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A rapid and sensitive method for separation of Cu^{2+} ions from industrial wastewater sample and water samples with methacrylamide-ethylene glycol dimethacrylate: A new synthesis of molecularly imprinted polymer

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Abstract

In this study, new molecularly imprinted polymer particles (MIP) were synthesised to extract Cu^{2+} ions from aqueous solutions using radical polymerisation. MIP was developed using the methacrylamide-ethylene glycol dimethacrylate (EGDMA) cross linking agent, methacrylamide monomer, and ACV initiator by the radical polymerisation method. A comparison of various cross linking agents in MIP production showed that the best cross linking agents are EGDMA and gallic acid. The template ions were removed by leaching with 0.100 M HCl. The polymer particles were characterised by FTIR spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The effect of different parameters such as cross linkers, pH, time, maximum adsorption capacity, and kinetic and isotherm adsorption were investigated. The best conditions were determined (pH = 8.0, t = 10 min, and q_m = 262.53 mg g^{-1}). The adsorption data were best fitted by Freundlich isotherm and pseudo second order kinetic models, as well. Due to its high adsorption capacity and multi-layer behaviour, this method is an easy, fast and safe way to extract cations. Removal of Cu^{2+} in certified tap water and rain water was demonstrated and the industrial wastewater sample (Charmshahr, Iran) with which the MIP was developed using Methacrylamide- Ethylene Glycol Dimethacrylate (EGDMA) was good enough for Cu^{2+} determination in matrices containing components with similar chemical property such as Co^{2+}, Zn^{2+}, Fe^2.

KEYWORDS

adsorption, isotherm, molecularly imprinted polymer (MIP), removal of Cu^{2+}

1 | INTRODUCTION

The covalent imprinting method was invented by Wulf and Sarahan in 1986 [1]. In this method, by a reaction of the imprint with a functional monomer and the formation of reversible covalent bonds between them, it changes to a monomer with polymerisation capability. The functional monomer and the imprint are mixed to form reversible covalent bonds. This imprint is converted by polymerisation in the presence of crosslinkage agents. In non-covalent imprinting, the reaction between the functional monomer and the imprint during the polymerisation is similar to the reaction between the polymer and the imprint at the re-bonding stage that is based on the non-covalent forces (the hydrogen bond, the sharing of the ion and the dipole-dipole bond) between the imprint and the functional monomer prior to polymerisation [2–4]. This method is first presented by Mosbach et al. [5]. This method has been most applicable to the production of molecularly imprinted polymers. The main reason is the simple experimental conditions and the existence of various functional monomers which are almost capable of reacting by any types of imprinted sites. However, this method

is not devoid of limitations. The interaction between the monomer and the imprint is a function of an equilibrium. Therefore, for the displacement of the equilibrium to the monomer-imprint formation, a large amount of monomer should be consumed. Moreover, the surplus monomer taken in the polymer matrices leads to the creation and formation of non-selective bonding sites. The most frequently used monomer is also the primary one for non-covalent imprinting, that is methacrylic acid [6–8]. Scientists have used methacrylic acid for imprinting a wide range of materials [9–11]. Other acid monomers such as 4-vinyl benzoic acid [12], and acrylic acid [13] are also used for imprinting several types of compounds. Synthesising the monomer compounds is also used to increase the bonding properties of molecularly imprinted polymers, including 2-vinyl pyridine with methacrylic acid [14–19]. The advantage of this method is the simplicity of the preparation steps, and the low speed of imprint removal and the low speed of a ligand-imprint bonding are the disadvantages of this method. The effect of various crosslinkages such as gallic acid and ACV as an effective initiator on MIP formation has not been investigated.

On the other hand, methacrylamide-based MIP was not used to remove Cu^{2+} ions. This work demonstrates the development of a rapid, efficient and highly sensitive method for selective removal of Cu^{2+} ions from aqueous industrial wastewater sample and water sample media using methacrylamide-based MIP and AAS determination. It appears that the presence of the amide group can bind to Cu^{2+} ions. Therefore, methacrylamide monomer was used for MIP synthesis. The results of this study show that the efficiency of this method is very high compared to other methods.

2 | EXPERIMENTAL

2.1 | Reagents and materials

All materials used include a monomer, cross linking agents, initiator and solvents provided from the German Merck factory with a high degree of purity, and double distilled water was used in all experiments. For methacrylamide purification, recrystallisation was carried out twice with distilled water and methanol, and the initiator was first suspended with distilled water to be purified. Then, sodium bicarbonate was added to its full dissolution, and finally, the initiator was deposited with the addition of 1.0 M of HCl and the obtained solid was washed with ice water and dried in a vacuum at room temperature and kept in the dark and in a refrigerator during the experiments.

2.2 | Apparatus

The Fourier transform infrared (FTIR) spectra at every stage of synthesis of magnetic nanobiosorbent were recorded by using FTIR spectrometer in the range 4000–400 cm^{-1} using the KBr pellet technique (Thermo, AVATAR). For the

determination of metal ions, flame atomic absorption spectrometer (FAAS) (Varian Spectra AA 200) was used. The size and morphology of the MIP was characterised by a scanning electron microscope (SEM, PHILIPS, CM120). The thermal stability of MIP was determined before and after ion adsorption using a TGA instrument (CHURCH STRETTON).

2.3 | MIP and NIP synthesis

In the first synthesis, citric acid was used as a cross linking agent. About 0.001 mol of copper sulphate equivalent of 0.1280 g was added to the Erlenmeyer flask followed by water and ethanol with the ratio of 1:3 to completely dissolve the copper sulphate. After dissolving copper sulphate, 0.004 mol of methacrylamide equivalent of 0.34 g was added and then 0.02 mol equivalent of 3.84 g citric acid was added as a cross linking agent to the Erlenmeyer flask and finally, 50 mg of ACV radical initiator has been added. Furthermore, de-airing was carried out using N_2 for 10 min and it was kept in a water pool for 24 h. In the synthesis that was carried out by citric acid cross linking agent, no solid was extracted. In this stage, ethanol Cu^{2+} was prepared in a mixture of water and ethanol, but since ethanol acts as a methacrylamide solvent, it prevented the formation of cross linking agents. Therefore, the removal of ethanol in the aqueous medium was performed during the all stages of synthesis. After the formation of the MIP polymer, it was removed from the Erlenmeyer flask and was washed by water and ethanol (in order to wash the non-grafted monomers). This process was performed several times for the excess wash of monomers, and finally, the filtration was carried out carefully.

It is worth mentioning that the extraction of Cu^{2+} from MIP by the citric acid cross linkers was carried out by 0.01 M HCl and surplus HCl was washed by methanol. In the next synthesis, ethylene glycol dimethacrylate cross linkers (EGDMA) were used. All the synthesised stages were similar to each other. In this synthesis, a large amount of MIP was produced after 24 h in a water bath at 70°C. This polymer was first washed by deionised water and then washed by HCl solvent and finally, surplus HCl was washed off by methanol. In the next synthesis, gallic acid cross linkers were used for the first time. All the synthesised stages were carried out in the same manners and the best performance was observed in the synthesis of polyethylene glycol dimethacrylate.

NIP synthesis was carried out in the absence of Cu^{2+}, unlike the former synthesis. In this step, after purifying the 4,4'-azobis 4-cyanovaleric acid (ACV) radical initiator and methacrylamide, 0.0040 mol of methacrylamide equivalent to 0.340 g was added to the Erlenmeyer flask and shaken, and then 0.002 mol of the ethylene glycol dimethacrylate cross linking agent equivalent of 3.77 ml was added into the Erlenmeyer flasks. Afterwards, we added 50 mg of ACV into the Erlenmeyer flask and then deairing was carried out in the water bath at the temperature of 70°C for 24 h, it is not necessary to do the extraction with HCl and ethanol after the formation of a polymer. The analysis was

performed after synthesis with three cross linking agents by MIP and NIP methods.

