Türkiye Teknoloji ve Uygulamalı Bilimler Dergisi

Turkish Journal of Applied Sciences and Technology

# Walnut Shell Immobilized Methacrylate-Based Polymeric Sorbent for the Extraction of Cu (II) and Cd (II)

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ISSN : 2528-8652
e-ISSN: 2822-2660

**Research Article**

**DOI:**10.70562/tubid.1777794

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**Received:** 04.09.2025
**Accepted:** 01.04.2026
**Published:** 08.04.2026

**Citation**
Teğin, İ., Akdeniz, S. and Canpolat, G. (2026). Walnut Shell Immobilized Methacrylate-Based Polymeric Sorbent for the Extraction of Cu (II) and Cd (II). *Turkish Journal of Applied Sciences and Technology*, 24-37.

**Abstract**
In this study, the potential of cross-linked poly(styrene-co-methacrylic acid) (PSMAA) as a support material for the immobilization of walnut shells was systematically investigated. The resulting immobilized walnut shell sorbent (WNS-PSMAA) was subsequently used for the extraction of Cu (II), and Cd (II) ions from spiked aqueous solutions. The removal efficiency was evaluated by analysing the influence of various experimental parameters such as pH of the solution, concentration of the eluent, flow rate, solution volume, mass of the sorbent, matrix interference and reusability. Under optimized conditions, the method enabled a 60-fold enrichment for Cu (II) and a 10-fold enrichment for Cd (II) with recoveries of 100.00% ± 2.30, and 99.89% ±2.83, respectively, confirmed by triplicate analyzes with a confidence level of 95. Method accuracy was verified by employing the certified reference material for aquatic plants (BCR-670). Consequently, the prepared low-cost adsorbent was successfully used for the determination of the mentioned metals in various real samples such as Van Lake water, Billoris Spa water and tap, salty, wastewater of Siirt (Türkiye).

**Keywords:** Solid phase extraction, heavy metal, polymeric sorbent, walnut shell

## 1. Introduction

Heavy metals that occur naturally in the earth's crust are considered persistent environmental pollutants that can enter the human body through various routes of exposure, e.g., inhalation of particles or ingestion of contaminated food, water, or soil. After bioaccumulation in biological systems, these metals can exert toxic effects on several organ systems (Jomova et al., 2025; Ismail et al., 2024). The increasing toxicity of these pollutants gives rise to great concern about their effects on ecology, the environment, and nutrition. The presence of heavy metals such as arsenic, cadmium, chromium, copper, lead, nickel, and zinc in wastewater is a major concern due to their toxic effects on humans and ecosystems (Lambert et al., 2000). Considering their high toxicity, continuous research on water resources with regard to metal contamination has become essential to ensure human health.

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Various techniques have been used to remove toxic heavy metals from environmental matrices, including electrocoagulation (Mansoorian et al., 2014), electro-floatation (Da Mota et al., 2015) electrodeposition (Wulan and Hariyadi, 2015), chemical precipitation (Benalia et al., 2022), ion exchange (Fu et al., 2022), photocatalysis (Gao and Meng, 2021) and solvent extraction (Merroune et al., 2024). However, these techniques often suffer from limitations such as high operational costs, generation of secondary waste, and the need for specialized equipment (Nnaji et al., 2023).

Given these limitations, adsorption has emerged as a more favorable alternative due to its low cost, ease of use, high efficiency, and environmental friendliness (Zheng et al., 2021; Ismail et al., 2024). A wide range of materials have been explored for this purpose, including activated carbon (AC) (Tu et al., 2020), clays (Buldağ and Yavuz, 2023), zero-valent iron (ZVI) (Li et al., 2017), graphene-based materials (Xu and Wang, 2017; Rout et al., 2023), carbon nanotubes (CNTs) (Xu and Wang, 2017; Krishna et al., 2023), and metal–organic frameworks (MOFs) (Abdollahi et al., 2022; Lin et al., 2023), and bio-sorbents.

Among these, biosorbents have gained considerable attention in recent years due to their natural occurrence, renewability and rich surface chemistry. The efficiency of biosorption is primarily attributed to the presence of various functional groups such as carboxyl, amino, hydroxyl, phosphate and thiol groups on the surface of biosorbents, which facilitate interactions with heavy metal ions. Commonly investigated biosorbents include microorganism-derived biosorbents (Nyika and Dinka, 2023), plant-derived materials, and agricultural waste. Agricultural waste, which is abundant in the biosphere and composed primarily of cellulose and lignin, is particularly attractive due to its low cost, minimal economic value, and high potential for future applications (Paranjape and Sadgir, 2023). As an agricultural waste, walnut shells are one of the largest agricultural wastes in the world and can be a potentially cost-effective biomass for the extraction of heavy metals due to having electron-donating functional groups such as hydroxyl, phenolic, and ketone (Li et al., 2019) on their surface. In addition to their widespread availability, walnut shells possess advantageous physicochemical properties, including high specific surface area, chemical and structural stability, and a lignocellulosic composition rich in cellulose, hemicellulose, and lignin. These characteristics collectively contribute to their high adsorption performance toward a broad range of environmental pollutants (Enache et al., 2023). Given these properties, numerous studies have investigated the potential of walnut shells for the extraction of metal ions, mainly through batch adsorption using modified or activated carbon-based materials derived from walnut shells (Zhang et al., 2024). To further advance these findings, the present study adopts a novel strategy by immobilizing walnut shell biomass within a polymeric matrix. This approach aims to enhance its efficiency in metal ion removal. It offers several advantages, including improved mechanical stability, ease of separation, and compatibility with continuous flow systems, thereby addressing some of the limitations of conventional biosorbents. In accordance with previous research on the immobilization of biosorbents, various supporting materials have been tested, especially for biosorbents derived from microorganisms. These include polysulfone, polyvinyl alcohol, polyacrylamide, polyurethane, silica gel, and carboxymethyl cellulose (Rusu et al., 2021).

