Reduction of Cr (VI) in Electroplating Wastewater and Investigation on the Sorptive Removal by WBAP

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ABSTRACT: Chromium (VI) that exists in many industrial wastewaters is considered highly toxic. The aim of the present investigation was to study the reduction of Cr (VI) to Cr (III) and then removing it with the help of Weathered Basalt Andesite Products (WBAP). Reduction of the Cr (VI) to Cr (III) by Hydrazinium Sulfate (HS) was investigated. The influence of hydronium ion concentration, contact time, HS dosage, and temperature has been tested in batch runs. The process was found to be acid, temperature and concentration dependent. The suitability of WBAP as a potential sorbent was assessed for the removal of Cr (III) following batch mode of operation. The effect of various parameters such as hydronium ion concentration, shaking time, sorbent dose, initial metal ion concentration, and temperature on the removal of Cr (III) from aqueous solution was studied. Thermodynamic parameters ($\Delta H°$, $\Delta S°$, and $\Delta G°$) for the sorption process were evaluated. Analysis of sorption results obtained showed that the sorption pattern followed the Freundlich, Langmuir, and Dubinin-Kaganer-Radushkevich isotherms. The process follows Pseudo second order rate and surface diffusion is identified as the predominating mechanism. The sorption process was shown to be reversible by the recovery of sorbed Cr (III) upon extraction with 0.5 M HNO_3. The sorbent before and after sorption, was characterized by FTIR, X-ray diffraction, SEM, TEM, and TGA methods. An increase in crystallanity after sorption of chromium was observed. An industrial effluent was successfully treated with the same sorbent.

INTRODUCTION

Chromium has extensive use in industrial applications such as metal finishing, leather tanning, pigment products, textiles, magnetic tapes, wood preservation, corrosion control agents in cooling waters etc. (Kirk *et al*., 1994). In nature, chromium exists in numerous oxidation states between –2 to +6, but only Cr (III) and Cr (VI) are stable. Cr (VI) is highly mobile and toxic, and also the form most widely present in industrial wastewaters (Cielslak-Golonka, 1995). Through refuse wastewater, chromium enters especially into fresh-water or soil and thereby into plant, animals, and human beings.

Chromium is non biodegradable and toxic beyond a given concentration. Chromium threshold concentration on inhibitory effect on heterotrophic organisms is 10 mg/L for Cr (III) and 1 mg/L for Cr (VI). All living organisms require varying amount of Cr (III) in micro amount for proper functioning. Cr (VI) is considered by International Agency for Research on Cancer (IARC)

as a powerful carcinogen that modifies the DNA transcription process causing important chromosomic aberration (US department of health and human services, 1991). Chromium (VI) is known to cause various health effects such as skin rashes, upset stomach and ulcers, respiratory problems, weakened immune system, kidney and liver damage, alteration of genetic material, lung cancer, and also death (HDR Engineering Inc., 2001). Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal. In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation. Maximum contaminant level for chromium set by EPA drinking water standard is 0.1 mg/L (US EPA, 2003). World Health Organization recommended maximum allowable concentration of 0.05 mg/L in drinking water for Cr^{+6}. According to the Indian standard institution, the desirable limit for Cr as

Cr^{+6} in drinking water is 0.05 mg/L. As per Indian standard institution, the tolerance limit for discharge of chromium containing wastewater in inland surface water, public sewers, and marine/coastal areas is 2.0 mg/L (Indian Standards, 1993).

As per studies carried out, Cr (VI) is 500 times more toxic to Cr (III) (Kowalski, 1994). As a consequence of the dramatic difference in the physical and chemical properties of two chromium types and benign character of Cr (III), the reduction of Cr (VI) to Cr (III) alone may be considered as a satisfactory solution. Reduction to Cr (III) is advantageous as it makes the removal and recovery by the natural sorbents. The reducing agents commonly used for hexavalent chromium are sodium sulfite and ferrous sulfate (Patterson, 1997; Eckenfelder, 1989). A number of iron based reductants such as waste shot blast fines (Smith *et al.*, 2006), iron sulfide (Erdem *et al.*, 2001), scrap iron (Gheju *et al.*, 2006), and siderite (Erdem *et al.*, 2004). Wang *et al.* (2004) used sucrose and starch for the reduction. Guha *et al.* (2005) utilized zero valent iron in conjunction with sulfate reducing bacteria for the conversion of Cr (VI) to Cr (III). Ekenberg *et al.* (2005) studied the probability of Cr (VI) reduction by anaerobic biological treatment in biofilm process. Taylor *et al.* (2000) and Parthasaraty *et al.* (2003) investigated clay minerals for the reduction of hexavalent chromium.

Aware of the importance of Integrated Waste Management, the authors of this study are involved in research concerning the removal and recovery of heavy metals from the wastewater (shah *et al.*, 1987, 1990, 2003, 2004, and 2006; Singh, 2007). We strongly believe that finding cost effective environmentally friendly methods for the reduction of Cr (VI) from industrial wastewater requires further investigation. All of the above mentioned research for Cr (VI) introduces other ions, thereby increasing the dissolved solids and making the sorption process more complicated which is proven economical process for the removal and recovery of metal ions in the developing countries. Therefore, the reduction of Cr (VI) by cheap and environment friendly "Hydrazinium Sulfate" was studied. For this purpose, batch experiments were conducted to study the parameters such as hydronium ion concentration, initial Cr (VI) concentration, HS dosage, equilibrium time, and temperature.

Reduction of Cr (VI) to Cr (III) is not the ultimate solution, as Cr (III) can be oxidized to the more mutagenic Cr (VI) by MnO_2 in the environment or by some bacteria in soil under proper conditions (Han *et al.*, 2006). So WBAP, a simple, effective, and economical sorbent was utilized for removal of Cr (III) from the wastewater.

