

Removal of Bromide from Desalinated Water Using Hydrotalcite

Takaaki Wajima

Abstract—Bromide (Br^-) can form disinfection by-products (DBPs) in drinking water sterilization (chlorination or ozonation) processes, and these DBPs have adverse effects on human health. In this study, we tried to remove Br^- from desalinated water, which was produced from seawater by spray flash desalination, using hydrotalcite (HT), before sterilization, for use as drinking water. Although HT did not remove Br^- from desalinated water by ion exchange, calcined HT removed Br^- by reconstruction. Br^- removal by reconstruction of calcined HT became saturated at sample/solution = 2 g/L after reaction for 2 h, and increased with increasing temperature. The adsorption kinetics was examined based on pseudo-first-order and pseudo-second-order reaction models, and the adsorption rate constants for these kinetics models were calculated. Adsorption experiments demonstrated that the adsorption process fitted a pseudo-second-order kinetics model better than a pseudo-first-order model.

Index Terms— Br^- removal, hydrotalcite, ion exchange, reconstruction.

I. INTRODUCTION

The development of sustainable water resources is a major issue for the 21st century [1]. Water resources are essential for agriculture, industry, environmental protection, ecology, and human life. Recently, with population growth, industrialization, and urbanization, problems caused by deteriorating water quality, climate change, and other factors have arisen in all parts of the world. Desalination is one possible solution, and many sectors have a keen interest in desalination technology, which produces fresh water from the almost inexhaustible supplies of seawater.

Multi-stage flash (MSF) and reverse osmosis (RO) membrane methods are widely known. Spray flash desalination uses relatively small temperature differences as the heat source, so this method can use the waste heat from MSF and other plants as an energy source. This technique is also expected to be an effective means of using waste energy, as a countermeasure against global warming and related issues [2], [3].

Desalination using untapped energy is one way of solving this problem, and upward jet spray flash desalination plants are promising in terms of efficiency and compactness. In a previous study, fresh water was produced from surface seawater in Imari Bay using an upward jet spray flash

desalination plant, and the principal components of seawater were removed; however, bromide (Br^-) remained in the water produced [4].

It is well known that disinfection is used to kill pathogens during drinking water treatment. However, an obvious drawback of disinfection is the formation of disinfection by-products (DBPs) [5], [6]. Although Br^- is generally considered to be non-toxic at the concentrations found in most drinking water sources, it reacts with a variety of commonly used disinfectants, most notably ozone, chlorine, and chloramine, to produce bromo-DBPs. For example, Br^- can be oxidized by ozone to generate bromate, which is highly toxic to humans. According to the World Health Organization standard, 25 $\mu\text{g/L}$ is the maximum concentration of Br^- permitted in drinking water [7]. Chlorine or chloramine can rapidly oxidize Br^- to hypobromous acid, yielding mixed bromo- or bromochloro-trihalomethanes (THMs) and haloacetic acids (HAAs) by reacting with natural organic matter [8–10]. The US Environmental Protection Agency limits for the maximum concentrations of THMs and HAAs in disinfectant/DBPs [rule (D/DBP) I] are 80 and 60 $\mu\text{g/L}$, respectively [11]. Bromo- or bromochloro-THMs and HAAs are generally considered to be more carcinogenic than their chlorinated analogs [4], [8], [9]. Accordingly, Br^- , which is a crucial precursor in the formation of bromo-DBPs, should be removed before disinfection during drinking water treatment.

Many studies have been conducted on Br^- removal. Electrochemical treatment is sufficient for removing Br^- through oxidation, but it generates by-products in the process [12]. Nanofiltration can also be used to remove this ion with good results, but the high cost limits its large-scale application [13]. Coagulation is also considered to be an effective alternative for removing Br^- [14]. However, treatment of the sludge after coagulation must be seriously considered as it contains most of the removed Br^- , which is harmful to the environment. Adsorption is one feasible method for Br^- removal from solution. For example, Br^- removal by Ag-doped activated carbon aerogels, and the effect of these aerogels on Br^- behavior, have been investigated [15].

In this study, we focused on hydrotalcite (HT) as a low-cost adsorbent for Br^- removal from desalinated water. Layered double hydroxides (LDHs), or HT-like compounds, can be represented by the general formula $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di- and tri-valent metal cations such as Mg^{2+} and Al^{3+} , which occupy octahedral sites in the hydroxide layers. A^{n-} is an exchangeable anion, and x is the ratio of $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$, and the layer charge depends on the $\text{M}^{2+}/\text{M}^{3+}$ ratio [16].

