

# Quaternized Wood as Sorbent for Hexavalent Chromium

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## Abstract

The potential of quaternized wood (QW) chips in removing hexavalent chromium from synthetic solution and chrome waste under both batch and continuous-flow conditions was investigated. Sorption was found to be dependent on pH, metal concentration, and temperature. QW chips provide higher sorption capacity and wider pH range compared with untreated wood chips. The equilibrium data could be fitted into the Langmuir isotherm model, and maximum sorption capacities were calculated to be 27.03 and 25.77 mg/g in synthetic chromate solution and chrome waste, respectively. The presence of sulfate in high concentration appeared to suppress the uptake of chromium by QW chips. Column studies showed that bed depth influenced the breakthrough time greatly whereas flow rate of influent had little effect on its sorption on the column.

**Index Entries:** Wood; chemical modification; biosorption; hexavalent chromium.

## Introduction

Many industrial activities, including iron and steel manufacturing, chrome leather tanning, chromium plating, textile dyeing, and wood preservation, contribute to the increase in chromium in aquatic and terrestrial ecosystems. This has caused great concern because chromium, especially in its hexavalent form, is highly toxic. It is carcinogenic, mutagenic, and in cells induces the formation of reactive oxygen species that damage cellular membranes (1,2).

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Various processes have been proposed to remove Cr(VI) from industrial wastewater. These include reduction followed by precipitation, ion exchange, reverse osmosis, solvent extraction, and adsorption by activated carbon. Most of these processes suffer from some drawback such as disposal of residual metal sludge or high capital and operational cost. Activated carbon, e.g., has been shown to be an efficient and effective adsorbent in the removal of Cr(VI) (3–5). However, its high cost has rendered its application unattractive. In recent years, attention has been focused on the use of various low-cost materials such as agricultural residues, industrial waste, and biologic materials as alternatives to activated carbon in the removal of heavy metal pollutants. Materials such as sugar beet pulp and sugarcane bagasse (6), leaf mold (7), coconut hulls and palm pressed fibers (8), quaternized rice hulls (9), sawdust (6,10), fly ash (11), sphagnum moss peat (12), water hyacinth roots (13), moss (14), and algae (15) have been reported to remove Cr(VI) with different degrees of success. Other than the report on the removal of Cr(VI) from electroplating wastes using phosphate-treated sawdust (10), the potential of using waste products from the wood industries in the removal of oxyanions has not been exploited much. Our earlier work on rice hulls has shown that the introduction of a quaternary ammonium group on the sorbent's surface greatly enhanced the sorption capacity for anionic species (9). In our continued effort to explore low-cost materials for the amelioration of the environment, this article reports the application of quaternized wood (QW) in the removal of Cr(VI) from synthetic solution as well as industrial chrome waste.

## Materials and Methods

### Materials

The wood used in most of the experiments was keruing (*Diterocarpus constulatus*). It was collected as wood chips from a timber factory in Selangor, Malaysia. The chips were ground and passed through a 1-mm sieve. One hundred fifty grams of ground wood was boiled with 4.5 L of 0.5 M NaOH solution for 2 h to remove color caused by the presence of lignin. It was subsequently filtered and rinsed with distilled water until the filtrate was near neutral. The alkali-treated wood was then dried in an oven overnight at 80°C and labeled as alkali-treated wood (HW). A portion of HW was quaternized according to the method reported by Laszlo (16) with some modifications. HW (100 g) was treated with 175 mL of 5 M NaOH for 30 min at room temperature. At the end of the incubation period, 125 mL of 4 M *N*-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride was added to the mixture. It was thoroughly mixed and left in the oven at 60–70°C for 4 h with intermittent stirring. The reaction mixture was then rinsed several times with distilled water and suspended in dilute HCl at pH 2.0. It was subsequently rinsed with distilled water and dried. The dried product was labeled QW.

A standard solution of 2000 mg/L of Cr(VI) was prepared by dissolving analytical reagent grade  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  in deionized water. Subsequent dilutions were carried out whenever necessary.

### *Batch Studies*

All the experiments were carried out in duplicate. Errors were calculated to be <7% from duplicate experiments. Sorption was measured by equilibrating 0.1 g of either QW or HW with 20 mL of 100 mg/L of Cr(VI) solution at pH 4.3 at an agitation rate of 250g on a gyratory shaker for 4 h at room temperature ( $28 \pm 2^\circ\text{C}$ ) unless otherwise stated. A control consisting of the Cr(VI) solution without the addition of sorbent to ascertain that there was no sorption of Cr(VI) on the surface of the container was included. At the end of equilibration, the reaction mixture as well as the control was filtered through Whatman no. 1 filter paper, and Cr(VI) in the filtrate was determined by inductively coupled plasma atomic emission spectrometry using a Perkin-Elmer instrument (P1000).

