FULL PAPER

Sorption capacity of Cs⁺ on titania nanotubes synthesized by solution processing

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Titania nanotubes (TNTs) have nanometer-sized tubular morphologies with layered structures. TNTs are candidate sorbents for the removal of many heavy metals and radionuclides. In this study, we investigated the Cs⁺ sorption capacity of TNTs synthesized by a solution chemical method in comparison with those of zeolite and TiO₂ particles. The TNT powder was shaken in 0.2–4.0 mM CsCl aqueous solution at 10, 25, and 40°C for up to 7 days. The sorption tests showed that the sorption density of Cs⁺ per gram of TNT was lower than that of zeolite. TiO₂ did not show Cs⁺ adsorption. The sorption isotherm of Cs⁺ on TNTs was fitted with the Langmuir model. The sorption of Cs⁺ on zeolite was well described with the Freundlich model. The TNT structure was maintained after sorption testing regardless of the concentration of CsCl aqueous solution. Elemental analysis of the TNTs showed uniformly adsorbed Cs⁺ throughout the TNTs. Na⁺ was also detected in the TNTs both before and after sorption, but the residual Na⁺ concentration decreased with increasing the adsorbed Cs⁺ concentration. These results clearly showed that the Cs⁺ was intercalated into the layered structures of the TNTs by ion-exchange with Na⁺.

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1. Introduction

Many heavy metals and radionuclides are released to the atmosphere, groundwater, and soil via industrial activity and natural disasters. These contaminants can cause serious health and environmental problems. The development of remediation materials is important in order to solve these problems. To remove heavy metals and radionuclides, titania of various crystal structures has been studied as an inorganic ion-exchanger. Among these materials, two-dimensional layered titanates, which show intercalation with interlayer cations, have been investigated using various cations as model sorbents for environmental remediation.^{1)–3)} In 1998, Kasuga et al. reported the synthesis of nanotubular TiO₂ (TiO₂ nanotubes, TNTs) by a simple solution process.^{4),5)} TNTs are a variety of titanate with a unique crystal structure. TNTs possess nanoscale tubular morphologies with inner and outer diameters of 5–7 and 8–10 nm, respectively. The unique structure of TNTs is expected to have significant advantages in environmental remediation. Many researchers have previously investi-

gated the synthesis and photocatalytic properties of TNTs synthesized by solution chemical processing, following Kasuga's proposed method.^{6)–8)} In addition, we reported the photochemical properties and photocatalytic functions of TNT-based materials synthesized by solution chemical processing.^{9)–11)} Also, TNTs show the high adsorption property of cationic molecule (methylene blue).¹¹⁾ Many researchers have investigated the adsorption or ion-exchange properties of TNTs, like the layered titanate compounds described above, with metal ions such as Pb²⁺, Cd²⁺, Cu²⁺, Li⁺, Cs⁺, and Ni²⁺.^{12)–19)} Na⁺ and H⁺ in the layered TNT structure can be exchanged with various cations. In addition, previous reports have described the main adsorption mechanism as an ion-exchange reaction; researchers have discussed the effects of pH, ionic strength, coexisting ion species, and crystal structure on adsorption behavior. Adsorption behavior remains a topic of study because the elucidation of the reaction mechanism is necessary in order to improve the adsorption capacity.

In the present study, we investigated the Cs⁺ sorption capacity of TNTs from solution in simple batch conditions. Cs⁺ was selected as a model target cation for the adsorption reaction. The sorption model and sorption density of Cs⁺ on TNT were investigated and compared with those of other sorbents or the results of previous reports regarding cation removal. Changes in the amount of Na⁺ in the

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TNTs were also discussed to investigate the ion-exchange reaction with Cs⁺ as the adsorption mechanism.

2. Material and methods

2.1 Synthesis of TNT by chemical solution method

TNTs were prepared using the reflux of an alkaline solution, similar to the method described by Kasuga et al.^{(4),(5)} TiO₂ nanoparticles (P25, Degussa, NIPPON AEROSIL Co., Ltd., Japan) (2.0 g) were added to 10-M sodium hydroxide (NaOH, Wako Pure Chemical Industries, Ltd., Osaka, Japan), and the suspension was stirred at 110°C under reflux conditions. The product was washed using ultrapure water to reach a conductivity of <5 μS/cm, washed in ethanol, and separated via filtration before freeze-drying.

