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Adsorption of silver ions from aqueous solutions using copolymer containing sodium methacrylate functional groups

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ABSTRACT

The negative effects of silver, which is one of the heavy metals, on the environment are known. Hence, to remove this dangerous heavy metal from the environment, poly(methacrylic acid), whose adsorption capability has been tested in previous studies, was used. But unfortunately, it performed poorly for silver ions. Therefore, this polymer was modified as poly(sodium methacrylate) using NaOH catalyst and used in the adsorption experiment process to obtain more efficient results. Some important functional groups in the modified copolymer were analyzed by FTIR measurement and the thermal stability of the copolymer by TGA measurement. To better interpret the adsorption process, some isotherms such as Freundlich, Langmuir, and Dubinin-Radushkevich (D-R) isotherms were examined. Using the (D-R) isotherm, the reaction energy was found to be 8.98 kJ/mol, which indicates that the adsorption process is of a chemical ion exchange type. The data from the experimental processes were also evaluated with some kinetic models such as the Elovich, the modified Freundlich, the pseudo-first-order, and the pseudo-second-order kinetic models. Among these models, the pseudo-second-order kinetic models of the adsorption of Ag(I) on poly(sodium methacrylate) showed the best agreement with the experimental data.

***Keywords**: Isotherm; Dimethyl aniline; Kinetic equations; Silver ions, Catalyst.*

1. Introduction

Effect of pollution on the environment should not be ignored as indicated in the regulation policy of the World Health Organization (WHO) [1]. Some industrial areas, such as the fertilizer industry, mining operations, battery manufacturing, smelting, and textile, cause a large number of heavy metals to be released into the environment [2]. The release of some heavy metals, such as cadmium (Cd), chromium (Cr), silver (Ag), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), and mercury (Hg) into nature can pose a very serious environmental threat [3, 4, 5]. Once they are released into the environment, it is very laborious and costly to remove them and can cause great harm to humans and various living species. Hence, it is very important to research methods of removing heavy metals from the environment, especially from the wastewater [6]. Among the detrimental heavy metals, one of the most useful and common heavy metals in industry and daily life is silver. [7]. However, due to widespread use of silver, when the accumulated amount of it in the human body reaches toxic levels, it causes various diseases and health issues. [8, 9]. The monovalent silver ion is more dangerous for living organisms than others and is known as an environmental threat due to the damage it can cause to humans and nature [10, 11]. Some health organization and environmental protection agencies have emphasized that the maximum level of silver in drinking water should be no more than 100ppb (100 µg/L) [12]. Therefore, extreme harmfulness in water makes it necessary to purify it from the environment, water, and wastewater [13, 14]. Many techniques have been developed to purify the aqueous solution from Ag(I), some of which are chemical precipitation, ion exchange [15], electrolysis [16], membrane separation [17], and adsorption [18, 19]. Most of these methods are not economically viable and in some cases they do not produce efficient results. Among these techniques, adsorption is more efficient, useful, simple, and economically more convenient than others [20, 21].

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Recently, in the process of separating metal ions from the aqueous solution, the use of adsorbents such as polymers [22, 23], chitosan [24, 25, 26], carbonaceous materials [27, 28], and fibers [29] with high capacity of linking and good performance for the removal of heavy metals has become a widespread method. Among these adsorbents, polymeric adsorbents are more advantageous in removing heavy metal ions from aqueous solutions by adsorption. Because they can contain some functional groups with a high metal binding capacity [30, 31, 32, 33, 34, 35]. In this research, Ethylene glycol dimethacrylate (EGDM) was used because the methacrylate units of this compound can copolymerize with methacrylic acid, and the ester link in its structure shows hydrolytic stability. Furthermore, methacrylic acid (MA) was chosen for its high chelating ability with metal ions. [31, 36, 37]. In this study, we first thought of using poly (methacrylic acid) for silver adsorption. However, the adsorption percentage and the other adsorption parameters were found to be quite low, which led us to look for a suitable catalyst for a stronger, high-capacity, and more efficient adsorbent. The use of catalysts can help to remove metal ions from the environment. In particular, catalysts such as alkaline-earth metal oxides and hydroxides [38], alkali metals (Na and K) hydroxides, zeolites [39], hydrotalcite [40] as well as some acid solids [41, 42], have been studied in numerous studies. Among the alkalis and metallic salts catalysts, NaOH is a highly efficient. So, we converted poly(methacrylic acid) to poly(sodium methacrylate) by adding NaOH to the copolymer containing methacrylic acid. The adsorbent we obtained has a very high adsorption capacity compared to the previous adsorbent. To show the presence of some important functional groups in the modified adsorbent and to examine the thermal behavior of the copolymer, Fourier-Transform Infrared Spectroscopy (FTIR) and Thermogravimetric Analysis (TGA) measurements were performed, respectively. All adsorption experiment results of silver ions on poly(sodium methacrylate) were measured with an ICP-MS device. The effects of different adsorbent amounts, pH change of solution, initial concentration of adsorbate, and shaking time on the adsorption process were investigated. To obtain more detailed information about adsorption, the obtained experimental data were evaluated with some isotherm and kinetic equations.

2. Experimental

2.1. Batch adsorption procedure

Adsorption experiments were carried out by keeping pH 7.45, contact time 60 minutes, adsorbent amount 0.04 g, and temperature constant at 303 K. Different initial concentration of Ag(I) solution was prepared from the stock 1000 ppm Ag(I) standard by appropriate dilution. The batch method was used to find the optimal values of pH, agitation time, initial Ag(I) concentration and copolymer mass in the adsorption experiment. To investigate the effect of adsorbent mass, 10 mL of 100 ppm as starting Ag(I) solution was added to different amounts of poly(sodium methacrylate) (0.005, 0.02, 0.04, 0.06 and 0.1 g) separately and in different beakers, then at 303 K for 60 minutes, it was shaken, after filtering, measurement was made with the ICP-MS device to determine the amount of silver in the solution. The amount of copolymer with the highest adsorption percentage was determined as 0.04 g and was used in the other stages of the experiment (the effect of Ag(I) concentration, temperature, pH, and contact time parameters). To investigate the effect of Ag(I) concentration, it was adjusted as 10.33, 22.78, 50.22, 103.3, 209.1 and 411ppm. In examining the temperature effect, T = 293, 303 and 323 K. contact time t = 1, 2, 4, 6, 10, 15, 20, 30 and 60 minutes, two different Ag(I) concentrations (100 and 50 ppm). In the pH study, the pH of the solution was adjusted between 1 and 11. Adsorption percentage (Ads.%), C_t, C_e concentrations, q_t amount and q_e were calculated using the following relations:

