

# Removal of silver (I) from aqueous solutions with clinoptilolite

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## Abstract

The aim of the present work was to investigate the ability of natural zeolite, clinoptilolite, to remove silver ions from aqueous solution. Towards this aim, batch adsorption experiments were carried out and the effect of various parameters on this removal process has been investigated. The effects of pH, adsorption time, metal ion concentration and the acidic treatment on the adsorption process were examined. The optimum pH for adsorption was found to be 4.0. It was found that acid treatment has a substantial effect on the metal uptake. In adsorption studies, residual  $\text{Ag}^+$  concentration reached equilibrium in a short duration of 45 min. Maximum adsorption capacity, 33.23 mg  $\text{Ag}^+$ /g zeolite, showed that this adsorbent was suitable for silver removal from aqueous media. Adsorption phenomena appeared to follow Langmuir and Freundlich isotherms.

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## 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 would endanger public health and the environment if discharged without adequate treatment. High concentrations of the metals in solution affect humans, animals and vegetation. The pollution of water and soil with metal cations increases proportionally with the expansion of industrial activities [3,4]. In order to minimize processing costs for these industrial wastewaters, most of the last investigations have focused on the use of low cost adsorbents [5,6].

In the last years, utilization of natural zeolites to control the pollution due to the effluents polluted with heavy metal ions has increased. Natural zeolites have ion-exchange capability to remove unwanted metal ions and this prop-

erty makes zeolites favorable for wastewater treatment. Beside this, price of zeolites is considered very cheap [7,8]. Basically, zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms and containing exchangeable alkaline and alkaline earth metal cations (normally  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) as well as water in their structural framework. The physical structure is porous, enclosing interconnected cavities in which the metal ions and water molecules are contained [9]. The fundamental building block of the 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 the site of each aluminum atom and is balanced by the exchangeable cation [10]. Clinoptilolite, thomsonite, gismondine and gonnardite are the commonly known natural zeolites. Clinoptilolite is most abundant in nature and has a typical chemical formula of  $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$  [11,12]. The chemical, surface, and ion-exchange properties of clinoptilolite has been concerned

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in many studies [13–16]. For example, in one of these studies, selectivity of Na-form clinoptilolite for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  was determined [17].

Silver is a very useful raw material in various industries due to its excellent malleability, ductility, electrical and thermal conductivity, photosensitivity and antimicrobial properties. Significant amounts of silver are lost in the effluents discharged from such industries and due to the toxicity of silver to living organisms, the removal of this metal from wastewaters is an important concern. The presently available technologies for the removal of silver include precipitation, electrolysis, solvent extraction, use of ion-exchange resins, chelating agents, etc. These processes can be profitably used on a large scale when the metal concentrations in effluents are sufficiently high, i.e., above 100 ppm [18–21].

Taking into account all the above, we have considered it of great interest to assess the ability of locally available natural zeolite, clinoptilolite, for the removal of  $\text{Ag}^+$  from aqueous solution and optimization of conditions for its maximum adsorption. To increase the efficiency of metal removal and to maximize the amount of metal recoverable from solution the effects of various parameters (especially that of pH of the medium and the acidic treatment of the zeolite) on the  $\text{Ag}^+$  removal process have been investigated. Also, the thermodynamics of the  $\text{Ag}^+$  adsorption have been investigated.

## 2. Experimental

### 2.1. Zeolite sample

The zeolite sample used in this study was obtained from Bigadiç region of Turkey. Zeolite was grinded to certain size and its particle size was determined. Also its porosity and surface area characteristics were determined by using Surface Area and Pore Size Analyser (Quantachrome NOVA 2200).

### 2.2. Adsorption studies

$\text{Ag}^+$  solution was prepared from its nitrate salt,  $\text{AgNO}_3$  (Merck, >99% purity) with deionized water with a conductivity value of 18.2 M $\Omega$  (supplied from Barnstead Nano pure Diamond). The effect of pH on the silver adsorption was investigated using 100 ppm  $\text{Ag}^+$  containing solution over the pH range 2.0–6.0. The pH of silver solutions was adjusted by appropriate using  $\text{HNO}_3$  or  $\text{NaOH}$ . Adsorption tests were conducted in polypropylene beakers. In each adsorption study, 50 mg zeolite (dry weight) was added to 25 ml of the  $\text{Ag}^+$  solution at 25 °C and magnetically stirred continuously. After 1 h, the aqueous phase was separated from the zeolite by centrifugation and the concentration of  $\text{Ag}^+$  in that phase was determined by using Atomic Absorption Spectrophotometer (AAS, Hitachi 180/80 Flame AAS). Each adsorption experiment was

performed in triplicate and the mean of 6 AAS measurements was recorded.

