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Removal of Ag(I) from Aqueous Solution by Japanese Natural Clinoptilolite

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Abstract

The present study examined the adsorption of silver ion in aqueous solution onto natural clinoptilolite zeolite from Futatsui Mine, Akita Prefecture, Japan. The effects of various parameters, *i.e.*, solution pH, adsorbent dosage, adsorption time, silver ion solution concentration, and temperature, on silver ion adsorption process onto clinoptilolite were examined. Additionally, the thermodynamics of the silver ion adsorption process was investigated. The optimum pH for silver adsorption was determined to be around 4.0. The adsorption process could be well described by the Langmuir isotherm model. The calculated maximum adsorption capacity was 0.64 mmol/g. Adsorption kinetics studies were also conducted. The results showed that the adsorption process preferentially followed the pseudo-second-order kinetics model over the pseudo-first-order model. Furthermore, with decreasing aqueous solution temperatures, the adsorption kinetics became slower and the amount of silver ion adsorbed increased. The thermodynamic values, ΔG^0, ΔH^0, and ΔS^0, indicated that adsorption was an exothermic and spontaneous process.

Keywords

Clinoptilolite, Ag(I) Removal, Adsorption, Natural Zeolite

1. Introduction

The removal of metal ions from industrial wastewaters using different adsorbents is always of great interest [1] [2] because industrial wastewaters often contain considerable amounts of metal ions that could pose a potential threat to the public health and environment if discharged without adequate treatment. High concentrations of problematic metals in solution can affect humans, animals, and vegetation. The pollution of water and soil by metal cations increases proportionally with the expansion of industrial activities [3] [4]. To minimize the costs associated with the treatment of such industrial wastewaters, most of the last investigations have focused on the use of low-cost adsorbents [5] [6].

In recent years, the use of natural zeolites to control heavy metal ions pollution of effluents has increased. Natural zeolites have ion-exchange capabilities toward removing metal ions, thus making them suitable for use in wastewater treatment. In addition, natural zeolites are considered to be inexpensive [7] [8]. Zeolites are a naturally occurring crystalline aluminosilicate that consists of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms, exchangeable alkaline and alkaline earth metal cations (typically Na^+, K^+, Ca^{2+}, Mg^{2+}), and water. Additionally, zeolites have a porous structure, enclosing interconnected cavities within which metal ions and water molecules are contained [9]. 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 the exchangeable cation [10]. Clinoptilolite, thomsonite, gismondine, and gonnardite are common known natural zeolites. Clinoptilolite is the most abundant in nature and has a typical chemical formula of $Na_6Al_6Si_{30}O_{72}\cdot 24H_2O$ [11] [12]. The chemical, surface, and ion-exchange properties of clinoptilolite have been examined in many studies [13]-[16]. For example, the selectivity of Na-form clinoptilolite toward Pb^{2+}, Cd^{2+}, Cs^+, Cu^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, N^{i2+}, Hg^{2+} was determined [17].

Silver is commonly used as a raw material in various industries owing to its excellent malleability, ductility, electrical and thermal conductivity, photosensitivity, and antimicrobial properties. Accordingly, copious amounts of silver are lost in the effluents discharged from such industries, and owing to its toxicity to living organisms, the removal of silver from wastewaters is important. Available technologies for the removal of silver include precipitation, electrolysis, and solvent extraction, and processes that use ion exchange resins and chelating agents. These methods can be used profitably on a large scale when metal effluent concentrations are sufficiently high, *i.e.*, >100 ppm [18]-[21]. To minimize processing costs and to reduce the metal concentration in industrial wastewaters, most recent investigations have focused on the use of low-cost adsorbents such as zeolites [22] [23].

