Removal of Perchlorate Ion in Tap Water with Montmorillonite Modified with Hexadecylpyridinium Chloride

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Abstract

Removal of perchlorate ion in tap water with montmorillonite which modified with hexadecylpyridinium chloride (CPC-montmorillonite) was investigated by column chromatography. Almost all anions except Cl^- ion in a tap water containing 0.518 and 0.540 mg dm^{-3} on average of perchlorate ion (ClO_4^-) and bromate ion (BrO_3^-), respectively, through the CPC-montmorillonite bed, are adsorbed at the beginning of the column experiment, whereas the Cl^- concentration in effluent immediately increases steeply. The anions exhibit breakthrough in the order of F^- , SO_4^{2-} , BrO_3^- , NO_3^- , Br^- and ClO_4^- . These results suggest that the anion uptake on CPC-montmorillonite proceeds through anion-exchange process, and the anion affinity of CPC-montmorillonite becomes $\text{F}^- < \text{SO}_4^{2-} < \text{BrO}_3^- < \text{NO}_3^- < \text{Br}^- < \text{ClO}_4^-$. The ClO_4^- concentration in effluent solution passing through the CPC-montmorillonite bed falls below detection limits of ion chromatography up to 4,500 bed volumes (BV) at the feed solution rate of space velocity (SV) 15 h^{-1} , thus the ClO_4^- ion in the tap water can be reduced to less than 0.025 mg dm^{-3} of the target value under consideration as a standard of water-purity for tap water at Ministry of Health, Labour and Welfare of Japan. The ClO_4^- concentration increases gradually between 5,000 and 10,000 of BV and becomes nearly constant at above near 10,000 of BV. The ClO_4^- uptake amount on the column experiment can be estimated as 0.04 mmol g^{-1} from the adsorption breakthrough curve of ClO_4^- ion. During 37 consecutive days of column experiment, 86 % of hexadecylpyridinium chloride molecules were eluted from an interlayer of CPC-montmorillonite and the basal spacing, (001) plane, of CPC-montmorillonite decreased from 4.05 nm to 2.11 nm.

Keywords: Ion exchange, Perchlorate ion, Tap water, Anion selectivity, Montmorillonite, CPC

1. Introduction

Perchlorate salts are strong oxidant and are used in solid propellants for missiles and rockets, pyrotechnic materials and detonators for air-bags in vehicles. Their use leads to the release of perchlorate salts into the environment¹⁾. The presence of perchlorate ion in dairy milk and human milk had been reported in Japan and United States²⁻⁴⁾. The perchlorate ion is similar in size of iodide ion and it can interfere with delivery of iodide ion to thyroid gland in the body. In this way, perchlorate can disrupt the production of thyroid hormones, and thus disrupt metabolism⁵⁾. Regular ingestion of perchlorate ion might therefore be associated with a risk of disorder of

child development. Ministry of Health, Labour and Welfare of Japan is considering carefully whether to establish an upper limit (0.025 mg dm^{-3}) of perchlorate ion on a standard of water-purity for tap water.

An adsorption process might be best suitable to remove the perchlorate in water, since some of the adsorbents show high selectivity toward ClO_4^- ion⁶⁻¹⁰⁾ compared with other process such as biological process¹¹⁾ and electrochemical process^{12,13)}. Recently, authors have reported that a CPC-montmorillonite exhibited excellent selectivity toward ClO_4^- ion¹⁴⁾. The ClO_4^- uptake capacity of 1.02 mmol g^{-1} by CPC-montmorillonite is comparable to 1.1 mmol g^{-1} of most efficient perchlorate

