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A comparison of the properties of natural clinoptilolites and their ion-exchange capacities for silver removal

Semra Çoruh*, Gaye Şenel, Osman Nuri Ergun

Department of Environmental Engineering, Ondokuz Mayıs University, 55139 Samsun, Turkey

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ABSTRACT

The aim of the present study is to investigate the removal of silver ions from aqueous solutions using natural clinoptilolites collected from Çankırı-Çorum and Manisa-Gördes regions of Turkey. The optimum conditions for adsorption/ion exchange by using a batch method were evaluated by changing various parameters such as particle size, contact time, initial pH of the solution, adsorbent amount, initial metal concentration and acidic treatment. The Langmuir, Freundlich and Temkin adsorption isotherm equations were derived form the basic empirical equations, and used for calculation of adsorption parameters. The equilibrium data fit well the Freundlich and Langmuir isotherm. The adsorption capacities of Çankırı-Çorum and Manisa-Gördes clinoptilolites as obtained from Langmuir isotherm were found to be 31.44 and 22.57 mg/g. The adsorption kinetic rates and metal recoveries were estimated by pseudo-first order, second order and intra-particle models.

1. Introduction

Industrial wastewater is often characterized by considerable heavy metal content and, therefore, treatment is required prior to disposal in order to avoid water pollution [1]. The presence of the above metals in the environment is of major concern of their toxicity accumulate in living organisms and threat for human life and for the environment, especially when tolerance levels are exceeded [2–4].

One of the most important heavy metal is silver. Silver is generally found in the combined state in nature, usually in copper or lead mineralization [5]. The major industrial use of silver is as silver halide in the manufacture of photographic film. In 1983, approximately 44% of silver was used in the manufacturing of chemicals for photographic products in the USA. Other industrial uses of silver include the production of electrical contacts and switching gear, batteries catalysts and mirrors. The main technologies used for silver removal wastewaters include precipitation, ion exchange, membrane processes, solvent extraction, cementation, electro coagulation, coagulation–flocculation, adsorption, reductive exchange and electrolytic recovery [6–14]. Adsorption has attracted attention because of new material types available for the recovery process. Cost-effective materials that have been investigated for their potential use as adsorbents for heavy metal uptake include sawdust [15], banana and orange peels [16], fly ash [17], red mud [18], tea industry waste [19], bagasse fly ash [20], phosphogypsum [21], bentonite [22], limestone [23] waste materials as refuse concrete [6], zeolite [1,3,24–30] and others (26–36(. Among the most frequently studied natural zeolite is shown to have selectivity for many cations mainly ammonium and heavy metals such as Pb, Cu, Zn, Cd. Zeolites are hydrated aluminosilicate minerals with a cage-like structure that offers large internal and external surface areas for ion exchange (1(. So far, some 40–50 different species of this mineral have been identified. The reasons for studying zeolites are their wide abundance in nature, low price of mining and processing, good mechanical, sorption and ion-exchanged properties. Clinoptilolite is the most abundant natural zeolite that occurs in relatively large sedimentary deposits in sufficiently high purity in many parts of the world (10–36(. Clinoptilolite is reported to have a classical alumina silicate age-like structure and therefore exhibits significant macro porosity. In nature, the cations present on clinoptilolite are calcium, sodium, potassium and magnesium (24,37(. The aim of this study is to investigate the efficiency of two clinoptilolites from Turkey in the removal of silver ions from aqueous solutions. The effects of particle size, clinoptilolite amount, adsorption time, metal ion concentration, pH and the acidic treatment on the adsorption process were examined. Experimental data have been analyzed by adsorption isotherms and kinetics parameters.

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* Corresponding author. Tel.: +90 362 312 19 19; fax: +90 362 457 60 35.
E-mail address: semcoruh@omu.edu.tr (S. Çoruh).

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Table 1
Chemical composition of natural clinoptilolite samples (wt%).

