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ORIGINAL PAPER

Kinetics and equilibrium study of the adsorption of silver ions by polymeric composites containing zeolite and methacrylic acid

Navid Allahyar[1,1] · **Cemal Özeroğlu**[1]

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Abstract
Environmental and water pollution caused by heavy metals, especially silver, is considered a threat to humans, ecosystem, and all living species. Therefore, with the development of industrialization, it is a very important effort to remove heavy metals from the environment and wastewaters. For this reason, in the present study, we synthesized two polymeric composites of ethylene glycol dimethacrylate (EGDM), methacrylic acid (MA), and different amounts of zeolite (25 g and 50 g) (PMAZ25 and PMAZ50) by using BPO-DMA initiator system at room temperature (298 K). Fourier Transform Infrared was used to show the presence of functional groups in the synthesized composites, and Thermal Gravimetric Analysis was used to test the thermal stability of the copolymeric composites. Batch adsorption method was applied to examine the effect of polymeric composites on silver ion adsorption at different pH values, contact time, initial Ag(I) concentrations, and adsorbent dosage. The adsorption process was found to be most efficient at pH 6. When we tested the most commonly used, Langmuir and Freundlich isotherm models, in the adsorption process in this study, both isotherm models fitted well. The monolayer adsorption capacity of poly(EGDM-methacrylic acid-25 g zeolite) (PMAZ25) and poly(EGDM-methacrylic acid-50 g zeolite) (PMAZ50) was found as 0.116 mg/g and 0.139 mg/g respectively. The adsorption data were also used for the Dubinin-Radushkevich (D-R) isotherm model, and the adsorption energies obtained from this model ($E_{PMZA25} = 15.384$ kJ/mol, $E_{PMZA50} = 14.72$ kJ/mol) indicated that the adsorption of Ag(I) on polymeric composites could be of ion exchange type. The time dependency experiments indicated that the adsorption rate of Ag(I) onto the polymeric composites was quite fast in the first 60 min and reached adsorption equilibrium after 100 min. Some kinetic models such as the Elovich, pseudo-first-order, and pseudo-second-order models were examined to deeply understand the adsorption kinetics. The kinetic data can be well fitted to the pseudo-second order kinetics model.

Keywords Isotherm · Methacrylic acid · Kinetic equations · Zeolite

Introduction

With the development of industrialization, the environment and drinking water have been polluted with wastewater emitted from the industry. Among the various organic and inorganic pollutants that contaminate nature, the most dangerous are heavy metals [1, 2]. Heavy metals emitted to the environment with wastewater from many industrial activities such as electroplating, metallurgy industry, battery, chemical production, fertilizer, pesticide industry, mining studies, and textile dyeing industry, and so on are a serious problem in recent years in terms of drinking water and the environmental pollution [3]. Heavy metals are defined as environmentally and biologically toxic substances if they are released into nature in sufficient quantities. Heavy metals do not decompose easily in nature and can be harmful to humans and many living species. Examples of some of these effects are deterioration of the body's nervous system, the collapse of the immune system. For this reason, the removal of these metals from wastewaters and the environment is very important in terms of public health. Some heavy metals are chromium (Cr), lead (Pb), copper (Cu), cadmium (Cd), nickel (Ni), silver (Ag), mercury (Hg), zinc (Zn) [4]. Among the toxic heavy metals, silver is used in many industrial areas such as battery, soldering, catalyst, electroplating, photography, coinage, and metal alloy industry due to its electrical and thermal conductivity, antibacterial properties, resistance

✉ Navid Allahyar
navid.allahyar@ogr.iuc.edu.tr

[1] Faculty of Engineering, Department of Chemistry, Istanbul University - Cerrahpaşa, 3420 Avcılar Istanbul, Turkey

to abrasion, and oxidation. When silver enters the human body, it damages the cell wall, denatures proteins, inhibits enzyme activity or lipid synthesis, all of which are essential for cell survival [5]. In addition, we can say that if the concentration of silver in the human body reaches toxic levels, it will cause various ailments such as kidney and liver diseases [6]. Therefore, with increasing concerns about the toxicity of water-soluble silver ions, it has become imperative to remove silver from wastewater and environment. [7]. Many methods have been developed to clean the environment from heavy metals. These methods include: flocculation [12], flotation [13], precipitation [14], coagulation [15], ion exchange [16], membrane filtration [17], electrolysis [18], photodegradation [19], extraction [20], radiation [21], oxidation [22], biological treatment [23], and adsorption [24]. In recent years, polymeric adsorbents provide some advantages for the adsorption of metal ions. Examples of these advantages are the broad physiochemical properties of polymers and the ability to be tuned by incorporating various ligands into their structures to produce specific adsorbents [8–11]. Functional polymers, including poly(methacrylic acid) (PMAA)-based materials, can be very effective as adsorbents in removing heavy metals from wastewater, because of the possible interaction between functional groups in their structures with pollutants. Although there are many methods, most of them are not useful or costly methods [25]. Among these methods, adsorption is simple, relatively low-cost, and effective method in removing heavy metals from wastewater [26]. Some natural materials such as zeolites, chitosan, clay are being considered as alternative low-cost adsorbents [27]. Zeolites are molecular sieves composed of covalent bonds between AlO4 and SiO4 tetrahedral. Zeolite has a three-dimensional lattice structure, and in these lattice framework structures, they can exchange abundant negative charges with cations [28]. The use of zeolites as an adsorbent for removing heavy metal ions from the aqueous solution has gained great interest due to its high ion exchange capacity [29–31]. Zeolite reserves in many countries provide many benefits to local industry in removing heavy metals from wastewater because zeolite is inexpensive [32]. However, it is difficult to separate the zeolite from the solution after the adsorption in large-scale wastewater treatment because of the small particle size of the zeolite, and the powder materials are not suitable for recycling. To overcome the above disadvantages, a composite of zeolite and the organic polymer was prepared in this work. Zeolite particles were dispersed and embedded in the polymer network and provided adsorption sites. The use of synthetic zeolites provides uniformity of structure and a high degree of purity and is also environmentally justified because it does not present hazard to aquatic life and will act as natural ones when released in nature, hydrolyzing irreversibly to silica, aluminum oxide, and natural aluminosilicates. Additionally, the selection of the appropriate monomers, such as methacrylic acid, for polymeric matrix, provides environmentally friendly adsorbents [33]. The present work aimed to study the adsorption behavior of Ag(I) ions on copolymeric composites containing zeolite and methacrylic acid as functional groups. For this reason, methacrylic acid, ethylene glycol dimethacrylate, and two different amounts of zeolite (25 g and 50 g) as mass were copolymerized using the benzoyl peroxide-N, N-dimethyl aniline initiator system. Finally, crosslinked copolymer composites containing zeolite and methacrylic acid as functional groups were synthesized. The obtained composites were characterized by elemental analysis, Fourier transform infrared spectroscopy (FTIR), and thermal gravimetric analysis, (TGA) to show the existence of carboxyl groups in the copolymer and thermal properties of copolymers, respectively. These composites were used for the investigation of the adsorption of silver ions from aqueous solution and for that batch adsorption method was applied. Effect of time, adsorbate dosage, and pH on the adsorption of silver ions from the aqueous solution were investigated. Inductively coupled plasma-mass spectroscopy (ICP-MS) measurements of the samples were taken using PerkinElmer Nexion 1000 model instruments.