MATERIALS AND METHODS

WBAP, gray in color, was obtained from weathered Basalt deposit in Kutch region of Gujarat (India). This material was first treated with H_2O_2 at room temperature for 24 hour to oxidize the adhering organic matter and washed with demineralized water. Preliminary sorption studies revealed that heating the sorbent at 100°C retards the sorption characteristics; therefore WBAP was dried in open atmosphere and then stored in a polypropylene container in a desiccator. No other physical or chemical treatments used prior to sorption experiment.

Demineralized water with conductivity 1.0 µS/cm was used after distillation. The chemicals used in the investigation were supplied by Rankem as analytical grade reagents. Synthetic stock solution (1000 ppm) of Cr (VI) were prepared by using potassium dichromate dried at 378 K for 24 hours in demineralized water. 0.25 M solution of Hydrazinium Sulfate (HS) was prepared by dissolving $NH_2NH_2.H_2SO_4$ (98.5%) in 1 L demineralized water. Solutions with different Cr (III) concentrations were prepared from reagent grade nitrate salt in demineralized water. Their pH values were adjusted to the predetermined values by adding small quantities of concentrated HNO_3 or NaOH solution and confirmed by pH measurements.

The Cr bearing wastewater samples were collected from electroplating unit situated at Valsad, M/s. Excel Shine Private limited. It has four major sections: Electro less Nickel Plating Section; Copper Plating Section; Chrome Plating Section; Other pre-treating sections. The highest Cr concentration was found to be 90 mg/L and pH 1.0–3.0.

The pH of all solutions was measured on Systronics (instrument model 361) pH meter. The concentration of metal ion was analyzed using Hach DR/2500 spectrophotometer after 1:10 dilution (APHA, 1992). The IR spectra of the samples were recorded on Thermo-Nicolet Nexus FT-IR spectrometer. SEM images were acquired by using a LEO 435 VP scanning electron microscope (LEO Electron Microscopy Ltd., Cambridge, England) operating at 15 kV. Philips EM-400 transmission electron microscope (Einhoven, The Netherlands) with a maximum accelerating voltage of 120 kV was employed to obtain the high resolution images and SAED patterns. X-ray diffraction patterns of the sample were recorded on a Bruker AXS D8 Advance diffractometer employing

Cu-K$_\alpha$ (λ = 1.54060 Å) radiations and Ni filter at 40 kV to record a pattern in the 2θ range of 5–1200. The thermal analysis of the samples were performed using a Perkin Elmer Pyris Diamond TG/TGA instrument at a fixed heating rate of 10°C/min over a temperature range of 26–1000°C using alumina powder (10 mg) as reference. The degradation runs were taken under oxidizing atmosphere (flowing dry air) at a flow rate of 200 ml/minute. The density of the sorbent was determined by specific gravity bottles. The sorption experiment were studied by batch technique using laboratory scale Stirred Tank Reactors (STR), equipped with six glass vessel of 1 liter and twin blade impeller driven by a variable speed motor.

Pre weighed sample of the sorbent and a measured volume of Cr (III) solution were taken in 1 L glass vessel of STR and the mixture was agitated for a constant time. The impeller speed was set at 100 rpm. At increasing time intervals aliquots of sample were withdrawn by plastic syringe, filtered, and after dilution of 1:10, analyzed with spectrophotometer.

CHARACTERIZATION OF WBAP

Chemical constituents of the WBAP as determined by using standard methods of chemical analysis (Corbin *et al.*, 1987; Vogel, 1989) are SiO$_2$, 55.09%; Al$_2$O$_3$, 10.48%; Fe$_2$O$_3$, 13.32%; CaO, 4.80%; Na$_2$O, 2.46%; K$_2$O, 0.19%; Loss on ignition, 16.88% by weight. Two gram sample of WBAP was stirred with demineralized water (100 ml, pH 6.59) for 24 h in an air tight stoppered conical flask. An enhancement in pH 9.66 was noticed. It is quite stable in water, salt solution, acids and bases.

The X-ray diffraction pattern (Figure 1) of the sorbent provided d spacing values which reflect the presence of Illite (4.447, 3.3466, 2.5704, 9.698, 2.455, 1.4928 Å), Montmorillonite (14.859, 4.447, 3.06, 1.4928 Å), Paragonite/Mica (2.515, 3.1915, 9.6985 Å), Tetrakalsilite (3.0697, 2.8969, 4.447 Å), Faujasite (14.859, 3.1915, 2.51 Å), Kaolinite (7.23302, 3.52494 Å), and Geothite (2.4555 Å) indicating a high chemical stability (JCPDS, 1971). After sorption, the change in diffraction pattern is clearly noticeable and new diffraction pattern is observed in the region of 10 to 60 Theta Scale. The original WBAP has a d-spacing of 14.859 Å which increased to 15.112 because of expansion in the interlayer spacing.

The SEM photograph indicates WBAP to be highly porous, which is in agreement with the porosity value. Based on the analysis of images taken by SEM before (Figure 2) and after sorption process (Figure 3), two types of sorption is observed. A horizontal layer type

of sorption is observed on the smooth surface, whereas accumulation of contaminants on the edges of the rough surfaces as well as in the macropores is observed. The images also indicate towards the possibility of multilayer sorption. After sorption, the WBAP particles seem to be more fluffy and porous. This may be due to the change in surface charge of the particle as a result of introduction of Cr (III) ions.
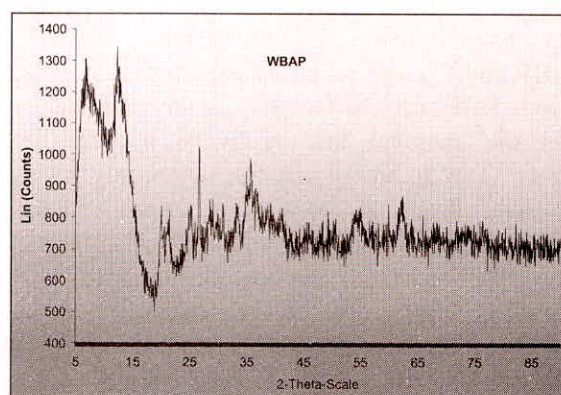
(a)
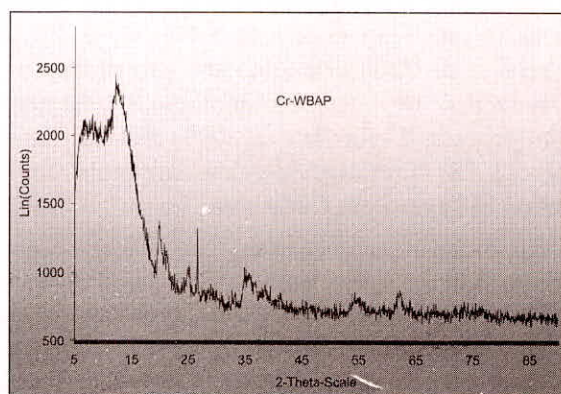
(b)