Major components	Çankırı-Çorum	Manisa-Gördes
SiO_2	64.28	71.00
TiO_2	0.17	0.10
Al_2O_3	12.07	11.80
Fe_2O_3	0.84	1.70
CaO	2.47	3.40
MgO	2.07	1.40
K_2O	0.83	2.40
Na_2O	5.62	0.40
SO_3	0.22	0.12
Others	11.43	7.68
Si/Al	3.68	4.69

2. Material and methods

2.1. Materials

The two natural clinoptilolites used in the experiments were obtained from Çankırı-Çorum (ÇÇ) and Manisa-Gördes (MG) locations in Turkey. They were crushed into small pieces from rock forms and then powdered in a mortar. The pulverized samples were then passed through the sieves to determine the grain size effect and classified into different size groups: 1.19–2 mm, 0.84–1.19 mm, 0.50–0.84 mm, 0.35–0.50 mm. Prior to batch adsorption experiments, the samples were washed with distilled water to remove the surface dust, and then dried in an oven at 70 °C. The chemical compositions of these materials are given Table 1. The crystalline phase composition of the Çankırı-Çorum and Manisa-Gördes clinoptilolites used in this work was characterized by SEM in Fig. 1. The cation-exchange capacity (theoretical capacity) of Çankırı-Çorum and Manisa-Gördes clinoptilolites were 83.6 and 65.4 meq/100 g, while specific surface areas of these materials were 75 and 54 m^2/g, respectively.

2.2. Method

All the chemicals used were of analytical reagent grade and were supplied by Sigma–Aldrich. $AgNO_3$ was used as a source for Ag(I). An ATI-UNICAM 929 model Atomic Absorption Spectrophotometer (AAS) was used for the determination of Ag(I) ions.

The effect of pH on the silver adsorption was investigated using 100 ppm Ag(I) containing solution over the pH range 2.0–8.0. The pH of silver solutions was adjusted by appropriate using HNO_3 or NaOH. Batch mode adsorption isotherm and kinetic studies were carried out 23 °C. Adsorption isotherms were performed for initial Ag(I) concentrations of 50, 100, 150, 200, 250 and 300 mg/L. Adsorption experiments were performed by shaking 0.125–3.0 g of clinoptilolite samples in a 100 mL of aqueous solutions of Ag(I) (solid/liquid ratio of 1.25–30 g/L). After the adsorption period, the mixtures were filtered with 0.45 (m filter and acidified with HNO_3 to decrease the pH to below 2 before the AAS measurement.

In order to obtain the adsorption capacity, the amount of silver adsorbed on the clinoptilolite (mg/g) was calculated the following expression:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of silver in the solution, respectively (mg/L), V is the volume of solution (L) and m is the weight of the adsorbent (g). Removal efficiency of silver ions by the adsorbent is considered in percentage as:

$$\text{Removal efficiency} = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

To determine desorption efficiency, the clinoptilolite sample loaded with the maximum amount of Ag(I) was added into the desorption solution (0.1 M HNO_3), and the sample was shaken in a shaker at 23 °C within 4 h. After shaking, the aqueous phase separated from the clinoptilolite and the concentration of Ag(I) in that phase determined.

The Ag(I) concentration desorbed was determined and the desorption efficiency (%) could be calculated by mass balance.

$$D = 100 \times \frac{C_d}{C_o - C_e} \tag{3}$$

where D is desorption efficiency (%), C_o and C_e are the initial and equilibrated concentrations of Ag(I) (mg/L) during the adsorption process, respectively. C_d is the desorbed equilibrium concentrations of Ag(I) (mg/L) during the desorption process.

3. Result and discussion

3.1. Effect of particle size

The samples were broken and sieved into the following particle sizes (mm): −2.0 + 1.19, −1.19 + 0.84, −0.84 + 0.50, −0.50 + 0.35, and −0.35 + 0.23. The adsorption characteristics of clinoptilolites with respect to particle sizes are given Table 2. Table 2 shows that decreasing in particle size of Çankırı–Çorum and Manisa-Gördes clinoptilolites causes an increase adsorption loading and adsorption efficiency. The difference between the minimum and maximum values of the removal efficiencies obtained for Çankırı–Çorum and Manisa-Gördes clinoptilolites samples of −1.19 + 0.84 and −0.35 + 0.23 mm were 1.87% and 6.01%. Therefore, increase in removal efficiency with decrease in particle size of natural clinoptilolites is not significant. Generally, the finer particle yields a higher adsorption capacity than the coarse one due to the higher specific surface area of the former (38–41(.