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

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

$$q_e = \frac{(C_0 - C_e)\,V}{m} \quad (3)$$

$$C_t = \left(1 - Ads.\% / 100\right) \times C_0 \quad (4)$$

In the above relations, 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 and at equilibrium at 60 min, respectively. q_t and q_e are the amount of adsorbed Ag(I) on the copolymer at the time and equilibrium (mg/g), respectively. V is the volume of Ag(I) solution (mL), and m is the mass of copolymer (g).

2. 2. Determining pH_{pzc}

The pH of a 10 mL series of 0.01 M NaCl solutions was adjusted to values between 1 and 11 by adding 0.01 M HCl and 0.01 M NaOH solution. The pH of these solutions was recorded as the initial pH (pH_i). Then, 0.1 g of poly(sodium methacrylate) was added and the final pH (pH_f) was measured after 24 h. Finally, the plot of ΔpH versus pH_i was drawn. So, the point of zero charges (pH_{pzc}) value of the solution was calculated to be 8.5.

2. 3. Physical measurements

The FTIR spectra of copolymer containing sodium methacrylate were recorded in the 4000- 400 cm^{-1} region using a Jasco 4700 FTIR spectrometers with KBr pellets. Thermogravimetric analysis was carried out with Mettler TG 50 thermobalance, under nitrogen flux over a temperature range from 50 to 525 °C at a scan rate of 10 °C/min.

3. Results and Discussion

3.1. Characterization of the adsorbent

3. 1. 1 FTIR spectrum analysis of poly(sodium methacrylate)

FTIR is a device for characterizing crystalline and amorphous materials [43]. As can be seen from **Fig. 1**, the peaks at 3662 cm^{-1} and 2974 cm^{-1}, are corresponding to O—Na, and the stretching vibration of the CH_4 group, respectively [44]. The peak at 1708 cm^{-1} was attributed to stretching vibration of the C═O from the methacrylate unit of sodium methacrylate. The peaks observed at 1250, 1115, and 1050 cm^{-1} should be assigned to the stretch vibrations of the C—O—C and C—O of eters respectively [45, 46].

3. 1. 2. Thermal Gravimetric Analysis (TGA) of the adsorbent

Thermal gravimetric analysis (TGA) of poly(sodium methacrylate) and copolymer bearing %25 methacrylic acid (MA) was compared under a nitrogen atmosphere from 50 °C to 525 °C with a heating rate of 10 °C/min. As given in **Fig. 2**, in the range of 60 – 150 °C, % mass loss for copolymer bearing MA was %12.97, while in the range of 70–150 °C, this percentage for poly(sodium methacrylate) was %1.76. The reason for the higher decomposition product of poly(methacrylic acid) at this temperature was interpreted as low molecular weight polymers containing methacrylic acid (MA) group gave a higher rate of degradation product. The reason why poly(sodium methacrylate) provided a lower decomposition product at this temperature was interpreted as low molecular weight polymers containing sodium methacrylate as a functional group giving the lower degradation product due to the ionic structure formation of the copolymer. The % mass loss of the poly(methacrylic acid) in the range of 150 – 300 °C was %1.49, while the % mass loss of the poly(sodium methacrylate) in the same temperature range was %11.06. These results showed that low molecular weight polymers containing sodium methacrylate groups in the copolymer structure gave more decomposition products at higher temperatures. % mass lossing at 500 °C was % 94.14 and % 80.30 for poly(methacrylic acid) and poly(sodium methacrylate) respectively. As a result at 500 °C, it was observed that poly(sodium methacrylate) containing inorganic structure gave fewer decomposition products.

3. 2. Effect of adding NaOH as a catalyst on the adsorption process

Different amounts of copolymer samples were weighed and placed in different beakers, and 10ml of 100ppm silver nitrate solution was added to all of them. This mixture was stirred for one hour (Fig. 3) at pH = 7.45. As we can see from figure 3, the copolymer containing methacrylic acid functional groups performed very poorly in Ag ion adsorption and the adsorption percentage was found low (Fig. 3, curve 2). For this purpose, to transform carboxylic acid groups in the copolymer to sodium methacrylates and modification of the copolymer, after processing 60 mL of 2 N NaOH solution as a catalyst with 3 g copolymer for 4 hours, it

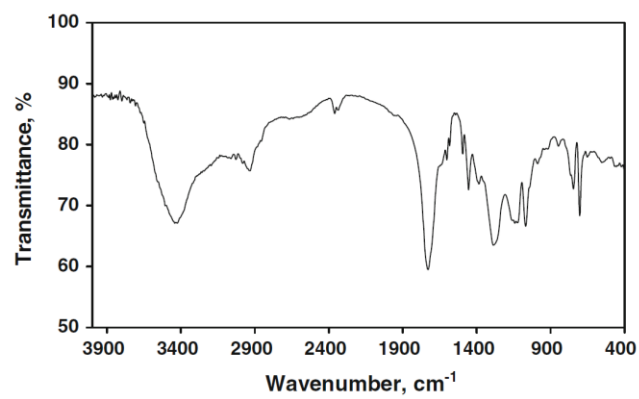


Fig. 1 The FT-IR spectrum of poly(sodium methacrylate)