In the present study, a cross-linked poly(styrene-co-methacrylic acid) matrix was used as an immobilization medium for the biomass from walnut shells. This copolymer was selected for its chemical stability, functional versatility, and potential to improve the performance of

biosorbents (Hayasi and Karimi, 2017). To our knowledge, the application of walnut shells immobilized in this particular polymer system for the extraction and determination of metal ions has not been reported before, representing a novel contribution to the field of biosorption.

## 2. Materials and Methods

### 2.1. Chemicals and sample preparation

All chemicals used in this study were of analytical grade. Stock solutions of Cu (II) and Cd (II) (1000 mg/L) were prepared by dissolving $Cu(NO_3)_2.3H_2O$ and $Cd(NO_3)_2.3H_2O$ (Sigma-Aldrich) in distilled water. Sample digestion was performed using nitric acid (65%, Sigma-Aldrich) and hydrogen peroxide (30%, Sigma-Aldrich). The pH adjustments were carried out with hydrochloric acid (36%, Merck) and sodium hydroxide (≥97%, Merck). Certified reference material (BCR-670) was sourced from the European Commission. Prior to use, all vessels were immersed overnight in 10% $HNO_3$ or HCl solutions and then thoroughly rinsed with deionized water and dried at 110 °C to ensure contamination-free conditions.

0.50 g of the BCR-670 sample was weighed into a PTFE digestion vessel for the acid digestion procedure. After adding 10 mL of $HNO_3$ and 2 mL of $H_2O_2$, the mixture was allowed to pre-react for 25 minutes before being digested in the microwave using a Berghof Speed Wave MWS-3 system. The microwave digestion conditions are listed in the literature (Teğin and Akdeniz, 2018). The resulting digestion was filtered, diluted to 50 mL with distilled water, and used for analysis.

### 2.2. Instrumentation and analytical procedures

The adsorption experiments were performed using a column-based system. The metal ion solutions were passed through the columns (1.0×10.0 cm) using a Watson-Marlow 120 S peristaltic pump. The pH of the solutions was measured and adjusted prior to the experiments using a HANNA pH/ORP meter.

The Cu(II) and Cd(II) ion concentrations after adsorption were determined using atomic absorption spectroscopy with the PerkinElmer AAnalyst 700 instrument. The operating parameters of the spectrometer were determined according to our previous study (Teğin and Akdeniz, 2018), while the details of the analytical calibration are given in Table 1.

**Table 1.** Analytical calibration parameters for Cu (II), and Cd (II)

| Element | Linear Range (mg/L) | Slope | Intercept | $R^2$ | Regression Equation |
|---|---|---|---|---|---|
| Cd (II) | 0.028–11 | 0.09157 | 0.001137 | 0.9975 | A = 0.09157·C + 0.001137 |
| Cu(II) | 0.077–5.8 | 0.06119 | -0.00191 | 0.9998 | A = 0.06119·C – 0.00191 |

A = Absorbance, C = Concentration (mg/L)

### 2.3. Preparation of a walnut shell-polymer based composite sorbent for column adsorption

The column packing material was prepared in three main steps: (i) synthesis and modification of the cross-linked copolymer, (ii) processing of the walnut shell biomass, and (iii) immobilization of the biomass on the copolymer and preparation for use in the column. Each step is described below.

*(i) Synthesis and Treatment of the Crosslinked Copolymer:*

Crosslinked poly(styrene-co-methacrylic acid) (C-PS-co-PMAA) was synthesized via bulk free-radical copolymerization under a nitrogen atmosphere. The monomers, styrene and methacrylic acid, were polymerized in the presence of α,α′-azoisobutyronitrile (AIBN) as an initiator and 1% (w/w) divinylbenzene as the crosslinking agent (Wang et al., 2015). The resulting copolymer was treated with 4 M HCl to enhance surface characteristics. The material was then thoroughly rinsed with deionized water until a neutral pH was reached and then washed with a 1:1 ethanol–water mixture. After a final rinse with deionized water, the sample was dried at 105 °C and preserved for further use.

