



## Synthesis of Metal Ion Imprinted Microspheres and Investigation of Their Detection Performance Against Some Metal Ions by ICP-OES

### Metal Baskılanmış Mikrokürelerin Sentezi ve Bu Mikrokürelerin ICP-OES ile Bazı Metallerle Karşı Tayin Performansının İncelenmesi

Sibel Çolak<sup>1</sup>, Derya Kılıçaslan<sup>2,3</sup>, Muharrem Karabörk<sup>1</sup>

<sup>1</sup> Department of Chemistry, Kahramanmaraş Sutcu Imam University, Kahramanmaraş, Turkey

<sup>2</sup> Afsin Vocational School, Department of Chemistry and Chemical Processing Technologies, Kahramanmaraş Sutcu Imam University, Kahramanmaraş, Turkey

<sup>3</sup> Research and Development Centre for University-Industry-Public Relations, Kahramanmaraş Sütçü İmam University, Kahramanmaraş, Turkey.

#### ABSTRACT

In this study, ion-imprinted polymers were prepared. These polymers can be used for the selective removal of Cu(II) ions from aqueous solutions. To this end, (E)-2-hydroxy-5-((vinylphenyl)diazonyl) benzaldehyde was used as a functional monomer in the synthesis stage of the polymeric adsorbent. Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres have been synthesized by dispersion polymerization technique through the interaction of the template molecule Cu(II) ion with the functional monomer. The specific surface area of Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres was 374.26 m<sup>2</sup>/g. The swelling rate was 80%. The maximum adsorption capacity, the optimum pH, and the adsorption equilibrium time were determined to be 153.03 mg/g, in the range of 8-10, and 30 min, respectively. According to the elemental analysis results, before imprinting; C%: 55.72, H%: 6.756, N%: 0.555 were found to be C%: 58.81, H%: 6.998, N%: 0.570 after imprinting. The increase in the percentages of C, H and N showed that the remaining molecule moved away from the structure. The relative selectivity coefficients of the imprinted microspheres were found to be 13.09, 57.88, 44.72, and 35.01 for the ion pairs as Cu(II)/Ni(II), Cu(II)/Pb(II), Cu(II)/Zn(II) and Cu(II)/Co(II), respectively. These results showed that the Cu(II)-imprinted microspheres were more selective with respect to Cu(II) ions. Reproducibility studies showed that Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres can be used repeatedly without a significant decrease in adsorption capacity.

#### Key Words

Ion imprinted polymer, Microsphere, Solid-phase extraction, Cu(II) ion, ICP-OES.

#### Öz

Bu çalışmada, sulu çözümlerden Cu(II) iyonlarının seçici olarak uzaklaştırılması için kullanılacak iyon baskılanmış polimerler hazırlanmıştır. Bu amaçla, polimerik adsorbentin sentez aşamasında fonksiyonel monomer olarak (E)-2-hidroksi-5-((vinilfenil)diazonyl) benzaldehit kullanılmıştır. Kalıp molekül Cu(II) iyonu ile fonksiyonel monomer etkileştirilerek dispersiyon polimerizasyon tekniği ile Cu(II) baskılanmış poli[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] mikroküreleri sentezlenmiştir. Cu(II) baskılanmış poli[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] mikrokürelerinin spesifik yüzey alanı 374,26 m<sup>2</sup>/g ve şişme oranı %80 olarak bulunmuştur. Maksimum adsorpsiyon kapasitesi, optimum pH ve adsorpsiyon denge zamanı sırasıyla 153,03 mg/g, 8-10 aralığı ve 30 dakika olarak tespit edilmiştir. Elementel analiz sonuçlarına göre baskılama öncesi; C%: 55.72, H%:6.756, N%:0.555 baskılama sonrası C%:58.81, H%:6.998, N%:0.570 olarak bulunmuştur. C, H ve N yüzdelerindeki artış yapıdan kalıp molekülün uzaklaştığını göstermiştir. Baskılanmış mikrokürelerin bağlı seçicilik katsayıları Cu(II)/Ni(II), Cu(II)/Pb(II), Cu(II)/Zn(II) ve Cu(II)/Co(II) için sırasıyla 13,09, 57,88, 44,72 ve 35,01 olarak bulunmuştur. Bu sonuçlar; Cu(II) baskılanmış mikrokürelerin Cu(II) iyonlarına karşı daha seçici olduğunu göstermiştir. Yapılan tekrarlanabilirlik çalışmaları Cu(II) baskılanmış poli[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] mikrokürelerin adsorpsiyon kapasitesinde önemli bir azalma olmaksızın tekrar tekrar kullanılabilir olduğunu göstermiştir.

#### Anahtar Kelimeler

İyon baskılanmış polimer, Mikroküre, Katı-faz ekstraksiyonu, Cu(II) iyon, ICP-OES.

**Article History:** Received: Sep 13, 2023; Revised: Nov 2, 2023; Accepted: Nov 20, 2023; Available Online: Jan 1, 2024.

**DOI:** <https://doi.org/10.15671/hjbc.1359536>

**Correspondence to:** M. Karabörk, Department of Chemistry, Kahramanmaraş Sutcu Imam University, Kahramanmaraş Turkey.

**E-Mail:** mkarabork@ksu.edu.tr

## INTRODUCTION

The environment is heavily polluted by inorganic ions, organic pollutants, organometallic compounds, radioactive isotopes, gaseous pollutants, and nanoparticles [1]. With the rapid growth of urbanisation, the use of heavy metal ions (such as copper (II), lead (II), silver (I), cadmium (II), arsenic (III), nickel (II) and mercury (II)) is increasing. Wastes from mining, mechanical engineering and chemical engineering processes cause serious water pollution worldwide. Contamination of surface and groundwater with heavy metal elements has become an important global problem both in terms of the environment and human health [2-7]. Unlike organic pollutants, heavy metals are not biodegradable and have a tendency to accumulate in living organisms. Many heavy metal ions are hazardous or carcinogenic [8]. Many of the heavy metals, such as cadmium, copper, and zinc, are associated with pollution and hazard concerns, especially when they are in solution. One of the properties of heavy metals is covalent bonding with organic groups. As a result, they form lipophilic ions and compounds and can have toxic effects when they are bound to non-metallic elements of the cellular macromolecules. The accumulation of heavy metals like cadmium and copper in humans can lead to cancer, neurological damage, liver and kidney failure, and death [9]. Some heavy metals, such as Cd, Pb, and Cr, have no known biological purpose, while others, such as Cu, Zn, and Mn, are required in small amounts for normal plant growth and development, but are seriously toxic to plants and animals at slightly higher concentrations than required [10]. Heavy metal toxicity is still a hot topic in science and further research is needed to better identify the effects of the mechanism of damage and to better understand how to control it to reduce medical problems. [11].

In the last few years, copper research has been tested for both toxicological and human health effects and copper has been evaluated as an environmental pollutant [12]. In small amounts, copper is essential for physiological processes. However, copper in excess of recommended doses can pose a threat to human health [12,13]. The 2002 Dietary Reference Intake for copper in adults aged 19 and over is 0.9 mg per day [14]. The estimated minimum requirement for Cu was set by The World Health Organisation (1996) at 0.6 mg/day for women and 0.7 mg/day for men [15]. Therefore, it has become necessary to develop new methods for the measurement of trace metals.

There are currently three main methods for treating heavy metal ions in wastewater: ion exchange, membrane separation and adsorption. [16-18]. Although ion exchange can significantly reduce solid waste reprocessing by performing reversible exchange reactions, its use is limited and prone to secondary pollution [19,20]. In membrane separation technology, selective permeability of membranes is used to block heavy metal ions and ensure adsorption. This method has problems such as membrane contamination and clogging [21]. Therefore, it is important to use new techniques to remove pollutants efficiently and selectively.