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selective strong-base anion exchange resin^{6,7}). The anion uptake on CPC-montmorillonite accompanied with release of chloride ion into solution through anion-exchange processes and the CPC-montmorillonite displayed exceptional selectivity for ClO_4^- ion with the sequence $\text{H}_2\text{PO}_4^- < \text{SO}_4^{2-} < \text{NO}_3^- < \text{ClO}_4^-$ similar to the Hofmeister series of anions based on the free energy of hydration¹⁵). In addition, authors have reported that the CPC-montmorillonite exhibited high selectivity toward BrO_3^- ion¹⁶). The BrO_3^- ion is human carcinogen¹⁷) and is formed by ozonation of water¹⁸). Consequently, regulatory agencies in the USA, European countries, and Japan established a maximum contaminant level of bromate of 0.01 mg dm^{-3} in drinking water. In the present study, removal of ClO_4^- ion or both ClO_4^- and BrO_3^- ions in tap water with the CPC-montmorillonite was investigated by column chromatography.

2. Experimental

2.1 Materials

CPC-montmorillonite was synthesized using natural Na-montmorillonite and hexadecylpyridinium chloride ($\text{C}_{12}\text{H}_{38}\text{NCl}$, cetylpyridinium chloride, CPC) monohydrate. The Na-montmorillonite (product name Kunipia-F) supplied by Kunimine Industries Co., Japan is a layered clay which has a cation exchange capacity of 1.19 meq g^{-1} . The hexadecylpyridinium chloride monohydrate was of a special grade chemical supplied by Wako Pure Chemical Industries Ltd., Japan.

A ClO_4^- ion or both ClO_4^- and BrO_3^- ions enriched tap water were used to evaluate the performance of perchlorate ion removal with the CPC-montmorillonite. A public drinking water that authors use daily was used as the tap water. The $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and NaBrO_3 used for preparation of the ClO_4^- ion or both ClO_4^- and BrO_3^- ions enriched tap water were of special grade chemicals supplied by Wako Pure Chemical Industries Ltd., Japan.

2.2 Synthesis of CPC- montmorillonite

The CPC-montmorillonite was prepared at room temperature in the same way as the literature¹⁴). Na-montmorillonite (5 g) was dispersed in deionized water (500 cm^3) and stirred for 90 min . An amount of CPC (10.5 g) corresponding to four times the cation exchange capacity of the Na-montmorillonite was dissolved in deionized water (250 cm^3) preheated to 60°C . The CPC solution was added slowly to the dispersion and the dispersion was stirred at 500 rpm for 1 day at room temperature. Solid products were separated by centrifugation, washed with deionized water, and dried at 40°C for 1 day . The sample was ground by a grinding mill (Model A10; Janke & Kunkel IKA Labortechnik) and was sieved in size from 0.063 to 1 mm using two standard sieves, for column chromatography.

2.3 Structural Analysis

Structure analysis was carried out using an X-ray diffractometer (RINT 2100; Rigaku Co., Ltd.), operating at 40

kV voltage and 24 mA current, with $\text{CuK}\alpha$ radiation ($\lambda=0.154052 \text{ nm}$). The X-ray diffraction (XRD) pattern of sample was collected with sampling width of 0.02° under scanning rate of 1° min^{-1} .

Thermal analysis was carried out using a thermogravimetric analyzer (Thermo plus TG8110; Rigaku Co., Ltd.) in a flowing air atmosphere ($100 \text{ cm}^3 \text{ min}^{-1}$). The TG-DTA data of sample was collected with a heating rate of $10^\circ\text{C min}^{-1}$.

