

Adsorption of Chromium on Activated Carbon Prepared from Coconut Shell

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ABSTRACT

Activated carbon was prepared from coconut shell by pyrolysis. It was characterized by PXRD, and SEM. Different physical properties such as bulk density, moisture content, volatile matter content, ash content, hardness, decolorizing power, phenol number, iodine number and surface area and porosity were also determined. The activated carbon was used as adsorbent for the removal of chromium from an electroplating industry. The effect of various parameters such as adsorbent dosage, particle size, pH, contact time and stirring speed was studied. The studies showed that the activated carbon can be used as a good adsorbent for the removal of hexavalent chromium from electroplating industries.

Key words - Activated carbon, adsorption, electroplating industry, hexavalent chromium, SEM.

1. Introduction

Chromium (VI) is highly toxic in nature. This is due to the fact that one of the reduction products of Chromium (VI) is Chromium (V). Chromium (V) is a known carcinogen and will lodge in any tissue to form cancerous growths. There are reports that Chromium (V) is also a factor leading to premature senility in parts of Russia. The Chromium (VI) is a very strong oxidizing agent (therefore very fast in reacting, unlike Chromium (III) and likely to form complexes). Chromium (VI) is not a very stable state when compared to Cr (III). 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 severe liver abnormalities. Chromium (VI) compounds are teratogenic to animals [1].

Effluents from electroplating and tannery industries is a major source of aquatic pollution in India with high chemical oxygen demand (COD), biological oxygen demand (BOD), and hexavalent chromium. In India, there are a large number of tanneries scattered all over the country but the main areas of their concentration are Tamilnadu, Uttar Pradesh and West Bengal. Nearly 80% of these tanneries are engaged in the chrome tanning processes. Most of them discharge untreated wastewater into the

environment. In such aqueous waste, Chromium (VI) is present as either dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in acidic environments or as chromate (CrO_4^{2-}) in alkaline environments.

Several treatment technologies have been developed to remove chromium from water and waste water. Common methods include chemical precipitation, ion exchange, membrane separation, ultrafiltration, filtration, electrocoagulation, solvent extraction, sedimentation, reverse osmosis, dialysis, electrodialysis, adsorption and filtration, evaporation, cementation, dilution, air stripping, steam stripping, flocculation and chelation [2-6].

Reduction and chemical precipitation has traditionally been the most used method. The most often used precipitation processes include hydroxide, sulphide, carbonate and phosphate precipitation techniques. The disadvantage of precipitation technique is the production of sludge. This process suffers from draw backs like incomplete removal, requirement of sizable quantities of treatment chemicals and production of voluminous toxic sludge. It constitutes a solid waste disposal problem. A variety of other treatment technologies were considered and evaluated. Techniques like ion exchange and adsorption with products obtained from naturally occurring materials like activated carbon were considered as better alternatives. The exorbitant cost involved with ion exchange makes it prohibitive for wide application [7-9].

Coconut shells are available in plenty in tropical countries. The utilization of this waste material helps in recycling waste and thus keeping the eco system clean. Mitigation measures based on low cost technologies hold promise of wide applicability in developing countries. This methodology can be profitably employed by least developed and developing countries in mitigating pollution due to the heavy metal ion chromium [10-12].

2. Materials and Methods

The coconut shells were washed with water to remove sticking and loose matter and then sun dried for 5 days (8 hours per day). The dried samples were then hammer broken to pieces and then converted to a powder using a mixer. Three temperature routes were followed for preparing

active carbon by taking known quantities of powdered coconut shell.

Samples were pyrolysed in a muffle furnace in the presence of steam flow. A two step procedure was followed. Sample was carbonized at 550 °C for 2 hours and then a physical activation method was followed for different periods of time. Through the inspection hole in the muffle furnace door a glass tube was introduced which was connected to a steam generator. Thus a continuous flow of steam was maintained. Three different samples were prepared and coded as 750S40, 750S100 and 800S30. The samples 750S40 and 750S100 were prepared by heating the powders to 750 °C and keeping them at 750 °C for 40 minutes and 100 minutes respectively. In case of sample 800S30, the powder was heated to 800 °C and then maintained at that temperature for 30 minutes.