Materials and methods

Reagent

Ethylene glycol dimethacrylate (Merck), methacrylic acid (Merck), N, N-dimethyl aniline (Fluka), dibenzoyl peroxide paste in dibutyl phthalate, silver nitrate (Merck) were used without further treatment and noted as EDGM, MA, DMA, BPO, and Ag(I), respectively, and we also used Lithofill MM zeolite.

Synthesis of crosslinked copolymeric composites

We aimed to synthesize an insoluble copolymer containing carboxylate groups to use in adsorption measurements of metal ions from solutions, and the dibenzoyl peroxide-N, N-dimethylaniline initiator system was used to initiate copolymerization of methacrylic acid and ethylene glycol dimethacrylate at room temperature.

BPO and DMA initiator systems were used to start copolymerization of EGDMA and MA. To synthesize two copolymeric composites, 75 g EGDMA and 25 g MA were mixed in a 250-mL beaker and 2.2 g benzoyl peroxide paste was added and the mixture was stirred. During stirring, 0.2 mL DMA was added to start copolymerization of EGDMA and MA at room temperature and then added 25 g and 50 g zeolite. Thus, crosslinked copolymer composites synthesized by adding different amounts of zeolite (25 g and 50 g) to the

EGDM mixture. For convenience, we named these composites PMAZ25 and PMAZ50.

Batch adsorption procedure

Adsorption experiments were carried out at desired pH value 7.15, contact time 60 min, adsorbent dosage 0.04 g, and the temperature 298 K. Different initial concentration of Ag(I) solution was prepared by proper dilution from stock 1000 ppm Ag(I) standard. Batch adsorption experiments were carried out to identify the optimum value of pH, contact time, and initial Ag(I) concentration. The effect of adsorbent dosage on removing metal ions from solutions was studied by using 10 mL of 100 ppm as initial Ag(I) solution in conjunction with 0.005, 0.02, 0.04, 0.06, and 0.1 g of PMAZ25 and PMAZ50. At the optimum dosage, other experiments were done. For measuring Ag(I) adsorption on the copolymeric composites, 0.04 g polymer sample was immersed in 10 mL Ag(I) solution. After shaking the mixture for sufficient time (60 min), the contents of the flask were filtered through filter paper and the filtrate was then analyzed for metal concentration by using inductively coupled plasma-mass spectroscopy (ICP-MS). The adsorption percentage (Ads. %) and the amounts of q_t were calculated by using the following equations.

$$\text{Ads.}\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_0 is the initial Ag(I) concentration (ppm); C_t and C_e are the Ag(I) concentrations (ppm) in solutions at the time, t, and at equilibrium at 60 min, respectively; q_t and q_e are the amounts of adsorbed Ag(I) in terms of mg/g on the crosslinked copolymer at the time, t, and equilibrium (t = 60 min), respectively; V is the volume of Ag(I) solution (mL) in the adsorption experiment; and m is the amount of adsorbent.

Results and discussion

Characterization of adsorbent

FTIR spectrum analysis of PMAZ25 and PMAZ50

FTIR spectroscopy was used to examine the presence of both PMA and zeolite in the copolymeric composites. As can be seen in Fig. 1, the peaks of both composites due to the functional groups were at almost the same frequencies for different zeolite amounts, indicating that the spectrum frequencies

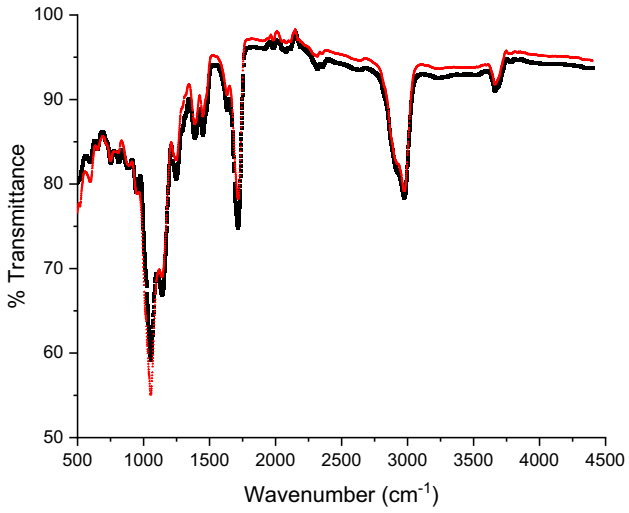


Fig. 1 The FT-IR spectrum of PMAZ25 and PMAZ50

are not dependent on the zeolite content. All characteristic peaks are present. Bands at 1716 cm^{-1} correspond to C=O stretching vibration of the carboxylic group and at 1139 and 1247 cm^{-1} correspond to the carboxyl (C–O) stretching. The peaks showing the O–H and C–O vibration bands in C–O–H are in 1387 and 1449 cm^{-1} [34, 35]. In spectra of zeolites, 1050 cm^{-1} is assigned to the asymmetrical stretching modes of the TO_4 units (T=Si or Al) in the zeolite framework [36]. Bands at lower wavenumbers represent symmetrical external stretching (920–790 cm^{-1}), symmetrical internal stretching (710–649 cm^{-1}), and external double-ring vibrations (650–500 cm^{-1}) [33].

