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REMOVAL OF SILVER(I) FROM AQUEOUS SOLUTION USING JAPANESE NATURAL ZEOLITES (MORDENITE AND CLINOPTILOLITE): A COMPARATIVE STUDY

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ABSTRACT: The adsorption of silver ion in aqueous solution onto Japanese natural zeolites, i.e., mordenite (MZ) and clinoptilolite (CZ), from Iizaka mine, Fukushima Prefecture and Koriyama mine, Kagoshima Prefecture, respectively, is analyzed in this study. The effects of various parameters, i.e., solution pH, adsorbent dosage, adsorption time, silver ion solution concentration, and temperature, on silver ion adsorption onto the Japanese natural zeolites are investigated as a comparative study. For both zeolites, the optimum pH for silver adsorption is determined to be 3–4, and the adsorption processes can be described better using the Langmuir isotherm model than the Freundlich isotherm model. The calculated maximum adsorption capacities of MZ and CZ are 0.728 $mmol \cdot g^{-1}$ and 0.546 $mmol \cdot g^{-1}$, respectively. Adsorption kinetics studies are conducted, and the results show that the adsorption processes for both zeolites correspond to the pseudo-second-order kinetics model instead of the pseudo-first-order model. These results suggest Japanese natural zeolites have a potential for removing silver ion from aqueous solution.

Keywords: Mordenite, Clinoptilolite, Silver ion, Adsorption, Kinetics

1. INTRODUCTION

The removal of metal ions from industrial wastewater using different adsorbents has received significant interest [1] because industrial wastewater often contains considerable amounts of metal ions that pose a potential threat to public health and the environment if discharged without adequate treatment. High concentrations of problematic metals in solution can affect humans, animals, and vegetation. Water and soil pollution by metal cations increases proportionally with the amount of industrial activities. To minimize costs associated with the treatment of such industrial wastewater, most previous investigations have focused on the use of low-cost adsorbents [2, 3].

Recently, the use of natural zeolites to control heavy metal ion pollution in effluents has increased. Natural zeolites exhibit ion-exchange capabilities for removing metal ions, rendering them suitable for use in wastewater treatment [4-6]. In addition, natural zeolites are inexpensive [7]. Zeolites are naturally occurring crystalline aluminosilicates that comprise a framework of tetrahedral molecules linked by shared oxygen atoms, exchangeable alkaline and alkaline earth metal cations (typically Na^+, K^+, Ca^{2+}, and Mg^{2+}), and water. Additionally, zeolites exhibit a porous structure that encloses interconnected cavities, which contain metal ions and water molecules [8]. The fundamental building block of zeolites is a tetrahedron of four oxygen atoms surrounding a relatively small silicon or aluminum atom. Because aluminum has one less positive charge than silicon, the framework has a net negative charge of one at each aluminum atom site and is balanced by exchangeable cations (ECs) [9].

Silver is typically used as a raw material in various industries owing to its excellent malleability, ductility, electrical and thermal conductivities, photosensitivity, and antimicrobial properties. Accordingly, copious amounts of silver are lost in effluents discharged from such industries. Furthermore, owing to the toxicity of silver to living organisms, it must be removed from wastewater. The applicable methods for removing silver include precipitation, electrolysis, solvent extraction, and those involving the use of ion-exchange resins and chelating agents. These methods can be used on a large scale when the metal effluent concentrations are sufficiently high (>100 ppm). To minimize processing costs and reduce the metal concentration in industrial wastewater, most recent investigations have focused on the use of low-cost adsorbents such as zeolites [10, 11].

Additionally, silver–zeolite composites have been reported to inhibit bacterial growth under aerobic and anaerobic conditions [12, 13]. Some microorganisms that exist in our living environment assist in ecological cycles, whereas others cause diseases in people, animals, and plants [14]. Microorganism growth and death are affected by environmental factors, such as temperature, pH, oxygen level, pressure, and light irradiation. Antimicrobial agents, such as alcohols, phenols, halogenated compounds, quaternary ammonium