*(ii) Preparation of the walnut shell powder:*

Initially, the walnut shells were thoroughly rinsed with deionized water to eliminate impurities, followed by drying at 80 °C for 48 hours. The dried material was then milled using a Memmert grinder and sieved through a 60-mesh screen to achieve uniform particle size distribution.

*(iii) Immobilization and formation of the composite:*

To prepare the composite sorbent, 1.00 g of the treated copolymer and 0.25 g of walnut shell powder were mixed in 10 mL of deionized water. The suspension was stirred at room temperature for 1 hour using a magnetic stirrer. The mixture was then dried at 105 °C. The slurrying and drying steps were repeated several times to ensure effective physical immobilization of the biomass on the copolymer matrix. The final dried composite was sieved again through a -60 mesh sieve and used as column packing material (Ozdemir et al., 2012).

### 2.4. Sorption process for Cd(II) and Cu(II)

The sorption of Cd(II) and Cu(II) ions was conducted using a continuous-flow column system. Aqueous test solutions containing 2.0 mg $L^{-1}$ of each metal ion were prepared from standard stock solutions. The pH of the solutions was adjusted before use, and the samples were passed through the column at a constant flow rate using a peristaltic pump.

After sorption, the column was rinsed with deionized water, and the retained metal ions were eluted with a suitable acid solution (HCl or $HNO_3$). The concentrations of Cd (II) and Cu(II) in the eluates were determined by flame atomic absorption spectrometry.

In the column-based adsorption experiments, the effects of operating parameters, including pH, flow rate, sorbent dosage, sample volume, eluent type, and analyte concentration, were systematically examined to assess their impact on sorption performance. The metal ion recovery (%) was calculated according to Equation (1).

$$Recovery(\% = \frac{(Co-Ce)}{Co} X100 \quad (1)$$

Where $C_o$ and $C_e$ represent the initial and equilibrium concentrations (mg $L^{-1}$) of the target metal ion in solution, respectively.

### 2.5. Real sample analysis

The applicability of the column system was evaluated using real water samples, including wastewater and tap water (Siirt), salt water (Tuzkuyu) and mineral-rich Billoris spa water. The samples were acidified with 0.1 mol $L^{-1}$ $HNO_3$ to pH < 2 to stabilize the metal ions (José Martínez-Pérez and Koelle, 2017), filtered through 0.45 μm membrane filters and stored at 4 °C until analysis.

## 3. Results and Discussion

### 3.1. Characterization

FTIR analysis of filler material was performed with a Perkin Elmer Spectrum 100 FT-IR, and the obtained results are shown in Figures 1A-1B.

In Figure 1, spectrum A corresponds to the cross-linked poly(styrene-co-methacrylic acid) polymer, whereas spectrum B belongs to the composite structure obtained after immobilizing walnut shells onto this polymer matrix. A comparative analysis reveals distinct structural modifications upon immobilization. In spectrum A, the absorption bands at 3026, 2922, and 2850 $cm^{-1}$ are assigned to aromatic and aliphatic C–H stretching vibrations, respectively, while spectrum B exhibits a pronounced band at 2921.49 $cm^{-1}$ attributable to aliphatic C–H groups originating from the cellulose and lignin components of the walnut shell (Farch et al., 2023). The carbonyl stretching band, located at 1703 $cm^{-1}$ in spectrum A, is shifted to 1695.62 $cm^{-1}$ in spectrum B with a noticeable decrease in intensity, suggesting possible hydrogen bonding or other interactions between hydroxyl groups and carbonyl functionalities within the lignocellulosic structure (Mccaffrey et al., 2024). The aromatic ring vibrations observed at 1602, 1493, and 1452 $cm^{-1}$ in spectrum A become more complex in spectrum B, with additional bands appearing at 1603.16, 1512.14, 1440.23, and 1372.84 $cm^{-1}$, indicating the contribution of phenolic moieties from the walnut shell to the composite (Farch et al., 2023). Moreover, new absorptions at 1236.11, 1192.31, and 1025.90 $cm^{-1}$ in spectrum B correspond to C–O and C–O–C stretching vibrations characteristic of lignocellulosic biomass (Mccaffrey et al., 2024), thereby confirming successful immobilization. In the fingerprint region (800–650 $cm^{-1}$), the emergence of new bands at approximately 775.33 and 670.04 $cm^{-1}$ in spectrum B, replacing the 756 and 700 $cm^{-1}$ absorptions in spectrum A, supports the occurrence of functional changes in the composite structure. These spectral assignments are consistent with previously reported FT-IR features of poly(styrene-co-methacrylic acid) and related copolymers, which typically exhibit aromatic C–H stretching near 3070 $cm^{-1}$, carbonyl stretching near 1730 $cm^{-1}$, and aromatic C=C stretching around 1600 $cm^{-1}$ (Naghash et al., 2007).

The results obtained from FT-IR analysis show that walnut shells have been successfully immobilized in a cross-linked poly(styrene-co-methacrylic acid) matrix and that new functional groups have been formed in the structure or interactions between existing groups have occurred during this process. These changes reveal that the functional properties of the composite structure have changed and that it may exhibit different performance in potential application areas.