2.4 | Adsorption experiment

First, a 100 ml balloon was used and 0.020 g of copper sulphate was added to the Erlenmeyer flask volume was made up with water. Thereupon, the pH of the mother liquor was calculated and it was carried out for four synthesised cases as well. . The ion adsorption tests were analysed by a batch technique. First, 0.020 g of produced MIP with various cross linking agents and NIP were weighted and added to a 50 ml flask. Then 20 ml of mother liquor was added to the 50 ml flask. These four flasks were covered with parafilm and transferred to the shaker with the rotation speed of 150 rpm. The temperature is set to 298 K and the time is set to 1 h. After 1 h, four flasks are evacuated and the solutions of each flask are poured into the test pipe. They were covered with parafilm and put into the centrifugal device (for 10 min by the rotation speed of 3000 rpm). After centrifugation, two separate phases were formed. The upper solution phase was carefully isolated and its adsorption was determined by atomic absorption spectrophotometer (Varian Spectra AA 200) and calculated based on the following equation.

$$q = C_0 - C_e/m \times V \tag{1}$$

In this equation, C_0 and C_e are initial and adsorbed concentration of at Cu^{2+}, respectively. SEM, FTIR spectroscopy and thermogravimetric analysis (TGA) were used to detect the adsorbate and confirming the adsorption of Cu^{2+} cation. The required standards are used as a witness to compare and draw the calibration curve were 10, 20, 30, 40 and 50 mg L^{-1}, respectively.

2.5 | Adsorption isotherm

In the four 20 ml Erlenmeyer flasks, we calibrated the concentrations of 20, 40, 60, and 80 mg L^{-1} and optimal pH of 8.0. Then, the polymers were put in the Erlenmeyer flasks, then the flask was put in the shaker with the rotation speed of 150 rpm and the temperature of 298 K. All samples were removed after an hour, then filtration and centrifugation were carried out on each of them, the adsorption of each solution was determined by FAAS and concentrations were determined using the calibration curves of concentrations. All adsorption and desorption experiments were repeated 5 times, and the particle efficiency did not decrease due to the high thermal stability of MIP. Thereupon, the results were evaluated in 324 nm with first type Langmuir, Temkin and Freundlich adsorption isotherms. In these equations, C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1})is the amount of adsorption at equilibrium state, q_m and K_a are constants of the Langmuir equation, K_f states the absorber capacity, and n represents the intensity of absorption, and a_e (mg g^{-1}) and B_0

(mg L^{-1}) are obtained from the empirical data after drawing the q_e-lnC_e curve.

$$\text{Langmuir,} \quad C_e/q_e = {}^1/q_m K + C_e/q_m \tag{2}$$

$$\text{Freundlich,} \quad \ln q_e = \ln k_f + {}^1/n \cdot \ln C \tag{3}$$

$$\text{Temkin,} \quad q_e = a_t + B_0 \ln C_e \tag{4}$$

2.6 | Adsorption kinetics

In this experiment, three flasks were used and 20 ml of mother liquor with a concentration of 20 mg L^{-1} was added to each flask and pH was calibrated to 8.0. Then, 0.020 g of the polymer was added to each of the flasks and finally, they were put into the shaker with the temperature of 298 K. The samples were removed after 5, 7.5, and 10 min, respectively, then filtration and centrifugation were carried out for each of the samples. The adsorption was determined by FAAS and evaluated with the pseudo-first-order, pseudo-second-order, and intramolecular diffusion models. The obtained results are summarised in Table 2. The relative standard deviations (RSDs) ($n = 5$)were calculated for intraday and interday. This reflects the favourable precision of the total procedure. As a result, the adsorption process is controlled by more than one adsorption limiting mechanism [18].

$$\text{Pseudo - first - order,} \quad \ln(q_e - q_t) = \ln q_e - k_a t \tag{5}$$

$$\text{Pseudo - second - order,} \quad \frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \tag{6}$$

$$\text{Intra - particle - diffusion,} \quad q = K_d \cdot t^{1/2+l} \tag{7}$$

3 | RESULTS AND DISCUSSIONS

3.1 | Characterisation

MIP recognition before and after the adsorption of Cu^{2+} ions were investigated by SEM, FTIR, and TGA methods. The MIP after the adsorption of Cu^{2+}, confirming that the range of approximately 1200–1300 cm^{-1}, determines the C-N group and a strong peak around 1630–1690 cm^{-1} denotes the carbonyl amide group. The two strong peaks observed, in addition to the N-H peak at 800–1100 cm^{-1}, confirmed the presence of MIP by the presence of the methacrylamide monomer. It is worth mentioning that the MIP is not destroyed after adsorption and the spectral variation is observed at approximately 2200 cm^{-1} (Figures 1 and 2). An imprinted cross linker, poly (methacrylamide-co-ethylene glycol dimethacrylate), using a double-imprinting approach for

the Cu^{2+} selective complex from aqueous medium was prepared. In the imprinting process, Cu^{2+} ions were employed as templates [20].

The TGA thermograms confirm that the synthesised MIP has high stability before and after adsorbing and has suitable thermal stability despite the adsorption of 200 mg L^{-1}, and the destruction temperature is approximately between 306 and 309 (Figures 3 and 4). Scanning electron microscopy images in MIP

confirmed the presence of empty cavities and then, after adsorbing as shown in Figures 5–7 with 20 KX and 40 KX magnifications, the empty spaces are filled with Cu^{2+} ions. The results obtained by the mentioned analyses confirm the formation of MIP and its effect on the absorption of Cu^{2+} ions.

3.2 | Effects of various cross linking agents

To this aim, a comparison of different cross linking agents for the synthesis of MIP was investigated in the presence of methacrylamide and 4,4'-azobis 4-cyanovaleric acid (ACV) initiator. Table 1 shows the results of these investigations. It has been observed that EGDMA and GA (gallic acid) cross linking agents have more adsorption, but citric acid has no suitable absorption for Cu^{2+}. The results of this study revealed that gallic acid can be used as a suitable new cross linking agent in the MIP and can be used as an effective cross linking agent for future studies.

TABLE 1 Effect of different cross-linking agents in adsorption of 20 mg L^{-1} Cu^{2+} ions

Crosslinkage	C_e (mg L^{-1})
Citric acid	15.5
Gallic acid	0.25
Ethylene glycol dimethacrylate	0.17
NIP	7.55

TABLE 2 Determination of Cu^{2+} ions in Iran water samples by the proposed adsorbent

RSD (%) ($n = 5$)	Removal (%)	After treatment (mg L^{-1})	Input (mg L^{-1})	Sample
1.2[a]	105	0.011	–	Charmshahr's wastewater sample
1.5	109	0.011	–	Sea water[c]
1.9	99	0.010	0.25	Rain water[d]
1.1	97	0.011	0.25	Tap water[b]

Abbreviation: RSD, relative standard deviation.

[a]Standard deviation ($n = 3$).

[b]From drinking water system of Tehran, Iran.

