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Abatement of Hexavalent Chromium Metal Ion from Aqueous Solution Using a Smart Meso-Porous Material

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Abstract*:- In the recent years, heavy metal pollution has become one of the most serious environment problems. Presence of heavy metals even in traces is toxic and detrimental to both flora and fauna. With the rapid development of many industries, wastes containing heavy metals are directly or indirectly being discharged into environment causing serious environmental pollution. Many heavy metals such as copper, lead, cadmium, chromium(VI) etc. are seriously affect the human health. 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 activated carbon derived from the bark of *Pongamia pinnata* (PPAC*)* 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 PPAC was found at pH 5.5, 5 gm/lit of adsorbent dose and 180 min contact time. Under optimum condition, 94.5% Cr(VI) was removed from aqueous solution. This investigation verifies that PPAC, a meso-porous 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, Hexavalent chromium, Pongamia pinnata bark

INTRODUCTION

The quality of life on Earth is linked inextricably to the overall quality of the environment. In early times, it was believed that land, water and other natural resources have unlimited abundance today, it is not true; in greater or lesser degree the human society has shown the carelessness and negligence in using them. The living conditions today have surely improved to a great extent at the cost of environmental degradation. Global development, however, raises new challenges, especially in the field of environmental protection and conservation [1]. Due to globalization, industrialization and urbanization creates the problem of pollution including heavy metal pollution The pollution due to heavy metals and metalloids is a widespread problem and causes a major environmental. degradation in each segment of environment. It is indeed a matter of concern to everybody as it has direct effect on human and environmental health [2]. Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater by human activities. All water pollution affects organisms and plants that live in these water bodies and in almost all cases the effect is damaging not only the individual species and population but also the natural biological communities. It occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful constituents. Water pollution is the major problem in the global context. It has been suggested that it is the leading worldwide cause for deaths and diseases and that it accounts for the deaths of more than 14,000 people daily [3]. About 93% of water contamination is generated by the chemicals, paper, petroleum and primary metal sectors. Several industries like sugar factories, dairies, paper and pulp, tanneries, metal plating, fertilizer industries etc. releases substantial quantities of toxic heavy metal in water. The removal of heavy metal contaminants from aqueous solutions is one of the most important environmental concerns because metals are biorefractory and are toxic to many life forms [4]. Metals, which are significantly toxic to human beings and ecological environments, include chromium, copper, lead, mercury, cadmium, nickel, iron etc.

Chromium exists usually in both trivalent and hexavalent forms in aqueous systems. The two oxidation states of chromium have different chemical, biological and environmental characteristics [5]. Cr(III) is relatively insoluble and required by microorganisms in small quantities as an essential trace metal nutrient[6], while Cr(VI) is a great concern because of its toxicity. Cr(VI) has been reported to be a primary contaminant to humans, animals, plants and microorganisms and is to be carcinogenic[7,8,9]. Sources of chromium waste leading to water pollution includes electroplating, steel fabrication, paints and pigments, mining, leather tanning, textile dyeing, aluminum conversion coating operations, plants producing industrial inorganic chemicals and wood treatment units[10,11,12]. The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L[13,14]. The Ministry of Environment and Forest (MOEF), Government of India has set minimal national standards (MINAS) of 0.1 mg/L for safe discharge of effluent containing Cr(VI) in surface water[15]. 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[16]. 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, cotton seed hulls, sugarcane bagasse, peanut hull etc. for the removal of Cr(VI) from contaminated water. The present investigation, studies were carried out for the removal of Cr(VI) from aqueous solution using 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 [17]. It is extensively used in Ayurveda, Unani and Haemeopathic medicine [18]. The tree is known for its multipurpose benefits and potential source of biodiesel [19]**.** The 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 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 Global Marketing (Nagpur, 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 700-850^{0}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 360W for 30 min. 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^{o}C for 3 hrs and stored in airtight bottle.

Characterization of PPAC

Characterization of PPAC 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 PPAC 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 308^{0}C. The residual concentrations were measured using atomic absorption spectrophotometer.

