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Sorption of Cr(VI) on the wood of Japanese larch treated with concentrated sulfuric acid

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Abstract A carbonaceous sorbent was prepared from the wood of Japanese larch (*Larix leptolepis*) by dehydration with concentrated sulfuric acid in a 69% yield. The abilities of the sorbent to remove Cr(VI) from aqueous solutions were investigated. Research parameters included the initial solution pH, temperature, and initial concentration of Cr(VI) in solution. The removal of Cr(VI) was highly solution pH dependent and was mainly governed by physicochemical sorption under weak acidic conditions. The equilibrium data fit well in the Langmuir isotherm model. The Langmuir constants were calculated at different temperatures, and the sorption capacity increased with rising temperature, indicating the endothermic nature of the Cr(VI) sorption onto the sorbent. The desorption experiments suggest that the Cr(VI) sorption is generally irreversible, owing to strong interaction of HCrO_4^- with the active sites of the sorbent.

Key words Sorption of Cr(VI) · Langmuir isotherm · Japanese larch wood · *Larix leptolepis* · Dehydration with concentrated sulfuric acid

Introduction

Chromium compounds are widely used in various industries, including electroplating, metal finishing, leather tanning, dye and pigment preparations, textile, and wood preserving, and as a result they are often found in industrial wastewaters. Chromium occurs in natural water in two main oxidation states, Cr(III) and Cr(VI). Although Cr(III) is an essential nutrient in mammalian metabolism, its compounds at high concentrations are both acutely and chronically toxic. Cr(VI) is 500 times more toxic than the trivalent form.¹

The most commonly employed process for treating industrial wastewater containing Cr(VI) includes its reduction to the trivalent state by the addition of reducing agents followed by alkaline precipitation of $\text{Cr}(\text{OH})_3$. However, this process is only effective at high Cr concentrations² and requires large settling tanks for the precipitation of voluminous quantities of hydroxides and subsequent sludge treatment. Although ion exchange has also been widely used for the decontamination of industrial wastewaters containing heavy metals, the poor selectivity of ion exchange resins for chromate over other anions³ and its high capital and regeneration costs limit the practical use of synthetic ion exchangers. Recent attention has been focused on cost-effective sorbents for removing toxic heavy metals from contaminated wastewaters.^{4–6}

Carbonaceous materials prepared from lignocellulosic wastes such as coconut shell^{7,8} and sawdust⁹ have received great interest as an inexpensive sorbent for Cr(VI). Char yield from wood by pyrolysis is generally as low as 30%. However, Kim et al.¹⁰ reported that the yield of carbon from cotton cellulose by pyrolysis was greatly improved by the addition of sulfuric acid, which catalyzed dehydration of the substrate instead of unfavorable levoglucosan formation. Cox et al.¹¹ also reported that a carbon from flax shive using sulfuric acid had a good sorption affinity for removing heavy metals from aqueous solutions. In the present study, a carbonaceous sorbent was prepared from the wood of Japanese larch (*Larix leptolepis* Gold.) by dehydration with concentrated sulfuric acid. The ability of the sorbent to remove Cr(VI) from aqueous solutions was investigated. The parameters studied include initial solution pH, temperature, and initial concentration of Cr(VI) in solution.

Materials and methods

Sorbent

The wood of Japanese larch was ground in a Wiley mill to pass through a 1-mm screen. The ground wood meal (P42–R80 mesh fraction) was treated with concentrated H_2SO_4 .¹²

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The sorbent was prepared by mixing 1 part of the wood meal, 1.8 parts of concentrated H_2SO_4 , and 0.1 part of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and keeping it in an electric oven at 353 K for 16 h. The reaction mixture was soaked in distilled water, and the supernatant was neutralized with dilute NH_4OH to remove any residual acid. The solid residue was washed with distilled water, dried in an electric oven at 378 K overnight, and pulverized in a vibration mill to pass a 100-mesh screen. The yield and ash content of the sorbent were $69.02\% \pm 0.24\%$ and $0.50\% \pm 0.01\%$ (mean \pm standard deviation, $n = 5$, dry material basis), respectively.