Additionally, it has been reported that silver-zeolite composites can inhibit bacterial growth under aerobic [24] and anaerobic conditions [25]. Some of the microorganisms existing in our living environment assist in ecological cycles, while others are responsible for diseases in people, animals, and plants [26]. Microorganism growth and death are influenced 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+}, Pd^{2+}), silver nanoparticles, metal oxides (ZnO, MgO, Ag_2O) and zirconium phosphates, and oxidizing agents (ozone, chlorine and its derivates), heat, and UV light are used to prevent contamination or sterilize contaminated materials [27]-[37]. Owing to its broad-spectrum antibacterial and antimicrobial properties, lack of toxicity to humans, high degree of biocompatibility, excellent resistance to sterilization conditions, and long-term antibacterial efficiency, silver either in metallic and nanoparticle form or as an ion is the most frequently used antibacterial agent for controlling bacterial growth [27] [31] [36]-[43]. An antibacterial agent such as a silver plate, silver nitrate solution, or silver sulfadiazine could be used directly but is not preferred because of its high cost. Alternatively, preparing antibacterial silver as a supported material with a high specific surface area and porosity is preferable. Examples of carrier support material for silver include polymers [29] [44]-[47], metal oxides [48] [49], silica [50] [51], glass [52] [53], clay [47] [54] [55], synthetic zeolites (such as LTA [44] [56]-[61], LTX [56] [62], LTY [56], and ETS-10 [63]), and natural zeolites (such as mordenite [56] and clinoptilolite [31] [64]-[69]). These exemplified supports are the most common and economical carriers owing to their user-friendly handling, nontoxicity, and controlled long-term release rate.

In the present study, we examined the potential of locally available natural zeolite, clinoptilolite, for the removal of Ag^+ from aqueous solution and optimization of conditions for its maximum adsorption. The effects of various parameters, *i.e.*, pH, adsorbent dosage, initial solution concentration, reaction time, and temperature, on the Ag^+ adsorption process were investigated to evaluate the adsorption properties of clinoptilolite as Ag-supported material for use either as a bactericide or for the removal of Ag^+ from polluted industrial waters. Additionally, the thermodynamics and kinetics of Ag^+ adsorption onto clinoptilolite were investigated.

2. Experimental

2.1. Zeolite Sample

The zeolite sample (clinoptilolite) used in this study was obtained from Futatsui mine, Akita prefecture, Japan. Before the experiments, clinoptilolite was ground to a certain particle size (<250 μm) and dried at 80˚C in a drying oven overnight. **Table 1** shows the exchangeable cations and cation exchange capacity of clinoptilolite determined using a modified Schollenberger method [70]. The cation exchange capacity (1.67 mmol/g) is relatively high, and most of the exchangeable cation sites are occupied by Na^+ and K^+.

2.2. Adsorption Studies

Ag^+ solution was prepared from its nitrate salt, $AgNO_3$ (>99% purity, Wako, Japan), and distilled water. The amount of Ag^+ adsorbed on unit mass clinoptilolite at equilibrium, q_e (mmol/g), and the Ag^+ removal from solution, R (%), were calculated from changes in the Ag^+ concentration in the medium by considering the adsorption volume

Table 1. Exchangeable cations and cation exchange capacity of natural clinoptilolite zeolite (mmol/g).

Cation exchange capacity	Exchangeable cations			
	Na^+	K^+	Mg^{2+}	Ca^{2+}
1.67	0.84	0.71	0.02	0.07

and amount of zeolite sample used:

$$q_e = (C_i - C_e)V/m, \tag{1}$$

$$R = (C_i - C_e)/C_i \times 100, \tag{2}$$

and C_i and C_e are the Ag^+ concentrations in the solution before and after adsorption for a certain adsorption time, respectively (mM), m (g) is the mass of zeolite, and V (L) is the Ag solution volume.

2.2.1. Effect of Solution pH

The effect of solution pH on Ag adsorption was investigated using 0.5 mM $AgNO_3$ solution over a pH range of 1 - 8. The pH of the Ag solution was adjusted with HNO_3 solution. Adsorption tests were conducted in 50-mL polypropylene centrifuged tubes. In each adsorption run, 0.1 g zeolite was added to 20 mL Ag^+ solution at room temperature, and the tube was shaken using a reciprocal shaker (200 rpm). After 2 h of mixing, the aqueous phase was separated from the solid (adsorbent) by centrifugation (3000 rpm, 10 min), the pH of the supernatant was measured by a pH meter (Horiba, D-53, Japan) and the concentration of Ag^+ in the supernatant was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Seiko, SPS5510, Japan) to determine q_e.

