

Adsorption of Chromium(VI) on Mesoporous Alumina

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ABSTRACT

Adsorption of Cr(VI) was investigated, employing mesoporous alumina (MA) as an adsorbent. The MA of γ -structure, having narrow pore size distribution of around 5.2 nm, was synthesized by hydrothermal synthesis method. The isoelectric point of the MA was $\text{pH} = 7.2$. The MA could thus adsorb anionic species of Cr(VI), $\text{Cr}_2\text{O}_7^{2-}$, and HCrO_4^- , in aqueous solution at acidic pH region. The adsorption of Cr(VI) at $\text{pH} < 4.2$ was decreased due to dissolution of the MA. The adsorption of Cr(VI) with MA is progressed by Langmuir mechanism with the maximum adsorption amount of 0.599 mmol/g and adsorption constant of 8.93 L/mmol at equilibrium $\text{pH} = 4.51$. Effective elution of the Cr(VI) loaded on the MA was achieved by weak alkaline solution of $\text{pH} \approx 9$.

Keywords: Adsorption; Chromium(VI); Mesoporous alumina

INTRODUCTION

Water pollution is one of the great concerns along with the advancement of chemical industries. Among the metals, Cr(VI) is one of the most toxic pollutants of the water environment, owing to its strong oxidizing ability, and its recovery from the water environment is therefore important from industrial waste solutions. There are several reports on the removal of Cr(VI), such as precipitation¹, solvent extraction^{2,3}, and adsorption/ion exchange⁴⁻⁷. Among the techniques, adsorption is most feasible due to advantages of easy process and high efficiency.

Alumina, especially having γ -structure, has been widely investigated as an adsorbent for pollutants in aqueous solution^{8,9}. The γ -alumina possesses high adsorption ability for the anionic species, such as As(V), Se(VI), and F^- , since the hydroxyl groups on the surface of γ -alumina becomes $-\text{OH}_2^+$ in acidic solution¹⁰. Several drawbacks of the γ -alumina are however pointed out, such as low adsorption capacity and slow kinetics owing to irregular pore. Recently, mesoporous alumina (MA) is thus paid attention as an adsorbent, due to its uniform pore size distribution and large surface area. There are several reports concerning the adsorption of As^{11-13} and phosphate¹⁴ with the MA, and concluded the MA possesses higher adsorption capacity and kinetics than conventional γ -alumina. The MA is

therefore expected to possess high adsorption ability for the removal of Cr(VI), since Cr(VI) mainly exists as anionic species¹⁵.

In the present work, the adsorption of Cr(VI) with the MA was investigated. MA was first synthesized by employing nonionic triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as a structure-directing agent and aluminum tri-isopropoxide as an aluminum source¹². The MA was characterized by X-ray diffraction (XRD), nitrogen gas adsorption, and zeta potential. The MA was then applied for the adsorption of Cr(VI), and the effect of pH on the adsorption, adsorption isotherm, and elution of Cr(VI) from the adsorbent were investigated.

EXPERIMENTAL

Reagents.

Nonionic triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and aluminum tri-isopropoxide (AIP) were supplied by Sigma-Aldrich (Tokyo, Japan). Commercial γ -alumina was supplied by Soekawa Chemicals (Tokyo, Japan). All other reagents used were supplied by Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

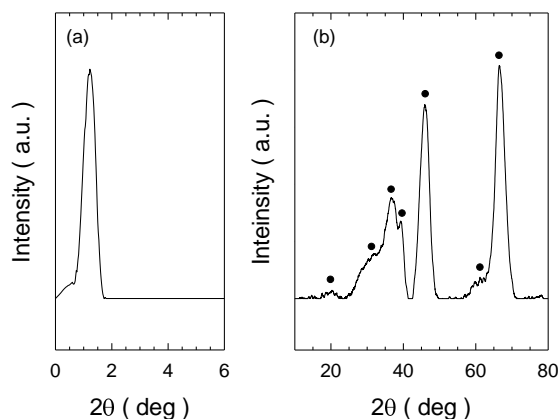


Figure 1 (a) Low and (b) wide angle XRD patterns of MA. ●: peaks for γ -alumina based on JCPDS #10-0425.

Synthesis and Characterization of Mesoporous Alumina (MA).