Molecular imprinting is the process of creating ligand-selective recognition sites in polymers by incorporating a template, which enables the formation of recognition sites during the covalent association of the bulk phase via a polymerisation or polycondensation process. [22]. Imprinted polymer technology is based on the development of highly stable synthetic polymers called molecularly imprinted polymers (MIPs) [23]. Molecular imprinting technique is widely used in the separation and purification of chemical and biological molecules of different dimensions [24-28]. MIPs are functional porous materials that offer analyte-based targeting via high-affinity binding sites that can be customized based on their size, shape, and function [29-31]. MIPs possess a high potential and practicality in wastewater treatment applications due to their special recognitions and affinity for cavities [3]. Compared to common adsorption materials, MIPs have many promising properties such as low cost, high stability against harsh chemical and physical conditions and excellent reusability [32]. As a result, ion imprinting technique has found its place in different application areas such as solid phase extraction (SPE) [33-35], sensors [36] and membrane separation of imprinted metal ions [37].

In this study, we aimed to develop a simple, fast and sensitive method for the selective determination and removal of copper ions from aqueous media by solid phase extraction method, considering that high molecular recognition properties can be obtained by using printed polymers. As a result, after the structures of the imprinted polymers were confirmed, adsorption-desorption, reproducibility, adsorption isotherms, selectivity in the presence of other ions and solid phase enrichment studies of Cu(II) ion in aqueous solution were carried out.

## MATERIALS and METHODS

### Materials

Azobisisobutyronitrile (AIBN) and ethylene glycol dimethacrylate (EGDMA) were purchased from Fluka AG (Buchs, Switzerland). Polyvinyl alcohol (PVA, MW:10,000) was obtained from Aldrich (Milwaukee, WI, USA). The other chemicals used were obtained from Merck (Darmstadt, Germany) with high purity, and Cu(II) 1000 mg/L stock solution used in the experiments was prepared using copper(II) chloride dihydrate. Copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) was obtained from Merck, Darmstadt, Germany. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Perkin Elmer brand Optima 2100 DV model ICP-OES) was used to determine the concentrations of Cu(II) ion and other ions in the aqueous phase. Wavelengths studied in ICP-OES measurements: Cu: 327.393, Ni: 231.604, Zn: 206.200, Pb: 220.353 nm. Surface morphology and cross-sectional structures were investigated using Zeiss EVO LS10 Scanning Electron Microscope (SEM). IR characterization of the synthesized materials was performed using a Perkin Elmer Spectrum 400FT-IR/FR-FIR spectrometer. The structure analysis of the synthesized ligand was carried out using Varian 400 (100) MHz  $^1\text{H}$  ( $^{13}\text{C}$ )-NMR spectrometer. The amounts of C%, H%, and N% were determined to check whether the copper ions in the structure of the synthesized substances were removed. This was done using Elemental Analysis (CHNS-932 (LECO), Sweden). Specific surface area measurements were made using the Nova 2200e, Surface Area

and Pore Size Analyzer (BET) device.

### Method

#### Synthesis of ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde ligand

4-Vinylaniline (0.01 mol) was taken, concentrated HCl (0.03 mol) and 5 mL of distilled water were added and stirred until completely dissolved. The temperature of this solution was then lowered below  $5^\circ\text{C}$  with the help of an ice bath. The solution of sodium nitrite (95% pure, 0.01 mol) in 1 mL of distilled water was added dropwise and the reaction was continued for 30 minutes (Figure 1) [38].

After diazotization of 4-vinylaniline, salicyl aldehyde was made basic with 10% NaOH solution for chelating. Then the synthesized diazonium salt was added dropwise onto salicyl aldehyde and mixed. During the addition step, pH was kept constant in the range of 9-10 with 10% NaOH solution. The resulting precipitate was filtered and dilute  $\text{CH}_3\text{COOH}$  solution was added to the filtrate. The synthesized product was dissolved in pure water and recrystallized with acetic acid. The resulting diazo compound is ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde. This synthesis reaction is given in Figure 2 [38].

#### Synthesis of $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)_2]$ complex monomer

In order to synthesize the Cu(II) complex monomer, ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde was dissolved in 0.025 mmol ethyl alcohol. To this solution,

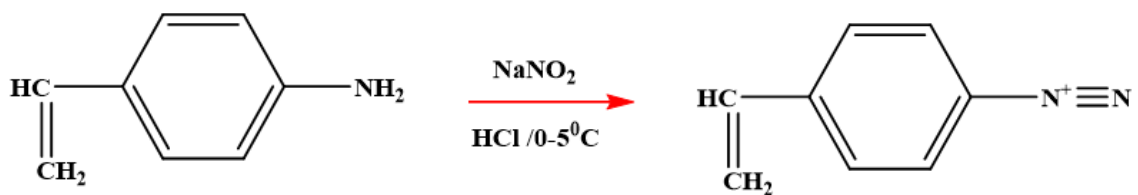


Figure 1. A schematic representation of diazotization reaction.

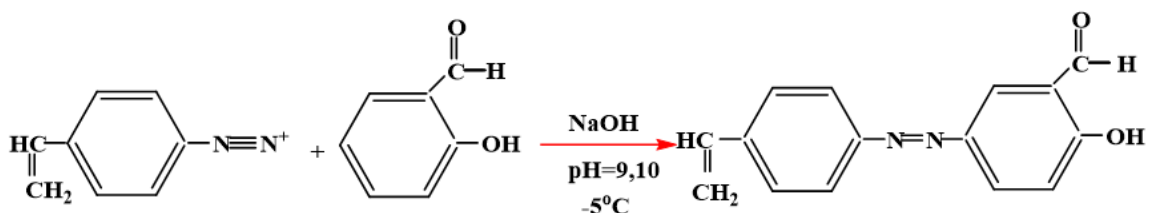


Figure 2. A schematic diagram for ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde synthesis.

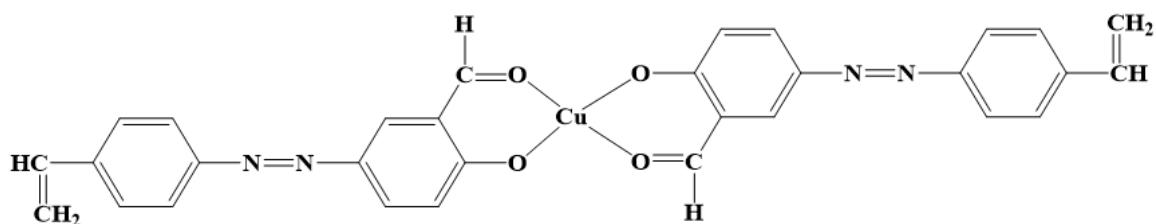


Figure 3.  $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)_2]$  complex monomer.

copper (II) chloride dihydrate, 0.0125 mmol was dissolved and added. It was stirred with a magnetic stirrer for 2 hours, filtered with blue banded filter paper, and left to dry in a vacuum oven. This synthesis reaction is given in Figure 3 [39].

### Synthesis of Cu(II) imprinted poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$ microspheres

For the synthesis of Cu(II) imprinted microspheres; 0.1 g of polyvinylalcohol (PVA) was dissolved in 30 mL of ultrapure water to provide a dispersion medium. To this solution 8 mL/12 mL of EGDMA/Toluene mixture, EGDMA- $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)_2]$  monomer complex dissolved in 25 mL of ethyl alcohol, and 0.06 g 2,2-Azobisisobutyronitrile as initiator were added. The polymerization process was started at 60°C for 6 hours, and completed

at 80°C for 24 hours. The resulting microspheres were washed continuously with ethanol, ethanol/water, and ultrapure water to remove unreacted monomers and other wastes. Removal of imprinted Cu(II) ions from microspheres was carried out using a 4M  $\text{HNO}_3$  solution. The Cu(II) ion-imprinted microspheres were then filtered and washed with ultrapure water, and allowed to dry at room temperature. Non-imprinted polymers (NIP) were synthesized by the same method without the use of Cu(II) ions [40]. The synthesis reaction of Cu(II) imprinted poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$  microspheres is given in Figure 4.