2.2 Cs⁺ sorption test

A Cs⁺ aqueous solution of 0.2–4.0 mM was prepared using cesium chloride (CsCl, Wako Pure Chemical Industries, Ltd., Osaka, Japan) with a pH of ~5 (no adjustment). For the sorption test, synthesized TNTs, P25 (TiO₂ nanoparticles), and type X zeolite (Na₂O·Al₂O₃·2.5SiO₂, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as sorbents (**Fig. 1**). Sorbents (0.01 g) were placed in plastic tubes to which 20 mL of CsCl solutions at various concentrations were added. The tubes were shaken at a constant speed of 150 rpm in a mechanical shaker (Bio Shaker, BR-43FL, TAITEC CORPORATION, Saitama,

Japan), at 10, 25, and 40°C for up to 7 days. Afterward, the sorbent and solution were separated by filtration, and the sorbents were freeze-dried to obtain powder samples.

2.3 Theoretical analysis

The Cs concentration of the solution after sorption testing was analyzed by atomic absorption spectrometry (AAS, AAnalyst 800, PerkinElmer Inc., Massachusetts, USA). The sorption results of Cs were fitted using the Langmuir equation:

$$\frac{C_{eq}}{Q} = \frac{1}{Q_{max}K} + \frac{C_{eq}}{Q_{max}} \quad (1)$$

where Q is the amount of adsorbed Cs per gram (mmol/g), C_{eq} is the equilibrium concentration of Cs (mmol/L), Q_{max} is the maximum adsorbed Cs (mmol/g), and K is a constant related to the adsorption rate coefficient. The sorption isotherm of Cs was also fitted to the Freundlich equation:

$$Q = K_F C_{eq}^{1/n} \quad (2)$$

where Q is the amount of adsorbed Cs per gram (mmol/g), C_{eq} is the equilibrium concentration of Cs (mmol/L), and K_F and n are the Freundlich constants corresponding to adsorption capacity and adsorption intensity. As in other reports, by assuming that the ion-exchange reaction can be approximated as the surface adsorption reaction, the sorption isotherm was investigated using the Langmuir and Freundlich models in this study. The distribution coefficient (K_d) of Cs was calculated as in Eq. (3):

Fig. 1. TEM images of sorbents for Cs⁺ sorption test of (a) TNTs, (b) P25, and (c) type X zeolite.

$$Kd = \frac{Q}{C_{eq}} \quad (3)$$

Kd is the ratio of target ions of the ion-exchange sorbent and the solution in equilibrium conditions. Therefore, the Kd value indicates the ion-exchanged amount of the sorbent from solution.

2.4 Characterization

The solution pH after sorption test was measured using a pH meter (D-52, HORIBA, Ltd., Kyoto, Japan). The crystallinity of the TNTs after sorption testing was identified by powder X-ray diffraction (XRD, D8 ADVANCE, Bruker AXS, Germany) using Cu K α radiation. The crystal size and morphology were observed by ultra-high-resolution scanning electron microscopy (SEM, SU9000, Hitachi High-Technologies Corporation, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100, JEOL Ltd., Tokyo, Japan). Elemental analysis of the sorbent was also performed by SEM equipped with energy-dispersive X-ray spectroscopy (EDX, EMAXEvolution X-Max, HORIBA, Ltd., Kyoto, Japan) and wavelength-dispersive X-ray fluorescence spectroscopy (XRF, ZSX-100e, Rigaku Corporation, Tokyo, Japan). The specific surface area (SSA) of the sorbents was measured by a multi-point Brunauer–Emmett–Teller (BET) method (NOVA4200e, Quantachrome Instruments JAPAN, Kanagawa, Japan).

3. Results and discussion

Figure 2 shows the changes in Cs⁺ concentration in the test solutions after sorption testing at 10, 25, and 40°C for up to 7 days. At 25°C, TNTs and zeolite show decrease in Cs⁺ concentration to ~3.4 and 3.1 mM within 1 h, respectively. Cs⁺ sorption on P25 is not observed in this condition. In this test, to investigate the effect of crystal structure of titanate on adsorption, P25 was used as reference. This result indicates that the Cs adsorption by electrostatic interaction is not large, because it is known that P25 or titanate nanotube are positively charged from neutral to acidic condition. Therefore, at 10 and 40°C, P25 was excluded for adsorption test. From the result, regarding the treatment temperature, the concentration reduction of Cs⁺ proceeds in the order of zeolite > TNTs. The reaction temperature shows no effect on the sorption of Cs⁺. From these results, the sorption test was performed at 25°C for 1 day to investigate the sorption density. The sorption isotherms of Cs⁺ on the sorbents are presented in **Fig. 3**. The order of sorption density per gram of Cs⁺ on the sorbents [Fig. 3(a)] is similar to the results of Fig. 2. That is, the sorption density per gram of Cs⁺ is in the order of zeolite > TNTs > P25. The adsorption equilibrium of Cs⁺ on TNTs is well described by the Langmuir model, as shown in **Table 1**. In general, Langmuir isotherms indicate monolayer adsorption and the presence of sorption sites in the material. Therefore, by assuming that ion-exchange can be approximated as surface adsorption, it is estimated that TNTs carry ion-exchange sites (adsorption sites) for Cs⁺. From the Langmuir model, the maximum adsorbed

Fig. 2. Changes in Cs concentration in solution after sorption test at (a) 25, (b) 10, and (c) 40°C up to 7 days.

