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Preconcentration and determination of Cu(II) and Cd(II) ions from wastewaters by using hazelnut shell biosorbent immobilized on Amberlite XAD-4 resin

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ABSTRACT

Hazelnut shell biosorbent immobilized on Amberlite XAD-4 polymer resin as solid phase extraction method was developed and used for preconcentration of Cu(II) and Cd(II) ions from aqueous solutions. Concentrations of analytes in solutions were determined by Flame Atomic Absorption Spectrometry after extraction with column technique. Functional groups of nutshell biosorbent immobilized on resin were characterized by Fourier transform infrared spectrometry. Optimized critical parameters for preconcentration of Cu^{2+} and Cd^{2+} ions from sample solutions with nutshell immobilized on the resin were the pH value of solution, type of eluent solutions, the flow rate of sample solution, quantities of nutshell biosorbent, Amberlite XAD-4 resin, and enrichment factors, respectively. Detection limits of Cu^{2+} and Cd^{2+} ions found were 0.29 µg L^{-1} and 0.25 µg L^{-1}, respectively. The method proposed was applied for determinations of Cu^{2+} and Cd^{2+} ions in standard reference material (BCR-670 aquatic plant sample) for accuracy and applied to real water samples such as wastewater and Van lake water. At the 95% confidence level, relative standard deviations (RSDs) were found as 1.44% for Cd^{2+} and 1.21% for Cu^{2+} ions with three replicate measurements.

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1. Introduction

Nowadays, toxic metal contaminations and their effects have widely increased in the environment and waters because of rapid developments in technology, industry, and social life of the people in the world [1-6]. Copper is one of the trace elements found in the body, but its higher level can cause toxic like other metals such as cadmium and lead, even if at low concentrations [7, 8]. Daily intake of copper is 1.0–1.1 mg for an adult woman and 1.2-1.6 mg for an adult man. Excessive or deficient copper causes different health problems such as heart failure, nausea, anaemia, hypertension, and vomiting [9]. Besides, cadmium accumulates in the human body and may increase the risk of lung cancer [10, 11]. Copper and cadmium are widely used in technology such as electrical supplies for construction, heat exchangers, electroplating, electroplate steel, medicine, painting, dying, surface treatment, etc. [12, 13]. For example, some industrial products that included cadmium are power stations, Ni-Cd batteries, alloy manufacture, dyeing, etc. Especially from industrial and agricultural activities, mining, unplanned urbanization, and household wastes, trace levels of copper and cadmium are emitted into the environment and accumulate in nature [14]. These problems have threatened the health of living beings in ecological nature and will affect future generations. Removing these metal contaminations from water solutions is a significant environmental problem because of their toxic effects on living conditions [15]. Therefore, determinations of copper and cadmium contaminants are important in waters because of their poisonous impacts on human health [16, 17].

Traditional methods such as chemical precipitation, ion flotation, ion exchange, coagulation and electrochemical methods have been applied to remove industrial pollution in wastewater in the field of environmental health [18, 19].

These methods are considered economically inexpensive, but they all have some disadvantages and inadequacies in environmental pollution removal. There is always a need for cheaper and more effective solutions. For this, it is seen that the adsorption method using biosorbent gives remarkable results [20-23]. Especially the use of waste materials as an adsorbent in adsorption processes is widespread for the synthesis of cost-effective materials. The peels of herbal products are very sympathetic to scientists within the framework of green chemistry thought [24-26].

In recent years, chelating resins have been functionalized in several assistance materials. The inclusion of commercially available XAD resins and their usage has increased for removing and recovering metals contaminated [27, 28]. Amberlite XAD resins are broadly used to develop chelating materials for preconcentration and enrichment procedures due to their excellent physical and chemical properties such as porosity, high surface area, durability, and purity [29]. Among these resins, Amberlite XAD-4 used as a solid sorbent has perfect physical features such as resistance to acids, bases, oxidizing and reducing agents, large surface area (>750 m^2g^{-1}), well-characterized medium size (0.49– 0.69 mm), and porosity [30].

The solid phase extraction (SPE) method is one of the most commonly used techniques for the preconcentration and enrichment of metals. It provides more elastic study conditions and well selectivity, steady, proximity, ability to work with large sample volume, high concentration capacity and high enrichment capability for metal ions, safety for hazardous samples, and minimum costs due to low consumption of reagents, ease and fast for automation [2, 10, 31, 32]. The fundamental mechanism of SPE is a transference of metals from the aqueous phase into active regions of the solid phase [29, 33].

Various Amberlite XAD resins and biological materials have been used as SPE for trace levels of toxic metals in water samples before instrumental analysis [34, 35]. The usage of natural materials such as yeast, plant leaves, and root tissues for recovery of heavy and toxic metal ions from aqueous solutions has increased in recent years because of the preferable performance and minimum cost of biosorbent materials. Biosorption processes are usually fast and appropriate for the extraction of metals from large volumes of water samples [36, 37]. Biological sorbent materials immobilized on a suitable XAD resin have been used to overcome some problems by offering ideal size, mechanical force, hardness, and porous characteristics to the biological material [35, 38, 39].

In this study, hazelnut shell biosorbent immobilized on Amberlite XAD-4 resin for SPE procedure was developed for preconcentration, enrichment, and determination of Cu^{2+} and Cd^{2+} ions in waters. There was no study observed in the literature with this procedure. The recovery conditions for Cu^{2+} and Cd^{2+} ions using resin immobilized with hazelnut shell as biosorbent in column technique were investigated. Effects of critical parameters such as pH of the solution, eluent type and concentration, solution flow rate, solution volume, foreign ion effects, and column reproducibility were examined in detail to optimize recovery and enrichment conditions for Cu^{2+} and Cd^{2+} ions by using standard solutions. The method proposed was applied to standard reference material (BCR-670 Aquatic plant sample) and real water samples to preconcentrate Cu^{2+} and Cd^{2+} ions, and the ions were determined by Flame Atomic Absorption Spectrometry (FAAS).