2.2.2. Effect of Adsorbent Dosage

The effect of adsorbent dosage on Ag^+ removal was determined using 0.5 mM $AgNO_3$ solution. The zeolite sample at varying amounts of 0.02 - 0.2 g was added to 20 mL Ag^+ solution in a tube at room temperature, and the tube was shaken for 2 h with a reciprocal shaker as per the above procedure. After shaking, the aqueous phase was separated from the solid by centrifugation as per the above procedure. The pH of the supernatant was measured using a pH meter, and the concentration of silver ion in the supernatant was determined using ICP-AES to calculate R.

2.2.3. Effect of Initial Ag^+ Solution Concentration

The effect of initial Ag^+ solution concentration on the adsorption capacity of clinoptilolite was determined using solutions of concentrations ranging from 0.1 to 5 mM. First, 0.1 g zeolite sample was added to 20 mL Ag^+ solution in a tube at room temperature, and the tube was shaken for 2 h as per the above procedure. After shaking, the aqueous phase was separated from the solid by centrifugation as per the above procedure, and the Ag^+ supernatant concentration was determined by ICP-AES to calculate q_e and R.

2.2.4. Effect of Temperature on Adsorption Time

To determine the adsorption time of Ag^+ from aqueous solution onto clinoptilolite, 1 g zeolite sample was added to 200 mL (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, and the Ag^+ concentration in the filtrate was determined by ICP-AES to calculate the amount of Ag^+ adsorbed on the zeolite at a sampling time t, q_t, using the difference between initial Ag^+ concentration and the Ag^+ concentration at sampling times. To study the effect of temperature on the adsorption time, the experiments were conducted at two additional temperatures, *i.e.*, 30˚C and 40˚C.

3. Results and Discussion

3.1. Silver Adsorption

Solution pH is an important factor that influences (Ag^+) adsorption at solid-liquid interfaces. The pH dependence of Ag^+ adsorption onto zeolite is shown in **Figure 1**. Experiments were conducted using silver ion solutions at different pH values. As observed, Ag^+ adsorption uptake, q_e, was low at low pHs, then increased with increasing pHs before decreasing with further increased in pH (>4), and subsequently reached a plateau at pH > 6.0. The highest q_e was obtained at equilibrium pH of around 4. These results agreed with the results of several investigations on Ag^+ removal [71]-[75]. These studies attributed the low adsorption capacity at pH < 4 to the competition between protons and Ag^+ for the exchange sites on the zeolite particle [76] [77]. With increasing pHs, precipitation of Ag on the zeolite at higher pH values can occur, thereby decreasing the adsorption/ion exchange uptake to reach equilibrium Ag^+ concentration.

Figure 2 shows the change in the solution equilibrium pH as a function of solution initial pH. The solution equilibrium pH increased when the initial pH was between 2 and 6. These results show that the zeolite has a negative surface charge at a pH of ~2 and that the lower uptake results from competition between the Ag^+ and H^+ ions for the adsorption/exchange sites. In the pH range of 2 - 6, Ag^+ uptake is accompanied by an increase in solution pH. Ag^+ uptake is believed to proceed via ion exchange and/or adsorption mechanism. However, this increase in pH suggests that the reaction likely proceeds via an ion exchange mechanism and exchangeable cations are released in the aqueous solution.

