Adsorption Study of Cr (VI) from Aqueous Solution Using Annona Reticulata and Pouteria Sapota

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Abstract: *Removal of heavy metals from aquatic environment is an issue of current interest and research for which adsorption is employed using many materials. Natural adsorbents are always preferred because of their easy availability and low cost. In this paper we have reported the removal of Cr (VI) by activated charcoal prepared from two natural materials namely Annona reticulata and Pouteria sapota. Both have exhibited good adsorption of Cr (VI) and the spectrophotometric, XRD and SEM analysis confirms the same. Hence such materials can be used for practical applications for effluents coming from the tanneries for the removal of Cr (VI).*

Keywords: Adsorption, chromium, Langmuir, spectrophotometric, chemisorption.

1. Introduction

Heavy metals are non biodegradable pollutants whose release in the environment poses toxicity, bio-accumulating tendency, threat to human life and the environment [1]. It is well documented that heavy metals can damage nerves, liver, and bones and could also block functional groups of essential enzymes. Unlike organic pollutants which can undergo biological degradation, heavy metals will not degrade and thus become toxic to human health and environment. Around twenty different known heavy metals were identified that can impact human health and their entry in to the body can lead to mental, cognitive, and physical defects and illness. Among the heavy metals Chromium has been considered as one of the toxic pollutants and because of its carcinogenic properties. Thus, treatment of aqueous wastes containing soluble heavy metals requires concentrations of the metals into smaller volume followed by recovery or secure disposal. Heavy metals can be found in a variety of industries, in particular mining, metal processing, finishing, leather tanning and plating etc [2,3].

The most common methods for removing dissolved heavy metal ions are precipitation, oxidation or reduction, filtration, ion exchange, electrochemical methods, biological treatment etc [4]. Many these methods are efficient, nevertheless, all these methods they have their inherent advantages and limitations [5].

Adsorption process is often considered as a better one than other methods because of it is easy in operation and simplicity of design. Adsorption can remove or minimize different types of pollutants and thus have wider applicability in many environmental applications. A good adsorbents should posses high porosity and larger surface area with more specific adsorption sites [6]. Activated carbons has a high adsorption capacity but are of high cost which is a disadvantage for practical applications, especially in the field of industrial effluent treatment where activated carbons may play a very useful role.

Therefore development of low cost adsorbents for the removal of heavy metals from aqueous solutions is the need of the hour and thus could revolunize the current scenario in effluent treatment. Plant wastes have been used as a raw material for activated carbon mainly because of their abundance. Production of activated carbon from this source may reduce the cost of waste water treatment and at the same time can be a step towards sustainable waste management as it will open new market for recycled agricultural waste product.

A sizable number of natural and synthetic adsorbents like agricultural waste's carbon [7], clay [8], neem leaves [9], cooked tea dust [10], zeolites [11], teak leaves activated carbon [12], cashew nut shell activated carbon [13], fly ash [14] etc were already studied for the removal of heavy metals. The present paper focuses on testing one such naturally derived activated charcoal material from two of commonly available economical materials namely annona reticulata and pouteria sapota seeds. These materials have shown to be promising adsorbents for Cr (VI) removal.

2. Materials and Methods

2.1 Preparation of active charcoal

The raw material for the preparation of activated carbon namely the custard apple (annona reticulata) and sapota (pouteria sapota) seeds were collected from agricultural fields from kurumberi village, Vellore district. The activated carbon was prepared by impregnating with Conc.HCl and further carbonized at 600°C. For impregnator ratio of acid volume to weight of plant material of 1:1 (w/v) was employed. Before utilization, the carbon particles washed with distilled water and dried in a hot air oven. The activated charcoals thus prepared were labelled as custard apple activated charcoal (CAAC) and sapota seed activated charcoal (SSAC).

2.2 Preparation of Cr (VI) Solution

A stock solution of Cr (VI) (1000 ppm) was prepared by dissolving appropriate quantity of analar grade $K_2Cr_2O_7$ using double distilled water. This solution was further diluted with distilled water to obtain standard Cr (VI) solutions of desired concentration. Hexavalent chromium is quantified using biphenyl carbazide which forms a red violet

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complex and intensity of this complex was read at 540 nm using the Varian cary 50 spectrophotometer.

2.3 Infrared Spectral Studies

The CAAC and SSAC samples (10 mg) were ground with 200 mg of KBr (spectroscopic grade) in a mortar pressed into 10mm diameter disks under 10 tonnes of pressure and high vacuum for 10 min. FTIR spectra were obtained on a PerkinElmer spectrometer. The analysis conditions used were 16 scans at a resolution of 4 cm^{-1} measured between 400 cm^{-1} and 4000 cm^{-1}.