[c]Caspian sea water, Iran.
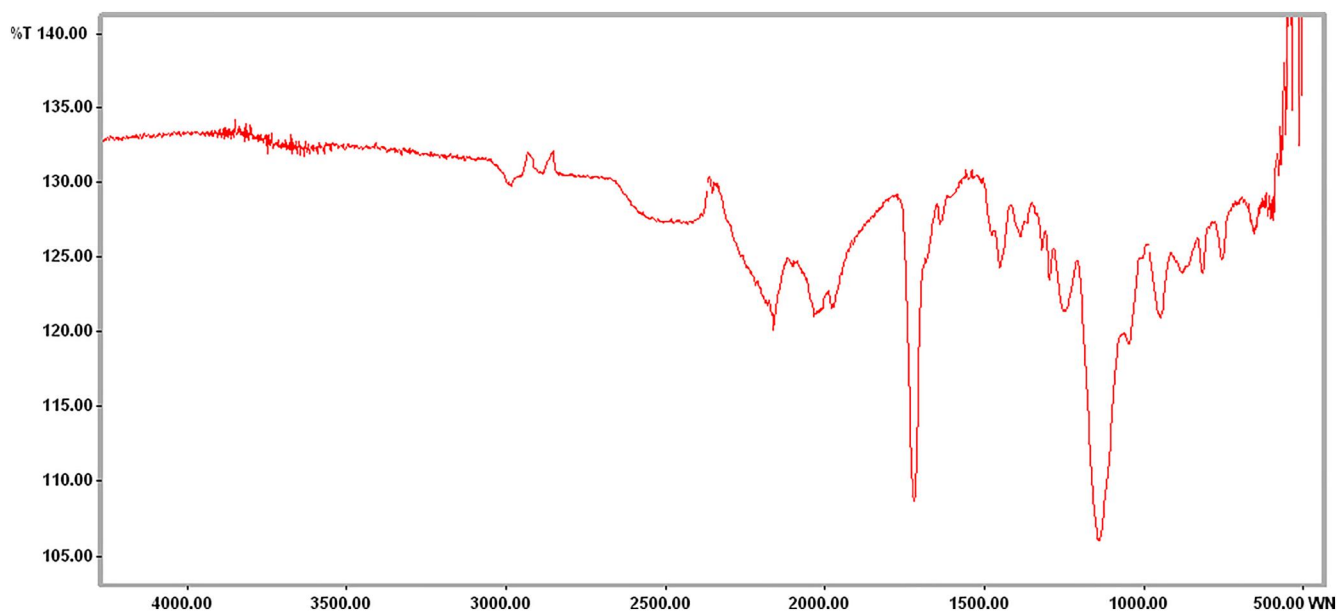
[d]Rain water (Tehran, 20 January, 2020).

FIGURE 1 Fourier transform infrared of the molecularly imprinted polymer before adsorption

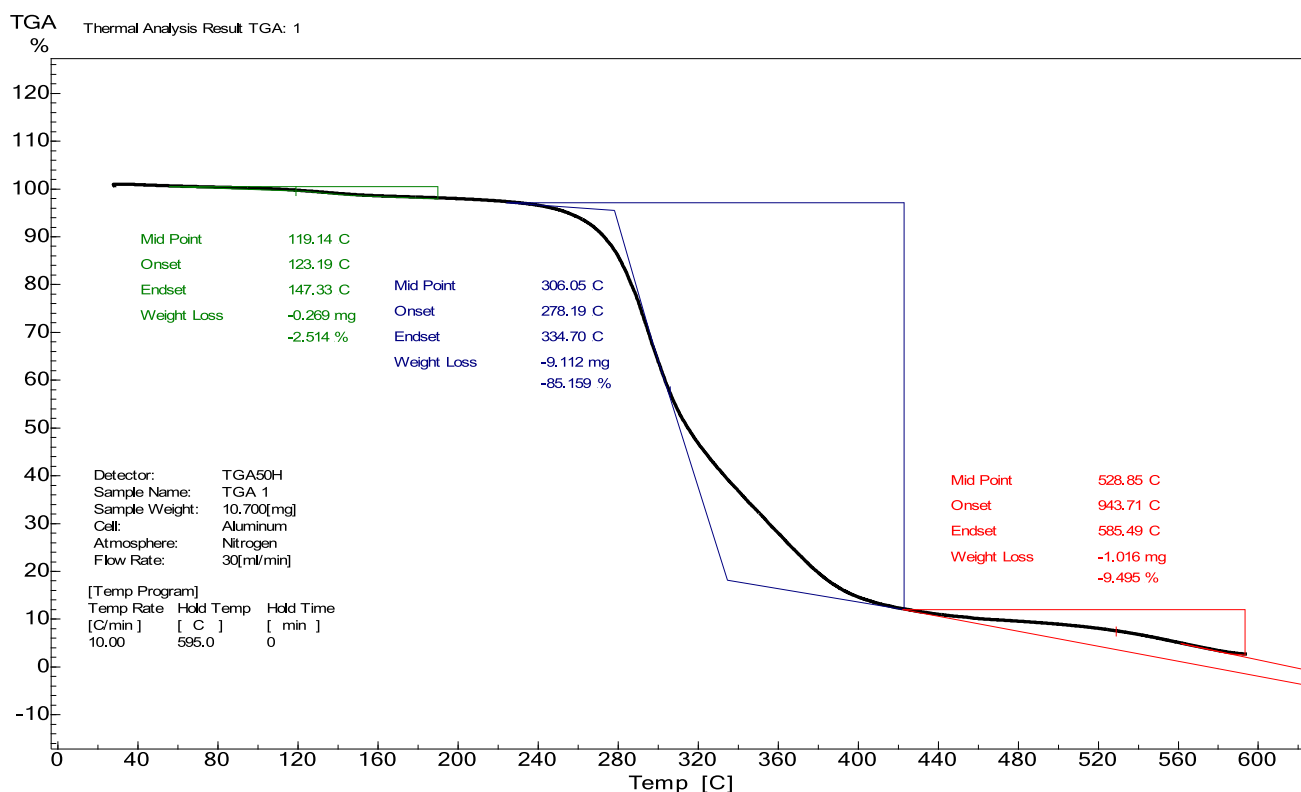**FIGURE 2** Fourier transform infrared of the molecularly imprinted polymer after adsorption

FIGURE 3 Thermogravimetric analysis of molecularly imprinted polymer before adsorption

3.3 | Calibration curve

In order to draw the calibration curve at $y = 0.0083x–0.0851$, $R^2 = 0.993$ concentrations, the adsorption is read by the AAS (PG 991 AAS) device, at the adsorption wavelength $\lambda_{max} = 324$ nm for Cu^{2+}.