Fig. 1: PXRD pattern of WBAP and Cr sorbed WBAP

TEM image of WBAP before and after sorption at 2700 magnification indicates the increase in electron density. Comparing the diffraction spots observed in the SAED pattern obtained for the virgin and sorbed WBAP, increase in diffraction spots is also observed. The number of diffraction spots Obtained for the rough surface is much more than that for smooth surfaces.

The DTA-TGA curves not shown here indicate first loss of weight (6.7%) between 25 and 125°C. These transformations are due to the removal of adsorbed water between the silicate sheets. The DTA curve shows the process to be endothermic. A small endothermic peak between 225–290°C is observed, which corresponds to loss of interlayer water molecules (1.04%). The third loss of weight (7%)

takes place between 370–500°C, and is completed at 750°C due to loss of structural water i.e. the hydroxyl groups from the WBAP. This step is also endothermic in nature. Further heating, does not show any change. The kinetic parameters for these decomposition steps were evaluated by Coats and Redfern method (Coats and Redfern, 1964). The value of energy of activation (*E*) and pre-exponential factor (*A*) was calculated from the slope and intercept of the best fit curve (Figure 4). Following equations were employed to calculate the entropy of activation (Eqn. 1), the enthalpy of activation (Eqn. 2), and free energy of activation (Eqn. 3):

$$S^* = 2.303 \ [\log (Ah/KT)] \ R \qquad \qquad ... (1)$$

$$H^* = E^* - RT \qquad \qquad ... (2)$$

$$G^* = H - TS \qquad \qquad ... (3)$$

where *h* and *K* are Planck's and Boltzmann constants, respectively. The data are given in Table 1. The negative value of S^* and positive value of G^* indicates that the decomposition reaction is slow.

(a)   (b)
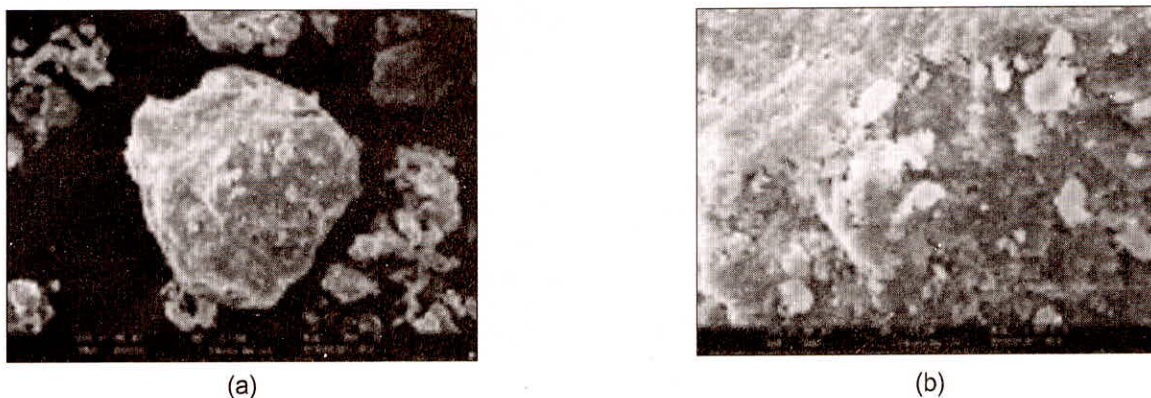
Fig. 2: SEM micrograph of WBAP: (a) 700 X and (b) 2 000 X magnification with smooth and rough surfaces

(a)   (b)
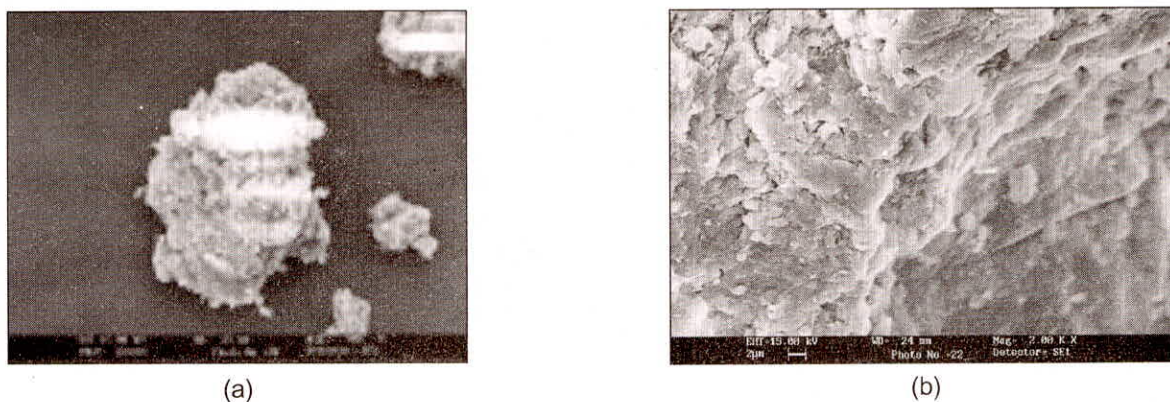
Fig. 3: SEM micrograph of Cr sorbed WBAP: (a) 700 X and (b) 2 000 X magnification
showing accumulation of contaminant