The effect of pH on Cr(VI) uptake was studied by equilibrating the reaction mixture at different initial pH values obtained by the addition of HCl or NaOH solutions. To study the effect of contact time and different initial concentrations, Cr(VI) solutions of 100, 150, and 250 mg/L were used. At predetermined time intervals, a set of reaction mixture was removed and filtered, and the filtrate was analyzed. To establish the sorption isotherm, Cr(VI) solutions of initial concentrations in the range of 100–400 mg/L were used.

A thermostatic shaking water bath was used to examine the effect of temperature on the sorption of Cr(VI). The experiments were carried out at 4–60°C. The initial concentration of Cr(VI) solution was 100 mg/L. The experiment on the effect of sorbent dosage on Cr(VI) sorption was performed using dosages of 0.0125–0.250 g.

The effect of competing anions on Cr(VI) sorption was studied by varying the molar ratio of Cr(VI) to  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  from 1:0 to 1:10 while keeping the Cr(VI) concentration constant at 4.0 mM and pH 4.3. Sodium salts were used throughout the experiments. These anions were selected because they are commonly present together with Cr(VI) species in wastewaters such as those from chrome-plating plants.

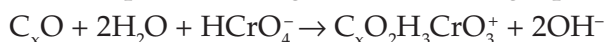
### *Column Studies*

Column experiments were conducted using a glass column of id of 1.0 cm. The column was packed to heights of 7.0, 15.0, and 20.0 cm using 1.10, 2.25, and 3.10 g of QW, respectively. The chrome waste, obtained from a nearby electroplating plant, containing 9.07 mg/L of Cr(VI), 16.65 mg/L of  $\text{SO}_4^{2-}$  at pH 4.3 (17) was passed through the column at a flow rate of 50 mL/min. The effect of flow rate was investigated using a column of 7.0 cm height, and the flow rate was varied from 10 to 50 mL/min. In all the continuous-flow experiments, the eluent was collected in 100-mL fractions and analyzed for Cr(VI).

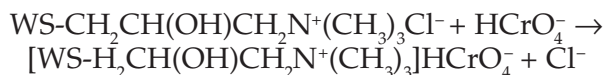
## Results and Discussion

### Effect of pH

The study of the effect of pH on the uptake of Cr(VI) by wood is important in establishing the optimum condition for the sorption of Cr(VI) at the solid/liquid interface and the chemical species of Cr(VI) in solution. Cr(VI) exists in different species of oxyanions, depending on pH and concentration. At pH < 2.0, the dominant species is  $\text{H}_2\text{CrO}_4$ , between pH 2.0 and 6.0 there exists an equilibrium between  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  that is concentration dependent, and above pH 6.0 the major component is  $\text{CrO}_4^{2-}$ . The predominant oxyanion present at pH 2.0–6.0 under experimental conditions was  $\text{HCrO}_4^-$  because  $\text{Cr}_2\text{O}_7^{2-}$  is practically absent at a concentration of  $\leq 0.1 \text{ M}$  (18). The results show that QW possessed much higher sorption capacity for Cr(VI) than the untreated wood (Fig. 1). Sorption of Cr(VI) on HW was highest at pH 2.0, with an uptake of 17%, and this value thereafter decreased rapidly as pH increased, a phenomenon normally observed with other biologic materials (6). No uptake of Cr(VI) occurred when the pH was >4.0. The sorption at a pH value of <4.0 is attributed to the attraction between the positively charged surface of the carbonaceous material with the  $\text{HCrO}_4^-$  ions at low pH according to the following equation (6):



However, sorption of Cr(VI) on QW remained unchanged as pH increased from 2.0 to 4.0 (about 88%) and decreased gradually thereafter. At pH 10.0, the sorption was 62%. It thus appears that  $\text{HCrO}_4^-$  forms the strongest bond with QW compared with  $\text{CrO}_4^{2-}$ ,  $\text{H}_2\text{CrO}_4$ , and  $\text{HCr}_2\text{O}_7^-$ . The sorption of Cr(VI) on QW may be considered an ion-exchange process between the oxyanion and the chloride group of the quaternary amine:



in which WS represents the surface of wood. An ion exchange between  $\text{PO}_4^{3-}$  on the surface of phosphate-treated sawdust and  $\text{Cr}_2\text{O}_7^{2-}$  in the solution at pH 2.0 was proposed to be the mechanism involved in the removal of Cr(VI) (11).