salts, heavy metal ions (Ag^+, Zn^{2+}, Cu^{2+}, $Fe^{2+/3+}$, Cd^{2+}, and Pd^{2+}), silver nanoparticles, metal oxides (ZnO, MgO, and Ag_2O), zirconium phosphates, oxidizing agents (ozone, chlorine, and its derivatives), heat, and ultraviolet light are used to prevent contamination or sterilize contaminated materials. Owing to its broad-spectrum antibacterial and anti-microbial properties, non-toxicity to humans, high biocompatibility degree, excellent resistance to sterilization conditions, and long-term antibacterial efficiency, silver, either in metallic or nanoparticle form or as an ion, is the most frequently used antibacterial agent for controlling bacterial growth. Antibacterial agents such as silver plates, silver nitrate solution, or silver sulfadiazine can be used directly but not preferred owing to the high cost incurred. However, preparing antibacterial silver as a support material with a high specific surface area and porosity is preferable. Examples of carrier support materials for silver include polymers, metal oxides, silica, glass, clay, synthetic zeolites (such as LTA, LTX, LTY, ETS-10), and natural zeolites (such as mordenite) and clinoptilolite) [15-19]. These exemplified supports are the most typical and economical carriers owing to their user-friendly management, non-toxicity, and controlled long-term release rate.

In the present study, we investigated the potential of locally available Japanese natural zeolites, i.e., mordenite (MZ) and clinoptilolite (CZ), for removing Ag^+ from aqueous solutions and the optimization of conditions for maximum adsorption. The effects of various parameters (pH, adsorbent dosage, initial solution concentration, reaction time, and temperature) on the Ag^+ adsorption process were investigated to evaluate the adsorption properties of Japanese natural zeolites MZ and CZ as Ag-supported materials for use as bactericides or for removing Ag^+ from polluted industrial waters.

2. RESEARCH SIGNIFICANCE

This research explores the potential of Japan's abundant natural zeolites, particularly from volcanic regions, as a sustainable and cost-effective resource for future development. By investigating the silver adsorption capacity of two Japanese natural zeolites, the study aims to assess their effectiveness in various applications, including wastewater treatment and the preparation of silver-supported materials. The findings could offer valuable insights into utilizing local, environmentally friendly materials for industrial purposes, promoting both resource efficiency and environmental sustainability. This work contributes to the development of innovative solutions for managing waste and enhancing material applications in Japan's growing technological landscape.

3. MATERIALS AND METHODS

3.1 Samples

Two natural Japanese zeolite samples, i.e., MZ and CZ, were used in this study. MZ was obtained from the Iizka mine, Fukushima Prefecture, Japan, whereas CZ was obtained from the Koriyama mine, Kagoshima Prefecture, Japan. Prior to performing experiments, the sample was ground to a certain particle size (< 250 μm) and dried at 80 °C in a drying oven overnight. Table 1 shows the ECs and cation exchange capacity (CECs) of the natural zeolites, which were determined using a modified Schollenberger method. The CECs (1.67 and 1.51 $mmol \cdot g^{-1}$) were relatively high, and most of the EC sites were occupied by Na^+ and Ca^{2+}. Therefore, these two Japanese natural zeolite samples exhibited similar CECs and ECs, although their crystal structures were different.

Table 1 Exchangeable cations and cation exchange capacities of natural zeolites, MZ and CZ.

	Exchangeable cations ($mmol \cdot g^{-1}$)				CEC ($mmol \cdot g^{-1}$)
	Na^+	K^+	Mg^{2+}	Ca^{2+}	
MZ	0.56	0.21	0.03	0.44	1.67
CZ	0.58	0.28	0.02	0.40	1.51

3.2 Experimental

Ag^+ solution was prepared from nitrate salt $AgNO_3$ (>99% purity, Wako, Japan) and distilled water. The amount of Ag^+ adsorbed per unit mass of zeolite at equilibrium, q_e ($mmol \cdot g^{-1}$), and the removal of Ag^+ from solution, R (%), were calculated based on changes in the Ag^+ concentration in the medium by considering the adsorption volume and amount of zeolite sample used, as follows:

$$q_e = (C_0 - C) \bullet V / w \quad (1)$$

$$R = (C_0 - C) / C_0 \times 100 \quad (2)$$

where C_0 ($mmol \cdot L^{-1}$) and C ($mmol \cdot L^{-1}$) are the initial and measured concentrations, respectively; V is the solution volume (L); w is the weight of zeolite sample (g).