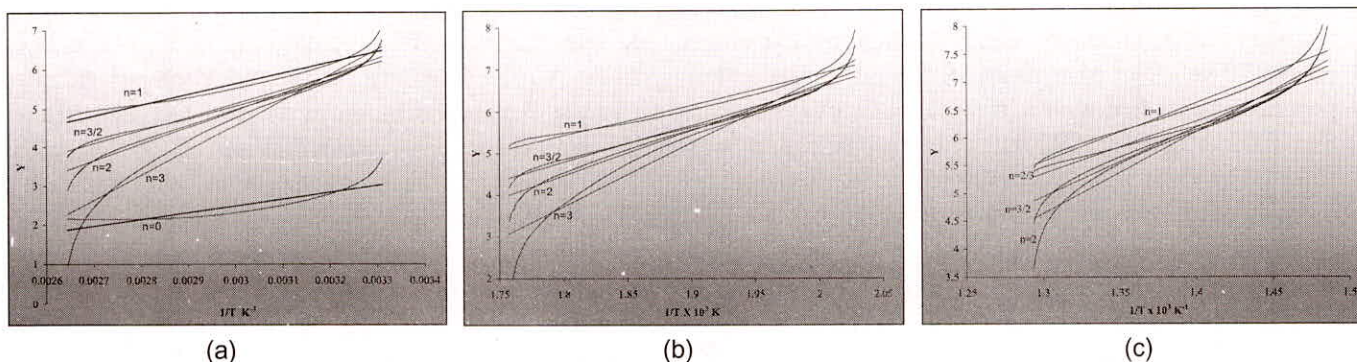(a)   (b)   (c)

Fig. 4: Plots of Coats and Redfern Method (a) Step I, (b) Step II, (c) Step III

Table 1: Kinetic Data of the Thermal Decomposition of the Sorbent

Step of Degradation	Parameters	Result
Step 1 (30–110°C)	Order of decomposition	2
	E^* (kJ/mol)	64.2636
	A (S^{-1})	7.0736×10^8
	S^* (J/K/mol)	−76.507
	H^* (kJ/mol)	61.469
	G^* (kJ/mol)	87.1818
Step 2 (210–290°C)	Order of decomposition	3/2
	E^* (kJ/mol)	121.145
	A (S^{-1})	3.212×10^{10}
	S^* (j/K/mol)	−48.652
	H^* (kJ/mol)	116.689
	G^* (kJ/mol)	142.761
Step 3 (370–530°C)	Order of decomposition	3/2
	E^* (kJ/mol)	142.557
	A (S^{-1})	2.697×10^8
	S^* (j/K/mol)	−33.669
	H^* (kJ/mol)	136.382
	G^* (kJ/mol)	161.387

The surface area was found to be 618.25 m²/g. The point of zero charge was determined by potentiometric titration method (Schwarz *et al.*, 1984). The characteristics of the sorbent are pHzpc 2.4, density 1.16 g/cm³, porosity 0.4378 fraction, and void ratio 0.779.

REDUCTION OF HEXAVALENT CHROMIUM

Effect of Hydronium ion Concentration and Equilibrium Time

Hydronium ions play an important role in the reaction mechanism; therefore the effect was investigated in the range of 0.5 to 3.0 pH. The study was limited to pH 3.0 considering the pH of electroplating industry wastewater pH. Also during the preliminary experiments it was observed that precipitation of Cr (III) as Cr(OH)₃ takes place above that which is not appropriate for the recovery of the metal by using sorption/ion exchange process. The effect of hydronium ion on the reduction process was studied with 520 mg/L of Cr (VI) solution and 0.02 M HS at 295 K. This concentration was selected as it was the maximum concentration for the electroplating wastewater under study.

Figure 5 shows Cr (VI) reduction percentage as a function of pH and contact duration. From figure, it appears that the Cr (VI) reduction was very fast up to pH 1.5, when hexavalent chromium was completely

reduced to trivalent form (98.98%) within 15 minutes of reaction time. The conversion is significantly slower for pH 2.0 and above, for which 180 minutes are required to achieve 98% conversion. This higher rate of reduction at low pH can be explained by considering the equation,
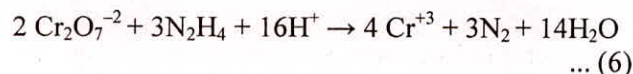
Reduction

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2\ Cr^{+3} + 7H_2O \qquad ...(4)$$

Oxidation

$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e^- \qquad ...(5)$$

Over all Reaction

$$2\ Cr_2O_7^{-2} + 3N_2H_4 + 16H^+ \rightarrow 4\ Cr^{+3} + 3N_2 + 14H_2O \qquad ...(6)$$

The increase in reduction at low pH is due to the stress imposed due to higher H⁺ ions. Also an increase in pH value was observed (embedded figure in Figure 5), this may be due to the consumption of hydronium ions during the reduction process.
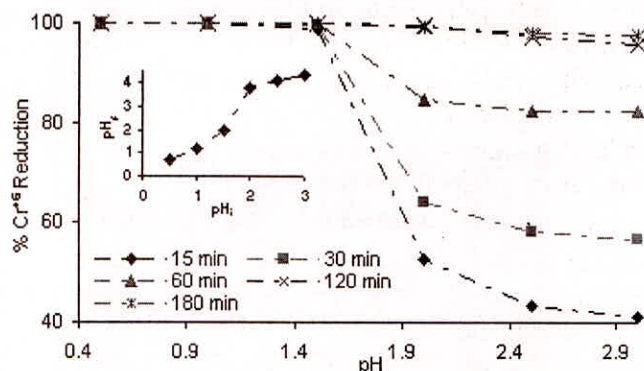

Fig. 5: Effect of initial pH on the reduction of Cr (VI). The embedded figure represents the change in final pH after 420 min of equilibrium

