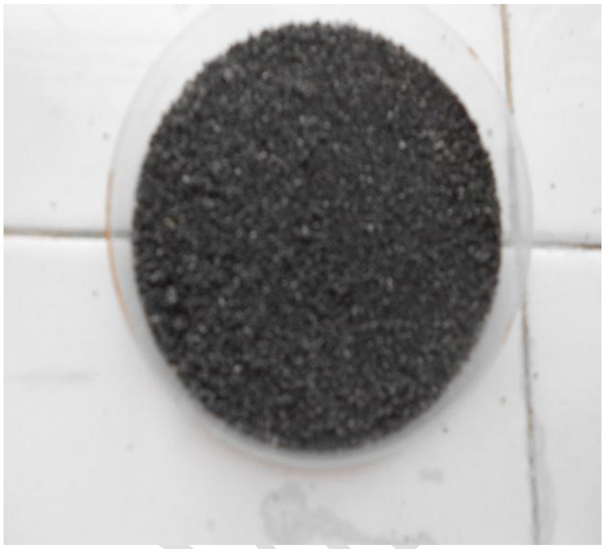

Fig.2. Chitosan Coated Activated Carbon (CCACBMB)

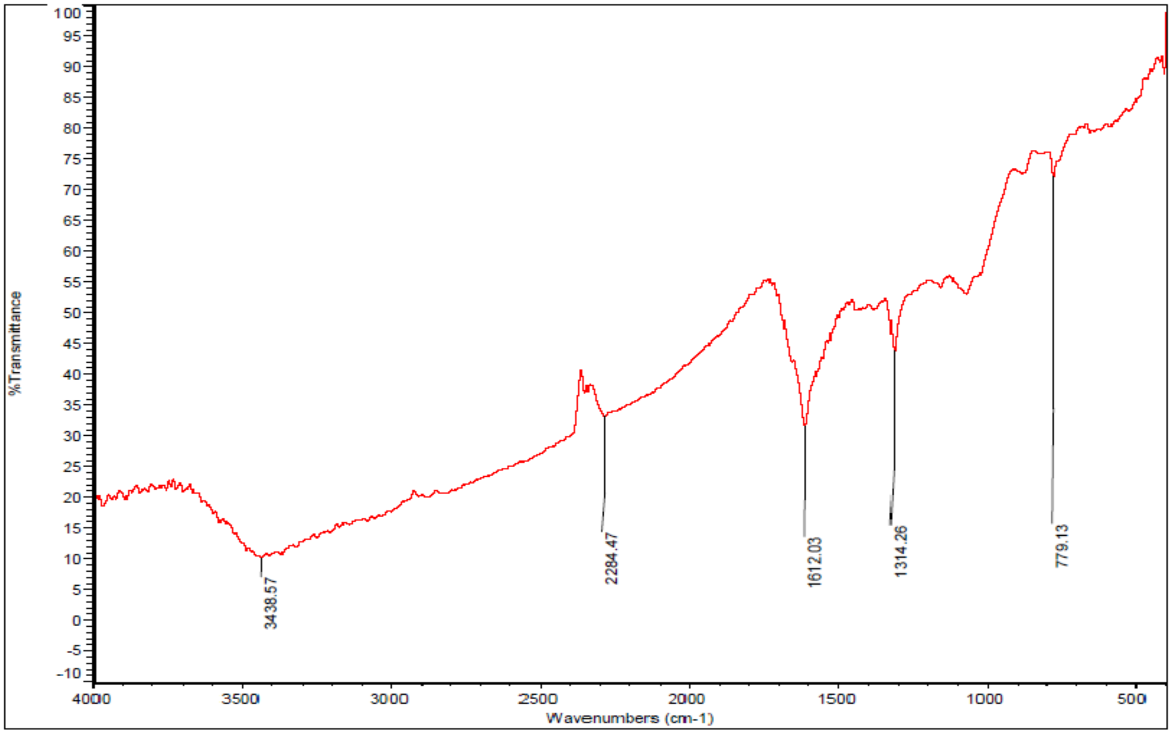

Fig. 3 : FT-IR Spectrum of Chitosan coated activated carbon of *Butea Monosperma* bark (CCACBMB)

