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Adsorption Study Of Cr (Vi) From Aqueous Solution Using Sesbania Grandiflora And Saraca Asocanuts

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1. Introduction

Heavy metal pollution in the aquatic environment poses a great threat to human health because the metals are toxic if their concentrations exceed threshold limits and are non-biodegradable. Chromium is one of the well known carcinogenic metals used in industries for electroplating, tanning, wood preservation, dyeing etc [1]. From these industries, the metals find their way into the aquatic environment through wastewater discharge. Because of their non-biodegradability, they tend to accumulate and lead to metal poisoning in animals and man. The increasing awareness about the environmental consequences arising from heavy metal contamination of the aquatic environment has led to the demand for the treatment of industrial wastewater before discharge into the aquatic environment.

Considerable attention has been given to methods for removal of toxic metals from industrial waste waters and a number of methods are available to remove toxic metals from water which includes ion exchange, reverse osmosis, precipitation, solvent extraction, membrane technologies, electrochemical treatment, sorption etc [2].

One of the most versatile materials used widely as a sorbent is the activated. However, the use of activated carbon is expensive, so there has been considerable interest in the use of other sorbent materials, particularly bio sorbents [3]. Adsorption is the far most versatile method for removing any contaminants like heavy metals, especially, if combined with appropriate regeneration steps. The activated carbons materials were found to be suitable candidates for removing Cr from the effluent water [4] through adsorption.

Chromium (VI) is highly toxic in nature due to the fact that one of the reduction products of chromium (VI) is chromium (V) which is a known carcinogen and will lodge in any tissue to form cancerous growth. It has been reported that chromium (V) leads to premature births in parts of Russia [5]. Chronic inhalation of chromium (VI) compounds increases the risk of lung, nasal and sinus cancer. Severe dermatitis skin ulcer can result from contact with chromium (VI) compounds. It can cause mild to serve liver abnormalities and Chromium (VI) compounds are teratogenic to animals [6]. Hence removal of chromium can curb a number of ailments that would otherwise affect the human population living in the vicinity of tanneries.

In India, there are a large number of tanneries scattered all over the country but the main areas of concentration are Tamil Nadu, Uttar Pradesh and West Bengal. Nearly 80% of these tanneries are engaged in the chrome tanning processes [7]. Most of them discharge untreated wastewater into the environment. In such aqueous waste, Chromium (VI) is present as either dichromate ions ($Cr_2O_7^{2-}$) in acidic environments or as Chromate ions (CrO_4^{2-}) in alkaline environments.

In the last few years, several approaches have been reported in this direction utilizing inexpensive and effective adsorption for removal of Cr (VI) from aqueous solution [8]. The advantage of low cost adsorbents over the conventional adsorbents as follows: The efficiencies of various non - conventional adsorbents towards adsorbate vary generally between 50 to 90% depending on the characteristics and the particle size of the adsorbent, and the characteristics and concentration of the adsorbate, etc. Hence low cost adsorbents can be used efficiently in removal of heavy metals. Non - conventional adsorbent require simple alkaline or acid treatment for the removal of lignin before application in order to increase their efficiency.

Among the various adsorbents that have been so far researched, materials of plant origin were found to be environmentally benign and cost effective [9]. Hence in this paper we have reported naturally obtained adsorbent materials from sesbania grandiflora and saraca asoca nuts for the effective removal of chromium.

2. Experimental methods

2.1 Saraca asocanut and sesbania grandiflora nut (agathi):

Sesbania grandiflora (agathi) nuts and Saraca asocanut (Asoka tree) were collected from local area. It was dried under sunlight until all the moisture got evaporated. The material was ground to fine powder. The ground powder was treated with 25 % orthophosphoric acid in the ratio of 1:10 (bagasse: acid w/ v) for 1 h. After one hour, extract was filtered out, washed with distilled water to remove free acid and activated at 300 °C in muffle furnace for 3 hours. The heated material was washed with distilled water to remove residual acid. The material was dried in an oven at 120 °C for 24 hours, and then powdered using a mortar and pestle to size that could be through ASTM sieved No.20 and was used for the further study. The activated carbonaceous materials obtained from sesbania grandiflora nuts (SGNAC) and Saraca asocanut (SANAC) were used as the adsorbents for the entire study.

2.2 Preparation of Chromium Metal Ion Solutions

In order to prepare chromium ion solutions of different concentrations, 1N $K_2Cr_2O_7$ solution was prepared using double distilled water and then it is then diluted to different concentrations (0.001 to 0.01N). The chemicals were obtained from Merck, India and used without any further purification.