Figure 3 illustrates the effect of adsorbent dosage on the solution pH and silver

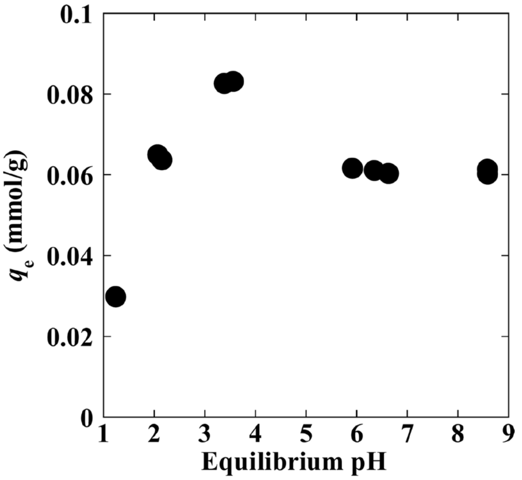

Figure 1. pH dependence of silver adsorption on natural clinoptilolite zeolite.

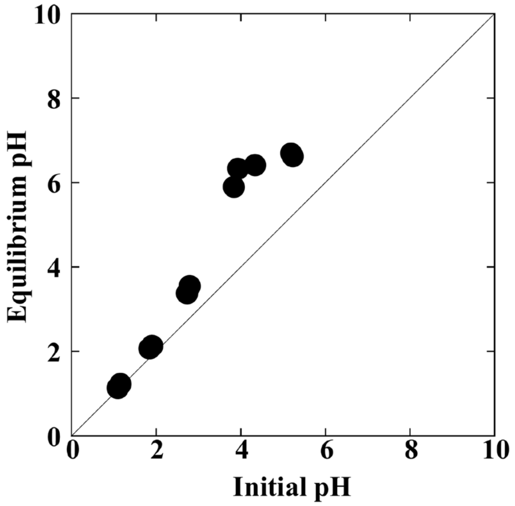

Figure 2. Variations in solution equilibrium pH as a function of solution initial pH.

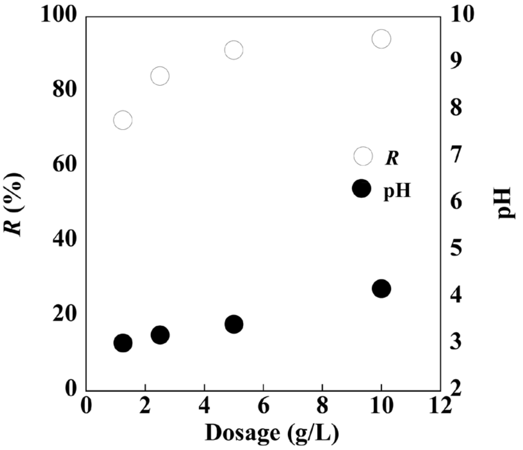

Figure 3. Effect of adsorbent dosage on solution pH and silver removal by clinoptilolite.

removal by clinoptilolite. With an increase in dosage, both the removal percentage and solution pH increased to approximately 95% and from 3 to 4, respectively. This result indicates that adsorbent dosages greater than 5 g/L are suitable to achieve efficient removal of silver from the solution.

Subsequently, the effect of varying the initial Ag^+ solution concentration (0.2 - 5 mM) on the Ag^+ uptake and removal from the solution was examined, and the results are shown in Figure 4. With increasing initial Ag^+ solution concentrations, the adsorption capacity increased, whereas the Ag^+ removal percentage decreased. These results indicate that energetically less favorable sites become involved with increasing Ag^+ concentrations in the aqueous solution.

Figure 6 shows the adsorption profiles of Ag^+ onto the zeolite sample at varying reaction temperatures of 20˚C, 30˚C, and 40˚C. The slopes of the lines joining the data points in the figure reflect the adsorption rates. As observed from Figure 5, with increasing solution temperatures, the uptake of Ag^+ decreased. However, the adsorption time was faster at the higher solution temperatures. Specifically, at 30˚C and 40˚C, the amount of adsorbed Ag^+ increased rapidly before reaching an equilibrium value after 20 min. In contrast, at a solution temperature of 20˚C, an equilibrium value was attained after 45 min. In a previous study, several adsorbents were examined toward the removal of Ag^+; an equilibrium adsorption time of 5 h was reported [78]. Short adsorption times are preferred owing to the lower energy consumption requirements. Thus, comparison between the adsorbents studied in the literature [78] and the present zeolite reveals that the latter is more efficient owing to the shorter adsorption time.

