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Solvent Impregnated Resins containing Quinizarin: Preparation and Application to Batch-mode Separation of Cd(II), Cu(II), Ni(II), and Zn(II) in Aqueous Media Prior to the Determination by Flame Atomic Absorption Spectrometry

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Abstract: Preparation of a high stable solvent impregnated resins (SIR) containing 1,4-dihydroxyanthraquinone (quinizarin, QNZ) was proposed using Amberlite XAD-16 beads. The SIR was applied for the separation of Cd(II), Cu(II), Ni(II), and Zn(II) in aqueous media prior to the determination by flame atomic absorption spectrometry (FAAS). The optimum conditions for batch mode extraction of the above metal ions were investigated and it was found that the sorption of these metal ions from a 1000-ml aliquots of the solution on 1.5 g of the SIR can be carried out quantitatively at pH of 9.5 and an ionic strength of 0.01 mol dm^{-3}. The sorbed metal ions were subsequently eluted with 10 ml 2 mol dm^{-3} HCl and the eluent was subjected to FAAS. Beer's law was obeyed in the range of $9 \times 10^{-9} - 1 \times 10^{-7}$ mol dm^{-3} for Cd(II) and Zn(II), and $9 \times 10^{-8} - 1 \times 10^{-6}$ mol dm^{-3} for Cu(II) and Ni(II) contents. Significant interference was not observed due to the various ions, which could be found in natural water samples. The practical applicability of the method was confirmed using a synthetic certificated reference material (CRM) and spiked natural water samples.

Keywords: Solvent impregnated resins, quinizarin, amberlite, XAD-16, FAAS

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INTRODUCTION

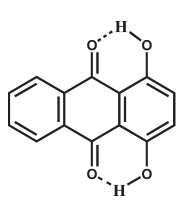
Efforts to determine trace metal ions directly and reliably by flame atomic absorption spectrometry (FAAS) is limited because of the low concentrations of analytes and matrix interferences. Therefore, the separation and enrichment techniques are of great importance in trace metal analysis by modern instrumental methods. To enhance the sensitivity and the precision of these methods, the preconcentration, and the separation techniques, such as coprecipitation (1–3), liquid-liquid extraction (4, 5), ion exchange (6, 7), and solid-phase extraction (8–10) are most frequently used. Solid-phase extraction using chelating resins is now widely used for the preconcentration of trace elements and cleaning up of various chemicals from a variety of predominantly aqueous solutions. There is continued interest in the development of chelating reagents for use in metal preconcentration systems. Appropriate chelating reagents can be chemically bounded to (11–16) or impregnated into support matrices (17–19), and provide complexing or chelating solid phases. Solvent impregnated resins (SIR) containing various types of reagents, are known as the simplest routes of conversion of the liquid-liquid extraction system into a solid-liquid one and have been widely used as extractants (20–23). The obvious advantages of SIR on traditional liquid-liquid systems are the ease of phase separation, the elimination of the problems attributed to form stable emulsions, and obtaining a high considerable preconcentration factor. Impregnation of an organic extractant into a polymeric support offers several advantages over the chemically bounding method, e.g.

i. the ease of preparation;
ii. the wide choice of reagents of desired selectivity;
iii. good extractant mobility in the resin phase and good metal mobility between the aqueous and the resin phase;
iv. high binding capacities;
v. good chemical and physical stability and low extractant loss (24–26).

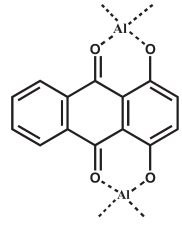
In spite of these advantages, the SIR systems frequently suffer from low stability due to the leak of the extractant from the polymeric support during their usage and gradual loss of SIRs capacity. Hence, the preparation of a high stable SIR system with time usage duration as long as the chelating resins or more should be desirable to eliminate this important drawback.

Dihydroxyanthraquinones (DHAQ) have been widely used as dye, chelating agent, and acid-base indicator (27–31). These reagents exist in phenolate anionic forms in moderately high pH media and are capable of binding readily with metal ions. Among the various DHAQ compounds, 1,4-dihydroxyanthraquinone (quinizarin, QNZ, 1) with the successive pK_a values of 9.26 and 11.79 (32), is one of the interesting reagents. As depicted in 2, it is capable of forming characterized chelates with a number of metal ions, such as aluminum through the ionized hydroxyl groups and adjacent carbonyl

moieties (33–37). However, it was reported that the metal chelation progresses very slowly in aqueous media so that it can not be used for the rapid determination of the metal ions (38). Previously, the chemisorption of QNZ on polar substrate, such as alumina has been investigated and showed that it is capable of bounding with the alumina surface via both adjacent carbonyl and hydroxyl functions (39). By considering the nonpolar exhibition of QNZ, which is attributed to the aromatic benzene rings and intra-molecular hydrogen bondings, it is expected that an inert support can be strongly impregnated with QNZ.