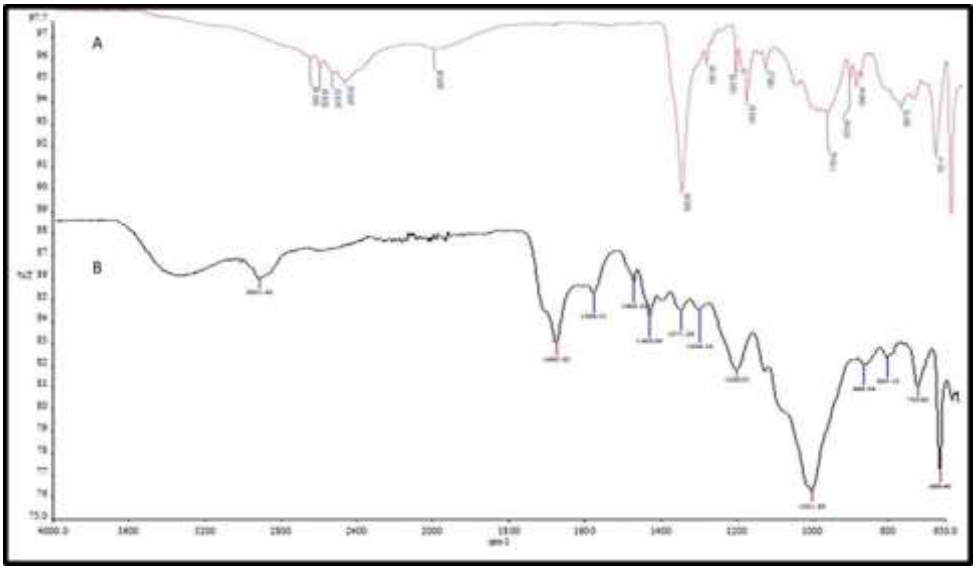


**Figure 1.** (A) FTIR image of cross-linked polymer, and (B) walnut shell immobilized on polymer

### 3.2. Effect of pH on metal ion extraction

The pH of the solution plays a critical role in the adsorption behavior of metal ions, as it influences both their solubility and the ionization state of the functional groups on the adsorbent surface, as well as that of the metal species in solution (El-Sayed et al., 2011). In this study, the effect of pH on the extraction of Cu(II) and Cd(II) ions was investigated using walnut shell-immobilized cross-linked poly(styrene-co-methacrylic acid) (WNS-PSMAA) in a pH range of 3.0 to 10.0. The adsorption experiments were performed with 50.0 mL test solutions containing 2.0 mg mL-1 of each metal ion. The influence of pH on the extraction of metal ions is shown in Figure 2. At a pH value of 3.0, the recovery rates were measured at 31.02% for Cu(II) and 33.56% for Cd(II). Under optimized conditions, the recovery rates were determined to be 100.00 ± 2.30% for Cu(II) and 99.89 ± 2.83% for Cd(II), based on triplicate measurements at a confidence level of 95. The relative standard deviations were calculated as 3.99% for Cu(II) and 4.90% for Cd(II). Maximum adsorption was achieved at pH 5.0 for Cu(II) and at pH 4.0 for Cd(II).

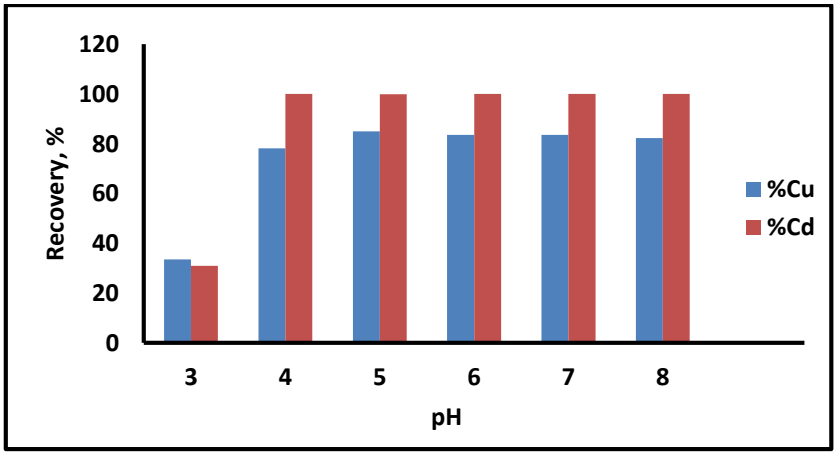


**Figure 2.** Effect of pH on solid phase extractions of Cu (II) and Cd (II)

### 3.3. Effect of the flow rate on metal ion extraction

The impact of sample solution flow rate on the adsorption efficiency of Cu(II) and Cd(II) ions on WNS-PSMAA was investigated in the range of 1.0 to 8.0 mL $min^{-1}$. The corresponding recovery data are shown in Figure 3. The optimum flow rates were found to be 2.15 mL $min^{-1}$ for Cu (II) and 2.95 mL $min^{-1}$ for Cd (II), at which the recovery efficiencies were 82.5% and 99.54%, respectively.

