

Removal of Hexavalent Chromium by Kendu Fruit Gum Dust

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ABSTRACT: The ability of a low cost adsorbent material, Kendu fruit gum dust (KGD), for removal of hexavalent chromium, Cr(VI), from aqueous solutions of both a synthetic and industrial (effluent) sample is successfully investigated through batch type experiments. The effects of contact time, Cr(VI) concentration, pH, adsorbent amount, and temperature on the extent of Cr(VI) removal are reported. At a lower initial concentration of Cr(VI) and a lower solution pH, the percent removal is found to be increased. A removal efficiency of 100% has been achieved. In the presence of cyanide ion the adsorption efficiency of KGD decreases. Recycling studies suggest that even after the sixth cycle, only ~ 20% loss of efficiency of KGD occurs. The adsorption process follows the Freundlich adsorption isotherm model. Another important feature of the investigation includes the studies on the characteristics and analysis of various constituents present in the newly developed adsorbent material (KGD). From the thermogravimetric analysis curves of the original KGD and Cr(VI) adsorbed KGD, it is observed that the thermal stability of KGD increases due to metal ion adsorption. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1485–1494, 1997

Key words: hexavalent chromium; Kendu fruit gum dust; batch experiments; thermogravimetric analysis

INTRODUCTION

Removal of toxic heavy metal ions from industrial and mining wastewater has received much attention in recent years. Different traditional (precipitation) and advanced technologies have been developed for the removal and recovery of heavy metals from wastewater.¹ However, the precipitation process using conventional precipitants like carbonates, hydroxides, etc., does not always provide a satisfactory removal rate to meet the pollution control limits whereas synthetic ion-ex-

change resins are often quite expensive. Many low cost agricultural by-products can bind heavy metal ions by adsorption, chelation, or the ion-exchange technique. Many low cost agricultural by-products, such as wool,^{2–5} cotton,⁶ onion skins,⁷ and peanut skins,^{8–10} for the adsorption of toxic heavy metal ions have been reported. Starch is a naturally low cost material and many starch-based products have been used for studies on adsorption removal of hexavalent chromium,¹¹ cadmium,¹² and gallium.¹³

Chromium and its compounds are extensively used in many industries. The two predominant forms of chromium, namely Cr(VI) and Cr(III), are found in many industrial wastewaters such as those from textile, leather tanning, electroplating,

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Table I Various Important Constituents of KGD

Constituents	Quantity (mg/L)
Na	40.0
K	185.0
Ca	190.0
Cr	0.5
Zn	19.0
B	150.0
NO ₃ ⁻ (as nitrogen)	4.5
Tannin and lignin	5300.0
F ⁻	0.28

and metal finishing industries.¹⁴ The toxicity of hexavalent chromium from the discharge of various industrial waste is well reported.¹⁵⁻¹⁷ One of the usual methods¹⁸ of removal of Cr(VI) from industrial effluents involves reduction to Cr(III) at low pH using reducing agents like FeSO₄ followed by precipitation of Cr(OH)₃ by increasing the pH. Removal of chromate by electrolytic treatment has been reported by Subramanian et al.¹⁹ The use of various adsorbents, such as activated carbon,²⁰ rice husk carbon,²¹ saw dust,²²⁻²⁴ bituminous coal,²⁵ and fly ash,²⁶ have been documented for the removal of Cr(VI) from aqueous solutions.

Botanically Kendu is known as *Diospyros cordifolia roxb* and it belongs to the family Ebenaceae.²⁷ The Kendu tree is distributed throughout India, Ceylon, and tropical Australia.²⁸ Kendu is a hardy tree that is found growing under diverse edaphic and environmental conditions. The fruit is a round, glabrous, green colored berry. At full maturity the color of the fruit turns yellowish brown. The fruits are bitter due to their high tannin content. A full grown tree on an average yields 100 kg of fruits per annum. The number of seeds per berry is generally four. In rural areas of India it is treated as *Kalpa Vriksha* due to its numerous

Table II Typical Characteristics of KGD

Characteristics	Result
pH	8.0
COD	640,000 mg/L
Elemental analysis (%)	
C	55.86
H	5.24
N	0.45

Table III Characteristics of Industrial Effluent

Characteristics	Result
pH	11.42
Total chromium	520.0 mg/L
Hexavalent chromium	410.0 mg/L
Suspended solids	90.0 mg/L

uses. Its leaves are used as wrappers for tobacco. The wood is used for making small articles of furniture, agricultural implements, matches, and carvings. Kendu has some medicinal value too. Its leaves and fruits are applied externally to boils and wounds. There is a good possibility of deriving gum adhesive from Kendu fruit, which is particularly important because it would be cheap.²⁹