### Effect of Contact Time and Initial Concentration

Figure 2 shows the results of contact time experiments using Cr(VI) solutions with initial concentrations of 100, 150, and 250 mg/L. The percentage uptake defined as  $[100(\text{C}_0 - \text{C}_t)/\text{C}_0]$ , in which  $\text{C}_0$  is the initial concentration and  $\text{C}_t$  is the concentration at time  $t$ , follows a trend of a greater percentage uptake with decreasing concentration. Sorption was very rapid, attaining equilibrium in 30 min irrespective of initial concentration. The rapid uptake of Cr(VI) by QW is a great advantage for its applications in the continuous-flow process when the contact time is generally short. Sorption capacities at equilibrium were 88.3, 60.1, and 42.0% for concentrations of 100, 150, and 200 mg/L, respectively.

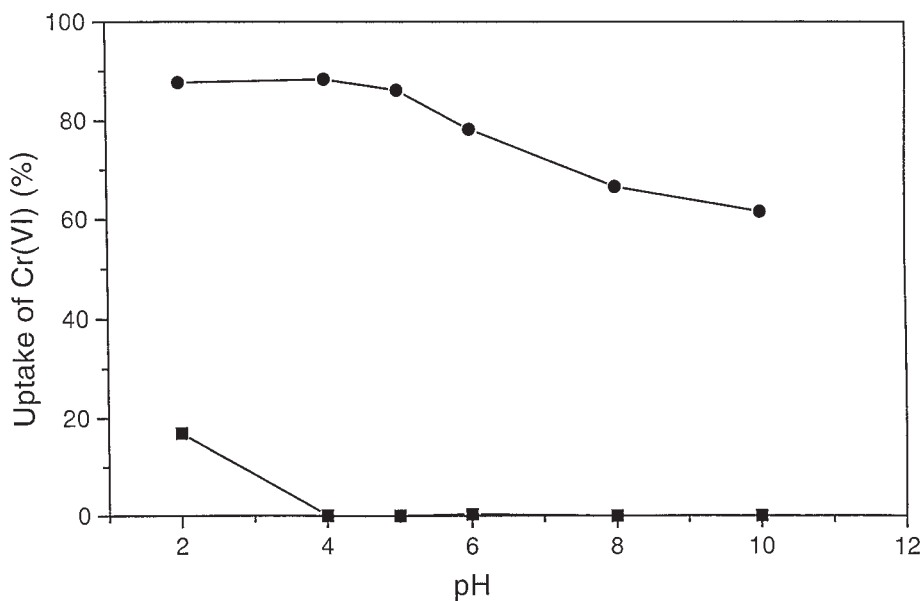


Fig. 1. Effect of pH on the uptake of Cr(VI) by HW (■) and QW (●).

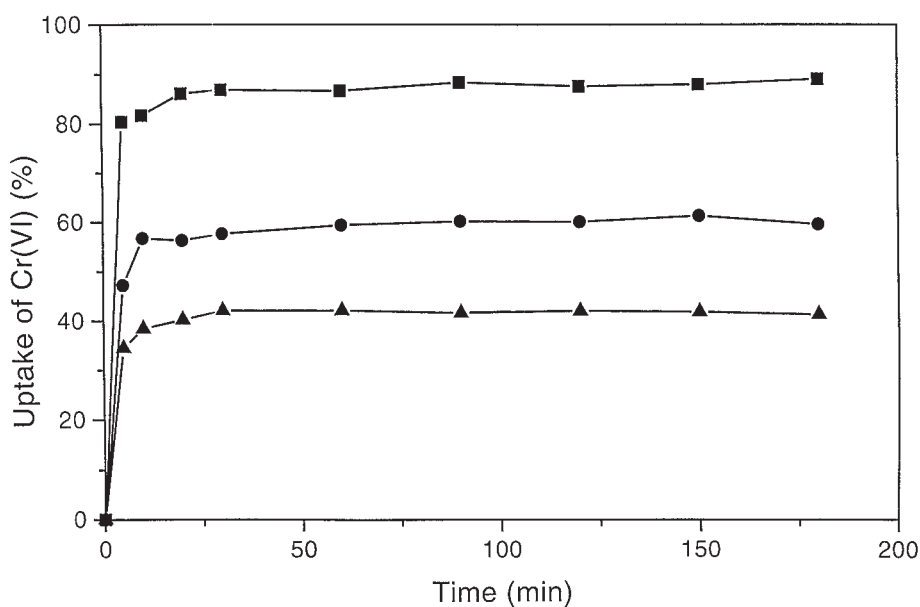


Fig. 2. Effect of contact time and initial concentration on the uptake of Cr(VI) by QW. (■) 100, (●) 150, and (▲) 200 mg/L.