2.1 Characterization of Activated Carbon Powders

2.1.1 Bulk Density

The activated carbon sample were packed in a previously weighed 25 cm³ specific gravity bottle by repeatedly tapping the bottle so that powder is filled upto the mark. The bottle was weighed again. The difference in the weights gives the weight of powder taken in the bottle. The bulk density of the powder was calculated using equation 1.

$$\text{Bulk density} = \frac{[\text{weight of powder taken in the bottle}]}{25} \quad (1)$$

2.1.2 Moisture content

About one gram of the powdered air dried activated carbon powder was taken in a previously weighed crucible. The crucible was placed in an electric hot air oven maintained at about 110 °C. After one hour the crucible is taken out, cooled in a desiccator and weighed again. The loss in weight of the powder reported on percentage basis gives moisture content in the sample.

2.1.3 Volatile Matter

About one gram of the powdered air dried activated carbon powder was taken in a previously weighed crucible. The crucible was placed in a muffle furnace maintained at about 925 °C. It was taken out after exactly 7 minutes. After first cooling in air, the crucible was cooled in a desiccator and weighed again. The loss in weight of the powder reported on percentage basis gives volatile matter content in the sample.

2.1.4 Ash Content

The residual activated carbon powder from the above step was then heated in a muffle furnace at 750 °C for about half an hour. After first cooling in air, the crucible was cooled in a desiccator and weighed again. The heating, cooling and weighing cycle was repeated till a constant weight was

obtained. The residue is reported as ash on percentage basis.

2.1.5 Hardness

The percentage of particles passing through a screen of 275 mesh was determined. Then the particles were subjected to hammer force for five minutes and then the particles which passed through a screen of 300 mesh were determined. The percentage of particles not broken to fine size was expressed as percentage of hardness.

2.1.6 Decolorizing Power

Decolorizing power is the ability of activated carbon to decolorize a dilute blue colored solution of methylene blue. It is expressed as mg/g.

2.1.7 Phenol Number

100 cm³ of 30 ppm solution of phenol was taken in a 250 cm³ leak proof reaction flask. The pH of the solution was adjusted to neutral by adding 0.1 N NaOH or 0.1 N H₂SO₄. A known weight of the activated carbon powder was added to it. The solution was equilibrated for 24 hours at room temperature followed by filtration and subsequent analysis of the filtrate for phenol concentration. The concentration of phenol was determined by spectrophotometric analysis for the colour resulting from the reaction of phenol with 4-amino antipyrine at a wave length of 600 nm.

2.1.8 Surface area and porosity

The BET surface area of activated carbon powder was determined by nitrogen adsorption desorption method. The instrument used was MICROMERITICS GEMINE 2375. Nitrogen gas was allowed to adsorb on the powder at 77 K. The nitrogen adsorption and desorption isotherms were used to determine parameters like surface area, pore volume and pore size.

2.1.9 Iodine Number

Iodine number is defined as the number of milligrams of iodine absorbed by one gram of activated carbon powder. Iodine solution is prepared by dissolving 13 grams of iodine in 50 cm³ of glacial acetic acid and then diluting up to the mark in a 1000 cm³ volumetric flask. A known weight of the activated carbon powder (about 0.25 g) was suspended in 10 cm³ of carbon tetra chloride taken in a 250 cm³ conical flask. To this a known volume of the prepared iodine solution was added. Similarly a blank solution was also prepared by taking same volumes of carbon tetra chloride iodine solution as in the previous case but without the activated carbon powder. Both the conical flasks were kept in a shaking machine for one hour. Then the solution were is rapidly filtered using Whatman filter paper no. 41. 20 cm³ of the filtrate was transferred into a 250 cm³ conical flask. To this 20 ml of 15%

potassium iodide and 100 ml of distilled water were added. The contents of both the flask were titrated against standard sodium thiosulphate using freshly prepared starch as indicator. The volume of sodium thiosulphate solution consumed in case of both back and ban titrations was determined. The difference in initial and final concentrations of iodine was determined and from this the iodine number was calculated using equation 2.

$$\text{Iodine number} = \frac{\text{Difference in concentration of iodine in mg}}{\text{Weight of activated carbon in g}} \quad (2)$$

2.2 X ray Diffraction

The structural analysis of the activated carbon powder was determined by PXRD. The PXRD pattern was recorded by using Philips PW 1051 X-ray diffractometer using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) with Nickel filter at a scanning rate of 2 $^\circ$ /minute.