3.4 | Investigation of pH effect

In order to obtain the best range of pH at a constant condition ($t = 60$ min, 150 rpm of rotation speed, the volume of a solution of 20 ml and constant adsorption concentration of 20 ppm) at different pH range from 2 to10 were investigated
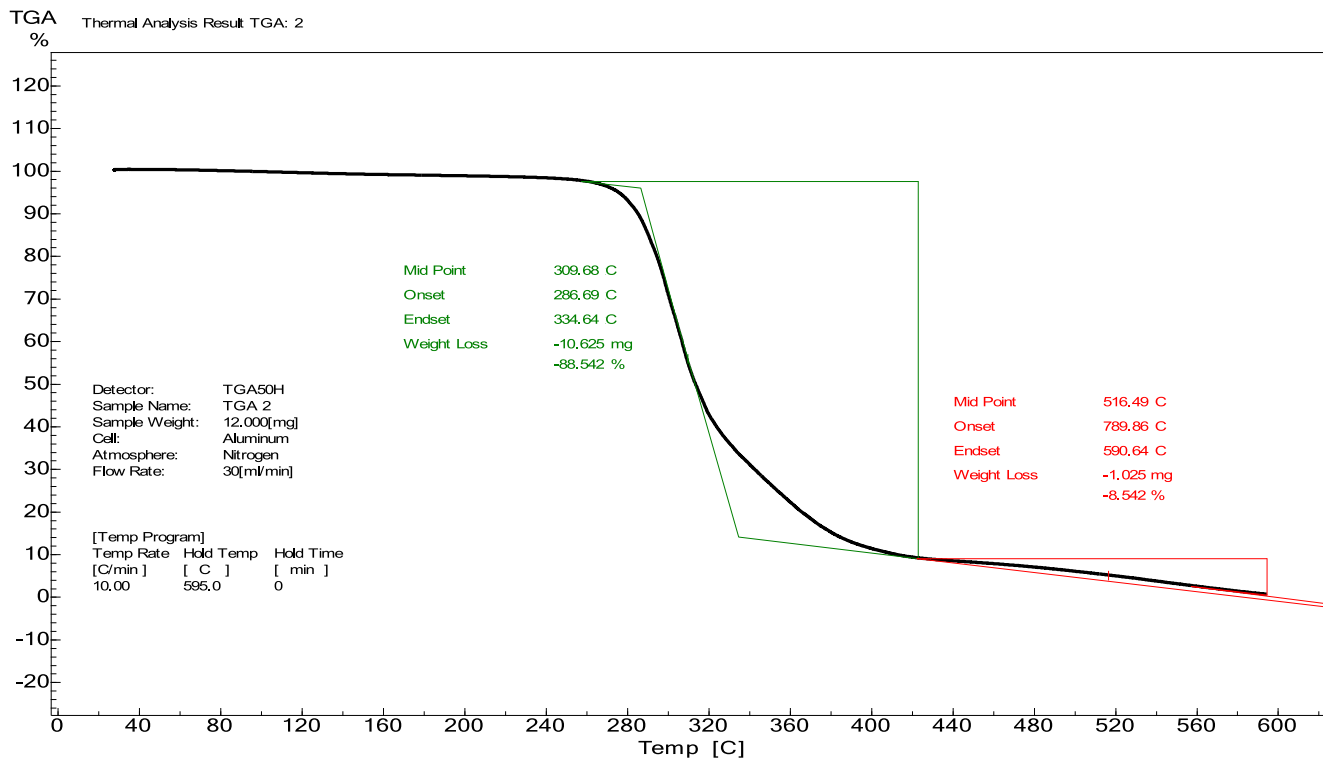
FIGURE 4 Thermogravimetric analysis of molecularly imprinted polymer after adsorption
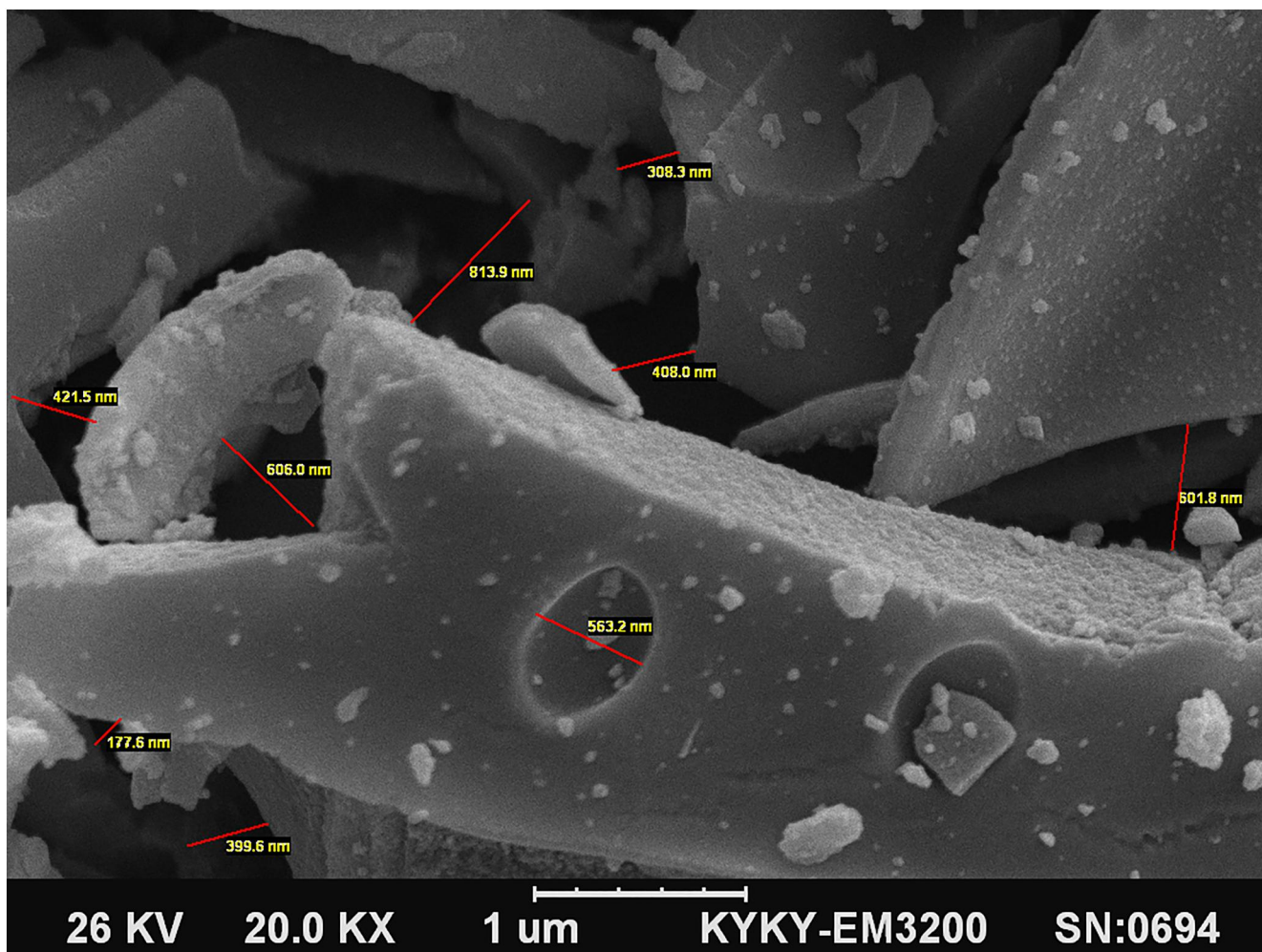