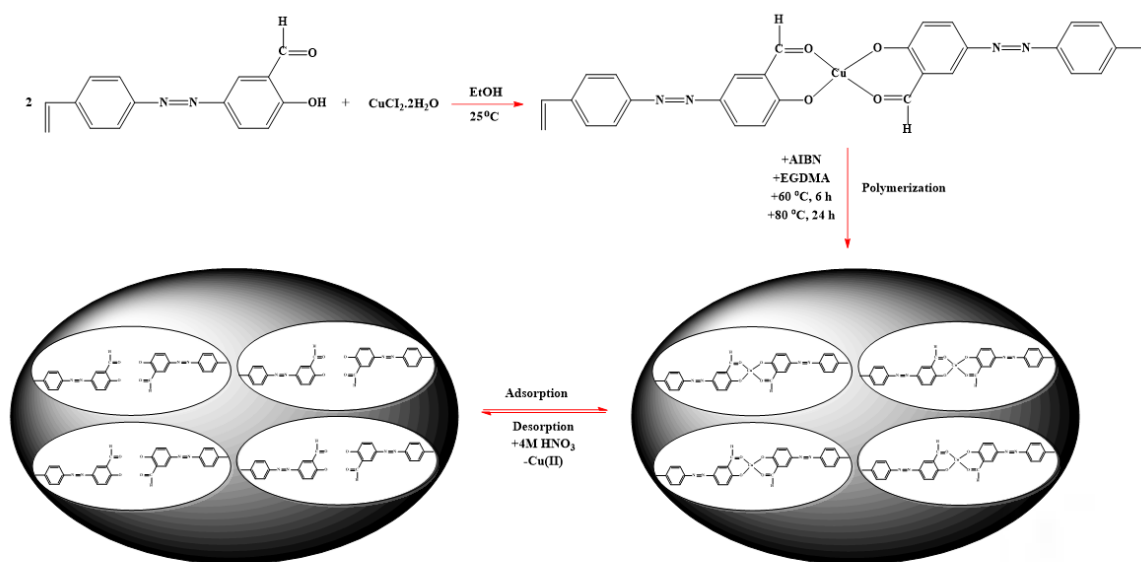


Figure 4. Synthesis reaction of Cu(II) imprinted poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$  microspheres.

## RESULTS and DISCUSSION

### Characterization of ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde Monomer

The characteristic peaks of FT-IR analyses used for the characterization of ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde monomer are as follows: FT-IR (KBr,  $\text{cm}^{-1}$ ): 1661.97  $\text{cm}^{-1}$  (aldehyde carbonyl band), 1617.08  $\text{cm}^{-1}$  (C=C band in the vinyl group), around 3300  $\text{cm}^{-1}$  (O-H band), 3049.25  $\text{cm}^{-1}$  (C-H band in aromatic ring), 1150.88  $\text{cm}^{-1}$  (C-OH band), 1596.10  $\text{cm}^{-1}$  (C=C band in aromatic ring), around 1385  $\text{cm}^{-1}$  (N=N band), around 1410  $\text{cm}^{-1}$  (C-N band).  $^1\text{H-NMR}$  was used to determine the chemical structure of ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde monomer as well. The  $^1\text{H-NMR}$  spectrum of the functional monomer is given in Figure 5. The characteristic peaks in this spectrum are as follows: The peak at 5.29 ppm is vinyl group ( $\text{CH}_2=\text{CH}-$ ), the peak at 10.74 ppm is hydroxyl group (-OH), the peak at 9.02 ppm is aldehyde group (-CHO), the peaks between 7.40-7.70 ppm are disubstituted benzene ring, the peak at 7.00 ppm is trisubstituted benzene ring.

### Characterization of $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)_2]$ Complex Monomer

The characteristic bands of FT-IR analyses used for the characterization of Cu(II) complex monomer are as follows: FT-IR (KBr,  $\text{cm}^{-1}$ ): 1597.24  $\text{cm}^{-1}$  (C=C band in aromatic ring), 2925.54  $\text{cm}^{-1}$  (C-H band in aromatic ring), 1172.00  $\text{cm}^{-1}$  (C-OH peak), 1383.97  $\text{cm}^{-1}$  (N=N band), around 1410  $\text{cm}^{-1}$  (C-N band), around 511  $\text{cm}^{-1}$  (Cu-O band). Here, the band at 511  $\text{cm}^{-1}$  indicated that the ligand and metal interacted.

### Characterization of Cu(II) Imprinted Microspheres

FT-IR spectra of synthesized Cu(II) imprinted poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$  microspheres before and after imprinting are given in Figure 6. As can be seen from the figure, the Cu-O peak at 511  $\text{cm}^{-1}$  was not observed after imprinting. These results showed that the Cu(II) ion was removed from the polymeric structure. The amount of carbon, hydrogen, and nitrogen in the structure of the synthesized Cu(II) imprinted microspheres before and after imprinting was determined using the elemental analysis method. According to the elemental analysis results obtained; C% before imprinting: 55.72, H%: 6.756, N%: 0.555 whereas C%: 58.81, H%: 6.998, N%: 0.570 after imprinting (Table 1). These results showed that an increase in the C, H, and N percentages occurred with the

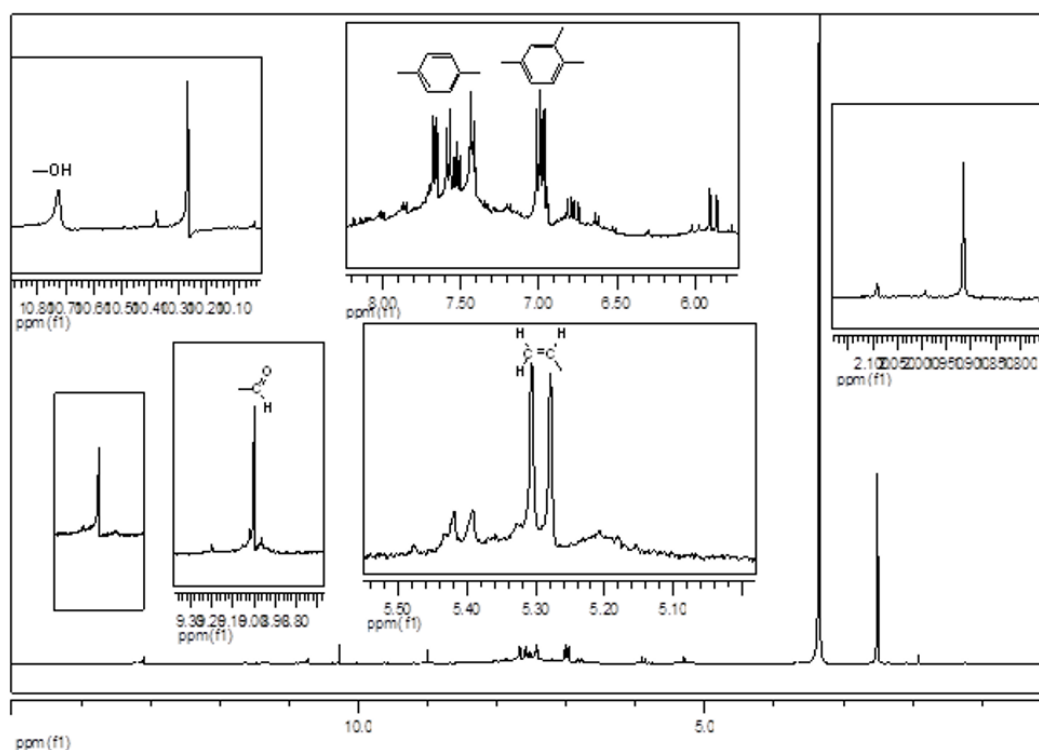
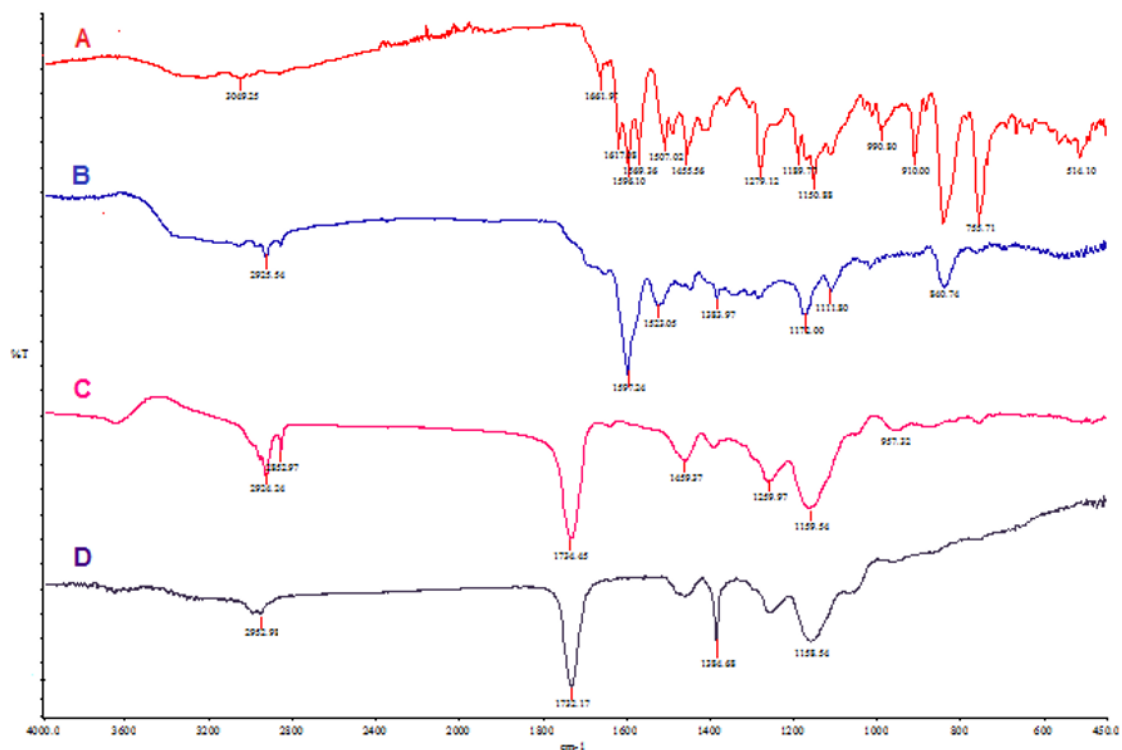