The effect of the initial  $\text{Ag}^+$  ion concentration on the adsorption capacity of the zeolite at the optimum pH was determined using solutions with concentrations ranging from 10 to 150 ppm. Again, 50 mg zeolite (dry weight) was added to 25 ml of the  $\text{Ag}^+$  solution at 25 °C and magnetically stirred continuously. After 1 h, the aqueous phase was separated from the zeolite by centrifugation and the concentration of  $\text{Ag}^+$  in that phase was determined by using AAS.

The amount of adsorbed  $\text{Ag}^+$  ions (mg  $\text{Ag}^+$ /g zeolite) was calculated from the decrease in the concentration of  $\text{Ag}^+$  ions in the medium by considering the adsorption volume and used amount of the zeolite:

$$q_e = [(C_i - C_e) \times V]/m \quad (1)$$

Here,  $q_e$  is the amount of metal ions adsorbed onto unit mass of the zeolite (mg  $\text{Ag}^+$ /g zeolite) at equilibrium;  $C_i$  and  $C_e$  are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for certain adsorption time, respectively (ppm  $\text{Ag}^+$ );  $m$  is the amount of zeolite used (g – gram) and  $V$  is the volume of silver solution (l – liter).

To determine the adsorption rate of  $\text{Ag}^+$  ions from aqueous solution, same batch adsorption and analysis procedure given above was used and optimum adsorption time was determined.

To determine the re-usability of the zeolite sample, adsorption/desorption cycles were repeated seven times using the same zeolite sample.  $\text{Na}_4\text{-EDTA}$  (10 mM) was used as desorption agent. Zeolite samples carrying 33.23 mg  $\text{Ag}^+$ /g were placed in this desorption medium (25 ml) and stirred magnetically for 1 h at 25 °C. After 1 h, the aqueous phase was separated from the zeolite and the concentration of  $\text{Ag}^+$  in that phase was determined.

Also, the zeolite sample loaded with the maximum amount of  $\text{Ag}^+$  ions was treated with  $\text{HNO}_3$  to determine the effect of acidic treatment on the adsorption capacity. In this part, 50 mg (dry weight) portion of zeolite containing 33.23 mg  $\text{Ag}^+$ /g was treated with 25 ml of 0.1 M  $\text{HNO}_3$  solution at 25 °C for 1 h. After stirring, the aqueous phase was separated from the zeolite and the concentration of  $\text{Ag}^+$  in that phase was determined. This adsorption/desorption cycle was repeated by using the same zeolite sample to monitor the effect of treatment with acid on the adsorption capacity.

## 3. Results and discussion

### 3.1. Porosity and surface area characteristics of the zeolite

The physical properties of the zeolite samples (grinded to 65 mesh) determined by nitrogen adsorption equipment are set out in Table 1. A parameter that denotes the accessibility of the pores is the BET specific area of these

Table 1  
The physical properties of the zeolite samples

Zeolite structure	Original zeolite	Ag <sup>+</sup> loaded zeolite	Acid treated
Surface area (m <sup>2</sup> /g)	16.76	19.25	133.30
Mean pore diameter (Å)	39.71	39.87	39.41

materials determined from N<sub>2</sub> adsorption/desorption isotherm at 77 K. It is seen that the specific surface areas of the materials studied differ from each other considerably and the surface area of the acid treated zeolite sample is the highest due to increasing microporosity of its structure. The acid treatment results in a significant increase of BET surface area and pore volume due to the modification of zeolite structure. The mean pore diameter is around 39 Å regardless of the kind of treatment. When the ionic diameter of the Ag<sup>+</sup> ions, 0.126 nm, is considered, pore characteristic of the original zeolite can be considered suitable for the elimination of diffusional limitations for the metal ions which will move through the channels of the lattice and interact with zeolite during the treatment.