RESULT AND DISCUSSION

Characterization of PPAC

FTIR spectrum of PPAC is shown in **Fig.1.** A band at 3442.21cm^{-1} is connected with –OH stretching band. The –OH groups are seem to be associated by means of hydrogen bonds, as the band for hydroxyl group not involved in hydrogen bonding usually appears as a sharp band located above 3500cm^{-1}. The band for –OH stretching in the range below 3700cm^{-1} was assigned by Zawadzki.**[20]** A band at 1633.75cm^{-1} is indicative of C=O stretching in aldehyde or ketone (carbonyl group). The sufficiently lowering in the band position suggest that C=O group may also involved hydrogen bonding. It is because of the reason that the intramolecular hydrogen bonded structure is stabilized by the phenomenon of resonance. The peak at 1084.14cm^{-1} is suggestive of ortho- substitution. Low band at 565.20 cm^{-1} is evidence of C-I stretching vibration.

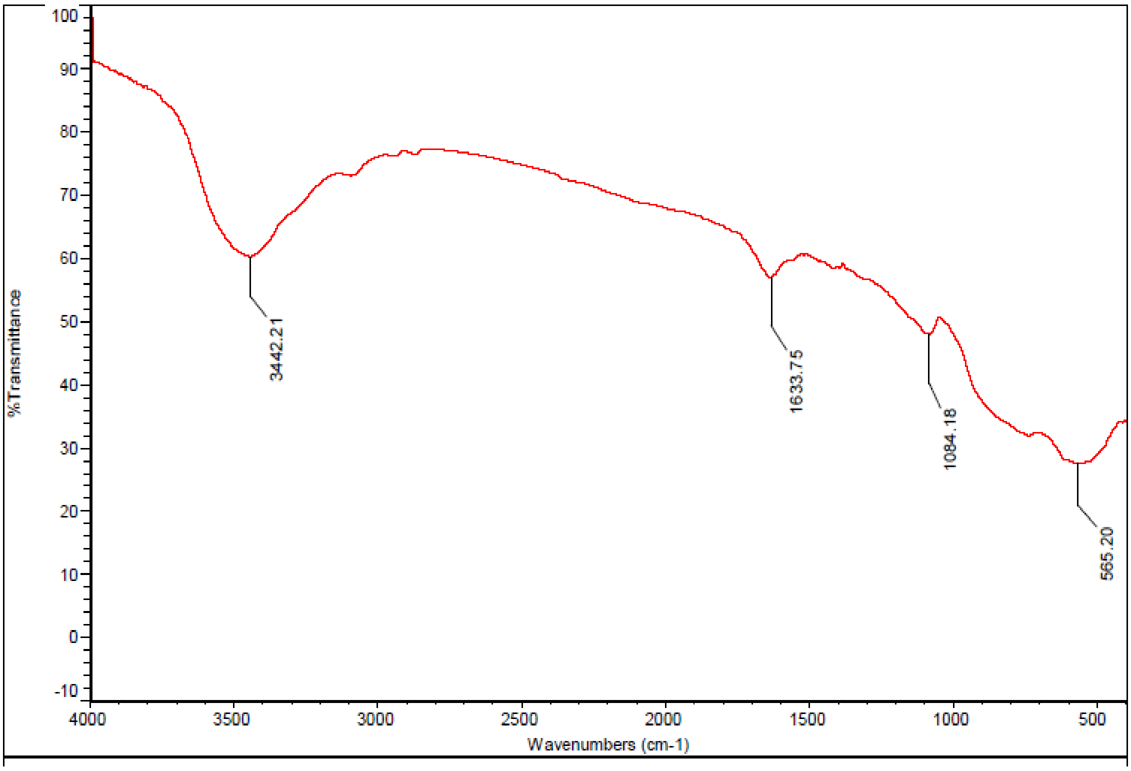

Fig.1 FTIR Spectrum of *Pongamia pinnata* Activated Carbon (PPAC)

Fig.2 shows SEM images of PPAC. SEM micrographs of PPAC show that the pores developed on the surface are deep, oval/hexagonal and elongated shaped. The surface pattern is honeycomb type. Micrograph under magnification of x4000 show that the surface of PPAC is well developed and closely packed structures accompanied with many holes and cavities. Several thin sheets/layers can be observed on the surface of PPAC. High magnification makes clear the presence of holes and cavities between the layers within the structure of PPAC. These features are inductive of an excellent quality of adsorbent, which may have very good adsorption efficiency.