Figure 5. Results of  $^1\text{H-NMR}$  analysis of ((E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde monomer.



**Figure 6.** FT-IR spectra of (A) functional monomer, (B)  $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$  complex monomer (C) non-imprinted and (D)  $\text{Cu}(\text{II})$  ion-imprinted poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$  microspheres.

**Table 1.** Elemental analysis results of  $\text{Cu}(\text{II})$  imprinted poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$  microspheres.

poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$ microsphere	% C	% H	% N
Non-Imprinted	55.72	6.756	0.555
Imprinted	58.81	6.998	0.570

removal of the imprinted metal ion from the polymer, i.e. selective regions specific to the imprinted metal ion were formed in the structure.

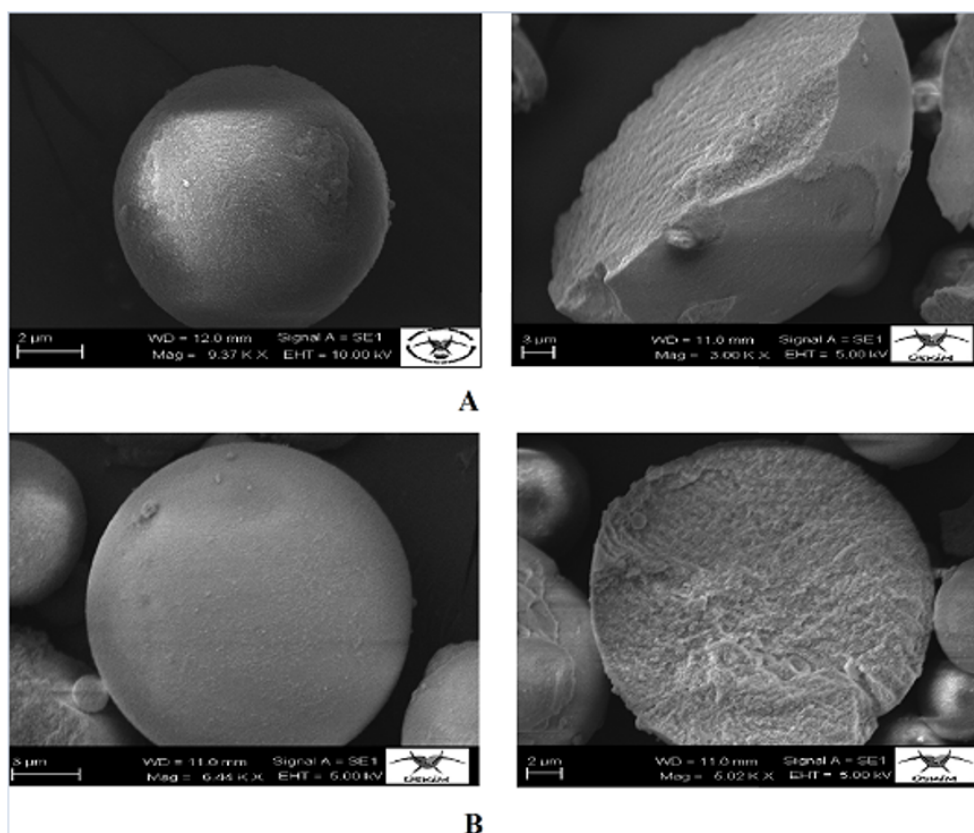
### Scanning electron microscopy (SEM)

The surface morphology and cross-sectional structures of the prepared  $\text{Cu}(\text{II})$  imprinted poly $[\text{Cu}(\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2)]$  microspheres were investigated using scanning electron microscopy (SEM). As seen in Figure 7, the polymeric structures obtained using the dispersion polymerization technique have a spherical form and uniform structure. In order to examine the interior of the polymeric structure before and after imprinting, the microspheres were broken and imaged. A comparison of Figure 7a and Figure 7b shows that  $\text{Cu}(\text{II})$  ion-imprinted polymers are more porous than non-imprinted polymers. This is an indication that the  $\text{Cu}(\text{II})$  ion moves away from the

polymeric structure and imprinted ion-specific selective sites are formed. This structure was also confirmed by BET analysis due to the increase in surface area. The fact that the microsphere surface does not have a smooth structure is a factor that increases the surface area. The microporous nature of the polymeric structure causes it to have a high internal surface area and this makes mass transfer relatively easy.

### Surface area measurements

The specific surface area of  $\text{Cu}(\text{II})$  imprinted microspheres before and after imprinting was determined by the Brunauer-Emmett-Teller (BET) analysis method. The specific surface areas of the obtained microspheres were  $309.49 \text{ m}^2/\text{g}$  and  $374.26 \text{ m}^2/\text{g}$  before and after removal of imprinted  $\text{Cu}(\text{II})$  ions, respectively. These re-



**Figure 7.** SEM images of A) non-imprinted and B) Cu(II) imprinted microspheres.

sults showed that an increase in the surface area of the imprinted polymer occurred with the removal of the imprinted Cu(II) ion from the polymer.

### Swelling test

The water retention of Cu(II) imprinted microspheres was determined by the volumetric method using deionized water. For this purpose, 100 mg of the imprinted polymer was placed in a thin glass column, the height was marked and filled with deionized water. After this procedure, the height of the swelling microspheres was marked every 30 minutes. After the microspheres stopped rising, the percentage swelling of the microspheres was calculated using Equation 1 below [41].

$$\text{Swelling rate\%} = \left[ \left( \frac{w_s - w_{dry}}{w_{dry}} \right) \times 100 \right] \quad (1)$$

In this equation;  $w_s$ : weight of swollen microspheres,  $w_{dry}$ : weight of dry microspheres.

Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres showed a swelling of 40% before imprinting and 80% after imprinting (Table 2). These results indicate that water ions enter the vacancies formed after the removal of Cu(II) ions from Cu(II) imprinted microspheres. This caused the imprinted microspheres to swell more.