FIGURE 5 Scanning electron micrograph of molecularly imprinted polymer (20KX)
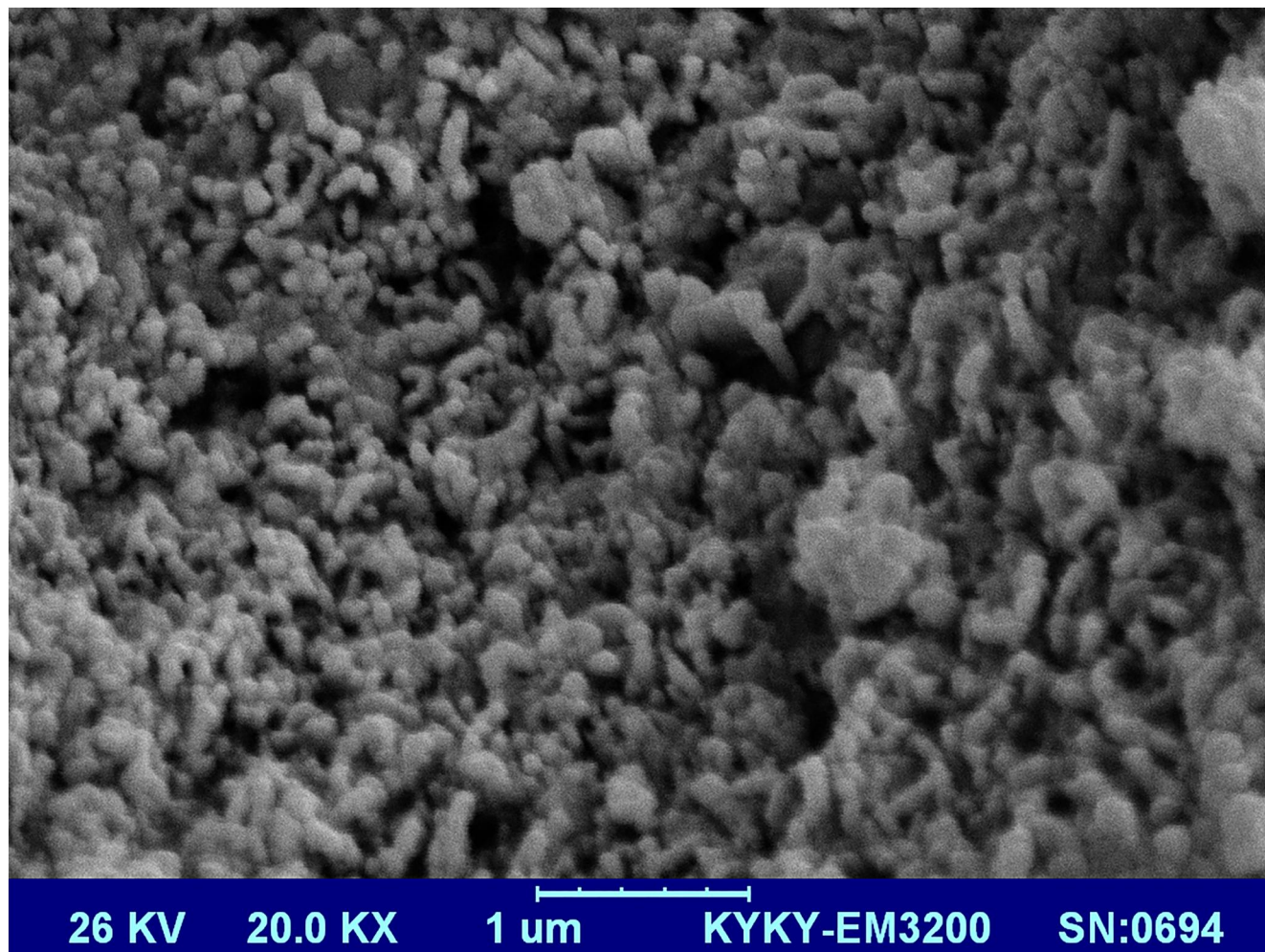
FIGURE 6 Scanning electron micrograph of molecularly imprinted polymer before adsorption (20KX)

for NIP and MIP. As observed in Figure 8, the maximum adsorption occurs at pH = 8.0. The results showed that in the acidic pH due to the high mobility of H^+ in comparison to Cu^{2+}, the diffusion and adsorption of the H^+ by the MIP was more than Cu^{2+}. Although in the pH range of 6–8, there was maximum adsorption which had a slight difference compared with the pH = 8.0. At a higher pH, adsorption reduction was observed.

3.5 | Investigation of adsorption time

In order to stabilise the best time of adsorption of Cu^{2+}, at a constant condition (at pH = 8, rotation speed = 10 rpm, adsorber = 20.0 mg L^{-1} and V = 20 ml) the adsorption operations were carried out in shaker at different times from 5 to 60 min. It is obvious from the results that the best time for the MIP adsorption is 10 min, which is a very fast process in adsorption pollutants and also shows more absorption in comparison to NIP (Figure 9).

3.6 | Investigation of adsorbate concentration

In order to determine the maximum adsorption at a constant condition ($t = 60$ min, rpm = 150 and pH = 8.0), absorber concentration varied from 5 mg L^{-1} to 340 mg L^{-1}. The results of the experiment are shown in Figure 10. The results showed that in MIP, the maximum adsorption capacity was observed at 340 mg L^{-1} and the amount of q was obtained at 262.53 mg g^{-1}. Whereas in NIP, maximum adsorption capacities were obtained at 24.89 mg g^{-1} for 140 mg L^{-1}. These results confirm that MIP has high strength in the absorption of ions and has a suitable industrial application compared to the previously reported absorbers.

3.7 | Adsorption isotherms

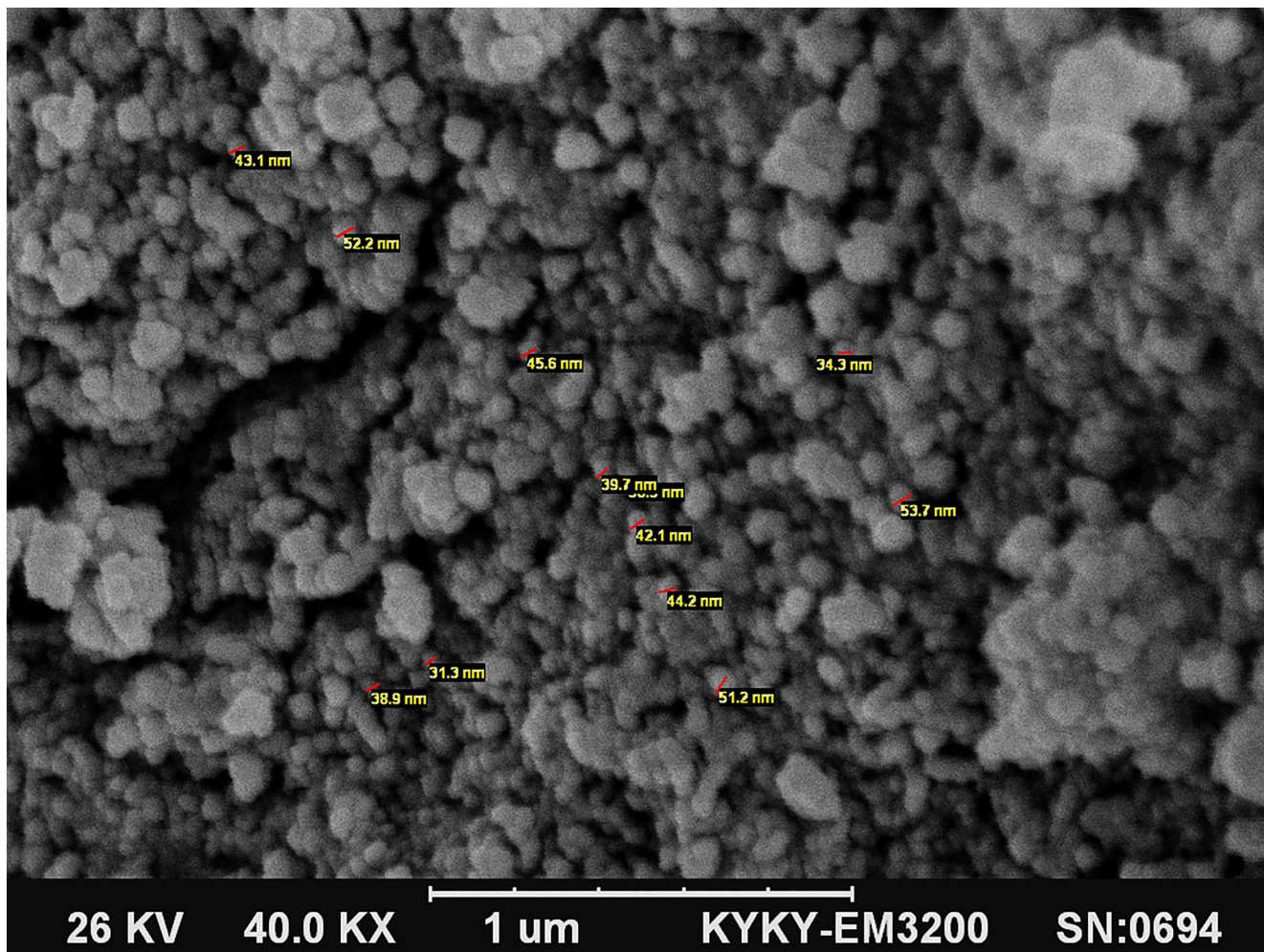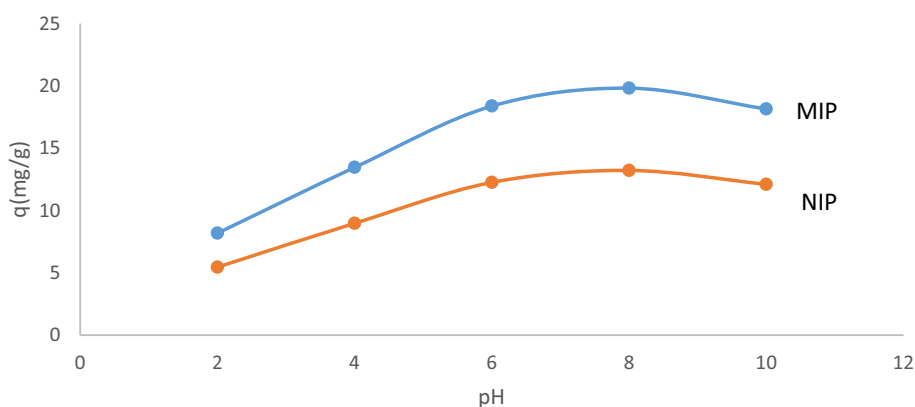The most stable isotherm model is based on the correlation coefficients obtained in the Freundlich model as it can be