In India most of the Kendu fruits go to waste or are noneconomically utilized. As far as a literature survey is concerned, the chemistry of Kendu fruit has not yet been studied thoroughly.²⁷ Recently we reported²⁹ on certain preliminary studies on basic chemistry and physicochemical properties of gum adhesive extracted from the much neglected Kendu fruit. The present article deals with studies of the removal of hexavalent chromium from industrial effluent as well as a synthetic sample using a low cost adsorbent, Kendu fruit gum dust (KGD).

EXPERIMENTAL

Preparation of Adsorbent (KGD)

For the present investigations Kendu fruits were collected from the village of Manijang in the Cuttack district in the state of Orissa (India) during the month of March 1996. The fruits were thoroughly washed with water, cut into pieces, and ground to a pasty mass in a grinder. The pasty mass was then squeezed through a piece of clean white cloth and the gummy extract thus collected was then overdried at 60 ± 2°C for 24 h. As a result of curing, ~ 70% weight loss of the gummy extract took place with the escape of moisture and volatile matter. The hard cured gum resin was then ground to 100 mesh size (ASTM). The KGD thus obtained was used as an adsorbent material to study the removal efficiency of hexavalent chromium.

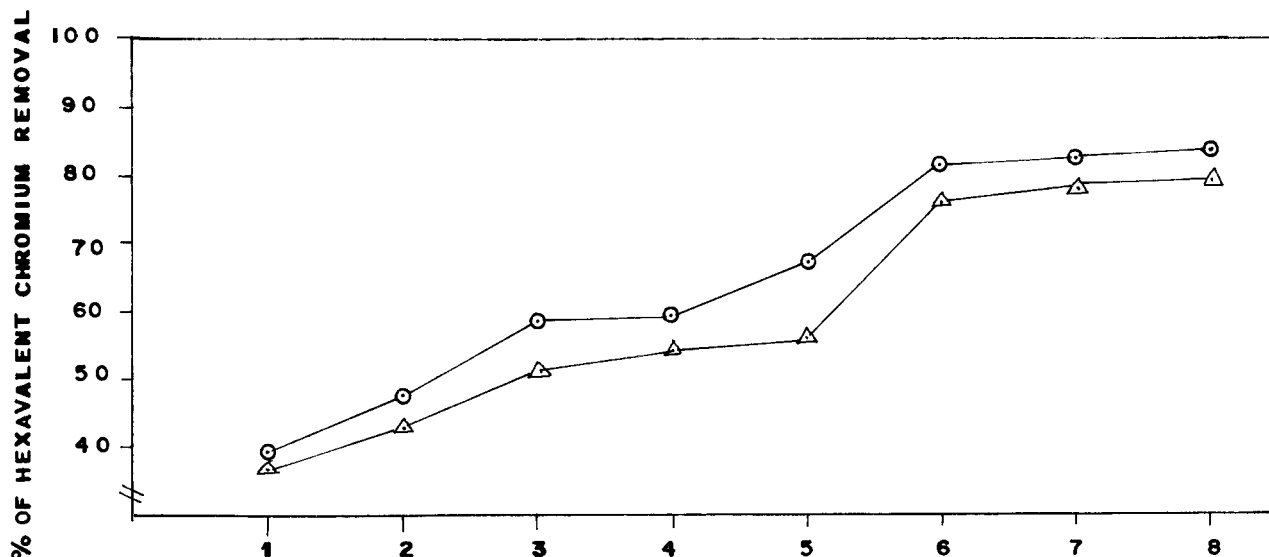


Figure 1 Effect of time: (○) synthetic sample, (△) industrial sample; KGD = 0.03 g, pH = 6.1, [Cr(VI)] = 6.0 mg/L, temperature = 30°C.

Analysis of Various Constituents and Characteristics of KGD

Because KGD is a new renewable resource based material as developed by us, this part of the experiment was carried out only to know about the characteristics and the various constituents present in the said material.

