

NATURAL ADSORBENT PREPARED TO ELIMINATION OF HEAVY METAL FROM SPIKED SOLUTIONS – BATCH MODE STUDY

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ABSTRACT

To study the effects of pH on the adsorption of Cr (VI), experiments were carried out using 100 mg of the adsorbent in 50 ml solution of 10 mg / lit of Cr (VI) concentration, adjusted to different pH values ranging from 2.0 to 9.0 using 0.1N H₂SO₄ and 0.1N NaOH solutions . The solutions after equilibrium for a period of 120 minutes were centrifuged. The centrifugates were tested for Cr (VI) concentration spectrophotometrically APHA 1995. The results are shown in Table – 1, maximum adsorption is 96.50. The high adsorption capacity of Cr (VI) in the lower pH range is due to protonation of adsorbent surface, which would favour the uptake of anionic forms HCrO₄⁻¹ and CrO₄⁻². Many authors have observed adsorption increases with decrease in pH for Cr (VI) removal. Dahe Fan *et al.*, (2006) reported maximum adsorption of Cr (VI) at pH 4.0 by Chitosan coated montmorillonite. With the increase in pH of the system, the degree of protonation of the surface is reduced gradually and hence decreased the adsorption. Similar trend has been observed for the removal of Cr (VI) by Fe (III) / Cr (III) hydroxide (Namasivayam and Ranganathan, 1993).

Key words: *Date nuts*, Heavy metals. Wastewater treatment, Removal, Advanced techniques.

Adsorbent : *Date nuts dust*

The *Date nuts* were collected near village of Visakhapatnam, Andhra Pradesh, cleaned thoroughly with water and soaked in distilled water for 24 hours and again washed with double distilled water and dried under sun light. The dried drupes were pulverized and the pulverized material was screened for various particle sizes like 0.430, 0.600 and 0.800 mm.

Adsorbate: Chromium solution

AR grade potassium dichromate solution was used to prepare Cr(VI) solution . A stock solution of 1000 mg /l of Cr(VI) was prepared by dissolving 2.830 g of dried potassium dichromate in double distilled water and made up to 1000ml.

INTRODUCTION

Heavy metals can be found in industrial wastewater/effluents from many sources and are deemed undesirable by many researchers / environmentalists. It ranks 21st in abundance among all elements with an average concentration of 100 ppm (Manonmani 2002) and enters into the environment through natural and anthropogenic sources. It is also used in metal plating, tanneries and oil drillings. Most of the chromium is present in wastewaters, especially Cr(VI), is the result of emissions from industries such as electroplating, metal finishing, magnetic tape manufacturing, pigment production, fungicides, paint and primer pigments manufacturing. The concentration of Cr(VI) found in the typical wastewater (such as electroplating or leather tanning wastewater), ranges of between 50 to 1000 mg/lutants defined by

United States Environmental protection agency (EPA 2003u). Chromium exists in nature mainly in two stable oxidation states +3 and + 6. In +3 state it acts as bio element, while in +6 state it causes mutagenicity. Therefore, the speciation of chromium in contaminated environments becomes critical for understanding its fate and exposure.

Batch mode study

Effects of pH on Chromium (VI) adsorption

The effects of pH on adsorption of Cr(VI) ion was carried out using 100 mg of Date nuts dust in 50 ml of solution of 10 mg/L Cr(VI) concentration. The pH of the solutions was adjusted to different pH values ranging from 2.0 to 10.0 and was equilibrated to 120 min. The equilibrated solutions were tested from Cr(VI) concentrations spectrophotometrically (Stewart 1975 & APHA 2005). The percentage of adsorption decreased with increase in pH. The maximum of 95.60% at pH 2.0 later decreased the percentage of adsorption up to 7.0 pH later 7-10 pH adsorption is almost constant. The adsorption of metal cations depends on the nature of metal ions, adsorbent surface and species of the metals

The high adsorption capacity of Cr(VI) in the lower pH range may be due to protonation of adsorbent surface which would favour the uptake of anionic forms HCrO_4^- and CrO_4^{2-} . Numerous studies consistently have demonstrated that pH is a dominant parameter in solutions, controlling adsorption and Cr(VI) adsorption (Singh et al, 1992) decreases dramatically as solution pH increases. Agrwal et al, 1989 also reported similar results. Studies shows the variation of percentage reduction of Cr(VI) as a function of solution pH. Also suggest that lower pH 2.0 appears to be the most favorable range for adsorption of Cr(VI), showing peak adsorption at 2.0. It can also observed that adsorption reduces sharply with increase in pH from 2.0 - 7.0 and thereafter no appreciable reduction is observed beyond pH 7.0 Gupta et , al, (1988) have reported

