

Removal of Chromium from Waste Water by Adsorption Method Using Agricultural Waste Materials

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ABSTRACT

Several low cost biomaterials such as rice husk, sugar cane bagasse, Tulsi Leaf & branches, coconut shell & coir and fly ash were tested for removal of chromium. All the experiments were carried out in batch process. The adsorbent, which had highest chromium (VI) removal, was coconut shell. An influence of chromium concentration, contact time on removal of chromium from effluent was investigated. In this study we will be see that tulsi leaf do not give fruitful result (23.340 % Removal). So, it is advise to not use Tulsi leaf as an adsorbent for removal of hexavalent chromium. Coconut Shell gives better result (81.999% removal) in comparison of other agricultural waste material.

INTRODUCTION

Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic. Its concentrations in industrial waste waters range from 0.5 to 270.000 mg/l. 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. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr(VI) to acceptable levels. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange,

electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption. Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual metal sludge. Many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials. Activated carbons with their large surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metals from industrial waste water. In this study two activated carbons prepared from agricultural wastes (Coconut coir & shell, Rice husk, sugar cane bagasse, Tulsi leaf &

Branches, fly ash) are used to remove Cr(VI) from aqueous solution.

MATERIALS AND METHODS

Materials

The adsorbents used in this study were agricultural waste material (Coconut coir & shell, Rice husk, sugar cane bagasse, Tulsi leaf & Branches, fly ash). All chemical solutions were prepared from certified lab grade chemicals. Potassium dichromate ($K_2Cr_2O_7$) was used as the source of Cr(VI) in the synthetic wastewater. The Cr stock solution (1000 mg/l) was prepared by dissolving 2.828 g of $K_2Cr_2O_7$ in 1000 ml of deionized water, while Cr concentration of synthetic wastewater was varied from 25 to 100 mg/l by diluting the stock solution. Before being used for adsorption studies, the pH of Cr solution at different of Cr concentration was measured using a pH meter. Adjustment of pH was carried out using 0.1N H_2SO_4 . Agitation of the system under investigation was carried out on a magnetic stirrer (2 MLH Model), while chromium concentration was analyzed by a spectrophotometer model SL -218 (ELICO).

METHOD

Preparation of various agricultural waste materials adsorbents

Agricultural waste materials (Tulsi leaf & branches, Coconut shell & coir, Rice husk, Sugar cane bagasse, Fly ash) were collected from local area of Kanpur, Uttar Pradesh. Then the sample were first washed with D.M. water to remove dirt particles. After washing it is sundried and then dried over night at $70^\circ C$ in the electrical oven. The size of sample was reduced by broken into very small pieces, then it was again broken in more small pieces in mixer used in home. The sample was sieved. The sieved sample was then soaked in H_3PO_4 (1:1 Wt%). It was then pyrolyzed at $170^\circ C$ for 0.5 Hrs in nitrogen atmosphere and activated at $450^\circ C$ for 1.0 Hrs. in nitrogen atmosphere in tube furnace. The sample was cooled over night in nitrogen atmosphere. The

sample was washed with D.M. water until the pH of the filtrate was more than 4.5. sample was dried and then used as Activated carbon.[1-4]

Determination of chromium content

The chromium concentration in raw and treated effluent was determined by SL-218 UV/VIS Spectrophotometer. For this purpose, $K_2Cr_2O_7$ solutions of different concentrations were prepared and their absorbance recorded by using a UV-spectrophotometer. A calibration plots for Cr(VI) were drawn between % absorbance and time.

Experimental Work

All the batch adsorption studies were carried out using 200 mL of solution of 100 ppm Cr concentration by dilution of the stock solution. Requisite quantity of adsorbent was added to 500 mL beakers. The beaker was placed on magnetic stirrer. At different intervals of time samples were drawn & filtered through a filter paper. The filtrate was analysed for pH and final chromium concentration using P^H meter & spectrophotometer respectively. The removal of Cr(VI) was studied by using different adsorbents. For all these runs the adsorbent dose was kept at 2 g. The pH was varied from 2 to 6. The contact time in batch was varied from 5 minutes to 210 minutes.