The standard solution of KGD was 1 g KGD dissolved in 100 mL of *N,N*-dimethyl formamide (DMF); the various constituents were measured by the usual techniques.³⁰ Na, K, and Ca were detected by the flame photometry technique using a Chemito digital flame photometer. The presence of total chromium (Cr) was detected by a GBC 902 double beam atomic absorption spectrophotometer. Photoelectric colorimetric analysis was performed on a model 943 Orbeco–Hellige portable water analyzer using the following methods: Zincon, Caramine, cadmium reduction, and tungstophosphoric and molybdophosphoric acid reduction. These methods were respectively employed for the detection of Zn, B, NO₃⁻ (as nitrogen), and tannin as well as lignin in the KGD. The electrode method was employed to detect fluoride ions in the adsorbent using a Sintalyzer. The results of all the above mentioned constituents are shown in Table I as measured by the standard procedures.³⁰ Table II shows some of the typical characteristics of KGD. Both pH and chemical oxygen demand (COD) were measured by taking the standard solution (1 g KGD dissolved in 100 mL of DMF)

using the usual procedures. A Systronics Griph 'D' pH meter 327 was used to measure the pH. Elements like C, H, and N of the solid KGD were estimated by a Carlo Erba 1108 elemental analyzer.

Test Solutions

For the present investigations, the test solutions containing hexavalent chromium were taken from a synthetic sample (a solution prepared by dissolving a required quantity of AR grade K₂Cr₂O₇ in distilled demineralized water) and the industrial effluent (collected from Orichem, Talcher, Orissa, India, a basic "chrome" sulfate manufacturing industry). Suspended solids, hexavalent chromium, total chromium content, and the pH of the effluent were analyzed by the standard procedures and the results are represented in Table III.

Batch Mode Experiment

Batch adsorption studies were carried out using glass stoppered conical flasks containing the required amount of test solutions at the desired pH and adsorbent materials. The pH of the solution was adjusted with HCl or a NH₄OH solution. The flasks containing the test solutions and adsorbents were shaken for the required time period at the desired temperature in an electric shaker. Except while studying the temperature effect, all

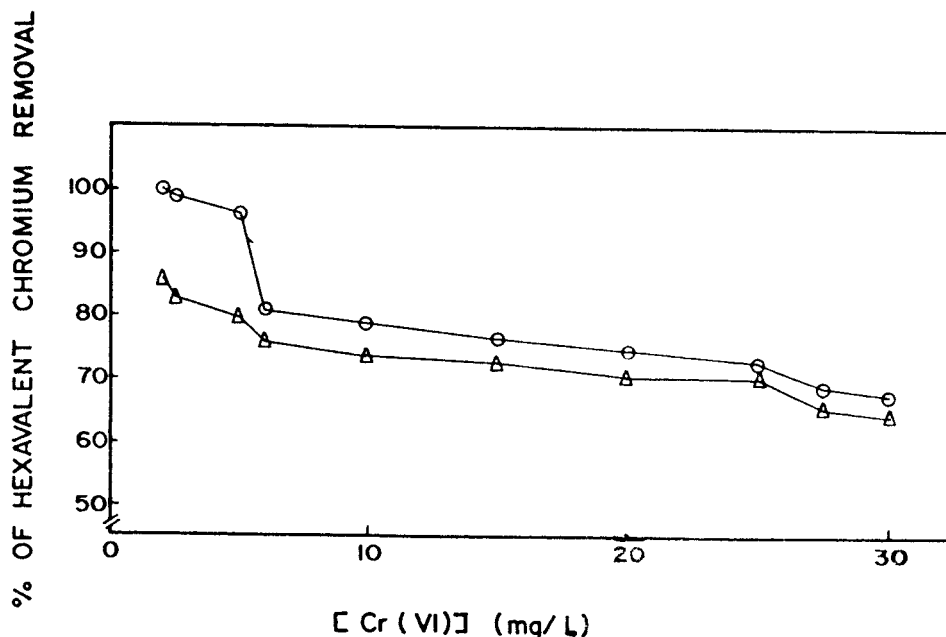


Figure 2 Effect of Cr(VI) concentration: (○) synthetic sample, (△) industrial sample; KGD = 0.03 g, pH = 6.1, temperature = 30°C, contact time = 6 h.

the experiments were carried out at 30°C. After the required time period, the contents of the flasks were filtered using Whatman No. 4 filter paper and were analyzed for Cr(VI) spectrophotometrically using 1,5-diphenylcarbazide.³⁰ The percent Cr(VI) removal was calculated from initial (C_0) and final/equilibrium (C_e) concentrations of test solutions as follows:

$$\% \text{ Cr(VI) removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

A GBC UV-VIS 911 spectrophotometer was used for spectrophotometric analysis of Cr(VI).