3.2. Adsorption Isotherm and Kinetics Studies

Figure 6 shows the silver adsorption isotherm of the zeolite sample. With increasing

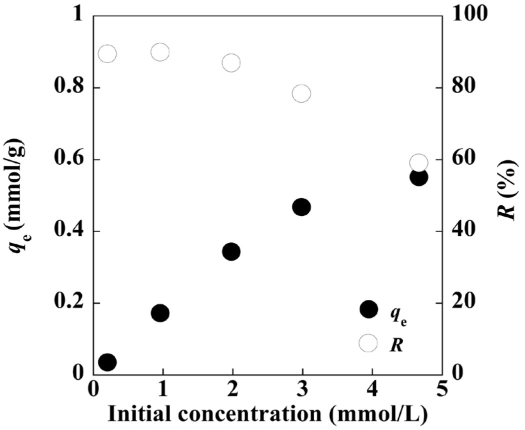

Figure 4. Variations in the silver ion uptake and silver removal as a function of initial silver ion solution concentration.

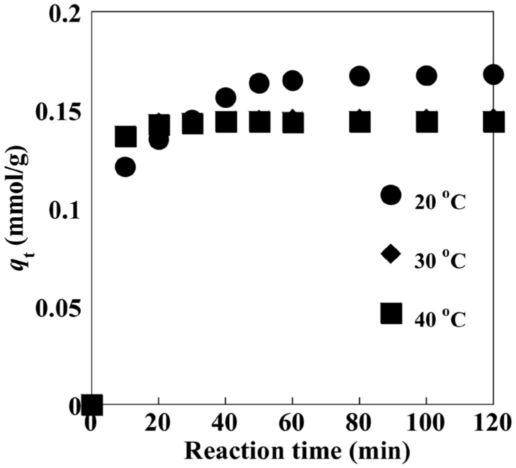

Figure 5. Silver ion adsorption on clinoptilolite at 20˚C, 30˚C, and 40˚C as a function of reaction time.

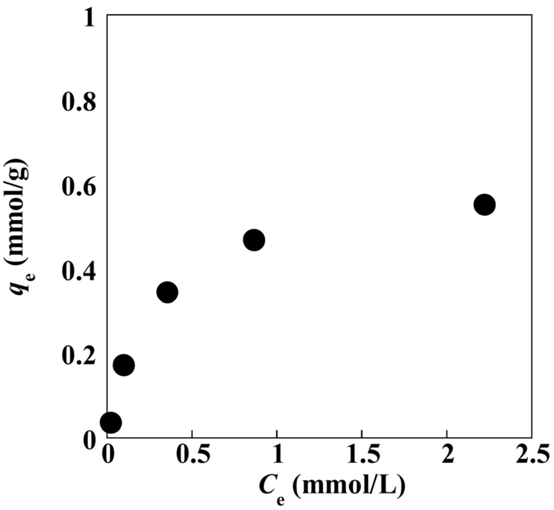

Figure 6. Silver ion adsorption capacity of clinoptilolite.

equilibrium concentrations, the silver ion uptake increased to approximately 0.6 mmol/g before reaching a plateau.

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

The linear form of the Langmuir model can be expressed as follows:

$$C_e/q_e = 1/(Q_{max}K_L) + C_e/q_{max}, \tag{3}$$

where Q_{max} (mmol/g) and K_L (L/mmol) are Langmuir constants related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites and a measure of adsorption energy (equilibrium adsorption constant), respectively. These constants can be respectively determined from the slope and intercept of the linear plot of C_e/q_e vs. C_e so that Q_{max} = 1/slope and K_L = slope/intercept.

The linear form of the Freundlich model can be expressed as follows:

$$\ln(q_e) = \ln(K_F) + \ln(C_e)/n, \tag{4}$$

where K_F and n are Freundlich constants determined from the slope and intercept of the plot of $\ln(q_e)$ vs. $\ln(C_e)$.