2.4 Column Chromatography for Removal of Perchlorate Ion in a Tap Water

Removal of perchlorate ion in a tap water was investigated by column chromatography at two different feed solution rates. The column experiments were carried out at 25°C in temperature-controlled room and the experiment was denoted by TEST 1 or TEST 2. For the TEST 1, a 0.82 g of CPC-montmorillonite was packed to 70.0 mm height in a chromatographic glass column (5 mm in diameter and 100 mm in length). The bed volume (BV) of CPC-montmorillonite was 1.37 cm^3 . A feed solution which contains $0.005 \text{ mmol dm}^{-3}$ of ClO_4^- in tap water was prepared by dissolving 10 cm^3 of 1 mmol dm^{-3} NaClO_4 in 1.99 dm^3 of tap water and was passed downward through the column at the flow rate of $7.3 \text{ cm}^3 \text{ h}^{-1}$ ($\text{SV } 5 \text{ h}^{-1}$) with a plunger pump. For the TEST 2, the same amount of CPC-montmorillonite as TEST 1 was packed in the chromatographic glass column. A feed solution which contains $0.005 \text{ mmol dm}^{-3}$ of ClO_4^- and BrO_3^- ions in tap water was prepared by dissolving 100 cm^3 of mixed solution of 1 mmol dm^{-3} NaClO_4 and 1 mmol dm^{-3} NaBrO_3 in 9.9 dm^3 of tap water and was passed downward through the column at the flow rate of $20.5 \text{ cm}^3 \text{ h}^{-1}$ ($\text{SV } 15 \text{ h}^{-1}$). The column experiments of TEST 1 and TEST 2 took 90 and 37 days , respectively. For both TEST 1 and TEST 2, the feed solutions were repurchased when needed, up to breakthrough of perchlorate ion. In actually, the concentration of anion such as chloride, sulfate, nitrate and other minor ions in the feed solution changed at every preparation, because each anion concentration in a tap water varied from day to day. For exactly the same reason, the concentration of cation also changed at every preparations. The anion concentrations in tap water used for TEST 1 and TEST 2 were provided with dashed lines in Figs. 4 and 5, respectively. The concentrations of main cations in tap water were in the range 5.01 to 6.14 mg dm^{-3} for Na^+ ion, 0.990 to 1.39 for K^+ , 1.38 to 1.88 for Mg^{2+} and 8.47 to 10.6 for Ca^{2+} . The solution pH of tap water was in the range 7.2 to 7.5 . The effluent through the column was collected by every 1 hour using an automatic sample collector. The anion concentrations in selected fractions were measured by ion chromatography (761 Compact IC; Metrohm AG).

3. Results and Discussion

3.1 Crystal Structure of CPC-Montmorillonite

Figs. 1a and 1b show X-ray diffraction patterns of natural Na-montmorillonite and synthetic CPC-montmorillonite,

respectively. The basal spacing, (001) plane, of the CPC-montmorillonite increased to 4.05 nm after modified with CPC from 1.26 nm of Na-montmorillonite. The basal spacing of 4.05 nm shows well agreement with that of 4.16 nm reported previously¹⁴). The small difference of basal spacing might be due to the amount of CPC intercalated between layers of montmorillonite. Contents of Na⁺, K⁺, Mg²⁺ and Ca²⁺ between layers of montmorillonite are given in **Table 1**. The contents were calculated from the amounts of dissolved cations from interlayer on acid treatment. The value for Mg²⁺ includes the dissolved Mg²⁺ ions from intralayer. Montmorillonite sample of 250 mg was dispersed in 100 mmol dm⁻³ HCl solution of 25 cm³ at room temperature and shaken frequently for 24 h. For the Na-montmorillonite, Na⁺ ions are located mainly in the interlayer and K⁺, Mg²⁺ and Ca²⁺ ions are located rarely. The 1.1 mmol g⁻¹ of Na⁺ content is in good agreement with 1.19 meq g⁻¹ of the

Fig. 1 XRD patterns of natural Na-montmorillonite (a), synthetic CPC-montmorillonite (b), CPC-montmorillonite after TEST 1 (c), and CPC-montmorillonite after TEST 2 (d).

Table 1 Cation contents in interlayer of montmorillonite.