2. Materials and methods

2.1. Equipment and working conditions

A Perkin Elmer 700 Analyst model flame atomic absorption spectrometry (Shelton, CT, USA) equipped with a deuterium lamp for background correction was used for absorbance measurements of Cu and Cd in solutions. Operating conditions of Cd and Cu were wavelengths (228.8 and 324.8 nm), bandpasses (0.7 and 0.5 nm), acetylene flow rates (1.8 and 2.0 L min^{-1}), and lamp currents (10.0 and 4.0 mA), respectively, and they were set according to the recommendations of the manufacturer. A Hanna model pH meter (Hanna Instruments, HI 2211 pH/ORP Meter, Romania) equipped with a glass electrode was performed to measure the pH values of all sample solutions. Extraction columns (1.0 cm inner diameter, 10.0 cm length, and 100 mL reservoir at upper end) equipped with polypropylene frites were utilized. A Watson Marlow 120 S brand (Milford, MA) peristaltic pump was utilized to pass solutions through a column and to control the flow rate. A Perkin Elmer 100 model Fourier transform infrared (FT-IR) spectrometer was utilized to analyse filler material to determine functional groups of nutshell immobilized Amberlite XAD-4 resin. Scanning electron microscopy (SEM) images were obtained with a LEO 440 Model Instrument to investigate surface structure. All chemicals and reagents (Merck, Germany) used during the experiments were analytical grade and utilized without purification. During the studies, ultrapure water obtained from a water system (resistivity 18.3 MΩ cm, Human power I+, Human Corporation, Korea) was used. Working standard solutions of Cd^{2+} and Cu^{2+} ions were prepared by diluting atomic absorption standard stock solutions (Merck, Germany, 1000 mg L^{-1} of each).

Glassware and plastic materials utilized in the works were cleaned by using 10% HNO_3 solution, rinsed three times with ultrapure water and dried in an oven at 110°C for use.

2.2. Collection and preparation of samples

Standard reference material (SRM, BCR-670 Aquatic plant sample) taken from Institute for Reference Materials and

Measurements (European Commission, Joint Research Centre) was decomposed by utilizing Berghof Speed Wave (MWS-3) microwave oven digestion system. The 0.50 g of SRM was weighed into a polytetrafluoroethylene (PTFE) digestion vessel. 5 mL of HNO_3 (65%, m/m) and 2 mL of H_2O_2 (30%, m/m) were poured into the vessel and waited for one night at laboratory condition by closing with a cover. The operating states of the digestion system in two steps were used as temperature (from 140 to 195 °C); pressure (50 to 50 bar); power (from 60 to 90 %); T_a (from 5 to 1 min) and time (10 to 10 min). After decomposition, the solution was diluted to 50 mL with ultrapure water. Water samples were collected from Siirt city waste and tap waters, from Van Lake water, Tuzkuyusu saline water, and Billoris spa water. The samples in 1.0 L polypropylene bottles were acidified with 0.1 mol L^{-1} HNO_3 to avoid the adsorption of ions on the walls of the container. In addition, the samples were filtered through ordinary filter paper to remove thick and suspended particles.

2.3. Preparation of Amberlite XAD-4 resin and nutshells

Approximately 50 g of Amberlite XAD-4 polymer resin (polystyrene divinylbenzene, taken from Sigma Aldrich) was mixed with 4 M HCl to modify its structure and remove organic and inorganic impurities. It was washed with ultrapure water until reaching neutral pH (pH was about 7.0) and put into an ethanol-water mixture (1:1) solution, respectively. After washing with ultrapure water, the resin was dried at 105°C and kept in a polyethylene bottle [29, 40]. Nutshells taken from Siirt bazaar were grained by Memert brand mill. After passing through a 60 mesh sieve, they were cleaned with ultrapure water to take out impurities and dried in an oven at 80°C. They were passed through 60 mesh sieves again to obtain powder nutshells [41].

2.4. Preparation of SPE columns for sorption studies

Amberlite XAD-4 resin (1.00 g) and nutshell powder (0.30 g) were mixed with a magnetic stirrer (IKA Werke RT-10P, Germany) for 1 h by adding 15 mL of ultrapure water. After mixing, the solid mixture was dried in an oven at 105°C for 1 h, passed through a 60 mesh sieve, and put into a column having a porous disk and a stopcock to prepare SPE columns [9]. The ultrapure column was conditioned by passing 1.0 mol L^{-1} HCl. 50.0 mL of two test solutions including 2.0 µg mL^{-1} of Cd^{2+} or 2.0 µg mL^{-1} of Cu^{2+} ions were separately prepared from standard stock solutions. Although FAAS could directly determine concentrations of these elements, they were used only to obtain optimization parameters [42]. The pH of each test solution was adjusted to a suitable value and passed from the SPE column by utilizing a peristaltic pump with an adjusted flow rate, and about 15 mL of ultrapure water was spent through the column. Cd^{2+} or Cu^{2+} ions taken by nutshells immobilized on the resin were eluted from two different columns with 5.0 mL of 1.0 mol L^{-1} HCl or 5.0 mL of 1.0 mol L^{-1} HNO_3 solution, separately. FAAS, respectively measured concentrations of Cu^{2+} and Cd^{2+} ions in eluent solutions [40].

3. Results and discussion

3.1. Characterization studies of filler material

The morphology and functional groups of a hazelnut shell, Amberlite XAD-4, and hazelnut shell immobilized on Amberlite XAD-4 resin were researched between 4000 and 400 cm^{-1} by FT-IR spectrometry and results of filler materials taken were shown in Figure 1. As seen in Figure 1, a series of absorption peaks were shown that the column packing material structure is complex. All spectra analyzed have bands at 3300-3500 cm^{-1}, indicating the presence of an alcoholic, phenolic, or acidic OH bond. The broad peak at 3394-3384 cm^{-1} indicates that macromolecular linkage has attached hydroxyl groups (cellulose, pectin, etc.). The peak points observed at 2923 and 2911 cm^{-1} may belong to C-H groups. At 2301-2068 cm^{-1}, the triple bond attached to the group C-N may be picked. The bands around the 1603 - 1601 cm^{-1} were indicated the presence of free and esterified carboxyl groups. FT-IR spectra showed that the carbon bands at 1484 and 1430 cm^{-1} were aliphatic, aromatic, and cyclic with different surface structures. Besides, the bands at 1023 and 981 cm^{-1} indicated that the alcohols and carboxylic acids were C-O [43].