MA was synthesized employing $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ and AIP similar to a previously reported¹². AIP (20.4 g) and 0.1 mol/L nitric acid (3 mL) were added to deionized water (160 mL), and the mixture was stirred at 40°C for 2 h to obtain aluminum hydroxide sol. Simultaneously, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (7.5 g) and 12 mol/L hydrochloric acid (20 mL) were added to deionized water (150 mL), and the mixture was stirred at room temperature for 2 h to obtain template solution. The template solution was then added into the aluminum hydroxide sol, and the mixture was shaken at 40°C for 12 h. During the shaking, the pH of the mixture was kept at ca. 7 by adding 10 mol/L sodium hydroxide solution. The mixture was then aged for 36 h at room temperature. Precipitates obtained were then filtered, and were washed with the mixture of deionized water and ethanol. After drying at 105°C for 24 h, the product was calcined at 400°C for 5 h.

The MA obtained was characterized by X-ray diffraction (XRD, 40 kV and 30 mA, $\text{CuK}\alpha$, Shimadzu XRD-6100), nitrogen gas adsorption (Bell Japan BELSORP-mini II), zeta potential (Otsuka Electronics ELSZ-1000).

Adsorption of Cr(VI).

Cr(VI) aqueous solution was prepared by dissolving sodium chromate tetrahydrate in deionized water, and the pH value was adjusted by adding hydrochloric acid solution or sodium hydroxide solution. The batch adsorption of Cr(VI) was carried out by contacting 0.1 g of MA or commercial γ -alumina and 10 mL of Cr(VI) aqueous solution. The suspended mixture was

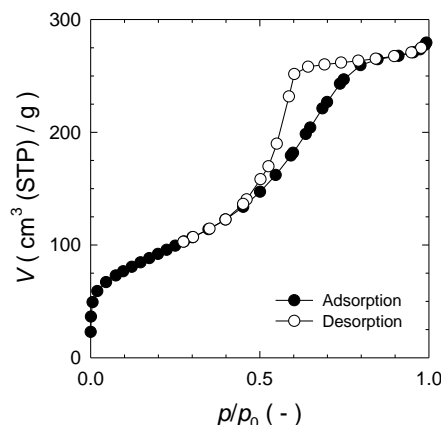


Figure 2. Adsorption and desorption isotherm of nitrogen for MA.

shaken at 25°C for 24 h. The feed concentration of Cr(VI) was set to 10 mmol/L in the case of effect of pH on the adsorption amount of Cr(VI) with MA and varied from 0.49 – 29.0 mmol/L in the case of adsorption isotherm of chromium(VI) with MA. The concentration of Cr(VI) was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000). The pH of the aqueous solution was measured with a pH meter (Horiba F-23). The adsorption amount of Cr(VI) (q) was calculated by:

$$q = \frac{([\text{Cr(VI)}]_{\text{feed}} - [\text{Cr(VI)}]) \cdot V}{w} \quad (1)$$

where $[\text{Cr(VI)}]_{\text{feed}}$ and $[\text{Cr(VI)}]$ are initial and equilibrium concentrations of Cr(VI), V is the volume of aqueous solution, and w is the weight of MA. Dissolution of aluminum from MA was determined by material balance based on the Al concentration in the aqueous solution, which was determined by ICP-AES (Shimadzu ICPE-9000), after batch adsorption.

Elution of Cr(VI) loaded on the MA was also investigated. In this case, adsorption of Cr(VI) was first carried out, and then 0.02 g of MA loaded by Cr(VI) was contacted with 10 mL of sodium hydroxide solution (0.001 mol/L – 0.1 mol/L), and the suspension was shaken at 25°C for 24 h. The suspension was then filtered, and the concentrations of Cr(VI) and Al were determined by ICP-AES.

RESULTS AND DISCUSSION

Characterization of MA.

MA was characterized with XRD. Figure 1 shows XRD patterns for the MA. Comparing the

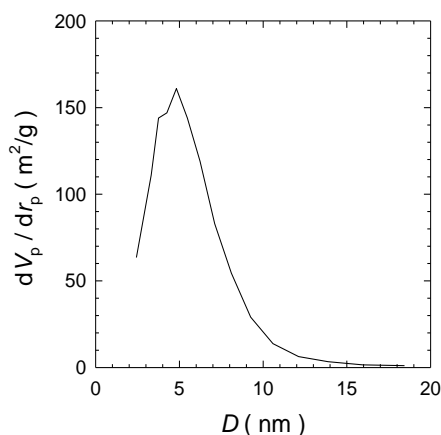


Figure 3. Pore size distribution of MA.