Sample	Cation content / mmol g ⁻¹			
	Na ⁺	K ⁺	Mg ²⁺ *	Ca ²⁺
Na-mont.	1.1 × 10 ⁰	1.4 × 10 ⁻²	2.5 × 10 ⁻²	3.8 × 10 ⁻²
CPC-mont.	1.4 × 10 ⁻³	7.9 × 10 ⁻⁴	3.0 × 10 ⁻³	2.2 × 10 ⁻⁵
CPC-mont. after TEST 1	1.5 × 10 ⁻³	1.1 × 10 ⁻³	1.7 × 10 ⁻³	8.0 × 10 ⁻⁵
CPC-mont. after TEST 2	1.1 × 10 ⁻³	7.1 × 10 ⁻⁴	1.7 × 10 ⁻³	1.0 × 10 ⁻⁴

* The value includes Mg²⁺ ion dissolved from intralayer.

cation exchange capacity of Na-montmorillonite. Conversely, Na⁺, K⁺, Mg²⁺ and Ca²⁺ ions hardly exist in interlayer of CPC-montmorillonite. These results indicate that almost Na⁺ ions of Na-montmorillonite exchanged with the hexadecylpyridinium ions (CP⁺).

Figs. 2a, 2b and **2c** show thermogravimetric curves of natural Na-montmorillonite, synthetic CPC-montmorillonite and CPC monohydrate, respectively. The weight loss of Na-montmorillonite became 8.3 % at the temperature below 110 °C, nearly zero in the range 110 to 600°C and 3.9 % in the range 600 to 800°C. The former weight loss corresponds to the amounts of the surface water and hydrated water of interlayer cation and the later weight loss might be due to a partial collapse of crystal structure. The weight loss of CPC-montmorillonite became 3.7 % at the temperature below 110°C and 56.6 % in the range 110 to 800°C. The weight loss of CPC monohydrate became 98 % at the temperature below 280.

These results indicate that the hydrated water of CP⁺ in CPC-montmorillonite is less than half that of Na⁺ in Na-montmorillonite and the weight loss of CPC-montmorillonite in the range 110 to 800°C is due to a thermal decomposition of CP⁺ and CPC molecule between layers of montmorillonite mainly and a partial collapse of the layers.

Fig. 2 Thermogravimetric curves of natural Na-montmorillonite (a), synthetic CPC-montmorillonite (b), CPC monohydrate (c), CPC-montmorillonite after TEST 1 (d), and CPC-montmorillonite after TEST 2 (e).

The contents of aluminosilicate layers of CPC-montmorillonite and of CP⁺ ions and CPC molecules between the layers were calculated from the weight losses in the range 110 to 800 °C from the thermogravimetric analysis, as given in **Table 2**, on the assumption that Na⁺ ions of 1.19 mmol g⁻¹ corresponding to the cation exchange capacity of Na-montmorillonite were ion-exchanged to CP⁺ from the result given in Table 1. The contents of layer, CP⁺ ion and CPC molecule of CPC-montmorillonite were 41, 16 and 43 wt%,

respectively. The CPC molecule content corresponds to 1.3 mmol g^{-1} of CPC and the value gives a theoretical limit of anion exchange capacity of CPC-montmorillonite, since the chloride ions of CPC molecules in CPC-montmorillonite can be ion-exchanged for the anions except chloride ion in an aqueous medium. The 1.3 mmol g^{-1} of anion exchange capacity compares well with 1.02 mmol g^{-1} of ClO_4^- uptake capacity calculated from a Langmuir fitting of a ClO_4^- uptake isotherm of CPC-montmorillonite determined at the initial ClO_4^- ion concentration of $0.50 \text{ mmol dm}^{-3}$ (equilibrium pH 5.8)¹⁴.

Table 2 Contents of aluminosilicate layer, CP^+ ion and CPC molecule in montmorillonite.

Sample	Content / wt% (mmol g^{-1})			
	layer	CP^+	CPC	CP-ClO_4
Na-mont.	100	0	0	-
CPC-mont.	41	16 (0.5)	43 (1.3)	-
CPC-mont. after TEST 1	68	26 (0.8)	4 (0.1)	2 (0.05)
CPC-mont. after TEST 2	65	25 (0.8)	8 (0.2)	2 (0.04)

Considering the layer thickness of montmorillonite as 0.97 nm and the length of the CPC molecule as 2.31 nm ¹⁹, the CPC-montmorillonite with basal spacing of 4.05 nm suggests a bi-layered arrangement of CPC in the interlayer space at the inclination angle of 42° ^{14, 16}, as shown in Fig. 3. The Cl^- ions of CPC molecules exchange with anions in solution.