3.2.1 Effect of pH

The effect of solution pH on Ag adsorption was investigated using a 0.5 mM $AgNO_3$ solution over a pH range of 1–8. The pH of the Ag solution was

adjusted using HNO_3 solution. Adsorption tests were conducted in 50 mL polypropylene centrifuged tubes. In each adsorption trial, zeolite (0.1 g) was added to 20 mL of the Ag^+ solution at room temperature, and the tube was agitated using a reciprocal agitator (200 rpm). After 2 h of mixing, the aqueous phase was separated from the solid (adsorbent) via centrifugation (3000 rpm, 10 min), the pH of the supernatant was measured using a pH meter (Horiba, D-53, Japan), and the concentration of Ag^+ in the supernatant was determined via inductively coupled plasma–atomic emission spectroscopy (ICP-AES; Seiko, SPS5510, Japan) to obtain q_e.

3.2.2 Effect of dosage

The effect of adsorbent dosage on Ag^+ removal was investigated using a 0.5 mM $AgNO_3$ solution. Varying amounts of zeolite samples ranging from 0.02 to 0.2 g were added to a 20 mL Ag^+ solution in a tube at room temperature, and the tube was agitated for 2 h using a reciprocal agitator as per the procedure above. Subsequently, the aqueous phase was separated from the solid via centrifugation, as described above. The pH of the supernatant was measured using a pH meter, and the concentration of silver ions in the supernatant was determined via ICP-AES to calculate *R*.

3.2.3 Effect of initial silver concentration

The effect of the initial Ag^+ solution concentration on the adsorption capacity of the natural zeolites was determined using solutions with concentrations ranging from 0.1 to 5 mM. First, a zeolite sample (0.1 g) was added to 20 mL of Ag^+ solution in a tube at room temperature, and the tube was agitated for 2 h. Subsequently, the aqueous phase was separated from the solid via centrifugation, and the Ag^+ supernatant concentration was determined via ICP-AES to calculate q_e.

3.2.4 Effect of temperature and adsorption time

To determine the adsorption time of Ag^+ from the aqueous solution onto natural zeolites, 1 g of the zeolite sample was added to 200 mL of 1 mM $AgNO_3$ solution in a 500 mL glass beaker, and the mixture was stirred using a magnetic stirrer at 20 °C. While stirring, 2 mL aliquots were sampled from the solution at varying times, filtrated, and the Ag^+ concentration in the filtrate was determined via ICP-AES to calculate the amount of Ag^+ adsorbed on the zeolite at sampling time *t*, q_t, by Eq. (1) based on the difference between the initial Ag^+ concentration and the Ag^+ concentration at the sampling times. To investigate the effect of temperature on the adsorption time, experiments were conducted at two additional temperatures, i.e., 30 °C and 40 °C. In addition, the concentrations of Na^+, K^+, Mg^{2+}, and Ca^{2+} from the ECs of the natural zeolites in the solution were determined via ICP-AES.

4. RESULTS AND DISCUSSION

Solution pH is an important factor that affects Ag^+ adsorption at solid–liquid interfaces. The pH dependence of Ag^+ adsorption on natural Japanese zeolites is shown in Figure 1. The experiments were conducted using silver ion solutions with different pH values. As observed for both MZ and CZ, the adsorption uptake of Ag^+ was low at low pH values; subsequently, it increased with the pH level before decreasing as the pH increased further (> 4); finally, it stabilized at pH > 6.0. The highest Ag^+ adsorption was achieved at an equilibrium pH ~ 4. These results are consistent with those of several investigations pertaining to Ag^+ removal [20-24]. In these studies, the low adsorption capacity at pH < 4 was attributed to the competition between protons and Ag^+ for exchange sites on zeolite particles [25, 26]. As the pH increases, the precipitation of Ag on the zeolites can occur, which decreases the adsorption/ion exchange uptake for achieving the equilibrium Ag^+ concentration. Notably, MZ affords a higher adsorption amount than CZ in acidic solutions (pH 1–4); however, the maximum adsorption at pH ~ 4 and the adsorption behavior above pH 4 are similar for both natural zeolites.