By taking scanning electron microscopes (SEMs) of Amberlite XAD-4 alone, hazelnut shell immobilized on resin, Cu^{2+} and Cd^{2+} ions pasted state of hazelnut shell immobilized resin were performed to examine their surfaces with LEO 440 Computer Controlled Digital Model Instrument, separately and the results obtained were shown in Figure 2. In addition, the Energy Dispersive X-Ray Analysis (EDX) image and thermo-gravimetric analysis (TG/DTA) graph of hazelnut shell immobilized on Amberlite XAD-4 resin were shown in Figures 3a and 3b. As shown in Figure 3a, no Cu and Cd contamination is observed in the column filler material. When Figure 3b was examined, the TGA chart could be viewed in 4 steps. In the first step, there was no mass loss between 68 and 225°C. In the second step, a mass loss of 19.3% was observed between 225 and 404°C. In the next step, 79.0% mass loss appeared between 405 and 479°C. In the final step, there was about 92.4% mass loss observed between 478 and 1006°C. It was also found that the decomposition temperature of column packing material was about 455°C from the derivative weight (mass %/min) analysis.

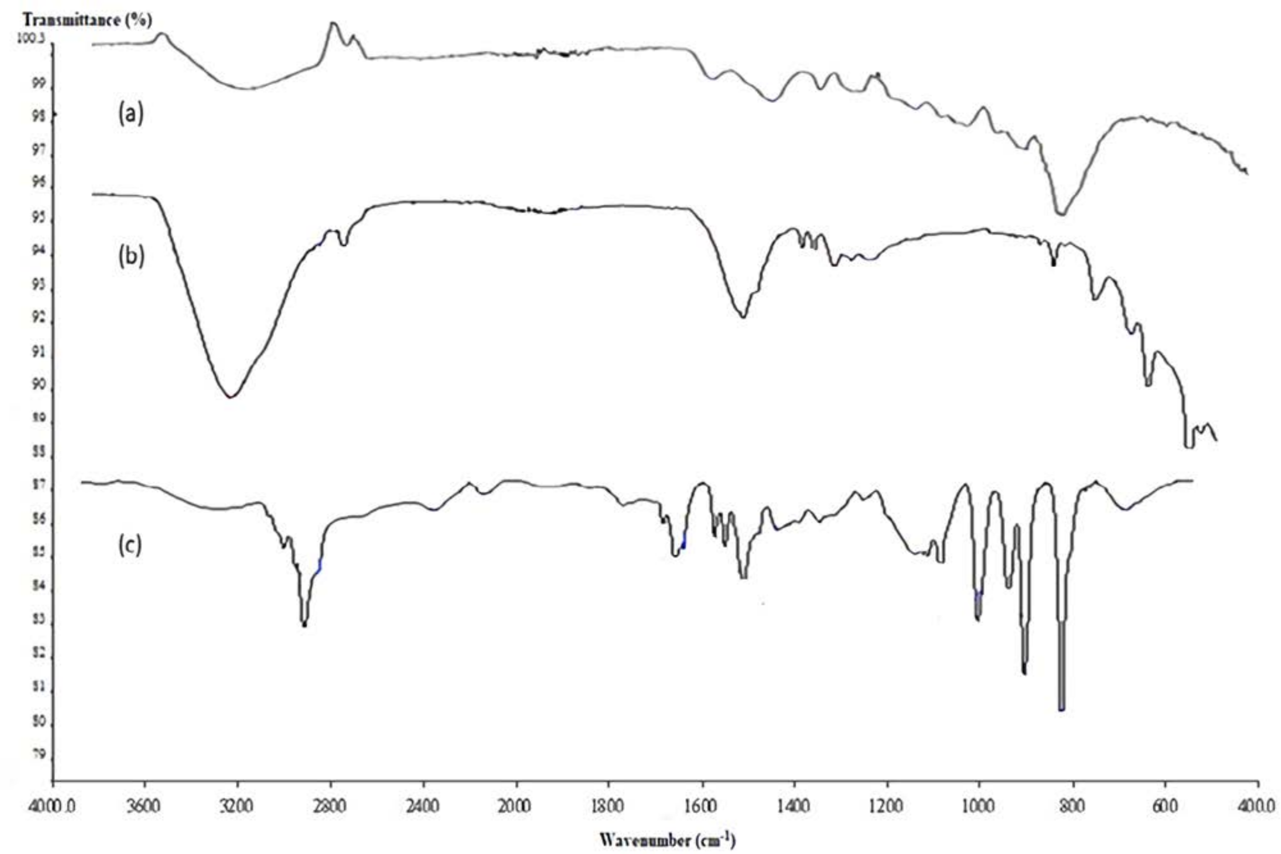

Figure 1. *Comparison of FT-IR images of (a) Hazelnut shell, (b) Amberlite XAD-4 and (c) Hazelnut shell immobilized on Amberlite XAD-4.*