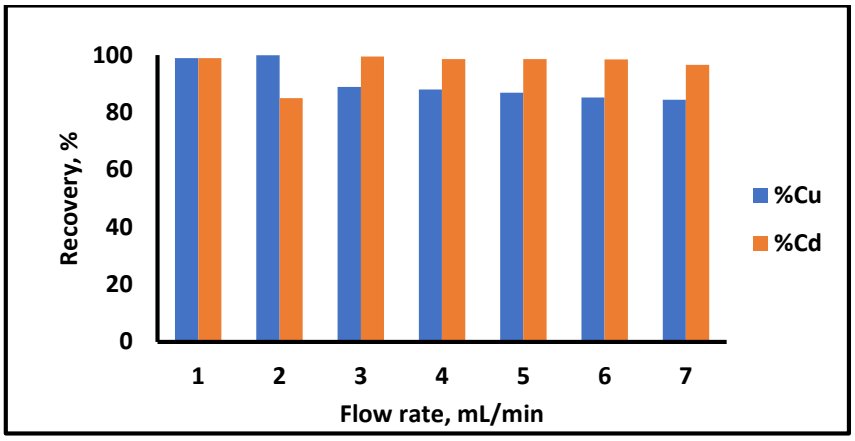


**Figure 3.** Effect of flow rate on the recovery of Cu (II), and Cd (II) ions using WNS-PSMAA sorbent

### 3.4.Effect of biosorbent amount on metal ion recovery

The effect of walnut shell amount on the adsorption performance of Cu(II) and Cd(II) ions was investigated at optimal pH values and flow rates of 2.15 mL $min^{-1}$ for Cu(II) and 2.95 mL $min^{-1}$ for Cd(II). The mass of the walnut shell used for the immobilized sorbent was varied between 150.0 and 450.0 mg. As Figure 4 shows, increasing the amount of walnut shell from 150.0 mg to 300.0 mg resulted in a significant improvement in Cu(II) recovery, which reached 91.06%, while Cd (II) at 250.0 mg achieved complete recovery (100.00%). Further increases in walnut shell amount beyond these values did not significantly improve recovery (Teğin et al., 2025).

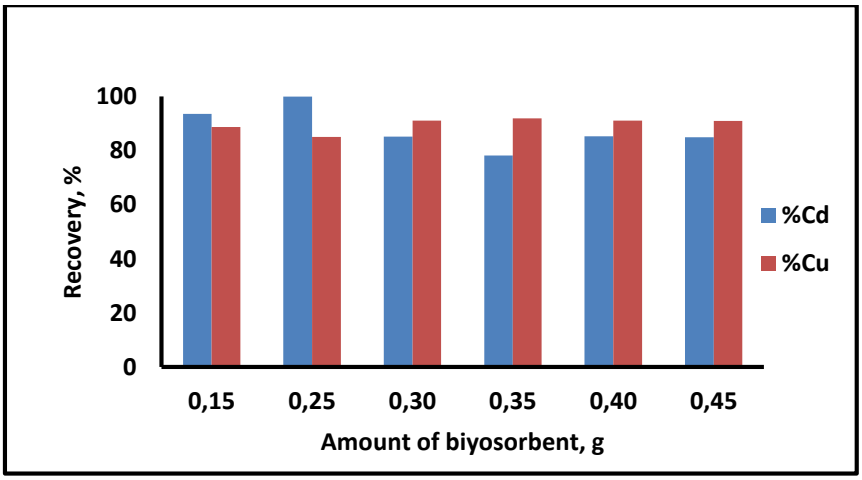


**Figure 4.** Effect of biosorbent dosage on the efficiency of SPE of Cu (II) and Cd (II)

### 3.5. Effect of cross-linked poly(styrene-co-methacrylic acid) (PSMAA) amount on metal ion extraction

The effect of the amount of polymeric support material PSMAA on the SPE of Cu (II), and Cd (II) ions was evaluated by varying the resin mass from 250.0 mg to 750.0 mg. As shown in Figure 5, the recovery improved with increasing resin amount and reached optimum values at 750.0 mg for both Cu(II), and Cd(II). Polymer support amounts above 750.0 mg did not lead to any further improvement in recovery, indicating a saturation point of the available binding sites. Therefore, 750.0 mg PSMAA was selected for the subsequent SPE experiments with both metal ions.

