Article

Adsorption and Separation of Hexavalent Chromium by Using Adsorption Gel Prepared from Grape Residue

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Abstract

Residue of grape generated during the wine production process consists of large amount of polyphenolic compounds which strongly bind heavy metal ions. An adsorption gel was prepared from such grape residue by cross linking with concentrated sulfuric acid. The adsorption behavior of the gel was investigated for Cr(III, IV) and Fe(III). The gel was found to adsorb Cr(VI) selectively over other metals. The maximum adsorption capacity of the gel for Cr(VI) was 4.72 mol/kg.

Key words: polyphenolic compounds, adsorption, hexavalent chromium

1 Introduction

The wastewater from industry contains heavy metals like lead, chromium, cadmium, copper and zinc. These heavy metals have an unfavorable effect on the environment and human health. Therefore, the emission standards of these metals are strictly regulated implying that the concentration of the heavy metals in the waste should be below these standards. However, sometimes, the concentration of heavy metals in soil and ground water are detected to be above the standards.

The treatment of heavy metals is performed with various methods such as aggregation, precipitation, membrane separation and ion-exchange. Membrane and ion-exchange resin treatments generally incur very high cost whereas aggregation method is not possible in case of low concentration of metal ions. Precipitation by metal hydroxide formation is relatively useful due to the ease of operation and low cost. However, since it produces a large amount of sludge, an alternative method of the heavy metal treatment is required which is not only environment friendly but also economically feasible. From this point of view, heavy metal adsorbents prepared from biomass wastes such as grape residue [1], apple residue [2], orange residue [3], and rice husk [4] were reported.

The grape residue is a kind of the biomass wastes produced after wine production. The grape residue contains a large amount of polyphenolic groups. The hydroxyl group of the polyphenol is known to have an affinity to the heavy metal ions. [5-7] With a view to utilize this biomass waste for the sustainable society, in the present study, we report on the adsorption of the heavy metals, especially hexavalent chromium on the gel prepared from grape residue whose polyphenolic groups have been prevented from leakage by cross linking.

2 Experimental

2.1 Preparation of the adsorbent

The lyophilized grape peel (45.3 g) was crushed with a mixer. The material was stirred in the concentrated sulfuric acid (60 cm^3) at 383 K for 24 h to cross-link the polyphenol in the grape peel. The resulting compound was neutralized with sodium hydrogen carbonate solution, filtered and stirred again in 1 mol/dm^3 HCl solution. After stirring, the product was filtered and washed with distilled water to remove excess acid, and washed with hot water at 323 K. It was then dried overnight in an oven at 333 K and its particle diameter was regulated with a sieve of 100 – 150 μm.

2.2 Metal adsorption on the cross-linked grape peel

Cross-linked grape peel (10 mg) was added to the 10 cm^3 metal solution (0.5 mmol/dm^3) and stirred at 303 K for a prescribed time. The pH was adjusted with 0.1 mol/dm^3 HEPES solution and 0.1 mol/dm^3 HCl solution. After adsorption, the adsorbent was removed by filtration and the concentration of the metal ion was measured by ICP-AES spectrometer (Shimadzu ICPS-8100). The concentration of Cr(VI) was measured by diphenyl carbazide method using UV spectophotometer (U-3310 Hitachi Co. Ltd.) The adsorption percentage and the amount of the metal adsorbed were calculated as follows:

$$\text{Adsorption \%} = 100\,(C_i - C_e)\,/\,C_i \qquad 1)$$

$$\text{Amount of metal adsorbed [mol/kg]} = (C_i - C_e)\,V\,/\,W \qquad 2)$$

where C_i [mmol/dm^3], C_e [mmol/dm^3], W [g], and V [dm^3] were the metal concentration before equilibrium, the metal concentration after equilibrium, the amount of the adsorbent and, the solution volume respectively.

3 Results and Discussion

3.1 Effect of pH

Figure 1 shows the effect of pH on the adsorption of metal ion on grape residue gel. The adsorbent showed high selectivity to Cr(VI) at pH <4. For Cr(III) and Fe(III), the adsorption % increased with increasing pH, demonstrating that these metals were adsorbed by the gel via a competitive reaction between proton and the metal ion. For Cr(VI), the adsorption % was optimal at pH 4. Above pH 4, the adsorption % of Cr(VI) decreased due to gradually increasing concentration of OH^-. On the other hand, below pH 4, Cr(VI) is reduced to Cr(III), decreasing the adsorption %. The adsorption mechanism of