Sorption experiments

The abilities of the sorbent to remove Cr(VI) from aqueous $\text{K}_2\text{Cr}_2\text{O}_7$ solutions were examined in batch mode conditions. Sorption experiments were conducted by agitating 60 mg of the sorbent with 30 cm^3 of the test solution containing 2 to 4.5 mM Cr in different stoppered bottles in a shaking thermostatic water bath. Preliminary runs showed that the sorption equilibrium could be attained within 72 h. The shaking speed used throughout the study, was $160\text{ strokes min}^{-1}$. The pH of the solution was adjusted to the desired values with 0.1 M H_2SO_4 or 0.1 M NH_4OH . The suspensions were then filtered off, and the residual Cr(VI) in the filtrate was determined by measuring absorbance of the purple complex of Cr(VI) with 1,5-diphenylcarbohydrazide at 540 nm with a Hitachi U-2810 spectrophotometer.¹³ The total Cr present in the solution was determined by oxidizing any Cr(III) formed with KMnO_4 followed by the same procedures described for the determination of Cr(VI). The sorption density was calculated by the difference between the initial concentration of Cr(VI) and the final concentration of total Cr in solution, while the difference between the final total Cr and Cr(VI) concentrations represented the Cr(III) concentration. All determinations were replicated five times and the means and standard deviations of analytical data were obtained.

Desorption experiments

The sorbent (3 g) was shaken with 1.5 dm^3 of a 5 mM $\text{K}_2\text{Cr}_2\text{O}_7$ solution (pH 2.5) at 298 K for 72 h. The suspension was filtered off, and the resulting solid residue was washed thoroughly with distilled water and dried in an electric oven at 378 K for 12 h. The Cr-laden sorbent (50 mg) was heated with a mixture of 30% H_2O_2 (10 cm^3) and concentrated sulfuric acid (2 cm^3) to afford a pale blue solution. The amount of total Cr in the resulting solution was determined by the same procedures described for the determination of total Cr. Total Cr content of the Cr-laden sorbent was $73.1 \pm 0.4\text{ mg Cr g}^{-1}$. The Cr-laden sorbent (30 mg) was soaked in 60 cm^3 of 0.1 M HCl or 1 M HCl at 298 K for 72 h. The resulting suspensions were filtered off, and the amounts of total Cr in the supernatants were determined by the same procedures described for the determination of total Cr.

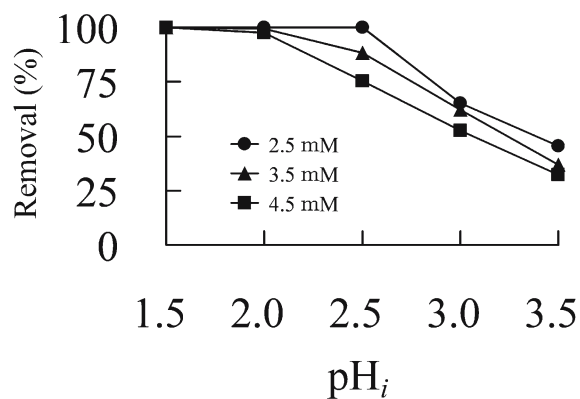


Fig. 1. Effect of initial pH of $\text{K}_2\text{Cr}_2\text{O}_7$ solution (pH_i) on the removal of Cr(VI) by the wood of Japanese larch treated with concentrated sulfuric acid

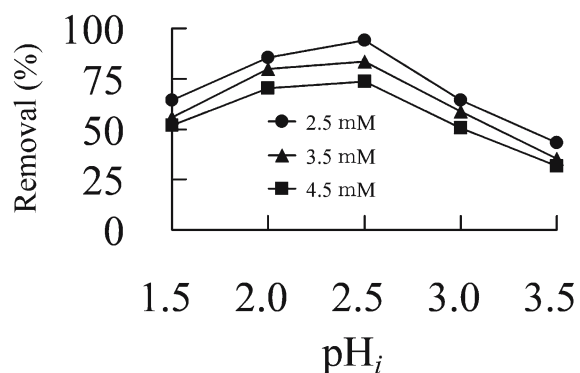


Fig. 2. Effect of initial pH of $\text{K}_2\text{Cr}_2\text{O}_7$ solution (pH_i) on the removal of total Cr by the wood of Japanese larch treated with concentrated sulfuric acid