2.3 FTIR Spectroscopy

The FTIR studies were conducted on activated carbon sample to determine the various organic and inorganic groups on the surface. The instrument used to record the FTIR spectrum Shimadzu with KBr as reference.

2.4 Scanning Electron Microscopy

The surface morphology of the activated carbon samples were studied by scanning electron microscopy. The SEM micrograph was recorded using JEOL JSM 5200 instrument.

2.5 Adsorption Studies

An adsorbate stock solution of 1000 mg/l of Cr (VI) was prepared by dissolving 2.829 g of potassium dichromate in double distilled water. The stock solution was diluted suitably to get 100, 200, 300, 400 and 500 mg of Cr (VI) solutions. Batch adsorption experiments were carried out by shaking 500 mg of activated carbon with 100 ml of potassium dichromate solution of known concentration in 200 ml Erlenmeyer flasks at specified temperatures in a thermostated water bath mechanical shaker.

The flasks were removed after the desired contact time. A definite volume (5ml) of the solution was withdrawn and quickly filtered through Whatmann No.40 filter paper. The filtrates were analyzed using UV-Visible spectrophotometer (Hitachi 2000) at a wavelength 540 nm using diphenyl carbazide as complexing agent. In acidic media some part of chromium (VI) was reduced to the trivalent state. Hence Cr (III) is oxidized to Cr (VI) by potassium permanganate and sodium azide. The adsorbed chromium (VI) was calculated by taking the difference of initial concentration and final chromium concentration in the filtrate.

The amount of chromium adsorbed q_t was calculated using equation 3.

$$q_t = \frac{(C_0 - C_t)V}{m_0} \quad (3)$$

where,

C_0 = initial chromium concentration in mg/L

C_t = chromium concentration at time t

m_0 = mass of activated carbon in g

V - Volume of chromium solution in cm 3

The effect of adsorbent dosage, particle size, pH, contact time, stirring speed, initial concentration of Cr (VI) and temperature were studied by varying any one of the parameters and keeping the other parameters constant.

3. Results and Discussions

3.1 Bulk Density measurements

Bulk density is an important parameter of powdered solids. The American Water Work Association has set a lower limit on bulk density at 0.25 gm/ml for activated carbon to be of practical use. The bulk density values of the prepared are given in table 1 of prepared samples satisfies this condition. The bulk density data are in agreement with the values reported in literature [13-15].

Table 1. Bulk density values of the samples

Sl. No.	Sample	Bulk density (g / cm 3)
1	750S40	0.2641
2	750S100	0.2592
3	800S30	0.2632

3.2 Moisture Content

The moisture content values of the prepared activated carbon samples are reported in table 2. The commercially available samples contain about 5-8% moisture [16].

Table 2. Moisture content values of the samples

Sl. No.	Sample	Percentage moisture content
1	750S40	5.11
2	750S100	5.31
3	800S30	5.21

3.3 Volatile matter

The coconut shell samples were weighed before and after pyrolysis. Table 3 gives the percentage conversion values for the samples after pyrolysis.

Table 3. Percentage conversion values for the samples after pyrolysis

Sl. No	Sample	Weight before Pyrolysis	Weight after Pyrolysis	Percentage of conversion
1	750S40	300 g	62 g	20.67

2	750S100	300 g	65 g	21.67
3	800S30	300 g	68 g	22.67

From table 3, it can be noticed that the yield of pyrolyzed carbon is around 20%. The samples used for the study contain substantial quantity of volatile matter.

3.4 Ash Content and Ash analysis

Table 4 gives the values of percentage ash content of the samples.