### Sorption Isotherm

The experimental data were fitted into the following modified Langmuir equation:

$$C_e/q_e = 1/Q_0b + C_e/Q_0$$

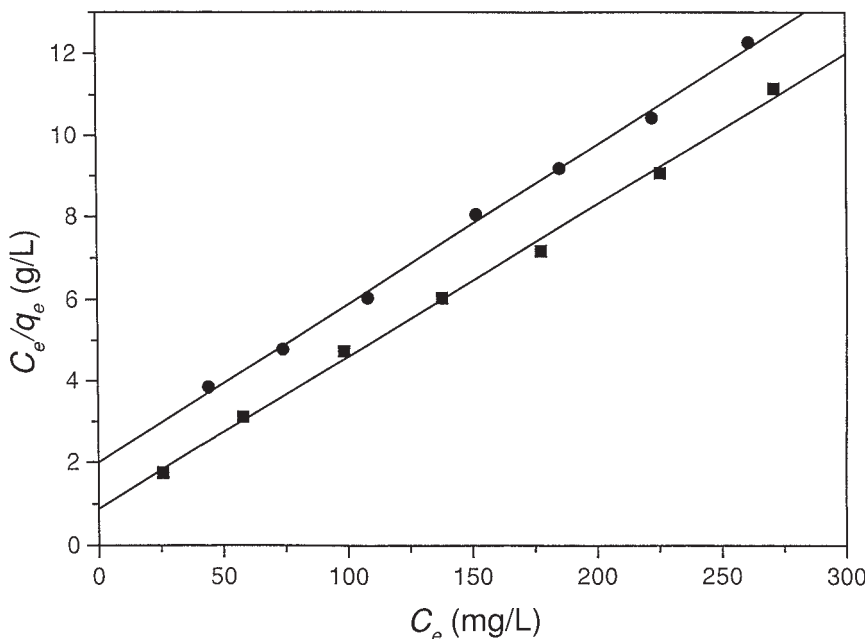


Fig. 3. Langmuir isotherms for the sorption of Cr(VI) on QW. (●) chrome waste; (■) synthetic chrome solution.

in which  $q_e$  is the amount of Cr(VI) sorbed (milligrams/gram) at equilibrium concentration  $C_e$  (milligrams/liter),  $Q_0$  is the maximum sorption capacity of QW (milligrams/gram), and  $b$  is the equilibrium constant related to sorption energy between the sorbate and sorbent (liters/milligram).

Although the Langmuir model is not really applicable to a system in which ion exchange is involved, it does provide some insight into the maximum sorption capacity. The maximum sorption capacities estimated from the slopes of the linear plots (Fig. 3) were 27.03 and 25.77 mg/g at pH 4.3 using synthetic solution and chrome waste, respectively. The slightly lower value in chrome waste could be owing to competitive uptake of other anions present such as  $SO_4^{2-}$ . These values compare favorably with those obtained using other sorbents (Table 1). Although sorbents such as sphagnum moss peat and activated carbon showed higher sorption capacities, these were values obtained at an optimum pH of 1.5–2.5. Sorption capacities decreased rapidly as pH increased. For example, in the case of sphagnum moss peat, as pH increased from 1.5 to 2.0, capacity decreased from 119.0 to 65.8 mg/g, and at pH 4.0, it was 21.7 mg/g (12). In a study on the removal of Cr(VI) with activated carbon, Perez-Candela et al. (19) reported that for very acidic conditions, up to pH 3.0, the amount of Cr(VI) removed increased with increasing pH up to a maximum and then decreased sharply and continuously for pH > 3. The same observation was also reported by Huang and Wu (5) in their study on the removal of Cr(VI) from dilute solution by activated carbon. QW has the advantage of maintaining its