Fig. 3 Schematic crystal structure of CPC-montmorillonite.

3.2 Removal of Perchlorate Ion in a Tap Water by Column Chromatography

Fig. 4 shows adsorption breakthrough curves of anions on the column experiment TEST 1 fed the tap water containing 0.483 mg dm^{-3} on average of ClO_4^- ion at $\text{SV } 5 \text{ h}^{-1}$. The dashed lines in the figure indicate the ion concentrations in feed solution. The ClO_4^- ion in the feed solution can be effectively

removed by passing through the CPC-montmorillonite column, although the concentration of ClO_4^- ion is markedly lower than those of Cl^- , SO_4^{2-} and NO_3^- ions. The ClO_4^- ion concentration in effluent is not detected up to 4,700 BV and breakthrough at around 5,000 BV. This indicates that the CPC-montmorillonite can reduce ClO_4^- ion concentration in tap water to less than 0.025 mg dm^{-3} of the target value under consideration as a standard of water-purity for tap water at Ministry of Health, Labour and Welfare of Japan. The ClO_4^- ion concentration increases gradually in the range of $5,000 < \text{BV} < 7,000$ and becomes substantially constant at $\text{BV} > 7,000$.

The Cl^- ion concentration decreases steeply in range 3 to around 1,000 BV and continues to decrease slowly up to the end of the column experiment. The F^- concentration in effluent shows about the same concentration as the feed solution during

Fig. 4 Adsorption breakthrough curves of ClO_4^- (a), Cl^- (b), F^- (c), SO_4^{2-} (d), NO_3^- (e) and Br^- (f) on the column experiment TEST 1 fed the tap water containing ClO_4^- ion at $\text{SV } 5 \text{ h}^{-1}$. Vertical and horizontal axes represent ion concentration (mg dm^{-3}) and bed volume, respectively. Dashed lines indicate the ion concentration in feed solution.

the column experiment. This result suggests that the CPC-montmorillonite adsorbs very little F^- ion. The concentrations of SO_4^{2-} , NO_3^- and Br^- ions in effluent decrease to almost zero at the beginning of the column experiment and the anion exhibits breakthrough in the order of SO_4^{2-} , NO_3^- , Br^- and ClO_4^- .

Fig. 5 shows adsorption breakthrough curves of anions on the column experiment TEST 2 fed the tap water containing 0.518 and 0.540 $mg\ dm^{-3}$ on averages of ClO_4^- and BrO_3^- ions at SV $15\ h^{-1}$. The ClO_4^- ion concentration in effluent is not detected up to 4,500 BV and breakthrough at around 5,000 BV as is the case of TEST 1. This result indicates that the ClO_4^- ion in the tap water can be effectively removed by column chromatography with CPC-montmorillonite under at least the SV $15\ h^{-1}$ of the feed solution rate, since the ClO_4^- ion is adsorbed relatively quickly to CPC-montmorillonite. Authors

Fig. 5 Adsorption breakthrough curves of ClO_4^- (a), Cl^- (b), F^- (c), SO_4^{2-} (d), BrO_3^- (e), NO_3^- (f) and Br^- (g) on the column experiment TEST 2 fed the tap water containing ClO_4^- and BrO_3^- ions at SV $15\ h^{-1}$. Vertical and horizontal axes represent ion concentration ($mg\ dm^{-3}$) and bed volume, respectively. Dashed lines indicate the ion concentrations in feed solution.