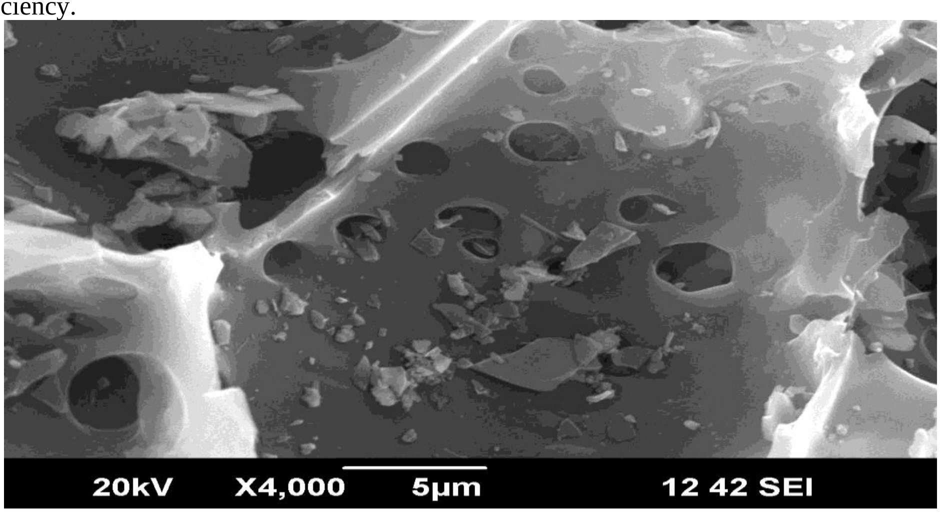

Fig.2 SEM image of *Pongamia pinnata* Activated Carbon (PPAC)

Effect of pH

The effect of pH on the adsorption of Cr(VI) by PPAC 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 8.0 and it is optimum at 5.5. The percent of adsorption increases from 60 to 95 as pH was increased from 1 to 5.5. The percentage of adsorption decreases steadily when pH increased above 5.5 and it was further decreased to 74% 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 PPAC increased with increase in contact time before equilibrium was reached. Other parameters such as dose of PPAC, 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 95% when contact time was increased from 10 to 180 min. Optimum contact time for PPAC was found to be 180 min. Cr(VI) removal efficiency remained nearly constant after 180 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 PPAC 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 PPAC 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 PPAC dosages, the adsorption efficiency for Cr(VI) removal increases. After 5g/l dose of PPAC, 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 PPAC 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 95 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.

