Cost-Effective and Eco-Friendly Technique for Attenuation of Cr(VI) From Aqueous Phase

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Abstract— The attenuation of chromium (Cr^{6+}) from aqueous solution by adsorption on chemically activated carbon derived from saw dust has been performed at room temperature. The removal by adsorption using Zinc chloride with varying Impregnation ratio's (I.R) were studied with respect to optimum dosages, and variation of pH and optimum time. It has been seen that the adsorption of Cr^{6+} increased with an increase in dosage in addition to an increase in Impregnation ratio. Additionally, it was observed that the surface area of saw dust carbon increased with an increase in Impregnation ratio. Thus, it is seen that the maximum removal efficiency is obtained at an I.R ratio of 0.75. Further, the optimum contact time, dosage and pH for carbon with I.R-0.75 was found to be 35min, 150mg and 1.5. The (Cr^{6+})removal efficiency was observed to be 84%, 90% and 99.80% respectively.

Key words— Chromium (Cr^{6+}), Contact time, Dosage, pH, Saw dust.

1.INTRODUCTION

Chromium is extremely insoluble in its natural state and cannot be converted into a more soluble form by weathering, oxidation, or bacteria. Its levels of water are normally low due to its low solubility. However, effluents containing chromium compounds have been pumped into rivers, causing chromium pollution of water, which has been severe in some cases. The amounts of chromium in finished water entering public supply systems are usually similar to raw water or slightly lower than natural water. Chromium is absorbed by the gastrointestinal and respiratory systems [1].

"Chromium enters environmental waters from anthropogenic sources such as electroplating factories, leather tanneries and textile manufacturing facilities. Chromium also enters groundwater by leaching from soil. Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur. Chromium is not known to usually accumulate in the bodies of fish, but excessive concentrations, mainly because of the disposal of metal products in surface waters, may affect the gills of fish swimming close to the point of disposal" [2]. In view of the teratogenic and carcinogenic qualities of(Cr^{6+})on the public, it is seen to result in grave health concerns. In accordance with W.H.O which provides the standard guidelines for drinking waters[3] and BIS 10,500[4], which specifies that the maximum allowable limit with respect to (Cr^{6+})in drinking water shall not exceed a concentration 0.05mg/L [5].

Core study Objectives:
The main objective of this study is to develop a technique for hexavalent chromium reduction or removal from the aqueous phase. The adsorption technique proposed in this study for significant hexavalent chromium reduction would be useful in solving chromium (Cr^{6+})problems in similar industrial waste streams.

2.LITERATURE REVIEW

Studies were carried out employing the shell of Schweinfurthii seeds adding activation agents

Phosphoric acid and zinc chloride. The results with respect to isothermsindicated that the maximum adsorption capacity amounting to a measured value of .757mg/g using Phosphoric acid for the preparation of AC [6].

Experiments with neem leaves for removing Chromium (Cr6+) from industrial effluents have been conducted. The carbon adsorbent made from neem leaves was seen to be highly effective with respect to chromium removal. The maximum removal efficiency for bio sorbent prepared from neem leaves was found to be up to 85 percent [7].

A recent research on adsorbent prepared from aloe vera for chromium (Cr^{6+}) removal involved batch adsorption studies, which show that the adsorbent prepared using aloe vera has a considerably good adsorption capacity for chromium (Cr^{6+}) from aqueous solution[8].

Activated carbon was prepared from coconut shell by pyrolysis. 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 studies showed that the activated carbon can be used as a good adsorbent for the removal of hexavalent chromium from electroplating industries [9].

Studies aimed at Chromium(Cr^{6+})removal from synthetic wastewater employing poly vinyl alcohol coated AC prepared from stem of Crotalaria burhia were carried out. It was reported that the chromium (Cr^{6+})adsorption followed both Langmuir and Freundlich's equation isotherms [10].

The work carried out here involves the chemically activated carbon preparation of by utilizingzinc chloride($ZnCl_2$). which serves as an activating agent, followed by an analysis of the basic physico-chemical properties of the newly prepared carbon and thus attempting to detect removal of chromium (Cr^{6+})with respect to contact time, pH and dosage .

3. MATERIALS AND METHODS

Material

The adsorbent selected for the removal of chromium (Cr^{6+})as saw dust. The saw dust was grounded and washed with deionized water and then it is dried at room temperature (32±1ºC).

Characteristics of Saw dust Carbon:

Before using the saw dust carbon as an adsorbent, the characteristics such as moisture content, ash content, pH, decolorizing power, surface area, specific gravity and bulk density of the prepared carbon [5] have been studied and the results are shown in Table 1.