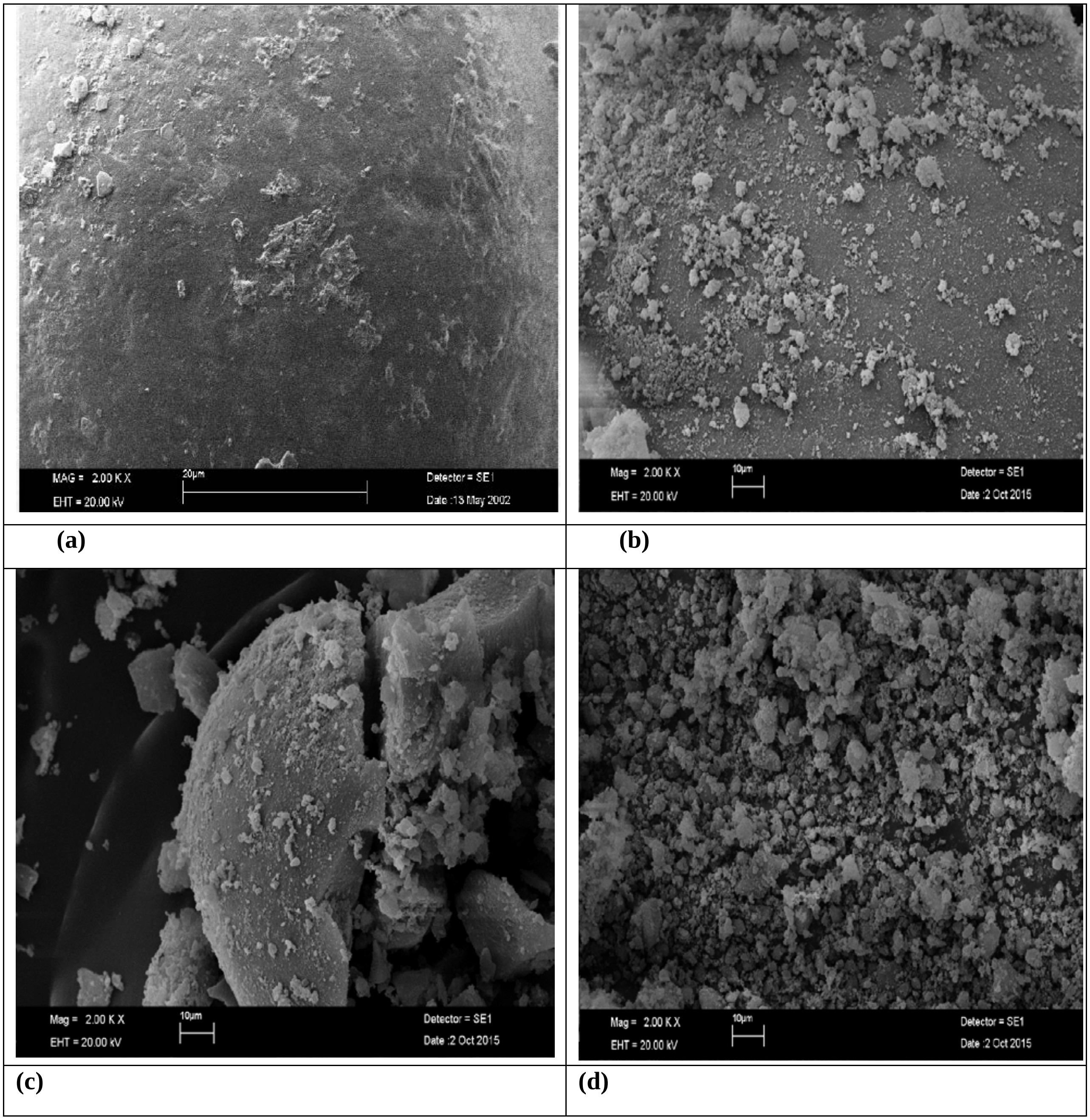

Figure 2. *Comparison of SEM images of (a) Amberlite XAD-4 [43], (b) Hazelnut shell immobilized on Amberlite XAD-4, (c) Cu^{2+} pasted state of hazelnut shell immobilized on Amberlite XAD-4 and (d) Cd^{2+} pasted state of hazelnut shell immobilized on Amberlite XAD-4.*