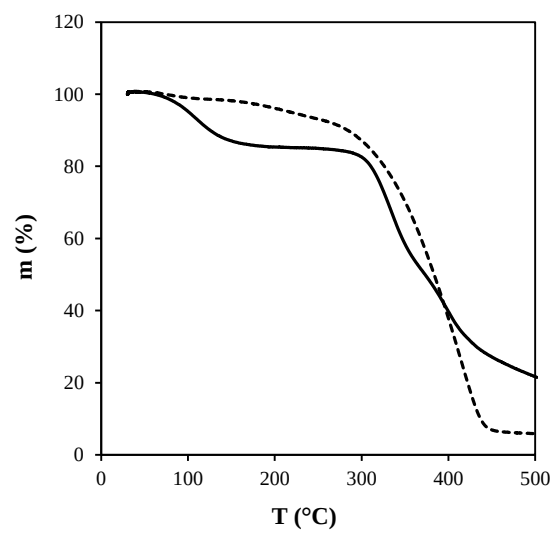
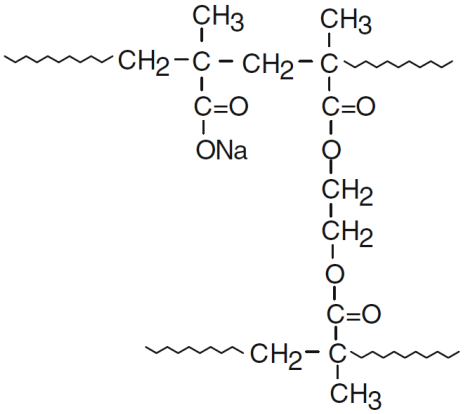


Fig. 2 Thermal gravimetric analysis of poly(sodium methacrylate) (—) and poly(methacrylic acid) (---)

was filtered through a paper sieve, then washed 6 times with 30 mL of distilled water to remove excess NaOH and placed in the oven at 60 °C to get dried. Thus, the poly(sodium methacrylate) seen in **Scheme 1** was obtained. The effect of the amount of adsorbent on the adsorption percentage and the amount of adsorbed silver were indicated in **Fig. 3**, curve 1, **Fig. 4**, curve 2, and **Table 1** for poly(sodium methacrylate). As can be seen from **Fig. 3** and **Table 1**, at Ag (I) concentration of 100ppm, by increasing the amount of adsorbent from 0.005 to 0.1 g in adsorption measurement at 303 K, the adsorption percentage increased from 90.874 to 99.856%.

The equilibrium adsorption capacity (q_e) of the adsorbent decreased from 1.07 to 0.056 mg Ag(I)/g copolymer.



Scheme 1 The chemical structure of crosslinked poly(sodium methacrylate).

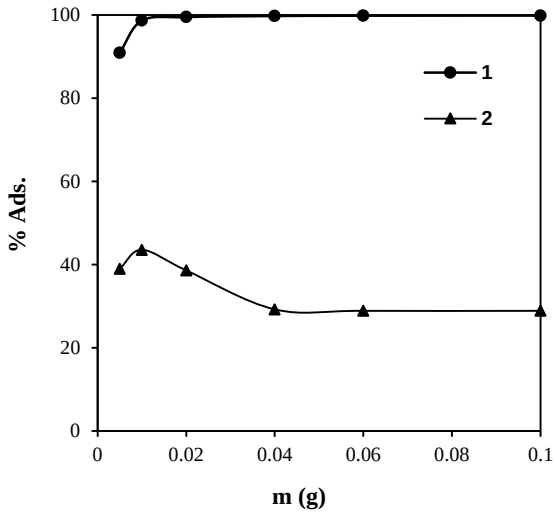


Fig. 3 The dependence of the percentage of Ag(I) adsorption on crosslinked poly(sodium methacrylate) (1) with the catalyst and poly(methacrylic acid) (2) without the catalyst at constant Ag (I) concentration of 100 ppm at 303 K. The initial pH of Ag (I) solution and contact time are 7.45 and 60 min, respectively

This event indicates that the adsorption of Ag(I) increased with increasing of available sodium carboxylate groups [47, 48]. By increasing the amount of adsorbent, the adsorption percentage of Ag(I) ions on the crosslinked copolymer increased and reached equilibrium at the amount of 0.04 g of the copolymer. For this reason, 0.04 g of adsorbent, which has an adsorption efficiency of 99.748 % was used for further experiments.

3.2. The effect of Ag(I) concentration

The effect of Ag(I) concentration change on the Ag(I) adsorption onto the copolymer was investigated at 303 K and 60 min shaking time. (**Fig. 5**). As can be seen from **Fig. 5**, by increasing the Ag(I) concentration from 10.33 to 411 ppm, the percentage of the adsorbed Ag(I) over the poly(sodium methacrylate) decreased (**Fig. 5**). However, the amount of Ag(I) adsorption on the copolymer increased (**Fig. 6**).

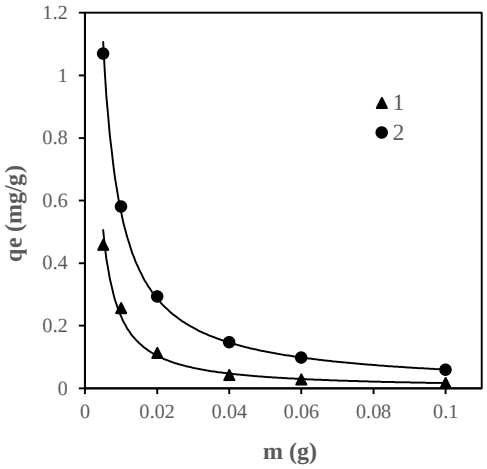


Fig. 4 The dependence of the amount of Ag(I) adsorption on poly(methacrylic acid) (1) and poly(sodium methacrylate) (2) as adsorbent at constant Ag(I) concentration of 100ppm at 303 K. The initial pH of Ag(I) solution and contact time are 7.45 and 60 min respectively

Table 1 The effects of percentage and the amount of adsorbed Ag(I) on densely crosslinked poly(sodium methacrylate) at constant Ag(I) concentration of 100ppm at 303 K

Adsorbent mass (g)	Ads. (%)	Q_e (mg Ag(I)/g copolymer)
0.005	90.874	1.07
0.010	98.636	0.58
0.020	99.495	0.29
0.040	99.748	0.147
0.060	99.824	0.09
0.10	99.856	0.058