QNZ, 1



QNZ-Al Complex, 2

Among the various types of inert supports that are candidates, for impregnating with QNZ, Amberlite XAD series are preferred owing to the nonionic hydrophobic behaviors, purity, and good adsorption properties. In this series, Amberlite XAD-16 is the most appropriate adsorbent because of its excellent physical resistance, hydraulic characteristics, and thermal stability. In addition, it benefits from high porosity, low polarity, and the largest surface area (825 $m^2\ g^{-1}$).

In this work, Amberlite XAD-16 was chosen as the adsorbent for the impregnation process using QNZ, which was mixed with dichloromethane. The prepared SIR was used for batch-wise enrichment of the interested metal ions and the determinations were finally carried out using the FAAS technique.

EXPERIMENTAL

Instrumentation

A Shimadzu AA 6300 flame atomic absorption spectrometer equipped with a deuterium arc was used for the metal ion determinations. The operating parameters for such determinations were set as recommended by the company. A Corning model 130 pH-meter was used for pH measurements.

Materials and Solutions

All the reagents were of analytical grade, obtained from Merck, Germany, and were used without further purification. Deionized and double distilled water was

used in all of the experiments. The metal ions stock solutions of 1×10^{-3} mol dm^{-3} were made up from nitrate salts. The working solutions were prepared by diluting aliquots of the stock solutions. The solutions of ammonia and ammonium nitrate with concentrations of 1 mol dm^{-3} were prepared to adjust the pH of the experimental solution.

Solid Support Preparation and the Impregnation Process

Initially, to eliminate each type of impurity, which may be found with the untreated Amberlite XAD-16 beads, they were kept in contact with 1:1 methanol-water solution containing 4 mol dm^{-3} HCl for 12 h. The solid residual was washed with water until the chloride ions were practically absent in the filtrate and then it was stored in distilled water. To carry out the impregnation process, 11 g of dry polymer adsorbent was contacted with 20 ml of dichloromethane containing 3.0 g QNZ. The mixture was shaken for 24 h and then the impregnated beads were separated through a porous filter using a water pump, rinsed with water and 2 mol dm^{-3} HCl, sequentially. Finally, it was stored in distilled water.

Metal Extraction Procedure

The extraction of Zn(II), Cd(II), Cu(II), and Ni(II) ions were carried out through the batch experiments at ambient temperature. 1.5-g of the SIR was immersed into aliquots of the standard/sample solutions (1000 ml) containing the first two metal ions with the maximum concentrations of 1×10^{-7} mol dm^{-3}, and the last two up to 1×10^{-6} mol dm^{-3}. The ionic strength and buffered pH were respectively adjusted to 0.01 mol dm^{-3} and 9.5 using the ammonium and ammonia solutions. The mixture was shaken for 35 min and then the SIR was separated by filtering. After eluting the SIR with 10 ml of 2 mol dm^{-3} HCl, the eluent solution was subjected to the FAAS measurements.

RESULT AND DISCUSSION

Preparation and Characterization of the SIR

The impregnation process onto the hydrophobic internal surface of a macroporous nonionic resin is thought to proceed via a combination of two mechanisms:

i. the attractive force between alkyl chains and/or aromatic rings of ligands in the solvent structure and those of the resin backbone;
ii. the subsequent physical entrapment of these ligands within the pores of the resin beads (40).

In the present study, the SIR system was prepared using Amberlite XAD-16, which has the largest surface area of Amberlite series. It is a nonionic, hydrophobic, macroreticular aliphatic crosslinked polymer based on divinylbenzene, which derives its adsorptive properties from its continuous polymer phase and continuous pore phase. Essentially, the impregnation efficiency is directly related to the solubility of the ligand in the organic solvent. To obtain the appropriate impregnation efficiency, various types of organic solvents including tri and dichloromethane, acetone, methanol, and ethanol were employed. It was found that QNZ can be solved respectively much better in tri and dichloromethane than the other solvents. However, in spite of the high solubility of QNZ in trichloromethane, the impregnation process was carried out using dichloromethane because of lesser toxic properties. Figure 1 illustrates the weight change of the impregnated polymers as a function of the impregnation ratio (g QNZ/g polymer adsorbent). As it is shown, a plateau is reached at the impregnation ratio of 1.5 g QNZ/g polymer adsorbent, and therefore this value was adopted as the optimum impregnation ratio.

