Removal of Hexavalent Chromium using Adsorbent Made from Drumstick Seeds Activated Carbon (DSSAC)

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Abstract— Saragava seeds (Moringa olefera) have been considered as agro-base product, which are very easily available. It is called drumstick. It is known that they have carbon contents. Attempts have been made to produce activated carbon (DSSAC) from them in a laboratory. They have been then employed for adsorption of chromium from the wastewater and they were found efficient for adsorption of chromium from the wastewater. All the experimental studies were batch studies, carried out in conical flask shacked with mechanical shaker. The filtration was done using Whatman No. 41 filter paper and the optical density was measured using the colourimeter. The weighing was done in digital balance. The adsorbents were prepared by impregnation with zinc chloride, at five different activation temperatures, i.e.3000 C, 4000 C, 5000 C and 6000 C. In the adsorption study of chromium, the effect of initial concentration of chromium solution on adsorption was studied at 0.5 mg/L,1.0 mg/L,2.0 mg/L and 3.0mg/L. The adsorbent dosage of 25mg/50mL, 30mg/50 mL, 35mg/50 mL, 40mg/50mL and 50 mg/50mL were used to determine the optimum dose of the adsorbents for removal of chromium from the wastewater. By using these optimum doses, optimum time were determined for each initial concentration and for the adsorbents prepared at various activation temperatures. Maximum removal of chromium was observed for all the four adsorbents but at temperature 5000C the effect is more. A comparative studies were made to evaluate the performance of DSSAC with commercially available PAC and GAC. It was observed that almost more of chromium removal was observed for DSSAC than PAC. In some cases, the removal of chromium using GAC was found to be lower than that of DSSAC.

Key words: DSSAC, Adsorption, Activation Temperature, Optimum Dose, Optimum Contact Time

I. INTRODUCTION

In recent years the use of adsorption technique for the removal of heavy metals has received global attention. [1] In adsorption, molecules distribute themselves between two phases, one of which is a solid whilst the other can be liquid or gas. [2]

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes. [3]

The three steps can be identified in the removal of a contaminant by adsorption. Firstly adsorbate must move from the liquid or gaseous phase through a boundary layer in the fluid to the exterior of the adsorbent. Next it must become attached to the adsorbent. Through the three stages are described as taking place sequence, in the practice all three may be occurring simultaneously in different parts of the adsorbent because conditions are not uniform throughout. Generally concentrations will be higher at the outer surface of an adsorbent than in the centre, until equilibrium conditions have been established. Also the pores structure will consist of a distribution of pore sizes, the spread of the distribution depending on the origin of adsorbent and its condition of manufacture. [4]

II. CHROMIUM – PRIORITY POLLUTANT

Chromium (Cr) is a metallic element, which is listed by Environmental protection Agency as one of 129 priority pollutants and is considered as one of the most noxious heavy metals. [5]

It does not occur free in nature. The metal chromium, which is the chromium (0) form, is used for making steel. Chromium (VI) and chromium (III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving. Chromium enters the air, water, and soil mostly in the chromium (III) and chromium (VI) forms. [6]

In air, chromium compounds are present mostly as fine dust particles, which eventually settle over land and water. Chromium can strongly attach to soil and only a small amount can dissolve in water and move deeper in the soil to underground water. Fish do not accumulate much chromium in their bodies from water. [7]

The hexavalent chromium compounds are reduced to the trivalent form in the presence of oxidizable organic matter. However in natural waters where there is a low concentration of reducing material hexavalent chromium compounds are more stable (EPA 1984) [8] Chromium enhances an alloy's hardenability, creep and impact strength, and resistance to corrosion, oxidation and wear. [9]

III. THE SCOPE OF PROPOSED WORK

In the proposed studies, adsorbents are proposed to be prepared from the agro product such as drum stick seeds. The prepared adsorbent will be employed for the synthetic waste containing chromium as major pollutant. The present study encompasses following steps:

- To prepare adsorbent by using drumstick seeds available in large quantity in our country.
- To prepare the adsorbents at various activation temperatures such as 300oC, 4000C, 5000C and 6000C.
- To study the physical properties of the adsorbents, which includes sieve analysis for average particle size, density

of adsorbents, moisture content, matters present in adsorbent soluble in water, and acid and ash content.