have reported that the ClO_4^- ion uptake of CPC-montmorillonite reached equilibrium within 4 h with an uptake amount of 0.75 $mmol\ g^{-1}$ at pH 5.8 from the initial concentration of 0.10 $mmol\ dm^{-3}$ $NaClO_4$ solution by a study of the kinetics on perchlorate uptake¹⁴), much higher than that reported for SBA-15 (0.55 $mmol\ g^{-1}$ ²⁰), MCM-41 (0.27 $mmol\ g^{-1}$ ²¹), Na-1-mica modified with hexadecyltrimethylammonium (0.35 $mmol\ g^{-1}$ ²²), MgAl-LDH(NO_3^-) (0.20 $mmol\ g^{-1}$ ²²), granular activated carbon coated with hexadecyltrimethylammonium bromide²³), or granular ferric hydroxide (0.03 $mmol\ g^{-1}$ ²⁴). The ClO_4^- ion concentration after the breakthrough increases slowly compared to that on TEST 1 in the range of $5,000 < BV < 10,000$ and became close to that in the feed solution at $BV > 10,000$.

The adsorption breakthrough curves of other anions on TEST 2 show the same tendency of those on TEST 1. The concentrations of SO_4^{2-} , BrO_3^- , NO_3^- and Br^- ions in effluent decrease to almost zero at the beginning of the column experiment and the anion exhibits breakthrough in the order of SO_4^{2-} , BrO_3^- , NO_3^- , Br^- and ClO_4^- . These results indicate that CPC-montmorillonite adsorbs ClO_4^- ion preferably than BrO_3^- ion and the anion affinity of CPC-montmorillonite becomes $F^- < SO_4^{2-} < BrO_3^- < NO_3^- < Br^- < ClO_4^-$. In our previous studies^{14,16}), we have reported that the selectivity of CPC-montmorillonite became $H_2PO_4^- < SO_4^{2-} < NO_3^- < ClO_4^-$ and $H_2PO_4^- < SO_4^{2-} < BrO_3^- < Br^- < NO_3^-$ based on the distribution coefficients of anions on the batch adsorption experiments with multi-anion solution of 0.1, 1.0 or 2.0 $mmol\ dm^{-3}$. The affinity order of Br^- and NO_3^- ions on the present column study is different with the selectivity order on the previous batch study. Since the concentrations of Br^- and NO_3^- ions in the tap water used in the present study are around 0.02 and 0.01 $mmol\ dm^{-3}$, respectively, CPC-montmorillonite probably adsorbs Br^- ion preferably than NO_3^- ion at the low concentration.

It is noticeable that the concentrations of SO_4^{2-} , BrO_3^- , NO_3^- and Br^- ions exceed those of the feed solution markedly after the breakthrough, though they become finally about the same concentration as the feed solution. The reason why is that the exchanged anion into CPC-montmorillonite are excluded from the site by the exchange with other anion having a higher affinity. Conversely, the ClO_4^- ion concentration increases up to the same level as that of the feed solution without a large exceedance. The exchanged ClO_4^- ion might not be excluded by any anion, since the CPC-montmorillonite shows the highest affinity toward ClO_4^- ion among the anions.

Table 3 shows the amounts of released chloride ion and adsorbed anions estimated from the adsorption breakthrough curves in Figs. 4 and 5. The ClO_4^- uptake amounts on TEST 1 and TEST 2 gave 0.05 and 0.04 $mmol\ g^{-1}$, respectively. The amounts of adsorbed F^- , SO_4^{2-} , BrO_3^- , NO_3^- and Br^- ions gave less than or equal to zero $mmol\ g^{-1}$. Though some anions gave negative values, the values are believed to be almost zero $mmol\ g^{-1}$, because there is no way that the uptake amount gives a

negative value theoretically. These results support that the exchanged anion in CPC-montmorillonite are excluded from the site by the exchange with other anion having a higher affinity and only ClO_4^- ions having the highest affinity might be finally remained in CPC-montmorillonite. The amount of released Cl^- ion is markedly higher than that of adsorbed ClO_4^- ion. This result suggests that the release of Cl^- ion is caused by the elution of CPC molecule mainly and the partial anion exchange.

Table 3 Amounts of released chloride ion and adsorbed anions estimated from the adsorption breakthrough curves in Figs. 4 and 5.