Table - 01

Adsorbent dose : 100 mg / 50 ml [Cr (VI)] : 10 mg / lit Agitation
 time : 120 min Particle size : 0.430 mm

PH	% Adsorption
2	95.60
3	88.22
4	79.66
5	65.88
6	34.46
7	14.18
8	14.18
9	14.18

Equilibrium time and initial metal ion concentration on the Cr (VI) Adsorption

To investigate the optimum equilibrium time, batch mode experiments were carried out with 50 ml of desired Cr (VI) solution (10 to 40 mg / lit) adjusted to pH 2.0 and 100 mg of the adsorbent. After equilibrating the solutions for different periods, solutions are centrifuged and centrifugates were analyzed and the percent adsorption in each case was determined (APHA 1995). The results are shown in Table - 2. From that, it is evident that for maximum adsorption, the solutions should be equilibrated for 150 min. At this equilibrium time, the amounts adsorbed were 4.77, 8.65, 11.61 and 13.42 mg / gm for Cr (VI) concentrations of 10, 20, 30 and 40 mg / lit respectively. The increase in initial Cr (VI) concentration decreased the percent adsorption and increased the amount of metal uptake per unit mass of the adsorbent (mg / gm). The equilibrium time was independent of initial Cr (VI) concentration. The percent adsorption vs time curve (Fig - 01) was smooth and continuous leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. Similar results have been reported in the literature (Kadirvelu *et al.*, 2003).

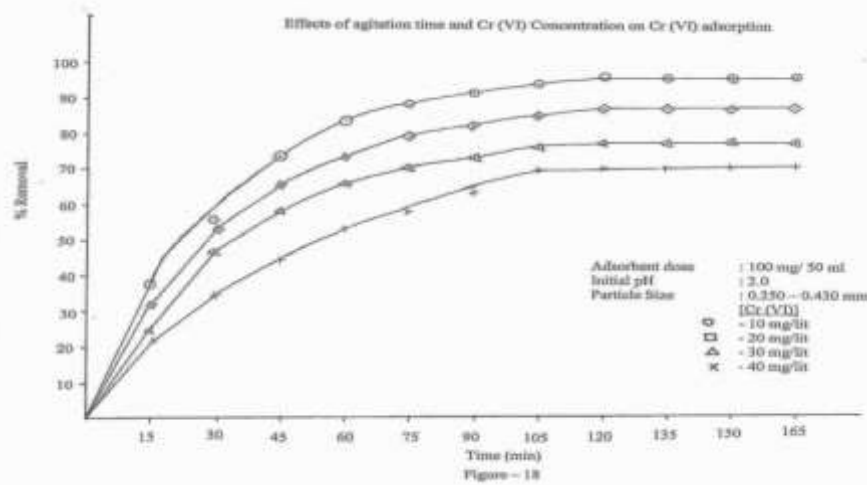


Fig. 01

Effects of Adsorbent dosage on the Cr (VI) Adsorption

The effects of adsorbent dosage on the chromium adsorption was studied by varying the amounts of adsorbent from 20 to 150 mg, the adsorbents were added to 50 ml of Cr (VI) solution of 10 mg / lit concentration, adjusted pH 2.0 and equilibrated for 120 min. After the equilibrium time, the solutions were centrifuged and centrifugates were analyzed for the amount of Cr (VI) and the percent adsorption was estimated (APHA 1995). The results are shows that, adsorption increased with increase in adsorbent dosage and the data is recorded in Table - 3 and suggest that, complete removal was possible with the *Datesnut power* dosage of 150 mg. The increase in percent adsorption with the increase in dosage is due to the availability of more surface area of the adsorbent. Similar results reported in the literature (Prabhavati Nagarajan *et al.*, 2005 and Prasanna Kumar *et al.*, 2006).

Table - 2

Effects of Adsorbent Dosage on Chromium (VI) Adsorption

[Cr (VI)] : 10 mg / lit Agitation time : 120 min
Particle size : 0.430 mm. Initial pH : 2.0

Adsorbent dosage (mg / 50 ml)	% Removal	Equilibrium concentration Ce (mg / lit)	Amount adsorbed (mg / gm)
20	35.87	6.41	8.98
40	59.65	4.03	7.46
60	73.41	2.66	6.12
80	84.88	1.51	5.31
100	95.72	0.43	4.79
150	100.00	0.00	4.17