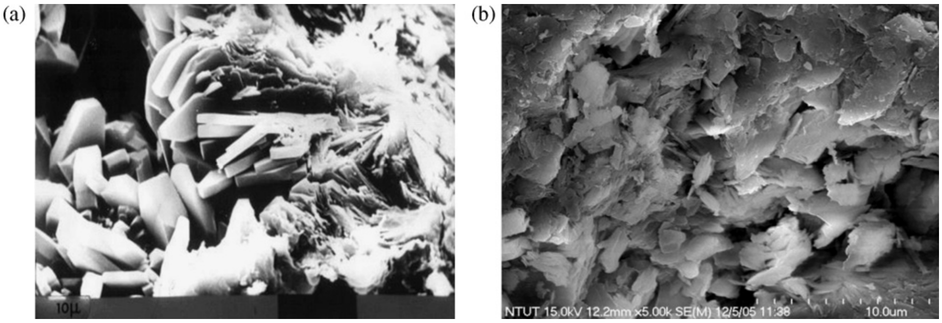

Fig. 1. Morphology of natural Çankırı-Çorum (a) and Manisa-Gördes clinoptilolites (b).

Table 2
Effect of particle size on removal of Ag(I).

Particle size (mm)	Metal adsorbed, q_e (mg/g)		Increase in adsorption (%)	
	Çankırı-Çorum clinoptilolite	Manisa-Gördes clinoptilolite	Çankırı-Çorum clinoptilolite	Manisa-Gördes clinoptilolite
−2.0 + 1.19	6.22	5.75	82.65	69.45
−1.19 + 0.84	8.02	6.69	96.68	80.74
−0.84 + 0.50	8.04	6.97	96.96	84.12
−0.50 + 0.35	8.13	7.27	98.11	87.72
−0.35 + 0.23	8.17	7.19	98.55	86.75

3.2. *Effect of pH*

It is well known that pH of the aqueous solution is an important controlling parameter in the adsorption and ion-exchange processes and metal removal typically increases with increasing pH values. Clinoptilolites are not only influenced by pH but in turn are capable of affecting solution pH especially in batch system and clinoptilolites tend to have a higher internal pH. In addition, the clinoptilolite surface may be influenced by the ambient pH which is not equal to the external solution pH value and precipitation within the channels of clinoptilolites and at the surface of clinoptilolites may occur. The removal efficiency of metal ions generally increased with increasing pH to a pH of around 6, and then increased only slowly thereafter, with further pH increases resulting in precipitation [9,22,42,43].

In order to determine the effects of pH on the adsorption of Ag(I) on the ÇÇ and MG clinoptilolites, batch equilibrium experiments were carried out 100 mg/L initial Ag(I) concentration and 10 g/L adsorbent at different pH levels ranging from 2 to 8. The effect of pH on Ag(I) adsorption by clinoptilolites was given in Fig. 2. As can be seen from Fig. 2, adsorption capacity of both materials increased the initial pH of the solution was increases from 2 to 4 and reached a maximum in the pH range of 6–8. The mechanism that governs the adsorption characteristics of clinoptilolite at pH ranges between 6 and 8 are adsorption and ion exchange the rapid increase at pH 8 can be attributed to the replacement of exchangeable cations present at the exchangeable sites, i.e. Na^+, K^+, Ca^{2+}, Mg^{2+} with Ag(I) cation in the aqueous solution. Similar results were reported in the literature [9,44–46].