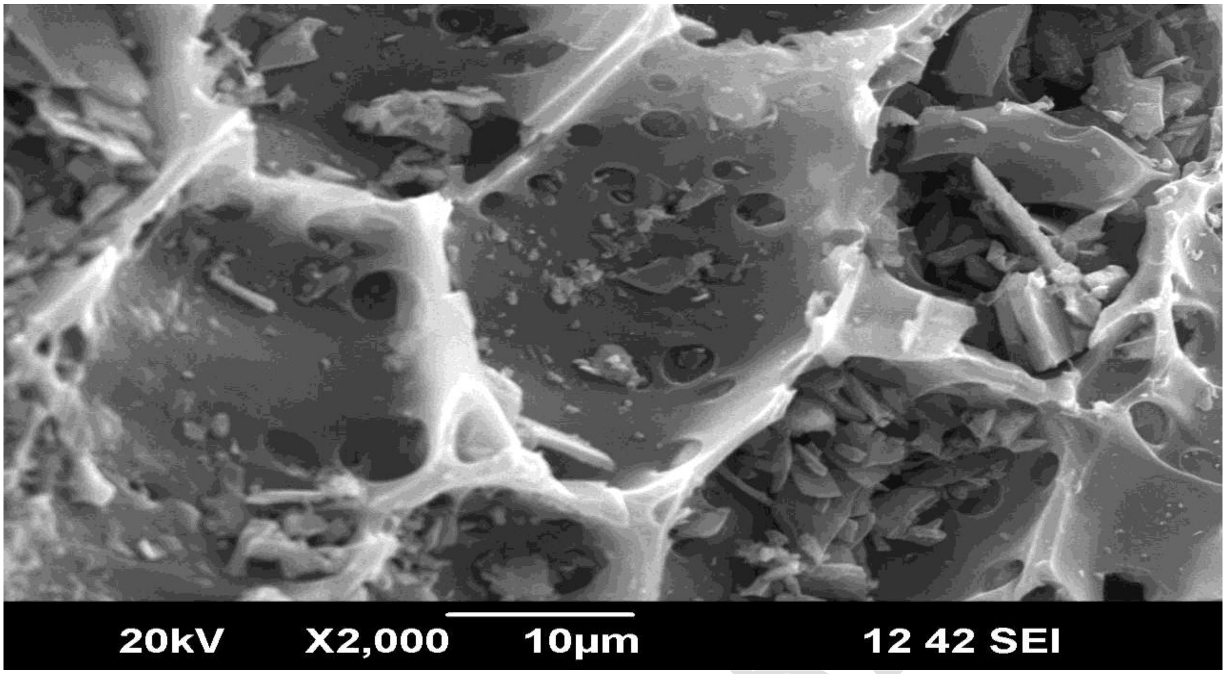

Fig. 4 : Scanning electron micrographs of the CCACBMB at 2000 x

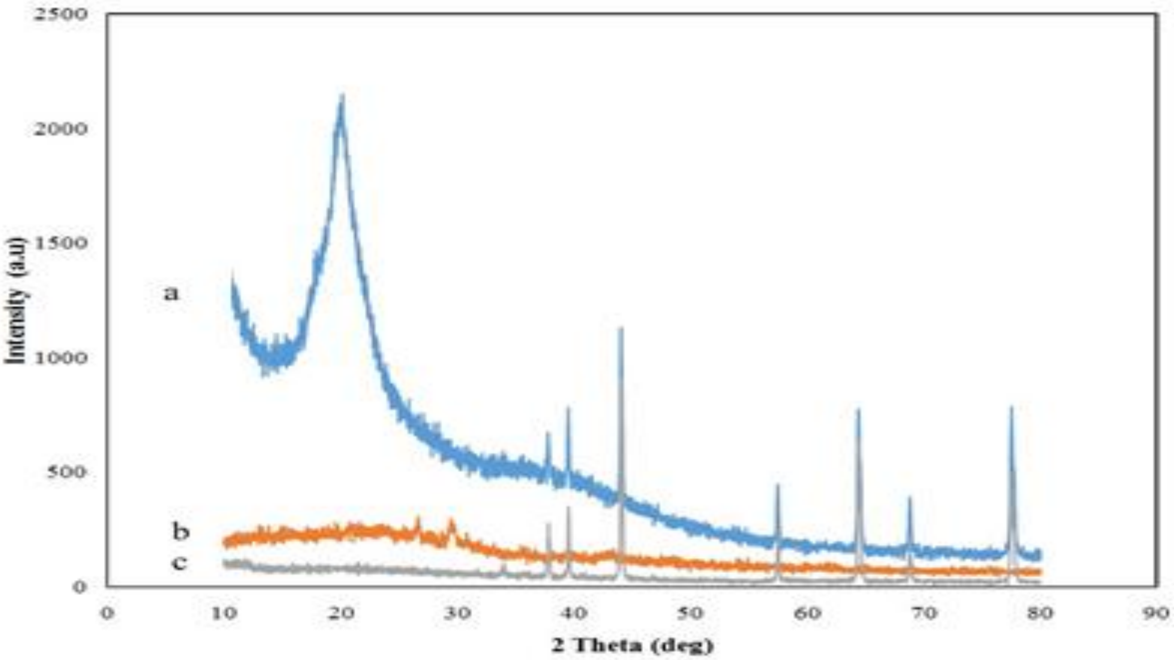

Figure 5. XRD patterns of chitosan film (a) activated carbon particles (b) and chitosan composite film (c).

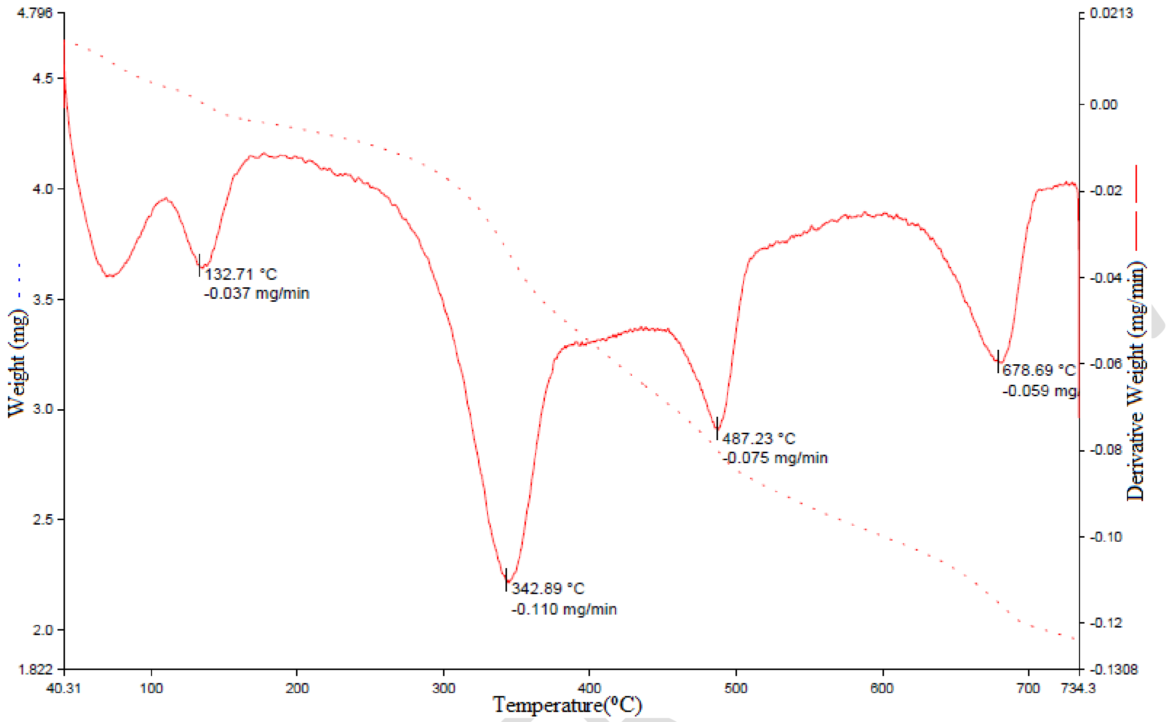

Fig.6 TG Curve of Chitosan Coated Activated Carbon of *Butea Monosperma* Bark(CCACBMB)