All the methods of analysis are as per "Standard Methods for the Examination of Water and Wastewater", 19th edition [11].

Table 1. Analysis results of Activated Carbon Characteristics

Sl. No.	Characteristics	Chemically activated		
		$ZnCl_2$		
		0.25	0.50	0.75
1	Moisture content (%)	7.00	7.10	8.00
2	Ash content (%)	14.83	13.88	13.80
3	Decolorizing power, (mg/g)	22.50	28.50	30.00
4	Surface area, (m^2/g)	618.39	633.57	661.39
5	pH	6.1	6.3	6.6
6	Specific gravity	0.946	1.086	1.543
7	Bulk Density, (g/cm^3)	0.230	0.217	0.204

Methods

Preparation of Activated carbon using $ZnCl_2$ as activating agent:

Afixed quantity of washed and dried saw dust powder of size 300 Micron was mixed with the activating agent ($ZnCl_2$), in required quantity[12], based on the impregnation ratio (I.R).

$$\text{Impregnation ratio (I.R)} = \frac{\text{Weight of the active agent added}}{\text{Weight of carbonizing material}}$$

Required quantity of distilled water was added in that mixture and boiled on till most of the water evaporated and slurry like mixture was retained. Then it was oven dried in a clean tray for 24 hours maintained at 105±5ºC. Preheated carbonizing material was filled in the small container in three layers. Each layer is compacted to remove any air space and avoid the loss in weight of the powder; otherwise it would result in burning of the material directly leaving behind only the ash. The small container is then placed inside a big container, such that sand surrounds the small container completely and the lid of the big container is tightly fitted. Pin hole was made on the lids of the containers for the escape of organic vapours. Then the setup was kept in a muffle furnace and heated at steady rate to attain the temperature of 800ºC. Thirty minutes after attaining the 800ºC temperature the furnace was allowed to cool for about 10 hours and then the container is taken out. Activated carbon thus prepared was washed with 0.1N HCl to remove the activating agent, followed by hot distilled water for about 8 times to remove the excess HCl present in the activated carbon. The activated carbon was dried at 105±5ºC, packed in polythene bags and kept in a desiccator [12].

Experimentation with BatchSorption

"In batch sorption, a pre-determined powder of adsorbent is mixed with the sample, stirred for a given contact time and subsequently separated by filtration. Powder adsorbent is more suitable for the batch type contact process.

Selection of Optimum Contact Time:

The adsorption is strongly influenced by the contact time. To study the effect of contact time, 100mL of 0.5mg/L chromium (Cr^{6+})solution of pH 2.0±0.02, was mixed with 0.1g of activated carbon, stirred at different contact times varying from (5mins, 10mins, 15mins up to 60mins). Then filtrate was analyzed for residual colour concentration using spectrophotometer.

Determination of Optimum Dosage of Adsorbent:

To determine the optimum dosage of activated carbon, adsorbent is added to a conical flask in different dosages varying from (25mg, 50mg, and 75mg up to 300mg), containing 100mL of 0.5mg/L concentration of chromium (Cr^{6+})solution and pH is adjusted to 2.0±0.02. The solution in the conical flask is subjected to stirring for pre-determined optimum contact time, filtered and analyzed for residual chromium concentration. The dosage which gives minimum residual concentration is chosen as optimum dosage"[1].

Selection of Optimum pH:

"The effect of pH on chromium adsorption was studied by performing equilibrium adsorption tests at different initial pH values. i.e. from 1.25 to 3.0 at an interval of 0.25. The pH of solution was adjusted by using 0.1N" H_2SO_4or 0.1N NaOH [5].The highest concentration of (Cr^{6+}) removal depicts the most optimum pH" [1].

4.RESULTS AND DISCUSSIONS

"The efficiency of removal of colour has been studied in terms of:

a) Effect of contact time
b) Effect of dosage
c) Effect of pH

Effect of Contact Time:

Contact time has greater influence in the adsorption process. The effect of contact time on removal of chromium (Cr^{6+}) from synthetic sample at pH 2.0±0.02 using chemically activated ($ZnCl_2$) carbon" prepared from saw dust [12]. This was with I.R. 0.25, 0.50 and 0.75 and are shown in figure 1. As I.R. increases optimum time decreases due to the increase in surface area. Optimum contact time [1] for all prepared carbons "is listed in table-II.