Cs⁺ masses (Q_{max}) on TNTs and zeolite were calculated as 1.06 and 1.76 mmol/g, respectively. For zeolite, the sorption isotherm of Cs⁺ was well fitted by the Freundlich model, as shown in **Table 2**, rather than by the Langmuir model (Table 1). Comparing the sorption density per SSA excluding P25 as shown in Fig. 3(b), the sorption density

Fig. 3. Sorption isotherms of Cs⁺ on TNTs, zeolite, and P25 at 25°C for 1 day. (a) Sorption density per gram (Q_g) (mmol/g) vs. C_{eq} (mmol/L), and (b) sorption density per specific surface area (Q_s) (mmol/m²) vs. C_{eq} (mmol/L).

Table 1. Langmuir isotherm constants for Cs adsorption on TNT and zeolite

Notation	$Q_{\max}$ (mmol/g)	K (L/mmol)	r^2
TNTs	1.06	23.03	0.999
Zeolite	1.76	3.78	0.969

Table 2. Freundlich isotherm constants for Cs adsorption on TNT and zeolite

Notation	K_F [mmol/g (L/mmol) ^{1/n}]	$1/n$	r^2
TNTs	0.946	0.196	0.921
Zeolite	1.235	0.260	0.978

of Cs⁺ on TNTs is greater than that of zeolite, because the average surface area of the TNTs (195.58 m²/g) is smaller than that of zeolite (450.94 m²/g) based on the BET measurements. This indicates that the TNTs contain slightly more ion-exchange sites than zeolite. The distribution coefficient (K_d values) of the sorbents against the

Fig. 4. (a) Distribution coefficient (K_d) of sorbents against the initial Cs⁺ concentration. (b) Changes in final pH of solution after sorption test.

initial Cs⁺ concentrations are presented in **Fig. 4(a)**. The K_d values are calculated using the sorption isotherms in Fig. 3. The K_d values of the sorbents are decreased with increasing Cs⁺ concentration. The K_d value of the TNTs is slightly lower than that of zeolite. Figure 4(b) shows the changes in the pH of the solution against the initial Cs⁺ concentration. The initial pH was ~5.5 before sorption testing. After testing, the pH of the TNTs and zeolite are increased to 6.5 and 8.2–7.5, respectively. The final pH of sorbents is gradually decreased with increasing initial Cs⁺ concentration.

Figure 5 shows the XRD patterns of the TNTs after sorption testing. From the XRD pattern, typical TNT peaks are detected both before and after sorption testing, regardless of the initial Cs⁺ concentration. However, the peak intensity of the TNTs is slightly decreased with increasing Cs⁺ concentration in the sorption tests. SEM images show that the typical tubular structures of TNTs are maintained even after the sorption tests using 1.0 and 4.0 mM Cs⁺ solutions (**Fig. 6**). Compared to SEM images of the TNTs before sorption testing [Fig. 1(a)], no precipitation or

Fig. 5. XRD pattern of TNT samples before and after Cs^+ sorption test at 25°C for 1 day.

changes on the surfaces of the TNTs are observed after the test. This result indicates that Cs^+ sorption by the TNTs probably occurs by the ion-exchange reaction. In addition, elemental analyses of the sorbents after the test were also performed (Fig. 7). Figure 7 shows the EDX maps of TNTs after sorption testing using 4.0-mM Cs solution. O, Ti, C, Cs, and Na are detected in the samples with traces of Al, Mg, Si, and Ca. The trace elements may have dissolved from the glassware during the synthesis of TNTs. Na^+ is incorporated from NaOH treatment during TNT synthesis. Previously, many researchers have studied the effects of Na^+ on the ion-exchange properties of TNTs. Therefore, to investigate the effect of Na^+ on the ion-exchange reaction, the changes in Cs^+ and Na^+ contents in the TNTs against the initial Cs^+ concentration were measured. As shown in Fig. 8, with increasing initial Cs concentration, the Cs amount is increased and the Na amount decreased in the TNTs. From these results, the sorption mechanism of Cs on TNTs is identified as ion-exchange of Cs^+ and Na^+ in the TNT structure.

