

Surface Modified Adsorbent for Removal of Hexavalent Chromium from Aqueous Solution

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Abstract

Environment is deteriorating day by day due to industrial pollution, toxic chemicals leads to the accumulation of heavy metals contamination in the waste water. 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 article reports the characterization and use of chitosan-coated activated carbon derived from the bark of *Pongamia pinnata* (CCPPAC) as a potential adsorbent after 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 CCPPAC was found at pH 4.5, 5 gm/lit of adsorbent dose and 140 min contact time. Under optimum condition, 96% Cr(VI) was removed from aqueous solution. This investigation verifies that CCPPAC, 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: Adsorption, Bio-sorbent, Chitosan, Hexavalent chromium, *Pongamia pinnata* bark

Introduction

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. Heavy metals account for a number of disorders in plants and animals and their removal from aqueous media is an important and challenging task [1,2]. Metals, which are significantly toxic to human beings and ecological environments, include chromium, copper, lead, mercury, cadmium, nickel, iron etc.

Chromium exists in aqueous media in two oxidation states, hexavalent Cr(VI), and trivalent Cr(III) and the toxicity of chromium depends upon its oxidation state. In a solution the Cr(VI) exists in various forms depending upon the pH, such as chromate ($\text{Cr}_2\text{O}_4^{2-}$) hydrochromate (HCrO_4^-), or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) [3]. 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 various industries and manufacturing plants such as tanneries, paints and pigments, electroplating, metal processing, wood preservatives, textile, dye industry, steel fabrication and canning and discharge large quantity into the environment [4–8]. Chromium enters into the body through breathing, eating, drinking or skin contact of chromium and its compounds. The toxic effects of Cr(VI) include skin rashes, nose bleeding, respiratory tract infection, suppressed immune system, hepatic diseases, and lung cancer [9,10]. According to WHO, 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 [11,12]. Ethiopian Environmental Protection Authority (EPA) also set a minimal standard to be 0.1 mg/l for hexavalent chrome containing industrial effluent [13]. Thus it is mandatory to treat the Cr-bearing wastewaters. Several chemical and physical methods have been developed to treat chromium bearing effluents to bring its level down to the permissible effluent standards [14-17].The most common methods include chemical precipitation, ion exchange, ultra-filtration, solvent extraction, sedimentation, reverse osmosis, dialysis and adsorption[18]. 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 [19]. 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 plant waste, coconut coir pith, sawdust, rice

husk, cotton seed hulls, sugarcane bagasse, peanut hull,), pomegranate peel, tea leaves etc. for the removal of Cr(VI) from contaminated water[20-26]. The present investigation, studies were carried out for the removal of Cr(VI) from aqueous solution using chitosan coated activated carbon derived from bark *Pongamia pinnata* belong to *Rhamnaceae* family which is an extremely drought hardy and native fruit of India. It is useful as food, fodder, nutrient and medicine. *Pongamia pinnata* having tremendous medicinal properties, attributed by adverse group of secondary metabolites such as alkaloids, flavonoids, terpenoids, saponin, pectin, triterpenoic acids and lipids. Chitosan{2-acetamido-2-deoxy- β -D-glucose-(N-acetylglucosamine)} 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 [27,28]. The composite sorbent was characterized by FTIR and Scanning Electron Microscopy (SEM) studies. Batch isothermal equilibrium method was conducted at 303K 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 composite have been proved to be very good adsorbent which can be successfully used for removal of carcinogenic hexavalent chromium from aqueous solution.

Material and Method:

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 *Pongamia pinnata* (PPAC)

The bark of *Pongamia pinnata* 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 min. The resulting activated carbon particles were ground 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 hrs and stored in airtight bottle.

Preparation of Chitosan Gel

Chitosan was procured from Otto Chemical, Mumbai (India). 30 g of chitosan was added into 1000 ml of 10% 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 PPAC with Chitosan Gel

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

Characterization of CCPPAC

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

Adsorption Studies

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

FTIR spectrum of CCPPAC is shown in **Fig.1**. The band at 3445.27 cm^{-1} indicates presence of the free hydroxyl group stretching of chitosan molecules. The band at 2662.41 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 cm^{-1}) due to the involvement of chitosan in composite formation. The absorption at 1633.30 cm^{-1} is due to the C=O stretching mode of the amido (CONH) group of chitosan.

The two characteristic bands appeared at 1005.85cm^{-1} and 911.73cm^{-1} (skeletal vibration involved in C-O-C stretching) prove the presence of saccharide structure¹⁰. The peaks at 532.07cm^{-1} and 464.47cm^{-1} corresponds to N-H bending.

Fig.2 represents SEM micrographs of CCPPAC. 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 CCPPAC 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- $10\mu\text{m}$.