### 3.2. Adsorption of metal ion on zeolite

The metal uptake is attributed to different mechanisms of ion-exchange and adsorption processes [22]. During the ion-exchange process, metal ions move through the pores of the zeolite and channels of the lattice, and they replace exchangeable cations (mainly sodium) and additionally exchange with protons of surface hydroxyl groups. In the case of exchange with sodium,  $\text{Na}_{(\text{zeolite})}^+ + \text{M}_{(\text{solution})}^+ \rightarrow \text{M}_{(\text{zeolite})}^+ + \text{Na}_{(\text{solution})}^+$  reaction, in which sodium ions placed on the zeolite surface exchange with the metal ions (M<sup>+</sup>) in the solution, occurs. When the exchange site is a hydroxyl group,  $\text{zeolite-OH}_{(\text{zeolite})} + \text{M}_{(\text{solution})}^+ \rightarrow \text{zeolite-O-M}_{(\text{zeolite})} + \text{H}_{(\text{solution})}^+$  exchange reaction occurs and in this case, metal ions (M<sup>+</sup>) exchange with the H<sup>+</sup> ions. Diffusion was faster through the pores and retarded when the ions moved through the smaller diameter channels. The ion-exchange processes in zeolites are affected by several factors such as concentration and nature of cations, pH, and crystal structure of the zeolite. The effect of these parameters has been investigated in several studies due to the importance of zeolite's mineral stability and its structural changes under in various environments (such as acidic media) in the applications of zeolite as an ion exchanger [23–25].

### 3.3. Influence of variables on Ag<sup>+</sup> adsorption

#### 3.3.1. Effect of time

Fig. 1 illustrates the adsorption of Ag<sup>+</sup> ions by zeolite as a function of time. The amounts of Ag<sup>+</sup> ions adsorbed were calculated using Eq. (1). The adsorption conditions are given in the figure legends. The slopes of the lines joining the data points in the figure reflect the adsorption rates.

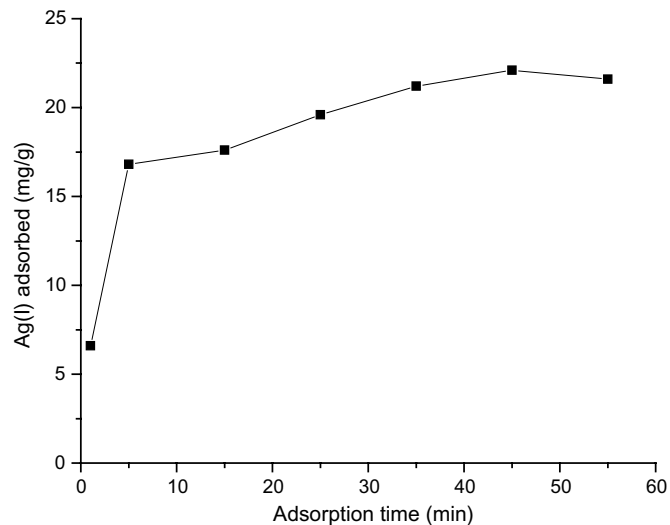


Fig. 1. Variation of the adsorbed amount of Ag<sup>+</sup> as a function of adsorption time (Ag<sup>+</sup> concentration = 100 ppm, pH = 4.0).

As it is seen, high adsorption rates were observed at the beginning and then plateau values were reached within 45 min. In a previous study, several adsorbents were used for silver (I) removal and 5 h is reported as an equilibrium adsorption time [26]. The adsorption rate obtained with the zeolite seemed to be very satisfactory. Due to the preference of short adsorption times for the minimum energy consumption, clinoptilolite can be accepted as an efficient adsorbent for Ag<sup>+</sup> removal when its short adsorption time is considered.