2.3 Analytical methods:

The concentration of Cr (VI) was analyzed using a spectrophotometer (Varian Cary 40, India) at 520 nm. The removal percent (%) of chromium was calculated using the equation:

$$\% \text{ Removal of Cr } = C_0 - Ce / C_0 \text{ X } 100\%$$

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

The distribution C_0 efficient (K_d) is regarded as a standard parameter in the assessment of the physiochemical behaviour of metal ions between solid and liquid phase. It can be calculated by the following equation:

$$Kd =(C_0 - Ce / C_0) \text{ X } /M$$

3. Results and Discussion

3.1 Grandifloranut activated charcoal (SGNAC) as adsorbent

3.1.1 Effect of Concentration

Different concentrations of $K_2Cr_2O_7$ solutions were diluted to 100 ml and taken in different beakers.

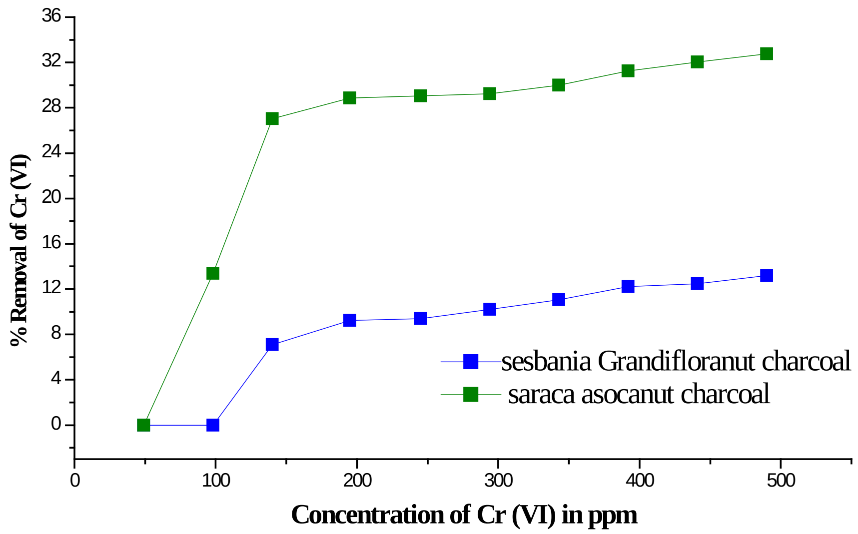

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Fig. 1 Effect of concentration of Cr (VI) on sesbania grandifloranut and Saraca asocanut activated charcoal.

To this a constant amount of 0.3 g of sesbania grandifloranut charcoal was added to each beaker followed by 50 ml of standard solution was added and then the solution was kept for 30 minutes in a magnetic stirrer. Followed by this the concentration of chromium was determined colorimetrically as described above.

The effect of concentration of chromium ion on both the SGNAC and SANAC (**Fig. 1**) reveals that, SANAC has shown a much increased efficiency than SGNAC. However as the concentration increases, the adsorption efficiency also increases for both the adsorbents. The extent of absorption was found to be maximum at about 350 ppm for both the adsorbents after which there isn't much rise in the chromium removal efficiency. This proves the efficiency of both the adsorbents, since both are capable of removing Cr (VI) beyond the lethal limits.

3.1.2 Effect of concentration of adsorbent:

50 ml of $K_2Cr_2O_7$ solutions were taken in ten different beakers with different quantities of sesbania grandifloranut charcoal (0.1g to 1g). The solutions were stirred using the magnetic stirrer for 30 minutes and the amount of chromium present in the solution were measured spectrophotometrically as before.

The effect of adsorbent concentration of SGNAC and SANAC on the removal of chromium is shown in **Fig. 2**. On increasing the amount of adsorbent, the adsorption and hence the removal