Effect of HS Dosage

The effect the HS dosage on reduction of Cr (VI) is shown in Figure 6(a) & (b). The effect of the molar ratio of Cr (VI) to HS at pH 2.20 and temperature 295 K was observed. With increase in HS dosage from 1:1 to 1:6 (Cr: HS) molar ratio, the reduction percentage of Cr (VI) increases. The molar ratio of 1:1 is insufficient to complete to complete reduction of Cr (VI) within 120 minutes, which is in accordance with equation 3. With molar ratio 1:2, it was possible to achieve 98% reduction of Cr⁺⁶ and 99.9% reduction of Cr (VI) was achieved with molar ration 1:3 and above within 30 minutes of reaction time. An increase in final pH was observed with the reduction process.
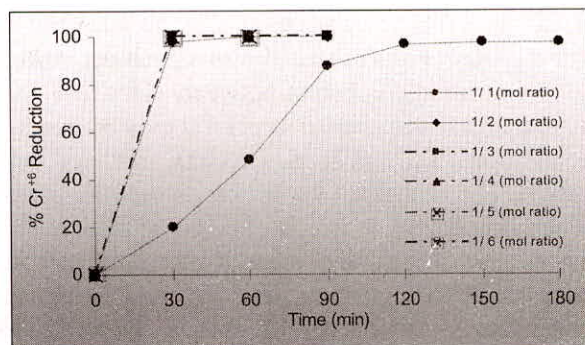
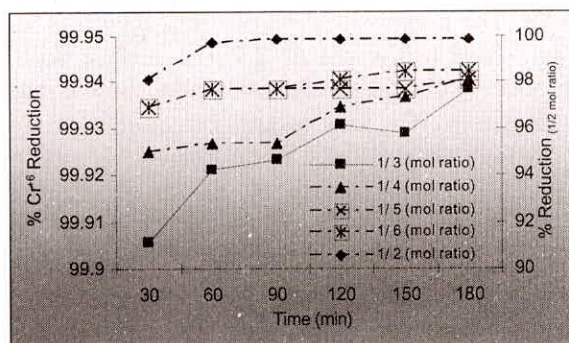**Fig. 6(a):** Effect of molar ratio of Cr (VI)/HS on the reduction of Cr^{+6}

Fig. 6(b): Effect of reaction time on the reduction of Cr (VI)

Effect of Temperature

The effect of temperature on the reduction of hexavalent chromium was investigated at 278, 295, and 315 K for Cr^{+6}/HS molar ratio ½ and initial pH 2.3. The results presented in Figure 7 indicate higher temperature favors the reduction of Cr (VI). The reduction was found to be completed in about 30 minutes at temperature 315 K and above. With the temperature 295 K, the reduction of 98.6% was achieved in 120 minutes. Each rise of 20 K temperature shortens the reaction time required about 90 minutes for the complete reduction. It can be concluded that the reduction process of Cr (VI) by HS is endothermic.
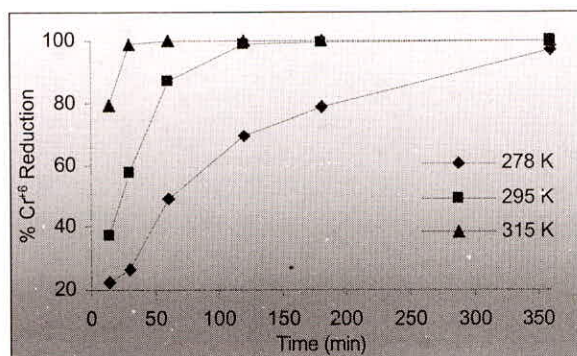
Fig. 7: Effect of temperature on the reduction of Cr (VI)

Study of Reaction Order with Respect to Cr (VI)

The first order reaction is,

$$\log [A_e - A_t] = \log A_e - (K_f \cdot t)/2.303 \quad \text{... (7)}$$

where, Where, [A_t] is the concentration of Cr (VI) reduced to Cr (III) at time t (mg/L), K_f is the rate constant of first order model (min^{-1}), and t is the time (min). A_e is Cr (III) concentration at equilibrium.

Plotting log [A_e] – log [A_t] against time creates a straight line with slope $-K_f$. The plots for the reduction of Cr (VI) were not linear indicating that the reaction order for conversion of Cr (VI) to Cr (III) is not of first order.

The second order rate model can be represented as,

$$t/[A_t] = 1/Ks \cdot [A_e]^2 + t/[A_e] \quad \text{... (8)}$$

where K_s is the rate constant for the second order model (M^{-1}min^{-1}). The plot of $t/[A_t]$ versus time should give a straight line if the reaction is of second order in nature.

The plots for Cr (VI) reduction were found to be linear (Figure 8a). The regression coefficients for the second order model were fond to be closer to unity (R^2 = 0.9891–0.9999). The obtained value of rate constant (K_s) was found to be 0.99 M^{-1}min^{-1}, 4.78 M^{-1}min^{-1}, and 66.45 M^{-1}min^{-1} for reduction at 278 K, 295 K, and 315 K.

The activation energy for the reduction process was determined by using Arrhenius equation,

$$\ln K = -E_a/RT + \ln A \quad \text{... (9)}$$

where, E_a is activation energy, R is the gas constant (8.314 J/mol.K), T is abloute temperature in Kelvin, and A is frequency factor,

$$A = p \cdot Z \quad \text{... (10)}$$

Where, Z is the collision rate and p is steric factor. Z turns out to be only weakly dependent on temperature. Thus the frequency factor is a constant, specific for each reaction. The plot of ln K versus 1/T yields a straight line with slope equals to $-E_a/R$. The activation energy of Cr (VI) reduction was calculated from Figure 8b and comes out to be 83.93 kJ/mol.