Effect of pH: The function of H$^+$ ion concentration was examined in the solution at different pH. pH is an vital parameter for adsorption of metal ions from the aqueous solution as it influence the solubility of the metal ions. The impact of preliminary pH on the elimination of Cr(VI) the use of CCACBMB tuned into studied (Fig.7) It is obvious that elimination of Cr(VI) will increases with an increase in pH from 1.0 to 3.0 and its maximum at 3.0 was observed. The percentage of adsorption will increases from 55.0 to 95.8 as pH accelerated from 1 to 3. The percent of adsorption decreases steadily to 80% whilst pH is accelerated from 3 to 6 and reduced in addition to 65 % as pH increase to 8.

Effect of Contact Time: Efficient uptake of Cr(VI) ion with impact of contact time with the aid of using CCACBMB was studied and end result are proven in fig.8 imply that the Cr(VI) elimination capacity of CCACBMB accelerated with increasing to bear before equilibrium is reached. Other parameters which includes dose of CCACBMB, pH of solution and initial concentration was unbroken optimum. It may be visible from Fig.4 that Cr(VI) ion removal potency accelerated from 50% to 95% while contact time turned into accelerated from 60 to 120 min. Optimum contact time for CCACBMB turned into observed to be 120 min. But after that time, elimination of Cr(VI) was nearly constant.

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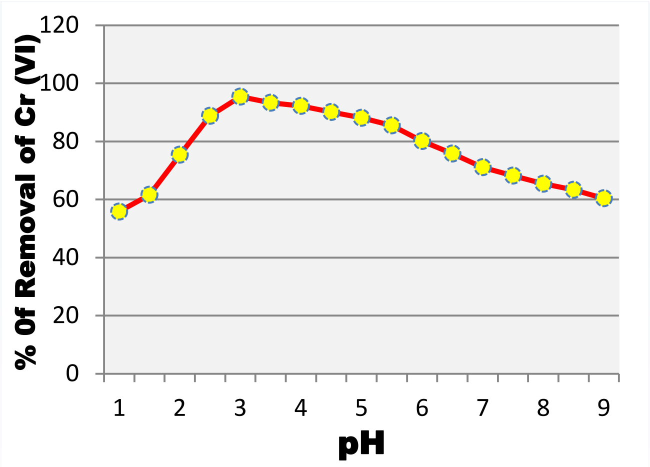

Fig.7. Effect of pH on Cr(VI) adsorption

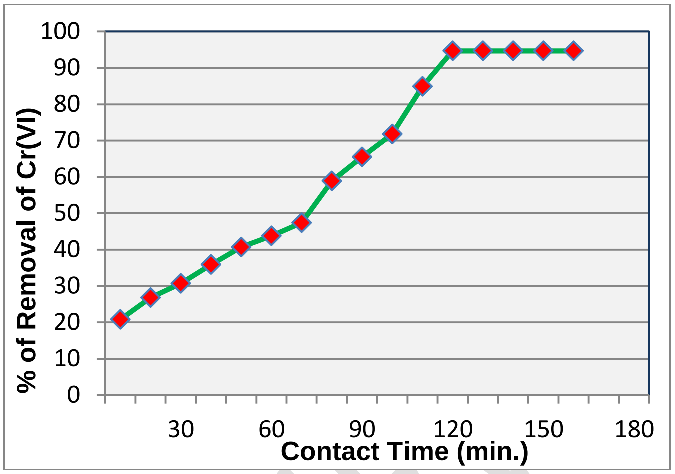

Fig.8.Effect of Contact time on Cr (VI) adsorption

Effect of Adsorbent Dosage: The impact of dosage at the elimination of Cr(VI) become studied with the aid of using various the quantity CCACBMB from 1 to 9 g/l whereas retaining other parameters (pH , contact time and initial concentration) constant as shown in fig.9. From the figure, it was discovered that percent of removal of Cr(VI) ion inflated with the rise within the quantity of CCACBMB and it had been found to 94.5% .This was due to availability of more pores as well as more availability of surface area. It is indicate that by increasing the CCACBMB dose, the adsorption potency of Cr (VI) ion will increases. But after certain quantity of adsorbent, the adsorption potency remains constant as a result of the utmost surface assimilation set in and Cr(VI) ion present in the solution bounded to adsorbent nearly constant.