Thermal Characteristics

Thermal characteristics of original KGD and Cr(VI) adsorbed KGD were investigated with thermogravimetric analysis (TGA) as recorded on a Shimadzu DT 40 thermal analyzer under atmospheric conditions at a heating rate of 10°/min up to 600°C.

RESULTS AND DISCUSSION

Effect of Contact Time

Batch adsorption studies were carried out at 30°C for different time periods, keeping the

amount of adsorbent, pH, and Cr(VI) content of the test solution fixed. Figure 1 shows the effect of the contact time of adsorbent (KGD) with the adsorbate (hexavalent chromium contained so-

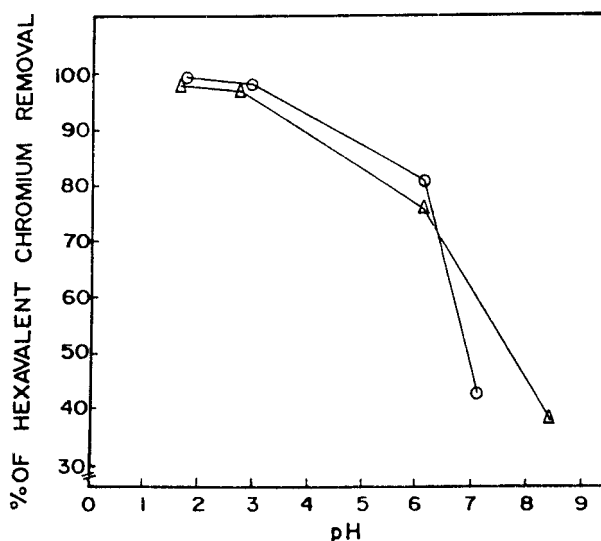


Figure 3 Effect of pH: (○) synthetic sample, (△) industrial sample; KGD = 0.03 g, [Cr(VI)] = 6.0 mg/L, temperature = 30°C, contact time = 6 h.

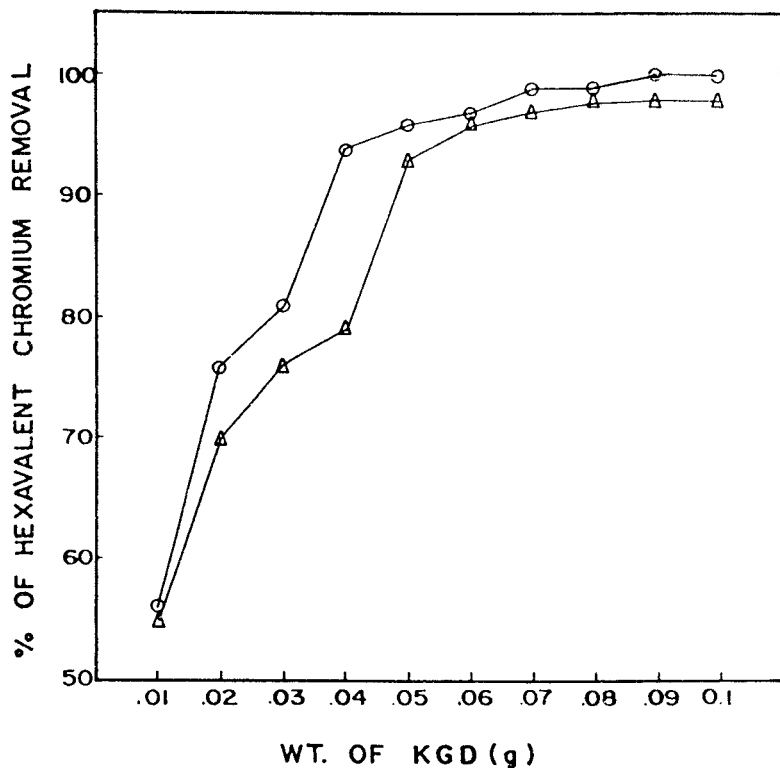


Figure 4 Effect of amount of adsorbent (KGD): (○) synthetic sample, (△) industrial sample; [Cr(VI)] = 6.0 mg/L, pH = 6.1, temperature = 30°C, contact time = 6 h.