Table 4. Percentage ash content of the samples

Sl. No.	Sample	Percentage ash content
1	750S40	1.42
2	750S100	1.54
3	800S30	1.37

From table 4, it can be seen that the ash content in activated carbon samples is low. The low ash content makes activated carbon an attractive candidate for adsorption studies. The ash content of commercial samples is around 2% (133,134). If ash content is high it will interfere with pore structure development and hence adsorption will be less.

3.5 Ash analysis

The ash obtained from various samples was mixed well and its analysis was conducted. Table 5 gives the composition of the various components in the ash.

Table 5. Ash analysis data for the samples

Sl. No.	Substance	Percentage
1.	SiO ₂	18.3
2.	K ₂ O	0.99
3.	CaO	0.95
4.	MgO	8.92
5.	P ₂ O ₅	0.09
6.	Na ₂ O	70.75
7.	Fe ₂ O ₃	1.22

3.6 Hardness

The activate carbon powder should possess sufficient mechanical strength to withstand the abrasion resulting from continuous use. The commercial samples have hardness in the range of 80-90%, where as prepared samples possess 90-98 % hardness.

Decolorizing power

Table 6 shows the values of decolorizing power of the samples.

Table 6. Decolorizing power values of the samples

Sl. No.	Sample	Decolorizing Power
1	750S40	66
2	750S100	68
3	800S30	69

3.7 Phenol Number

It is the amount of activated carbon required for 90% removal of phenol. This indicates the ability to remove taste and odor. It is expressed as mg/g.

Table 7. Phenol number values of the samples

Sl. No.	Sample	Phenol number
1	750S40	27
2	750S100	31
3	800S30	37

3.8 Surface area, pore volume and pore size

Table 8 gives the values of BET surface area, pore volume and pore size values of the samples.

Table 8. BET surface area, pore volume and pore size values of the samples.

Sl. No.	Sample	BET Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (Å)
1	750S40	695	0.38781	17.88
2	750S100	730	0.40734	18.78
3	800S30	790	0.44082	19.82

The above results show that surface area of activated carbons is in agreement with other studies. Average pore volume of 0.4 cm³/g suggests good pore structure development. The BET surface area increases with increase in temperature of activation, soaking time and porosity as well. Increase in surface area results in an increase in chromium adsorption. This can be explained as due to the increases in the number of adsorption sites.

3.9 Iodine Number

Table 9 gives the values of the iodine number of the samples. The iodine numbers of activated carbons prepared in this investigation lies between 480-700. This is quite comparable with the values reported by other workers. The iodine numbers reported by other workers lies between 550 – 850 . Generally, higher the iodine number, greater is the sorption capacity. ASTM D 4607 describes the procedure for determining the iodine number.

The iodine number recommended as a minimum by the American Water Works Association for a carbon to be used in removal low molecular weight compounds is 500. The two factors that determine good iodine number are activation temperature and dwell time. At 800 °C even a dwell time of 30 minutes is sufficient. For lower temperatures dwell time of more than one hour is required. Hence samples 750S100 and 800S30 conform to these specifications. The sample 750S40 has an under developed pore structure. From figure 1, it can be observed that the iodine number increases as the temperature of activation increases. This suggests that surface area has increases in terms of microscopic pores. Iodine adsorption is usually

associated with micro pores because of the small size of iodine molecule.

Table 9. Iodine number values of the samples

Sl. No.	Sample	Iodine Number
1	750S40	478
2	750S100	562
3	800S30	682

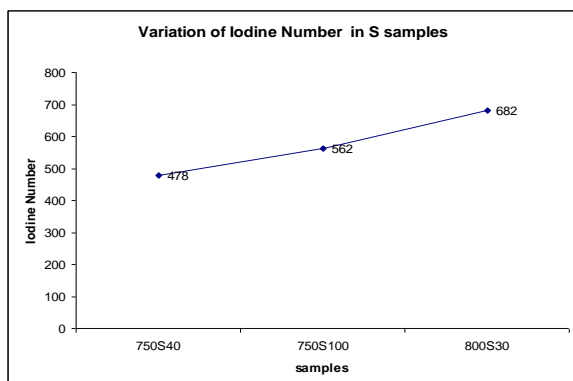


Figure 1. Variation of iodine number of the samples

3.10 X-Ray Diffraction Studies

Figure 2 shows the PXRD profile of the powdered sample. The PXRD pattern shows the presence of amorphous carbon in the sample. The crystalline phases of Si, KCl, Fe, Zn are also present. The peaks in the PXRD profile correspond to those reported in the literature for activated carbon.