Results and discussion

Effect of solution pH

Solution pH is an important factor for removing heavy metals from aqueous solution. The effect of solution pH on the ability of the sorbent to remove Cr(VI) from aqueous solutions was examined using acidic $\text{K}_2\text{Cr}_2\text{O}_7$ solutions. The initial pH of the solution varied from 1.5 to 3.5, because both the Cr(VI) sorption onto sphagnum moss peat and the chemical reduction of Cr(VI) to Cr(III) occur favorably in acidic media.¹⁴

Dependence of the removal of both Cr(VI) and total Cr on the initial pH of $\text{K}_2\text{Cr}_2\text{O}_7$ solution at 298 K is shown in Figs. 1 and 2, respectively. Figure 1 shows that the removal ratio of Cr(VI) is favored both by low initial solution pH values and low Cr(VI) concentrations. The removal of Cr(VI) decreased steadily with an increase in the solution pH from 2.0 to 3.5, while the removal of total Cr peaked at pH 2.5 (Fig. 2). The originally added Cr(VI) could be completely removed from $\text{K}_2\text{Cr}_2\text{O}_7$ solutions containing Cr(VI) up to 4.5 mM by the sorbent, when the initial pH of the solutions were 1.5. However, significant amounts of Cr

(36%–48%) still remained in the supernatants as Cr(III). The results indicate that the chemical reduction of Cr(VI) to Cr(III) occurs extensively below pH 2.

It is well known that chromic ions exhibit typical cationic sorption behavior.^{15,16} Low uptake of the Cr(III) formed at low pH may be caused by an increased ability of protons to compete with Cr(III) for the binding sites of the sorbent.¹² Further chromic ion species exist in acidic solution as bulky hydrated species such as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$,¹⁷ which has a molecular diameter of 0.922 nm.¹⁸ Chromic ion in aqueous solution is accessible only to pores larger than 1 nm. The value of the Brunauer-Emmet-Teller (BET) surface area of the sorbent ($2.3 \text{ m}^2 \text{ g}^{-1}$) suggests that the sorbent possesses negligible porosity. The result implies that surface of the sorbent may be inaccessible to bulky hydrated Cr(III) ions. Although the sorbent possesses negligible porosity, when the sorbent (60 mg) was contacted with an acidic $\text{K}_2\text{Cr}_2\text{O}_7$ solution containing 2.5 mM Cr (30 cm^3 , pH 2.5) at 298 K for 72 h, 94% of Cr present in the solution could be sorbed onto the sorbent. In contrast, untreated larch wood meal could capture only 19% of Cr from the solution under the same sorption conditions. Therefore, certain active sites for Cr(VI) sorption may be formed by the treatment of larch wood meal with concentrated sulfuric acid.

After 72 h of contact time, only small amounts of Cr(III) were detected in the supernatants (0.06–0.02 mM Cr) at higher initial solution pH values (pH \geq 3). In addition, the sorption of Cr(VI) increased with increasing equilibrium pH of the sorption system. This implies that the uptake of Cr(VI) by the sorbent may be responsible for the depletion of protons in the system.¹⁵ The speciation diagram for the Cr(VI) solution containing 2.5 mM Cr was calculated using the formation constants reported previously.¹⁹ As shown in Fig. 3, HCrO_4^- anions exist predominantly in acidic $\text{K}_2\text{Cr}_2\text{O}_7$ solutions (pH 2.0–3.5), suggesting that this anion species is taking part in the sorption process. The consumption of protons in the system is possibly explained by an exchange reaction with hydroxyl ions during sorption, which is shown in Eq. 1.^{14,20} Hydroxyl ions can be released by the reaction

of the oxo groups (C_xO) on the surface of the sorbent with water molecules. HCrO_4^- anions, dominant Cr(VI) species in solution, can bind with the positively charged surface of the sorbent. Hence, the removal of Cr(VI) by the sorbent may be mainly governed by physicochemical sorption in moderately acidic media (initial solution pH \geq 2.5).