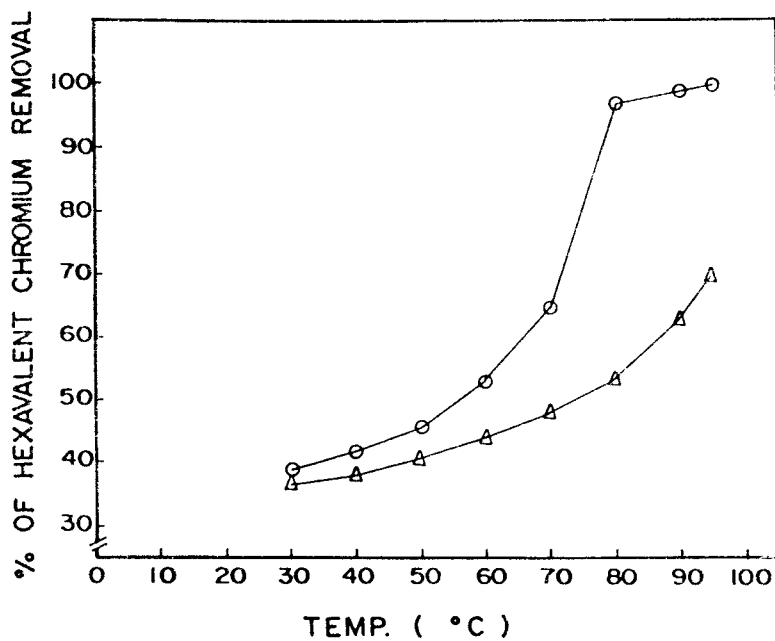


Figure 5 Effect of temperature: (○) synthetic sample, (△) industrial sample; KGD = 0.03 g, [Cr(VI)] = 6.0 mg/L, pH = 6.1, contact time = 1 h.