Table 1  
Maximum Sorption Capacities of Some Cr(VI)-Sorbent Systems

Sorbent	$Q_0$ (mg/g)	Optimum pH	Reference
Sugar beet pulp	17.2	2.0	6
Sugarcane bagasse	13.4	2.0	6
Leaf mold	43.0	2.0	7
Coconut husk fibers	29.0	2.1	8
Palm pressed fibers	15.0	2.0	8
Quaternized rice husk	32.3	4.0–6.0	9
Sawdust	39.7	2.0	10
Sphagnum moss peat	119.0	1.5	12
Water hyacinth roots	8.9	2.0	13
Copper-coated moss	7.1	2.0	14
<i>Cladophora crispata</i> (algae)	39.5	1.0	15
Activated carbon (Filtrisorb-400)	145.0	2.5	6
Activated carbon (Filtrisorb-400)	57.7	—	5
Quaternized wood	27.0	2-5	Present study

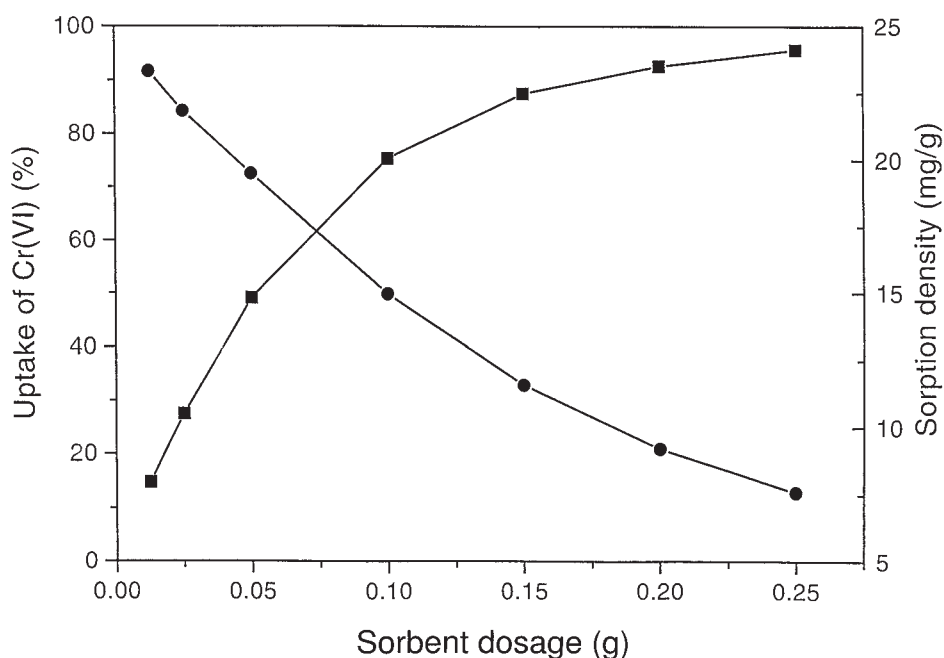


Fig. 4. Effect of sorbent dosage on Cr(VI) uptake (■) and sorption density (●).

sorption capacity over a wide pH range, and, hence, adjustment of pH is not required in the treatment of wastewater.

#### Effect of Sorbent Dosage

The study of uptake as a function of sorbent dosage is important in establishing the optimum use of sorbent for any sorption process. Figure 4

Table 2  
Effect of Temperature  
on Sorption of Cr(VI) by QW

Temperature (°C)	Uptake (%)
4	79.2
26	75.3
40	73.7
50	72.8
60	71.1

shows the effect of dosage on percentage uptake and sorption density of Cr(VI) on QW. By increasing the sorbent dosage from 0.0125 to 0.25 g, the percentage uptake increased from 14.68 to 95.61% whereas the sorption density decreased from 23.3 to 7.6 mg/g. The decrease in sorption density is owing to the greater number of binding sites available to Cr(VI) with increasing dosage.

### *Effect of Temperature*

The effect of temperature on the sorption of Cr(VI) by QW was also investigated (*see* Table 2). Sorption decreased from 79.2 to 71.1% in the temperature range of 4–60°C, indicating that sorption was exothermic in nature. No plausible explanation for the observed trend is possible until a more in-depth study on the sorption mechanism has been investigated.

The variation of uptake with temperature is represented by the relationship between the distribution coefficient,  $k_d$ , defined as  $q_e/C_e$  in which  $q_e$  is the amount of Cr(VI) sorbed at equilibrium concentration  $C_e$  and the absolute temperature  $T$ (K). This can be expressed in the form of van't Hoff equation:

$$\log k_d = \Delta S^\circ/2.303R - \Delta H^\circ/2.303RT$$

It is clear that  $\log k_d$  decreased linearly with increasing temperature, indicating that sorption was an exothermic process (Fig. 5). The enthalpy ( $\Delta H^\circ$ ) obtained from the slope of the plot is  $-5.80$  kJ/mol. It has been reported that the sorption of Cr(VI) from wastewater by quaternized rice husk (9) and fly ash (11) decreased with increasing temperature, probably owing to the weakening of sorptive forces between the binding sites and Cr(VI) ions. A similar process is likely to occur in the present system.