TGA of PMAZ25 and PMAZ50 composites

TGA of crosslinked copolymer composites synthesized by adding different amounts of zeolite (25 g and 50 g) to the EGDM mixture is given in Fig. 2. When TGA of PMAZ25 and PMAZ50 composites given in Fig. 2 is investigated, the % mass losses observed in the range of 60–150 °C are 2.20% and 3.27%, for PMAZ25 and PMAZ50 composites, respectively. These mass losses were interpreted as PMAZ25 and PMAZ50 composites may contain water, monomers, or low molecular weight oligomers. When the % mass loss of copolymeric composites in the range of 150–300 °C was examined, the % mass loss for PMAZ25 composite was 16.98%, and for the PMAZ50 composite was 11.19%. The % mass loss amounts of P(MA-EGDM) composites containing different amounts of zeolite in this temperature range decrease with the increase of zeolite in the composite content. As a result, with the increase in the amount of zeolite in this temperature range, the thermal strength of the composite structure increases. At temperature above 300 °C, the degradation of the composite structure increases, but with a

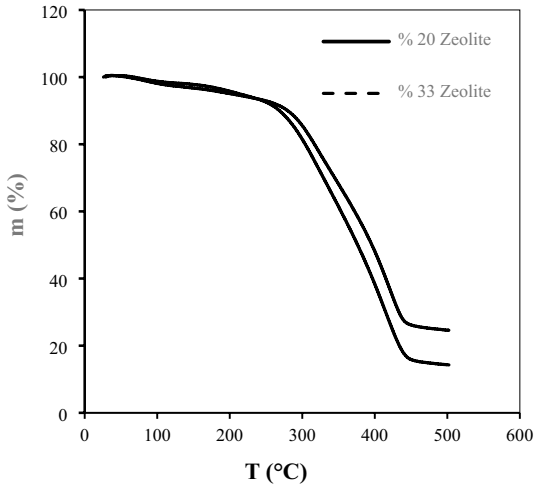


Fig. 2 Thermal gravimetric analysis of polymeric composites containing %20 (—) %30 zeolite (--)

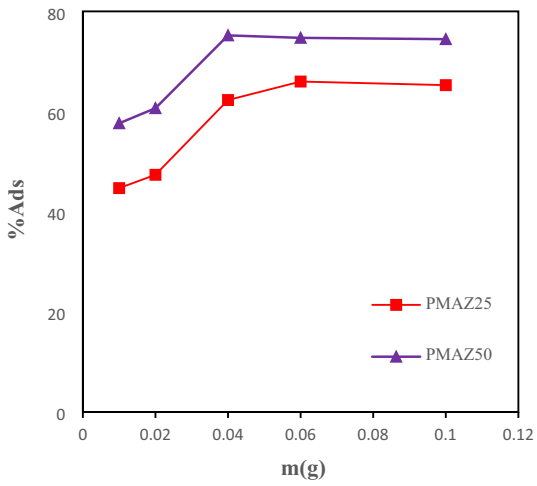


Fig. 3 The dependence of the mass of polymeric composites containing different amounts of zeolite as adsorbents on the percentage of Ag(I) adsorption at constant Ag(I) concentration of 100 ppm at 298 K. The initial pH of Ag(I) solution and contact time are 7.15 and 60 min, respectively

high amount of zeolite, this degradation increase occurs at a higher temperature. At 500 °C, % mass loss of PMAZ25 and PMAZ50 composites was found 73.36% and 64.55%, respectively. As can be seen from TGA results of P(MA-EGDM) composites containing different amounts of zeolite, it is observed that P(MA-EGDM) containing less zeolite has a higher rate of degradation.

Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. Various amounts of the crosslinked copolymeric composites were mixed with 10 mL of Ag(I) solution (100 ppm) at 298 K and pH 7.15. Investigation of the effect of adsorbent weight on Ag(I) removal percentage (Fig. 3) and the adsorption amount of 100 ppm at 298 K (Fig. 4) are summarized in Table 1. The graph presented in Fig. 3 shows that as the weight of adsorbent increased from 0.015 g to 0.1 g, the percentage of Ag(I) removed increased from 44.7 to 65.26% and from 57.64 to 74.44% for PMAZ25 and PMAZ50 composites, respectively. It could be noticed that firstly the percentage of the removed Ag(I) increases fast and linearly with the increase in the adsorbent mass, but then it slowed down and finally reached equilibrium. The equilibrium for Ag(I) adsorption was observed at 0.04 g of composites. For this reason, 0.04 g of adsorbent which has an adsorption efficiency of 62.30% and 75.2% for PMAZ25 and PMAZ50 composites, respectively, was used for subsequent experiments. Although the removal of Ag(I) increases in the composite mass due to the higher amount of active sites, the adsorption capacity reduced from 0.515 to 0.075 mmol/g for PMAZ25 composites and from 0.664 to 0.086 mmol/g for PMAZ50 composites. It is easily understood that the increase in the adsorption sites of Ag with the increase of the adsorbent dose causes an increase in the adsorption percentage [37, 38]. It is also interesting to observe that at the lower weight of adsorbents, PMAZ50 composites contain more zeolite and show much better performances in terms of the considerably higher amount of the removed silver ions, because, based on the literature, an ion exchange mechanism

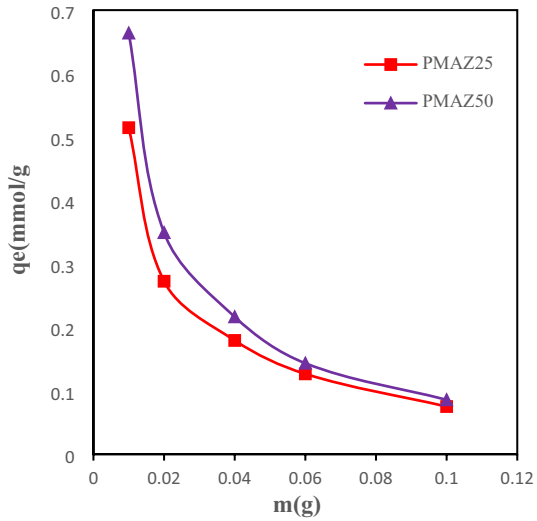


Fig. 4 The dependence of the mass of the polymeric composites as adsorbent on amount of Ag(I) adsorption at constant Ag(I) concentration of 100 ppm at 298 K. The initial pH of Ag(I) solution and contact time are 7.15 and 60 min, respectively

Table 1 The effects of mass of the PMAZ25 and PMAZ50 composites on percentage and the amount of adsorbed Ag(I) at constant Ag(I) concentration of 100 ppm at 298 K