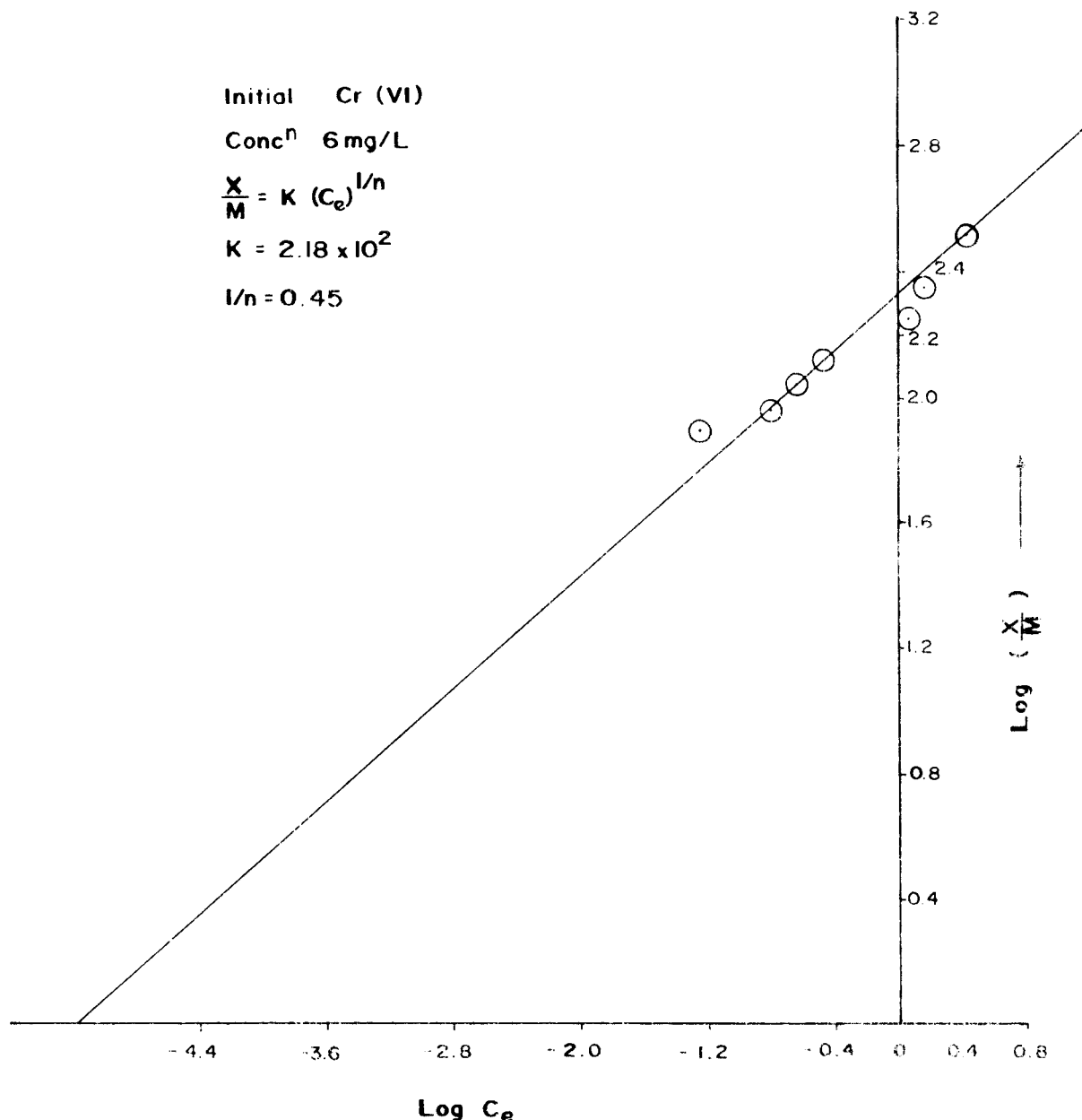


Figure 6 Freundlich adsorption isotherm at 30°C. pH = 6.1; contact time = 6 h.

lutions of synthetic and effluent samples) on the percent removal of Cr(VI). The uptake of Cr(VI) by KGD increased with an increase of contact time up to 6 h and thereafter leveled off. Siddiqi and Paroor³¹ reported that uptake of Cr(VI) by activated charcoal increased with an increase of contact time and it took 7 h for maximum adsorption (92.62%) of Cr(VI) under their optimum reaction conditions. Figure 1 shows that the percent removal of Cr(VI) from

the synthetic sample is comparatively higher than that from the industrial effluent. The presence of suspended solids or impurities of the effluent might cause a slight hindrance in Cr(VI) adsorption by the adsorbent (KGD) as compared to the pure synthetic sample. While studying the effects of different variables on the percent removal of Cr(VI) by KGD from the synthetic and effluent test solutions, we observed a similar trend: the percent removal from the syn-

Table IV Effect of Cyanide

Concn Cyanide, CN ⁻ (mg/L)	Removal of Cr(VI) (%)
0	60.2
5	56.6
10	52.0
15	51.6
20	48.3
25	46.6
30	42.5

KGD = 0.1 g; pH = 6.1; [Cr(VI)] = 30 mg/L; temperature = 30°C; contact time = 2 h.

thetic sample was comparatively higher than that from the effluent.

Effect of Cr(VI) Concentration

The effect of variation of Cr(VI) concentration in the test solution (both synthetic and effluent) on the percent removal of Cr(VI) by KGD is shown in Figure 2. Observe that the percent removal of Cr(VI) from the test solution decreased with an increase of solute concentration from 2 to 30 mg/L. The reason for the above observation may be attributed to the larger increase in the denominator (C_0) value in comparison to that of the ($C_0 - C_e$) value in eq. (1). Again this decrease in adsorption may be attributed to the monolayer coverage of solute molecules on the surface area of the adsorbent.³²

Effect of pH

The variation of pH of the test solution plays an important role on Cr(VI) adsorption by KGD. Figure 3 represents the effect of variation of pH on percent removal of Cr(VI) of both the synthetic and industrial samples. In the synthetic sample at pH 1.66, a 99% Cr(VI) removal occurred; whereas at pH 7.1 a 42.6% Cr(VI) removal occurred. For the effluent at pH 1.85, a 97.8% removal occurred and almost remained the same (97.5%) at pH 2.7. With a further increase of pH from 2.7 to 6.1, a sharp decrease in percent removal value occurred and at pH 8.35 the removal was only 39.2%. Huang and Wu¹⁷ reported that under low pH conditions, the Cr(VI) species are converted into dichromate ions. Because of this, the oxidizing ability of Cr(VI) over KGD might have been increased. Thus, a high reduction process on the adsorbent surface may occur at lower

pH, thereby increasing the efficiency of adsorption. Again the effect of pH on the adsorption capacity of KGD may be considered for the results from the combined effect of pH on the nature of the KGD surface, adsorbed Cr(VI) species, and the acid-base used to adjust the solution pH. The effect of increasing pH on the nature of the KGD surface may be manifested in altering the chemical nature of the surface sites of KGD. This means the decrease in net positive surface potential as a result of competitive effects of OH⁻ ions, which ultimately leads to the reduction in adsorption capacity. The decrease in adsorption capacity may have been accomplished with the weakening of the electrostatic forces between the KGD surface and negatively charged Cr(VI) species. Again, the protolysis of the KGD surface with H⁺/H₃O⁺ ions under the reduced pH may have produced the increased adsorption capacity.