The chemical stability of the SIR was examined by sequentially treating a portion of 0.2-g of the SIR with 50-ml aliquots of 6 mol dm^{-3} HCl and 0.01 mol dm^{-3} NaOH and absorbance measurements of the solutions, spectrophotometrically, after 30 min and 48 h of shaking the mixtures. The results obtained are detailed in Table 1. It was found that no considerable amount of QNZ was released with such treatments. However, if the SIR should be exposed to more concentrated alkaline media, a slightly amount of the impregnated ligand was released.

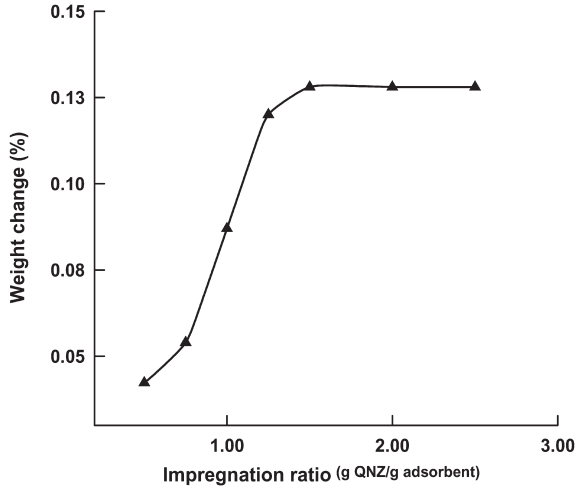


Figure 1. Effect of the impregnation ratio on the SIR preparation at the condition that portions of 1-g of the dry polymer beads of Amberlite XAD-16 was subjected to the impregnation process.

Table 1. Effect of acidic and basic media on stability of the SIR. The absorbance measurements were carried out at $\lambda_{max} = 545$ nm, and reported as the average of triplicate measurements with the related standard deviations

	Absorbance	
Medium	After 30 min	After 48 h
0.01 mol dm^{-3} NaOH	0.015 ± 0.03	0.028 ± 0.03
6 mol dm^{-3} HCl[a]	0.017 ± 0.03	0.021 ± 0.03

[a]The acidic solutions were initially neutralized and the media were made basic before the absorbance measurements.

Sorption and Desorption of the Metal Ions

As pointed above, the metal chelation with QNZ is a very slowly progress (41). In spite of such exhibition, the reaction between the SIR containing QNZ and some metal ions including Cd(II), Cu(II), Ni(II), and Zn(II) is significantly very fast. This phenomenon provides a situation in which the SIR can be employed for the separation and the preconcentration of these metal ions via the sorption/desorption process. It should be considered that the time required for the total sorption of a metal ion is attributed to the type of the metal ion and its kinetic behavior. To verify the time requested for the equilibrium for each one of these metal ions, aliquots of 500-ml of the buffered solutions, pH = 9.5, containing 0.1 μmol of the metal ion were subjected to a portion of 1.5-g of the SIR for several time durations. After that, the concentration of the metal ion in the eluent was measured by FAAS. As shown in Fig. 2, the total sorption of Zn(II) ions is completed relatively earlier than the others. However, to ensure from total sorption of the others, the shaking was continued for 35 min.

The effect of the pH on the sorption process was investigated in treatment with the solutions containing the interested metal ions in which the pH was varied within the range of 2–10.5. The pH values were adjusted using several buffering systems, such as hydrochloric acid–glycine (pH 1–3), acetic acid–sodium acetate (pH 3–6), ammonium acetate–ammonia (pH 6–8), and ammonium nitrate–ammonia (pH 8–10.5). As shown in Fig. 3, maximum sorption was achieved at pH of 9.5. Essentially, the low efficiencies of the sorption process at the pHs less than 9.5 are related to low acidic dissociation constants of QNZ, which in turn related to the presence of strong intra-molecular hydrogen bonding in its molecule. On the other hand, low efficiencies at the pHs greater than 9.5 are attributed to either precipitation as hydroxide compounds or complexation with ammonia and hydroxyl agents. With regard to these considerations, the buffering pH of 9.5 was selected for subsequent investigations.