The selectivity of metal ion by clinoptilolites is influenced by the character of the metal complex that predominates at a particular solution pH. Clinoptilolites are not only influenced by pH but in turn are capable of affecting solution pH especially in batch system and clinoptilolites tend to have a higher internal pH. In addition, the clinoptilolite surface may be influenced by the ambient pH which is not equal to the external solution pH value and precipitation within the channels of clinoptilolites and at the surface of clinoptilolites may occur. The adsorption capacity generally increased when the initial pH of solution was increased. This was because clinoptilolites were highly selective for H_3O^+ ions when the H_3O^+ ions concentration was high. Thus, at lower pH values, the H_3O^+ ions competed with metal ions for the exchange sites in clinoptilolite [47–49]. This result can be considered as an evidence for the Ag(I) removal by ion-exchange mechanism in the present study.

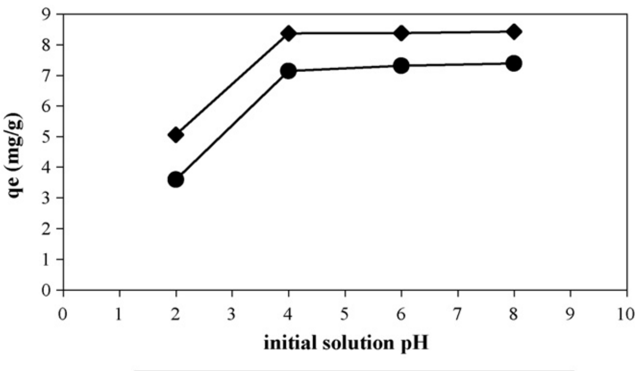

Fig. 2. Changes in the adsorbed amount of Ag(I) as a function pH (Co: 100 mg/L, contact time: 60 min, clinoptilolite amount: 10 g/L)

3.3. *Effect of contact time*

Fig. 3 shows the effect of contact time on the removal of Ag(I) ions from aqueous solution by two natural clinoptilolites. The contact time ranges between 5 and 480 min. The results showed that the adsorption of Ag(I) increases with time rapidly (in the first 5 min for Çankırı-Çorum clinoptilolite) and saturation in about 90–120 min.

3.4. *Effect of adsorbent dosage*

Fig. 4 shows the effect of the amount of ÇÇ clinoptilolite and MG clinoptilolite dosages on the silver removal. As it can be seen from Fig. 4 that while the removal efficiency of Ag(I) increased with the increase adsorbent dosage, but the amount of Ag(I) adsorbed by unit weight of the adsorbed decrease (Fig. 4). The removal efficiencies for 1.25 g/L of ÇÇ and MG samples were found to be 88.0 and 65.0%, respectively but as the clinoptilolite amount were increased to 20 g/L, removal efficiencies were found to be 99.0% and 95.0%, respectively. From Fig. 4, the decrease the adsorbed amount with the increase in adsorbent dosage may result from the electrostatic interactions, interference between binding sites, and reduced mixing at higher adsorbent densities. Also, the reason for decrease in the sorption capacity was due to the increasing interface area when the suspension was diluted [22,50,51].

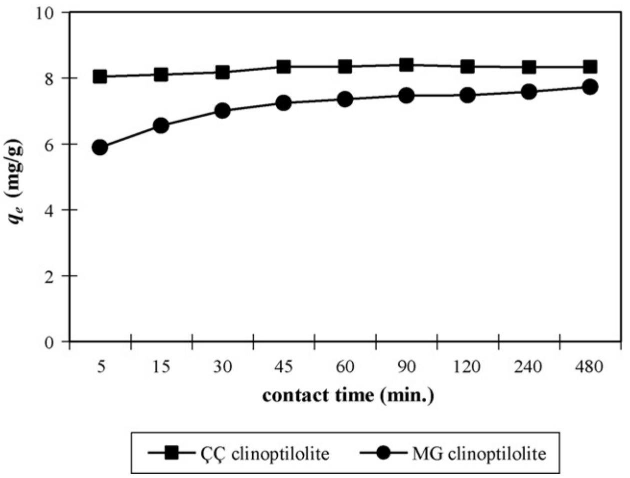

Fig. 3. Changes in adsorption capacity as a function of contact time (Co: 100 mg/L, clinoptilolite amount: 10 g/L).