The Langmuir and Freundlich isotherm models were applied to the experimental data presented in Figure 5, and the associated parameters calculated from the fitted data are shown in Table 2. As observed from Table 2, the Langmuir model fitted the data better than the Freundlich model owing to the higher correlation regression coefficient R^2 (measure of the goodness-of-fit) of the data fitted with the Langmuir model. As discussed in a previous study [79], the uptake of various metals by natural zeolite can be attributed to different ion-exchange mechanisms and adsorption processes. Q_{max}, as calculated from the Langmuir isotherm model, was 0.64 mmol/g. The Q_{max} value obtained here is comparable with those reported in the literature. For instance,

Table 2. Langmuir- and Freundlich-fitted adsorption parameters and associated correlation regression coefficients.

Langmuir model			Freundlich model		
$Q_{\max}$ (mmol/g)	K_L (L/mmol)	R^2	n	K_F	R^2
0.64	3.7	0.995	1.64	0.55	0.898

the adsorption of Ag^+ onto H-Na-ZDM-5 zeolite [80], mordenite [81], different types of chitosan [82], and coal [83] generated maximum adsorption capacities of 0.57, 0.04 - 0.21, 0.4, and 0.017 mmol/g adsorbent, respectively.

The kinetics adsorption data obtained from **Figure 5** were analyzed using different kinetics models, *i.e.*, the Lagergren pseudo-first-order [84]-[86] and pseudo-second-order [87]-[102] models. The Lagergren pseudo-first-order model can be described as follows:

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - k_1 t, \tag{5}$$

where q_t (mmol of Ag^+/g zeolite) is the amount of Ag^+ adsorbed on the zeolite at time t and k_1 ($\min^{-1}$) is the adsorption rate constant. Parameters k_1 and $\ln(q_e)$ can be respectively deduced from the slope and intercept of the linear plot of $\ln\left(q_e - q_t\right)$ vs. t.

The linear form of the pseudo-second-order model can be expressed as follows:

$$t/q_t = 1\Big/\left(q_e^2 k_2\right) + t/q_e, \tag{6}$$

where k_2 (g/mmol min) is the adsorption rate constant, and k_2 and q_e can respectively be determined from the intercept and slope of the plot of t/q_t vs. t so that q_e = 1/slope and k_2 = slope²/intercept. The rate constants of the pseudo-first-order, k_1, and pseudo-second-order, k_2, reaction for Ag^+ adsorption were determined from **Figure 6**. The values of k_1, k_2, R^2, and q_e (*i.e.*, $q_{e,1}$ and $q_{e,2}$) are presented in **Table 3**. Comparison of the R^2 values reveals that the adsorption process follows the pseudo-second-order model better than the pseudo-first-order model.

As can be deduced from **Table 3**, $q_{e,2}$ and k_2 were dependent on the reaction temperature. To gain insights into the thermodynamic nature of the adsorption process, several thermodynamic parameters were calculated. The Gibbs free energy change, ΔG^0, was negative, as calculated from the following equation:

$$\Delta G^0 = RT \ln K_c, \tag{7}$$

where K_c is the adsorption equilibrium constant, R (8.314 J/(mol·K)) is the gas constant, and T(K) is the absolute temperature. K_c can be calculated as follows:

$$K_c = F_e\Big/\left(1 - F_e\right), \tag{8}$$

where F_e is the fraction of Ag^+ adsorbed at equilibrium and is obtained by the expression:

$$F_e = \left(C_0 - C_e\right)\Big/C_e. \tag{9}$$

Parameters C_0 and C_e are the initial and equilibrium concentrations of Ag^+ in solution (mmol/L).

Table 3. Adsorption kinetics parameters and associated correlation regression coefficients.