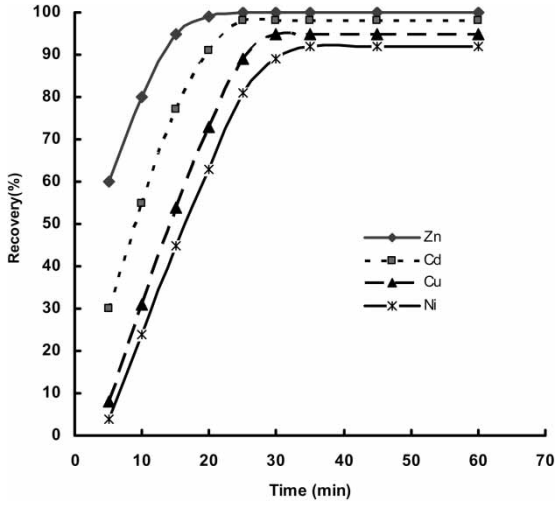


Figure 2. Effect of the shaking time on the sorption process. The metal ion initial concentrations are all equal to 2×10^{-7} mol dm^{-3}. The liquid volume is 500 ml, 1.5 g dried SIR, pH = 9.5.

The effect of the ionic strength on the sorption process was also studied by adjusting the pH of the solutions to 9.50 using various concentrations of ammonia/ammonium agents. It was seen that the sorption efficiencies were diminished at the ionic strength values greater than 0.1 mol dm^{-3}. Hence,

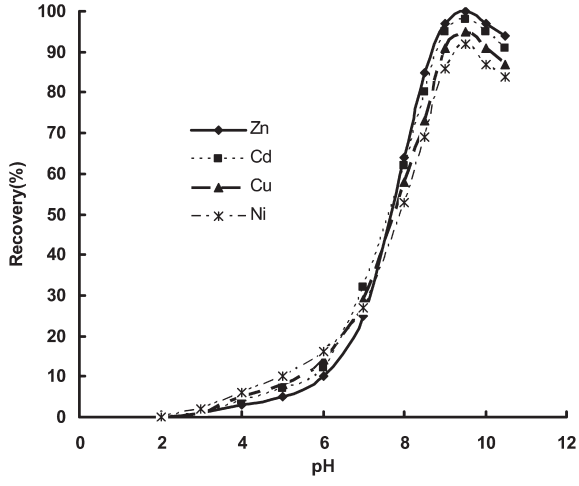


Figure 3. Effect of sample pH on sorption of the metal ions on the SIR. The metal ion initial concentrations are all equal to 2×10^{-7} mol dm^{-3}. The liquid volume is 500 ml, 1.5 g dried SIR.

the ionic strength was not exceeded from this value at subsequent investigations.

To find the appropriate eluent for desorption the metal ions from the SIR, various types of acid solution including nitric, sulfuric, and hydrochloric acid were examined at different concentration values. It was found that regardless of the type of the acid the elution process was not completed using the diluted solutions. The application of the concentrated solutions of nitric and sulfuric acids (more than 4 mol dm^{-3}) caused the SIR to be slowly oxidized and clogged with the precipitates that may have occurred. Since the SIR exhibited a considerable stability in acidic media of concentrated hydrochloric acid, solutions with the appropriate concentration of this acid were chosen as the elutent. The experiments showed that 10.0 ml of 2.0 mol dm^{-3} HCl was sufficient for the complete elution of the total sorbed metal ions.

To investigate the maximum sorption capacities of each type of the metal ions on the SIR, aliquots of the solutions (250 ml) containing each of the metal ions with concentration of 1×10^{-4} mol dm^{-3} were treated with portions of 1.5-g of the resin for 24 h at the optimum pH and room temperature. The loading capacity of the resin for each metal ion was calculated from the difference between the metal ion concentrations before and after the sorption processes. The values obtained were 226.3, 263.1, 211.9, and 299.7 μmol g^{-1} for Cd(II), Cu(II), Ni(II), and Zn(II) ions, respectively. The difference between the above quantities may be attributed to the distribution coefficients of these metal ions, which in turn related to stability constants of the metal-QNZ chelates. The preconcentration capability of the SIR was investigated in a series of experiments in which 1.5 g of the SIR was subjected to 1.0×10^{-4} mol of each type of the metal ions dissolved in various aliquots of the solutions (100, 250, 500, 1000, and 1500 ml). It was seen the recoveries obtained were satisfactorily the same and did not diminish by increasing the volumes up to 1000 ml. Hence, to obtain a high available preconcentration factor, further investigations were carried out using aliquots of 1000-ml of the standard/sample solutions. In another investigation, the sorption capacity of 1.5 g of the SIR associated with Zn(II) ions was tested semimonthly during a six-month employment. As shown in Fig. 4, the capacity of the SIR did not change significantly over the time usage.