Adsorbent	Mass (g)	Ads. (%)	q_e (mmol Ag(I)/g composite)
PMAZ25	0.01	44.703	0.514
	0.02	47.361	0.272
	0.04	62.294	0.179
	0.06	65.987	0.126
	0.1	65.267	0.075
PMAZ50	0.01	57.65	0.663
	0.02	60.664	0.35
	0.04	75.204	0.216
	0.06	74.711	0.143
	0.1	74.45	0.085

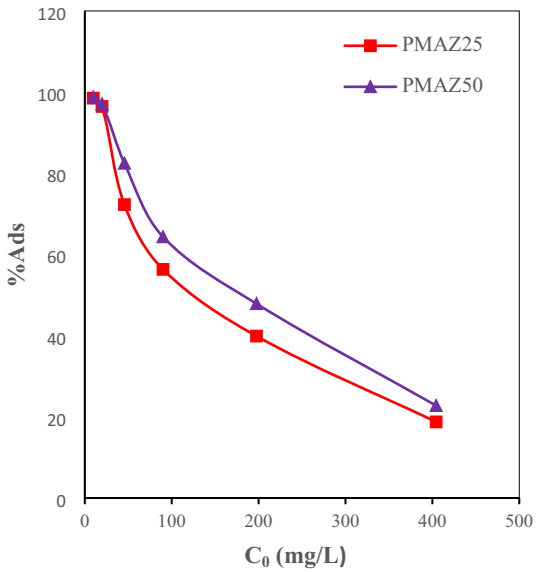


Fig. 5 The effect of the initial Ag(I) concentration on the percentage of the adsorbed Ag(I) ions on the two polymeric composites at 298 K. The contact time is 60 min, and the pH of the initial Ag(I) solution is 7.15

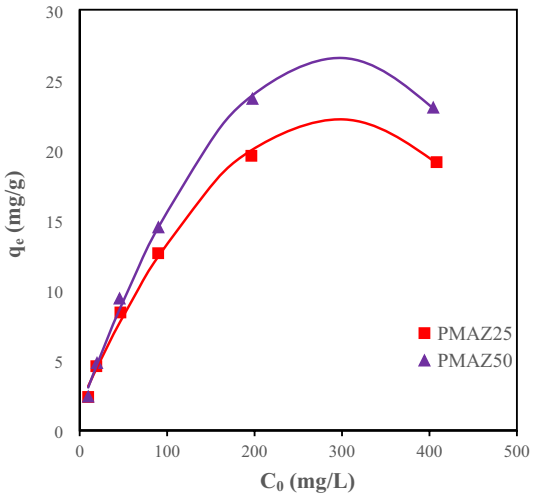


Fig. 6 The effect of the initial Ag(I) concentration on the amount of the adsorbed Ag(I) ions on the polymeric composites at 298 K. The contact time is 60 min, and the pH of initial Ag(I) solution is 7.15

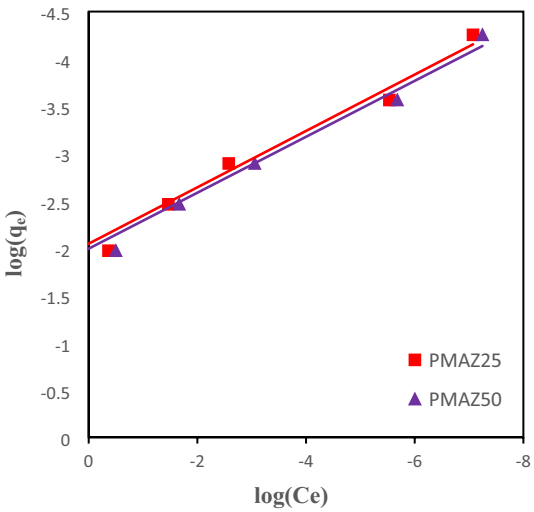


Fig. 7 The relation between log q_e against log C_e of linearized Freundlich isotherm equation for the Ag(I) adsorption on the PMAZ25 and PMAZ50 composites for various Ag(I) concentrations at constant temperature of 298 K and time of t = 60 min

has been realized between the negative charges existing in the zeolite structure and silver cations [39, 40].

Influence of initial Ag(I) concentration

The effect of initial silver ion concentrations in the solution for different concentrations of Ag(I) (9.772, 19.806, 45.61, 90.01, 197.55, and 404.323 ppm) on the adsorption is shown in Figs. 5 and 6. It can be seen from Fig. 5 that there was a decrease in the adsorption percentage of silver with increasing silver ion concentration. However, the amount of adsorbed Ag(I) increased with a rise in initial Ag(I) concentration (Fig. 6). These results indicate that with increasing metal concentration in the aqueous solution, favorable sites for adsorption have decreased.

Adsorption isotherm

Compatibility of adsorption data to the Freundlich, Langmuir, and D-R isotherm was examined for Ag(I) adsorption on the copolymeric composites at initial Ag(I) concentration ranging from 9.772 to 404.323 ppm at the constant time (t = 60 min) and temperature (T = 298 K) (Fig. 7).

Freundlich isotherm

The Freundlich isotherm model is one of the most widely used isotherms. This model describes the adsorption on an energetically heterogeneous surface and does not restrict to the formation of the monolayer. The Freundlich isotherm is expressed as Eq. (3) [41, 42]:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where q_e is the amount of Ag(I) adsorbed at equilibrium (mmol/g) and C_e is the equilibrium solution concentration in (mmol/L), K_F is the Freundlich constant which relates to adsorption capacity (L/mg), and 1/n is the heterogeneity factor which relates to the adsorption intensity. The value of 1/n ranges from 0 to 1 and indicates the degree of nonlinearity between the solution concentration and the adsorption. If the value of 1/n is equal to 1, the adsorption is linear. If the value is below 1, the adsorption process is chemical. If the value is above 1, the adsorption is a favorable physical process. The more heterogeneous the surface, the closer the value of 1/n is to 0 [43, 44]. For determination of these constants, taking the logarithm of both sides of Eq. 3 and obtaining the following linear equation

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

K_F and 1/n can be determined from the slope and intercept of the linear plot of log q_e versus log C_e. The Freundlich parameters of Ag(I) adsorption onto the two polymeric composites are listed in Table 2.