Effect of adsorbent dosage":

"Effect of adsorbent dosage has been studied and graph of percentage of residual chromium (Cr^{6+})removal versus dosage is plotted as shown in figure 2. From the graph it is observed that, as the dosage of carbon increases, amount of residual chromium decreases sharply and attains equilibrium. The dosage, at which maximum removal is attained, is taken as optimum dosage. After this not much change is observed even after increase in the amount of carbon dosage. The optimum dosage for all prepared carbon are listed in table-II

Effect of pH on chromium (Cr^{6+})removal:

The pH of solution has an influence on the extent of adsorption removal efficiencies of chromium (Cr^{6+})by prepared activated carbon at different pH values as shown in figure 3. From the figure, it is observed that chromium (Cr^{6+})is removed more effectively in acidic range. As pH increases, the removable efficiency decreases appreciably. This is due to the precipitation of carbon surface by nucleation" [1]. The optimum pH for all prepared carbons are listed in Table 2.

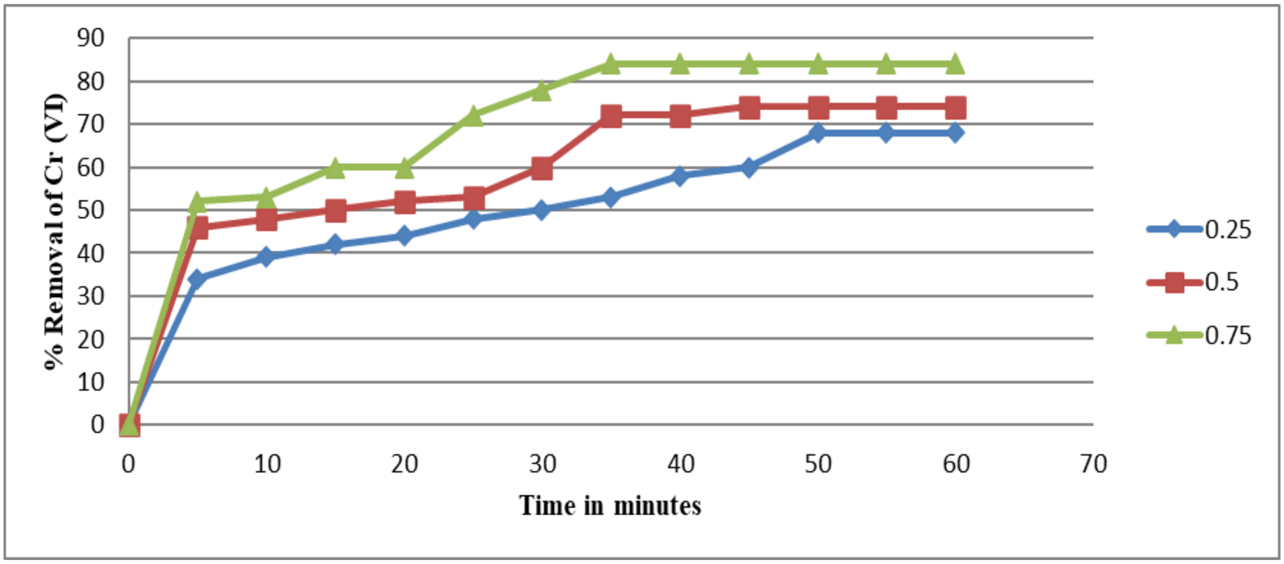

Fig1. Effect of contact time on chromium (Cr^{6+}) removal (chemically with $ZnCl_2$) by activated carbon