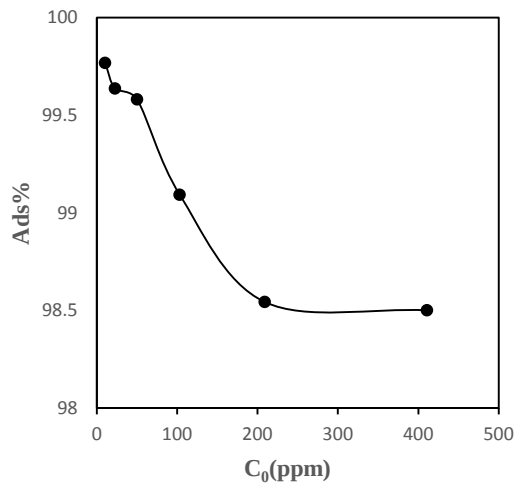


Fig. 5 The effect of the initial Ag(I) concentration on the percentage of the adsorbed Ag(I) ions on the poly(sodium methacrylate) at 303 K. The contact time is 60 min, the pH of the initial Ag(I) solution is 7.45

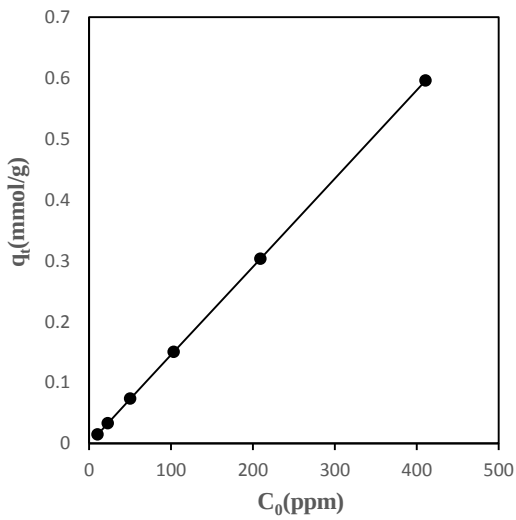


Fig. 6 The effect of the initial Ag(I) concentration on the amount of the adsorbed Ag(I) ions on the poly(sodium methacrylate) at 303 K. The contact time is 60 min, the pH of the initial Ag(I) solution is 7.45.

3.3. The adsorption isotherms

Adsorption isotherms can be very useful to obtain information about the behavior of metal ion concentration with the adsorbent surface, some properties of the adsorbent, and the adsorption experiment. There are many isotherms. Among them, the Dubinin-Radushkevich (D–R), Freundlich, and Langmuir's isotherms were studied by adjusting the Ag(I) concentration between 10.54 to 394.31 ppm at 303 K and at constant adsorption time (t = 60 min) [49, 50, 51].

3.3.1 Langmuir isotherm model

The Langmuir equation was derived by Langmuir for chemical adsorption. This equation is used in gas-solid adsorption in every pressure range. It is based on three assumptions: (1) Adsorption cannot go beyond the monolayer coating. (2) All adsorption sites are equivalent. (3) The ability of a molecule to be adsorbed at a particular site is not affected by whether neighboring sites are full or empty [52]. The Langmuir equations are shown:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \qquad (5)$$

Where q_e is the amount of the adsorbed Ag(I) at equilibrium (mmol/g), and C_e is the equilibrium solution concentration as mmol/L. The constant Q_0 (mmol/g) and b (L/mmol) are Langmuir constants. As can be seen on **Fig. 7**, the graph of $1/q_e$ versus $1/C_e$ is a straight line and the Langmuir constants are found from the slope and intercept of this graph.

3.3.2 Freundlich isotherm model

The correlation between the amount of gas adsorbed on the solid surface and the gas pressure was discovered by Herbert Freundlich in 1909. The same relation is also applicable for the concentration of a solute adsorbed onto the surface of a solid and the concentration of a solute in the liquid phase [53]. Freundlich equation has been written as follows

$$q_e = k_F C_e^{\frac{1}{n_F}} \qquad (6)$$

Where k_F(L/g) and $1/n_F$ are the Freundlich constants. The q_e and C_e are the same as described in the Langmuir isotherm. The linear form of Freundlich's equation is as follows:

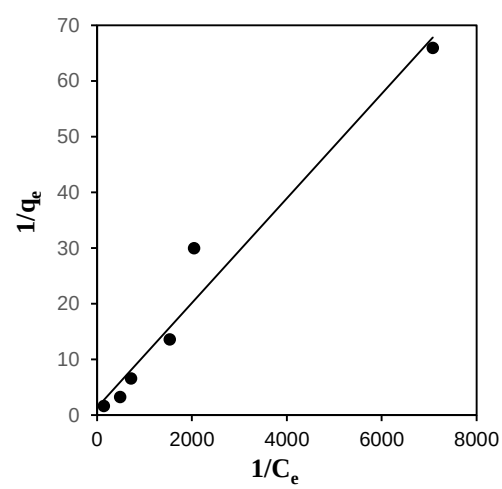


Fig. 7 Evaluation of adsorption data on the Langmuir adsorption isotherm at 303 K. Initial Ag(I) concentration is 100ppm, t = 60 min, and the pH of initial Ag(I) solution is 7.45

$$\log q_e = \log k_F - \frac{1}{n_F} \log C_e \quad (7)$$

The plot of log q_e against log C_e shows a straight line in the linearized Freundlich Eq. (6) for the Ag(I) adsorption on the crosslinked poly(sodium methacrylate). The n_F ve K_F constants in the Freundlich equation are found from the slope and intercept of the log q_e against log C_e at the constant time (t = 60 min), temperature (303 K), and various initial Ag(I) concentrations (10.33, 22.78, 50.22, 100.3, 209.1 and 411 ppm) (**Fig. 8**). The value of k_F gives information about the adsorption capacity. The n_F gives information about whether the adsorption is chemical or physical. If $n_F > 1$, the adsorption is physical, if $0 < n_F < 1$ adsorption is chemical. The n_F value also gives information about the heterogeneity of the adsorbent surface. The closer the n_F value is to zero, the higher the heterogeneity of the surface [54]. Langmuir and Freundlich's constants are shown in **Table 2**. The n_F value we obtained in this study is between 0 and 1, which indicates that the adsorption of Ag(I) on poly(sodium methacrylate) is of chemical type. The R^2 values for both isotherms showed the compatibility of the experimental data with these isotherms.