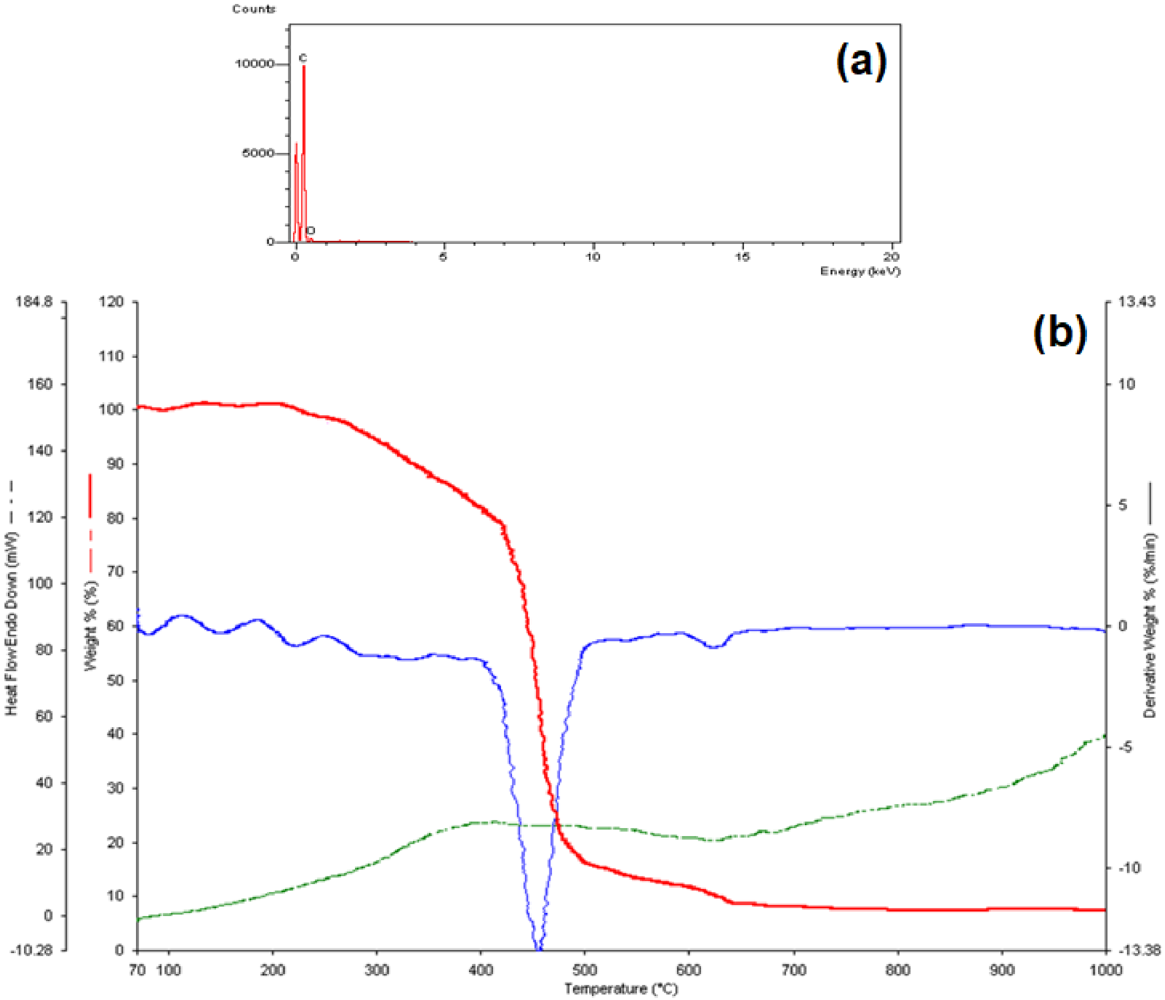

Figure 3. *(a) EDX graph of hazelnut shell immobilized on Amberlite XAD-4 column filler material, (b) TGA graph of hazelnut shell immobilized on Amberlite XAD-4 column filler material.*

3.2. Effect of pH

The pH effect is an important test parameter for the adsorption of metal ions because it affects solubility and ionic attraction of metal ions with functional groups of Amberlite XAD-4 resin immobilized with hazelnut shell sorbent [29]. The pH effect of sample solutions on recoveries of Cu^{2+} and Cd^{2+} ions in hazelnut shells immobilized on the resin was investigated in the pH range from 3.0 to 10.0 by using 1 mol L^{-1} HCl solution or 1 mol L^{-1} NaOH solution. The solutions prepared were passed through the column, and they were eluted by HCl solution or HNO_3 solution. For this purpose, extraction experiments from the column were carried out by utilizing 50.0 mL of test solutions containing 2.0 µg mL^{-1} Cu^{2+} and 2.0 µg mL^{-1} Cd^{2+} ions. Percent recoveries of Cu^{2+} and Cd^{2+} ions versus pH values of solutions for the SPE process were depicted in Figure 4a. As seen in Figure 4a, optimum pH values of solutions were found as 7.0 for Cu^{2+} and 9.0 for Cd^{2+} ions. At these pH values, average percent recoveries of Cu and Cd for three replicate measurements with standard deviations (below 2%) were found as 64.7 ± 1.3% and 76.7 ± 1.8%, respectively. The recovery efficiency for both analytes between pH 3.0 and 5.0 was low due to the acidic medium of the solution. All following solutions were regulated to pH 7.0 for Cu^{2+} and to pH 9.0 for Cd^{2+} ions. The Cu^{2+} and Cd^{2+} ions in eluent solutions were determined by FAAS.

3.3. Effect of solution flow rate

The flow rate effect of the sample solution was investigated to obtain the optimum retention of analytes in Amberlite XAD-4 immobilized with hazelnut shells. Transfer of ions from sample solution into active sides or binding groups of biosorbent could be influenced by the flow rate of sample solution and must be controlled for biosorption recovery.

Therefore, the effect of the flow rate of a sample solution containing only Cu^{2+} at pH 7.0 and another solution containing only Cd^{2+} at pH 9.0 on the recoveries of analytes with the resin immobilized nutshell powder as biosorbent was examined in the range from 1.0 to 6.0 mL min^{-1} by using a peristaltic pump. Average recovery results of Cu^{2+} and Cd^{2+} ions with three replicate measurements found versus flow rate of solution were shown in Figure 4b. As shown in Figure 4b, optimum flow rates of sample solutions were found as 1.8 mL min^{-1} for Cu^{2+} and 2.7 mL min^{-1} for Cd^{2+} ions. Means of Cu^{2+} and Cd^{2+} ions recoveries at these flow rates were found to be 64.7 ± 1.5% and 100.0 ± 1.7%, respectively. When the flow rate of solution was increased above 2 mL min^{-1}, percent recovery of Cu^{2+} ions on biosorbent decreased significantly. This decrease may be due to the less interaction of the analyte with the sorbent species. Percent recovery of Cd^{2+} ions reached a plateau at 2.7 mL min^{-1} and stable by increasing flow rates. These optimized flow rates of sample solutions containing analytes were performed in the following studies.

3.4. Effect of amount of nutshell and resin

The amount of column supporting material is an essential parameter for quantitative recovery of metals in SPE studies. Increasing the mass of biosorbent or mass of resin, percent recoveries of metals can rise to an optimum value because active surfaces and binding groups for biosorption of heavy and toxic metals increase. If biosorbent mass or resin mass was increased over optimum mass, interference between active sides and binding groups could occur, and recovery of metals could reduce [44]. An example of the nutshell as biosorbent for Cu^{2+} and Cd^{2+} ions was examined using optimized sample solutions' optimised individual flow rates and pH values, respectively. The amount of hazelnut shells varied from 0.15 to 0.45 g, while the quantity of Amberlite XAD-4 resin was kept constant as 1.0 g during experimental studies. The means of percent recovery results of Cu^{2+} and Cd^{2+} ions for three replicate measurements with standard deviations (less than 3%) found versus to mass of biosorbent were depicted in Figure 4c. As seen in Figure 4c, recovery values of Cu^{2+} and Cd^{2+} ions increased by the increasing amount of nutshell powder up to 0.3 g and then reached a constant value above this amount. Therefore, 0.3 g of hazelnut shell was adequate for both Cu^{2+} and Cd^{2+} ions. The averages of percent recoveries for Cu^{2+} and Cd^{2+} ions were found as 98.9 ± 1.6% and 99.0 ± 1.9%, respectively.

Effect of Amberlite XAD-4 resin mass on recoveries of Cu^{2+} and Cd^{2+} ions was also examined in the range of 0.25–1.50 g while the mass of nutshell biosorbent was kept constant as 0.3 g during studies. Means of percent recoveries of ions for three replicate measurements with standard deviations (less than 3%) obtained versus the resin mass were shown in Figure 4d. As seen in Figure 4d, maximum percent recoveries (above 90%) were found using 1.0 g resin for both Cu^{2+} and Cd^{2+} ions. When above 1.0 g of resin was used, percent recoveries of Cu^{2+} and Cd^{2+} ions decreased. Therefore, 0.3 g of hazelnut shell powder and 1.0 g of resin optimized were mixed and used for further studies.