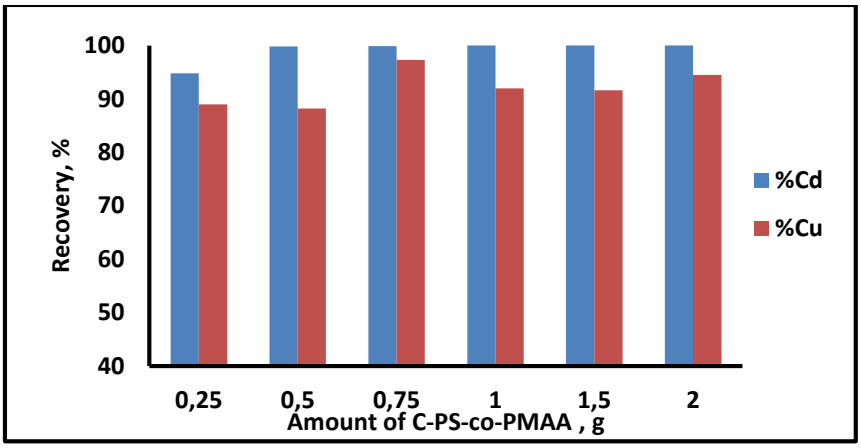


**Figure 5.** Effect of polymeric support material dosage on the efficiency of solid phase extraction of Cu (II), and Cd (II)

### 3.6. Effect of sample solution volume on the solid-phase extraction

In trace metal analysis, the volume of the sample solution plays a critical role in effective enrichment. To evaluate this parameter, the effect of different sample volumes (25.0–400.0 mL) on the solid phase extraction of Cu(II) and Cd(II) ions was investigated using walnut shells immobilized on PSMAA as a sorbent. The concentration of each metal ion was maintained at 2.0 µg $mL^{-1}$ throughout the experiments. As shown in Figure 6, the highest recovery for Cu(II) (99.89%) was achieved at a sample volume of 200.0 mL, while Cd(II) showed complete recovery (100.00%) at 50.0 mL under the specified optimum conditions.

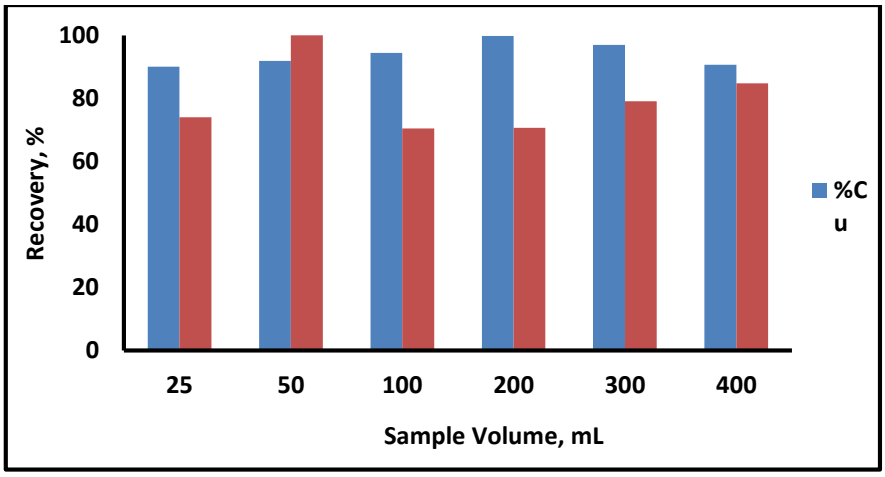


**Figure 6.** Effect of sample solution volume on the SPE efficiency of Cu(II) and Cd(II)

### 3.7. Effect of type and concentration of eluent on the desorption of metal ions

The effect of eluent type, volume, and concentration on the desorption efficiency of Cu(II) and Cd(II) ions from the biosorbent immobilized column was investigated to optimize desorption efficiency. Different acids and volumes were tested to determine the conditions that allow complete elution of the adsorbed metal ions from the sorbent (Table 2). The results indicated that both the chemical nature and the volume of the eluent significantly influenced recovery, with optimal recoveries achieved under specific conditions for each metal ion. These findings emphasize the importance of selecting appropriate elution parameters to ensure quantitative desorption in metal ion analysis.

**Table 2.** Effect of type and concentration of eluent on the extraction of Cu(II) and Cd(II)

| Type of elution solution | Concentration ($molL^{-1}$) | Recovery (%) | |
|---|---|---|---|
| | | Cu (II) | Cd (II) |
| HCl | 0.5 | 91.55 | 81.45 |
| | 1.0 | 91.65 | 84.11 |
| | 1.5 | 92.73 | 80.97 |
| | 2.0 | 91.92 | 82.61 |
| $HNO_3$ | 0.5 | 88.38 | 81.91 |
| | 1.0 | 93.94 | 82.73 |
| | 1.5 | 87.74 | 89.62 |
| | 2.0 | 88.08 | 89.29 |

As presented in Table 2, the optimum recoveries were obtained with 5.0 mL of 1.5 mol $L^{-1}$ $HNO_3$, resulting in 95.7 % recovery for Cu(II), and 100.0 % for Cd(II).

The type of elution solution significantly influences the recovery rates of Cu(II) and Cd(II), with hydrochloric acid (HCl) generally providing better results, particularly for Cu(II) at certain concentrations. Further experiments may be necessary to optimize conditions for maximum recovery and to explore the effects of varying elution volumes.