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Carbonates are the interlayer anions in naturally occurring HT. LDHs have large surface areas (20–120 m²/g) and high ion-exchange capacities for adsorption/ion-exchange of various anionic pollutants. LDHs decompose at 500–800 °C to a magnesium–aluminum oxide solid solution, which is rehydrated and reconstructs the original structure from water containing anions [17]; they are therefore potential adsorbents for anionic solutes. Calcined LDHs are particularly interesting adsorbents because they have the potential to remove F⁻, Cl⁻, and other toxic anions from contaminated water [18–24].

In this work, the removal of Br⁻ from desalinated water by calcined and uncalcined MgAl–CO₃ LDHs, by reconstruction and ion exchange, respectively, was studied.

II. EXPERIMENTAL METHOD

A. Samples

The desalinated water used in this study was produced by the flash desalination plant at the Institute of Ocean Energy, Saga University, Japan [4]. The conductivity, salinity, chemical composition, and pH of the desalinated water and the seawater before the flash desalination treatment are shown in Table I. Although seawater has high conductivity and high salinity, the conductivity (<0.5 mS/m) and salinity of the desalinated water were quite low, indicating a higher degree of purity than that of fresh water (1 mS/m) produced by RO desalination of common tap water (20 mS/m). The seawater contained high concentrations of Na⁺, Cl⁻, and other ions. The principal components and B fulfilled the criteria for tap water, but the Br⁻ concentration in the sample (1.9 mg/L) was higher than that in tap water (10–100 µg/L). The pH of the desalinated water was 5.0. The desalinated water could therefore be used for drinking water after Br⁻ removal.

TABLE I: CONDUCTIVITY, SALINITY, CHEMICAL COMPOSITION, AND PH OF DESALINATED WATER AND SEAWATER

	Desalinated water	Seawater
Conductivity (mS/m)	0.497	4350
Salinity (%)	N.D.	2.71
Content (mg/L)		
Na ⁺	1.1	10 329
K ⁺	N.D.	471
Mg ²⁺	N.D.	1305
Ca ²⁺	N.D.	376
Cl ⁻	N.D.	19 410
Br ⁻	1.9	58
SO ₄ ²⁻	N.D.	2140
B	0.2	8.2
pH	5.0	8.1

N.D.: Not determined.

HT was synthesized as follows. MgCl₂ solution (0.6 M, 100 mL) and AlCl₃ solution (0.2 M, 100 mL) were mixed and stirred with a magnetic stirrer at room temperature. During stirring, the pH of the solution was adjusted to 10.5 by dropwise addition of 0.15 M Na₂CO₃ solution. After stirring for 48 h, the slurry was filtered, washed with distilled water, and then dried overnight in a drying oven to obtain the HT

sample. The calcined HT (CHT) sample was prepared by heating HT at 600 °C for 1 h in an electric oven.

B. Experimental Procedure

1) Addition of HT and CHT

Different amounts of HT or CHT (0–0.3 g) were added to 100 mL of desalinated water. The mixtures were stirred with a magnetic stirrer for 1 d at room temperature. After stirring, the slurries were filtered and the pHs of the filtrates and their Br⁻ concentrations were determined.

2) Reaction time for Br⁻ removal

HT (1 g) or CHT (1 g) was added to 500 mL of desalinated water and the mixture was stirred with a magnetic stirrer at room temperature. During stirring, the pH of the solution was monitored, and 3 mL aliquots of each slurry were removed at various times, from 0 to 24 h. The aliquots were filtered, and the concentrations of Br⁻ in the filtrates were determined.

3) Effect of temperature on Br⁻ removal

CHT (1 g) was added to 500 mL of desalinated water and the mixture was stirred with a magnetic stirrer at 5–80 °C. During stirring, the pH of the solution was monitored, and 3 mL aliquots of each slurry were removed at various times, from 0 to 3 h. The aliquots were filtered, and the concentrations of Br⁻ in the filtrates were determined.

4) Chemical analysis

The electrical conductivities and salinities of the seawater and desalinated water were measured using a conductivity meter (ES-51, Horiba, Japan). The concentration of B, which is vital in desalination, was measured using inductively coupled plasma atomic emission spectroscopy (ICPS-7500, Shimadzu, Japan). The solution pH was measured with a pH meter (D-53, Horiba, Japan), and the Br⁻ concentration in the solution was determined using ion chromatography (ICS-3000, Dionex, Japan). The Br⁻ uptake by CHT, q (mg/g), and the percentage Br⁻ removal, R (%), were evaluated using the following equations:

$$q = \frac{(C_0 - C)V}{m} \quad (1)$$

$$R = \frac{(C_0 - C)}{C_0} \times 100 \quad (2)$$

where C_0 and C are the initial and residual Br⁻ concentrations in the solution (mg/L), respectively, V is the solution volume (L), and m is the mass of adsorbent (g).