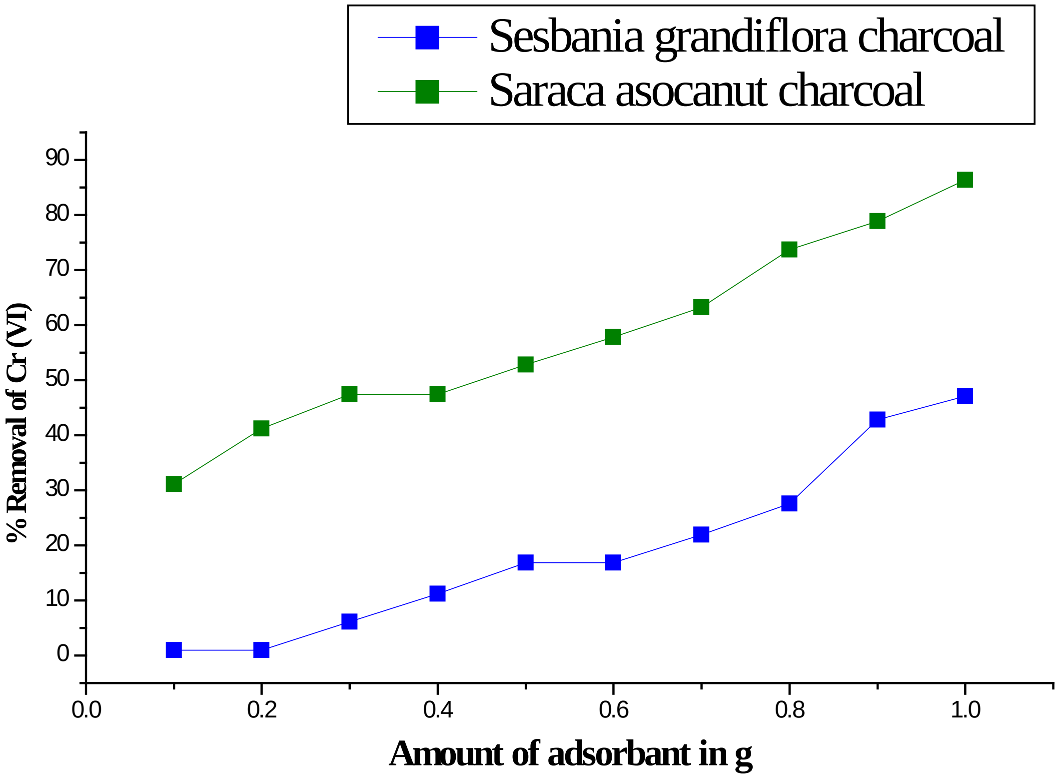

Fig.2 Effect of adsorbate concentration on the SGNAC and SANAC.

of chromium was also greatly pronounced. The extent of removal of Cr (VI) was again higher in the case of SANAC than the SGNAC. In the case of SANAC, a maximum of 86.3 % removal of Cr (VI) was observed for a meager 1 g of the adsorbent which shows the efficiency of the adsorbent. Further increase in the adsorbent quantity did not yield any significant change in the removal of chromium and hence 1 g is found to be the optimum.

3.1.3 Effect of contact time

In order to evaluate the effect of contact time of the adsorbent, 50 ml aliquots of $K_2Cr_2O_7$ solutions were taken in ten different beakers followed by the addition of 0.3g of sesbania grandifloranut charcoal. Each solution was stirred magnetically with different time interval (from 30 min to 300 min) and then the concentration of chromium was measured spectrophotometrically.

The comparative graph on the effect of contact time (**Fig. 3**) demonstrates a different behavior by these two adsorbents. Initially the calculations obtained reveal that the SGNAC adsorbent exhibits a better Cr removal than the SANAC. This may be due to the micro structural features of it which makes it as the time progresses. But on prolonging the time, both the adsorbent show a remarkable removal of Cr from the solution peaking up to 89 and 94 % respectively. Hence it could be ascertained that the morphology of these adsorbents are in very much favorable for adsorption.

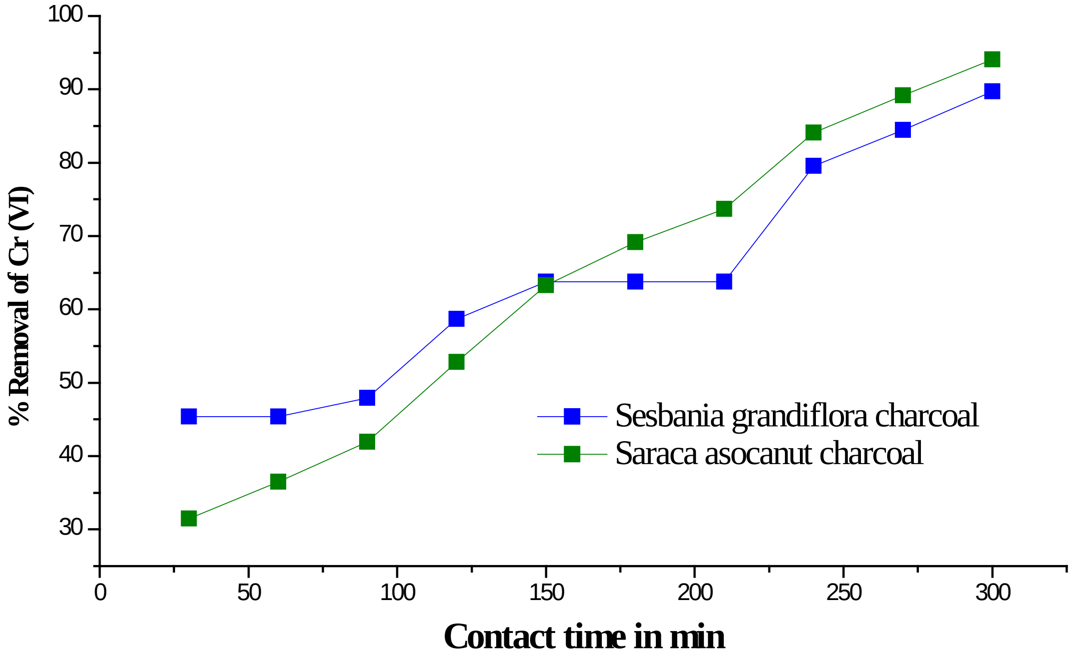

Fig.3 Effect of contact time on the sesbania grandifloranut and Saraca asocanut charcoal.