FIGURE 7 Scanning electron micrograph of molecularly imprinted polymer after adsorption (40KX)

FIGURE 8 Effect of pH

seen in the Figures 11–13. Adherence to the Freundlich isotherm model indicates that the adsorption process is multilayered. In this study, isotherms were surveyed by varying the concentration of Cu^{2+} ion solutions from 10 to 350 mg L^{-1} at pH 8.0 with a 0.05 g of the MIP EGDMA

and gallic acid. The Langmuir, Freundlich, Temkin, Dubinin–Radushkevich isotherm models were applied to elucidate the adsorption mechanism. Figures 11–13 summarises all parameter values obtained from the isotherms used for the Cu^{2+} removal by the MIP. Moreover, the model has larger R^2
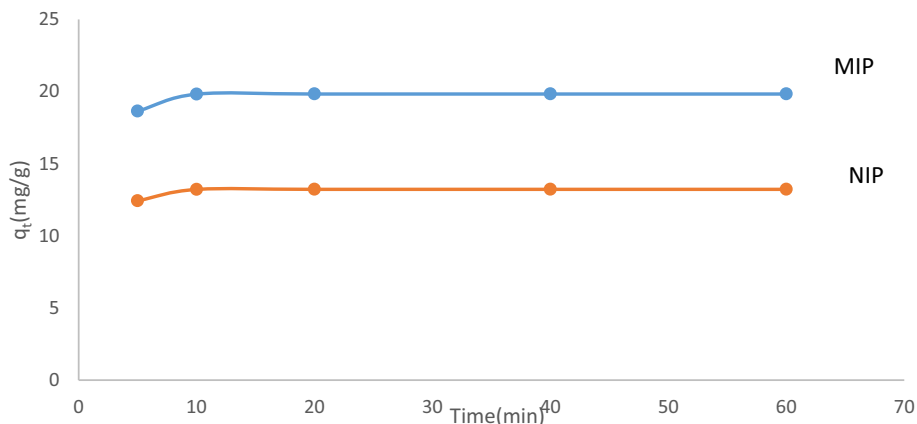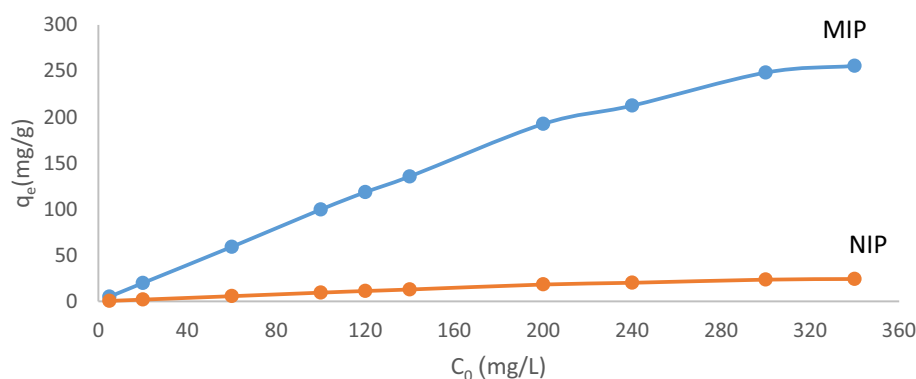
FIGURE 9 Effect of time

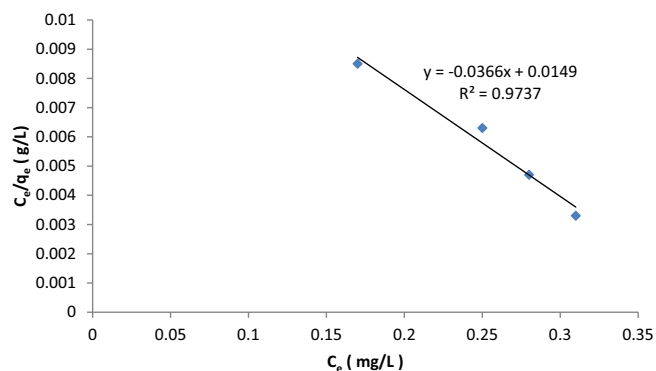**FIGURE 10** Effect of Cu^{2+} concentration

FIGURE 11 Langmuir (first model) isotherm (298 K)
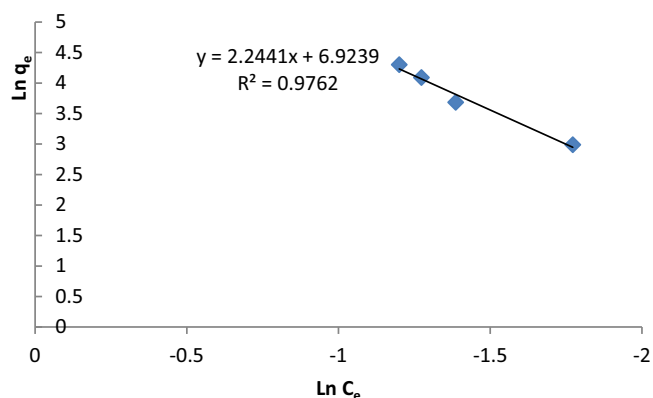

FIGURE 12 Freundlich isotherm (298 K)

values after the Freundlich model to fitting experimental data of Cu^{2+} removal by MIP EGDMA and gallic acid. In this work, three kinetic models were employed to study the adsorption time and rate. For these intentions, the experiments were performed at optimum conditions at various time intervals up to 10 min. The equilibrium times were observed to be 15 min for adsorption of Cu^{2+}ions by, MIP- EGDMA and gallic acid.

3.8 | Adsorption kinetics

The kinetic results of adsorption are investigated and analysed based on three kinetic models.