In Table 2, it can be seen that the linear correlation coefficients (R^2) for the Freundlich model are not much lower than Langmuir's, which indicated that the Freundlich model can also be used to describe the adsorption process of the PMAZ25 and PMAZ50 adsorbents for Ag(I) ions.

Table 2 Parameters of investigated adsorption isotherm models for adsorption of Ag(I) from aqueous solution onto PMAZ25 and PMAZ50

İsotherm model	Parameters	PMAZ25	PMAZ50
Langmuir	K_L	2.177	3.22
	q_L	0.116	0.139
	R_L	0.82	0.75
	R^2	0.99	0.99
Freundlich	$1/n_F$	0.27	0.29
	K_F	0.108	0.136
	R^2	0.97	0.97
D-R	K_D	0.0021	0.0023
	q_m	0.195	0.257
	E	15.384	14.74

The values of 1/n were calculated as 0.2734 and 0.2956 for PMAZ25 and PMAZ50 composites, respectively. This suggested that the adsorption process of Ag(I) ions on the composites is chemical, and the surface of the adsorbents is heterogeneous [45]. In addition, 1/n values obtained for composites containing different amounts of zeolite showed that excess zeolite caused a decrease in adsorbent surface heterogeneity.

Langmuir isotherm

Langmuir isotherm is widely used to describe the adsorption phenomenon in solutions and is valid for monolayer adsorption on a surface containing a finite number of identical sites [46, 47]. The Langmuir isotherm is described by Eq. (5) as follows

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{b}{K_L} C_e \tag{5}$$

where q_e and C_e are defined in the Freundlich isotherm. K_L (L/g) and b (L/mg) are constants of the Langmuir equation. The graph C_e/q_e versus C_e is a linear graph as shown in Fig. 8. The intersection of this linear graph is equal to $1/K_L$, and its slope is equal to b/K_L. Thus, b and K_L values can be calculated. The maximum adsorption capacity, or saturation capacity (q_m), is numerically equal to K_L/b. Langmuir parameters of Ag(I) adsorption on copolymeric composites are listed in Table 2.

In Table 2, it can be seen that the correlation coefficients (R^2) are close to 1. This indicated that the adsorption process

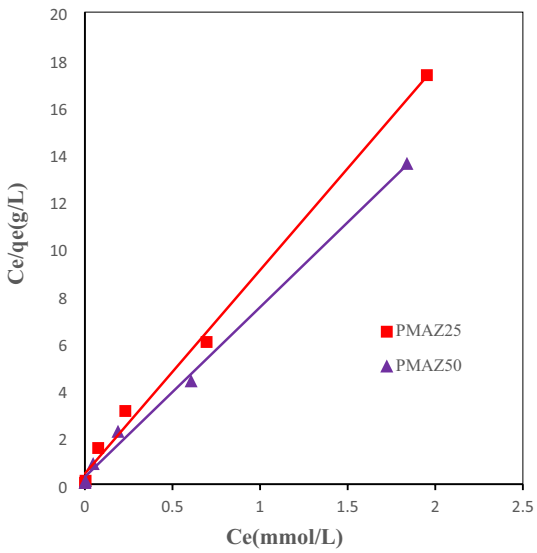


Fig. 8 Dependence of adsorption data on the Langmuir adsorption isotherm at 298 K. $C_{Ag(I)}$ = 100 ppm, t = 60 min, the pH of initial Ag(I) solution is 7.15

fitted well with the Langmuir model. So, it can be considered that Ag(I) was adsorbed with a monolayer on the particle surface of the adsorbents. Compared with 25 g zeolite-containing composite (PMAZ25), the Langmuir maximum adsorption capacity (q_m) of 50 g zeolite-containing composite (PMAZ50) is high. This indicated excess zeolite in the composite leads to increased adsorption capacity.

The dimensionless constant separation factor or equilibrium parameter, R_L, is another factor that can express the essential features of the Langmuir isotherm. It is defined by the following relationship:

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

A favorable adsorption process, the value of R_L should be ranged from 0 to 1. If the value of R_L is beyond 1, it implies that the adsorption process is unfavorable [48]. The values of R_L for both composites are given in Table 2. Values of R_L for PMAZ25 and PMAZ50 composites were in the range of 0 to 1, which indicated the adsorption process of the copolymeric composites of two different amounts of zeolite as adsorbent for Ag(I) is favorable.

D-R isotherm

The D-R isotherm model can be applied to distinguish between physical and chemical adsorption. The D-R isotherm model can be written as [39]:

$$\ln q_e = \ln q_m - k_D \varepsilon^2 \tag{7}$$

where q_e (mol/g) is the equilibrium metal ion concentration on the adsorbent; q_m (mol/g) is the maximum adsorption capacity of the adsorbent; k_D is the constant related to adsorption energy (mol^2/kJ^2); ε is the Polanyi potential that is equal to $RT\ln(1+(1/C_e))$. C_e is the equilibrium concentration mol/L; R is the gas constant; and T is the absolute temperature. The experimental data were fitted into the D-R isotherm model as illustrated in Fig. 9. The values of isotherm constants and correlation coefficient (R^2) are presented in Table 2. The value of the adsorption free energy can be calculated from the following equation [49]

$$E = \frac{1}{\sqrt{2k_D}} \tag{8}$$

It is known that the value of free energy could determine the type of adsorption mechanism. Physical adsorption processes have adsorption energy in the range of 1–8 kJ/mol. If the E value lies between 8 and 16 kJ/mol, the adsorption type can be explained by ion exchange [50]. The E values in this study were found to be 15.384 kJ/mol and 14.74 kJ/mol for PMAZ25 and PMAZ50, respectively, suggesting that the

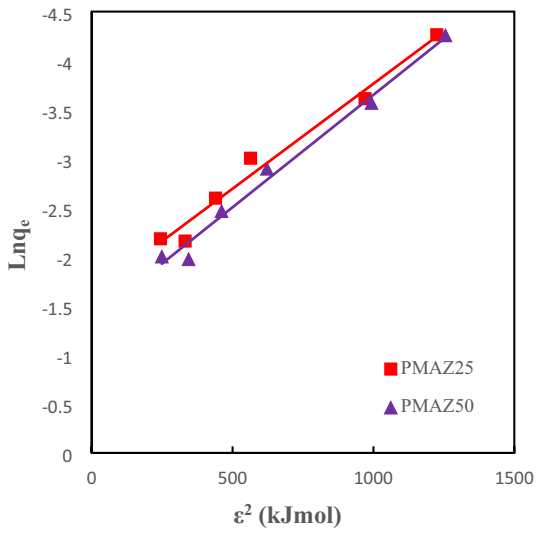


Fig. 9 The relation between $\ln q_e$ and ε^2 in the D-R adsorption isotherm for Ag(I) adsorption on the copolymeric composites at 298 K. $C_{Ag(I)} = 100$ ppm, t = 60 min, the pH of initial Ag(I) solution is 7.15