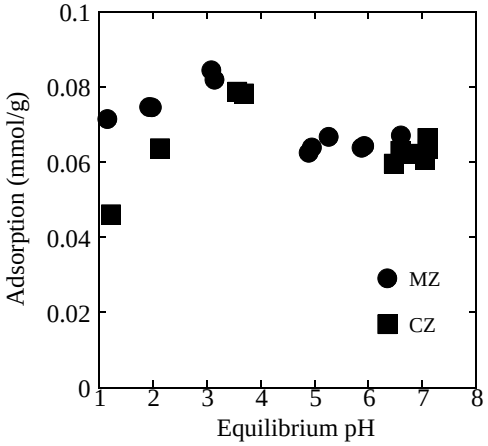

Fig.1 pH dependence of silver adsorption on Japanese natural zeolites, MZ and CZ

Figure 2 shows the change in solution equilibrium pH as a function of the initial pH. The solution equilibrium pH increased when the initial pH was between 2 and 6. This implies that the zeolites have a negative surface charge at a pH lower than 2, and that the lower uptake is due to competition between the Ag^+ and H^+ ions for the adsorption/exchange sites. In the pH range between

2 and 6, the Ag^+ uptake is accompanied by an increase in solution pH owing to the decrease in H^+ in the solution. This Ag^+ uptake is believed to have occurred via ion exchange and/or adsorption. Notably, the equilibrium pH values of the solution containing MZ are lower than those containing CZ, which implies that MZ is more acidic than CZ.

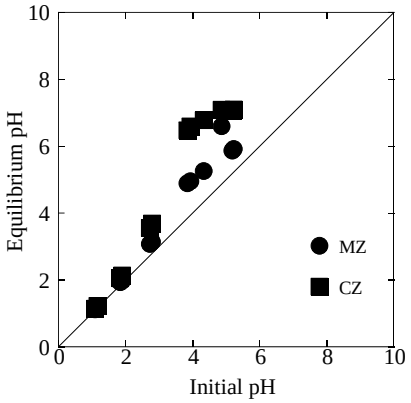

Fig.2 Variation in solution equilibrium pH as a function of solution initial pH

Figure 3 illustrates the effect of adsorbent dosage on the solution pH and silver removal by the natural zeolites. For both MZ and CZ, as the absorbent dosage increased, both the removal percentage and solution pH increased. Furthermore, adsorbent dosages greater than 5 g/L efficiently removed silver (approximately 95%) from the solution. Regardless of the dosage, the pH of the solution containing MZ was lower than that containing CZ, whereas the removal of Ag+ using MZ was more effective than that using CZ.

Figure 4 shows the Ag adsorption isotherms of the zeolite samples. The silver ad-sorption of MZ was higher than that of CZ, and as their equilibrium concentrations in-creased, the silver ion uptake of MZ and CZ increased to approximately 0.6 and 0.5 mmol·g^{-1}, respectively, before reaching a plateau.

The equilibrium distribution of Ag^+ between the zeolite and solution is important for determining the maximum sorption capacity. Several isotherm models are available to describe the equilibrium sorption distribution. In the present study, two models, i.e., the Langmuir and Freundlich models, were used to fit the experimental data.

The linear forms of the Langmuir and Freundlich models can be expressed as follows:

$$C_e/q_e = 1/(q_{\max} \bullet K_L) + C_e/q_{\max} \quad (3)$$

$$\ln(q_e) = \ln(K_F) + \ln(C_e)/n \quad (4)$$

where C_e is the equilibrium concentration (mmol·L^{-1}), and q_e (mmol·g^{-1}) is the amount sorbed at equilibrium (mmol·g^{-1}). Additionally, q_{max} (mmol·g^{-1}) and K_L (L·mmol^{-1}) are the Langmuir constants associated with the maximum adsorption capacity (which corresponds to the complete coverage of the available adsorption sites) and the adsorption energy (equilibrium adsorption constant), respectively; K_F and n are the Freundlich constants.