III. RESULTS AND DISCUSSION

Fig. 1 shows (a) the solution pHs and (b) the Br⁻ concentrations in the solutions after treatment with HT and CHT. The solution pH after treatment with CHT was higher than that after treatment with HT, increasing to pH 11 and pH 8.5 with increasing addition of CHT and HT, respectively, as a result of the production of OH⁻ ions [25], [26]. Little decrease in the Br⁻ concentration occurred on treatment with HT, but the Br⁻ concentration decreased significantly when treated with CHT at more than 2 g/L; this was in good agreement with the pH behavior of the solution. It is considered that the reconstruction reaction for the uptake of

Br⁻ from the solution occurred strongly on addition of more than 2 g/L of CHT.

shown in Fig. 4(a). The equilibrium state was reached more quickly with increasing temperature.

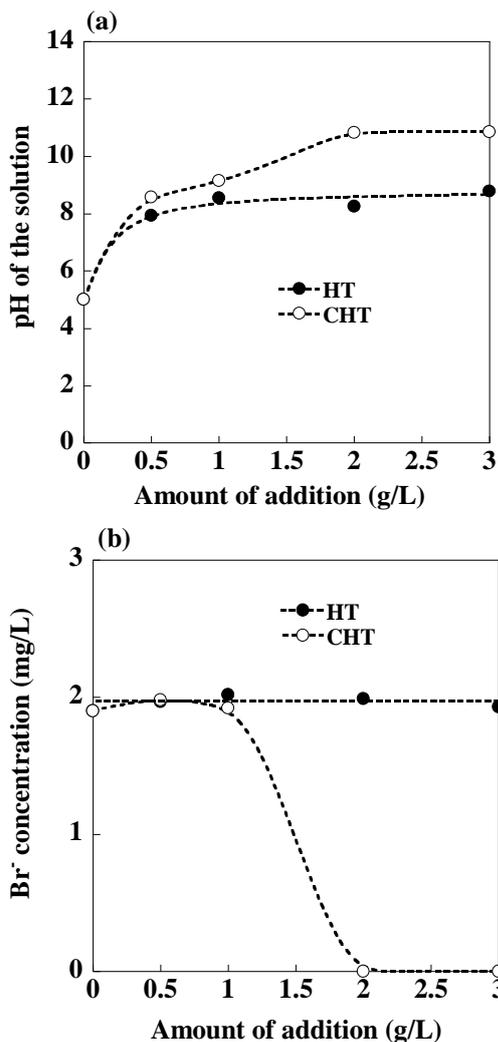


Fig. 1. Effects of HT and CHT addition on (a) solution pH and (b) Br⁻ concentration.

Fig. 2 shows the (a) pHs and (b) Br⁻ concentrations of solutions during treatment with HT and CHT. The solution pH rapidly increased to 8.5 and 11 in the initial stage, and then became almost constant, on treatment with HT and CHT, respectively. Although the concentrations of Br⁻ were unchanged by treatment with HT because the anion selectivity order of the ion-exchange reaction with HT is Br⁻ << CO₃²⁻ [27–29], they gradually decreased over 2 h to zero on treatment with CHT. Br⁻ can therefore be removed from desalinated water using CHT.

Fig. 3 shows the Br⁻ concentrations of the solutions and the removal of Br⁻ from desalinated water during treatment with CHT at 5, 15, 25, 50, and 80 °C. With increasing temperature, the decrease in Br⁻ concentration in the solution to zero became faster, and the removal of Br⁻ from desalinated water was promoted. Above 50 °C, Br⁻ removal reached 100% within 0.5 h. These results suggest that desalination treatment with CHT at high temperatures gives better Br⁻ removal than treatment at low temperatures does.

