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REMOVAL OF CHROMIUM FROM AQUEOUS SOLUTIONS USING *DERRIS INDICA* WOOD BASED ACTIVATED CARBON. ADSORPTION BATCH STUDIES

Adsorption efficiency in removal of chromium from waste water has been studied using *Derris indica* based activated carbon by conducting batch adsorption tests. Adsorption kinetics of chromium removal by *Derris indica* was examined by varying factors such as pH and concentration of synthetic solution and dosage of activated carbon. It has been found that the *Derris indica* based activated carbon is able to remove 80 mg/dm³ of chromium from aqueous solution by dosage of 0.8 g/150 cm³ with optimum contact time of 15 min. The isotherm data confirms with both Langmuir and Freundlich isotherm forms.

1. INTRODUCTION

Heavy metals such as nickel, cadmium, chromium, zinc and arsenic are toxic in nature even when they are mixed with water at low concentrations. Chemicals, dyes, electroplating, and leather industry are the prime sources of discharging waste water containing toxic heavy metals. Normally heavy metals are not easily degradable in biological way and will be present on Earth for a considerable period. The concentrations of these heavy metals should be reduced to allowable standards before they are let out in either soil or water bodies. Otherwise it will be a greater threat to living organisms such as man, animals and plants. When they consume polluted water, these heavy metals get accumulated in their body and cause several diseases depending upon individual strength. Various treatment methods are available for the removal of chromium from industrial waste water such as chemical precipitation, ion exchange, filtration, membrane separation, oxidation and reduction and adsorption. When com-

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paring with other methods, adsorption is found cost effective and technically easy to adopt.

Commercial activated carbon is used throughout the world for the removal of heavy metals from the industrial waste water. The cost of commercial activated carbon and its efficiency in removing the heavy metals make the industries to prefer the same. Mostly developing countries and under developed countries suffer due to non-removal of heavy metals from the industrial waste water. Thus, there is a necessity for developing a new activated carbon which is of low cost and easily available. Various types of low cost activated carbon were recommended; still there is a requirement to make a proper adsorbent for the removal of chromium from the industrial waste water.

Many agricultural waste to be used for preparing activated carbon were suggested, e.g. *Avena Monida* biomass [1] rice hulls [2], rice husk carbon [3], coconut shell carbon [4], saw dust [5], biogas slurry [6], polyacrylamide grafted sawdust [7], hazel nut shell [8], *Fagus orientalis* L. [9], coirpith [10], and coconut tree saw dust [11].

Derris indica is a locally available tree in all parts of south India. It is not used for any medical purpose and it is cheap. Normally it is considered as an agricultural waste. Hence, experiments were conducted in removal of chromium from aqueous solution using *Derris indica* wood based activated carbon to determine their removal efficiency. The main objective of this research is to explain the removal efficiency of *Derris indica* wood based activated carbon for the removal of chromium from aqueous solution.

2. MATERIALS AND METHODS

Preparation of activated carbon. *Derris indica* is the agricultural waste material which is available in Tamil Nadu, South India. *Derris indica* was collected and its size was diminished into small pieces by breaking it. It was kept in oven for drying at a temperature of 170 °C for one day. It was then kept in air tight cylindrical iron mould with top completely covered air tight during charring process. The sealed iron mould was kept in muffle furnace and the temperature is raised up to 600 °C and the same was maintained up to 60 minutes. During this process, wood of *Derris indica* was converted to activated carbon. The activated carbon thus manufactured was broken down into small pieces and then sieved using 710–500 μ sieve. The carbon pieces of the size in-between 710–500 μ are washed in distilled water, dried in oven and kept in an air tight container for further experiments.

Preparation of synthetic solution. Synthetic solution of concentration of 80 mg/dm³ of chromium was prepared by dissolving 409.950 mg of CrCl₃·6H₂O in 1 dm³ of distilled water. The synthetic chromium solution thus prepared was used for all experiments.

Instrumentation and chemicals. Double beam spectrophotometer (systrons 2202 model) was used to find out the concentration of chromium. The minimum detection

limit was within EPA standards. Various concentrations of chromium solutions were used as standard solutions to calibrate the instrument. All the experiments were repeated twice and the results with the deviation higher than 0.1 mg/dm³ were ignored. pH meter (ECGO) was used for all pH measurements.

Chemicals such as concentrated hydrochloric acid and sodium hydroxide (Madras scientific company) were used for adjusting required pH of samples. In all experiments, distilled demineralised water was used.