- To prepare the calibration curve for the sample.
- To prepare the solution of 1, 5 – diphenyl carbazide.
- To prepare solutions of different concentrations of chromium which may be present in the industrial effluent and cause serious environmental problems. The proposed solutions of chromium which are to be used are having following concentration: 0.5 ppm, 0.75 ppm, 1.0 ppm and 1.5 ppm
- To study the parameters affecting the adsorption of chromium from the solution, which include the effect of activation temperature, adsorbent dosage, contact time, initial concentrations of chromium solutions.
- To study the equilibrium condition of the chromium adsorption process which include the study of adsorption isotherms (not reported in this paper)
- To compare the results of low cost adsorbents with the commercially available powdered activated carbon and granular activated carbon and draw the inferences from the results obtained by the investigations made therein.

IV. MATERIALS AND METHODS

The experiments of adsorption for present investigation were carried out in Environmental Engineering Laboratory of Civil Engineering Department of B.V.M. Engineering College, V. V. Nagar.

V. SELECTION OF ADSORBENT

Activated carbon can be produced with relative ease and at reasonable cost from a number of different raw materials and with a variety of surface properties to meet the requirements of specific applications. The importance of investigations in the preparation of the activated carbon from the raw material available locally can hardly be overestimated. [10, 11]

In view of the multipurpose use of activated carbon in water and effluent treatment in the industry, the present investigation was undertaken to prepare activated carbon from indigenous raw materials. Here, the adsorbent is prepared from the agro base product drumstick seeds powder and use them for the removal of chromium from the industrial effluent.

VI. PREPARATION OF ADSORBENT- DSSAC [12]

The schematic representation for preparation of the activated carbon from DRUMSTICK is shown in Figure. 1

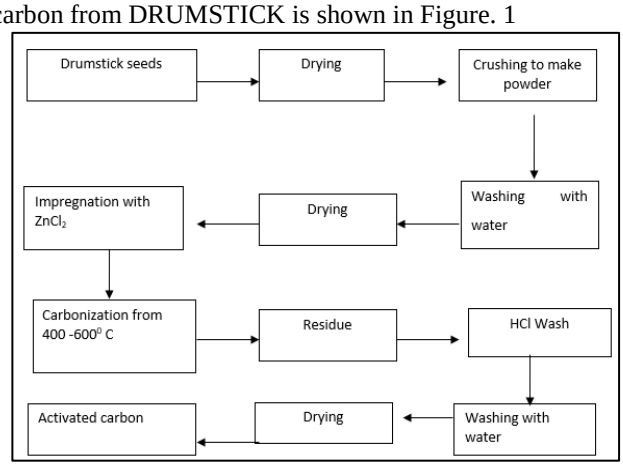

Fig. 1:

A. Preparation of the Raw Material:

Drumstick seeds were collected from nearby village farm and then it is allowed for sun drying. The pods and shells of stick is removed and seeds were collected for the experiment. Seeds are allowed for further sun drying. The dried sample was then ground thoroughly and screened through standard sieves of 20 mesh to get uniform particle size for the preparation of powdered activated carbon.

B. Preparation of Activated Charcoal:

The prepared raw materials were first washed with distilled water to remove soluble impurities, if any. Then it was kept in oven for drying at 1100 C for 30 min. thereafter, an impregnation was done with the solution of zinc chloride in a mixing cylinder. Impregnation time given for desire absorption of zinc chloride was 12 hrs. The recommended impregnation time varies from 12 to 36 hrs.

The impregnated samples were placed in a muffle furnace for carbonization. The air was excluded from the furnace to prevent the oxidation. The carbonization was carried out at different carbonizing temperatures such as 300oC, 4000C, 5000C and 6000 C. The carbonization time was 4 to 5 hours. After 5 hours, the carbonized product was cooled to room temperature by putting it in to desiccators, and then the product is crushed from coarse lumps to small particles.

The activated product contains the considerable amount of the zinc chloride used for impregnation. Therefore, the sample was then washed with concentrated hydrochloric acid until practically all the traces of zinc chloride have been dissolved. The nature of zinc chloride is basic and so concentrated hydrochloric acid was used to make the pH neutral. This was followed by water wash until the pH of the filtrate liquor is neutral. This washed activated product was dried in the hot air oven at 100 + 50 C for 2 hours. Grinding the material followed by sieving to 400 meshes ASTM gave the uniform particle size of the adsorbent.