#### 3.3.2. Effect of pH

The pH dependence of Ag<sup>+</sup> adsorption onto zeolite is shown in Fig. 2. Experiments were carried out using metal ion solutions at different pH values. As it is seen in Fig. 3,  $q_e$  is low at low pH values. The value of  $q_e$  is increased by

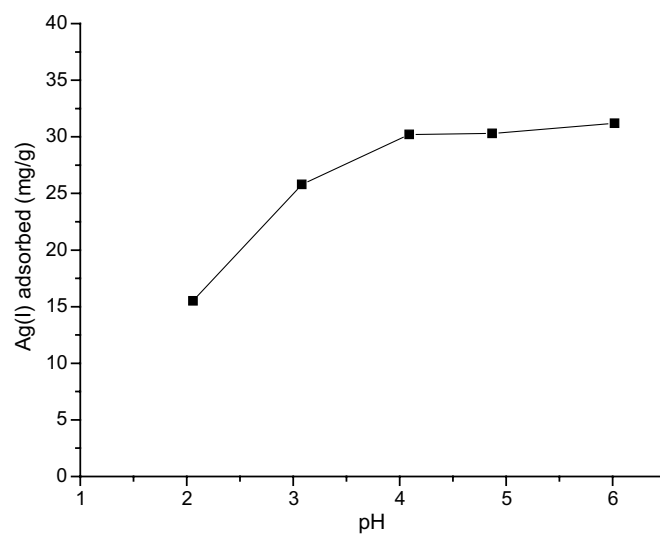


Fig. 2. Variation of the adsorbed amount of Ag<sup>+</sup> as a function of pH (Ag<sup>+</sup> concentration = 100 ppm; temperature = 25 °C).

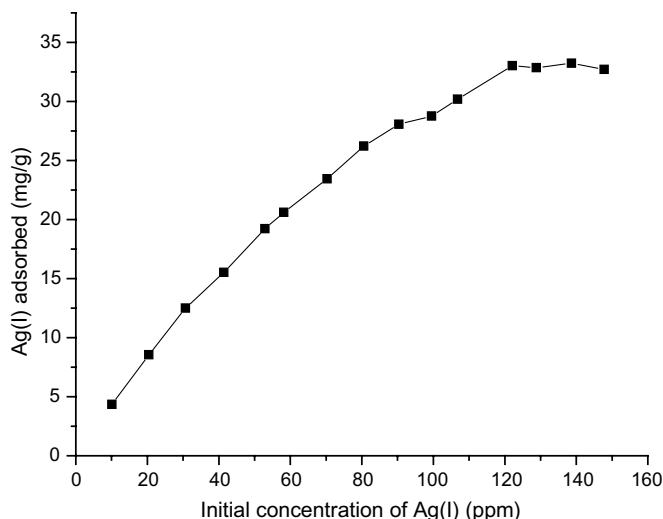


Fig. 3. Variation of the adsorbed amount of  $\text{Ag}^+$  ions as a function of  $\text{Ag}^+$  concentration (pH = 4.0; temperature = 25 °C).

increasing the pH value and reaches a plateau at a pH value of 4.0. It is apparent that using solutions at pH values between 4.0 and 6.0 gives the highest  $q_e$  values. So, we can carry out this  $\text{Ag}^+$  adsorption process not only at a certain pH value, but also in a wide range of pH values. These results are in agreement with several previous investigations on metal removal by a variety of materials which revealed that the adsorption capacity is low at pH values below 4.0 because of the competition between the protons and metal ions for the exchange sites on the zeolite particle [27,28]. So, increased external  $\text{H}^+$  concentration (due to lowered pH) may have effected silver ion removal via ion-exchange by direct competition effects between the protons and silver ions for the exchange sites on the zeolite. This result can be considered as an evidence for the silver ion removal via ion-exchange mechanism in this study.

### 3.3.3. Effect of initial $\text{Ag}^+$ concentration

Experiments conducted with different initial  $\text{Ag}^+$  concentrations show that the amount of  $\text{Ag}^+$  ions adsorbed per unit mass of zeolite (i.e., the adsorption capacity) increases with the initial concentration of  $\text{Ag}^+$  ions (Fig. 3). This increase continues up to 120 ppm  $\text{Ag}^+$  and beyond this value, there is not a significant change at the amount of adsorbed  $\text{Ag}^+$  ions. This plateau represents saturation of the active sites available on the zeolite samples for interaction with metal ions, the maximum adsorption capacity. It can be concluded that percentage adsorption for  $\text{Ag}^+$  decreases with increasing metal concentration in aqueous solutions. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution. The metal uptake can be attributed to different mechanisms of ion-exchange and adsorption processes as it is concerned in many previous work [22]. The maximum adsorption capacity was calculated as 33.23 mg  $\text{Ag}^+$ /g zeolite. Different adsorbents