Figures 14–16 indicate that the pseudo-second-order model is the best fit for the kinetics of adsorption kinetics of Cu^{2+} ions ($C_e = 20.0$ mg L^{-1}). It seems that this model can confirm the rapidity of MIP EGDMA and gallic acid reaction
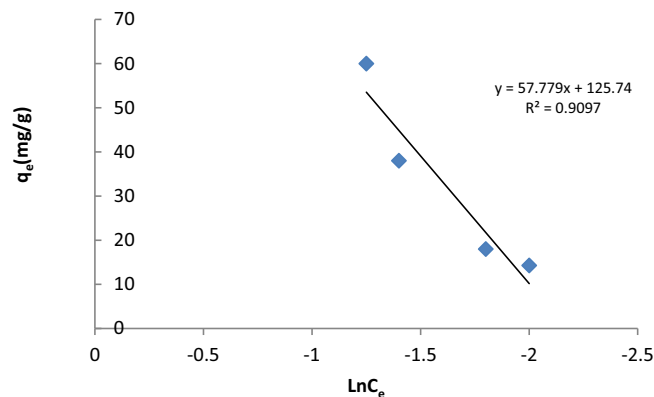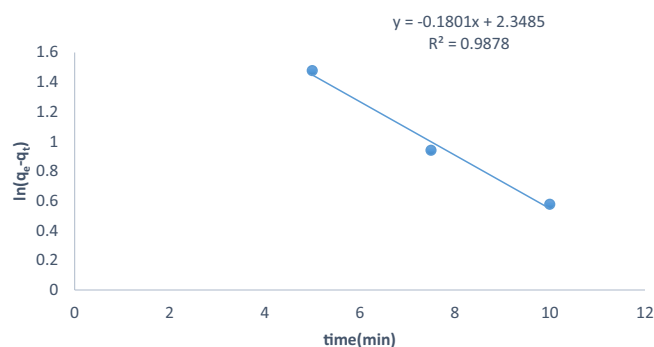
FIGURE 13 Temkin isotherm (298 K)

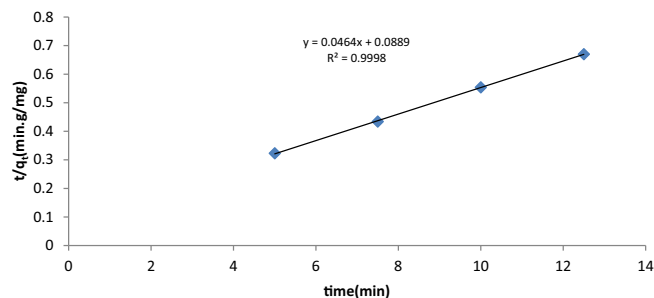**FIGURE 14** Pseudo-first order kinetics

FIGURE 15 Pseudo-second order kinetics

with Cu^{2+} ions. Examination of the effect of adsorption time and completion of adsorption in 10 min confirms this mechanism. In this work, three kinetic models were employed to study the adsorption time and rate. For these intentions, the experiments were performed at optimum conditions at various time intervals up to 10 min. The equilibrium times were observed to be 180 min for adsorption of Cu^{2+} ions by MIP EGDMA and gallic acid. The adsorption of Cu^{2+} ions by the MIP-EGDMA and gallic acid can be revealed by the pseudo-second-order kinetic type, and this model proposed that the rate in the adsorption process controlled by the chemical adsorption mechanism.
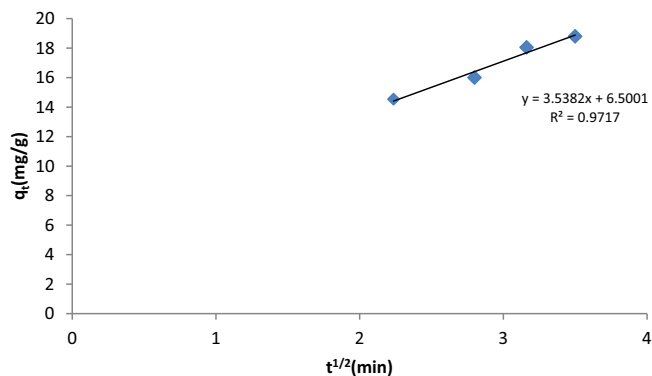

FIGURE 16 Intra-particle diffusion kinetics

3.9 | Analysis of water samples

The proposed method was then applied for the determination of Cu^{2+} in tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20 January 2020), and sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples and industrial Charmshahr's wastewater (Varamin, 15 February 2020). Meanwhile, the standard addition method was applied to check the selectivity of the imprinted copolymers for Cu^{2+} against matrix elements. The recoveries were in the range of 97%–105%, demonstrating that the interference species in the matrix were eliminated after the MIIP and removal procedure. The results listed in Table 2 indicate the suitability of the present Cu^{2+} imprinted copolymers for the removal of Cu^{2+} from natural water and industrial Charmshahr's wastewater samples.

3.10 | Pollutants in Charmshahr's wastewater sample

The average colour range of the untreated tannery effluent was found to be 1650 Pt-Co units, which was 110 times higher than all the recommended values of standard (15 Pt-Co units). The colour appearance of untreated effluent was found yellowish. The analysis results indicate that the untreated effluents contained highly coloured compound which has the potential to pollute the environment Table 3.

3.11 | Selectivity of copolymers for matrix ions

Competitive adsorption of Cu^{2+}/Co^{2+}, Cu^{2+}/Zn^{2+}, Cu^{2+}/Fe^{2+} from their binary mixture was also investigated in the batch procedure. The D values of the Cu^{2+} molecularly imprinted polymer developed using EGDMA cross linking agents, methacrylamide monomer, and ACV initiator by the radical polymerisation method show increase for Cu^{2+}, while they decrease significantly for Zn^{2+}, Fe^{2+}, and Co^{2+}, as shown in Table 4. The α_r values for Cu^{2+}/Co^{2+}, Cu^{2+}/Zn^{2+}, Cu^{2+}/Fe^{2+}, are 36.7, 51.8, 86.7, respectively. This means that Cu^{2+} can be determined even

in the presence of Co^{2+}, Zn^{2+}, and Fe^{2+}. In order to further check the selectivity of the method for Co^{2+}, Zn^{2+}, and Fe^{2+}, solutions containing Cu^{2+} and other metal ions were prepared and analysed by the proposed procedure. Studies with $1.0 \, \mu g \, L^{-1}$ of Cu^{2+} showed that the concentration of $25 \, \mu g \, L^{-1} \, Zn^{2+}, Co^{2+}, Fe^{2+}$ did not interfere with Cu^{2+} determination after the MIIP and removal procedure.

T A B L E 3 The physico-chemical characteristics of tannery effluents (before and after filtration processes)

Parameters	Untreated effluents (raw effluents)
Colour units (Pt-Co)	1650 ± 2.35[a]
pH	7.6 ± 0.15
EC (mS cm^{-1})	18.25 ± 0.65
TSS (mg L^{-1})	6200 ± 34.05
TDS (mg L^{-1})	12000 ± 50.19
TS (mg L^{-1})	20500 ± 55.20
DO (mg L^{-1})	0.9 ± 0.07
BOD5 (mg L^{-1})	920 ± 15.20
COD (mg L^{-1})	3900 ± 20.50
SO$_4^{2-}$ (mg L^{-1})	5200 ± 15.02

[a]Standard deviation ($n = 3$).