### *Effect of Competing Anions*

Industrial wastewater may contain anions other than chromate. Hence, the effect of other anions commonly present in wastewater on the sorption of Cr(VI) was investigated. Table 3 shows the effect of  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  on the sorption of Cr(VI) on QW. The trivalent  $\text{PO}_4^{3-}$  had little

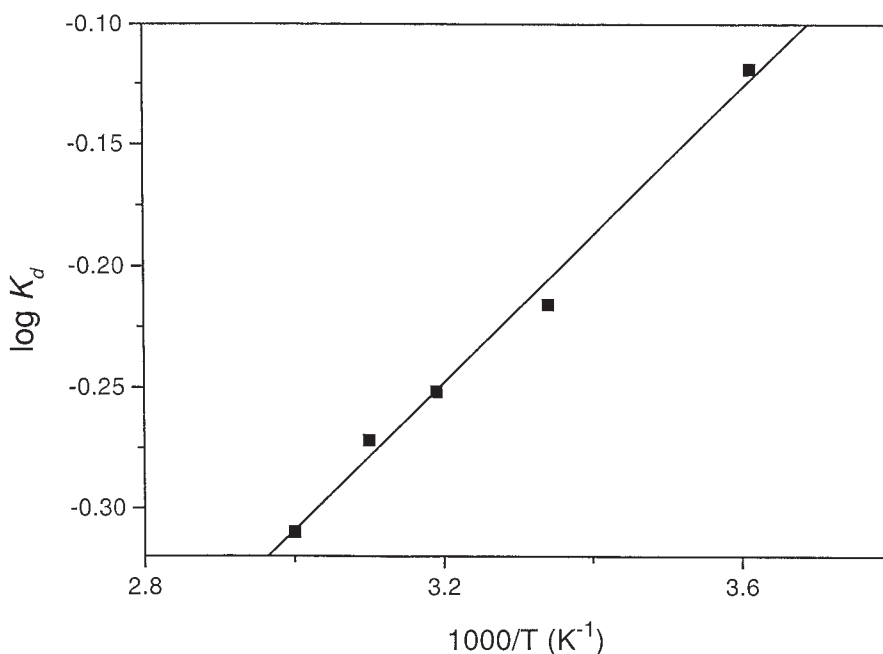


Fig. 5. van't Hoff's plot for the Cr(VI)-QW system.

Table 3  
Effect of Competing Anions on Uptake of Cr(VI) by QW

Molar ratio of Cr(VI):anions	Uptake of Cr(VI) in presence of anion (%)		
	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>
1:0	76.99	76.99	76.99
1:1	72.46	48.29	70.65
1:2	70.43	41.89	65.38
1:5	64.05	40.27	57.71
1:10	59.95	31.70	48.28

effect on the uptake whereas Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> reduced the uptake of Cr(VI) from 77 to 48 and 32%, respectively, when these anions were present at 10 times the molar concentration of Cr(VI). The competitive uptake of these anions may pose a problem when QW is used as a sorbent to remove Cr(VI) from effluents containing such anions.

### Continuous-Flow Studies

Parameters obtained in batch processes are useful in providing information on the effectiveness of the Cr(VI)-QW system. However, the data obtained are generally not applicable to treatment under continuous-flow conditions in which the contact time is too short for the attainment of equi-