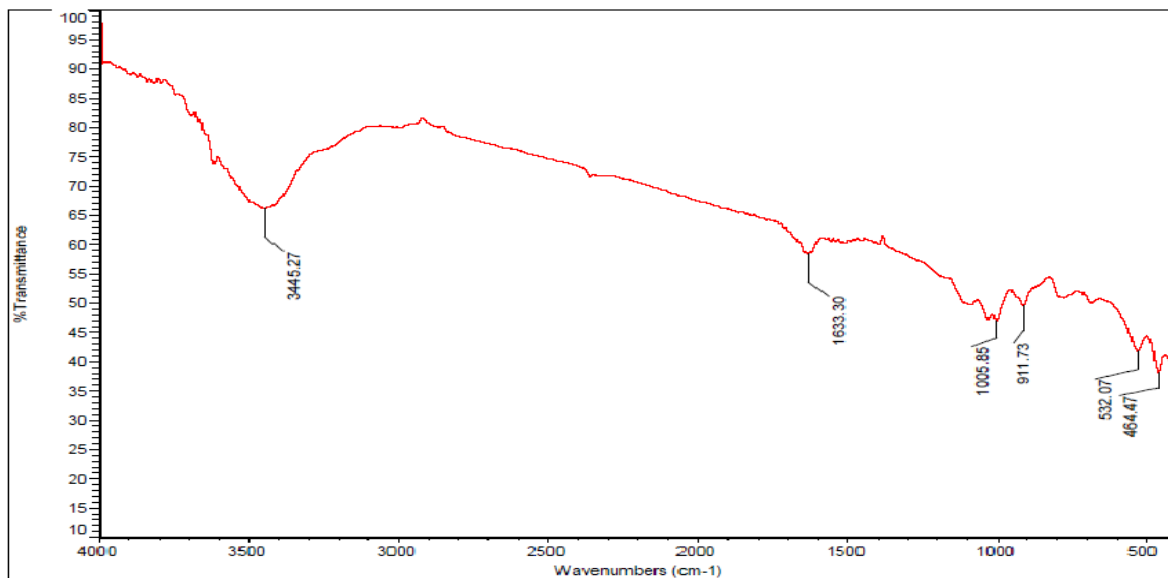


Fig.1 FTIR Spectrum of Chitosan Coated *Pongamia pinnata* Activated Carbon (CCPPAC)

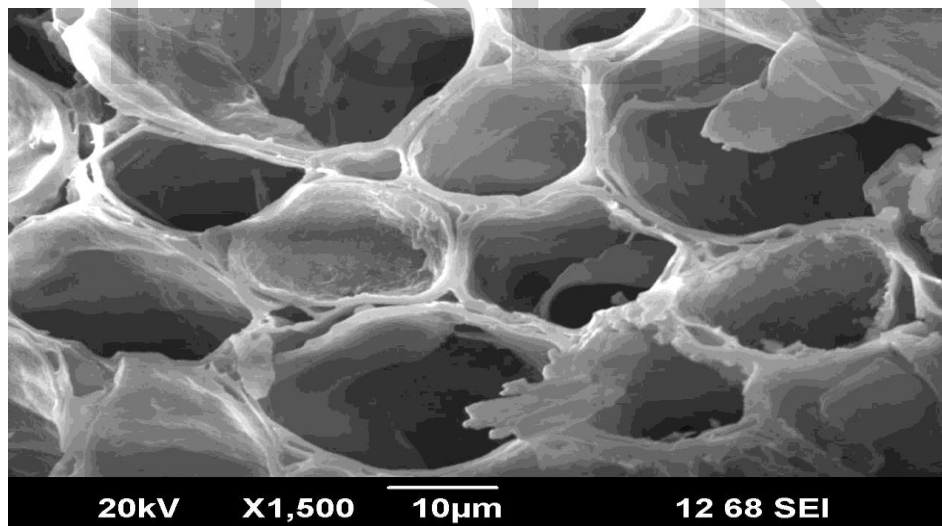


Fig.2 SEM image of Chitosan Coated *Pongamia pinnata* Activated Carbon (CCPPAC)

Effect of pH

The effect of pH on the adsorption of Cr(VI) by CCPPAC 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 5.0 and it is optimum at 4.5. The percent of adsorption increases from 60 to 96 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 **Fig.4**. It can be observed that Cr(VI) removal ability of CCPPAC increased with increase in contact time before equilibrium was reached. Other parameters such as dose of CCZMAC, pH of solution and initial concentration were kept optimum. It

can be seen from fig.4 that Cr(VI) removal efficiency increased from 25 to 96% when contact time was increased from 10 to 160 min. Optimum contact time for CCPPAC was found to be 140 min. Cr(VI) removal efficiency remained nearly constant after 130 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 CCPPAC 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 CCPPAC doses and it was found to be maximum i.e. 95% at the dose of 5g/l. This is due to availability of more surface area. It indicates that by increasing the CCPPAC dosages, the adsorption efficiency for Cr(VI) removal increases. After 5g/l dose of CCPPAC, 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 CCPPAC 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 49%. This can be justified by the fact that adsorbent have limited number of active sites which are saturated beyond certain concentration of adsorbate.