3.5. Effect of sample volume

The effect of sample volume is another critical parameter for obtaining reliable analytical results and high enrichment factors (EFs). Since natural waters especially contain trace metal ions, the highest volume of sample solution must be passed through SPE systems under optimum conditions [10, 29, 35]. Volume effect of sample solution on recoveries of Cu^{2+} and Cd^{2+} ions in nutshells immobilized on Amberlite XAD-4 resin was examined in the range of 25.0-400.0 mL solutions containing 2.0 µg mL^{-1} Cu^{2+} and Cd^{2+} ions by passing through SPE column under optimized experimental conditions. Means of recoveries of Cu^{2+} and Cd^{2+} ions found from three replicate measurements with standard deviations (less than 3%) versus volume of sample solution were shown in Figure 4e. As seen in Figure 4e, the averages of recoveries for Cu^{2+} and Cd^{2+} ions were found as 99.0 ± 1.8% and 98.3 ± 2.3%, respectively. When the sample volume was increased above 50 mL, recoveries of metal ions decreased slowly and constantly. It was observed that 50 mL sample solution was adequate for the preconcentration of Cu^{2+} and Cd^{2+} ions at optimized conditions for the next studies.

3.6. Reusability of SPE column

Reusability and cost of column workings in SPE are important for column stability in biosorption studies. The stability of the column was tested by using a 50.0 mL sample solution containing 2.0 µg mL^{-1} Cu^{2+} and Cd^{2+} ions. Cu^{2+} and Cd^{2+} ions retained on the sorbents were eluted with 5.0 mL of HNO_3 (1.0 mol L^{-1}) solution for Cu^{2+} and 5.0 mL of HCl (0.5 mol L^{-1}) solution for Cd^{2+} ions. If concentrations of ions were out of the calibration range, they were diluted with ultrapure water to measurable concentrations and analyzed by FAAS. Column reusability studied was shown in Figure 4f. As seen in the figure, the average percent recovery was higher than 85% for nearly 10 cycles. The column could be reused for 10 cycles sufficiently without reducing the retentions of Cu^{2+} and Cd^{2+} ions in column stability.

3.7. Effect of type, concentration and volume of eluent

The type, concentration and volume of eluent were investigated for reusability of nutshells biosorbent immobilized on Amberlite XAD-4 resin by minimizing damage and retention of metals [10, 29, 35, 45]. A suitable eluent was carried out to obtain a high EF for Cu^{2+} and Cd^{2+} ions from the SPE column. HCl and HNO_3 elution solutions were tested for desorption of Cu^{2+} and Cd^{2+} ions from biosorbent and resin at various volumes and concentrations. The averages of recovery results obtained with standard deviations (less than 2.5%) for three replicate measurements were given in Table 1. As seen in Table 1, when 5.0 mL of 1.0 mol L^{-1} HNO_3 eluent was used for Cu^{2+} ion, the percent recovery value found was about 96.5 ± 1.8%, and when 5.0 mL of 0.5 mol L^{-1} HCl eluent was used for Cd^{2+} ion, the percent recovery value was found as 94.2 ± 1.9%. Therefore, 5.0 mL of 1.0 mol L^{-1} HNO_3 for Cu^{2+} ion and 5.0 mL of 0.5 mol L^{-1} HCl for Cd^{2+} ion were suitable for studies. The EF for both analytes was found as 10 (50 mL sample/5 mL eluent). As result, we can say that the Cu^{2+} and Cd^{2+} ions in water samples can be directly determined at low concentrations using the method proposed and FAAS.