Effect of Amount of Adsorbent (KGD)

Figure 4 shows the effect of variation in the amount of adsorbent (KGD) on the percent removal of Cr(VI). It is observed that within the range studied, the percent removal increases with an increase in the amount of adsorbent for both the synthetic and industrial samples up to an optimum amount of KGD (0.05 g) beyond which the percent removal remains nearly the same, approaching 100%. The increase in the percent removal with an increase in the amount of adsor-

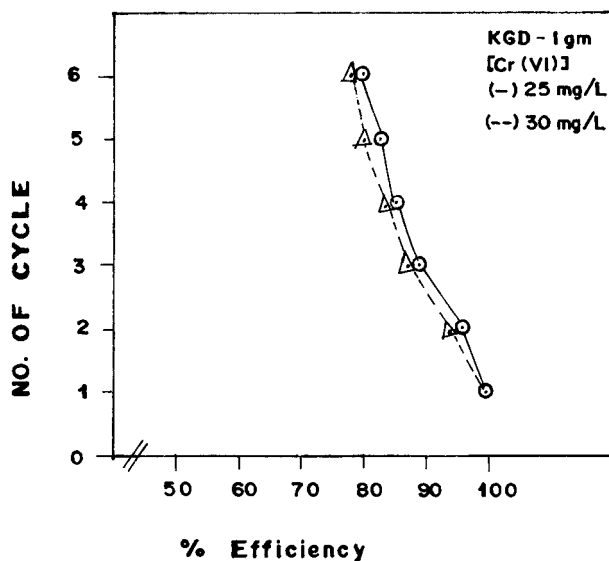


Figure 7 Removal efficiency of KGD with successive cycles. pH = 6.1; temperature = 30°C; contact time = 6 h.