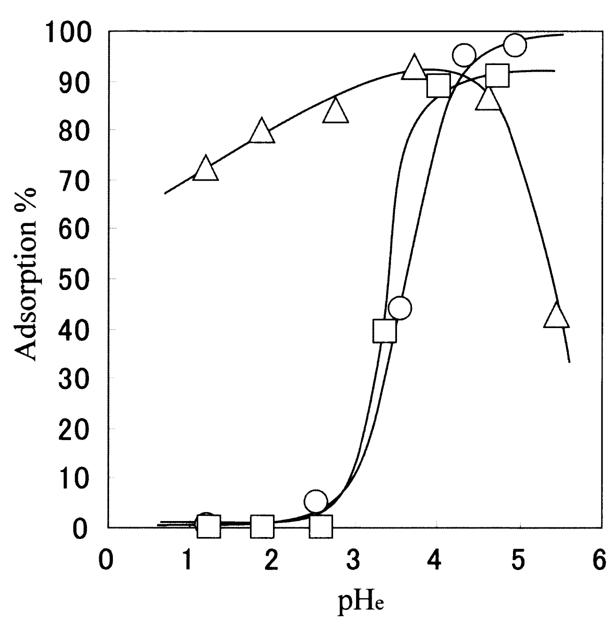
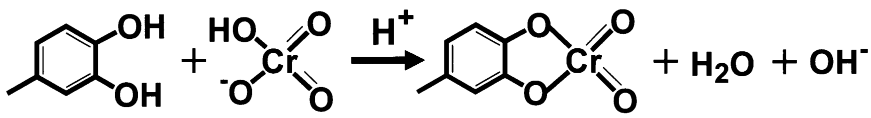


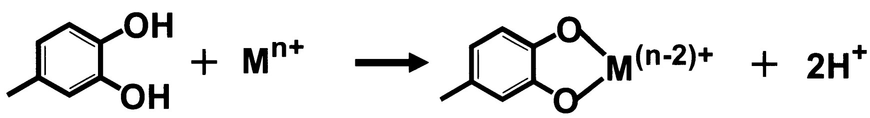
Fig.1 Effect of pH on the adsorption of metal ions on the grape residue gel. [○:Cr(Ⅲ), △:Cr(Ⅵ), □:Fe(Ⅲ)]

Cr(VI) was different from the other metals possibly due to the following reason (Scheme 1): Cr(VI) forms a complex with the cathecol in polyphenol compounds by the esterification reaction [5], whereas the other metals are adsorbed via ion-exchange reaction [8, 9].

(a) esterification reaction



(b) ion exchange reaction



Scheme 1 Adsorption mechanism of (a) chromium(VI) and (b) other metals binding to catechol group in the grape residue.

3.2 Adsorption kinetic

Figure 2 shows the time variation curves of Cr(VI) adsorption onto the gel with varying pH. At low pH region, adsorption of Cr (VI) reached equilibrium quickly, and then it slightly decreased, which demonstrates that either Cr(VI) was eluted from the gel or it was reduced to Cr(III) by the gel. Figure 3 shows the time dependence of Cr(VI) and Cr(III) in the solution at pH 1.93. Along with the adsorption of Cr(VI) onto the gel, Cr(VI) that remained in the solution was changed to Cr(III). At lower pH, the reduction rate of Cr(VI) increased, however, above pH 3, the reduction was not observed. Hence, the concentration of proton was found to be the dominant factor for the adsorption and the reduction of Cr(VI) rather than the esterification reaction.

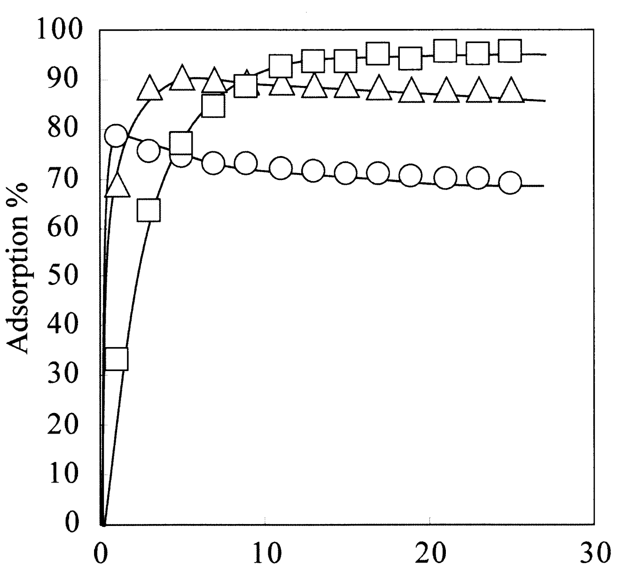


Fig.2 Adsorption rate of chromium(Ⅵ) on grape residue gel. [○:pH1.03, △pH1.93, □:pH3.03]