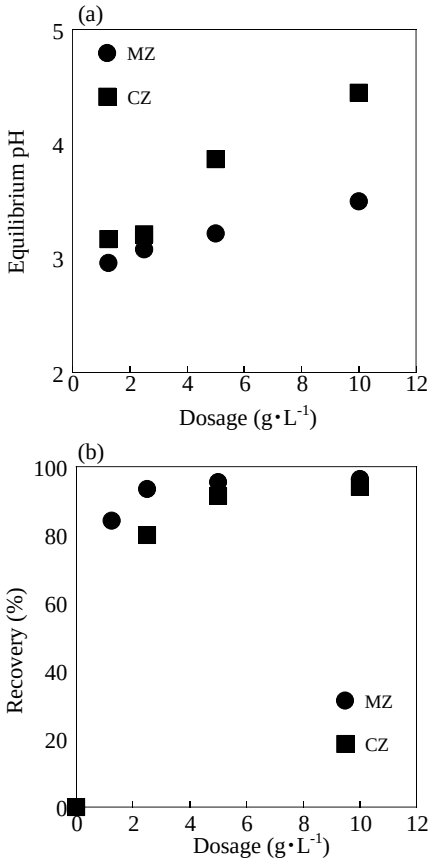

Fig.3 Effect of adsorbent dosage on (a) solution pH and (b) silver removal by natural zeolites, MZ and CZ

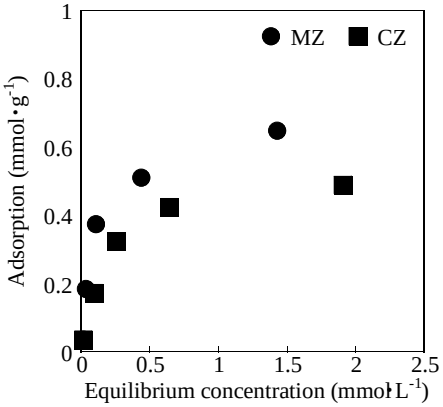

Fig.4 Silver ion adsorption capacities of natural zeolites, MZ and CZ

The Langmuir and Freundlich isotherm models were applied to the experimental data presented in Figure 4, and the associated parameters calculated from the fitted data are listed in Table 2. For both natural zeolites, the Langmuir model fitted the data better than the Freundlich model owing to the

higher correlation regression coefficient R^2 (a goodness-of-fit indicator) of the data fitted with the Langmuir model. As discussed in a previous study [27], the uptake of various metals by natural zeolites is attributable to different ion-exchange mechanisms and adsorption processes. The maximum silver adsorption capacities (q_{max}) of MZ and CZ, as calculated using the Langmuir isotherm model, were 0.728 and 0.546 mmol·g^{-1}, respectively, which are comparable with those reported in the literature. For instance, the adsorption of Ag^+ onto H-Na-ZDM-5 zeolite [28], mordenite [29], different types of chitosan [30], and coal [31] generated maximum adsorption capacities of 0.57, 0.04–0.21, 0.4, and 0.017 mmol•g^{-1} of adsorbent, respectively.

Table 2 Isotherm parameters and correlation regression using Langmuir and Freundlich models for Ag^+ adsorption of Japanese natural zeolites

Langmuir			Freuldlich		
q_{max}	K_L	R^2	n	K_F	R^2
0.728	5.68	0.982	1.77	0.485	0.790
0.546	4.75	0.998	1.77	0.218	0.897

Figure 5 shows the adsorption profiles of Ag^+ onto the natural zeolites at reaction temperatures of 20 °C, 30 °C, and 40°C. For MZ, as the solution temperature increased, the uptake of Ag^+ increased, and the amount of adsorbed Ag^+ increased rapidly before reaching an equilibrium value after 20 min. For CZ, regardless of the temperature, the uptake behavior of Ag^+ was similar, and the amount of adsorbed Ag^+ increased rapidly before reaching an equilibrium value after 10 min. Notably, the temperature dependence of silver adsorption for MZ was greater than that for CZ.

The kinetic adsorption data obtained from Figure 5 were analyzed using different kinetic models, i.e., the Lagergren pseudo-first-order and pseudo-second-order models, as follows:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \bullet t \quad (5)$$

$$t/q_t = 1/(k_2 \bullet q_e^2) + t/q_e \quad (6)$$

where q_t is the amount removed from the adsorbent at any time (mmol·g^{-1}); k_1 (min^{-1}) and k_2 (g·(mmol·min)$^{-1}$) are the adsorption rate constants. The values of k_1, k_2, R^2, and q_e (i.e., $q_{e,1}$ and $q_{e,2}$) are listed in Table 3. A comparison of the R^2 values revealed that the adsorption process for both natural zeolites corresponded to the pseudo-second-order model instead of to the pseudo-first-order model. Regardless of temperature, the adsorption rate constants, k_2, of CZ (123.6–158.8) were higher than those of MZ (12.7–20.9), indicating that the adsorption kinetics of CZ for silver is faster than that of MZ. Meanwhile, the adsorption amounts of silver, q_e, for both natural zeolites were similar.