The removal percentage (% R) of chromium was calculated for each run by using Eq.

$$\% \text{ Removal (\% R)} = [C_i - C_e / C_i] \times 100$$

Where, C_i - Initial Concentration (ppm)

C_e - Equilibrium Concentration (ppm)

RESULT AND DISCUSSION

Performance of adsorbents for Cr removal

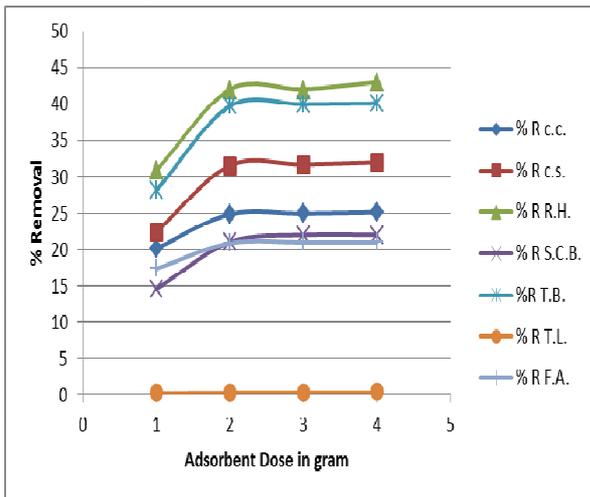
The performances of these sorbents were evaluated for the percent removal of chromium. The maximum (81.999%) removal of chromium was achieved with Coconut shell. The percent chromium removal with other sorbent (Tulsi leaf) was significantly

low(23.340%) as compared to coconut shell therefore tuls leaf not considered for further investigations. The variation in the sorption capacity between the various adsorbents could be related to the nature and concentration of surface groups responsible for interaction with the metal ions.

The adsorptive properties of activated carbon are due to its porous nature. Over 99% of the active sites for adsorption in activated carbon are located in the interior of the particle. Results of our investigation revealed that Coconut shell has highest percent removal and sorption capacity. Further investigations were made with this sorbent while Tuls leaf does not give fruitful results So, it is advise to not use Tuls leaf as an adsorbent for removal of hexavalent chromium.

Effect of adsorbent dose

The percentage adsorption of Cr⁶⁺ ions onto Activated carbon of Agricultral waste materials was studied at different adsorbent doses (1.0,2.0,3.0 and 4.0 gram) , keeping P^H=2 at room temperature, Contact time = 30 minute and initial Cr⁶⁺ ions concentration of 100 ppm (Part Per Million). The result showed that optimum removal was observed with adsorbent dose of 2.0 gram.



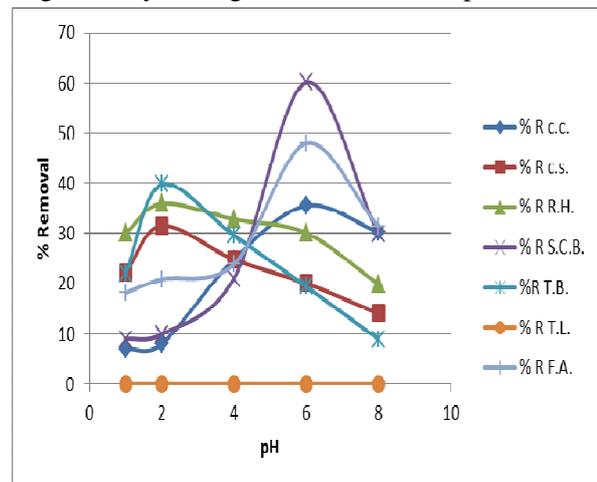
Graph between adsorbent dose and % Removal

Effect of the pH on the uptake of Hexavalent Chromium

Chromium exists mostly in two oxidation states which are Cr (VI) and Cr (III) and stability of these forms is dependent on the pH

of the system. It is well known that the dominant form of Cr (VI) at higher pH is HCrO₄⁻. Increase in pH shifts the concentration of HCrO₄⁻ to other forms CrO₄²⁻ and Cr₂O₇²⁻. At higher pH maximum adsorption indicates that it was the HCrO₄⁻ form of Cr (VI) which was the predominant species. When the pH was further increased after 3 a decrease in percentage adsorption was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in adsorption capacity. Beyond 6 sharp decrease is observed this is due to the competition between OH⁻ and chromate ions (CrO₄²⁻).

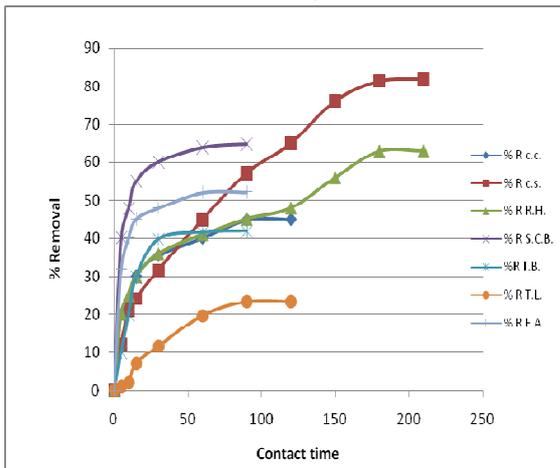
The net positive surface potential of the adsorbent decreased with increasing pH resulting in weakening of electrostatic force between adsorbate and adsorbent which ultimately lead to lowering of sorption capacity [5].For Agricultural waste materials the P^H of the solution is an important variable which controls the adsorption of the metal ions at the solid water interface. Hence, the influence of P^H on the adsorption of Cr⁶⁺ ions onto activated carbon was examined in the P^H=1,2,4,6and 8. The result showed that maximum removals of Cr⁶⁺ ions by adsorbents for contact time 30 minutes were carried out at P^H= 2, concentration of solution is 100 ppm& adsorbent dose 2gram. Some Agricultural waste materials (Coconut coir, sugar cane bagasse, Fly ash) give better result at pH =6.