Adsorption isotherms. Freundlich isotherm and Langmuir isotherm equations were used to explain the experimental isotherm data:

- the Freundlich equation:

$$\lg \frac{X}{m} = \lg K_F + \frac{1}{n} \lg C_e \quad (1)$$

where: X/m – weight of chromium adsorbed per unit weight of adsorbent, g/kg, C_e – equilibrium concentration of adsorbate in solution after adsorption, mg/dm³, $K_F n$ – empirical constants.

- the Langmuir equation:

$$\frac{1}{\left(\frac{X}{m}\right)} = \frac{1}{q_m} + \frac{1}{K_a q_m} \frac{1}{C_e} \quad (2)$$

where: X/m – weight of chromium adsorbed per unit weight of adsorbent, g/kg, K_a , q_m – constants, C_e – equilibrium concentration of adsorbate in solution, mg/dm³.

Experimental procedure. To calculate optimum dosage and optimum contact time for chromium removal using *Derris indica* wood based activated carbon, 8 conical flasks containing 150 cm³ of 80 mg/dm³ chromium solution were taken. 0.2–1.6 g of activated carbon prepared from *Derris indica* wood was placed in every flask. Then the conical flask was kept in magnetic stirrer for continuous agitation. Samples were taken out from every conical flask at intervals of 5, 10, 15, 20, 25 and 30 min. Samples which were taken out from every conical flask were kept in a test tube after filtering using Whatman filter paper No. 41. The remaining metal ion concentration was determined by UV spectrophotometry.

Optimum pH and optimum concentration for chromium removal were determined in other sets of experiments. All the batch mode experiments were carried out at 20±2 °C. All the experiments (except those for optimum pH) were carried out at pH of 3.37 (original pH). The concentration of remaining chromium ions was calculated from:

$$\text{Chromium removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad [\%] \quad (3)$$

where C_0 – initial chromium concentration, mg/dm^3 , C_e – residual chromium concentration, mg/dm^3 .

3. RESULTS AND DISCUSSION

3.1. EFFECT OF DOSAGE

Increase in quantity of activated carbon increased the percentage removal of chromium. This was due to more surface area availability and more surface functional groups. The effect of carbon dosage on the removal of chromium metal ions is illustrated in Figs. 1, 2, and Tables 1, 2.

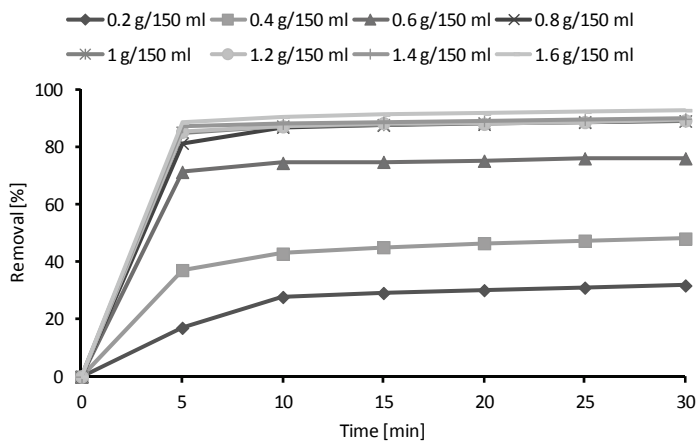


Fig. 1. Time dependences of percentage removal of chromium for various carbon dosages

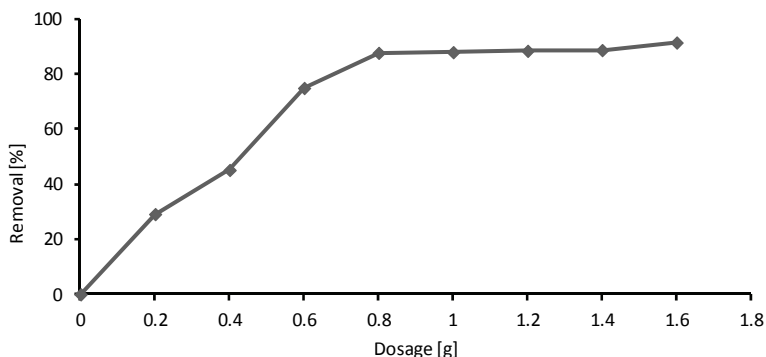


Fig. 2. Dependence of percentage removal of chromium at optimum time 15 min on carbon dosage