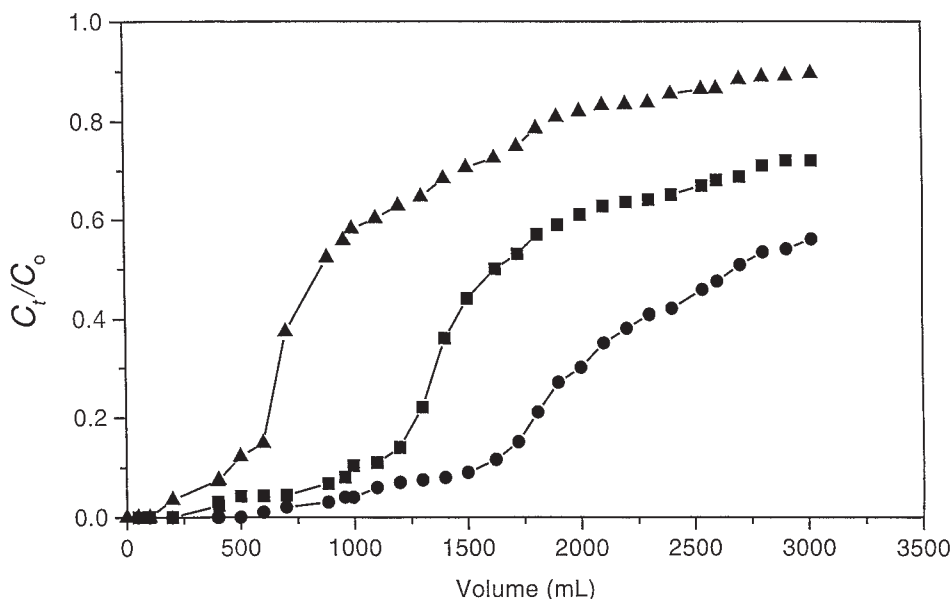


Fig. 6. Breakthrough curves of Cr(VI) at different bed depths with a sample containing 9.07 mg/L of Cr(VI), 16.65 mg/L of  $\text{SO}_4^{2-}$  at pH 4.3. ( $\blacktriangle$ ) 7, ( $\blacksquare$ ) 15, and ( $\bullet$ ) 20 cm.

librium. Hence, it is necessary to assess the performance of the system under flow conditions.

To evaluate the usefulness of QW in removing Cr(VI) from a real sample situation, chrome waste collected from an electroplating factory was passed through a QW column. Typical composition of raw waste streams from common metal plating contained 0.005–334.5 mg/L of Cr(VI) (20). The breakthrough curves of Cr(VI) at a fixed flow rate of 50 mL/min for different bed depths are shown in Fig. 6. Breakthrough at  $C_t/C_0 = 0.5$  occurred at 847, 1636, and 2695 mL of Cr(VI) solution for bed depths of 7, 15, and 20 cm, respectively. It is clear that the higher the bed depth the greater the load that can be passed through before breakthrough occurs. Various models have been proposed to correlate the service time of fixed sorption bed with other variables such as bed depth. One such model is the bed-depth service time (BDST) model proposed by Hutchins (21), which states that bed depth ( $x$ ) and service time ( $t$ ) bear a linear relationship that can be expressed as

$$t = (N_0/C_0 v)x - (v/kN_0)\ln(C_0/C_t - 1)$$

in which  $t$  is the service time,  $N_0$  is the sorption capacity,  $C_0$  is the initial concentration of the influent,  $v$  is the linear flow rate,  $x$  is the bed depth,  $k$  is the constant of sorption, and  $C_t$  is the eluent concentration at time  $t$ . At 50% breakthrough ( $C_0/C_t = 2$ ), the second term in the BDST equation is reduced to zero, giving a simplified equation:

$$t_{1/2} = (N_0/C_0 v)x$$

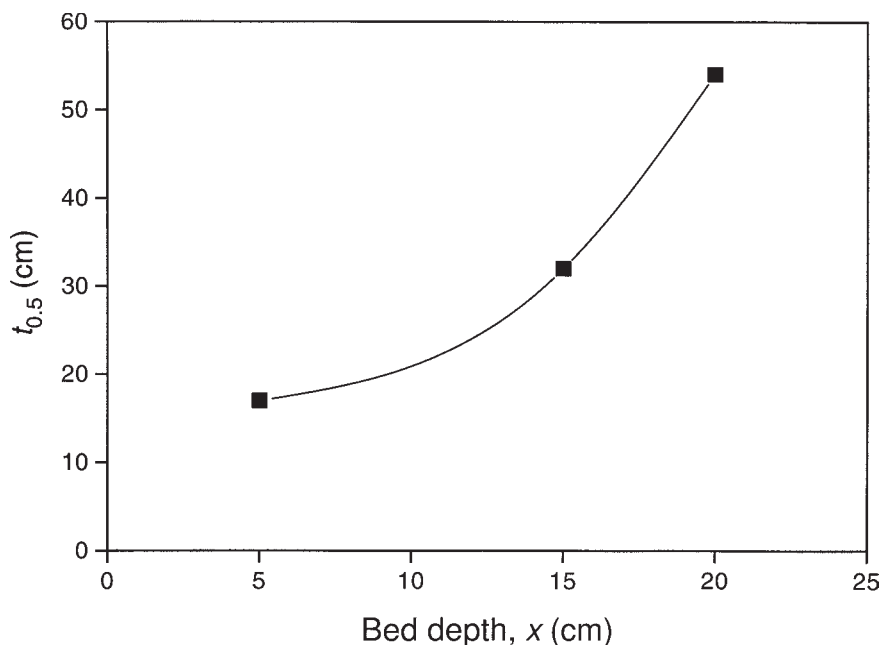


Fig. 7. Plot of bed depth vs service time at  $C_i/C_0 = 0.5$  breakthrough for Cr(VI)-QW column at a flow rate of 50 mL/min.