The kinetics of the adsorption of Br⁻ from desalinated water at 5, 15, and 25 °C, and the adsorption capacities of CHT for Br⁻ at 5, 15, and 25 °C were studied; the results are

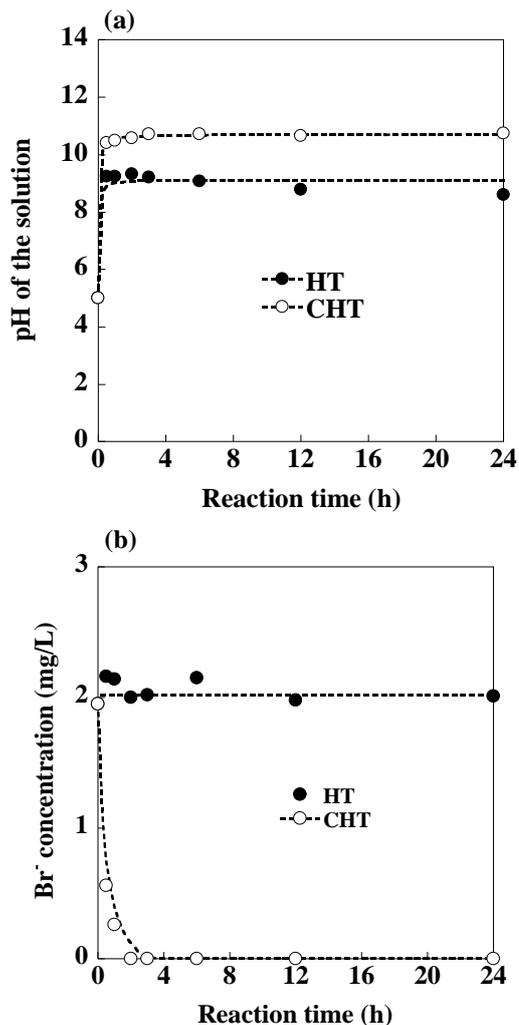


Fig. 2. Effects of reaction time on (a) solution pH and (b) Br⁻ concentration in solutions treated with HT and CHT.

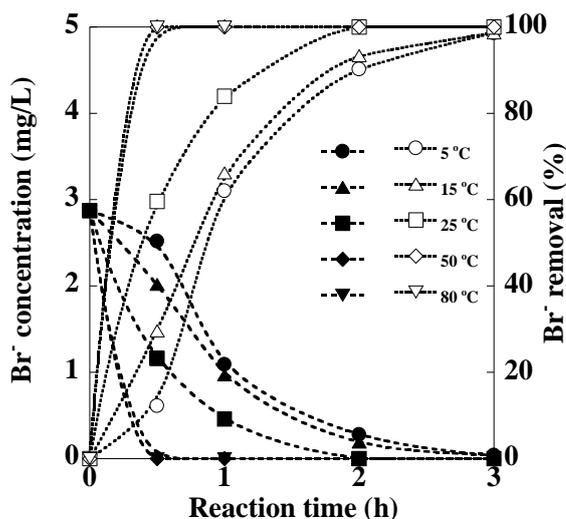


Fig. 3. Br⁻ concentrations in solutions and removal of Br⁻ from desalinated water during treatment with CHT at 5, 15, 25, 50, and 80 °C.

The kinetics of the adsorption process were investigated using pseudo-first-order and pseudo-second-order equations, i.e., equations (3) and (4), respectively, to analyze the experimental data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (4)$$

where q_e and q_t are the amounts of Br^- adsorbed at equilibrium and at time t (h), and k_1 (h^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$) are the adsorption rate constants of the pseudo-first-order and pseudo-second-order equations, respectively. Fig. 4(b) and Fig. (c) show the linearized forms of the pseudo-first-order and pseudo-second-order models for Br^- adsorption onto CHT. The kinetics parameters were calculated from the slopes and intercepts of the linear plots of $\ln(q_e - q_t)$ versus t , and t/q_t versus t ; the results are summarized in Table II.