2.4 Analytical Method

The concentration of Cr (VI) was determined by spectrophotometer at wavelength of 540 nm by using biphenyl carbazide as chromomegenic reagent. The removal percent (%) is calculated by using the equation.

Removal % = C_0 – Ce / C_0 X 100 %...................(2.1)

Where,
C_0 is the initial concentration of Cr (VI) in suspension,
Ce is the equilibrium concentration of Cr (VI) in supernatant after centrifugation.

The distribution Coefficient (Kd) is regarded as a standard parameter in the assessment of the physiochemical behavior of metal ions between solid and liquid phase. It can be calculated by the following equation,

Kd = (C_0 – Ce / C_0) X /M……………………(2.2)

Where, M= mass of adsorbate.

3. Results and Discussion

3.1FTIR Studies of Adsorbents

The FTIR spectra of CAAC and SSAC after adsorption are shown in **Fig. 1 & Fig. 2**. The FTIR spectra of CAAC showed peaks at 2909, 1577, 1213, 1069 and 719 cm^{-1}, which may be assigned to OH group, aliphatic C–H group, unsaturated groups like alkene, amide, CH deformation, OH deformation, aromaticity and OH stretch, respectively. The intensity of the peaks were either minimized or shifted slightly in case of treated and adsorbed samples.
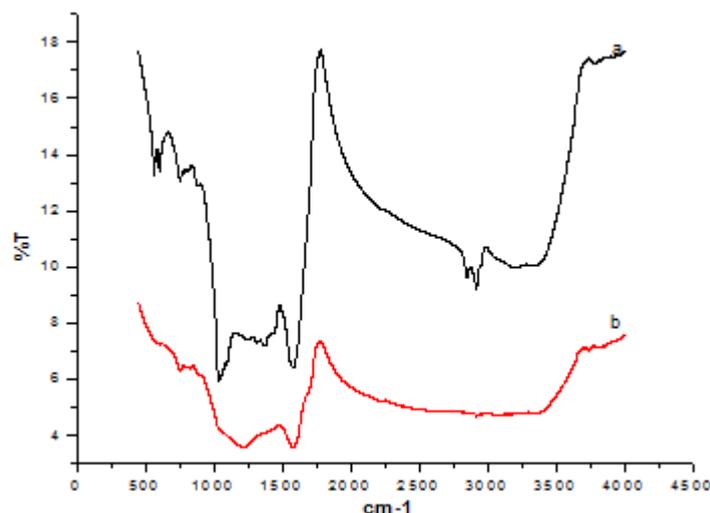
Figure 1: FTIR Spectra of (a) CAAC before adsorption of chromium (b) CAAC after adsorption of chromium

These results are similar to the ones reported earlier [15]. The FTIR spectra of Sapoto seed charcoal after adsorption are shown in Fig. 2. The FTIR spectra of SSAC showed peaks at 3381, 2921, 1641, 1411, 1096, 853, 774 and 607 cm^{-1}, which may be assigned to OH group, aliphatic C–H group, unsaturated groups like alkene, amide, CH deformation, OH deformation, aromaticity and OH stretch, respectively.
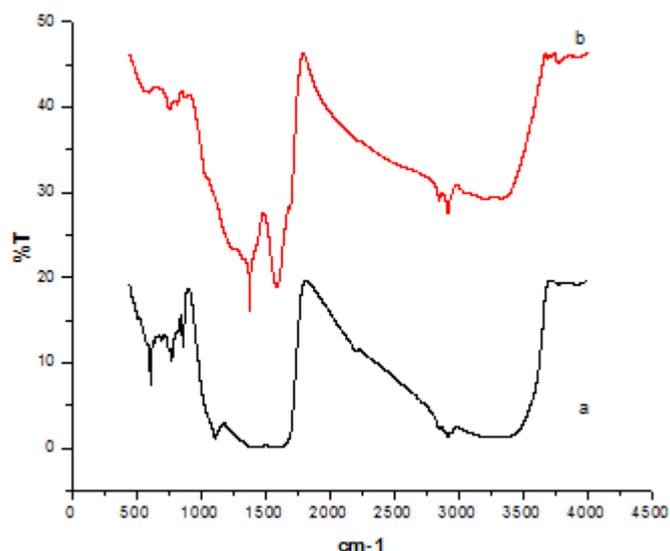
Figure 2: FTIR Spectra of (a) SSAC before adsorption of chromium (b) SSAC after adsorption of chromium.