Sorption isotherm

Sorption data are generally described by the Langmuir isotherm that represents one of the first theoretical treatments of nonlinear sorption. The Langmuir isotherm is given by Eq. 2:

$$C_e/q_e = 1/Q^0b + C_e/Q^0 \quad (2)$$

where C_e is the equilibrium concentration of the solution (mg dm^{-3}), q_e is the amount sorbed at equilibrium (mg g^{-1}), Q^0 (mg g^{-1}) and b ($\text{dm}^3 \text{ mg}^{-1}$) are the Langmuir constants related to sorption capacity and the energy of sorption, respectively. The linearized plots of C_e/q_e versus C_e for total Cr at different temperatures are shown in Fig. 4. The Langmuir constant Q^0 increased from 85.5 to 99.0 mg g^{-1} with increasing temperature from 288 to 308 K (Table 1), indicat-

Table 1. Langmuir constants and thermodynamic parameters

Temperature (K)	Langmuir constant			Thermodynamic parameter	
	Q^0 (mg g^{-1})	b ($\text{dm}^3 \text{ mg}^{-1}$)	r^2	K_0	ΔG^0 (kJ mol^{-1})
288	85.5	0.098	0.997	5.58	-4.12
293	88.5	0.133	0.999	6.38	-4.52
298	90.9	0.162	0.998	7.58	-5.02
303	95.2	0.288	0.999	8.85	-5.50
308	99.0	0.342	0.999	9.05	-5.64

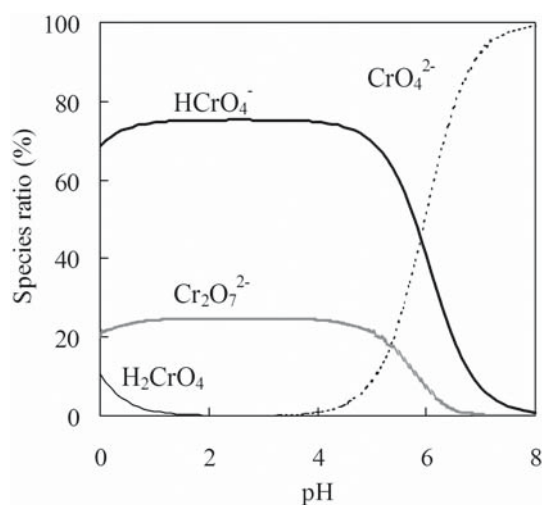


Fig. 3. Speciation diagram for Cr(VI) complexes present in an aqueous solution containing 2.5 mM Cr(VI)

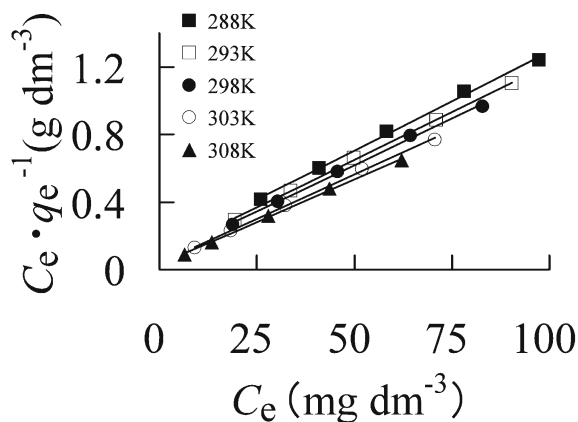
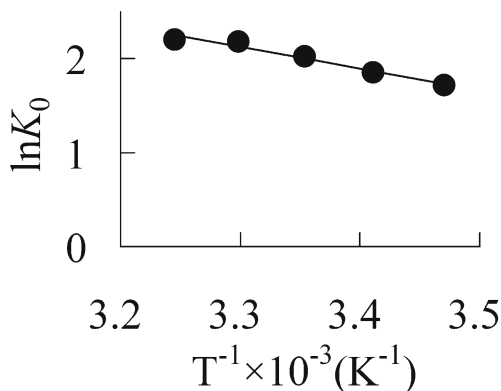


Fig. 4. Langmuir plots for the sorption of Cr(VI) on the wood of Japanese larch treated with concentrated sulfuric acid