Graph between pH and % Removal

Effect of contact time

The effect of contact time on adsorption was studied at different initial concentrations with various adsorption dosages in Fig. It is obvious that increase in contact time from 05min to 210 min enhance significantly the percentage removal of Cr (VI). The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available adsorption sites affected the time needed to reach the equilibrium. Coconut Shell gives better result (81.999 % Removal) in comparison of other agricultural waste material. Tulsi Leaf does not give any result at 100ppm Cr⁶⁺ Solution, so different Concentration of Cr⁶⁺ solutions (100,50,25 ppm) are checked and The result showed that maximum removals of Cr⁶⁺ ions at 25ppm concentration by adsorbents gives better result for contact time 90 minutes were carried out at P^H= 2 & adsorbent dose 2gram.



Graph between contact time and % Removal

Adsorption Isotherm

To examine the relationship between adsorbed (q_e) and the aqueous concentration C_e at equilibrium sorption isotherm models are widely employed. The isotherm results were analyzed using the Langmuir & Freundlich isotherm. The amount of adsorption at equilibrium, q_e (mg/g) was calculated by equation [6], [7].

$$q_e = (C_0 - C_e) V / W \text{ ----- (1)}$$

Where, C₀ and C_e (mg/L) are the liquid-phase concentrations of hexavalent chromium at initial and equilibrium respectively. V is the

volume of the solution (L) and W is the mass of dry adsorbent used.

Langmuir Isotherm: The Langmuir isotherm model assumes that the uptake of metal ions occur on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir isotherm constants were calculated from the following linearized form.

$$C_e / q_e = 1/a_m b + 1/a_m (C_e) \text{ ----- (2)}$$

Where a_m and b are Langmuir constants determined from the slope and intercept of the plot, indicative of maximum adsorption capacity (mg/g) of adsorbent and energy of adsorption respectively, while C_e is the remaining concentration of adsorbate after equilibrium(mg/l) and q_e is the amount adsorbed at equilibrium(mg/g)

The linear plot of 1/q_e and 1/C_e show that the experimental data reasonably well fitted the linearized equation of the Langmuir isotherm over the whole chromium concentration range.[8]

Freundlich Isotherm: The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems[9]. Freundlich isotherm assumes that the uptakes of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich isotherm is expressed as :

$$q_e = K_f \cdot C_e^{(1/n)} \text{ ----- (3)}$$

Where, K_f and n are constants of Freundlich isotherm incorporating adsorption capacity (mg/g) and intensity.

Table: Adsorption capacity of various adsorbents

Adsorbent	Max. adsorbent capacity (mg/g)	pH	Max. Concentration (mg/l)
Coconut coir	8.9964	6	100
Coconut shell	16.30998	2	100
Rice Husk	12.6226	2	100
Sugar Cane bagasse	12.8760	6	100
Tulsi branches	8.3908	2	100
Tulsi Leaf	4.6680	2	25
Fly ash	10.4208	6	100

CONCLUSION

The study indicated the suitability of the adsorbents used for removal of Cr (VI) from aqueous solution. Coconut shell an agricultural waste was found to be the most effective one, for which the removal efficiency reached to 81.999% of Cr(VI) at room temperature at adsorbent dose of 2gm. The optimum pH for the removal was found to be at 2. Increase in the concentration of the adsorbent and contact time were found to increase the % removal of Cr(VI). While increasing the initial Cr(VI) concentration, removal percentage decreases for all the four adsorbents by keeping the other conditions like pH, concentration of the adsorbent and temperature constant. Results obtained were modeled using three isotherm models: Langmuir & Freundlich. Equilibrium isotherms were well described by the Langmuir equation, giving maximum adsorption capacity of 16.30998 mg/g at room temperature for coconut shell. Removal of poisonous hexavalent form of chromium from solutions was possible using selected adsorbents. Tulsi Leaf was the not effective for which the removal reached only 23% for Cr(VI) at concentration of 25ppm and at pH 2. Increase in the dose of adsorbent, initial concentration of Cr(VI) and increase in contact time upto 2 h are favorable for all increase the adsorption of Cr(VI). So, it is advice to not use Tulsi leaf as an adsorbent for removal of hexavalent chromium.

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