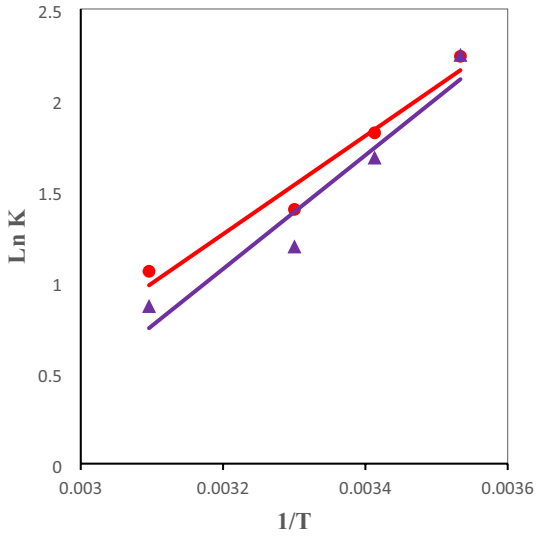


Fig. 10 The plot of ln K_d vs 1/T for calculation of thermodynamic parameters for the Ag(I) adsorption on the copolymer containing 25 g zeolite (PMAZ25) (*triangle*) and copolymeric composite containing 50 g zeolite (PMAZ50) (*circle*) from aqueous solutions. Initial Ag(I) concentration is 100 ppm, t = 60 min, and the pH of initial Ag(I) is 7.15

adsorption of Ag(I) onto polymeric composites involved an ion exchange process.

Thermodynamic parameters

Removal of Ag ions by the adsorbents at different temperatures and the corresponding plot are shown in Fig. 10. This curve was plotted based on the following equations and used

Table 3 The results obtained thermodynamic of Ag(I) removal by PMAZ25 and PMAZ50

Adsorbent	T(K)	ΔG(kJ/mol)	ΔS(J/molK)	ΔH(kJ/mol)
PMAZ25	283	− 5.28	− 74.293	− 25.997
	293	− 4.10		
	303	− 3.0		
	323	− 2.32		
PMAZ50	283	− 5.27	− 61.414	− 22.47
	293	− 4.43		
	303	− 3.52		
	323	− 2.84		

for calculating the thermodynamic parameters of the adsorption process (Table 3). In these equations, K_d (mLg^{-1}) is the distribution coefficient.

$$\Delta G = -RT \ln K_d \tag{9}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

As the results show, with the increase in temperature, ΔG becomes less negative confirming that the removal of Ag(I) by the adsorbents is less favorable at higher temperatures because the process is an exothermic process (ΔH < 0). In this process, interaction between Ag(I) and the adsorbent is stronger than interaction between Ag(I) and solvent, causing a negative ΔG value and a driving force for re-distribution of Ag(I) ions from solution to the surface of the adsorbent [51, 52]. In this case, adsorbed Ag(I) cations have less freedom causing a negative entropy for the process. The negative values of entropy also confirm that a lower amount of ion replacement occurred during the removal process and the process is accompanied by a chemisorption process [53].

Effect of contact time and adsorption kinetic

Due to equilibrium nature of the removal process of Ag(I) by the copolymeric composites containing different amount of zeolites, it seems that contact time affects the removal efficiency of the used adsorbent. Hence, the effect of contact time on the removal extent of Ag(I) by PMAZ50 and PMAZ25 was studied in the batch experiments. Ten milliliters of Ag(I) solution at a concentration of 50 ppm and 100 ppm was taken and mixed with 0.04 g polymeric composites at 298 K. The corresponding results are given in Fig. 11. It can be seen that the removal of Ag(I) from aqueous solution using the PMAZ50 and PMAZ25 increased during the time and reached to the nearly constant amount at equilibrium conditions after 60 min. This variation of

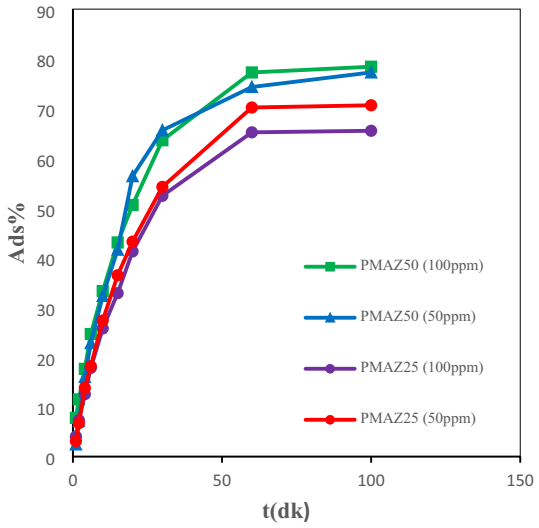


Fig. 11 The relation between adsorption percentage and the contact time for initial Ag(I) concentrations of 50 ppm and 100 ppm of PMAZ25 and PMAZ50 at 298 K and t = 60 min

the adsorption percentage over time may be because initially, all sites on the surface of the adsorbents are empty and at 60-min equilibration time, the surface of the adsorbents becomes saturated with respective silver ions and the removal efficiency becomes almost constant [54, 55]. To explore the kinetics of adsorption, three adsorption kinetics models, the pseudo-first-order, pseudo-second-order, and Elovich models, are often considered.