Table 1

Effect of carbon dosage on chromium removal

| Sample No. | Contact time [min] | % of Cr removal for 150 cm ³ | | | | | | | |
|------------|--------------------|---|-------|-------|-------|-------|-------|-------|-------|
| | | 0.2g | 0.4g | 0.6g | 0.8g | 1.0g | 1.2g | 1.4g | 1.6g |
| 1 | 5 | 17.00 | 37.13 | 71.38 | 81.38 | 85.13 | 85.38 | 87.13 | 88.63 |
| 2 | 10 | 27.75 | 42.88 | 74.50 | 87.00 | 87.38 | 87.25 | 88.25 | 90.63 |
| 3 | 15 | 29.13 | 45.13 | 74.88 | 87.63 | 87.88 | 88.38 | 88.63 | 91.38 |
| 4 | 20 | 30.13 | 46.50 | 75.25 | 88.00 | 88.50 | 88.75 | 89.25 | 91.75 |
| 5 | 25 | 31.00 | 47.38 | 76.13 | 88.63 | 88.88 | 89.00 | 89.63 | 92.38 |
| 6 | 30 | 31.75 | 48.13 | 76.13 | 89.13 | 89.13 | 89.37 | 89.88 | 92.88 |

Table 2

Effect of dosage of activated carbon on chromium removal at equilibrium state

| Weight of adsorbent [g/150 cm ³] | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| Per cent of chromium removal | 29.13 | 45.13 | 74.88 | 87.63 | 87.88 | 88.38 | 88.63 | 91.38 |

It is apparent from the results obtained that the percentage removal of chromium increases upon increasing dosage; it was found that the percentage removal reaches equilibrium after certain time. Up to the carbon dosage of 0.6 g/150 cm³ the removal of chromium varied and at the dosage of 0.8 g/150 cm³ it was around 88% and the equilibrium state is almost achieved. The optimum time for removal of chromium using *Derris indica* wood based activated carbon was 15 min.

3.2. EFFECT OF pH

In order to determine the adsorption mechanism, the effect of pH was studied. pH is one of the major factors controlling the removal of chromium from the waste water. Figure 3 shows the impact of pH on trivalent chromium removal efficiencies with the use of *Derris indica*. The study was performed at synthetic solution containing 80 mg/dm³ chromium, adsorbent dosage of 0.8 g with pH varying from 1 to 8. It was found that the percentage removal increases upon increasing pH and at certain point it reaches an equilibrium state. At pH 1 and 2 precipitation of trivalent chromium took place. The percentage removal of trivalent chromium was 84.50% at its original pH and from there onwards there was a slight increase in removal. Optimum pH for the removal was 3.37 at optimum contact time of 15 min. Hence all the experiments were conducted at original pH.

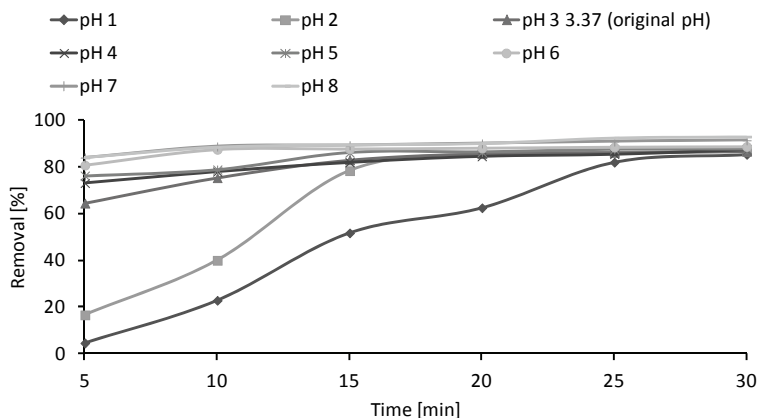


Fig. 3. Time dependences of percentage removal of chromium for various pH

3.3. EFFECT OF INITIAL CONCENTRATION:

To demonstrate the chromium adsorption at various initial concentrations, solutions of 10, 20, 30, 40, 50, 60, 70 and 80 mg/dm³ were used. The samples were analysed for the residual chromium concentration at intervals of 5 min up to the contact time of 30 min. The results obtained are shown in Fig. 4.