3.1.4 X-ray diffraction studies

Figure 4 shows the XRD pattern of the powdered activated charcoal adsorbent samples. 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 (**SANAC** and **SGNAC**).

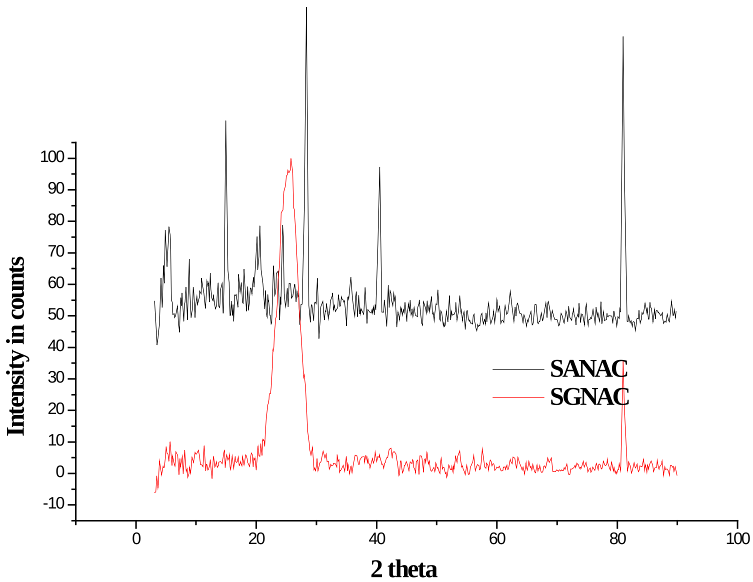

Fig. 4 XRD pattern of SANAC and SGNAC after adsorption of chromium.

3.1.5 Langmuir model

The Langmuir plot of Ce/qe(ppm) Vs Ce (ppm) was employed for both the adsorbents and they showed a similar pattern of adsorption which is shown in **Fig.5**. 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.

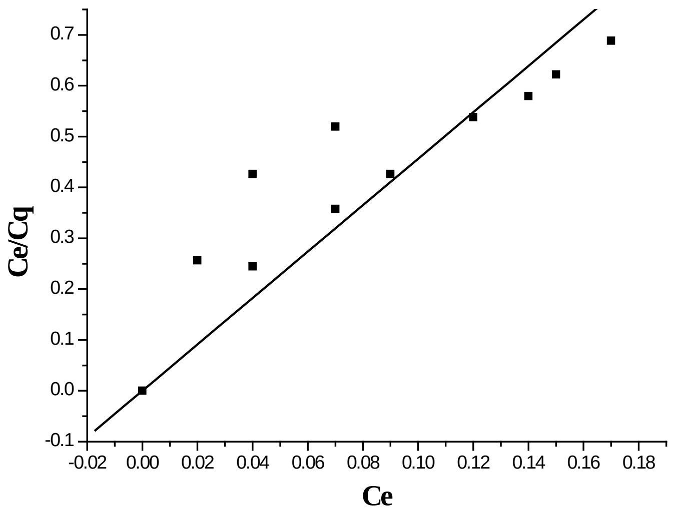

Fig. 5. Langmuir isotherm for Cr (VI) adsorption.

Conclusions

The fore going results have proven that the adsorbents SGNAC and SANAC are very much suitable to remove chromium (VI). Excellent results on the effect of concentration, contact time and adsorption dose on the removal of chromium could be demonstrated using these adsorbents and the adsorption followed Langmuir adsorption isotherms. Among the adsorbents, SANAC obtained from saraca asocanut was found to display a superior adsorption efficiency which is evident from the datas. On the other hand, SGNAC obtained from sesbania grandiflora nut is found to be efficient when contact time is adjusted and hence could be useful for appropriate environments. Since the cost and material preparation involves less effort and cost, these materials could be an efficient substitute for their expensive counter parts. Further works on controlling the particle size of the adsorbents and modifying their micro structural features are being currently carried out the results of which are also would be communicated soon. Hence these two adsorbents could very well be employed in real time removal of Cr (VI) from tanneries.

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