The intensity of the peaks were either minimized or shifted slightly in case of treated and adsorbed charcoal.

3.2. Standardization of Cr (VI)

Different concentration of Potassium dichromate solution was diluted to 50 ml and 1 ml of biphenyl carbazide was added, and then standardized using spectrophotometer at 540 nm.
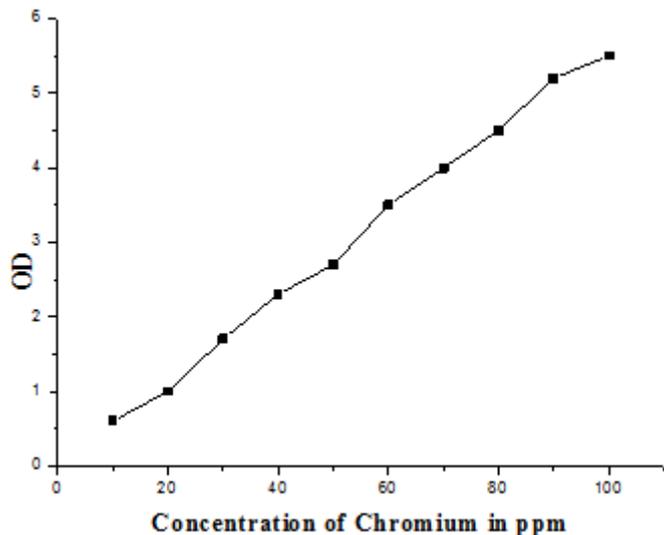
Figure 3: Standardization of Cr (VI)
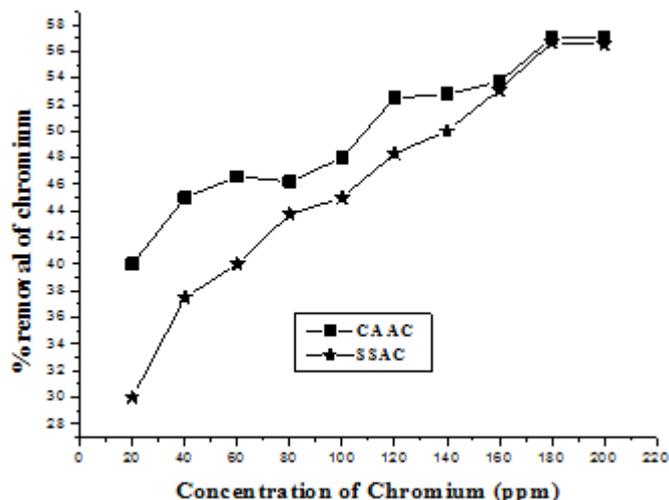
Figure 4: Effect of Adsorbate Concentration on the Adsorption Efficiency of Custardapple (CAAC)

3.3 Effect of Adsorbate Concentration

Different concentration of Potassium dichromate solution were diluted to 50 ml and taken into different beakers. Then 1ml of biphenyl carbazide was added to each solution, to this 0.5g of CAAC and SSAC charcoal were added then the solution was stirred for 30 minutes using magnetic stirrer. After that the concentration of chromium was determined colorimetrically as mentioned above.

3.4 Effect of Adsorbent Dosage

50ml of Potassium dichromate solution were taken in eight different beakers, to this 1ml of biphenyl carbazide was added. Then different quantities of CAAC and SSAC (0.1 to 1g) were added. The solutions were stirred using the magnetic stirrer for 30 minutes. After the amount of chromium present in the solution were measured as before.

3.5 Effect of Contact Time

50 ml of Potassium dichromate solution were taken in eight different beakers, together with 1ml of biphenyl carbazide. Then 1g CAAC and SSAC powders were added. Each solution was stirred magnetically with different time interval (15 to150 mins) then the concentration of chromium was measured.

3.6 Effect of Concentration of Cr (VI)

Adsorption of chromium by charcoal is shown in **Fig 4**. The results show that maximum adsorption takes place at lower concentrations. At higher concentration of chromium, for a fixed amount of charcoal, the removal efficiency decreases.