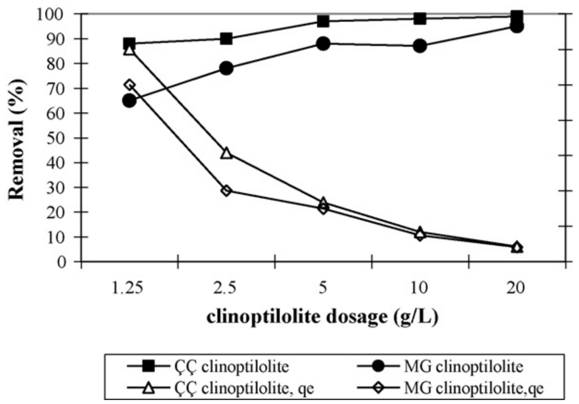

Fig. 4. Changes in Ag(I) removal and adsorption capacity as a function of clinoptilolite dosage (Co: 100 mg/L, contact time: 60 min).

3.5. Effect of initial metal concentration

The effect of initial metal concentration on the adsorption was investigated by varying the initial concentration of Ag(I) between 50 and 300 mg/L. The initial metal concentration provides an important driving force to overcome all mass transfer resistance of Ag(I) between the aqueous and solid phase. Fig. 5 shows the adsorption of Ag(I) on natural clinoptilolites as an initial metal ion concentration. The percent adsorption of Ag(I) is inversely related to the initial metal ion concentrations. Percentage of Ag(I) removal decreased as its concentration increased at fixed adsorbent dosage. As can be seen from Fig. 5, increasing the metal ion concentration led to an increase in the Ag(I) adsorption by natural clinoptilolites. This can be attributed to the effective pore diffusivity decrease with increasing initial metal concentration [52].

3.6. Effect of acidic desorbent on desorption

Desorption studies help to elucide the mechanism of adsorption and to estimate the degree of recovery of precious metals adsorbed from the waste waters. The utilization of natural clinoptilolites for removing metals from the solutions is commonly cycling and accounts for the regeneration of clinoptilolite in order to its reuse. Generally, common diluted acids such as nitric acid, hydrochloric acid was considered as desorbents for heavy metal ions [7,53].

The desorption efficiency for Ag(I) from the adsorbents were calculated using Eq. (3). When the Ag(I) carrying clinoptilolite samples were treated with 0.1 M HNO_3, it was observed that desorption efficiency and adsorption capacity for Ag(I) increase the increasing desorption time, as can be from Fig. 6. The desorption efficiencies of 0.1 M HNO_3 increasing abruptly within 60 min, reached equilibrium after approximately 120 min. The desorption efficiencies of Manisa-Gördes clinoptilolite were higher than Çankırı-Çorum clinoptilolite. The maximum desorption efficiencies of Manisa-Gördes and Çankırı-Çorum clinoptilolites were obtained as 58.41% and 45.70% Ag(I), respectively.

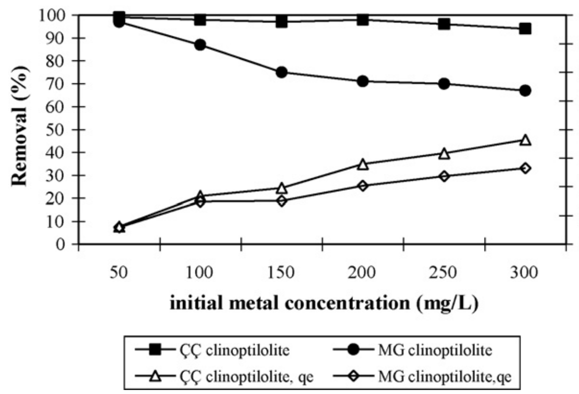

Fig. 5. Changes in Ag(I) removal and adsorption capacity as a function of initial metal concentration (Clinoptilolite amount: 10 g/L, contact time: 60 min).