have been reported for the adsorption of  $\text{Ag}^+$ . H-Na-ZSM-5 zeolite was used and an adsorption capacity of 61 mg  $\text{Ag}^+$ /g zeolite was found [29]. In another study, a series of mordenite samples were used and an adsorption capacity range was found to be 4–23 mg  $\text{Ag}^+$ /g zeolite [30]. In a recent work, different types of chitosan were used for  $\text{Ag}^+$  adsorption and the maximum adsorption capacity achieved in this case was 43 mg  $\text{Ag}^+$ /g adsorbent [31]. In another one, coal used for the removal of silver and maximum adsorption capacity was found as 1.87 mg  $\text{Ag}^+$ /g coal [32].

If it is considered that we have used a natural clinoptilolite sample, which is locally available and no pre-treatment applied, a maximum adsorption capacity of 33.23 mg  $\text{Ag}^+$ /g zeolite is a comparable value to those obtained with other adsorbents given above.

### 3.3.4. Effect of acidic treatment

When the  $\text{Ag}^+$  carrying zeolite samples were treated with 0.1 M  $\text{HNO}_3$ , it was observed that treatment of zeolite with acid solution decreases the adsorption capacity of the zeolite sample with progressing cycles, as can be seen from Fig. 4. Despite the fact that, about 90–100% of the initially adsorbed amount of  $\text{Ag}^+$  has released into the acidified water, certain loss of metal removal efficiency during progressing adsorption/desorption cycles was reported. In an earlier study, this behavior was related to the structural changes (such as the dealumination of zeolite framework) formed as a result of the interaction of zeolite with the acid solution [33].

### 3.4. Desorption studies

In metal ion removal process, it is important to easily desorb the adsorbed metal ions under suitable conditions.

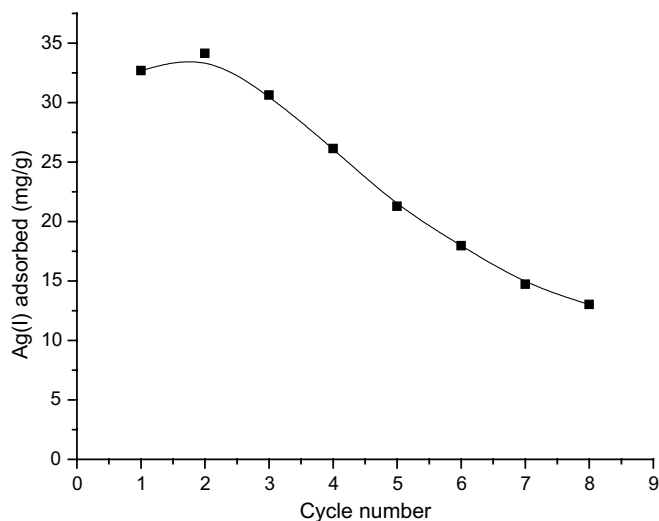


Fig. 4. Adsorption capacity of the zeolite towards  $\text{Ag}^+$  ions during the acidic treatment cycles. Experimental conditions for  $\text{Ag}^+$  adsorption: initial concentration of  $\text{Ag}^+$  ions = 120 ppm, pH = 4.0, temperature = 25 °C.

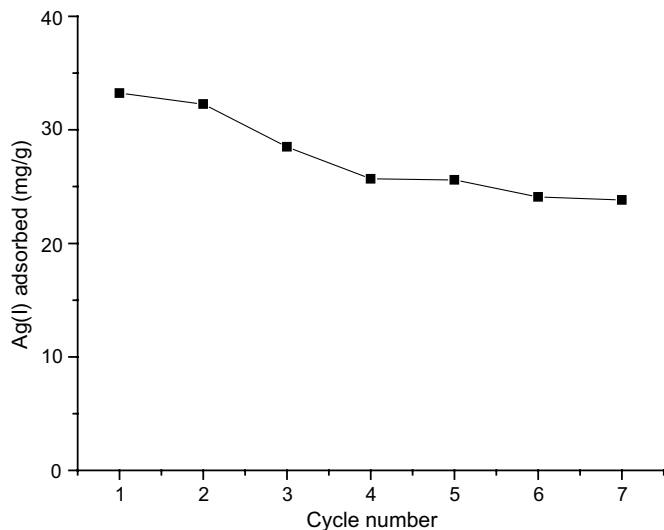


Fig. 5. Adsorption capacity of the zeolite towards  $\text{Ag}^+$  ions during repeated adsorption/desorption cycles. Experimental conditions: initial concentration of  $\text{Ag}^+$  ions = 120 ppm, pH = 4.0, temperature = 25 °C.