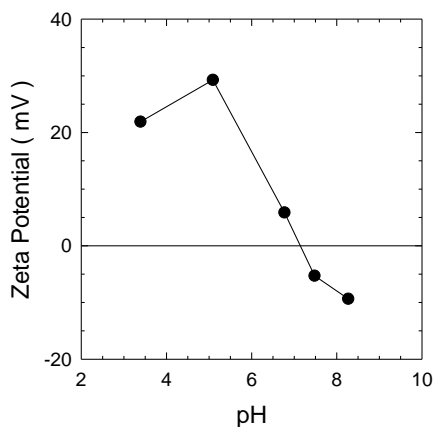


Figure 4. Effect of pH on the zeta potential of MA.

XRD pattern in wide angle, shown in Figure 1b, with the database (JCPDS #10-0425) shows that the γ -alumina could be obtained by the hydrothermal synthesis procedure. In addition, a single diffraction peak was observed in 2θ region below 2° , as shown in Figure 1b, indicating mesostructure was successfully formed^{12,16}. Figure 2 shows nitrogen gas adsorption isotherms of the MA. Hysteresis loop was seen at relative pressure of ca. 0.5 – 0.8, which also confirms the synthesized MA possesses mesopores. The pore distribution of the MA, determined by BJH method, revealed that the MA possess narrow pore size distribution around in 5.2 nm, as shown in Figure 3. Surface area, pore size, and pore volume of the MA determined by BET method are 330 m²/g, 5.2 nm, and 0.43 m³/g, respectively, which are similar values with the data previously reported¹². Figure 4 shows the zeta potentials of the MA in aqueous solutions at various pH values.

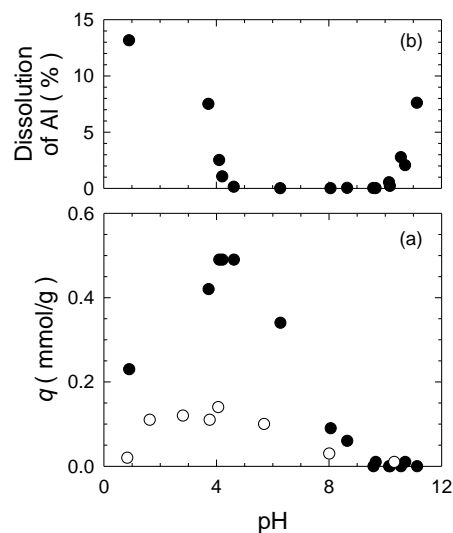


Figure 5. Effect of equilibrium pH on (a) the adsorption amount of Cr(VI) with MA and commercial γ -alumina and (b) dissolution of aluminum from MA. ●: MA, ○ commercial γ -alumina.

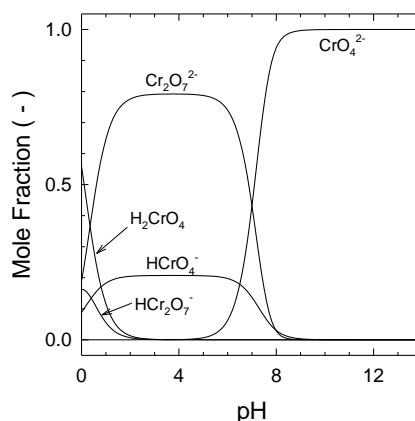


Figure 6. Mole fraction of Cr(VI) in aqueous solution.

The zeta potential of MA decreased with pH, and the isoelectric point was observed at pH = 7.2.

Adsorption of Cr(VI).

The MA was then applied for the adsorption of Cr(VI). Figure 5 shows the effect of pH on the adsorption amount of Cr(VI) with the MA synthesized and commercial γ -alumina, together with the dissolution of Al from the MA. The MA could adsorb Cr(VI) and the adsorption ability was higher than that with the commercial γ -alumina. The adsorption of Cr(VI) increased with increasing pH up to pH 4.6, and then the adsorption amount decreased. Figure 6 shows the

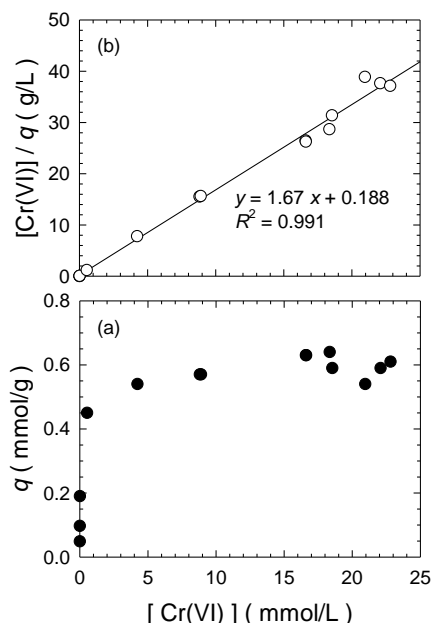
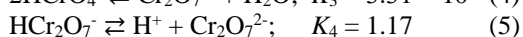
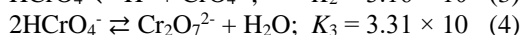
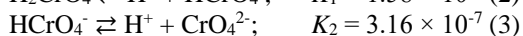
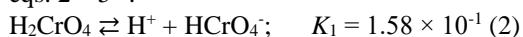