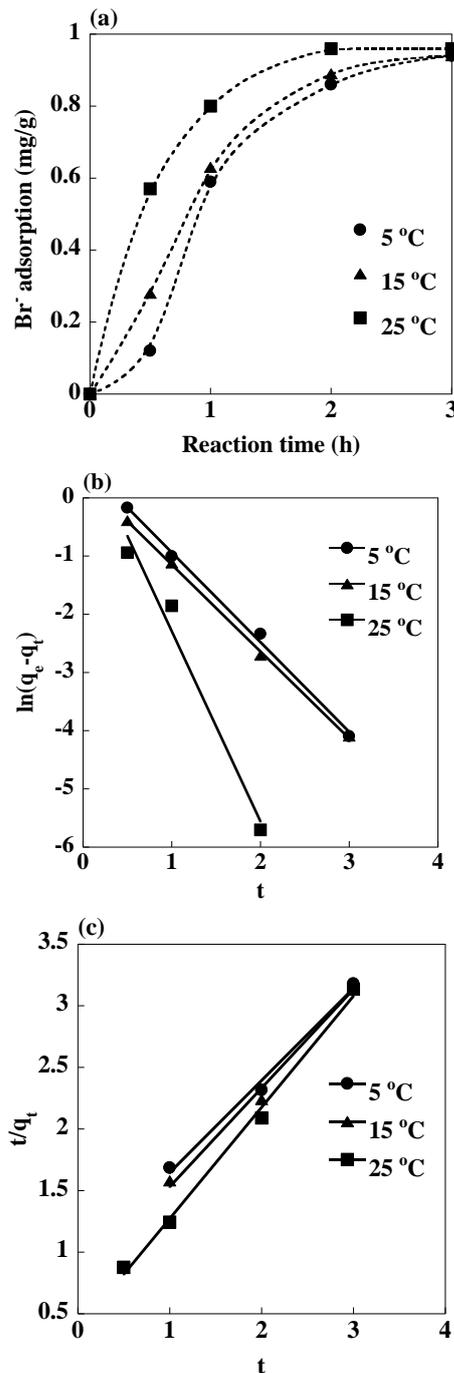


Fig. 4. (a) Adsorption of Br^- from desalinated water onto CHT at 5, 15, and 25 °C, (b) pseudo-first-order kinetics study of Br^- adsorption onto CHT at 5, 15, and 25 °C, and (c) pseudo-second-order kinetics study of Br^- adsorption onto CHT at 5, 15, and 25 °C.

Temperature (°C)	Pseudo-first-order equation			Pseudo-second-order equation		
	k_1 (h^{-1})	q_e (mg/g)	R^2	k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$)	q_e (mg/g)	R^2
5	1.542	1.831	0.997	0.621	1.34	0.992
15	1.493	1.417	0.999	0.876	1.25	0.990
25	3.271	2.674	0.977	2.210	1.11	0.995

The R^2 coefficients for the pseudo-first-order and pseudo-second-order models are high (>0.99) and have almost the same values, except in the case of the pseudo-first-order model at 25 °C. The theoretical q_e for the pseudo-second-order model is 1.11–1.34 mg/g, which is closer to the experimental q_e than the q_e for the pseudo-first-order model is. These results indicated that the pseudo-second-order model adequately describes the kinetics of Br^- adsorption from desalinated water onto CHT.

The activation energy for Br^- adsorption from desalinated water onto CHT was calculated using the Arrhenius equation:

$$k_2 = A \cdot \exp\left(-\frac{\Delta E}{RT}\right) \quad (5)$$

where ΔE is the activation energy (kJ/mol), A is the frequency factor, T is the absolute temperature (K), and R is the gas constant. The activation energy for the adsorption of Br^- from desalinated water onto CHT was calculated to be 43.5 kJ/mol from the plot of $\ln k_2$ versus $1/T$ (Fig. 5).

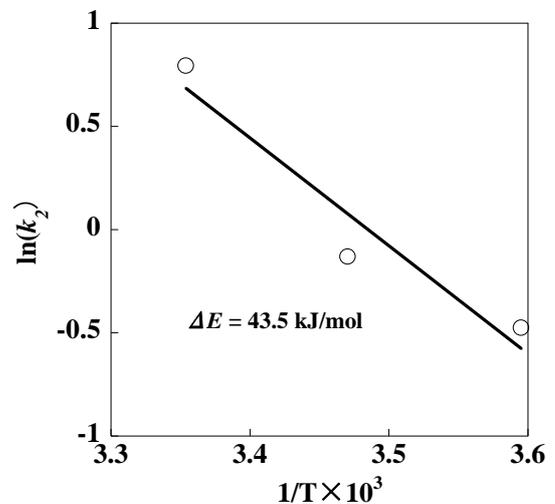


Fig. 5. Arrhenius plot for Br^- adsorption from desalinated water onto CHT.

IV. CONCLUSION

To establish an effective use of ocean resources, we used an inorganic anion exchanger, i.e., HT, for Br^- removal from desalinated water produced from seawater using upward spray flash desalination. CHT removed large amounts of Br^- from desalinated water, whereas non-calcined HT removed little Br^- . The removal of Br^- from desalinated water using CHT increased with increasing temperature. The adsorption kinetics of Br^- from desalinated water onto CHT followed a pseudo-second-order model rather than a pseudo-first-order model. These results indicate that CHT can reduce the Br^- concentration in desalinated water, and has possible

applications as an adsorbent for removal of ions from drinking water before sterilization.

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