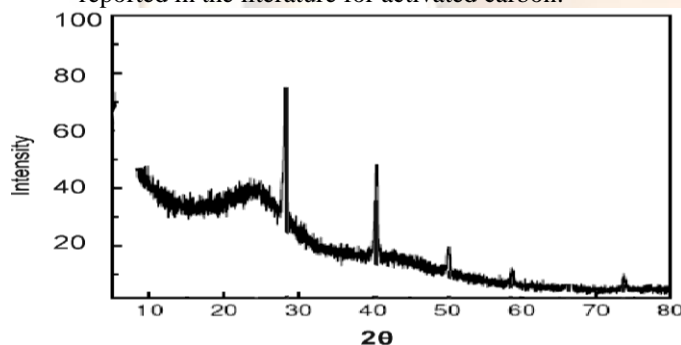


Figure 2. PXRD profile of activated carbon sample

3.11 Scanning Electron Microscopy Studies

Figures 5 and 6 show the SEM micrographs of the sample before and after chromium coating. The porosity is less in case of figure 6 compared to that in case of figure 5 which indicates the adsorption of chromium in the pores of the sample.

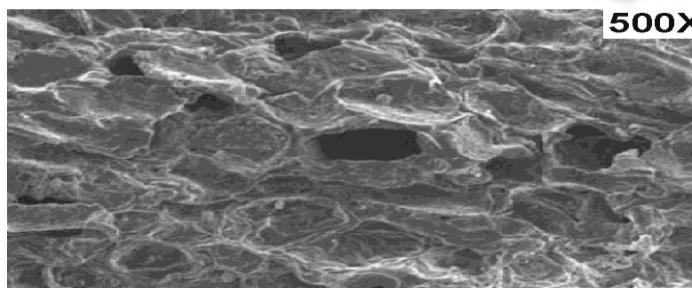


Figure 5 SEM micrograph of sample before adsorption of chromium

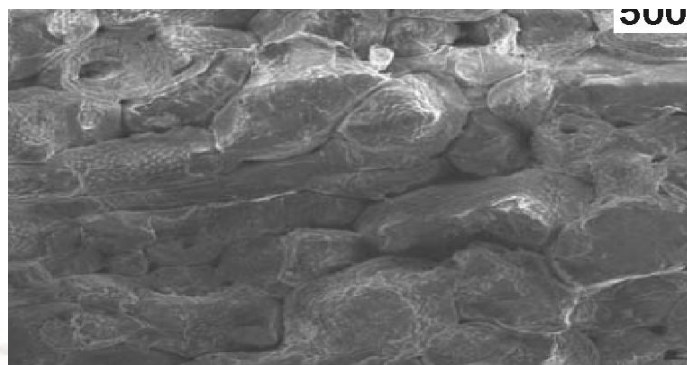


Figure 6 SEM micrograph of sample after adsorption of chromium

3.2 Adsorption Equilibrium Studies

3.2.1 Effect of Adsorbent Dosage

Figure 7 shows the effect of adsorbent dosage on the removal of chromium. It is clear from the figure that as the adsorbent dosage increases, the adsorption also increases. This is due to fact that an increase in adsorbent dosage increases the number of active sites available for adsorption. Optimum removal of chromium (about 94%) was achieved for an adsorbent dosage of 2 g of the adsorbent. Beyond the optimum dosage, the adsorption negligible increase in adsorption occurred.