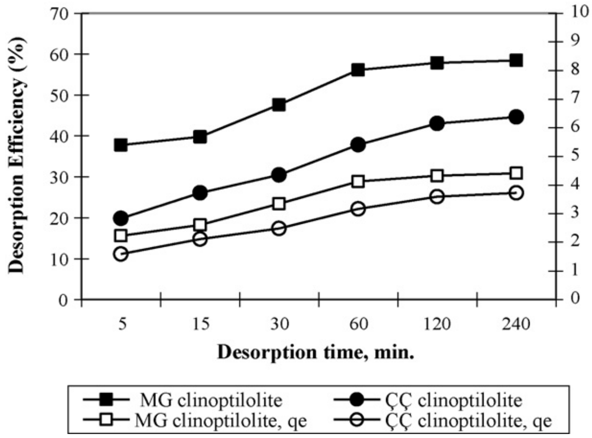

Fig. 6. Effect of time on desorption of 0.1 M HNO_3 desorbent solution (100 mL desorbent solution was contacted with 1 g/L of Çankırı-Çorum and Manisa-Gördes clinoptilolites which adsorbed Ag(I) solution, 100 mg/L, for 60 min at 23 °C).

Acidic pre-treatment of the clinoptilolite leads to the creation of new sites accessible for ion exchange. Also, the structural changes formed as a result of the interaction of clinoptilolite with the acidic solution. Thus, there is an increase in the uptake of silver because the natural clinoptilolite is transformed into its H^+ form with more effective ion-exchange ability than that the raw material. This has been found for the sorption of some heavy metals on H^+-form of clinoptilolites. The ion-exchange reaction of silver is with H^+ ions. It should be noted that results of previous investigations on desorption with HNO_3 show a continuous and rather fast decrease in the adsorption ability with progressing desorption time [7,54].

3.7. Comparison of adsorption isotherms

The equilibrium data for the adsorption are commonly known as adsorption isotherms. In this research, in order to determine the mechanism of silver adsorption on the Manisa-Gördes and Çankırı-Çorum clinoptilolites the experimental data were applied to the Langmuir, Freundlich and Temkin isotherm equations.

The Langmuir equation is valid for the monolayer adsorption onto surfaces a finite number of identical sites and the Langmuir isotherm equation could be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

where q_e is the amount adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_m and K_L are the Langmuir constants related to the saturated monolayer sorption capacity and the sorption equilibrium constant, respectively. q_m and K_L were calculated from the slope and intercept of the plots [49,50,55,56].

The Freundlich equation is employed to describe heterogeneous systems, and the equation in logarithmic form is given by Eq. (5),

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration in mg/L, K_F and n were the empirical Freundlich constants and indicative of adsorption capacity and adsorption intensity, respectively [57,58].

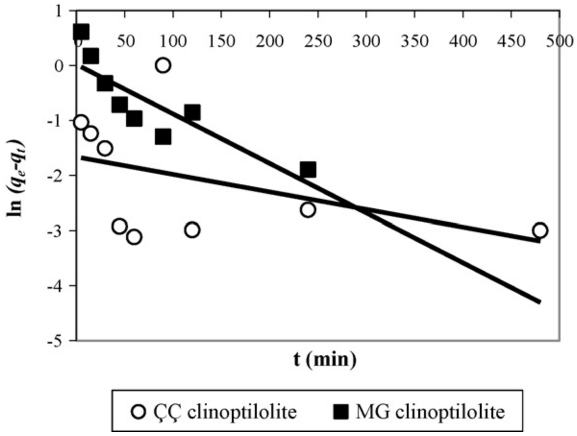

Fig. 7. Linearized pseudo-first order kinetics plots for the adsorption of Ag(I).

Temkin isotherm model is given in Eq. (6):

$$q_e = B\ln A + B\ln C_e \tag{6}$$

where $B=(RT)/b$, q_e (mg/g) and C_e (mg/L) are the amounts of adsorbed Ag(I) per unit weight of adsorbent and unadsorbed Ag(I) concentration in solution at equilibrium, respectively. Also, T the absolute temperature in K and R is the universal gas constant, 8.314 J/mol K. The constant B is related to the heat of adsorption [59,60].