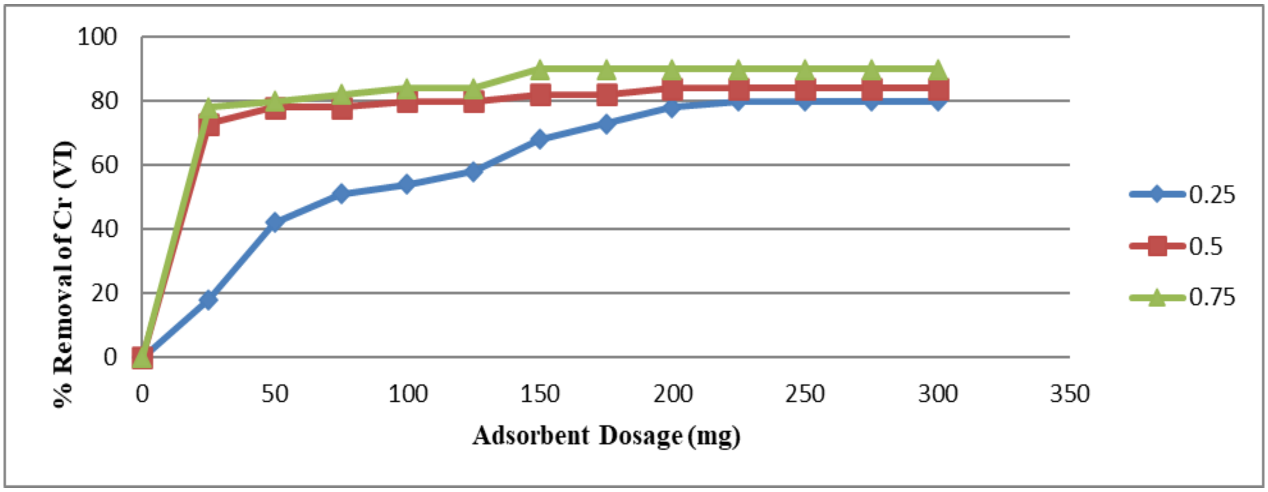

Fig.2.Effect of adsorbent dosage on chromium (Cr^{6+}) removal (chemically with $ZnCl_2$) by activated carbon

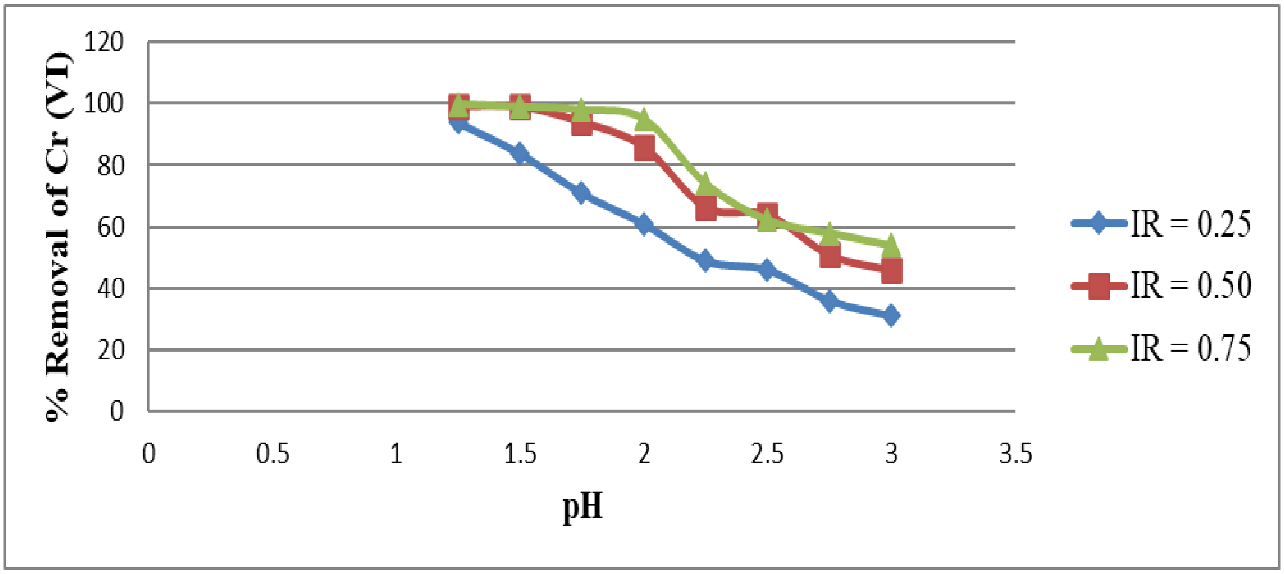

Fig.3.Effect of pH on chromium (Cr^{6+}) removal (chemically with $ZnCl_2$) by activated carbon

Table 2. "Optimum time, optimum dosage and optimum pH for prepared carbons".
Initial concentration = 0.5 mg/L pH = 2.0±0.02
Volume of sample = 100mL Temperature = 32 ± 1° C"

Type of Carbon	I.R	Optimum Time (min)	Optimum Dosage (mg)	Optimum pH
Chemically activated ($ZnCl_2$)	0.25	50	225	1.5
	0.50	45	200	1.5
	0.75	35	150	1.5

5.CONCLUSION

The following conclusions have been arrived at, based on the experimental studies. Chromium (Cr6+) adsorption increases over time and eventually reaches equilibrium. The experimental findings on the optimal dosage shows that increasing the adsorbent quantum tends to increase the chromium removal (Cr6+) and subsequently after the saturation dosages for varying impregnation ratios, the chromium (Cr6+) removal from the sample almost becomes constant. Further it is seen that the enhanced surface area of the corresponding adsorbent increases the removal of chromium (Cr6+). Chromium (Cr6+) adsorption is pH based, and the efficiency of an adsorbent for removing chromium (Cr6+) increases as the pH value decreases.

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