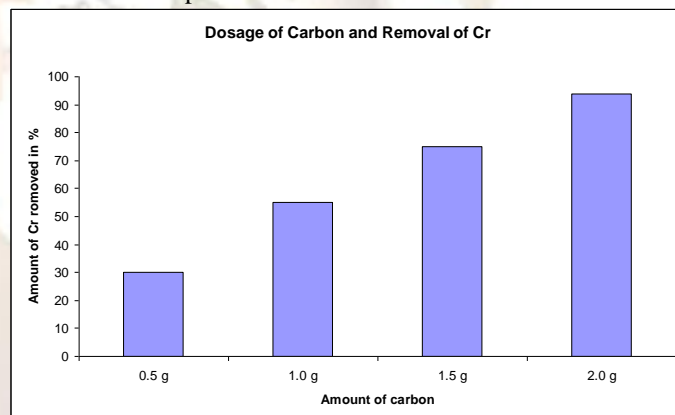


Figure 7. Effect of adsorbent dosage

3.2.2 Effect of Particle Size

Various particle sizes of carbons were used to conduct experiments to determine % removal of chromium at 25 °C at an initial concentration of 200 mg /dm³. The removal of chromium at different particle sizes illustrated that removal rate increases as the particle size decreases. As can be seen from figure 8 that the adsorption increases as the particle size decreases. The relatively higher adsorption rate as the particle size decreases is due to the increase in surface area. There is a tendency as fine particles exhibit lesser time to equilibrate in shorter time.

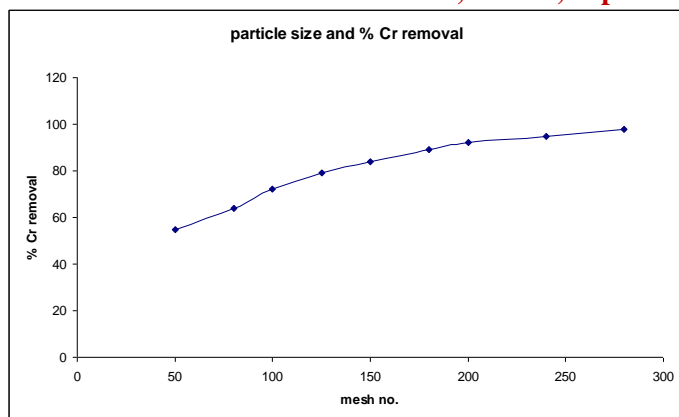


Figure 8. Effect of particle size on adsorption

3.2.3 Effect of pH

The effect of pH on the adsorption of chromium by activated carbon was studied at pH values of 1 to 7. 0.5g of activated carbon was suspended in 100 ml of solution which contained 80 mg of chromium per liter. Different pH conditions were maintained by adding HCl and acetic acid-sodium acetate buffer. The adsorption of chromium was determined after an equilibration time of one hour at a stirring speed of 200 rpm.

pH influences the adsorption of Cr(VI) ions on the adsorbate as it affects the solubility of metal ions and hence the electrostatic binding of ions. From figure 9, it is evident that at lower pH between 2 and 3 the adsorption is maximum. This could be attributed to the high concentration of H⁺ ions at lower pH values which neutralizes the negatively charged adsorbate Cr₂O₇²⁻ ions. The decrease in the adsorption efficiency at higher pH can be attributed to increase in the concentration of OH⁻ ions which hinder the diffusion of Cr (VI) ions.

The process of adsorption of metal ions on the adsorbent involves the binding of metal ions by electrostatic forces of attraction. The surface of the adsorbent is positively charged and hence negatively charged Cr₂O₇²⁻ ions are held by electrostatic forces of attraction.

It has been suggested that the mechanism for metal adsorption is due to the acidic functional C=O groups on the adsorbent surface. The presence of oxygen functional groups make the adsorbent surface negatively charged and therefore a repulsive electrostatic interaction between the adsorbent and the anion where as for a cation the negatively charged group enhances the electrostatic interaction with the negatively charged surface of the adsorbent mainly through carboxylic ligands.

According to the fig, the rates of adsorption are weak with low values of pH (<2). Between 2 and 3 the rates of absorption increase rapidly. This is due to the surface charge of the metal, which is strongly related to the pH of the solution. Maximum adsorption capacity is observed in the pH range 2 to 3. This indicates that the pH corresponds to the zero

point charge (pHzpc) which lies between the two values. The pHzpc is a point at which the adsorbent surface groups either acidic or basic no longer contribute to the pH of the solution. Maximum adsorption of Cr (VI) ions at lower pH has been reported [17, 18].