Effects of agitation time and particle size on Cr (VI) adsorption

To study the effects of particle size, adsorbent particle of sizes 0.250 - 0.430, 0.430 - 0.60 and 0.600 - 0.800 mm were selected. In each study, 100 mg of adsorbent in 50 ml of 10 mg / lit of Cr (VI) solution was adjusted pH 2.0 and equilibrated. After equilibrium time, the adsorbent was separated and the supernatant solution was analyzed for Cr (VI) concentration (APHA 1995). The results (Fig - 2) indicate that increase in particle size decreased the percent removal of Cr (VI). The amount adsorbed for particle sizes 0.250 - 0.430, 0.430 - 0.600 and 0.600 - 0.800 mm are 4.77, 4.23 and 3.45 mg / gm respectively. At a fixed adsorbent dosage, the decrease in particle size increased the metal uptake and decreased the equilibrium time, Kannan *et al.*, 2003 reported. The shorter equilibrium time for smaller particles may be due to the dominance of intraparticle diffusion. This has been generally found in adsorption studies. The increase in the uptake by smaller particles is due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent. Similar type of results has been reported in the literature (Suwannee Junyapoon *et al.*, 2006 and Venkateswarulu *et al.*, 2008).

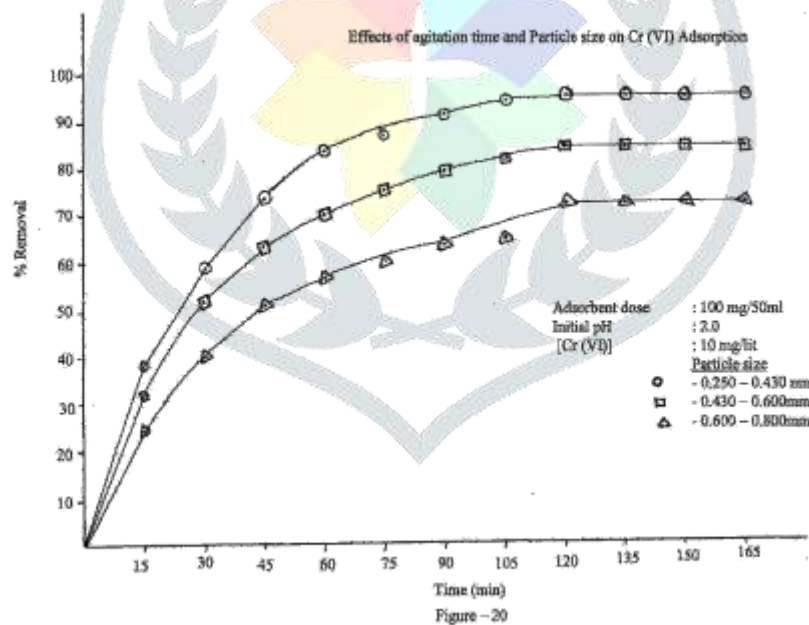


Fig-2

ADSORPTION KINETICS

Effects of Cr (VI) Concentration on Lagergren rate Constant

The kinetics of Cr (VI) adsorption followed the first order rate equation given by Lagergren *et al.*, 1898.

Effects of Particle Size on Lagergren Rate Constant

The effects of particle size on the rate of adsorption is shown and the rate constant K_{ad} values calculated from slopes of linear plots are given in Table - 05.

Table - 04
Effects of Particle Size on Lagergren Rate Constant

Adsorbent dose : 100 mg / 50 ml

Initial pH : 2.0

[Cr (VI)] : 10 mg / lit

Particle size (mm)	Rate Constant K_{ad} (min^{-1})
0.250 - 0.430	3.37×10^{-2}
0.430 - 0.600	3.02×10^{-2}
0.600 - 0.800	2.67×10^{-2}

For the adsorption of Cr (VI), increase in particle size from 0.250 - 0.430 mm to 0.600 - 0.800 mm decreased the rate of adsorption from 3.37×10^{-2} to 2.67×10^{-2} . The higher rate of metal uptake by smaller particles is due to greater accessibility to pores and greater surface area for bulk adsorption per unit weight of the adsorbent. Weber and Morris (1963) have stated that the breaking up of larger particles to form smaller ones and opens tiny sealed channels, those become available for adsorption and therefore the rate of uptake by smaller particles is higher than that by larger particles. Similar results reported in the literature (Singh *et al.*, 2004).

Desorption studies

The desorption studies of Cr (VI) was tried with various sodium hydroxide concentrations and the results are shown in Fig - 2. Maximum desorption of 81.33 percent was possible with 0.014M sodium hydroxide. There is no further increase in the percent desorption with increase in the concentration of sodium hydroxide. This is due to the fact that at alkaline pH, the surface of the adsorbent is deprotonated and hence the alkaline surface of the adsorbent leached out the negatively charged HCrO_4^{-1} , CrO_4^{-2} species. Desorption of Cr (VI) by alkaline solution was reported by many authors. Desorption by alkaline solution shows that the mechanism of adsorption involved an ion - exchange phenomenon. A similar result was reported by Selvaraj *et al.*, 1998.