### Adsorption-Desorption and Reproducibility Studies on Synthesized Cu(II) Imprinted Poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] Microspheres

#### The effect of pH on Cu(II) adsorption

25 mg of Cu(II) imprinted microspheres were taken and 25 mL of 25 ppm Cu(II) solution was added. The pH of the medium was changed between 3-10 and stirred for 2 hours. These mixtures were then filtered and the Cu(II) ion concentration in the filtrate was determined by ICP-OES. As can be seen from Figure 8, Cu(II) imprinted microspheres showed low adsorption under acidic conditions and the adsorption capacity increased as the pH of the medium increased. The maximum adsorption value was found as 24.95 mg/g in the pH range of 8-10.

**Table 2.** Swelling ratios of Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres.

Poly[Cu(C <sub>15</sub> H <sub>11</sub> N <sub>2</sub> O <sub>2</sub> )] microsphere	Unit height h <sub>dry</sub>	Unit height h <sub>swollen</sub>	Average swelling rate %
Non-imprinted	10 unit	14 unit	40
Imprinted	10 unit	18 unit	80

In non-imprinted microspheres, no significant plateau value was reached. The maximum adsorption amount was found as 5.49 mg/g.

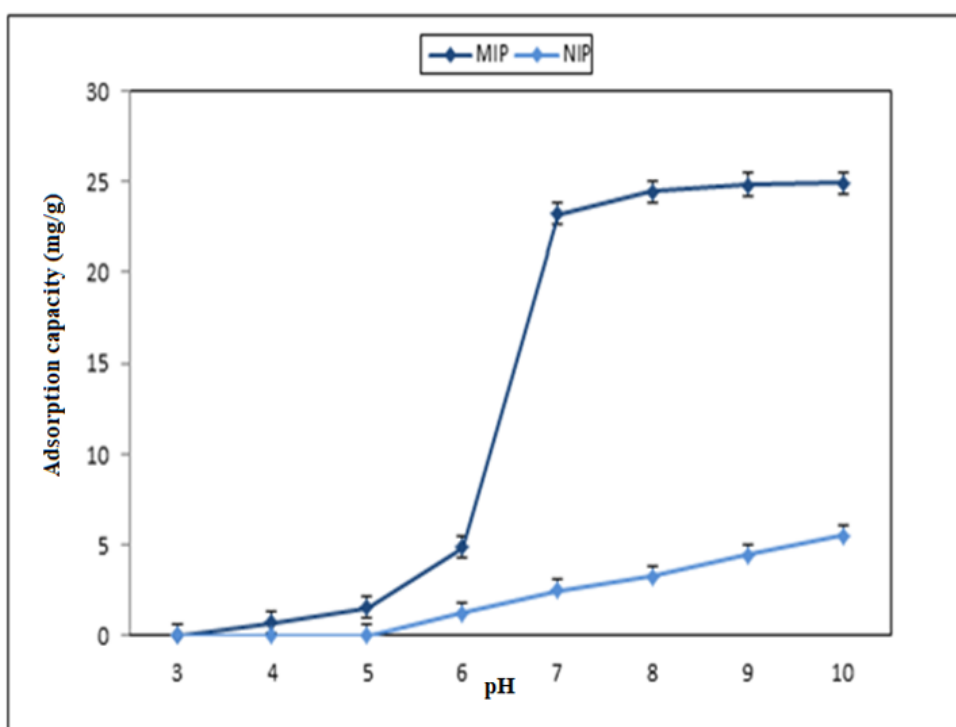
### Adsorption equilibrium time

25 mg of Cu(II) imprinted microspheres were taken and 25 mL of 25 ppm Cu(II) solution was added. The pH of the medium was adjusted in the range of 8-10 and mixed at different times (0-180 minutes). These mixtures were then filtered and the Cu(II) ion concentration in the filtrate was determined by ICP-OES. As shown in Figure 9, the adsorption capacity of the imprinted microspheres increased with time and reached saturation at 30 minutes. The maximum Cu(II) ion adsorption value of imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres was de-

termined as 24.96 mg/g. In the case of NIPs, a plateau value was not obtained and the maximum adsorption amount was found to be 4.26 mg/g.

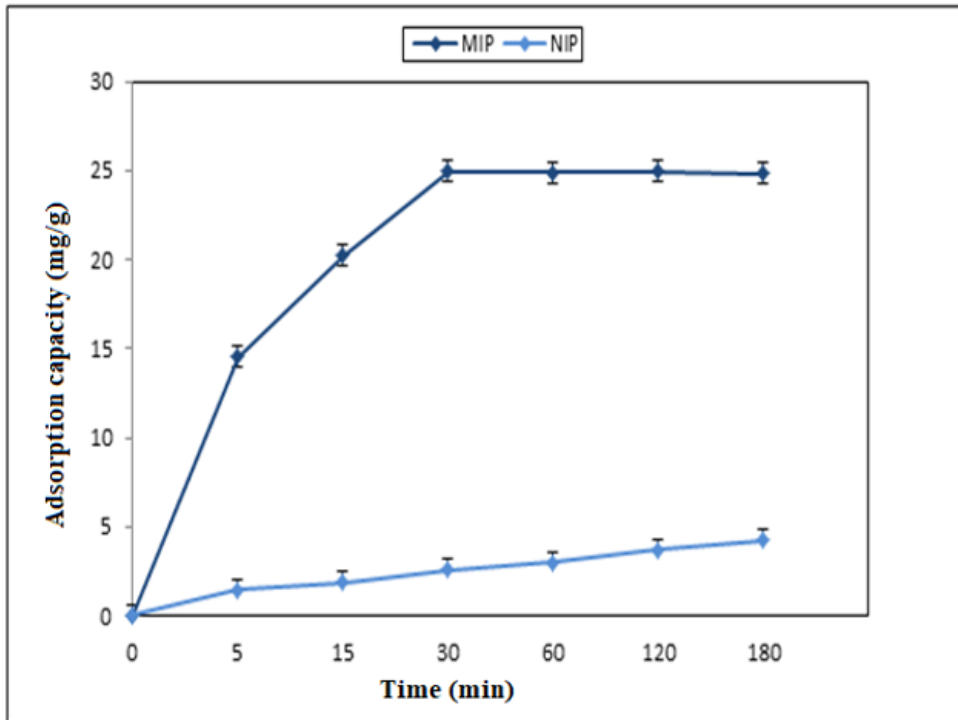
### Effect of Cu(II) initial concentration

25 mg of Cu(II) imprinted microspheres were taken and 25 mL of solutions prepared in the range of 0 -750 ppm were added separately. The pH of the medium was adjusted in the range of 8-10 and mixed in a multiple mixer for 30 minutes. These mixtures were then filtered and the Cu(II) ion concentration in the filtrate was determined by ICP-OES. As the Cu(II) concentration in the solution increased, the adsorption capacity of the imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres increased and reac-