Potential Industrial Application

The wastewater from the electroplating industry with initial pH 1.44, and Cr (VI) concentration 180 mg/L was treated with HS in the 1:2.5, 1:5, and 1:10 molar ratio. The results of reduction are shown in Figure 9. The reduction was almost completed in 15–30 minutes of contact duration.
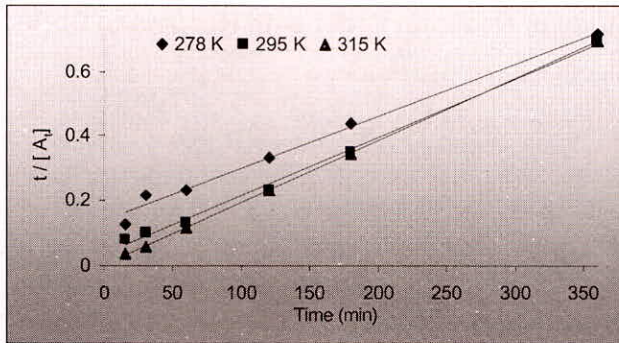
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Effect of Shaking Time

Figure 11 shows the variation in removal of Cr (III) with contact time (0–420 min) at pH 2.36, 210 mg/L of Cr (III) solution, stirring rate 100 rpm, temperature 295 K, and sorbent dose 20 g/L. The rate of uptake is quite rapid in the beginning and typically 70% ultimate sorption occurs with in the first 15 minutes of contact duration and concentration of Cr (III) ions becomes asymptotic to time axis after that. Sorption slowed down in later stages due to reduction in the number of vacant surface sites available for sorption and the increase in the repulsive forces between solute molecules of solid and bulk phase. The contact time required for the removal of Cr (III) by *WBAP* is very short, thus implying that this material could be used for the economic removal of Cr (III) from wastewater.
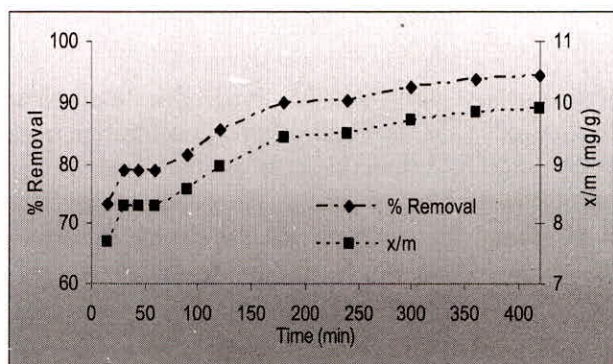

Fig. 11: Effect of shaking time on sorption of Cr^{+3}

Effect of Sorbent Dosage

The results for the sorptive removal of Cr (III) with respect to sorbent dose are shown in Figure 12 over the range 5–40 g/L, at pH 2.36, temperature 295 K, contact time 60 minutes, stirring rate 100 rpm, and initial Cr (III) concentration 220 ppm. The results shown in Figure 9 demonstrate that the rate of sorption of Cr (III) ions increases when mass of WBAP increased from 5–30 g/L and than attains equilibria. Sorption increases from 36.95% to 93.86%; while the increase in the removal efficiency on introducing an additional 5 g/L WBAP was not so significant. The optimum WBAP dosage was 30 g/L for the wastewater under study. It is apparent that the percent removal of Cr (III) increases rapidly with increase in the dose of WBAP due to the greater availability of the sorption sites or surface area.

Effect of Initial Metal Ion Concentration

A given mass of sorbent can sorb only a fixed amount of sorbate. So the initial concentration of sorbate is very important. The effect of initial Cr (III) concentration on sorption was investigated over the concentration range 30–500 mg/L at fixed pH, 2.38; temperature, 298 K; contact time, 60 minute; and sorbent dose, 20 g/L. At lower initial concentration, sufficient sorption sites are available for sorption of the Cr (III). Therefore, the fractional sorption is independent of initial metal ion concentration. However, at higher concentration the number of ions is relatively higher compared to availability of sorption sites. Hence, the percent removal of Cr ions depends on the initial concentration and decreases with increase in initial concentration as shown in the figure. However, the amount of Cr (III) ion sorbed per unit sorbent mass increased with increase in initial concentration due to the difference in the sorbate concentration in bulk and solid phase.
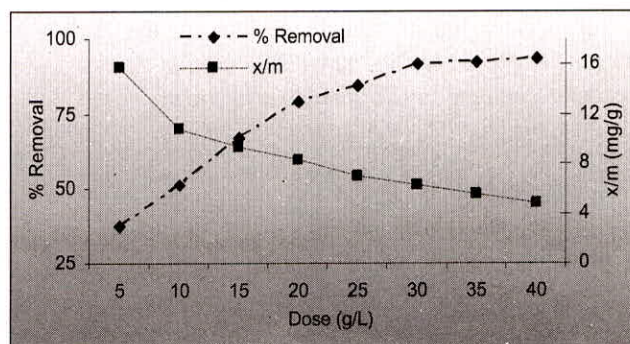
Fig. 12: Effect of sorbent dose on sorption of Cr^{+3}

Effect of Temperature

The effect of temperature on the sorption of Cr (III) by *WBAP* was investigated at concentration, $C_0 = (100$ ppm, 200 ppm, and 300 ppm); temperature, $T = (276, 295, 313,$ and $333)$ K; pH 2.38; stirring rate, 100 rpm; contact duration, 60 minutes; and sorbent dose, 20 g/L is shown in Figure 13. The thermodynamic parameters were calculated from the slope and intercept of ln K_d against 1/T (Figure 11) by using the equation,

$$\ln K_d = (\Delta S°/R) - (\Delta H°/RT) \qquad ...(11)$$

where K_d is distribution coefficient, $\Delta H°$, $\Delta S°$, R, and T are the enthalpy, entropy, gas constant, and temperature in Kelvin, respectively. Gibbs free energy $(\Delta G°)$ of specific sorption was calculated from the well known equation,

$$\Delta G° = \Delta H° - T.\Delta S° \qquad ...(12)$$

The values of thermodynamic parameters for the sorption of Cr ions on WBAP are given in Table 2.