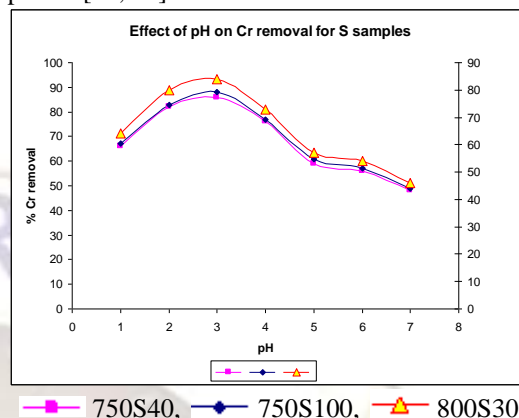


Figure 9. Effect of pH on adsorption

3.2.4 Effect of contact time on Adsorption

Adsorption experiments were conducted as a function of contact time and the results are shown in figure 10. The rate of Cr (VI) binding with adsorbent was greater in the initial stages, then gradually decreased and remained almost constant after an optimum period. After 60 minutes the adsorption reaches an optimum value of 92%. This is because initially a large number of vacant sites are available for adsorption and after some time the remaining sites may be difficult to occupy due to repulsive forces between adsorbate ions on the solid and in the solution. Similar results have been reported by other investigators.

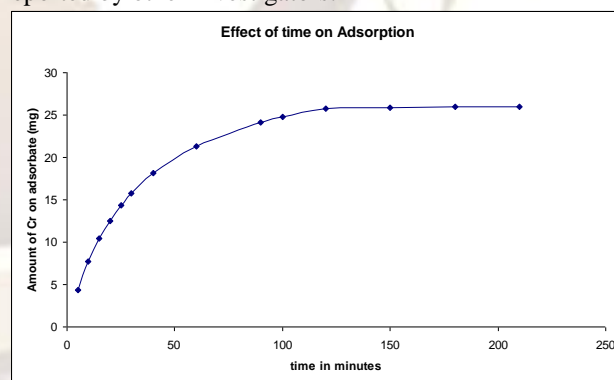


Figure 10. Effect of contact on adsorption

3.2.5 Effect of Stirring Speed

The effect of the agitation of the sorbent/sorbate system in chromium adsorption was monitored at low, medium and high- agitation speeds (80, 100, 120, 150, 200 rpm). The results are shown in figure 11.

0.5 gm of adsorbent and 50 ml of the solution containing 100 mg/l of chromium at pH 3 was agitated between 90 and 210 rpm. Maximum of 97.77 % chromium removal was achieved at 200

rpm. The effect of chromium adsorption on low and high agitation speed was observed. An increase in adsorption was observed from 66.66 % to 97.77 %, when the agitation speed was increased from 90 to 200 rpm. Due to agitation, proper contact was developed between metal ion in solution and the binding sites, which promoted effective transfer of adsorbate ions onto the adsorbent sites.

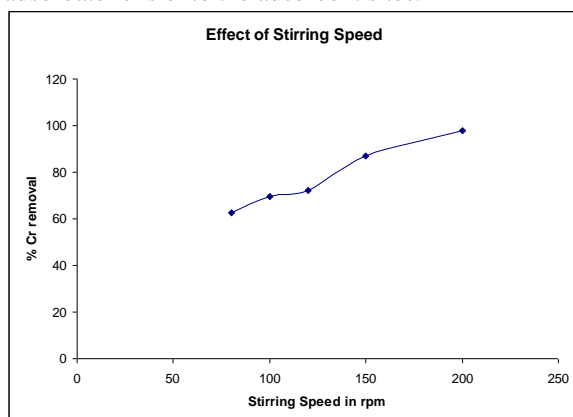


Figure 11. Effect of stirring speed on adsorption

4. Summary and Conclusions

Activated carbon was successfully prepared by pyrolysis. The results indicated that the adsorption capacity depends upon the pore size, surface area and temperature of activation of the activated carbon. At pH 3, the adsorption was found to be maximum. The activated carbon can act as a good adsorbent for the adsorption of chromium from industrial effluents such as electroplating industries.

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