The Elovich kinetic model

Elovich equation is one of the most useful models for describing chemisorption, which is given as [56]

$$\frac{dq_t}{dt} = \alpha \exp\left(-\beta q_t\right) \tag{11}$$

where q_t is the amount of Ag(I) adsorbed by the copolymeric composites at time t, α is the initial Ag(I) adsorption rate (mmol/g min), and β is related to the extent of surface coverage and activation energy for chemisorption (g/mol). The linearized form of Elovich Eq. (10) can be given as follows

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{12}$$

When the linear plot of q_t versus ln t is performed, the constants of α and β can be obtained from slope and intercept. In this case, a linear relationship was obtained between the adsorbed Ag(I) (q_t) on the adsorbents and ln t as seen in Fig. 12. The α and β values for two amounts (50 ppm and 100 ppm) of PMAZ25 and PMAZ50 are given in Table 4. It was indicated from the estimated Elovich parameters

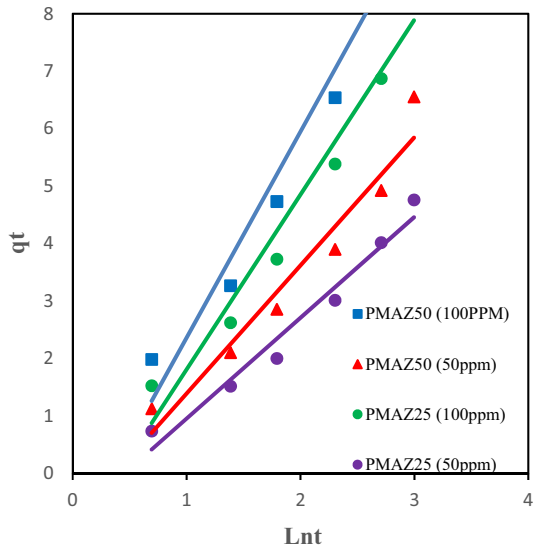


Fig. 12 The relationship between q_t and lnt in the Elovich adsorption equation for Ag(I) adsorption on the densely crosslinked copolymeric composites at 303 K. The initial Ag(I) concentration is 50 ppm and 100 ppm, and the pH of initial Ag(I) solutions is 7.15

(Table 4) that the R^2 values obtained from the Elovich equation were in the range of 0.96–0.97 for the different initial Ag(I) concentrations. Also, the q_e values calculated from the Elovich equation agreed quite well with the experimental values. This suggests that the sorption process may be explained by the Elovich equation. This confirms that the adsorption system is controlled by the chemisorption process [33].

Pseudo-first-order kinetics model

In 1898, Lagergren suggested a pseudo-first-order equation for the sorption of liquid/solid systems based on solid capacity. The Lagergren equation is the most widely used rate equation in liquid-phase sorption. The general equation is expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{13}$$

After integrated by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (12) becomes the following [57]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{14}$$

where q_t and q_e are the amounts (mg/g) of metal ions adsorbed at contact time t and equilibrium time (min) and k_1 is the pseudo-first-order rate constant (min^{-1}). The values of k_1, q_e, and R^2 are presented in Table 4. In Table 4, it is indicated that the values of the correlation coefficients are low for the different Ag(I) concentrations. Furthermore, the estimated values of q_e calculated from the equation differ from those measured experimentally. That confirms that the adsorption process of Ag(I) using polymeric composites containing different amounts of zeolites did not obey the pseudo-first-order model [58].

Pseudo-second-order kinetic model

"Ho and Mckay developed a pseudo-second-order equation based on the assumption that the occupation rate of adsorption sites is proportional to the square of unoccupied sites, and the number of occupied sites is proportional to the fraction of the metal ion adsorbed" [59], which has been widely (Fig. 13) applied to different adsorption processes, given by [60]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{15}$$

By applying boundary conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$), we obtained the following form

Table 4 The Elovich, pseudo-first-order, and pseudo-second-order kinetics parameters for Ag(I) adsorption onto PMAZ25 and PMAZ50 at 298 K and t = 60 min

Kinetic model	Parameters	PMAZ25(50 ppm)	PMAZ25(100 ppm)	PMAZ50(50 ppm)	PMAZ50(100 ppm)
Elovich	α	1.109	2.014	1.8	2.962
	β	0.57	0.328	0.64	0.53
	q_e	6.365	11.734	8.2	8.571
	R^2	0.97	0.96	0.97	0.96
Pseudo-first-order	q_e(mol/g)	6.428	6.095	5.87	4.81
	k_1(min^{-1})	0.092	0.09	0.036	0.03
	R^2	0.8	0.84	0.7	0.56
Pseudo-second-order	q_e(mol/g)	11.627	19.12	9.96	8.55
	k_2(g/min mol)	0.0029	0.0021	0.006	0.018
	R^2	0.99	0.99	0.99	0.99

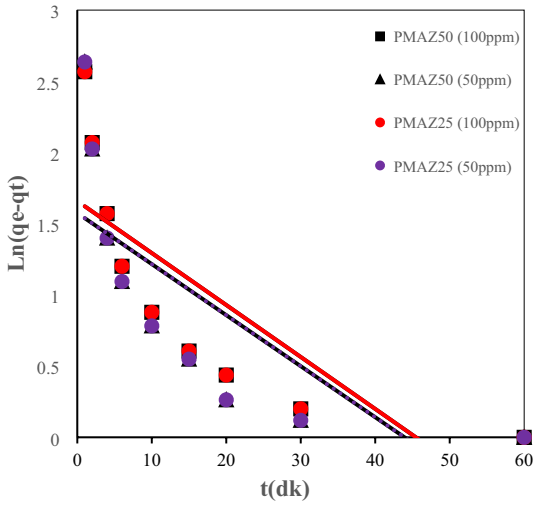


Fig. 13 The dependence of ln ($q_e - q_t$) on the time for the adsorption of initial Ag(I) concentrations of 50 ppm and 100 ppm on PMAZ25 and PMAZ50 from aqueous solutions at 298 K. The pH of initial Ag(I) solutions is 7.15

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{16}$$

where q_t and q_e are the amounts adsorbed (mg/g) at contact time t and equilibrium (min), respectively, and k_2 is the adsorption rate constant (g/mg min). The parameters calculated from the kinetic models are listed in Table 4. The kinetic plots of t/q_t versus t shown in Fig. 14 reveal that t/q_t has a significant linear correlation with t, which is proved by the considerably high correlation coefficients (R^2) greater than 0.99. Also, as Table 4 shows, the q_e determined from the model is close to q_{exp}. The experimental data fitted well to the pseudo-second-order kinetic model with a high correlation coefficient, which indicates that the sorption system could be well described by the pseudo-second-order model. This obedience from this kinetic model recommends that the adsorption of Ag(I) onto PMAZ25 and PMAZ50 is most likely be controlled by the chemisorption process [61, 62]