The corresponding Langmuir, Freundlich and Temkin parameters along with correlation coefficients are given Table 3. It was found that the experimental data are better fitted with the Freundlich equation. The Freundlich model predicts mathematically an infinite surface coverage of the sorbent by the sorbate, indicating the formation of multilayers on the surface [53]. The maximum adsorption capacities of ÇÇ and MG clinoptilolites were found to be 31.44 and 22.57 mg/g, respectively. Different adsorbents have been reported for the adsorption of Ag(I) [61]. H–Na–ZMS-5 zeolite was used and an adsorption capacity of 61 mg Ag(I)/g zeolite was found. In another study, molecular-imprinted biosorbent was used and adsorption capacity range was found to be 49.83 mg Ag(I)/g [7].

3.8. Adsorption kinetics

The parameter values obtained from the application of kinetic models were used to predict the variation of adsorbed Ag(I) ion with time using natural clinoptilolites. The rate constants of chemical adsorption and intra-particle diffusion for silver adsorption on Çankırı-Çorum and Manisa-Gördes clinoptilolites were determined using the equations of the pseudo-first order and pseudo-second order models. Pseudo-first order model is one of the most widely used procedures for the adsorption of a solute from aqueous solution [4,26,62,63]. The pseudo-first order equation can be expressed as follows:

$$\ln(q_e - q_t) = \ln\ q_e - k_1 t \tag{7}$$

where q_e and q_t were the amounts of silver adsorbed (mg/g) at equilibrium and at time t, respectively and k_1 is first order rate constant for adsorption (L/min). The rate constant, k_1, was calculated from the plots of $\ln(q_e - q_t)$ versus t for silver adsorption. The pseudo-first order rate constants k_1 and correlation coefficients are presented in Table 4. The adsorption of silver on Çankırı-Çorum and Manisa-Gördes clinoptilolites were not fitted to a first-order model and is shown in Fig. 7.

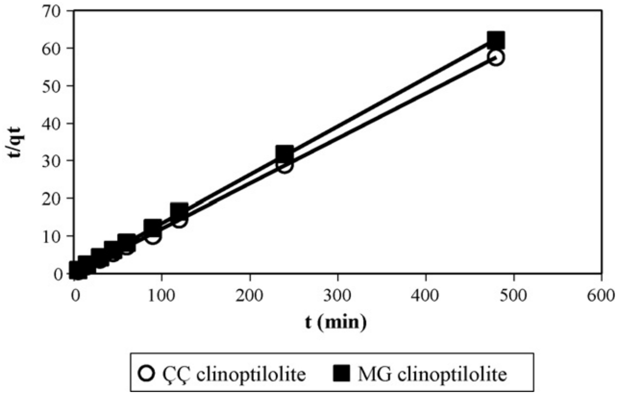

Fig. 8. Linearized pseudo-second order kinetics plots for the adsorption of Ag(I).

Pseudo-second order kinetics may be expressed as the following equation [10,57,64]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where q_e and q_t are the amount of the heavy metal (mg/g) adsorbed at equilibrium (mg/g), k_2 (g/mg min) is the rate constant of the second-order kinetic equations. The pseudo-second order kinetic for Ag(I) removal using Çankırı-Çorum and Manisa-Gördes clinoptilolites is presented Fig. 8. The second-order kinetic rate constants k_2 and correlation coefficients are presented in Table 4. The correlation coefficients for the second-order kinetic model were higher than 0.999 indicating the applicability of this kinetic model of the adsorption process of silver ions on clinoptilolites.