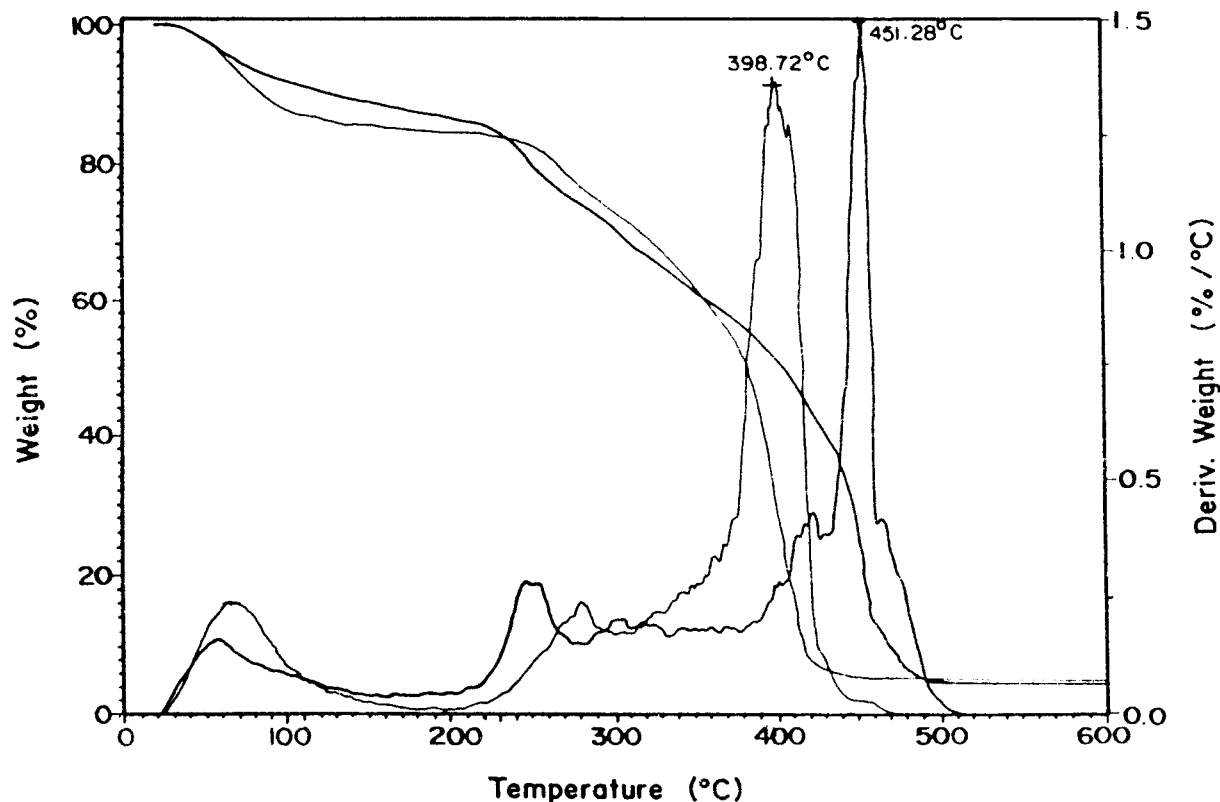


Figure 8 TGA curves of original KGD and Cr(VI) adsorbed KGD. Original KGD and Cr(VI) adsorbed KGD are shown by light and dark lines, respectively.

bent might be attributed to the availability of increased surface area or active sites of the adsorbent (KGD).

Effect of Temperature

The effect of variation of temperature on percent removal of Cr(VI) of both the synthetic and industrial samples is represented in Figure 5. For both the samples percent removal is found to increase with an increase of temperature from 30 to 100°C, indicating the process is endothermic. The increase in adsorption with temperature suggests that the active surface centers available for adsorption increases with temperature. The increase of uptake with temperature may be due to the desolvation of adsorbate species, the change in the size of pores,³³ and the enhanced rate of intraparticle diffusion of metal ions because the diffusion is an endothermic process.³⁴ The activation of the reacting species is also responsible for the increase of adsorption with temperature.³⁵

Adsorption Isotherm

The adsorption studies conducted at fixed initial Cr(VI) concentrations (synthetic sample) and

varying adsorbent amounts were fitted to the linearized Freundlich adsorption isotherm that is of the form

$$\log\left(\frac{x}{M}\right) = \log K + \frac{1}{n} \log C_e \quad (2)$$

where x/M is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of Cr(VI), K is the adsorption capacity, and $1/n$ is the adsorption intensity. K and $1/n$ values as obtained from the plot (Fig. 6) are 2.18×10^2 and 0.45, respectively. The high value of K as well as low value of $1/n$ (less than 1)³⁶ indicate a greater adsorption efficiency of our newly developed adsorbent (KGD) for Cr(VI) removal.

Effect of Cyanide

It is not unexpected that many of the effluent streams, especially those of electroplating and metal finishing plants, contain a substantial concentration of cyanide as CN^- . To study the effects

of cyanide on the adsorption capacity of KGD, we took the synthetic sample. The results are shown in Table IV. The reduction in adsorption capacity in the presence of cyanide may be due to the fact that the cyanide as CN^- are competitively adsorbed, covering a portion of the surface sites of KGD that in turn disallow more Cr(VI) anions to be adsorbed on the surface. Moreover, cyanide adsorption may bring the KGD surface to a stronger electronegative state that prevents Cr(VI) from being adsorbed to the surface via electrostatic forces. Cyanide adsorption can also give rise to significant anion effects in the diffused double layer³⁷ that causes the reduction in Cr(VI) adsorption by KGD.

Recycling of KGD

In any waste treatment process recycling of the adsorbent is an important aspect of treatment costs. Hence, the feasibility of recycling and regeneration of KGD was studied by determining the efficiency of KGD after successive recycling by carrying out batch experiments at initial Cr(VI) concentrations (synthetic sample) of 25 and 30 mg/L. The results presented in Figure 7 indicate that there is gradual decrease of efficiency with each successive cycle. However, we observed that there was no significant decrease in efficiency. Even after the sixth cycle, only an $\sim 20\%$ loss of efficiency of KGD occurred, indicating that KGD is an efficient adsorbent for Cr(VI). A decrease in adsorption efficiency with successive uses may be because of the diminishing surface area of the adsorbent. While studying the removal of Cr(VI) by blast furnace flue dust (BFD), Das and Patnaik³⁸ reported that there was a loss of efficiency of the adsorbent (BFD) after the second cycle and use after the fourth cycle was not viable.

Thermal Behavior

The TGA curves of the original KGD and Cr(VI) adsorbed KGD are shown in Figure 8. The Cr(VI) adsorption improved the thermal stability of KGD as evidenced from the maximum decomposition temperature (T_D) values. The original KGD shows a T_D value at 398.72°C. The Cr(VI) adsorbed KGD shows a T_D value at 451.28°C, indicating possible stabilization of the polymeric adsorbent (KGD) by Cr(VI). A similar observation that the metallization enhances thermal stability was also reported earlier.³⁹

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