The positive value of $\Delta H°$ confirms the endothermic nature of the overall sorption process. The endothermicity of the heat of sorption may be due to

Table 2: Thermodynamic Parameters for the Sorption of Cr^{+3} on WBAP

Concentration of Cr^{+3}	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/K/mol)	$-\Delta G°$ (kJ/mol)			
			276 K	295 K	313 K	333K
100 mg/L	67.9	291.256	12.486	18.020	23.263	29.088
200 mg/L	54.57	236.74	10.770	15.268	19.529	24.264
300 mg/L	34.34	156.52	8.859	11.833	14.651	17.781

the removal of water molecules from the solid/solution interface and from the sorbing cations. This dehydration process of the ions requires energy. This energy of dehydration supersedes exothermicity of the ions getting attach to the surface. The enthalpy change of sorption suggests the possibility of strong bonding between sorbate and sorbent. The Gibbs free energy indicates the sorption process to be spontaneous in nature, more favorable at higher temperature. The positive value of $\Delta S°$ shows the increased randomness at the solid/solution interface during the sorption process. The positive value of $\Delta S°$ also suggests some structural changes in the sorbate and the sorbent.
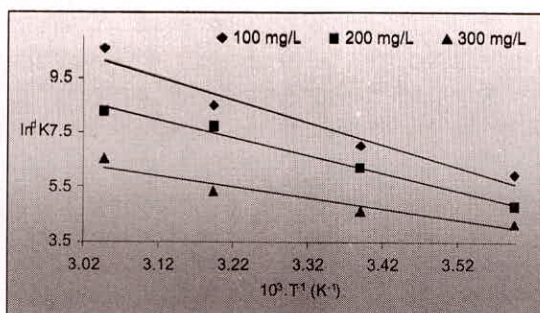

Fig. 13: Effect of temperature on thermodynamic behavior of Cr^{+3} sorption

Modeling of the Sorption Isotherms

To optimize the design of a sorption system for the sorption of sorbates, it is important to establish the most appropriate correlation for the equilibrium curves. To understand the sorption behavior in solution of metal ions by the sorbent '*WBAP*', Freundlich (Freundlich and Hatfield, 1926), Langmuir (Langmuir, 1918), and Dubinin-Kaganer-Radushkevitch (Krishna *et al.*, 2000) models have been used. These models had been widely used by many workers. The obtained experimental data are commonly well fitted with the Langmuir (Eqn. 13), Freundlich (Eqn. 14), and DKR (Eqn.15) models,

$$1/q_e = 1/Q_0 + 1/Q_0.b.C_e \qquad \text{... (13)}$$

where q_e is the amount sorbed (mg/g), C_e is the equilibrium concentration of the sorbate (mg/L), and Q_0 and b are the Langmuir constants related to maximum sorption capacity and energy of sorption, respectively,

$$\log q_e = \log K + 1/n \log C_e \qquad \text{... (14)}$$

where q_e is the amount sorbed (mg/g), C_e is the equilibrium concentration of the sorbate (mg/L), and K and n are Freundlich constants related to sorption capacity and sorption intensity, respectively,

$$\ln q_e = \ln X_m - \beta\varepsilon^2 \qquad \text{... (15)}$$

where q_e is the amount sorbed (mg/g), X_m is DKR monolayer capacity, β is the activity coefficient related to mean sorption energy, and ε is Polanyi potential, which is equal to,

$$\varepsilon = RT \ln(1/C_e) \qquad \text{... (16)}$$

where R is gas constant (J/K/mol), T is temperature (Kelvin), and C_e is the equilibrium concentration of the sorbate (mg/L). When $\ln q_e$ is plotted against ε^2, a straight line is obtained. The slope of the plot gives the value of β and the intercept yields the value of sorption capacity, X_m. The value of β is related to sorption energy, E, via following relationship:

$$E = -1/(-2 \beta)^{1/2} \qquad \text{... (17)}$$

The linearized form of isotherm models for Cr (III) removal by WBAP can be seen in Figure 14. The correlation factors and other parameters for Freundlich, Langmuir, and DKR isotherm are presented in Table 3. The correlation factors confirms good agreement between theoretical models and our experimental results. The correlation coefficients for Freundlich and DKR isotherm are highest. The $1/n << 1$ indicates that sorption capacity is slightly suppressed at lower equilibrium concentration. This isotherm does not predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer sorption on the surface. The influence of sorption isotherm shape to know whether the sorption is favorable or not, has been discussed in terms of a dimensionless constant R_L; referred to as separation factor (30), defined as follows,

$$R_L = 1/(1 + b.C_0) \qquad \text{... (18)}$$

Where b is Langmuir constant (L/mg) and C_0 the initial concentration (mg/L). The value of R_L was found to be less than 1. This indicates a highly favorable sorption.
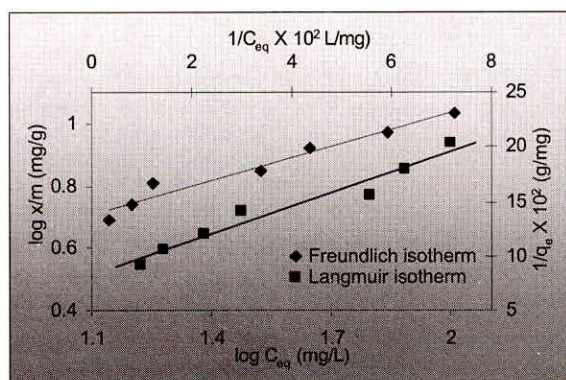
(a)
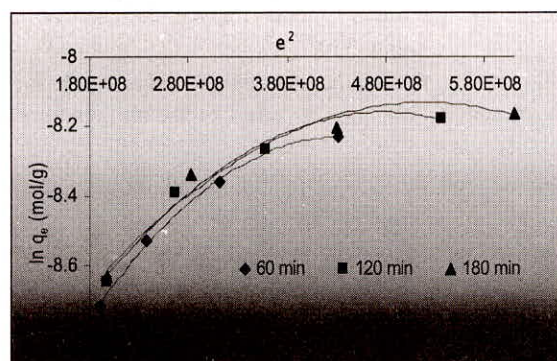
(b)

Fig. 14: (a) Freundlich and Langmuir isotherm and (b) DKR sorption isotherm

The sorption capacity of Indian *WBAP* for Cr (III) at pH 2.36 and 295 K was found to be 12.07 mg/g. The sorption capacity obtained for *WBAP* was found to be comparable to and in some cases better than, the other sorbents and activated carbons as reported by Hasany *et al.*, 2006 for coconut husk (0.949 mg/g); Gode *et al.*, 2007 for b-DAEG-sporopollenin resin (1.23 mg/gm) and CEP-sporopollenin resin (133.33 mg/gm); Han *et al.*, 2006 for Chlorella miniata (14.73 mg/g); Natale *et al.*, 2006 for char of South African coal (0.285 mg/g) and granular activated carbon (2.21 mg/g); Entezari *et al.*, 2005 for tire rubber (0.85 mg/g); Meunier *et al.*, 2003 for cocoa schells (2.52 mg/g); Chakir *et al.*, 2002 for bentonite (4.29 mg/g) and perlite (1.4 mg/g); and Abollino *et al.*, 2002 for Na-montmorillonite (5.13 mg/g).