3.7 Effect of Adsorbent Concentration

The effect of different amount of charcoal used to adsorb chromium metal ion is shown in **Fig 5**.The concentration of Potassium dichromate solution and stirring time 30 minutes are constant and the amount of charcoals of the two adsorbents varied from 0.1 to.1g. This results reveals that minimum amount of charcoal is enough to absorb chromium from solution.
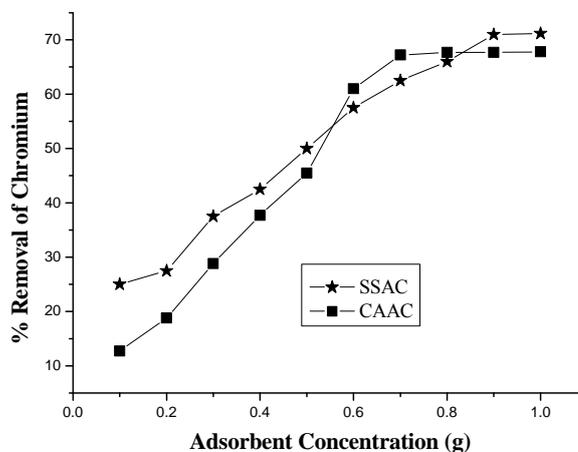
Figure 5: Effect of Adsorbent Dosage on the Adsorption Efficiency of custard apple (CAAC)

From the results, it is evident that both the adsorbents significantly removed the chromium and the optimum amount for efficient adsorption was found to be 0.7 g for both custard apple and SSAC. There is no significant increase in the removal of chromium and the efficiency of sapota seed activated carbon (SSAC) was marginally superior to the custard apple activated carbon (CAAC). Further increase of adsorbent did not show any marked efficiency in the chromium removal.

3.8 Effect of Contact Time

The effect of contact time on removal of chromium metal ion from solution by SSAC and CAAC is shown in **Fig. 6.** Both concentration of chromium and amount of charcoal were fixed while the contact time was varied from 15 minutes to 150 minutes.
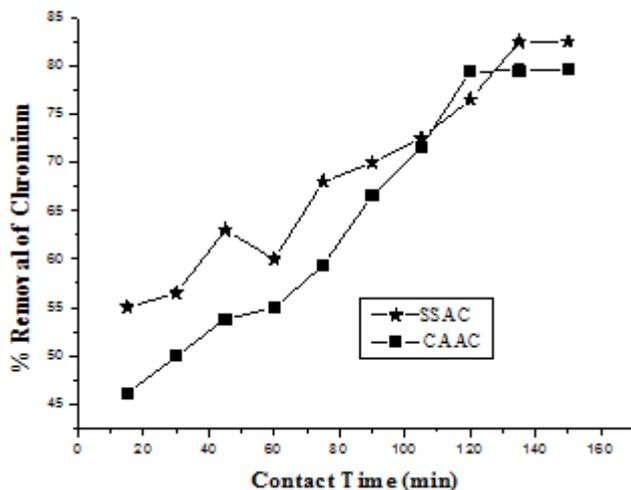
Figure 6: Effect of Contact time on the Adsorption Efficiency of custard apple activated charcoal (CAAC).

The result shows that the maximum adsorption occurred at 120 minutes there is no considerable change in further increase in the contact time.

3.9 Langmuir Model

The Langmuir plot of Ce/qe(ppm) Vs Ce (ppm) at 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2 ,2.4 and 2.6 ppm is shown in **Fig.7**. The Langmuir isotherm fits the experimental data very well for both the materials, which may be due to homogeneous distribution of active sites on the particle surface. The nature of adsorption is Chemisorption.
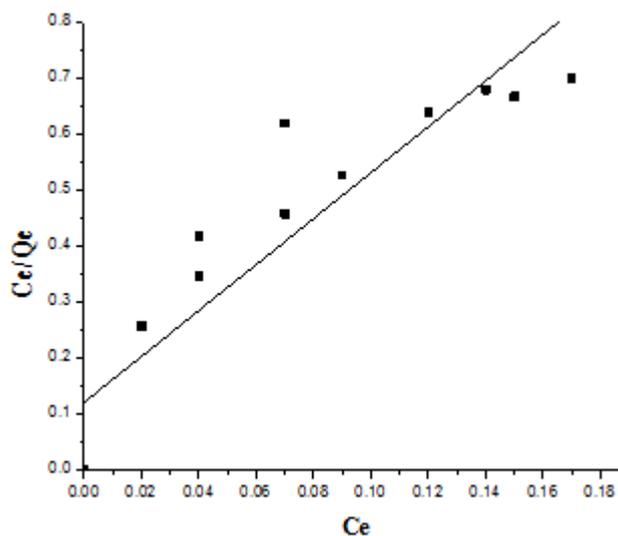
Figure 7: Langmuir isotherm for Cr (VI) adsorption