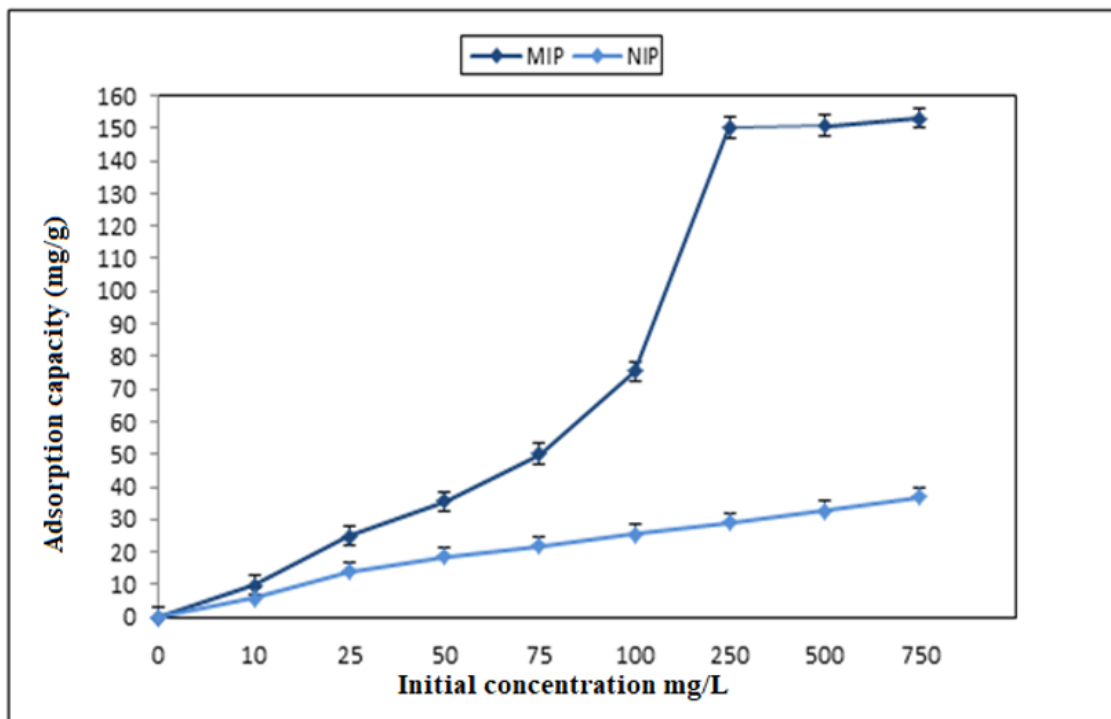


**Figure 8.** Effect of pH on the adsorption of Cu(II) ion: 25.0 mg/g; T: 25°C each point was determined by averaging 3 parallel runs.





**Figure 9.** Effect of time on the adsorption of Cu(II) ion: pH 8-10: 25.0 mg/g; T: 25 °C each point was determined by averaging 3 parallel runs.



**Figure 10.** Effect of initial concentration on the adsorption of Cu(II) ion: pH 8-10: T:25 °C: 30 min, each point was determined by averaging 3 parallel runs.

hed a maximum at 250 mg/L (Figure 10). The maximum adsorption capacity for MIP and NIP microspheres was found to be 153.03 mg/g and 36.99 mg/g, respectively.

### Desorption and reusability of Cu(II) ion-imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres

#### Eluent selection by desorption

A suitable washing solution must be selected so that Cu(II) ion-imprinted microspheres can be used many times after extraction. For this purpose, five different acids including HCl, HNO<sub>3</sub>, CH<sub>3</sub>COOH, HCOOH, and EDTA were compared for the desorption of Cu(II) ions from Cu(II) ion-imprinted microspheres after adsorption. The desorption rate of acids (D) was calculated using Equation 2 [42].

Desorption rate(%) =  $\frac{[\text{Cu(II) ions released into the desorption medium}]}{[\text{Cu(II) ions released into the absorbing medium}]} \times 100$  (2)

As seen in Figure 11, the highest desorption rate was observed when 4 mol/L 100 mL HNO<sub>3</sub> solution was used and was found to be 95.0%. Since the interaction between the metal and the ligand is a covalent interaction, HNO<sub>3</sub>, which is a strong acid, was chosen because it has

a higher desorption rate than other acids.

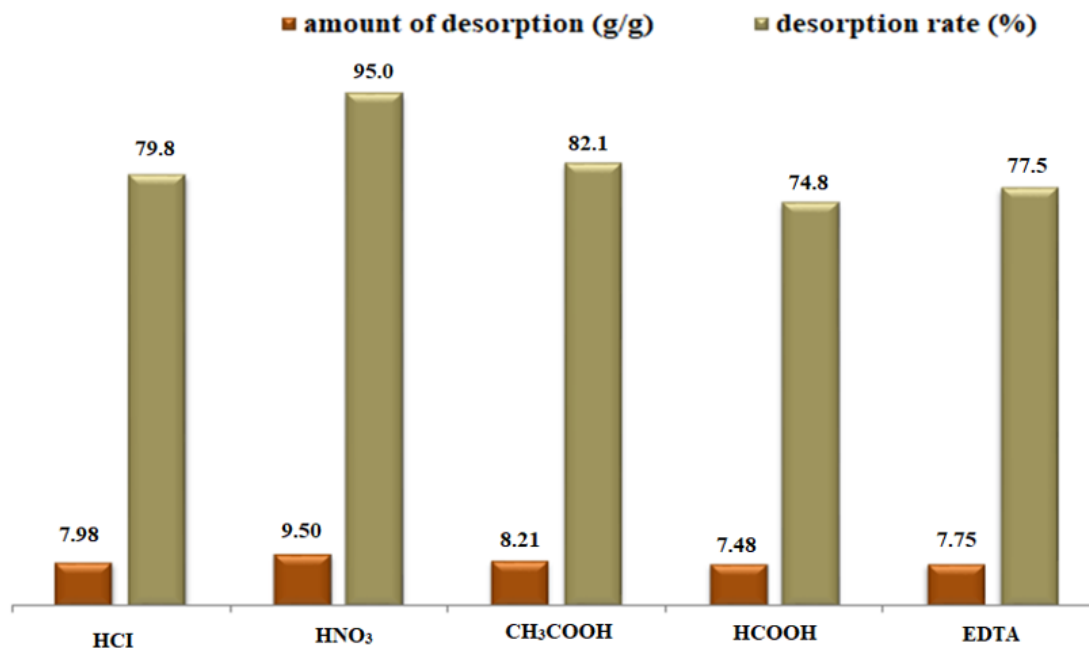
#### Reusability

Desorption of the adsorbed Cu(II) ion was carried out by using 4 M HNO<sub>3</sub> solution at room temperature for 3 hours at 700 rpm with a magnetic stirrer.

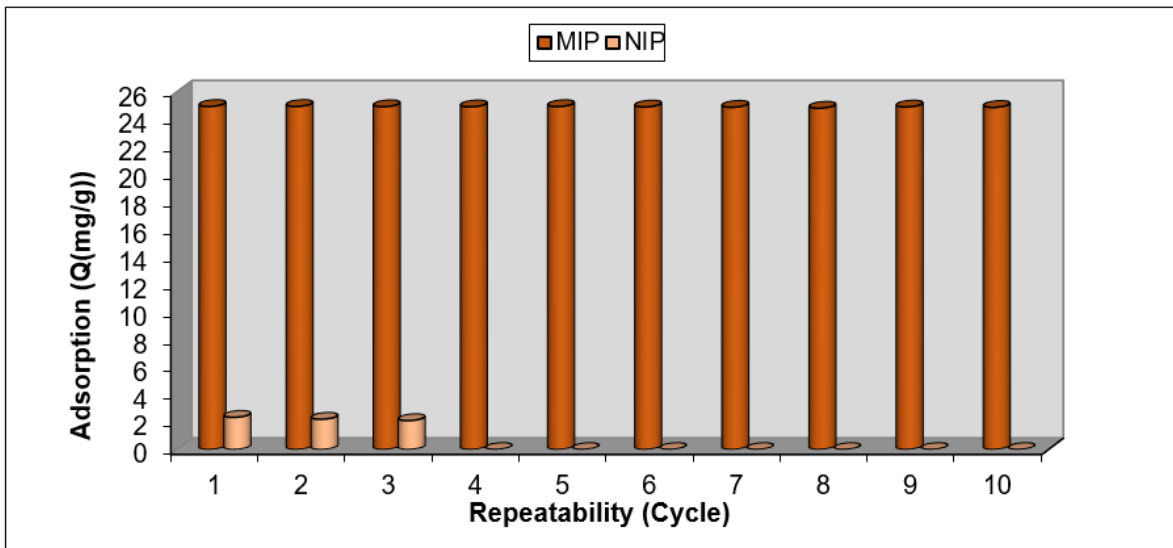
The concentration of Cu(II) ions remaining in the aqueous phase was determined by ICP-OES. The reusability of Cu(II) imprinted and non-imprinted polymers was determined by using the same polymers 10 times for consecutive Cu(II) adsorption-desorption processes. As seen in Figure 12, it was observed that Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres can be used repeatedly without a significant decrease in adsorption capacity.