### 3.8. Effect of matrix interference on the recovery of metal ions

The presence of interfering ions in complex matrices often complicates the determination of trace metals in environmental samples (Alan et al., 2007). To evaluate the effects of such interfering species, various salts and metal ions were spiked in solutions containing Cu(II) and Cd(II) under optimized experimental conditions. The recovery results are presented in Table 3.

**Table 3.** The effect of interfering ions on the recovery of Cu(II) and Cd(II) ions

| Ion | Added Salts | Concentration ($mgL^{-1}$) | Recovery (%) | |
|---|---|---|---|---|
| | | | Cu(II) | Cd (II) |
| **$Na^+$** | NaCl | 10000 | 93.27 ± 1.89 | 85.33 ± 1.79 |
| **$Cl^-$** | $BaCl_2$. $2H_2O$ | 20 | 92.97 ± 1.36 | 88.78 ± 1.65 |
| **$SO_4^{-2}$** | $MnSO_4.H_2O$ | 50 | 92.81 ± 1.76 | 88.14 ± 1.18 |
| **$Mg^{2+}$** | $Mg(NO_3)_2.6\ H_2O$ | 5000 | 92.62 ± 1.87 | 84.78 ± 1.66 |
| **$Ca^{2+}$** | $CaCl_2.2H_2O$ | 3000 | 92.55 ± 1.69 | 83.69 ± 1.47 |
| **$F^-$** | KF | 1000 | 92.27 ± 1.91 | 80.56 ± 1.83 |

The results indicate that the recovery of Cu(II) remained relatively stable within the range of 92–93%, suggesting that the sorbent exhibited high selectivity and was not significantly

influenced by the presence of competing ions. In contrast, Cd(II) recovery showed greater variability, ranging from 80.56% to 88.78%, indicating higher sensitivity to matrix interferences. The observed analytical errors remained ≤2 %, and this error value is determined by the AAS determination methods (Saygi et al., 2008). These results demonstrate the robustness of the method against common matrix interferences and support its applicability for trace metal analysis in complex sample matrices.

Among the tested ions, $Cl^-$ and $SO_4^{2-}$ exerted the least impact on Cd(II) recovery, which remained above 88%. However, the presence of $F^-$ resulted in the most pronounced reduction, lowering Cd(II) recovery to 80.56%. Intermediate effects were observed with $Na^+$, $Mg^{2+}$, and $Ca^{2+}$, which decreased Cd(II) recovery to values between 83% and 85%. Overall, the findings demonstrate that the method exhibits high tolerance toward foreign ions, with Cu(II) being more selectively recovered than Cd(II).

### 3.9. Repeatability of the walnut shell-immobilised polymeric column

The repeatability of the column was analyzed by performing ten consecutive adsorption–desorption cycles under constant experimental conditions. In each cycle, 50.0 mL of sample solution containing 2.0 mg of Cu(II) and Cd(II) ions was passed through the column, followed by elution of the retained metal ions with 5.0 mL of 1.0 mol $L^{-1}$ $HNO_3$ for Cu(II) and 5.0 mL of 1.5 mol $L^{-1}$ $HNO_3$ for Cd (II). The results presented in Figure 7 clearly demonstrate that the column preserved consistent efficiency during ten consecutive cycles of use, confirming its robustness and reusability.

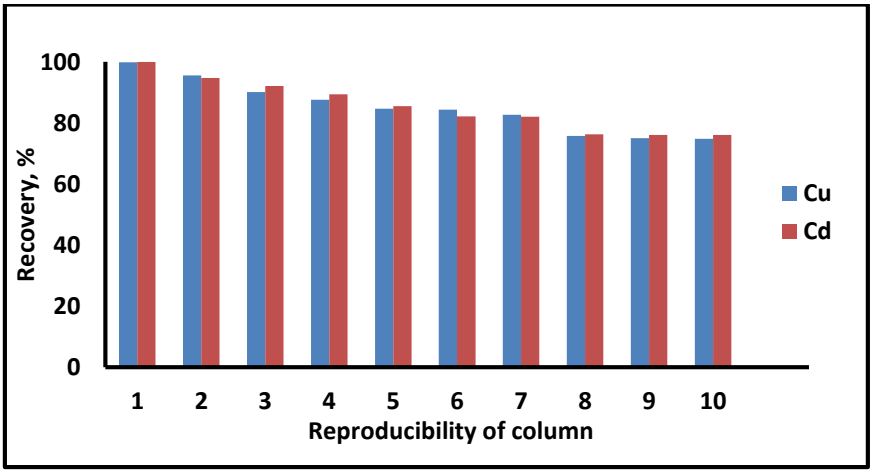


**Figure 7.** Repeatability of the column for SPE of Cu (II) and Cd (II)

The column demonstrated stable performance, indicating that it can reliably retain and elute the targeted metal ions across multiple uses. The data illustrates the potential for this sorbent system in applications requiring the separation and recovery of Cu(II) and Cd(II) ions. The effectiveness of the column for the retention and elution of Cu(II) and Cd(II) ions, with an average recovery yield exceeding 80% over repeated usage, suggests that it is a viable option for applications in metal ion recovery or analytical sample preparation.