Table 2. Sorption capacities of various carbonaceous sorbents

Sorbent	Langmuir constant Q^0 (mg g ⁻¹)	Solution pH	Cr(VI) concentration (mg dm ⁻³)	Reference
Larch wood treated with concentrated H ₂ SO ₄	90.9	2.5	156–260	Present study
Char from coconut shell	2.2	6.0	5–25	[27]
Activated carbon from hazelnut shell	170.0	1.0	1000	[26]
Activated carbon from coconut tree sawdust	3.5	3.0	5–20	[28]
Activated carbon from sawdust	2.2	2.0	100–1000	[9]
Sphagnum moss peat	119.0	2.0	10–1000	[14]
Activated carbon (Filtrisorb-400)	48.5	2.0	100–1000	[9]

**Fig. 5.** van't Hoff plot for the sorption of Cr(VI) on the wood of Japanese larch treated with concentrated sulfuric acid

ing that the process is endothermic. The increase in the sorption of Cr with rising temperature is explained by the thermodynamic parameters such as changes in Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0), which are determined using the following equations:

$$K_0 = C_s/C_e \quad (3)$$

where K_0 is the equilibrium constant and C_s and C_e are the equilibrium concentrations (mg dm⁻³) of the sorbate on the sorbent and in the solution, respectively^{21–23}

$$\Delta G^0 = -RT \ln K_0 \quad (4)$$

$$\ln K_0 = \Delta S^0/R - \Delta H^0/RT \quad (5)$$

where T is the temperature in Kelvin, and R is the universal gas constant (8.315 J mol⁻¹ K⁻¹). Thermodynamic equilibrium constants (K_0) for the sorption were obtained by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e .^{24,25} ΔH^0 and ΔS^0 were obtained from the slope and intercept of the van't Hoff plot of $\ln K_0$ versus T^{-1} (Fig. 5).

The ΔG^0 values at 288, 293, 298, 303, and 308 K were found to be -4.12 , -4.52 , -5.02 , -5.50 , and -5.64 kJ mol⁻¹, respectively, indicating the spontaneous nature of sorption. The positive value of ΔH^0 (19.2 kJ mol⁻¹) suggests the process to be endothermic. The positive value of ΔS^0 (80.9 J mol⁻¹ K⁻¹) shows the increased randomness at the

solid–solution interface during the sorption of HCrO₄⁻ onto the sorbent.^{22,24}

A comparison of the sorbent capacity with various carbonaceous sorbents studied in the literature is given in Table 2. The sorption capacity of *Larix leptolepis* wood meal treated with concentrated sulfuric acid for Cr(VI) compares favorably with those of other sorbents, except for activated carbon from hazelnut shell²⁶ and sphagnum moss peat.¹⁴

Desorption

Recovery of the sorbed metals and regeneration of the sorbent are important steps in treating wastewaters containing heavy metals. Studies have also been carried out for the desorption of Cr using dilute acids. Only 0.2% and 13.8% of sorbed Cr could be eluted by contact with 0.1 M HCl and 1 M HCl, respectively, at 298 K for 72 h. The result suggests that Cr(VI) sorption is generally irreversible, owing to strong interaction between HCrO₄⁻ and the surface active sites of the sorbent.

Conclusions

A carbonaceous sorbent was prepared from the wood of Japanese larch by dehydration with concentrated sulfuric acid in a 69% yield. The sorbent had high ability to remove Cr(VI) from aqueous systems. The removal of Cr(VI) was highly solution pH dependent and was mainly governed by physicochemical sorption under weak acidic conditions. However, extensive chemical reduction of the Cr(VI) species in solution to Cr(III) occurs at low solution pH (pH \leq 2.0). The sorption capacity increased with rising temperature, indicating the endothermic nature of the Cr(VI) sorption onto the sorbent. The desorption experiments suggest that the Cr(VI) sorption is generally irreversible, owing to strong interaction of HCrO₄⁻ with the surface active sites of the sorbent. Strong bonding between sorbate and sorbent does not make the regeneration of the exhausted sorbent economically viable. The waste sorbent can be disposed of without expensive regeneration. The recovery of Cr can be easily carried out by burning the exhausted sorbent followed by extraction with mineral acids.

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