3.3.3 Dubinin-Radushkevich (D-R) isotherm

Dubinin-Radushkevitch (D-R) isotherm is the frequently used isotherm method to determine the type of adsorption. This isotherm can be used to determine the porosity and adsorption energy of the adsorbent [55, 56]. The equation for the Dubinin-Radushkevich isotherm can be written as shown in equation (8) [57].

Where ε is the poleni potential given as RTln(1+1/C_e)(kJ/mol), R is the ideal gas constant (8.314 J/mol K), q_e and C_e are the same as described in the Langmuir isotherm, T is the absolute temperature (K), and q_m is the maximum absorption capacity of the adsorbent (mol/g). K_D (mol^2/kJ^2) is a constant related to the sorption energy. By taking the natural logarithm of both sides of the equation, the following linear equation is obtained:

$$q_e = q_m \exp(-K_D \varepsilon^2) \quad (8)$$

If a straight line is obtained in plotting ε^2 versus Lnq_e, this indicates that the adsorbing material is suitable and the energy of the adsorption sites is low. Using the intercept and the slope of the line (Fig. 9), the maximum sorption capacity q_m and the energy of adsorption ($E = (-2K_D)^{1/2}$) can be calculated [36, 58]. The R^2 of straight lines was found to be 0.964. The K_D and q_m were found as 6.2×10^{-3} and 0.21 mmol Ag(I)/g copolymer, respectively. The energy value to be found is between 8-16 kJ/mol, which means that the adsorption is generally of the ion exchange type. If the energy is less than 8 kJ/mol, the adsorption can be explained by physical interactions. Conversely, if the energy value is greater than 8 kJ/mol, the adsorption mechanism can be explained by chemical interactions [59, 60, 61]. The E value was calculated as 8.98 kJ/mol, indicating that the adsorption process can be carried out via an ion exchange mechanism.

$$\ln q_e = \ln q_m - K_D \varepsilon^2 \quad (9)$$

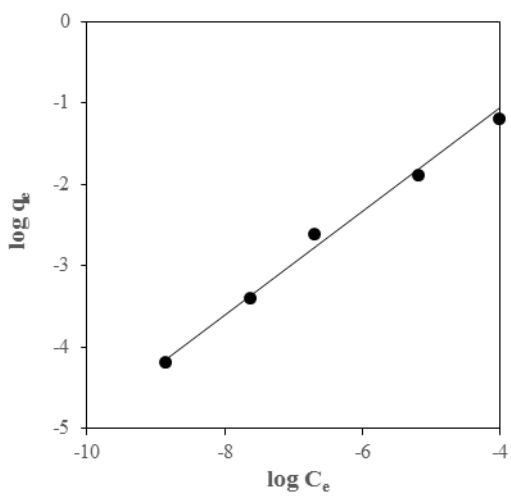


Fig. 8 The relation between log q_e against log C_e for the Ag(I) adsorption on the poly(sodium methacrylate) for various Ag(I) concentrations at a constant temperature of 303 K and time of t = 60 min

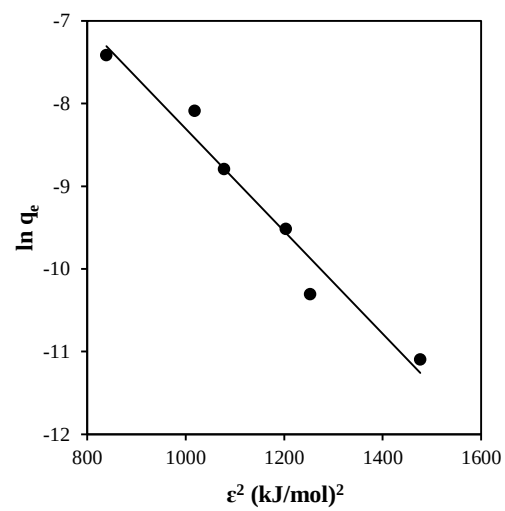


Fig. 9 The relation between ln q_e and ε^2 in the D–R adsorption isotherm for Ag(I) adsorption on the poly(sodium methacrylate) at 303 K. $C_{Ag(I)}$ = 100ppm, t = 60 min, the pH of initial Ag(I) solution is 7.45

Table 2 The Langmuir, Freundlich, and D-R constants of isotherm models at 303 K, contact time 60 min.

Langmuir isotherm			Freundlich isotherm			D-R isotherm			
Q_0	b	R^2	n_F	K_F	R^2	K_D	q_m	E	R^2
0.72	147	0.96	0.98	0.116	0.97	6.2×10^{-2}	0.21	8.98	0.964

3.4. Effect of contact time

To examine how adsorption changes over time and how long it takes to reach equilibrium, 10 ml of Ag(I) solutions at 100 ppm and 50 ppm concentrations were added to 0.04 g adsorbent and an adsorption experiment was carried out at different Agitation times (1, 2, 4, 6, 10, 15, 20, 30 and 60 min). As seen in **Fig. 10**, the amount of silver adsorbed on the copolymer increases over time and the adsorption percentage reaches very high values in the first 10 minutes, then the increase slows down and reaches equilibrium up to 60 minutes.

3. 5. Adsorption kinetics

3.5.1 The modified Freundlich kinetic model

The modified Freundlich equation is given as the Eq. 10 [62, 63].

$$q_t = at^b \quad (10)$$

If the logarithm of both sides is taken, this equation becomes linear (Eq. 11).

$$\ln q_t = \ln a + b \ln t \quad (11)$$

Where q_t is the amount of Ag(I) adsorbed by poly(sodium methacrylate) at time t. a and b are the constants for the modified Freundlich kinetic equation. As seen on **Fig. 11**, there is a linear relationship between ln q_t and ln t values. The values of a, b, and R^2 values were calculated (**Table 3**). Based on the R^2 values, it is understood that Ag(I) adsorption does not fit this kinetic model very well.