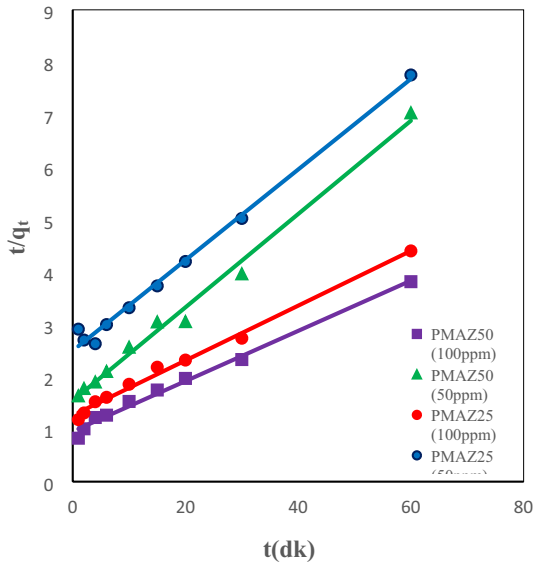


Fig. 14 The fitting of adsorption data to the pseudo-second-order kinetic model for Ag(I) adsorption on PMAZ50 and PMAZ25 at the initial Ag(I) concentration of 50 ppm and 100 ppm at 298 K. The pH of the initial Ag(I) solution is 7.15

Effect of pH value on adsorption

The pH of the aqueous solution is an important parameter in the adsorption of metal ions from the aqueous solution onto the adsorbent [63]. This is partly because hydrogen ions themselves are strongly competing with an adsorbate . Since the surface charge of an adsorbent could be modified by changing the pH of the solution, pH is one of the most important parameters affecting the adsorption process of Ag ions. The initial pH of the solution containing 10 mL of 100 ppm and 0.04 g of adsorbent was determined as 7.15. The pH values of the mixtures were adjusted by adding 2 N HNO_3 solutions. The pH values were varied between 1 and 6 keeping other parameters constant as adsorption temperature of 298 K and initial Ag(I) concentration of 100 ppm. The dependence of adsorption percentage of Ag(I) on the pH of the solution is given in Fig. 15. As can be seen from Fig. 15, the adsorption of Ag(I) was strongly dependent on solution pH. The adsorption percentage of the Ag(I) ions adsorbed on both composites indicated a marked increase with increasing pH of solutions from 1.0 to 3.0 and reaches a plateau at a pH value of 3.0. Using the solution at pH values between

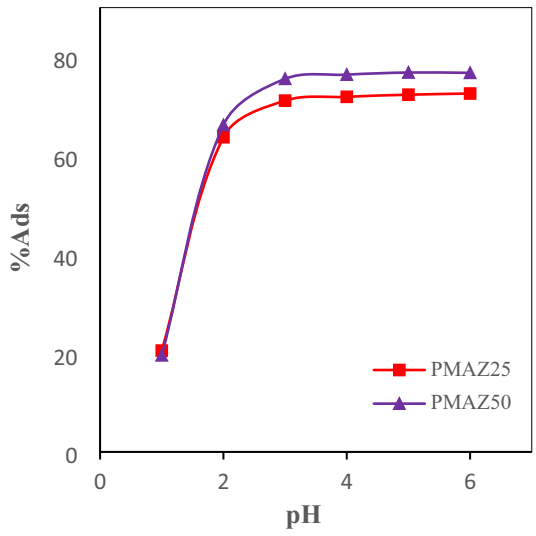


Fig. 15 The effect of pH on the Ag(I) adsorption on the PMAZ25 and PMAZ50 from aqueous solutions at 303 K. The contact time and initial Ag(I) concentration are 60 min and 100 ppm, respectively

3.0 and 6.0 gives the highest adsorption percentage. It could be easily seen that the adsorption capacity of PMAZ25 and PMAZ50 for Ag(I) in weak acidic or natural solution was better than that in strongly acidic solutions. This was because zeolite was highly selective for H^+ ions when the H^+ ions concentration was high [64]. Thus, at lower pH values, the hydrogen ions strongly competed with metal ions for the same negatively charged adsorption sites on the surface of the adsorbent. As the solution pH value increased, the concentration of hydrogen ions as a competitor decreased and this caused an increase in the amounts of adsorbed metal ions. These results can be considered as evidence for the silver ion removal via ion exchange in this study.

Conclusion

İn this study we have synthesized and characterized two porous adsorbents of PMAZ25 and PMAZ50 and investigated their performance of removing Ag(I) from aqueous solution. It is found that the initial Ag(I) concentration, the solution pH, and the adsorbent mass have a significant influence on the adsorption process as well as the adsorption kinetics. The increase in the amount of adsorbent showed an increase in the percentage of the adsorbed Ag(I) ions and reached equilibrium at 0.04 g of adsorbents. So, 0.04 g was taken as an equilibrium adsorption value and used in the adsorption experiments. When the dependence of adsorption percentage of Ag(I) on the pH of the solution was examined, it was observed that the adsorption percentage of Ag(I) adsorbed on the copolymeric composites indicated a marked influence with increasing the pH of the solution ranging from 1 to 6. With increasing initial Ag(I) concentration from 9.7 to 408.11 ppm, it was observed that the adsorption percentage decreases from 98.515 to 18.752% and 98.761 to 22.767% for PMAZ25 and PMAZ50, respectively. However, adsorption capacity increases from 2.38 to 19.13 and 2.41 mg/g to 23.01 mg/g for PMAZ25 and PMAZ50, respectively. The obtained adsorption data depending on initial Ag(I) concentration was analyzed by the Freundlich, Langmuir, and D-R isotherms. The n_F value obtained from the Freundlich equation was determined to be lower than 1. This meant that the surface of the adsorbent was heterogeneous. The average free energy of adsorption E calculated from the examination of D-R isotherm indicated that the adsorption of Ag(I) onto copolymeric composites was carried out via a chemical ion exchange mechanism. The negative ΔG values indicate the spontaneous nature of the Ag(I) removal process, and the negative ΔH values suggest the process is exothermic and negative values of entropy change show a decreased disorder at the solid/liquid interface during Ag(I) adsorption. The fitting of adsorption data obtained from experimental results produced as depending on contact time was analyzed by the Elovich, the pseudo-first-order, and the pseudo-second-order kinetic models. It was observed that the adsorption data obtained depending on contact time provided much better fitting for the pseudo-second-order kinetic equation with high correlation coefficients ($R^2 > 0.99$). This indicated that Ag(I) adsorption on the PMAZ25 and PMAZ50 occurred by chemisorption mechanism.

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