Effect of initial metal ion concentration: The impact of initial metal ion concentration on the percentage elimination of hexavalent chromium through CCACBMB as shown in fig.10. It may be visible that the percent removal of Cr(VI) decreases with the increase in initial Cr(VI) concentration. In this examine, the experiment was performed to examine the initial concentration effect in the range 10mg/l to 50mg/l .The adsorbent quantity changed into preserve 5g/l .The end result proven the decrease in elimination from 96% to 73%.This may be justified through reality that adsorbent have constrained wide variety of active sites that are saturated beyond certain concentration.

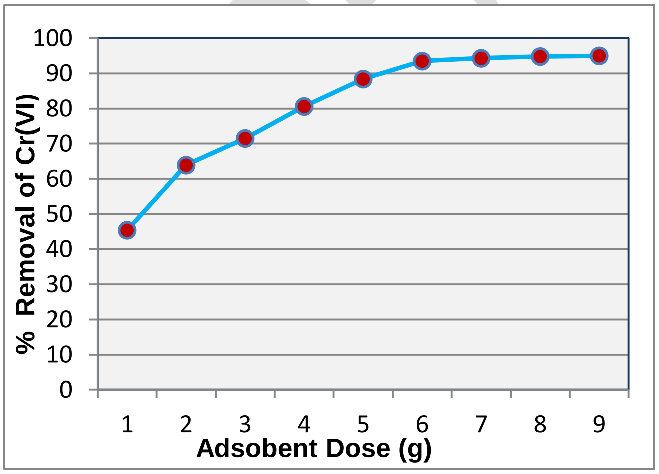

Fig.9. Effect of Adsorbent doses on Cr (VI) adsorption

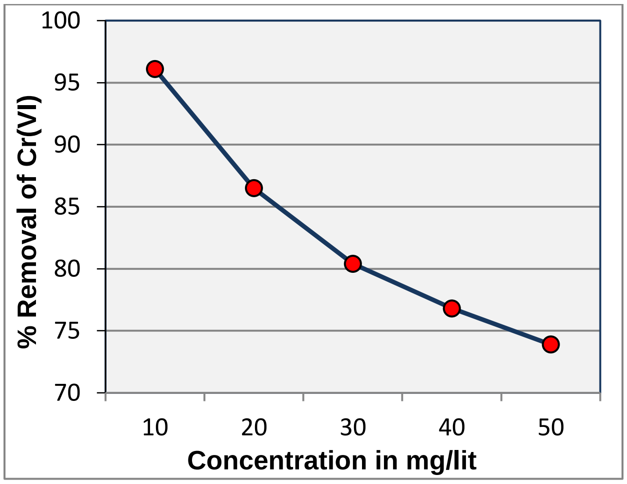

Fig.10 Effect of concentration on Cr(VI) adsorption

Conclusion:

- The activated carbon derived from the bark of *Butea monosperma* tree was efficaciously synthesized and characterised using FTIR, SEM and XRD studies.
- The study show that the batch elimination of hexavalent chromium from aqueous solution usage CCACBMB become investigated.
- CCACBMB was most effective for elimination of Cr(VI) ion at pH= 3 with 96%. Show that adsorption was extremely pH dependent. Above pH 3, there was decreased in Cr(VI) removal capacity.
- Further increase of quantity of dose and contact time were found to extend the proportion removal of Cr(VI) up to 94% to 96%.
- Adsorption of Cr(VI) decreases with the rise in the initial Cr(VI) ion concentration as quantity of CCACBMB was fixed.
- The CCACBMB being appropriate biosorbent are often used for the elimination of Cr(VI) from aqueous solution through cost effective and environment friendly method.

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