3.5.2 The Elovich kinetic model

The Elovich kinetic model is generally expressed as following equation [36, 64, 65]:

$$\frac{dq_t}{dt} = A\exp(-Bq_t) \quad (12)$$

İn this equation, A and B are Elovich kinetic constants. The linear form of the Elovich equation (12) is as follows:

$$q_t = B\ln(AB) + B\ln t \quad (13)$$

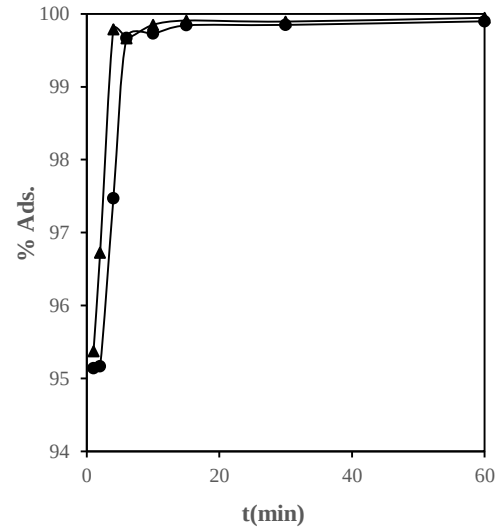


Fig. 10 The relation between adsorption percentage and the contact time for initial Ag(I) concentrations of 50ppm (*triangle*) and 100ppm (*circle*) at 303 K and t = 60 min

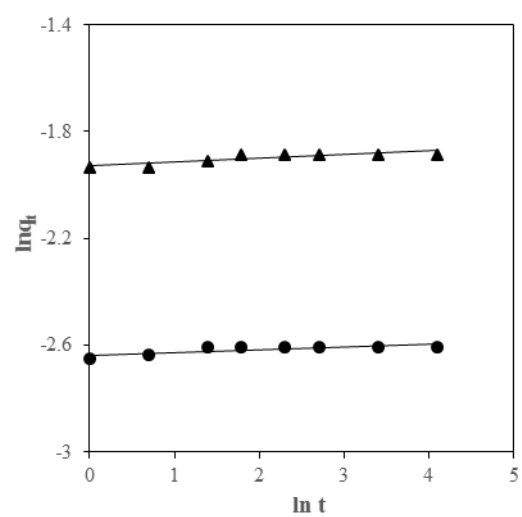


Fig. 11 Dependence of adsorption data on the modified Freundlich adsorption model for Ag(I) adsorption on the poly(sodium methacrylate) at 303 K. The initial Ag(I) concentrations are 50 ppm (*circle*) and 100 ppm (*triangle*), the pH of initial Ag(I) is 7.45

The values of A and B are found from the slope and intercept of the graph of q_t against ln t (**Table 3**). In this case, the correlation coefficient ($R^2 = 0.753$) for the lines in **Fig. 12** was found to be low in this model as well.

3.5.3 The pseudo-first-order kinetic model

The pseudo-first-order kinetic equation can be written as follows

$$\frac{dq_t}{dt} = k(q_e - q_t) \qquad (14)$$

The k (1/min) is the rate constant for pseudo first-order kinetic equation. The linearized pseudo-first-order kinetic (Eq. 14) can be given below

$$\ln(q_e - q_t) = \ln q_e - kt \qquad (15)$$

The k and R^2 values for different Ag(I) concentrations obtained from plot of ln ($q_e - q_t$) against t (**Fig. 13**), are given in **Table 3** for this kinetic model.

3.5.4 Pseudo-second-order kinetic model

The following equation was used to examine the compatibility of the experimental data with the pseudo-second-order kinetic model at different silver concentrations (50ppm and 100ppm)

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (16)$$

For the boundary conditions from t = 0 to t = t and q_t = 0 to $q_t = q_t$, the integrated form of Eq. (16) becomes

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \qquad (17)$$

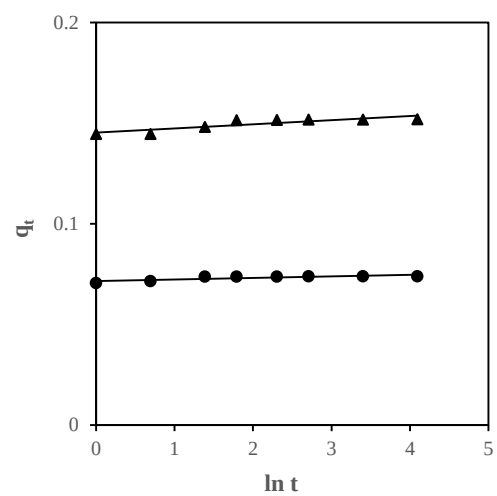


Fig. 12 The relation between q_t and ln t in the Elovich adsorption equation for Ag(I) adsorption on the poly(sodium methacrylate) at 303 K. The initial Ag(I) concentrations are 50 ppm (*circle*) and 100 ppm (*triangle*), the pH of initial Ag(I) solutions is 7.45

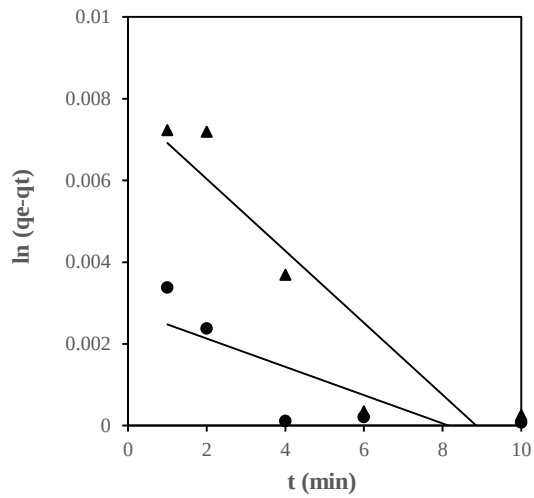


Fig. 13 The dependence of ln ($q_e - q_t$) on the time for the adsorption of initial Ag(I) concentrations of 50 ppm (*circle*) and 100 ppm (*triangle*) on the poly(sodium methacrylate) from aqueous solutions at 303 K. The pH of initial Ag(I) solutions are 7.45

The linearized form of the Eq. (19) can be written as given

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (18)$$

The graph of t/q_t to t (**Fig. 14**) is linear and the constants of the model are calculated from the slope and intercept of this graph (**Table 3**). In these calculations, the R^2 value was found to be 0.99. The q_e determined from the model is close to q_{exp}. These values indicated that the adsorption process had the best compatibility with the pseudo-second-order kinetic model.