In the desorption studies 10 mM  $\text{Na}_4\text{-EDTA}$  was used as desorption agent. The zeolite samples loaded with the maximum amount of  $\text{Ag}^+$  ions were placed in the desorption medium and the amount of ions desorbed within 45 min measured. Fig. 5 shows the data of repeated adsorption/desorption cycles for  $\text{Ag}^+$  ions after 7 cycles. The data show that there is a slight decrease in the adsorption capacity of the zeolite with progressing cycles. Hence, we can infer that adsorbent, clinoptilolite, can be used repeatedly without sacrificing its adsorption capacity towards  $\text{Ag}^+$  ions.

### 3.5. Thermodynamics of the adsorption process

Adsorption of  $\text{Ag}^+$  has been investigated in terms of adsorption isotherms and it was found that adsorption isotherm data fitted to the Langmuir model (Eq. (2)) and the Freundlich model (Eq. (3)):

$$q_e = (K_d \times q_{\max} \times C_e) / (C_e \times K_d + 1) \quad (2)$$

$C_e$  = concentration of  $\text{Ag}^+$  at equilibrium ( $\text{mg}/\text{dm}^3$ );  
 $K_d$  = energy of adsorption ( $\text{dm}^3/\text{mg}$ );  $q_{\max}$  = maximum surface coverage ( $\text{mg}/\text{g}$ ):

$$q_e = k_f \times C_e^{1/n} \quad (3)$$

$C_e$  = concentration of  $\text{Ag}(\text{I})$  at equilibrium ( $\text{mg}/\text{dm}^3$ );  
 $k_f$  = adsorption capacity;  $n$  = intensity of adsorption.

Linear forms of these models can be written as

$$C_e/q_e = (1/K_d \times q_{\max}) + (C_e/q_{\max}) \quad (4)$$

$$\ln q_e = \ln k_f + (1/n) \times \ln C_e \quad (5)$$

Plotting the experimental data using Eqs. (4) and (5) indicated that these models give good fit for the data. It was determined that the equilibrium removal of  $\text{Ag}(\text{I})$  by

the clinoptilolite can be represented by the following equations:

$$q_e = [(0.074) \times (38.91) \times (C_e)] / [(C_e) \times (0.074 + 1)] \quad (6)$$

$$q_e = 6.45 \times C_e^{0.40} \quad (7)$$

When the maximum adsorption capacity values are compared, it is seen that 33.23  $\text{mg Ag}^+/\text{g}$  zeolite (experimentally found) and 38.91  $\text{mg Ag}^+/\text{g}$  zeolite (calculated according to Langmuir model) values are close to each other. The correlation coefficient ( $R^2$ ) was 0.99, indicating that the Langmuir model can be applied to this sorbent system.  $n = 2.5$  value obtained from the Freundlich model with  $R^2 = 0.98$  and  $k_f = 6.45$ .  $k_f$  is a parameter related to the temperature and  $n$  is a characteristic constant for the adsorption system under study. Values of  $n$  between 2 and 10 show good adsorption [34].

## 4. Conclusion

In this study, the interaction between  $\text{Ag}^+$  and zeolite has been investigated. The results indicated that several factors such as pH, adsorption time,  $\text{Ag}^+$  concentration and acidic treatment effect the adsorption process. The physico-chemical characteristics of wastewaters from varying sources can be much more complex compared to the aqueous metal solution used in this study. Because of this, the effects of other components of wastewaters on commercial metal adsorption process should be determined. However, this work can be considered a preliminary study to conclude that clinoptilolite is suitable and efficient material for the adsorption of  $\text{Ag}^+$  from aqueous solution. Despite the fact that natural clinoptilolite has been extensively used for the metal ion removal, the performance of the zeolite considered in this work cannot be compared due to the lack of literature data including interaction between the zeolite and silver ion in this way.

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