#### Selectivity studies on Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres

The selectivity of Cu(II) ion-imprinted and non-imprinted microspheres in the presence of different metals (Cu, Ni, Pb, Co, and Zn) was investigated in a batch system. For this purpose, 25 mg of the imprinted microspheres were taken, and 25 mg/L of Cu(II)/Ni(II), Cu(II)/Pb(II), Cu(II)/Co(II) and Cu(II)/Zn(II) solution mixtures were added. Then, the pH was adjusted in the range



**Figure 11.** Desorption rates of Cu(II) ions from Cu(II) ion-imprinted microspheres with different acids (4 mol/L 100 mL acid solutions were used).



**Figure 12.** Reusability of Cu(II) ion-imprinted and non-imprinted microspheres: pH 8-10, concentration: 25.0 mg/L; T: 25 °C. Each point was determined by averaging 3 parallel runs. 4M HNO<sub>3</sub> was used as a desorption agent.

of 8-10 and stirred in a multiple mixer until the equilibrium adsorption time (30 minutes). At the end of the adsorption period, the metal ion concentration in the solution was determined by ICP-OES. The imprinting effect in selectivity was calculated using Equation (3) [42].

$$K_d = \left( \frac{C_i - C_f}{C_f} \right) \times \left( \frac{V}{m} \right) \quad (3)$$

In this equation;  $K_d$  = Dispersion coefficient,  $C_i$  = Initial concentration,  $C_f$  = Final concentration,  $V$  = Volume of the solution used in extraction and  $m$  = Weight of the polymer used in extraction.

The selectivity coefficient for the selective binding of the target ion to the imprinted polymers in different metal species was determined by Equation 4 [42]:

$$k = K_{Metal\ ion\ analyzed} / K_{Mixture\ metal\ ion} \quad (4)$$

In this equation;  $k$  = Selectivity coefficient,  $K_{metal\ ion\ analyzed}$  = Distribution coefficient of the imprinted metal ion,  $K_{Mixture\ metal\ ion}$  = Distribution coefficient of the mixed metal ion

In order to reveal the effect of imprinting on selectivity, the relative selectivity coefficient was found by com-

paring the selectivity coefficient of imprinted polymers and nonimprinted polymers using Equation 5 [42]:

$$k' = k_{imprinted\ polymer} / k_{Non-imprinted\ polymer} \quad (5)$$

Here;  $k'$  = Relative selectivity coefficient,  $k_{imprinted\ polymer}$  = Selectivity coefficient of imprinted polymers,  $k_{Non-imprinted\ polymer}$  = Selectivity coefficient of non-imprinted polymers.

As shown in Table 4, the relative selectivity coefficients of the imprinted microspheres were 13.09, 57.90, 44.72 and 35.01 for Cu(II)/Ni(II), Cu(II)/Pb(II), Cu(II)/Zn(II), and Cu(II)/Co(II), respectively. These results showed that Cu(II) ion was 13.09, 57.88, 44.72, and 35.01 times more selective than Ni(II), Pb(II), Zn(II), and Co(II) ions, respectively, in Cu(II) ion-imprinted microspheres.

## CONCLUSION

In this study, it was aimed to selectively remove copper ions from aqueous media by solid phase extraction method using imprinted polymers. For this purpose, firstly, (E)-2-hydroxy-5-((vinylphenyl)diazonyl)benzaldehyde monomer was synthesized using 4-vinyl aniline, sodium nitrite and salicylaldehyde. The resulting functional monomer was complexed with Cu(II) ion. Then, Cu(II) imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microsp-

**Table 4.** Selectivity study of Cu(II) ion-imprinted poly[Cu(C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>)] microspheres.

Metal ion	Cu(II) Ion-imprinted Microsphere (MIP)		Non-imprinted Microsphere (NIP)		
	Kd	k	Kd	k	k'
Cu(II)	3129.501	-	2094.825	-	-
Ni(II)	433.979	7.211	3802.151	0.551	13.09
Pb(II)	431.516	25.062	9647.359	0.433	57.90
Zn(II)	268.006	27.055	6217.090	0.605	44.72
Co(II)	385.502	12.287	2680.556	0.351	35.01

heres were synthesized by dispersion polymerization technique using this complex monomer. The amount of carbon, hydrogen and nitrogen in the structure of Cu(II) printed microspheres before and after imprinting was determined using the elemental analysis method. The results showed an increase in the percentages of C, H and N after imprinting. This shows that the template molecule moves away from the polymer and selective regions specific to the template molecule are formed in the structure. Specific surface areas for MIP and NIP microspheres were found to be 374.26 m<sup>2</sup>/g and 309.49 m<sup>2</sup>/g, respectively. The swelling rates of microspheres before and after imprinting were found to be 40% and 80%. The maximum adsorption value for MIP and NIP microspheres was found to be 24.95 mg/g and 5.49 mg/g, respectively. The selectivities of Cu(II) imprinted and nonimprinted microspheres against Cu(II), Ni(II), Pb(II), Zn(II) and Co(II) ions were examined in the batch system. The results showed that Cu(II) imprinted microspheres were 13.09, 57.88, 44.719 and 35.006 times more selective for Cu(II) ions over Ni(II), Pb(II), Zn(II) and Co(II) ions, respectively.

As a result; the large surface area and high porosity of Cu(II) imprinted microspheres allow Cu(II) ions to be more easily localized to the active sites. The ion imprinting method increases the adsorption capacity and rate of Cu(II) ion-imprinted microspheres. This advantage shows that ion imprinting is a useful solid-phase extraction technique that can also be used for the removal and selective preconcentration of Cu(II) ions.

This study showed that further development of MIPs could lead to the formation of promising adsorbents for the removal of copper(II) ions from water. The use of MIPs in the removal of not only copper but also other

inorganic contaminants is considered a very important issue with great potential for future applications in water treatment. The main advantage of these materials is that they are very selective towards the contaminant of interest. This improved selectivity is then attributed to the incorporation of specific templates that can almost completely adsorb the contaminant of interest. Therefore, the main problem in adsorption processes is the competition for adsorption sites by other water components such as phosphates, nitrates, carbonates and sulphates, which can be avoided by the use of MIP-type adsorbents.

**Acknowledgments** - This study was financially supported in the scope of the research project coded "2013/6-4YLS" by Kahramanmaraş Sutcu Imam University Scientific Research Projects Unit (KSÜ BAP). We would like to thank Dr. Mukerrem Kurtoğlu for his contributions in the synthesis phase.