TEST	Amounts of released Cl^- and adsorbed anions / mmol g^{-1}						
	Cl^-	ClO_4^-	F^-	SO_4^{2-}	BrO_3^-	NO_3^-	Br^-
1	1.15	0.05	< 0	< 0	-	< 0	0.00
2	0.48	0.04	0.00	< 0	0.00	< 0	0.00

3.3 CPC-Montmorillonite after the Column Experiment

Figs. 1c and 1d show XRD patterns of CPC-montmorillonite after column experiments of TEST 1 and TEST 2, respectively. The basal spacing, (001) plane, decreased to 2.11 nm for TEST 1 and 2.14 nm for TEST 2 from 4.05 nm of CPC-montmorillonite in Fig. 1b. Figs. 2d and 2e show thermogravimetric curves of CPC-montmorillonite after TEST 1 and TEST 2, respectively. The weight losses of CPC-montmorillonite after TEST 1 and TEST 2 at the temperature below 110°C were 1.3 and 2.1 wt%, respectively. This result indicates that the hydrated water of CP^+ in CPC-montmorillonite is much lower than that of Na^+ in Na-montmorillonite. The weight losses of CPC-montmorillonite after TEST 1 and TEST 2 in the range 110 to 800°C were 30.8 and 33.3 wt%, respectively. Table 1 shows that CP^+ ions remain in interlayer of CPC-montmorillonite after TEST 1 and TEST 2, since Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions hardly exist in the interlayer. These results suggest that the amount of CPC molecules in CPC-montmorillonite decrease during the long-term column experiments.

The contents of aluminosilicate layers, CP^+ ions, CPC molecules and CP-ClO_4 molecules which exchanged Cl^- ions in CPC for ClO_4^- ions of CPC-montmorillonite after TEST 1 and TEST 2 were calculated from the weight losses in the range 110 to 800°C from the thermogravimetric analysis and the ClO_4^- uptake amounts of 0.05 mmol g^{-1} for TEST 1 and 0.04 mmol g^{-1} for TEST 2, as given in Table 2. Since the CP^+ ions between layers of CPC-montmorillonite is not exchanged for any cations in the tap water, the ratios of CP^+ to layer after TEST 1 and TEST 2 coincide with that of CPC-montmorillonite before

column experiment. When the weight of layer of samples is normalized as 1, CPC and CP-ClO_4 values become 1.05 and 0.0 for CPC-montmorillonite, 0.057 and 0.030 for CPC-montmorillonite after TEST 1 and 0.12 and 0.023 for CPC-montmorillonite after TEST 2, respectively. These results suggest that the CPC of CPC-montmorillonite is eluted during the long-term column experiment. The decreases become 92 mol% for TEST 1 on 90 consecutive days and 86 mol% for TEST 2 on 37 consecutive days.

The CPC molecule is used for sterilization of throat in a mouthwash, since it exerts bactericidal effect. Therefore, the desorption of CPC from CPC-montmorillonite might not causes a health damage, even if a small amount of CPC molecule is contaminated in the drinking water.

4. Conclusions

The ClO_4^- ion in the tap water can be effectively removed by passing through the CPC-montmorillonite column and be reduced to less than 0.025 mg dm^{-3} of the target value under consideration as a standard of water-purity for tap water at Ministry of Health, Labour and Welfare of Japan. The anion affinity of CPC-montmorillonite on the present study becomes in the order of $\text{F}^- < \text{SO}_4^{2-} < \text{BrO}_3^- < \text{NO}_3^- < \text{Br}^- < \text{ClO}_4^-$ from the adsorption breakthrough curves of anions on the column experiment. The ClO_4^- uptake amounts until the ClO_4^- ion concentration reaches to equilibrium after the breakthrough is estimated as about 0.05 mmol g^{-1} . During the long-term experiment, about 90 % of CPC molecules were eluted from an interlayer of CPC-montmorillonite and the basal spacing, (001) plane, of CPC-montmorillonite decreased from 4.1 nm to 2.1 nm.

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