Previously many researchers have reported the ion-exchange of TNTs with cations such as Pb^{2+} , Sr^{2+} , Cd^{2+} , Cu^{2+} , Li^+ , K^+ , and Cs^+ from aqueous solutions, and the sorption mechanism of cations by TNTs has been discussed.^{12)–19)} The present study clearly shows that the sorption isotherm of Cs is well fitted by the Langmuir model, consistent with other research results.^{12)–14)} In addition, in previous reports, the sorption mechanism of TNTs was also proposed as ion-exchange by intercalated Na^+ or H^+ in the TNTs. As shown in Fig. 8, the ion-exchange reaction of Na^+ and Cs^+ in the TNTs is clearly observed in this study. These results are similar to previous results. The increase of pH [Fig. 4(b)] indicates the release of Na^+ from the sorbent and ion-exchange reaction with H^+ in solution. In addition the decrease in final pH depending

Fig. 6. SEM images of TNT samples before and after Cs^+ sorption test using (a) 1.0 mM and (b) 4.0 mM solution.

on the initial concentration of Cs also indicates the loss of H^+ by ion-exchange is suppressed, in other words the increase of ion-exchange ratio of Na^+ and Cs^+ . Therefore, from these pH changes, it can be seen that the contribution of Na^+ on the sorbent ion-exchange is large. The maximum adsorbed Cs (Q_{max}) on TNT was calculated as 1.06 mmol/g, lower than that of sodium titanate nanotubes as reported by Yang et al.¹⁹⁾ This difference is attributed to the Na^+ content of TNT. Liu et al. reported that the sorption capacity of Cu^{2+} on TNTs was increased with increasing Na^+ contents in the TNT structure.¹²⁾ Therefore, the present study shows that, although existing TNTs show sorption capacities lower than that of zeolite, increasing the content of Na^+ in the TNTs can improve the sorption capacity of Cs^+ . In addition, the sorption capacity of TNTs may be affected by both the amount of cation and cation species, because the interlayer distance or balance of TNTs may change with changing ionic radii and cation charge balance, as discussed in the study of layered titanate by Li et al.³⁾ In fact, we have reported that TNTs has larger ionic organic molecule (methylene blue) sorption capacity than common TiO_2 crystal due to its unique crystalline and morphological structures.¹¹⁾ Further, the organic molecule adsorption to titania nanotube could be much enhanced by the trivalent cation doping such as Sm(III) mainly due to the electrostatic charge control.²⁰⁾ It was considered

Fig. 7. SEM images and EDX maps of TNT samples after sorption tests using 4.0 mM Cs⁺ solution.

Fig. 8. Changes in Cs and Na contents of TNT samples after Cs sorption test, measured by XRF. (H, C, and O are not included)

that the M³⁺ doping to Ti(IV)O₂ lattice formed oxygen vacancy associated with compensating the mass and charge balance of the lattice, which contributed to the formation of negatively-charged surface by an electron trap and resultant increase in electrostatic adsorption of cationic molecules.²⁰⁾ This fact implies us that the doping

of some cations might also contribute to the enhanced sorption of inorganic cations. Hence, in future work, the TNT structure will be modified to improve the sorption capacity and ion selectivity. Considering the characteristics of excellent photocatalytic activity,^{6)–11)} TNTs remain good candidates as improvable sorbents for water purification.

4. Conclusions

We investigated the Cs⁺ sorption capacity of TNTs synthesized by solution chemical method by simple batch tests using 0.2–4.0 mM CsCl solution, compared to the capacities of zeolite and P25 (TiO₂ nanoparticles). The sorption capacity of Cs per gram showed the order of P25 < TNT < zeolite. The sorption isotherm of Cs on TNTs followed the Langmuir model, and the calculated maximum sorption ($Q_{\max}$) was 1.06 mmol/g. No changes in crystal morphology or layer structure of TNTs were observed with Cs⁺ sorption. In addition, Cs⁺ sorption on TNTs was most likely a result of the ion-exchange reaction, because no precipitate formed on the TNT surfaces. After sorption testing, O, Ti, C, Cs, and Na were detected in the TNTs, and the amount of Na remaining in the TNTs was decreased with increasing sorption amounts of Cs. This result indicated the ion-exchange of Cs⁺ with Na⁺ by the TNTs. These results clearly show that Na⁺ in

the TNT layer structure is important for improving the sorption capacity of Cs^+ by the ion-exchange reaction.

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