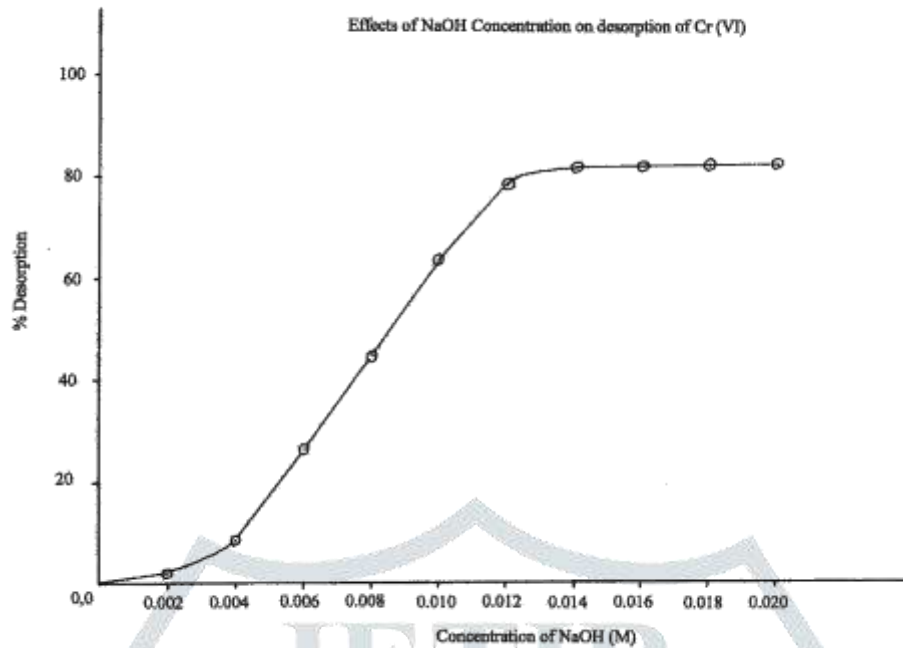


Figure - 25

Fig - 04

Removal of Cr (VI) from Chromium Plating Wastewater

Since the pH of the electroplating wastewater was acidic (pH - 1.64), it was taken for the study with the correction of its pH as 2.0. Fig - 05 shows the effects of adsorbent dosage on the removal of Cr (VI) from industrial electro plating wastewater. The results reveal that increase in adsorbent dosage increased the percent removal and quantitative removal of 85.33 % was achieved by 1000 mg of adsorbent for 50 ml of wastewater containing Cr (VI) concentration of 26.40 mg / lit. Similar results reported in the literature, Selvaraj *et al.*, 1998.

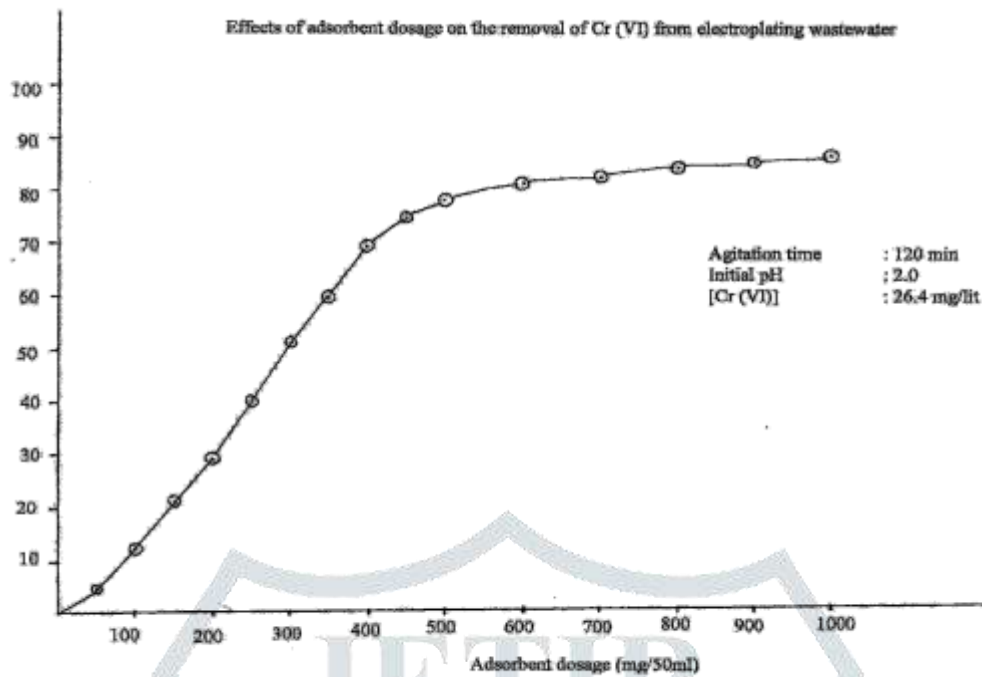


Fig - 05

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