Reaction temperature (˚C)	Pseudo-first-order kinetics model			Pseudo-second-order kinetics model		
	$q_{e,1}$ (mmol/g)	k_1 ($\times 10^{-2}$) (1/min)	R^2	$q_{e,2}$ (mmol/g)	k_2 (g/(mmol·min))	R^2
20	0.047	1.76	0.824	0.18	1.1	0.999
30	0.005	1.96	0.782	0.15	13.0	1.000
40	0.003	1.88	0.495	0.14	23.0	1.000

The K_c values associated with the adsorption of Ag^+ on the zeolite at different temperatures were calculated using Equations (8) and (9), and the results are presented in Table 4. The K_c value obtained at 20˚C was higher than those at 30˚C and 40˚C. This result implies the strengthening of the adsorbate-adsorbent interactions at the lower temperature of 20˚C. Additionally, the obtained negative ΔG^0 values confirmed the feasibility and spontaneous nature of the adsorption process.

The Gibbs free energy can also be represented as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \tag{10}$$

The enthalpy change (ΔH^0) and entropy change (ΔS^0) change, which were calculated from the intercept and slope of the plot of ΔG^0 versus T, are presented in Table 4. The negative ΔH^0 value obtained confirmed the exothermic nature of the adsorption process. The negative ΔS^0 value indicated the decrease in the degree of randomness at the solid-solution interface with some structural changes in the adsorbate and adsorbent.

The activation energy related to the silver adsorption on clinoptilolite was calculated by the Arrhenius equation:

$$k_2 = A\exp\left(-\Delta E/RT\right), \tag{11}$$

where ΔE (kJ/mol) is the activation energy, A is the frequency factor, T (K) is the absolute temperature, and R is the gas constant. From the plot of ln(k_2) vs. $1/T$ (Figure 7), the activation energy for the adsorption of silver was found to be 116 kJ/mol.

4. Conclusion

In the present study, the interaction between Ag^+ and clinoptilolite zeolite was investigated. The results indicated that several factors, *i.e.*, pH, adsorbent dosage, adsorption time, initial Ag^+ solution concentration, and temperature, influenced the adsorption process. Of particular interest, the amount of Ag^+ adsorbed on clinoptilolite was highest at around pH 4, and the Ag^+ uptake increased with decreasing solution temperatures. The experimental data were fitted with the Langmuir and Freundlich adsorption isotherm models. The results revealed that the process was best described by the Langmuir model. The maximum adsorption capacity of the zeolite, as calculated from the Langmuir model, was 0.64 mmol/g. The Ag^+ adsorption kinetics from aqueous solution followed the pseudo-second-order model. The thermodynamic studies revealed that Ag^+

Table 4. Thermodynamics parameters of silver ion adsorption on clinoptilolite.

Reaction temperature (K)	K_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))
293 (20˚C)	3.95	−3.35	−12.7	−32.5
303 (30˚C)	2.72	−2.52		
313 (40˚C)	2.81	−2.70		

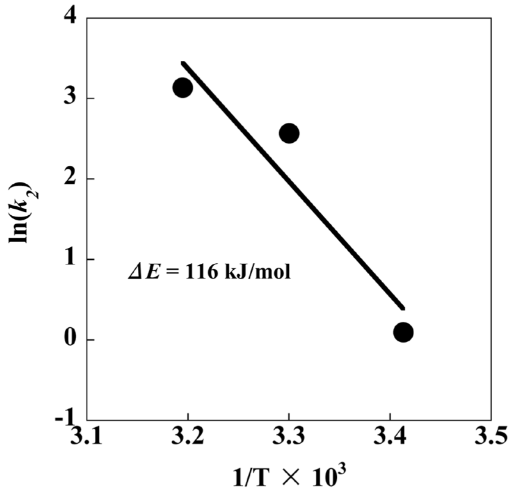

Figure 7. Arrhenius plot of silver adsorption on clinoptilolite.

adsorption on the zeolite was an exothermic and spontaneous process. In summary, the current findings demonstrate the potential of Japanese clinoptilolite as a suitable and efficient material for the removal of Ag^+ from aqueous solution.

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