3.10 X-ray Diffraction Studies

Figure 8 shows the XRD pattern of the powdered sample. The XRD pattern shows the presence of amorphous carbon in the sample. The peaks in the XRD peaks correspond to the adsorption of chromium by both the activated carbons (SSAC and CAAC).
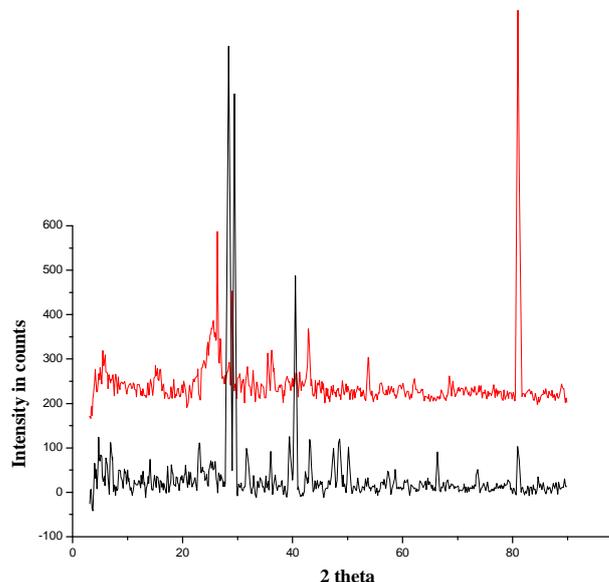
Figure 8: XRD pattern of SSAC and CAAC after adsorption of chromium

3.11 Scanning electron microscopic studies
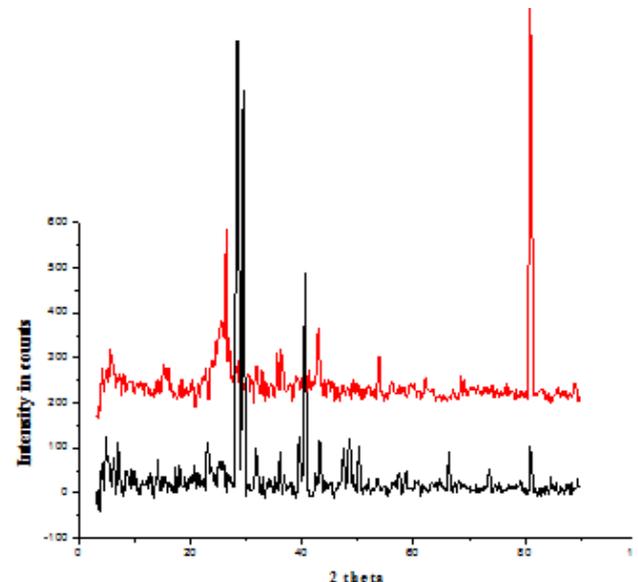
Figure 9and 10 show the SEM micrographs of the sample before and after chromium coating. The porosity is less in case of **figure 10** compared to that in case of **figure 9** which indicates the adsorption of chromium in the pores of the sample.

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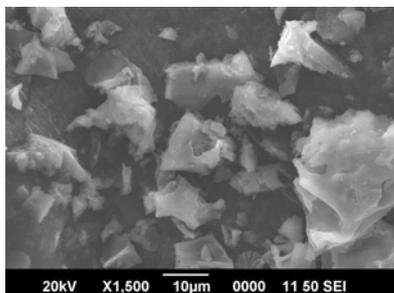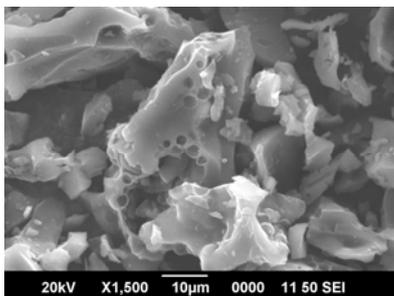
Figure 9 &10: SEM images of adsorbents CAAC and SSAC after adsorption of chromium

4. Conclusions

From the experimental results it can be concluded that both activated carbon materials obtained from CAAC and SSAC were found to be effective adsorbents of Cr (VI). This adsorption of Cr (VI) onto activated carbon is found to be time and concentration dependent. The adsorption isotherm values also confirm the above observations. Thus the use of custard apple seed and sapota seeds activated charcoal as an adsorbent seems to be an economical and promising an alternative over the conventional methods for removal of Cr (VI) from industrial effluents.

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