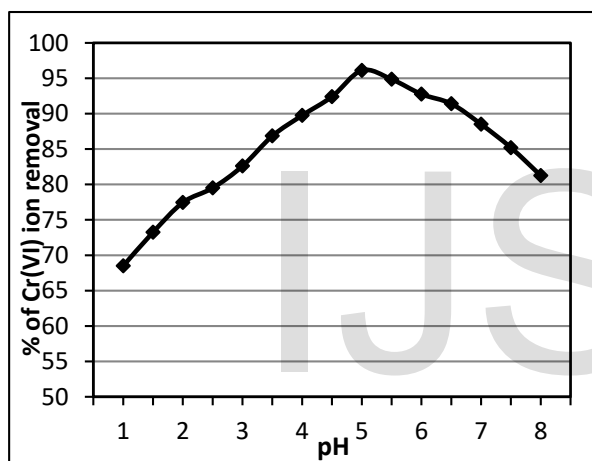


Fig.3 Effect of pH on Cr(VI) removal by CCPPAC

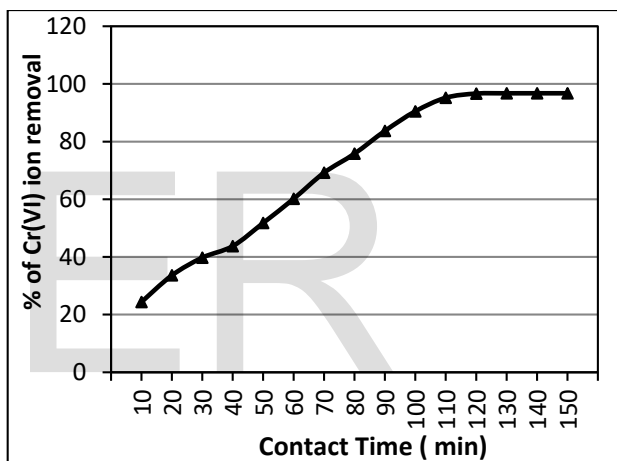


Fig.4 Effect of Contact time on Cr(VI)

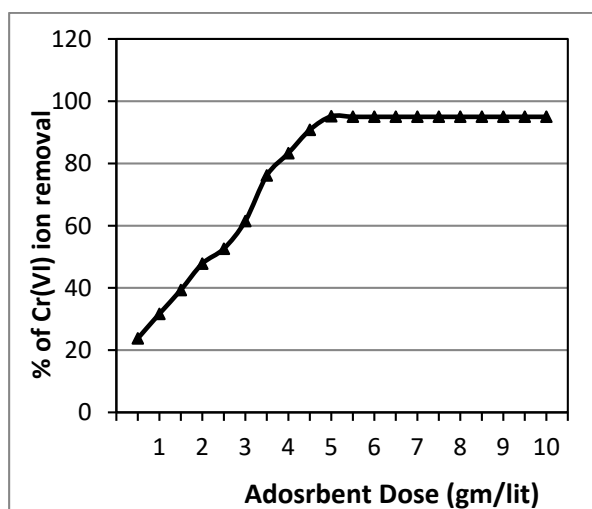


Fig.5 Effect of Adsorbent dose on Cr(VI) removal

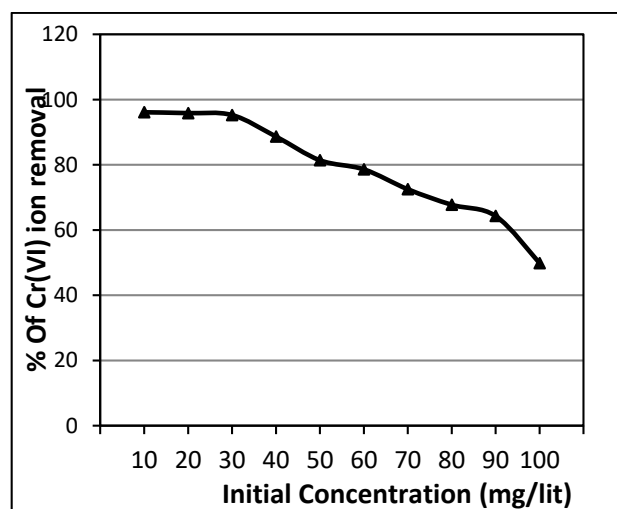


Fig.6 Effect of initial concentration of Cr(VI) Removal

Conclusion

- The activated carbon derived from the bark of *Pongamia pinnata* tree and surface was successfully coated with chitosan and characterized employing FTIR and SEM studies.
- The newly developed CCPPAC high porous structure and excellent surface area.
- CCPPAC was most effective for Cr(VI) removal. At pH 4.5, 96% of Cr (VI) was removed from aqueous solution. Adsorption was found to pH dependent. Above pH 5.0, 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 130 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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