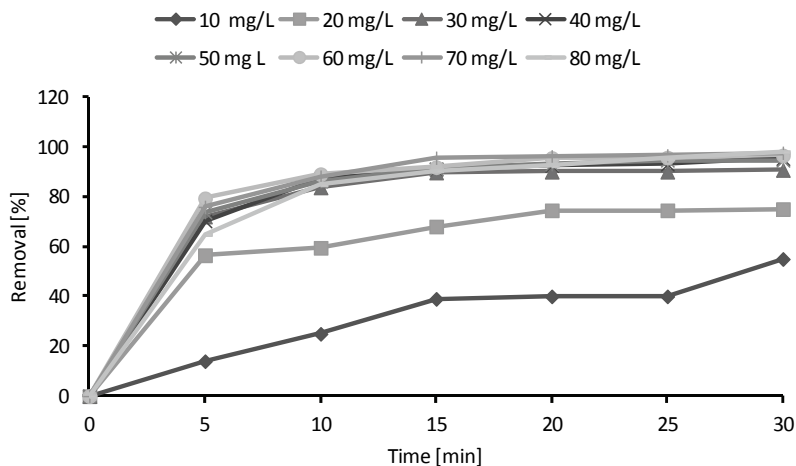


Fig. 4. Time dependences of percentage removal of chromium for its various initial concentrations

It is visible from the picture that initial concentration has a significant effect on adsorption prospective application. The percentage of chromium removal increases up to initial concentration of 70 mg/dm³ and reaches equilibrium.

3.4. ISOTHERM STUDY

A permanent volume (150 cm³) of synthetic chromium solution was equilibrated with various quantities of *Derris indica* wood based activated carbon (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6) for 20 min. Chromium concentrations at the equilibrium state were determined for each of 8 reactors. The statistics needed for isotherm plot for *Derris indica* wood based activated carbon is given in Table 3 (Langmuir isotherm) and Table 4 (Freundlich isotherm).

Table 3

Data for Langmuir isotherm
for chromium removal

| $1/C_e$ [dm ³ /mg] | x/m [g/kg] | $1/(x/m)$ [kg/g] |
|----------------------------------|-----------------|---------------------|
| 0.0176 | 0.00875 | 114.28 |
| 0.0227 | 0.00677 | 147.71 |
| 0.0497 | 0.00748 | 133.68 |
| 0.1010 | 0.00656 | 152.43 |
| 0.1030 | 0.00527 | 189.75 |
| 0.1075 | 0.00442 | 226.24 |
| 0.1098 | 0.00379 | 263.85 |
| 0.1449 | 0.00342 | 292.40 |

Table 4

Data for Freundlich isotherm
for chromium removal

| $x/m \times 10^{-3}$ [g/kg] | $\lg C_e$ | $\lg(x/m)$ |
|--------------------------------|-----------|------------|
| 0.00875 | 1.753 | -2.058 |
| 0.00677 | 1.642 | -2.169 |
| 0.00748 | 1.303 | -2.126 |
| 0.00656 | 0.996 | -2.183 |
| 0.00527 | 0.987 | -2.278 |
| 0.00442 | 0.968 | -2.354 |
| 0.00379 | 0.959 | -2.421 |
| 0.00342 | 0.839 | -2.466 |

The isotherm test data was observed to be in shape with Langmuir and Freundlich isotherm models (Figs. 5, 6). While plotting the values in terms of the Langmuir and Freundlich isotherm models, it was observed that R_L value was 0.058 and $n = 0.667$, which is appropriate for removal of chromium by adsorption process.