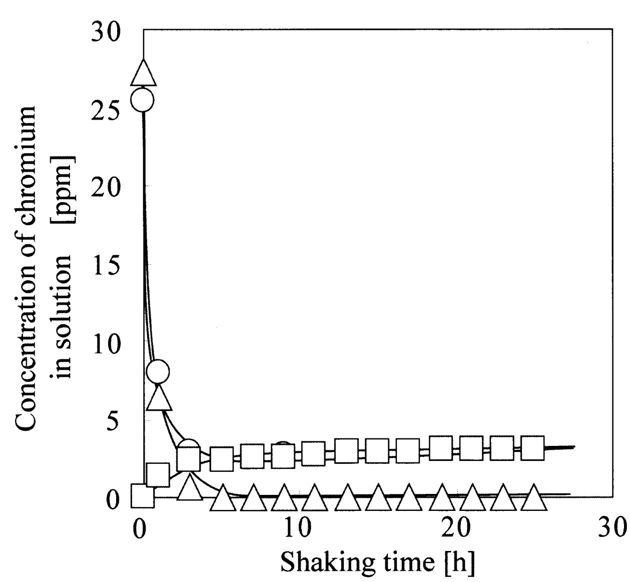


Fig.3 Concentration in solution of total Cr, chromium(Ⅵ) and chromium(Ⅲ) at the pH=1.93 [○:Total Cr, △chromium(Ⅵ), □:chromium(Ⅲ)]

3.3 Adsorption isotherm

Figure 4 shows the isotherm curve for the adsorption of Cr(VI) onto the gel at different pH values. With increasing pH, the amount of Cr(VI) decreased, demonstrating that the concentration of proton highly influences the adsorption process i.e., the change of chromic acid to bi-chromic acid occurs at high concentration of proton leading to the higher amount of chromium adsorption. Because the isotherm curves were apparently Langmuir adsorption type, the curves were fitted to the Langmuir plots as shown in Fig. 4 (b). From the plots, the maximum adsorption capacity of the gel for Cr(VI) at pH 1.05, 2.02 and 3.03 were evaluated as 4.72, 3.60 and 1.93 mol/kg, respectively. At pH <3, Cr(VI) is easily reduced to Cr(III) which is difficult to be adsorbed on the gel. However, at pH $\geqq 3$, since no such reduction occurs, the maximum adsorption capacity of the gel is constant regardless of pH. The maximum adsorption capacities for the other metal ions are summarized in Table 1. Compared to the adsorption of other metal ions, this adsorbent exhibits a higher affinity to Cr(VI). Table 2 summaries the saturated adsorption capacities of the other adsorbents compared to this gel, which shows that the polyphenol-containing adsorbents such as Mimosa tannin (condensed tannin) [5] and persimmon tannin [6] showed higher adsorption capacities than other biomasses such as sugarcane bagasse [10] and chitosan[11,12]. The grape residue gel containing the polyphenolic groups also demonstrated a high adsorption capacity for Cr(VI) comparable to those of other tannin containing gels. However, compared to other gels, the preparation process of the grape residue gel is simple and economical and it does not produce a large amount of effluent or terrible smell like that during production of chitosan. Therefore, utilizing this biomass for the preparation of a more sophisticated adsorbent for Cr(VI) ion looks highly promising for environmental remediation.