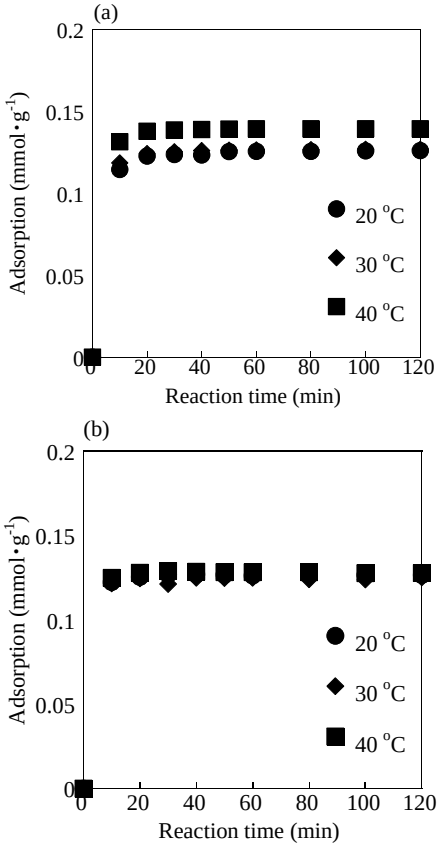

Fig.5 Silver ion adsorption on natural zeolites (a) MZ and (b) CZ at 20, 30 and 40 °C as a function of reaction time

Table 3 Kinetics parameters and correlation regression using pseudo-first-order and pseudo-second-order kinetics models

	Temperature (°C)	Pseudo-first-order kinetics model			Pseudo-second-order kinetics model		
		k_1	q_e	R^2	k_2	q_e	R^2
MZ	20	0.169	0.060	0.794	14.0	0.184	1.000
	30	0.165	0.062	0.792	12.7	0.180	1.000
	40	0.182	0.052	0.773	20.9	0.172	1.000
CZ	20	0.220	0.022	0.967	133.2	0.155	1.000
	30	0.208	0.008	0.841	158.8	0.156	1.000
	40	0.382	0.013	0.886	123.6	0.167	1.000