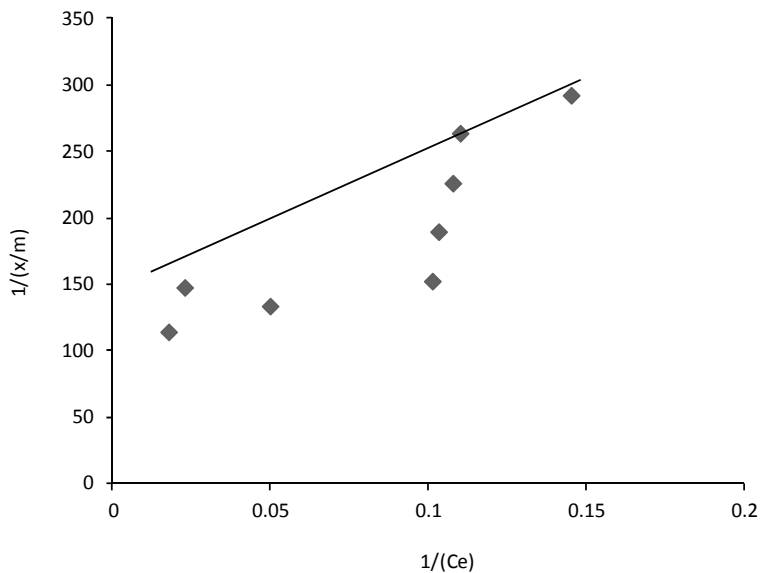


Fig. 5. Langmuir isotherm for chromium removal

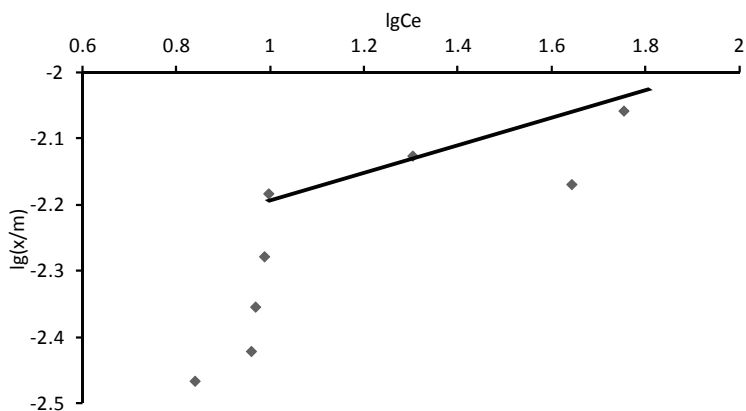


Fig. 6. Freundlich isotherm for chromium removal

4. REGENERATION OF ACTIVATED CARBON

Various regeneration techniques such as thermal regeneration, chemical regeneration and wet air oxidation are available for the recovery of heavy metals. Thermal regeneration method is one of the most widely applied one, it needs to maintain temperature as high as 800 °C, which leads to high energy consumption and we can recover around 60% of chromium from the carbon.

5. CONCLUSIONS

Activated carbon was made by using *Derris indica* wood. Experiments were conducted in a batch mode to analyse the capacity of this carbon to eliminate chromium from waste water. The following conclusions were arrived from the present studies on chromium removal capacity on *Derris indica* wood based activated carbon:

- For *Derris indica* wood based activated carbon the percentage of chromium removal increases upon increasing pH. But there is no remarkable change there after compared to original pH.

- Optimum dosage for the eliminating of 80 mg/dm³ of chromium in aqueous solution is 0.8 g/150 cm³ at an optimum contact time of 20 min.

- From the isotherm models, it is detected that *Derris indica* wood based activated carbon confirms Langmuir and Freundlich isotherms.

- In the present study, wood of *Derris indica* based activated carbon was not subjected to any physical or chemical modification for strong and better activation.

REFERENCES

- [1] GARDEA-TORRESDEY L., TIEMANN K.J., ARMENDARIZ V., BESS-OBERTO L., CHIANELLI R.R., RIOS J., PARSONS J.G., GAMEZ G., *Characterisation of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of Avena monida (Oat) biomass*, J. Hazard. Mater., 2000, B80, 175.
- [2] LOW K.S., LEE C.K., NG A.Y., *Column study on the sorption of Cr(VI) using quaternized rice hulls*, Bioresour. Technol., 1999, 68, 205.
- [3] BISHNOI N.R., BAJAJ M., SHARMA N., GUPTA A., *Adsorption of Cr(VI) on activated rice husk carbon and activated alumina*, Bioresour. Technol., 2004, 91, 305.
- [4] BABEL S., KURNIWAN T.A., *Cr(VI) Removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan*, Chemosphere, 2000, 54, 951.
- [5] HAMADI N.K., CHEN X.D., FARID M.M., LU M.G.Q., *Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust*, Chem. Eng. J., 2001, 84, 95.
- [6] NAMASIVAYAM C., YAMUNA R.T., *Adsorption of chromium(VI) by a low-cost adsorbent: biogas residual slurry*, Chemosphere, 1995, 30, 561.
- [7] RAJ C., ANIRUDHAN T.S., *Batch Cr(VI) removal by polyacrylamidegrafted sawdust: kinetics and thermodynamics*, Water Res., 1998, 32, 3772.
- [8] KOBYA M., *Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies*, Bioresour. Technol., 2004, 91, 317.
- [9] ACAR F.N., MALKOC E., *The removal of chromium(VI) from aqueous solutions by Fagus orientalis L.*, Bioresour. Technol., 2004, 94, 13.
- [10] KADIRVELU K., THAMARASELVI K., NAMASIVAYAM C., *Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith*, Sep. Purif. Technol., 2001, 24, 497.
- [11] SELVI K., PATTABHI S., KADIRVELU K., *Removal of Cr(VI) from aqueous solution by adsorption on to activated carbon*, Bioresour. Technol., 2001, 80, 87.