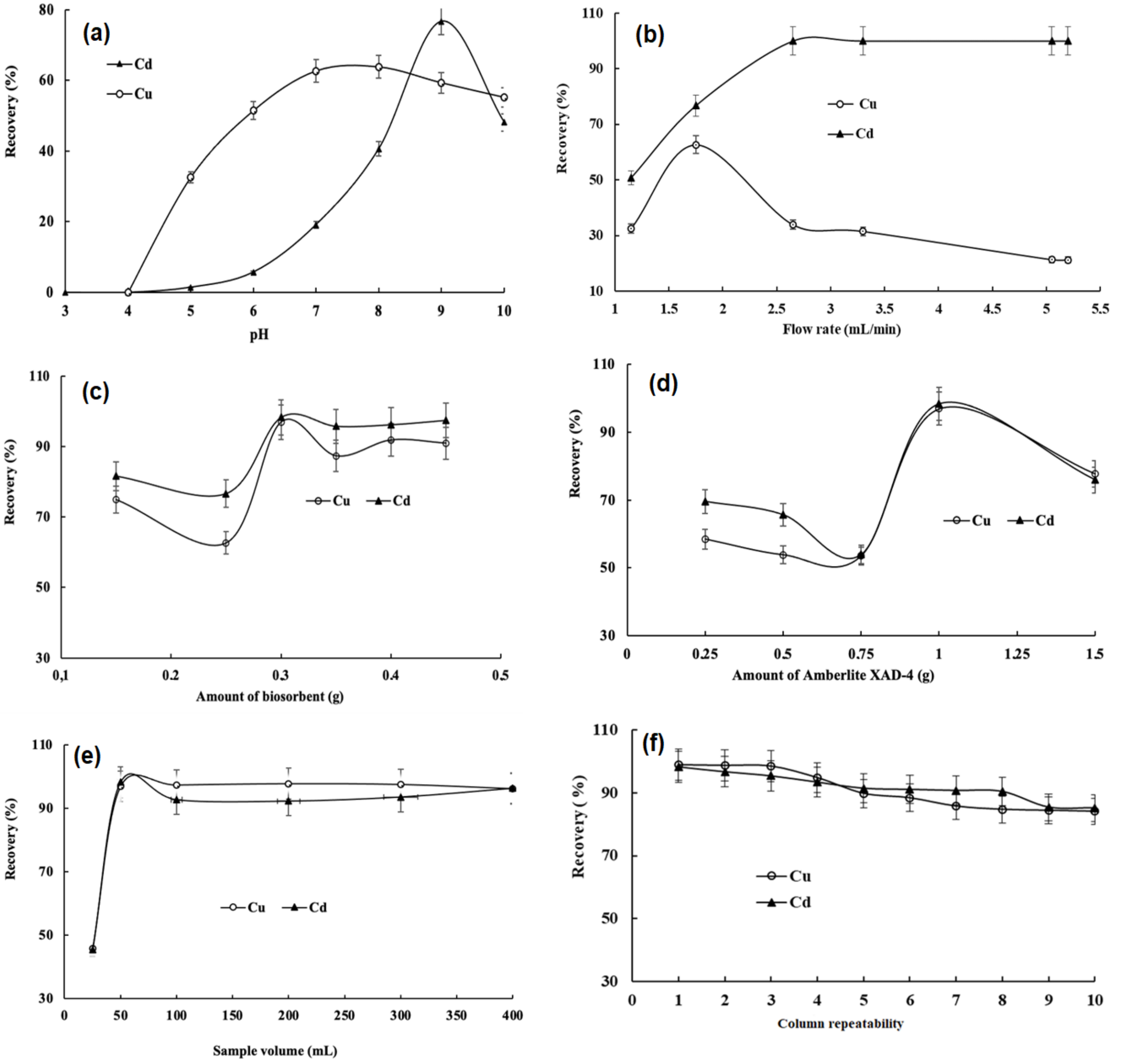

Figure 4. *(a) Recoveries of Cu^{2+} and Cd^{2+} ions with various pH of solutions, (b) Recoveries of Cu^{2+} and Cd^{2+} ions with various flow rates of a solution, (c) Effect of amount of hazelnut shell biosorbent for recoveries Cu^{2+} and Cd^{2+} ions by using 1.0 g of XAD-4, (d) Effect of Amberlite XAD-4 quantity for recoveries of Cu^{2+} and Cd^{2+} ions by using 0.3 g of hazelnut shell biosorbent, (e) Recoveries of Cu^{2+} and Cd^{2+} ions with various volume of sample solution, (f) Stability and reusability of the column with hazelnut shell immobilized on Amberlite XAD-4 for recoveries of Cu^{2+} and Cd^{2+} ions.*

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Table 1. *Optimization of type and volume of eluent solution for recoveries of Cu^{2+} and Cd^{2+} ions (N=3).*

Eluent type	**Concentration (mol L^{-1})**	**Eluent Volume (mL)**	**Recovery (%)[a]**	
			Cu^{2+}	**Cd^{2+}**
HCl	0.5	5	90.8 ± 1.7	94.2 ± 1.9
	1.0	5	87.9 ± 2.1	88.6 ± 2.0
	1.5	5	88.3 ± 1.9	88.5 ± 2.3
	2.0	5	87.6 ± 2.0	88.2 ± 2.1
HNO_3	0.5	5	90.8 ± 2.1	89.3 ± 1.8
	1.0	5	96.5 ± 1.8	80.5 ± 2.0
	1.5	5	93.7 ± 2.2	80.2 ± 2.3
	2.0	5	93.0 ± 2.0	80.1 ± 2.2

[a] 95% confidence level, N= 3, $\bar{x} \pm 4.30 \cdot s/\sqrt{N}$

3.8. Influence of interfering ions on recovery of metals

Due to foreign ions' matrix effects, the determination of trace levels of Cu^{2+} and Cd^{2+} ions in real water samples by FAAS is complicated [10, 46]. The effects of interfering ions on the determination of the analytes were studied by using optimized conditions obtained. Different interfering cations and anions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO4^{2-} and F^- were added to 50 mL test solution containing 2.0 µg mL^{-1} of Cu^{2+} and Cd^{2+} ions. Means of percent recovery results found from three replicate measurements with standard deviations (about 2%) by using FAAS were summarized in Table 2. As seen in Table 2, the average percent recoveries of analytes were generally higher than 80% for Cu^{2+} (except Ca^{2+} ion) and 83% for Cd^{2+} ions, respectively.

Table 2. *Optimization of type and volume of eluent solution for recoveries of Cu^{2+} and Cd^{2+} ions (N=3).*

Ion	**Salts added**	**Interference to metal ion ratio**	**Recovery[a] (%)**	
			Cu^{2+}	**Cd^{2+}**
Na^+	NaCl	2500	86.3 ± 2.0	97.1 ± 1.1
Cl^-	$BaCl_2$. $2H_2O$	5	81.9 ± 1.9	84.6 ± 1.5
SO_4^{2-}	$MnSO_4.H_2O$	12.5	86.2 ± 1.8	93.1 ± 1.6
Mg^{2+}	$Mg(NO_3)_2.6\ H_2O$	1250	82.9 ± 1.7	84.1 ± 1.8
Ca^{2+}	$CaCl_2.2H_2O$	750	72.4 ± 1.5	83.7 ± 1.7
F^-	KF	250	100 ± 1.0	90.2 ± 1.9

[a] 95% confidence level, N= 3, $\bar{x} \pm 4.30 \cdot s/\sqrt{N}$

3.9. Analytical features and applicability

Under optimized experimental conditions, the analytical features of the method proposed were performed and assessed. Analytical parameters obtained for Cd^{2+} and Cu^{2+} with the method developed were given in Table 3. By applying to preconcentrated blank solutions, limits of detection (LOD) and quantification (LOQ) values for Cu^{2+} and Cd^{2+} ions were determined. The LODs for Cu^{2+} and Cd^{2+} ions were depended on the ratio of three times standard deviations of absorbance signals for the blank solution to the slope of the calibration curve (LOD = $3x(S_b/m)$, N=12). After dividing the EF, the analytical LODs for Cu^{2+} and Cd^{2+} ions were found as 0.29 µg L^{-1} and 0.25 µg L^{-1}. Moreover, the LOQ values (LOQ = $10x(S_b/m)$, N=12) for Cu^{2+} and Cd^{2+} ions from related calibration curves were also found as 0.97 µg L^{-1} and 0.83 µg L^{-1}, respectively.