The rate parameter for intra-particle diffusion equation is given using the following equation [65,64]:

$$\log R = \log k_{id} + \alpha \log t \tag{9}$$

where R is the percent silver adsorbed, t is the contact time (min), α is the gradient of linear plots, and k_{id} is the intra-particle diffusion rate constant (mg/g min$^{1/2}$). Consistent with Eq. (9), the values of R correlated linearly with values of log t and the rate constant k_{id} directly evaluated from slope of the regression line. In this model, due to the porous nature of the adsorbent, pore diffusion is expanded to be surface adsorption. Fig. 9 exhibits the intra-particle diffusion model of silver adsorption on Çankırı-Çorum and Manisa-Gördes clinoptilolites. The intra-particle diffusion rate constants k_{id} and correlation coefficients are presented in Table 4.

The correlation coefficients (R^2) of the pseudo-second order model were high, indicating that the pseudo-second order kinetic model best describe the adsorption of silver ion on clinoptilolite.

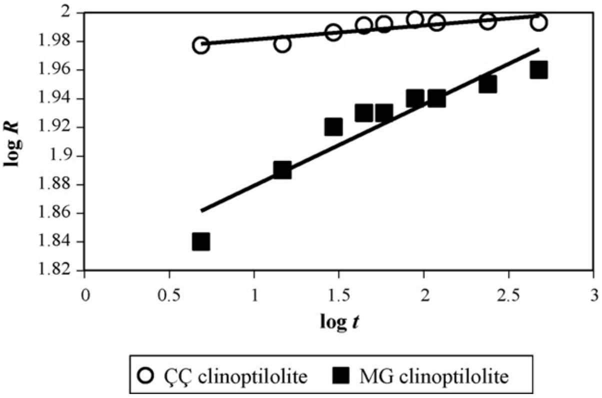

Fig. 9. Linearized intra-particle diffusion kinetics plots for the adsorption of Ag(I).

Table 3
The parameters for Langmuir, Freundlich and Temkin isotherms.

Materials	Langmuir constants			Freundlich constants			Temkin constants		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	$1/n$ (g/L)	R^2	A (L/g)	B (j/mol)	R^2
ÇÇ clinoptilolite	31.44	0.381	0.9396	5.98	0.596	0.9354	19.05	3.557	0.7762
MG clinoptilolite	22.57	0.051	0.8397	3.96	0.337	0.9328	1.80	3.454	0.7733

Table 4
Kinetic values calculated according to pseudo-first order, second order and intra-particle models.

	First-order model			Second-order model			Intra-particle diffusion		
	q_e (mg/g)	k_1 (L/min)	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2	k_{id} (mg/g min$^{1/2}$)	α	R^2
ÇÇ clinoptilolite	45.70	0.003	0.3845	8.34	0.202	0.9998	93.62	0.009	0.7598
MG clinoptilolite	1.04	0.009	0.7418	7.76	0.035	0.9999	66.42	0.056	0.8859

4. Conclusion

The aim of this study was to investigate the effectiveness of the natural clinoptilolites to remove silver ions from aqueous solutions. In the present study, it was observed that silver adsorption is dependent on the adsorbent amount, particle size, contact time, initial pH of the solution and initial metal concentration.

As the clinoptilolite amounts increased, the removal efficiencies increased, but on the other hand the adsorbed amount on the clinoptilolite decreased with the increasing clinoptilolite amounts. These results show that removal efficiency was increased with increasing amounts of the Çankırı-Çorum and Manisa-Gördes clinoptilolites. It had been found that the highest removal efficiency with Çankırı-Çorum clinoptilolite was obtained. The removal efficiency of natural clinoptilolites is strongly affected by the pH of the solution. The effect of pH of the solution could significantly improve the adsorption rate and adsorption capacity of Ag(I) ions.

The maximum adsorption capacities of Çankırı-Çorum and Manisa-Gördes clinoptilolites were found to be 31.44 and 22.57 mg/g, respectively. The experimental data were well fitted to the Freundlich equation, with good correlation coefficients. The adsorption kinetics of Ag(I) ions onto clinoptilolite well describe by pseudo-second order model. These results showed that Çankırı-Çorum and Manisa-Gördes clinoptilolites which may represent a valid alternative to traditional treatments based on precipitation can be used effectively as an adsorbent/ion-exchange material for the removal Ag(I) ions from aqueous solutions and wastewaters.

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