VII. PROPERTIES OF DSSAC

The characteristics of adsorbent DSSAC prepared in the lab were determined and the same were compared with the powdered activated carbon

Adsorbents	**PAC**	**DSSAC**
Bulk density, g/mL	0.7	0.42
Matter soluble in water, (%)	1.5	2.9
Matter soluble in acid, (%)	2.5	4.15
Moisture content (%)	5.6	9.10
Ash content (%)	6.8	9.5

Table 1: Characteristics of the Adsorbents

VIII. ADSORBATE

In this study, the synthetic waste solution of chromium was prepared in the laboratory to avoid the interference of other metals.

A. Preparation of the Synthetic Chromium Waste [13]:

Standard solutions of chromium are required for preparation of the calibration curve. The calibration curve is needed for converting the measured optical density with colorimeter in to corresponding chromium concentration in terms of mg/L.

Stock solution of chromium is required for preparing the synthetic effluent of chromium of particular concentration for the experimental study. The prepared stock solution is taken for subsequent dilution to get the series of different concentrations of chromium.

Steps for preparation of stock and standard solutions are:

1) Weighing the sample accurately in weighing balance.
2) Weighed sample is dissolve in partially filled measuring cylinder with distilled water and shaken well to ensure complete dissolution of the sample.
3) The solution is finally diluted up to the mark in measuring cylinder.

– Stock Chromium Solution:

This was prepared by dissolving 14.14 mg of anhydrous potassium dichromate in distilled water and then it was further diluted to 100 ml. This makes 1.00 ml = 50 microgram chromium

– Standard Chromium Solution

This was prepared by diluting 20 ml of stock chromium solution to 1000ml. In this, 1.00 ml = 1.00 microgram hexavalent chromium.

Preparation of 1, 5 – Diphenyl carbo-hydrazide Reagent

This was prepared by dissolving 200mg of 1, 5– diphenyl carbo-hydrazide in 100 ml 95 % ethyl alcohol solution. Then, the acid solution prepared from 40 ml concentrated sulphuric acid and 360 ml of distilled water was added in to this with mixing. This solution was then refrigerated to maintain the stability for about a month. In this, the colour change from colourless to tan does not affect reagent's usefulness.

B. Measuring the Concentration of the Samples:

The standard solutions of varying concentrations were used for the preparation of the standard calibration curve by plotting concentration versus optical density by measuring the optical density of the standard solution of specific concentration. To measure the chromium concentration, optical density of the prepared solution was measured in a colorimeter and then corresponding chromium concentration was estimated from the standard calibration curve. After preparing the concentrated chromium solution, the subsequent chromium concentration solutions were prepared by serial dilution of that concentrated solution.

The concentrations in treated and untreated chromium solutions were measured similarly as described above. However, care was taken during measuring the optical density, like rinsing the measuring tube with distilled water after each measurement.

While using colorimeter, a maximum wavelength, at which the solution shows maximum optical density or minimum transmission, as compared to other wavelengths is required to be determined. Since we are concerned only about the visible wavelength, the optical density is to be found out only over the wide range of wavelength from 450 to 750 nm. Calibration of the colorimeter should be done by using distilled water in the measuring tube of 1 cm diameter for a set of infinite transmission and black rubber tube for set of zero transmission. For chromium maximum wavelength is 550 nm.[14] The calibration curve thus obtained is available in Figure.2

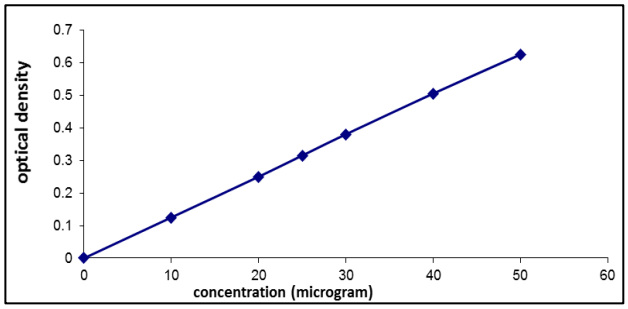

Fig. 2: Calibration curve for removal of cr^{+6} using colourimeter

IX. RESULTS AND DISCUSSIONS

The experiments were conducted to study the effect of dose and activation temperature on Percentage Removal of chromium (VI)

The Experiments were also conducted to study the effect of contact time and activation temperature on Percentage Removal of chromium (VI)

The Summary Tables (Table-2 to Table 6) shows the results of the experiments.