### 3.10. Evaluation of the analytical performance of the method

Under optimal experimental conditions, the limit of detection (LOD) and limit of qualification (LOQ) of the study were calculated by application of the preconcentration procedure to blank solutions. The limits of detection for Cu(II) and Cd(II) depend on three times the standard deviations of the blank (k=3. N=12), thus the limits for the ions mentioned above were 1.40 μg $L^{-1}$ and 5.10 μg $L^{-1}$, respectively. Correspondingly, the LOQ values of Cu (II) and Cd (II) were found as 4.80 μg$L^{-1}$ and 17.20 μg$L^{-1}$. The enrichment factors were calculated to be 60 for Cu(II) and 10 for Cd(II), indicating a significant improvement in detection sensitivity.

### 3.11. Analytical validation and application of the developed method

After optimizing the enrichment conditions, the accuracy and precision of the method were evaluated, and the results are summarized. The mean recovery values were 100.00% for Cu (II) and 99.89% for Cd (II), indicating that both analytes were measured with high accuracy, very close to their theoretical values. The associated uncertainty values were ±2.30% for Cu(II) and ±2.83% for Cd(II), suggesting that the results for cadmium were characterized by slightly greater variability compared to copper. The higher RSD observed for Cd (4.90%) relative to Cu (3.99%) supports this observation, implying that the repeatability of Cd measurements is somewhat lower. The regression coefficients were determined as 0.9998 for Cu(II) and 0.9975 for Cd(II), confirming the strong linearity of the calibration curves. Pre-enrichment factors of 60 for Cu(II) and 10 for Cd(II) further highlighted the higher enrichment efficiency achieved for copper ions.

Overall, the findings demonstrate that both analytes can be determined with high accuracy; however, copper displays superior precision and lower variability compared to cadmium. Depending on the intended application, such as regulatory compliance or quality control, these differences in measurement uncertainty and precision may be of practical importance.

The accuracy of the method was confirmed by analyzing the certified aquatic plant reference material BCR-670. The values given correspond to the average of three replicate measurements, calculated with a confidence of 95%. The results presented in Table 4 show a strong correlation between the measured concentrations and the certified values for both Cd(II) and Cu(II).

**Table 4.** Analytical validation of the developed method for BCR-670 reference material

| Element | Certified value (μg$g^{-1}$) | Found[a] (μg $g^{-1}$) | Recovery[a] (%) | Relative Standard Deviation (RSD) (%) |
|---|---|---|---|---|
| Cd (II) | 75.5 ± 2.50 | 73.4 ± 2.34 | 99.89 ± 2.83 | 4.90 |
| Cu (II) | 1.82 ± 0.30 | 1.80 ± 0.12 | 100.00 ± 2.30 | 3.99 |

[a] $x \mp 4.30xs \sqrt{3}$

The optimized method was used for the quantitative determination of Cu(II) and Cd(II) in various water matrices, including wastewater and tap water (Siirt), salt water (Tuzkuyu), and mineral-rich Billoris spa water. According to the method applied in this study, Cd(II) ions were

not detected (n.d.) in any of the analyzed water samples. The recovery values for Cu (II) ions varied significantly depending on the type of water matrix. High recovery rates were obtained for tap water (99.53 ± 1.1%) and Billoris spa water (99.31 ± 1.2%), indicating the high efficiency and reliability of the applied method in these matrices. In contrast, considerably lower recovery rates were observed for wastewater (31.65 ± 1.9%) and saline water (27.17 ± 2.0%), which may be attributed to matrix interferences or the negative impact of high ionic strength on analytical performance. Overall, while the method yielded results below the detection limit for Cd(II) in all samples, it demonstrated high accuracy for Cu(II) in matrices with low ionic interference.

## 4. Conclusions

This study presents an effective and sustainable SPE method using walnut shells immobilized on a methacrylate-based polymer (WNS-PSMAA) for the extraction and determination of Cu(II), and Cd(II) ions. The sorbent showed high recovery rates (100.00 ± 2.30% for Cu(II) and 99.89 ± 2.83% for Cd(II)), low detection limits (1.40 µg $L^{-1}$ for Cu(II) and 5.10 µg $L^{-1}$ for Cd(II)), and significant enrichment factors. Validation with certified reference material confirmed the accuracy of the method, while application to different water samples proved its robustness. The sorbent retained an efficiency of over 80 % after ten reuse cycles, indicating good stability. This method offers a cost-effective and environmentally friendly strategy for the removal of heavy metals and shows that it is scalable and can be applied to other metals in future research.

## Acknowledgment

This study was supported by the Scientific Research Projects Unit of Siirt University with project number 2015-SİÜFEB-34

## Ethics Statement

The authors declare that ethical approval was not required for this research.

## Author Contribution Statement

The authors declare that they contributed equally to the article and that they have seen/read and approved the final version of the manuscript for publication.

## Conflict of Interest Statement

All authors declare that there is no conflict of interest for this study.

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