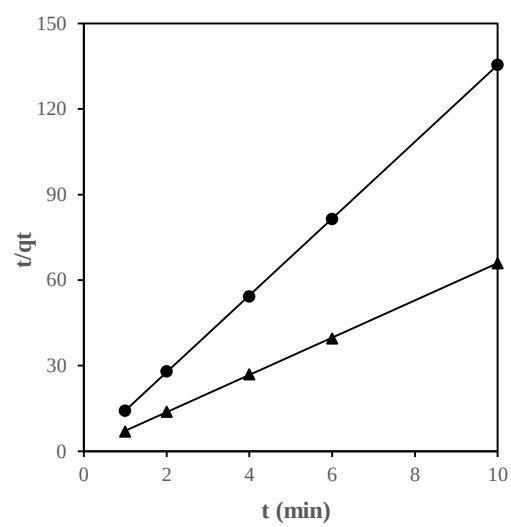


Fig. 14 At the initial Ag(I) concentration of 50 ppm (*circle*) and 100 ppm (*triangle)*, The fitting of adsorption data to the pseudo second-order kinetic model for Ag(I) adsorption on the poly(sodium methacrylate) at 303 K, The pH of initial Ag(I) solution is 7.45

Table 3 The kinetic constants obtained from four kinetic models (The modified Freundlich, the Elovich, the pseudo-first-order, and pseudo-second-order kinetic models) for the Ag(I) adsorption on poly(sodium methacrylate)

Model	Parameters	50ppm Ag(I)	100ppm Ag(I)
The modified Freundlich	a	0.072	0.145
	b	0.0108	0.0139
	R^2	0.716	0.752
The Elovich	A	8×10^{-4}	24×10^{-4}
	B	1250	476.2
	R^2	0.753	0.644
Pseudo first-order	k_1 (min^{-1})	3×10^{-4}	9×10^{-4}
	R^2	0.831	0.891
Pseudo second-order	q_e (mol/g)	0.074	0.153
	k_2 (g/min mol)	247.63	71.4
	R^2	0.998	0.999

3.6 . Thermodynamic parameters

In this section, Ag(I) adsorption onto copolymer for two different silver concentrations (50 ppm and 100 ppm) at different temperatures (293, 303, and 323 K) was attempted, and some thermodynamic parameters like enthalpy (ΔH, kJ/mol), entropy (ΔS, J/mol K), and Gibbs free energy (ΔG) were calculated using the following equations to better understand the nature of this adsorption.

$$K_e = \frac{q_e}{C_e} \quad (19)$$

$$\Delta G = \Delta H - T\Delta S \quad (20)$$

$$\Delta G = -RT\ln K_e \quad (21)$$

$$\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (22)$$

In the above equation, K_e (L/g) is the equilibrium constant of adsorption, R (8.314 J/mol K) is gas constant and T is temperature. Using equation 22, the graph of $\ln K_e$ against 1/T is drawn (**Fig. 15**). Using the slope and intercept of this graph and other equations, thermodynamic parameters were calculated for different temperatures and different concentrations (**Table 4**). As can be seen on **Table 4**, the thermodynamic parameters for different concentrations were found to be negative at all temperatures. The negative ΔG values at all temperatures indicate the process of removing Ag(I) from the aqueous solution using poly(sodium methacrylate) occurs spontaneously. The enthalpy being negative means the experiment is exothermic. In some work, there is an explanation about ΔG, "If ΔG values are greater than -20 kJ/mol, it corresponds to physical adsorption. This event is due to the electrostatic interaction between the sorption sites and the metal ions. A value of ΔG less than -40 kJ/mol also corresponds to chemical adsorption due to charge sharing or transfer between adsorbent and adsorbate" [66, 67, 68]. Based on this information, the ΔG values calculated in the current study appear to be all smaller than -40 kJ/mol, giving some clues to the chemical nature of the adsorption as previously described. During adsorption, as silver ions adsorbing on the adsorbent surface, they got rid of their dispersed state in the solution and thus caused a decrease in disorder, which may have caused the entropy to be negative [69, 70, 71].

3.7. Effect of pH

To examine how the pH change of the solution consisting of silver ions and copolymer affects the adsorption process, 10 mL of 100 ppm Ag(I) solution at pH 7.45, and 0.04 g of adsorbent were mixed. The pH of the solution was varied between 1 and 11 by carefully

adding HNO_3 and NaOH to the solution separately. Other parameters are kept constants as adsorption temperature (T = 303 K) and contact time (t = 60 min). Adsorption percentage, which changes according to the pH changes, is given in **Fig. 17** and **Table 5**. As seen in **Fig. 17** and **Table 5**, the adsorption percentage is quite low at pH 1. But after pH 2, a large increase was seen and the increase from pH 3 to pH 6 slows down and the system reaches equilibrium at pH 6. To better understand the behavior of the adsorption percentage concerning to the pH changes, the pH_{pzc} of the solution was calculated (**Fig. 16**, pH_{pzc} = 8.5). At pH < pH_{pzc}, the surface of the adsorbent has positively charged, due to the distribution of H^+ over the surface, while it has negatively charged at pH > pH_{pzc}, due to the excess of OH^-. As the pH of the solution decreases (pH < pH_{pzc}), positive charges (H^+) competes with metal ions to diffuse into the adsorbent surface. After the surface becomes positively charged, a electrostatic repulsion force has occurred between the positive surface and the silver cations. These events may have caused a smaller amount of silver to be adsorbed on the copolymer surface. As the pH value increased, the H^+ ion density on the adsorbent surface decreased, which allows more silver ions to adsorb on the surface. At higher pH values, (pH > pH_{pzc}= 8.5), the adsorbent surface was negatively charged and an electrostatic attraction force was formed between them and the silver ions, which helped the adsorption process of the silver ion on the copolymer [72, 73].