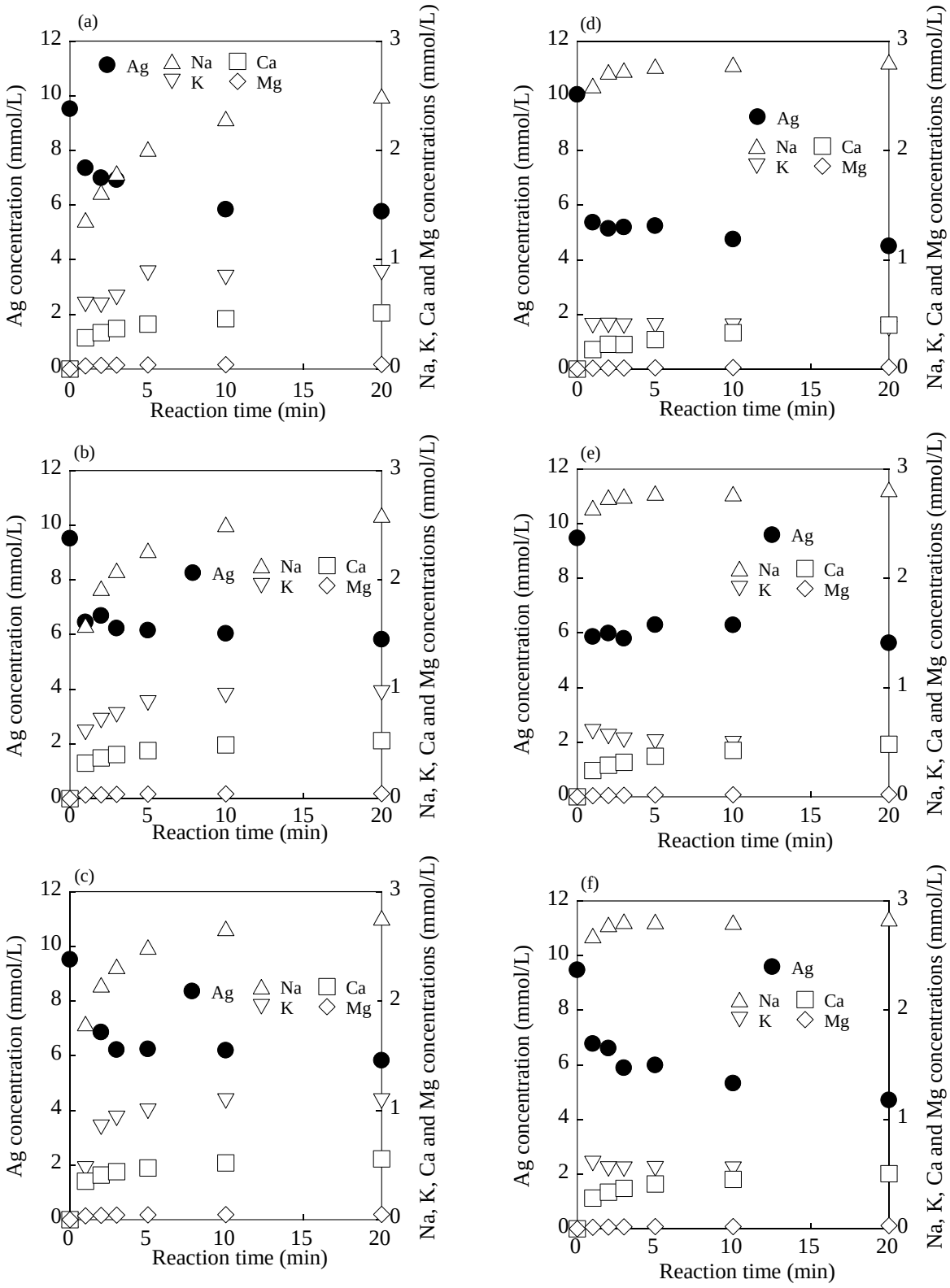

Fig.6 Concentrations of Ag^+, Na^+, K^+, Ca^{2+} and Mg^{2+} in solution with 10 mM Ag^+ at reaction temperatures of 20, 30 and 40 °C after MZ and CZ additions, as a function of reaction time: (a) MZ, 20 °C; (b) MZ, 30 °C; (c) MZ, 40 °C; (d) CZ, 20 °C; (e) CZ, 30 °C; (f) CZ, 40 °C

Figure 6 shows the concentrations of Ag^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} in the solution with 10 mM Ag^+ at reaction temperatures of 20 °C, 30 °C, and 40 °C after the addition of MZ and CZ. Regardless of temperature and the zeolite type, the concentration trend of the divalent cations, Mg^{2+} and Ca^{2+}, was similar, whereas the concentrations of monovalent cations, Na^+ and K^+, by adding CZ increased faster than those by adding MZ, resulting in the decrease in Ag^+ concentration due to CZ being faster than that due to MZ. It is speculated that the silver adsorption of natural zeolites primarily depends on the ion exchange be-tween Ag^+ and the monovalent ECs in the natural zeolites, i.e., Na^+ and K^+.

5. CONCLUSION

In the present study, the interaction between Ag^+ and Japanese natural zeolites was investigated, and the different properties of Japanese natural zeolites, i.e., MZ and CZ, for removing silver from aqueous solutions were clarified. The results indicated that several factors, such as pH, adsorbent dosage, adsorption time, initial Ag^+ solution concentration, and temperature, affected the adsorption process using those natural zeolites.

The optimum pH for silver adsorption by both natural zeolites was approximately 4. The equilibrium adsorption capacities of both natural zeolites for silver ions were measured and extrapolated using the Langmuir and Freundlich isotherm models, and the experimental data fitted better with the Langmuir isotherm model. The calculated maxi-mum adsorption capacity of MZ was 0.73 $mmol \cdot g^{-1}$, which was higher than that of CZ (0.55 $mmol \cdot g^{-1}$). The adsorption kinetics of both natural zeolites were tested for pseudo-first-order and pseudo-second-order reactions, and the rate constants of adsorption for these kinetic models were calculated. Adsorption experiments on both natural zeolites demonstrated that the adsorption process corresponded to a pseudo-second-order kinetics model instead of a pseudo-first-order.

In summary, the current findings demonstrated the potential of natural Japanese zeolites as effective and efficient materials for removing Ag^+ from aqueous solutions.

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