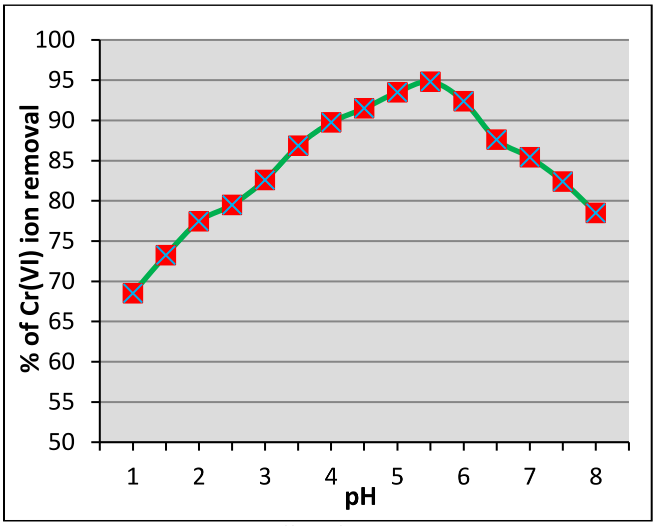

Fig.3 Effect of pH on Cr(VI) removal by PPAC

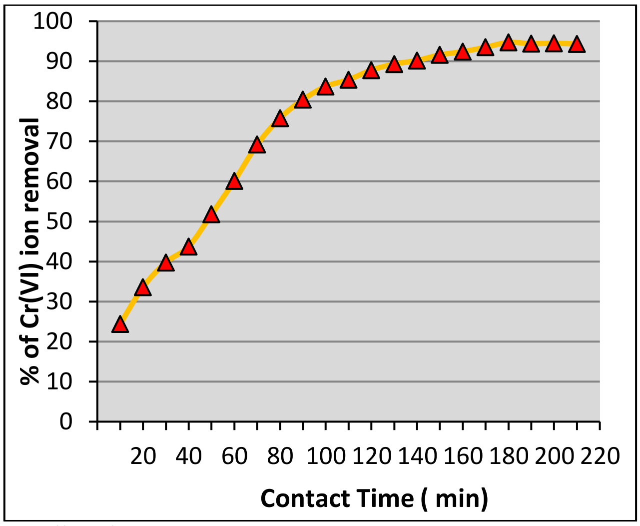

Fig.4 Effect of Contact time on Cr(VI) removal by PPAC

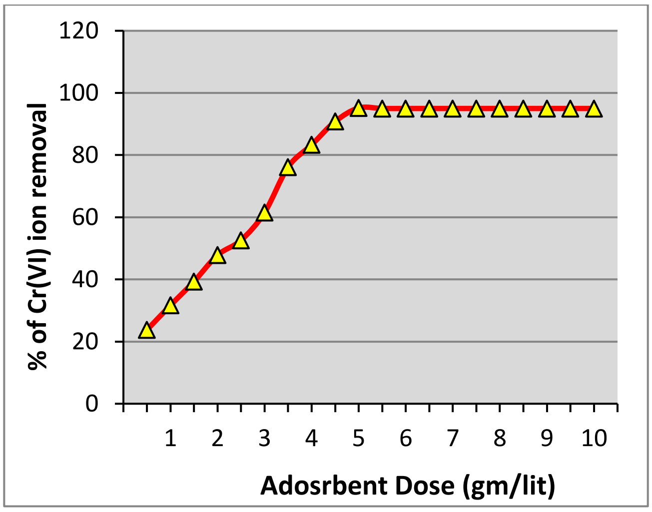

Fig.5 Effect of Adsorbent dose on Cr(VI) removal

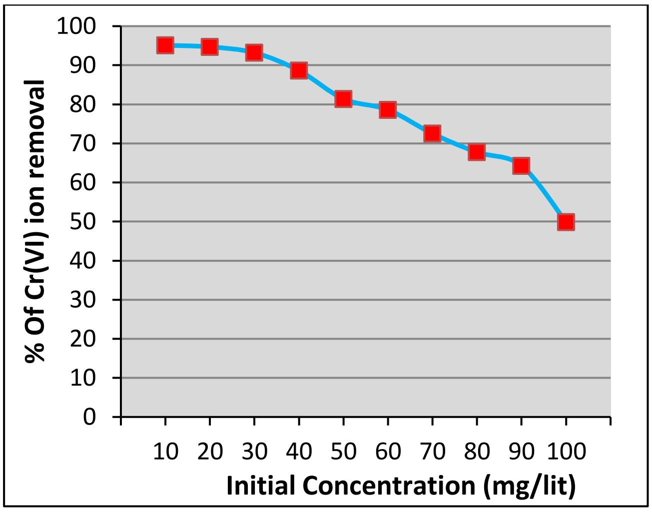

Fig.6 Effect of initial concentration of Cr(VI) removal

CONCLUSION

- The activated carbon derived from the bark of *Pongamia Pinnata* tree was successfully prepared and characterized employing FTIR and SEM studies.
- The newly developed PPAC high porous structure and excellent surface area.
- PPAC was most effective for Cr(VI) removal. At pH 5.5, 95% 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 180 min. of contact time.
- The 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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