Table 4 The thermodynamic parameters of Ag(I) removal by poly(sodium methacrylate)

C_0(mg/L)	T(K)	ΔG(kJ/mol)	ΔS(J/mol K)	ΔH(kJ/mol)
50ppm	293	-41.76	-20.49	-35.76
	303	-41.98		
	323	-42.30		
100ppm	293	-56.72	-46.88	-42.98
	303	-57.18		
	323	-58.12		

Table 5 The adsorption percentage behavior with changing pH values

pH_i	pH_f	ΔpH	Ads. (%)
1	3.63	2.63	27.61
2	4.5	2.5	35.56
3	5.8	2.8	85.33
4	6.93	2.93	97.171
5	7.68	2.68	99.784
6	7.83	1.83	99.854
7	7.91	0.91	99.873
8	8.22	0.22	99.891
9	8.72	-0.28	99.896
10	9.11	-0.89	99.905
11	10.03	-0.97	99.9

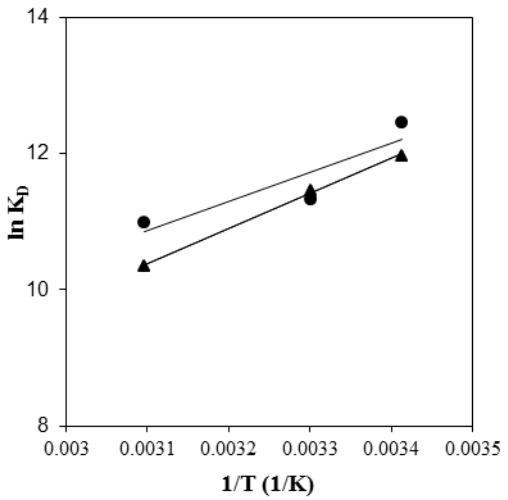


Fig. 15. Calculating of some thermodynamic parameters by plot of ln K_d versus 1/T for the adsorption of Ag(I) onto the poly(sodium methacrylate). Initial Ag(I) concentrations are 50 ppm (*circle*) and 100 ppm (*triangle*), t = 60 min, the pH of initial Ag(I) is 7.45

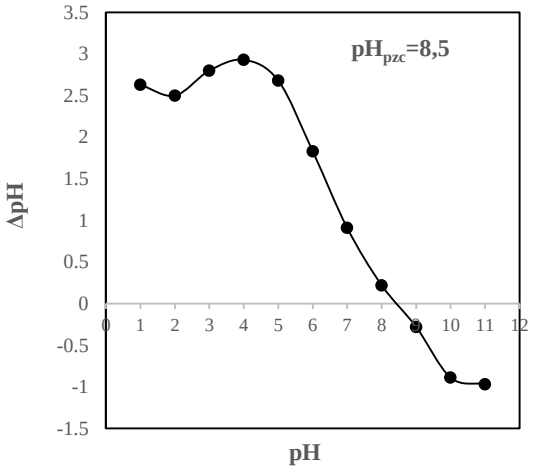


Fig. 16 The pH_{pzc} (zero-point charge) of adsorbent (C_{NaCl}=0.01 M, adsorbent mass = 0.04 g, initial pH = 1-11, T = 303 K, contact time = 60 min and concentration of solution $AgNO_3$ solution 100ppm)

4. Conclusions

The adsorption of Ag(I) onto crosslinked copolymer containing sodium methacrylate as a functional group was tested in the batch method. Poly(sodium methacrylate) is a powerful adsorbent for the removal of Ag(I) from aqueous solutions. The effect of the amount of adsorbent, contact time, pH of the solution, and the temperature was examined. It was observed that with increasing the amount of adsorbent from 0.005 to 0.1 g, the adsorption percentage showed a significant increase and reached equilibrium at the $m_{copolymer}$ = 0.04 g. This adsorption mass was taken as the adsorption equilibrium

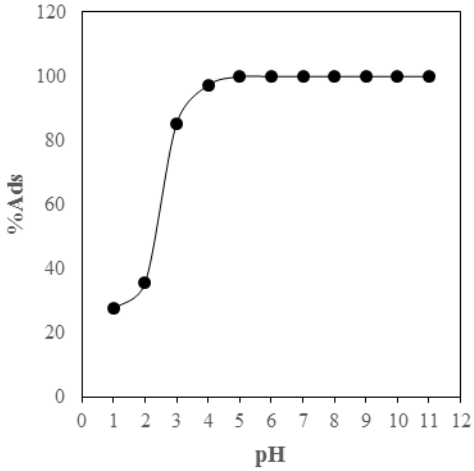


Fig. 17 The effect of pH on the Ag(I) adsorption on the poly(sodium methacrylate) from aqueous solutions at 303 K. The contact time and initial Ag(I) concentration are 60 min and 100 ppm, respectively

mass and was used in the continuation of the experiments. By the increase in the pH of the solution, an increase in the adsorption percentage was observed, and it reached equilibrium at a certain pH value. The thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were negative at all temperatures. The negative ΔH ve ΔG values indicate that the adsorption reaction is exothermic and occurs spontaneously. A negative ΔS value means that the disorder in the adsorption mechanism is reduced. An inverse correlation was observed between the concentration of the $AgNO_3$ solution diluted with distilled water and the adsorption percentage. When the adsorption data were evaluated with some isotherms (n_F was between 0-1 in the Freundlich isotherm and the free energy value was 8-16 in the D-R isotherm) it was revealed that the adsorption of the Ag(I) ions exchange chemical type. The pseudo-second-order kinetic model showed the best fit among the adsorption kinetic models examined (0.998< R < 0.999).

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