A. Summary Tables for Results of DSSAC, PAC & GAC:

Optimum Time = 30 min

Sr.No.	Dose (mg/50 mL)	% Removal of Cr^{+6}					
		DSSAC					
		300° C	400° C	500° C	600° C	PAC	GAC
1	25	48	50	55	45	54	60
2	30	53	65	67	52	60	63
3	35	60	72	74	60	72	65
4	40	65	80	83	65	76	70
5	45	70	82	85	72	80	73
6	50	70	82	85	72	80	74

Table 2: Initial Concentration = 0.5 mg/L

Sr.No.	Dose (mg/50 mL)	% Removal of Cr^{+6}					
		DSSAC					
		300 °C	400 °C	500 °C	600 °C	PAC	GAC
1	25	52	54	56	45	50.25	48.25
2	30	60	62	60.27	68.51	53.49	53.51
3	35	64	65	72.27	72	58.51	59.49
4	40	70	72.25	78	75.33	66	64
5	45	75	81	84.23	80.53	79.25	72.27
6	50	75.50	82	86.27	81	80	72.23

Table 3: Initial Concentration = 0.75 mg/L

Sr.No.	Dose (mg/50 mL)	% Removal of Cr^{+6}					
		DSSAC					
		300 °C	400 °C	500 °C	600 °C	PAC	GAC

1	25	45	48	50	46	48.5	38
2	30	58	60	62	53	65	42.5
3	35	62	62	65	65	69.25	55
4	40	65	74	72	68	70.25	59.25
5	45	70	80	88	76	72	64
6	50	70	80	89.5	76	72	64

Table 4: Initial Concentration = 1 mg/L

Sr.No.	Dose (mg/50 mL)	% Removal of Cr^{+6}					
		DSSAC					
		300 °C	400 °C	500 °C	600 °C	PAC	GAC
1	25	18.67	44.27	46.5	34.5	38.25	32
2	30	48.5	48	50	42.27	48.25	45
3	35	53.25	55.25	55.2	45	55	52
4	40	53	57.5	56	54	55	53
5	45	58.53	62	63	59	62.25	58
6	50	59	62	63	60	62.48	58

Table 5: Initial Concentration = 1.5 mg/L

Sr. No.	Concentration mg/L	% Removal Of Cr^{+6}					
		DSSAC					
		300 °C	400 °C	500 °C	600 °C	PAC	GAC
1	0.5	79.5	88.5	92.4	84.6	86.2	78
2	0.75	84	86.53	89.07	83.07	84	77.5
3	1	78.5	84.25	90.5	82	78.3	70.2
4	1.5	63.27	68.27	72.53	65.5	67	65.27

Table 6: Equilibrium Time=60 Min, equilibrium dose = 45 Mg/50ml

X. Conclusions

Based on the experiments following conclusions have been drawn:

1) During the experimentation it was found that removal of chromium using Drumstick seeds is feasible from the synthetic waste water prepared in the lab.
2) Irrespective of any concentration and temperature the optimum dose is found to be 45mg/50mL in all cases. IT is shown in table 6.1 to table 6.4.
3) At any given concentration of Cr+6 in the wastewater, the maximum removal is found at activation temperature 500oC.The maximum percentage removal at 500oC with 0.5mg/L concentration is found to be 90.5%.
4) Compared with PAC &GAC the performance of DSSAC at any given concentration of Cr+6 is found to be better.

At 1.5 mg/Concentration the percentage removal of Cr+6 by PAC & GAC are found to be 67% &65.27% respectively. However percentage removal of Cr+6 using DSSAC at 500oC is found to be 75.53%.

5) At any given activation temperature as concentration increases percentage removal of Cr+6 decreases. When concentration of 0.5 mg/L at 300oC percentage removal is 79.5%, which is reduces 63.5% when concentration is 1.5mg/L. Similar results have been obtained during experimentation with PAC & GAC.
6) When concentration Cr+6 0.5mg/L percentage removal by commercial available PAC & GAC is 86% &78%, which is found reducing as concentration increases to 1.5 mg/L to 67% & 65.27%
7) Activation temperature 500oC has shown the greatest amount of removal compared with the result obtained when activation temperature are 300oC & 400oC. However, when the activation temperature is further increases to 600oC the percentage removal reduces.
8) The optimum contact time is found to be 30min. However the equilibrium time is 60min and equilibrium dose is 45mg/50mL.

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