Figure 7. (a) Adsorption isotherm of Cr(VI) with MA at equilibrium pH = 4.51 ± 0.07 , and (b) linearized Langmuir plots of the adsorption isotherm.

effect of the pH value on the mole fraction of the differing species Cr(VI) in an aqueous solution, as calculated using the equilibrium constants from eqs. 2 – 5¹⁵.



The Cr(VI) mainly exists as $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- in the acidic solution, while surface charge of the SMA is positive at pH < 7.2. These results indicate that the change in the relative concentrations of the Cr(VI) species in the aqueous solution affects the adsorption ability with MA, and $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- are considered to be adsorbed. Decrease in the adsorption amount of Cr(VI) at pH < 4.2 is considered to be due to dissolution of MA.

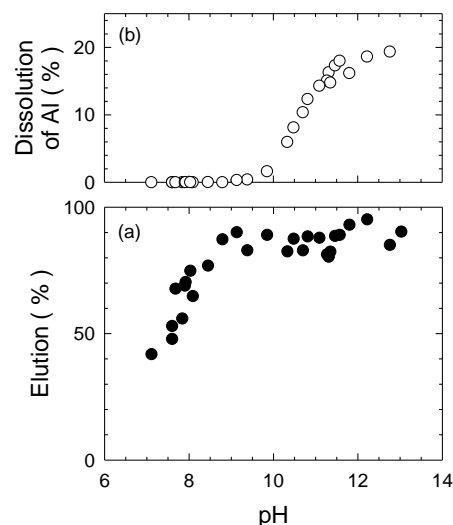


Figure 8. Effect of equilibrium pH on (a) the elution yield of Cr(VI), and (b) dissolution of aluminum from MA during the elution.

Adsorption isotherm of Cr(VI) with MA at equilibrium pH = 4.51 ± 0.07 is shown in Figure 7a. The adsorption isotherm of Cr(VI) with MA fits well with the linear relationship of the Langmuir adsorption mechanism, as shown in Figure 7b. The maximum adsorption amount (q_{\max}) and adsorption constant (K) of Cr(VI) with MA obtained from the Langmuir adsorption isotherm are $q_{\max} = 0.599$ mmol/g and $K = 8.93$ L/mmol, respectively. The constants obtained are also summarized in Table I, together with those of other inorganic adsorbents previously reported^{17,18}, although pH values applied for adsorption isotherms were different. The MA prepared in the present work possesses higher adsorption capacity than other inorganic adsorbents, while the adsorption constants are competitive values.

Table I. Comparison of maximum adsorption amount (q_{\max}) and adsorption constants (K).

Adsorbent	pH	q_{\max} (mmol/g)	K (L/mmol)	Ref.
MA	4.51	0.599	8.93	Present work
Hematite	8.0	0.0442	20.2	[17]
Goethite	8.0	0.0376	13.6	[17]
α -Alumina	8.0	0.0415	9.46	[17]
Activated alumina	3.0	0.492	5.93	[18]
Fly ash	3.0	0.459	2.24	[18]

Elution of Cr(VI).

Elution of Cr(VI) from the MA loaded was investigated. Alkaline solution is considered to be suitable for the elution of Cr(VI), based on the adsorption behavior shown in Figure 3. Figure 8 shows the effect of pH on the elution yield of Cr(VI), together with dissolution of aluminum during the elution. High elution yield of Cr(VI) was obtained at $\text{pH} > 8.8$, which is corresponded to the adsorption behavior. Since dissolution of Al was however progressed in $\text{pH} > 9.8$, the suitable pH for elution is considered around pH 9.

CONCLUSIONS

We described adsorption of Cr(VI) with MA. The important features are summarized as follows. MA having narrow pore size distribution around 5.2 nm could successfully prepared by a hydrothermal synthesis method employing nonionic triblock copolymer as a structure-directing agent and aluminum tri-isopropoxide as an aluminum source. The MA possesses higher adsorption ability for Cr(VI) than the commercial γ -alumina. The Cr(VI) species, $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- , are the possible species adsorbed on the MA. The adsorption of Cr(VI) is progressed via Langmuir mechanism. Effective elution of Cr(VI) was achieved with weak alkaline solution of $\text{pH} \approx 9$.

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