The numerical value of mean sorption energy E from DKR isotherm in the present system was found to be 12.909 kJ/mol indicating the sorption process to be of ion exchange in nature. The sorption capacity X_m was found to be 5.83 mg/g for Cr (III), which is less than the sorption capacity observed at the Langmuir region. This may be attributed to different assumptions taken into consideration while formulating the isotherms. Moreover, these isotherms were devised to

explain the sorption of gases on solid surfaces and have further been extended to sorption of metal ions from aqueous solution to solid sorbents.

From the regression coefficient values, it was concluded that sorption of Cr (III) ions on WBAP followed Freundlich and DKR isotherm postulates.

Table 3: Langmuir, Freundlich, and DKR Parameters of Sorption Isotherm for Cr (III) on WBAP

Parameters	Value
Langmuir isotherm	
Q_0 (mg/g)	12.067
b (L/mg)	0.05257
R^2	0.9554
R_L	0.0831
Freundlich isotherm	
1/n	0.3643
K	2.028
R^2	0.9657
DKR isotherm	
Xm (mg/g)	5.826
β (mol^2/J^2)	-0.3×10^{-8}
E (kJ/mol)	12.909
R^2	0.9726

Table 4: Kinetic Parameters for Removal of Cr (III) by WBAP (T = 295 K, m = 20 g/l, pH = 2.46, Stirring Rate = 100 rpm)

Pseudo first order model			
C_0 (mg/g)	q_e (mg/g)	$K_f \times 10^{-3}$ (min^{-1})	R^2
100	0.786	9.670	0.9602
200	2.969	7.599	0.9977
300	5.978	4.854	0.9827

Pseudo second order model				
C_0 (mg/g)	q_e (mg/g)	h (mg/g min)	$K_s \times 10^{-3}$ (g/mg min)	R^2
100	5.079	0.6501	25.20	0.9999
200	10.194	0.5726	5.510	0.9998
300	14.514	0.5018	2.382	0.9982

Kinetics and Rate Parameters

Kinetics is another important aspect in evaluatioin of sorption as a unit operation. The sorption of Cr (III) from liquid phase to solid phase is normally assumed to be controlled by physicochemical processes. To quantify the extent of uptake in sorption kinetics, pseudo first order (Eqn. 7) and pseudo second order (Eqn. 8) as cited by Ho and McKay, 1999 were used.

The initial sorption rate, h (mg/g/min), at $t \rightarrow 0$ is defined as,

$$h = K_s \cdot q_e^2 \qquad \qquad ...(19)$$

The best fit values of h, q_e, and K along with correlation coefficients for the pseudo first order and pseudo second order (Figure 15) models are 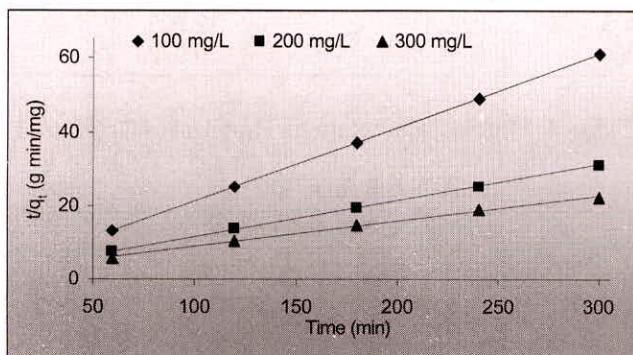shown in Table 4. The calculated correlation coefficients are closer to unity for pseudo second order kinetic model than that for the pseudo first order kinetic model. Therefore, the sorption can be approximated more appropriately by the pseudo second order kinetic model for the sorption of Cr (III) by *WBAP*.
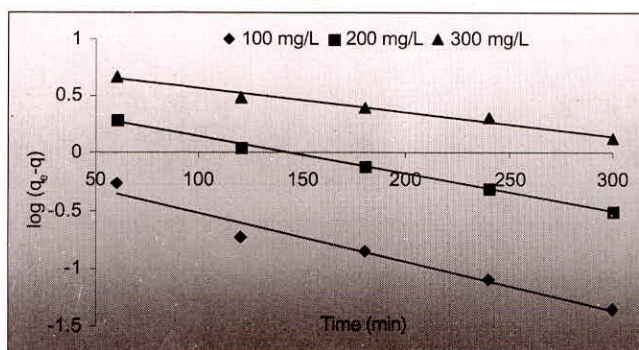
(a)

(b)

Fig. 15: (a) Pseudo-first-order and (b) Pseudo-second-order kinetic plots for removal of Cr^{+3} ions sorption on WBAP

CONCLUSIONS

WBAP is very efficient in removal of Cr (III) from the acidic solutions/wastewater. Very short time of 15 minutes is required for the removal. The presence of other metals does not substantially influence the uptake of Cr by WBAP. The sorption process follows Freundlich sorption isotherm indicating multilayer sorption, which is also evident from the SEM micrographs. The sorption process is endothermic in nature. The uptake of Cr (III) ions takes place by ion exchange. The kinetics of Cr (III) sorption process can be described by pseudo second order rate equation. Additional efforts are planned to invesigate the sorption potential of the sorbent, so that it could utilized for practical applications.

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