T A B L E 4 The selectivity parameters of copolymers MIIP for Cu^{2+}

Metal ions	D_i	D_n	α_i	α_n	α_Γ
Co^{2+}	35	150	72	2.60	36.1
Zn^{2+}	26	235	85	1.90	51.5
Fe^{2+}	39	402	78	1.09	86.2

3.12 | Comparison of the applied method with other reported methods

The features of the proposed adsorbent were compared with previously published adsorbents for the removal of heavy metals. The obtained results are summarised in Table 5. According to the results presented in the table, short equilibrium time and high adsorption capacity along with simultaneous removal of several metals are important properties of the synthesised adsorbent compared to other adsorbents.

4 | CONCLUSIONS

In this study, a new molecularly imprinted polymer was developed using EGDMA cross linking agents, methacrylamide monomer, and ACV initiator by the radical polymerisation method. A comparison of various cross linking agents in MIP production showed that the best cross linking agents are EGDMA and gallic acid, but citric acid did not present good results in the production and synthesis of MIP. Synthesised MIP was investigated for the selective extraction of Cu^{2+} ions from aqueous solutions using the batch technique water samples and various parameters such as pH, adsorption time and maximum adsorption capacity were investigated. The optimum value of these parameters were determined as follows: pH = 8.0, time = 10 min and the maximum adsorption capacity of $262.53 \, mg \, g^{-1}$. This adsorption capacity is very high compared to the previously reported absorbers and is used in the most polluted environments as an efficient adsorber. MIP identification was confirmed by three methods including TGA, FTIR and SEM, and the results showed that polymer destruction was not observed after adsorption of the ion in MIP. The adsorption data were processed with different isothermal and kinetic models and was determined that the best isothermal model was

T A B L E 5 Comparison of the proposed method with some of the methods reported in the research study for removal of the metal ions

Metal ion	Adsorbent	q_{max} (mg g^{-1})	Sample's pH	Contact time (min)	Ref.
Cu^{2+}	l-Arginine modifying magnetic chitosan	134.19	5.5	13	[21]
Cu^{2+}	Chitosan–oxalate	227.27	5.0	1440	[22]
Cu^{2+}	Chitosan/sporopollenin microcapsules	84.42	6	240	[19]
Cd^{2+}		86.55			
Cr^{3+}					
Ni^{2+}					
Zn^{2+}					
Cu^{2+}	Chi-MG/Fe$_3$O$_4$	172.4	5.5	40	[18]
Cd^{2+}		175.4			
Pb^{2+}		163.9			
Cu^{2+}	MAm-EGDMA	262.53	8.0	10	Present work

[a]Data not reported.

the Freundlich model and the best kinetic model was the pseudo-second-order model. According to the results, this adsorbent has a very high speed and reusability. When compared to effective composites, it is cheap and accessible.

CONFLICT OF INTEREST
None.

PERMISSION TO REPRODUCE MATERIALS FROM OTHER SOURCES
None.

DATA AVAILABILITY STATEMENT
Data openly available in a public repository that issues data sets with DOIs.

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REFERENCES
1. Wulff, G., et al.: An enzyme-analogue built polymers, on the synthesis of polymers containing chiral cavities and their use for the resolution of racemates. Macromol. Chem. 178, 2799–2816 (1977)
2. Sellergren, B.: Molecular imprinting by noncovalent interactions tailor-made chiral stationary phases of high selectivity and sample load-capacity. Chirality. 163–168 (1989)
3. Sellergren, B.: Molecularly imprinted polymers: man-made mimics of antibodies and their applications in analytical chemistry. Tech. Instrum. Anal. Chem. 23, 113–184 (2001)
4. Azizinezhad, F.: Kinetic investigation of grafting of poly(ethylene terephthalate) fibers with 2-hydroxypropyl methacrylate using 4,4'-azobis4-(cyanovaleric acid). Asian J. Chem. 23(2), 899–902 (2011)
5. Mosbach, K., Arshady, R.: Synthesis of substrate-selective polymers by host-guest polymerization. Makromol. Chem. 182, 687–692 (1981)
6. Nomura, Y., et al.: Selective recognition of 2, 4-dichlorophenoxyacetic acid using a molecularly imprinted polymer. Anal. Lett. 31, 973–980 (1998)
7. Kempe, M.: Oxytocin receptor mimetics prepared by molecular imprinting. Lett. Pept. Sci. 7, 27–33 (2000)
8. Moghimi, A.: Review of preconcentration and solid phase extraction for the determination of trace Lead. Int. J. Bio-Inorg. Hybr. Nanomater. 5(1), 5–18 (2016)
9. Kim, J.M., Chong, B.O., Ahn, K.D.: Molecular recognition by hydroquinidine-imprinted polymers. Bull. Kor. Chem. So. 19, 143–145 (1998)
10. Dong, H., Tong, A.J., Li, L.D.: Syntheses of steroid based molecularly imprinted polymers and their molecular recognition study with spectrometric detection. Spectrochim. Acta Mol. Biomol. Spectrosc. 59, 279–284 (2003)
11. Shojai, M., Moghimi, A.: Extraction of lead (II) with functionalization of nano graphene oxide with prior to determination by flame atomic absorption spectrometry orient. J. Chem. 31, 85–94 (2015)
12. Andersson, L., Sellergren, B., Mosbach, K.: Imprinting of amino-acid derivatives in macroporous polymers. Tet. Lett. 25, 5211–5214 (1984)
13. Sellergren, B., Ekberg, B., Mosbach, K.: Molecular imprinting of amino-acid derivatives in macroporous polymers-demonstration of substrate selectivity and enation-selectivity by chromatographic resolution of racemic mixtures of amino-acid derivatives. J. Chromatogram. 15, 754–761 (1985)
14. Ramström, O., Andersson, L.I., Mosbach, K: Recognition sites incorporating both pyridinyl and carboxy functionalities prepared by molecular imprinting. J. Org. Chem. 58, 7562–7564 (1993)
15. Ramström, O., Ye. L., Gustavsson. P.E.: Chiral recognition by molecularly imprinted polymers in aqueous media. Chromatographic. 48, 197–202 (1998)
16. Moghimi, A., Yari, M.: Review of procedures involving separation and solid phase extraction for the determination of cadmium using spectrometric techniques. J. Chemical Reviews. 1, 1–18 (2019)
17. Salehi, N., Moghimi, A., Shahbazi, H.: Preparation of cross-linked magnetic chitosan with methionine-glutaraldehyde for removal of heavy metals from aqueous solutions. Int. J. Environ. Anal. Chem. 1753718 (2020). https://doi.org/10.1080/03067319.2020
18. Salehi, N., Moghimi, A., Shahbazi, H.R.: Magnetic nanobiosorbent (MG-Chi/Fe$_3$O$_4$) for dispersive solid-phase extraction of Cu(II), Pb(II), and Cd(II) followed by flame atomic absorption spectrometry determination. IET Nanobiotechnol. (2021). https://doi.org/10.1049/nbt2.12025
19. Sargına, I., Arslan, G.: Chitosan/sporopollenin microcapsules: preparation, characterisation and application in heavy metal removal. Int. J. Bio. Macromol. 75, 230 (2015)
20. Germiniano, T.O., et al.: Synthesis of novel copper ion-selective material based on hierarchically imprinted cross-linked poly(acrylamide-co-ethylene glycol dimethacrylate). React. Funct. Polym. 82, 72-80 (2014)
21. Wu, Z., et al.: Removal of Cu(II) ions from aqueous water by l-arginine modifying magnetic chitosan. Colloid. Surface. Physicochem. Eng. Aspect. 499, 141 (2016)
22. Mi, F.L., Wu, S. J., Lin, F.M.: Adsorption of copper(II) ions by a chitosan–oxalate complex biosorbent. Int. J. Bio. Macromol. 72, 136 (2015)