Table 3. *Analytical parameters of metals studied by FAAS with proposed method.*

Analytical Parameter	**Cd^{2+}**	**Cu^{2+}**
LOD (µg L^{-1})	0.25	0.29
LOQ (µg L^{-1})	0.83	0.97
Linear range (mg/L)	0.002 – 8.0	0.002 - 5.8
Regression equation	A = 0.1841 x C + 0.0023	A = 0.1339 x C + 0.0119
R^2	0.9975	0.9998

A = Absorbance, C = Concentration

The precision of the proposed method was tested by using 50 mL of a standard solution containing 2.0 µg mL^{-1} Cu^{2+} and Cd^{2+} ions. Means of recovery results obtained at 95% confidence level (N = 3) were given in Table 4. Relative standard deviations (RSDs) were found as 1.44% for Cu^{2+} and 1.21% for Cd^{2+} ions. Regression coefficients (R^2) were determined as 0.9998 and 0.9975 for Cu^{2+} and Cd^{2+} ions (Table 3), respectively.

To evaluate the accuracy of the method proposed, Cu^{2+} and Cd^{2+} ions in the certified BCR-670 aquatic plant sample (SRM) were determined under optimized conditions. The means of results found were illustrated in Table 4, and they were well consistent with certified values of SRM.

Table 4. *Precision and applicability of method proposed to SRM (BCR-670 Aquatic plant sample).*

Element	**Precision**		**BCR-670 aquatic plant sample**		
	$R \pm 4.30 \cdot s/\sqrt{N}$ (%)	**RSD (%)**	**Certified value (µg/kg)**	**Found (µg/kg)^a**	**Relative error (%)**
Cd^{2+}	98.3 ± 0.8	1.44	75.5 ± 2.5	74.2 ± 1.6	-1.72
Cu^{2+}	99.0 ± 0.2	1.21	1820 ± 300	1890 ± 214	3.85

^{a} 95% confidence level, N= 3, $\bar{x} \pm 4.30 \cdot s/\sqrt{N}$

Comparison of analytical characteristics of the method proposed with the recent methods developed for preconcentration of Cu^{2+} and Cd^{2+} ions with different instruments were illustrated in Table 5. It was clear that detection limits (LODs) and RSDs of Cu^{2+} and Cd^{2+} were compatible with the literature [47]. Besides, EFs found in this study were lower than the literature values [38, 39, 48, 49]. Because of this, the method proposed can be applied for the determination of trace levels of Cu^{2+} and Cd^{2+} ions in various samples.

Table 5. *Comparison of Analytical Features of Pre-concentration Methods for Cu^{2+} and Cd^{2+} ions.*

Method	**Instrument**	**Cu^{2+}**			**Cd^{2+}**			**Reference**
		LOD (µg L^{-1})	**EFs**	**RSD (%)**	**LOD (µg L^{-1})**	**EFs**	**RSD (%)**	
Synthesized 8-hydroxy-2-quinoline carboxy-aldehyde functionalized Amberlite XAD-4	FAAS	0.35	22.3	-	0.14	27.6	-	[48]
Mucor pusillus immobilized Amberlite XAD- 4 biocomposites	HR-CS FAAS	74	50	<8	62	50	<8	[39]
Synthesis and application of a new functionalized resin for use in an on-line, SPE system	FAAS	0.29	27.3	-	0.13	27.6	-	[49]
Preconcentration and determination of trace elements with 2,6-diacetylpyridine functionalized Amberlite XAD-4	FI-ICP-MS FI-FAAS	0.34 10	-	1.2–8.5	0.33 22	-	1.2–8.5	[47]
Bacillus subtilis – immobilized amberlite XAD-16	ICP-OES	0.21	36.4	4.9	-	-	-	[38]
Nutshell biosorbent immobilized on amberlite XAD-4	FAAS	0.29	10	1.44	0.25	10	1.21	This study

The method proposed was also applied to the determinations of Cu^{2+} and Cd^{2+} ions in actual water samples collected from different regions of Siirt city under optimum conditions. Results of analytes found in samples were demonstrated in Table 6. As seen in Table 6, the proposed method can be successfully applied to actual waters such as waste and tap waters.

Table 6. *Recoveries of metal ions in real water samples by applying the method proposed.*

Samples	**Recovery (%)[a]**	
	Cu^{2+}	**Cd^{2+}**
Waste water	99.2 ± 1.2	n.d.
Van lake water	40.1 ± 1.9	n.d.
Tap water	99.6 ± 1.3	n.d
Saline water	46.3 ± 2.0	n.d
Billoris spa water	67.9 ± 1.8	n.d.

[a] 95% confidence level, N= 3, $\bar{x} \pm t\cdot s/\sqrt{N}$, n.d.: Not detected

4. Conclusion

Using hazel nutshell powder as biosorbent immobilized on Amberlite XAD-4 resin, the SPE method was improved for recoveries of Cu^{2+} and Cd^{2+} ions from water solutions. It was discovered that both Cu^{2+} and Cd^{2+} ions were adsorbed by nutshell immobilized resin in the column at pH values 7.0 for Cu^{2+} and 9.0 for Cd^{2+} ions, respectively. In addition, the experimental parameters such as type and concentration of eluent, solution flow rate, solution volume, foreign ions on the recoveries of Cu^{2+} and Cd^{2+} ions, and column reusability were optimized. The feasibility of the proposed method was

validated by analyzing Cu^{2+} and Cd^{2+} ions in the BCR-670 aquatic plant sample. It was demonstrated that the concentrations of analytes found were in good consistent with certified values. Analytical characteristics of Cu^{2+} and Cd^{2+} ions obtained by the proposed method were compared with literature values and found in good agreement with reported values. The method proposed was applied to the determinations of Cd^{2+} and Cu^{2+} ions in actual water samples. It may be used to determine Cd^{2+} and Cu^{2+} ions in any solutions obtained from various samples in the future. It can be concluded that the method proposed is suitable in terms of simplicity, low analytical cost, sensitivity, precision, accuracy, reliability, and column stability.

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