---

## References

---

1. C.H. Walker, R.M. Sibly, S.P. Hopkin, D. B. Peakall, Principles of Ecotoxicology; Group, T. And F., Ed.; 4th Edition, CRC Press, 2012.
2. D. Türkmen, M. Bakhshpour, S. Akgönüllü, S. Aşır, & A. Denizli, Heavy metal ions removal from wastewater using cryogels: A review. *Frontiers in Sustainability*. 3 (2022) 765592.
3. H. Wu, G. Lin, C. Liu, S. Chu, C. Mo, & X. Liu, Progress and challenges in molecularly imprinted polymers for adsorption of heavy metal ions from wastewater. *Trends in Environmental Analytical Chemistry*. 36 (2022) e00178.
4. S. Nam, & P.G. Tratnyek, Reduction of azo dyes with zero-valent iron. *Water Research*. 34 (2000) 1837-1845.
5. A.R. Bagheri, N. Aramesh, A.A. Khan, I. Gul, S. Ghotekar, & M. Bilal, Molecularly imprinted polymers-based adsorption and photocatalytic approaches for mitigation of environmentally-hazardous pollutants— A review. *Journal of Environmental Chemical Engineering*. 9 (2021) 104879.
6. L. Duan, Y. Zhang, M. He, R. Deng, H. Yi, Q. Wei, & A. Uddin, Burn-in degradation mechanism identified for small molecular acceptor-based high-efficiency nonfullerene organic solar cells. *ACS applied materials & interfaces*. 12 (2020) 27433-27442.
7. Y. Gao, N. Yan, C. Jiang, C. Xu, S. Yu, P. Liang, & X. Huang, Filtration-enhanced highly efficient photocatalytic degradation with a novel electrospun rGO@TiO<sub>2</sub> nanofibrous membrane: Implication for improving photocatalytic efficiency. *Applied Catalysis B: Environmental*. 268 (2020) 118737.
8. F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management*. 92 (2011) 407-418.
9. P. Häyrynen, J. Landaburu-Aguirre, E. Pongrácz, R.L. Keiski, Study of permeate flux in micellar-enhanced ultrafiltration on a semi-pilot scale: Simultaneous removal of heavy metals from phosphorous rich real wastewaters. *Separation and Purification Technology*. 93 (2012) 59-66.
10. M. Adrees, S. Ali, M. Rizwan, M. Zia-Ur-Rehman, M. Ibrahim, F. Abbas, M. Farid, M. F. Qayyum, M. K. Irshad, Mechanisms of silicon-mediated alleviation of heavy metal toxicity in plants: A review. *Ecotoxicology and Environmental Safety*, 119 (2015) 186-197.
11. M. Singh, J. Kumar, S. Singh, V.P. Singh, S.M. Prasad, M. Singh, Adaptation strategies of plants against heavy metal toxicity: A short review. *Biochemistry and Pharmacology (Los Angeles)*. 4 (2015) 501-2167.
12. C. K. Yap, M. Saleem, W. S. Tan, W. M. Syazwan, N. Azrizal-Wahid, R. Nulit, L. S. Wong, Ecological–Health Risk Assessments of Copper in the Sediments: A Review and Synthesis. *Pollutants*, 2 (2022) 269-288.
13. R. N. Khalef, A. I. Hassan, H. M. Saleh, Heavy Metal's Environmental Impact. (2022).
14. Food and Nutrition Board, Institute of Medicine, 2002. Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iron, Iodine, Manganese,
15. L.M. Gaetke, & C.K. Chow, Copper toxicity, oxidative stress, and antioxidant nutrients. *Toxicology*. 189 (2003) 147-163.
16. C.F. Carolin, P.S. Kumar, A. Saravanan, G.J. Joshiba, & M. Naushad, Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *Journal of environmental chemical engineering*. 5 (2017) 2782-2799.
17. R. Chakraborty, A. Asthana, A.K. Singh, B. Jain, & A.B.H. Susan, Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*. 102 (2022) 342-379.
18. C. Tang, P. Brodie, Y. Li, N. J. Grishkewich, M. Brunsting, & K.C. Tam, Shape recoverable and mechanically robust cellulose aerogel beads for efficient removal of copper ions. *Chemical Engineering Journal*. 392 (2020) 124821.
19. A.M. Donia, A.A. Atia, & D.H. Mabrouk, Fast kinetic and efficient removal of As (V) from aqueous solution using anion exchange resins. *Journal of hazardous materials*, 191 (2011) 1-7
20. L. Joseph, B.M. Jun, J.R. Flora, C.M. Park, & Y. Yoon, Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere*, 229 (2019) 142-159.
21. J. Landaburu-Aguirre, V. García, E. Pongrácz, & R.L. Keiski, The removal of zinc from synthetic wastewaters by micellar-enhanced ultrafiltration: statistical design of experiments. *Desalination*. 240 (2009) 262-269.
22. A.K. Tolkou, G.Z. Kyzas, & I.A. Katsoyiannis, Arsenic (III) and Arsenic (V) Removal from Water Sources by Molecularly Imprinted Polymers (MIPs): A Mini Review of Recent Developments. *Sustainability*. 14 (2022) 5222.
23. E.Y. Bivián-Castro, A. Zepeda-Navarro, J. L. Guzmán-Mar, M. Flores-Alamo, & B. Mata-Ortega, Ion-imprinted polymer structurally preorganized using a phenanthroline-divinylbenzoate complex with the Cu (II) ion as template and some adsorption results. *Polymers*, 15 (2023) 1186.
24. S.M. Muk Ng, R. Narayanaswamy, Fluorescence sensor using a molecularly imprinted polymer as a recognition receptor for the detection of aluminium ions in aqueous media. *Anal. Bioanal. Chem*. 386 (2006) 1235–1244.
25. H. Su, J. Li, T. Tan, Adsorption mechanism for imprinted ion (Ni<sup>2+</sup>) of the surface molecular imprinting adsorbent (SMIA). *Biochem. Eng. J*. 39 (2008) 503–509.
26. I. Dakova, I. Karadjova, V. Georgieva, G. Georgiev, Ion-imprinted polymethacrylic microbeads as new sorbent for preconcentration and speciation of mercury. *Talanta*. 78 (2009) 523–529.
27. Y. Lu, C.L. Yan, S.Y. Gao, Preparation and recognition of surface molecularly imprinted core–shell microbeads for protein in aqueous solutions. *Appl. Surf. Sci*. 255 (2009) 6061–6066.
28. G. Bayramoglu, M.Y. Arica, Synthesis of Cr(VI)-imprinted poly(4-vinyl pyridine-co-hydroxyethyl methacrylate) particles: Its adsorption propensity to Cr(VI). *J. Hazard. Mater*. 187 (2011) 213-221.
29. S. Akgönüllü, S. Kılıç, C. Esen, & A. Denizli, Molecularly imprinted polymer-based sensors for protein detection. *Polymers*. 15 (2023) 629.
30. K. Haupt, K. Mosbach, Molecularly Imprinted Polymers and Their Use in Biomimetic Sensors. *Chem. Rev*. 100 (2000) 2495–2504.
31. D.A. Spivak, Optimization, Evaluation, and Characterization of Molecularly Imprinted Polymers. *Adv. Drug Deliv. Rev*. 57 (2005) 1779–1794.
32. H. Wang, C. Huang, S. Ma, C. Bo, J. Ou, & B. Gong, Recent advances of restricted access molecularly imprinted materials and their applications in food and biological samples analysis. *TrAC Trends in Analytical Chemistry*. (2022) 116526.

33. B. Rezaei, S. Mallakpour, N. Majidi, Solid-phase molecularly imprinted preconcentration and spectrophotometric determination of isoxicam in pharmaceuticals and human serum. *Talanta* 78 (2009) 418e423.
34. S. Ansari, M. Karimi, Recent progress, challenges and trends in trace determination of drug analysis using molecularly imprinted solid-phase microextraction technology, *Talanta* 164 (2017) 612e625.
35. M. Contin, P. Bonelli, S. Lucangioli, A. Cukierman, V. Tripodi, Synthesis and characterization of molecularly imprinted polymer nanoparticles for coenzyme Q10 dispersive micro solid phase extraction, *J. Chromatogr. A* 1456 (2016) 1e9.
36. J.W. Lowdon, H. Diliën, P. Singla, M. Peeters, T.J. Cleij, B. van Grinsven, K. Eersels, MIPs for commercial application in low-cost sensors and assays - an overview of the current status quo, *Sensor. Actuator. B Chem.* 325 (2020) 128973.
37. K. Araki, T. Maruyama, N. Kamiya, M. Goto, Metal ion-selective membrane prepared by surface molecular imprinting. *J. Chromatogr. B*, 818 (2005) 141–145.
38. M. Karabörk, E. Kirveli, H. Kırpık, D. Suluoğlu, M. Köse, Competitive Liquid–Liquid Extraction of Cu (II) Ion from Aqueous Using New Diazo-Compounds. *Water, Air, & Soil Pollution*, 234 (2023) 130.
39. R. Kose, S. A. Gungor, S. E. Kariper, M. Kose, M. Kurtoglu, The new O, O and N, O type ligands and their Cu (II) and Ni (II) complexes: Crystal structure, absorption-emission properties and superoxide dismutase mimetic studies. *Inorganica Chimica Acta*, 462 (2017) 130-141.
40. M. Karabörk, A. Ersöz, E. Birlik, S. A. Y. Rıdvan, Preconcentration of Fe III Using Fe III-Ion Imprinted Polymeric Traps and Its Analytical Performance for FAAS. *Hacettepe Journal of Biology and Chemistry*, 35 (2007) 135-142.
41. M. Karabörk, A. Ersöz, A. Denizli, R. Say, Polymer– clay nanocomposite iron traps based on intersurface ion-imprinting. *Industrial & engineering chemistry research*, 47 (2008) 2258-2264.
42. M. Karabörk, Solid-Phase Extraction Applications Based On Ion Imprinting (Doctoral dissertation, Anadolu University (Turkey)) (2015).