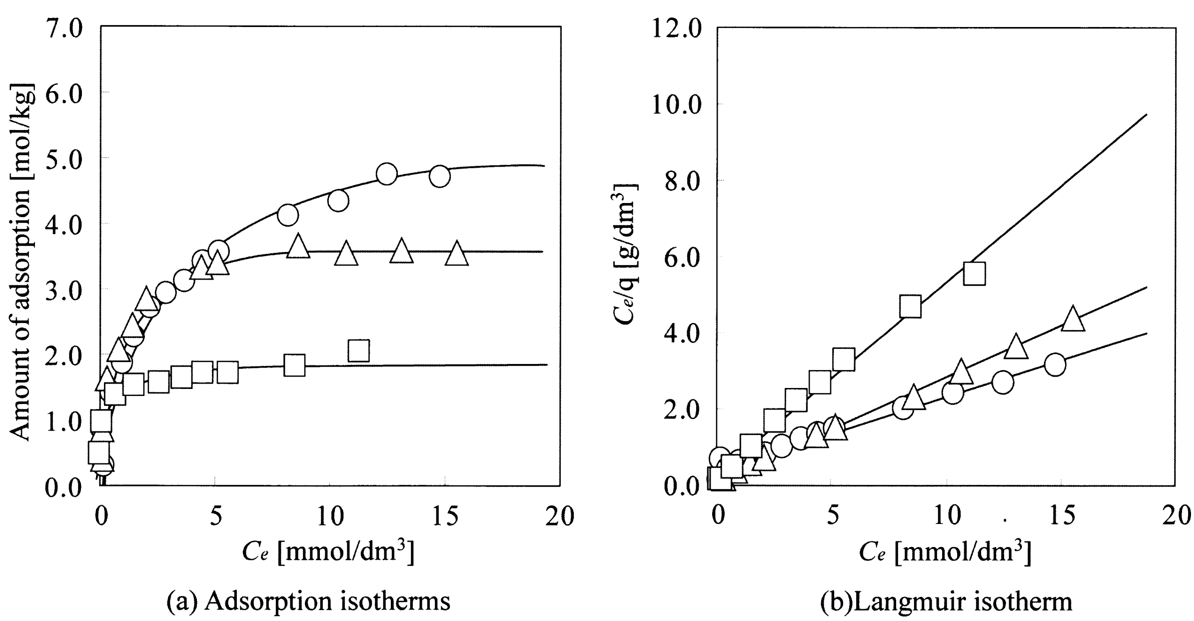


Fig.4 (a) Adsorption isotherms of metal ions by the grape residue gel. (b) Langmuir isotherm of chromium(Ⅵ) [○:pH1.05, △pH2.02, □:pH3.03]

Table 1 The maximum adsorption capacity for the other metals.

Metal	Optimum pH	Adsorption capacity [mol/kg]
Cr(III)	4.23	1.38
Cr(VI)	1.05	4.72
	2.02	3.60
	3.03	1.93
Fe(III)	4.09	0.78

Table 2 Comparison of the maximum adsorption capacity for Cr(VI) on different adsorbents.

Adsorbent	pH	Temperature (℃)	Adsorption capacity [mol/kg]	Reference
Mimosa tannin	2.0	30	5.52	Y.Nakano et al. [5]
Persimmon tannin	3.0	30	5.27	A.Nakajima et al. [6]
Sugarcane bagasse	3.0	25	1.97	L.H.Wartelle et al. [10]
Quaternary chitosan salt	4.5	25	1.31	V.A.Spinelli et al. [11]
Cross-linking chitosan	5.5	25	1.01	T.Tan et al. [12]
Grape residue gel	1.1	30	4.72	This work

3.4 Elution test

Figure 5 shows the elution % of Cr(VI) by acid (HCl or H_2SO_4) treatment at various concentrations. At 3 mol/dm^3, the elution % was only about 60%by H_2SO_4, revealing that complete elution with acid treatment was difficult due to a very strong complex of Cr(VI) with polyphenols. The other possible methods for Cr(VI) recovery are the alkali treatment and the incineration which are further to be investigated in our study.

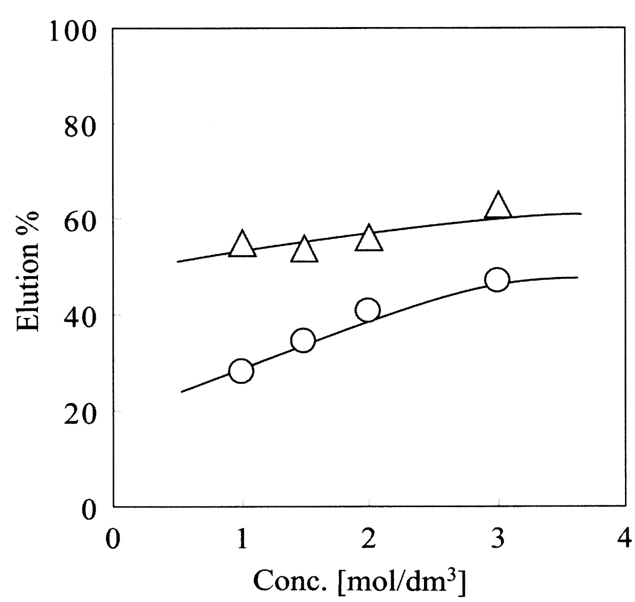


Fig.5 Elution of chromium adsorbed on the grape residue gel. [○:HCl, △:H_2SO_4]

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