A plot of  $t_{1/2}$  vs  $x$  therefore yields a straight line where the slope represents the time required to exhaust a unit length of the fixed bed under test conditions. However, this is not seen in the Cr(VI)-QW system at a flow rate of 50 mL/min (Fig. 7). This deviation may be owing to the presence of more than one rate-limiting step in the sorption process, as suggested in earlier studies (22,23).

Figure 8 shows that for a bed depth of 7 cm, increasing the flow rate from 10 to 50 mL/min had very little effect on the breakthrough volume of the column, indicating that Cr(VI) was sorbed by the column to a similar degree at the flow rates investigated. This is owing to the rapid sorption of Cr(VI) on QW, as was shown in the batch studies. Thus, by choosing an appropriate combination of bed depth and flow rate, the process can be made to quite time-efficient.

### Cost Analysis

Although QW shows good potential in removing Cr(VI) over a wider range of pHs, the cost of preparation has yet to be determined. Laszlo (16) estimated that the chemical cost of quaternizing sugarcane bagasse would be two orders of magnitude less expensive than commercially available quaternized cellulose. This does not take into account processing and related costs, which would increase the price. A similar situation is likely to occur in our preparation. However, other factors such as durability of sorbents need to be addressed before a final assessment can be made and this is beyond the scope of our present study.

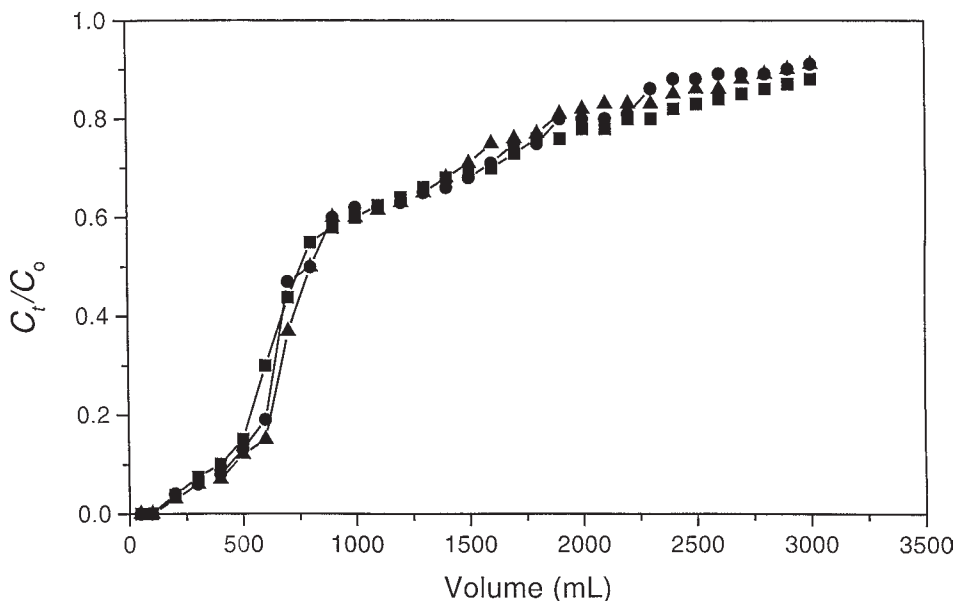


Fig. 8. Breakthrough curves of Cr(VI) at different flow rates. (■) 10, (●) 25, and (▲) 50 mL/min.

## Conclusion

The results show that QW, a low-cost material, is an efficient sorbent for the removal of Cr(VI) from aqueous solutions. It has a wider pH range in which sorption capacity remains constant than most of the other sorbents that had been investigated. The very rapid uptake is an advantage in its application in the continuous-flow system in which contact time between sorbent and sorbate is generally very short. Flow rate in the range of 10–50 mL/min had very little effect on the sorption of Cr(VI) on the column. However, the presence of other anions, such as  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , must be taken into consideration in the removal of Cr(VI) from industrial effluents because these anions do compete for sorption sites on QW. The full implication of the effect of these competing anions has yet to be assessed in detail. Such a study is currently being conducted.

## Acknowledgment

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