Analytical Figures of Merit

Under the optimum conditions, the calibration curves for the determination of the above metal ions were linear over the ranges of $9 \times 10^{-9} - 1 \times 10^{-7}$ mol dm^{-3} for Cd(II) and Zn(II), and $9 \times 10^{-8} - 1 \times 10^{-6}$ mol dm^{-3} for Cu(II) and Ni(II) contents. The linear equations

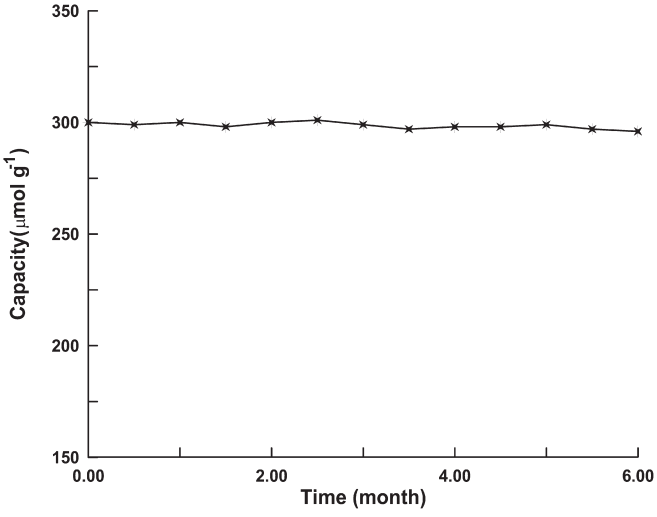


Figure 4. Effect of time usage on sorption capacity of the SIR. A portion of 1.5-g of the SIR was tested semimonthly for measurement of its Zn(II) sorption capacity during a six month employment.

along with regressions (R^2) are as follows.

$$\text{Cd(II)}: \quad A = 1.87 \times 10^6 C + 0.0022; \quad R^2 = 0.9992$$

$$\text{Zn(II)}: \quad A = 1.70 \times 10^6 C + 0.0157; \quad R^2 = 0.9991$$

$$\text{Cu(II)}: \quad A = 5.73 \times 10^5 C + 0.0020; \quad R^2 = 0.9987$$

$$\text{Ni(II)}: \quad A = 2.59 \times 10^5 C + 0.0012; \quad R^2 = 0.9984$$

Where A is the peak area of absorbance and C is the concentration in mol dm^{-3}. All the statistical calculations are obtained based on the average of triplicate reading for each standard solution in the given ranges.

The quantities of limit of detection (blank + 3σ) where σ is S.D. of the blank estimations were evaluated as given in the parentheses: Cd (5×10^{-10} mol dm^{-3}), Zn (3×10^{-9} mol dm^{-3}), Cu (1×10^{-8} mol dm^{-3}), and Ni (1×10^{-8} mol dm^{-3}).

The relative standard deviation values were measured by seven successive sorption/desorption cycles using the solutions with the concentration of 5×10^{-8} mol dm^{-3} (Cd(II) and Zn(II)), and 5×10^{-7} mol dm^{-3} (Cu(II), and Ni(II)). The obtained results were as 1.71%, 2.15%, 1.53%, and 1.01% for Cd(II), Zn(II), Cu(II), and Ni(II) ions, respectively.

Effect of Interfering Ions

The effect of interfering ions on the sorption process was studied in treatment with 1000- ml aliquots of the solutions containing the interested metal ions with the concentration of 1×10^{-7} mol dm^{-3} and each one of the interfering ions with the concentration of 1×10^{-4} mol dm^{-3}. Before the sorption process, the solution was filtered for separation of each type of precipitate that may be formed during the preparation process. The results are given in Table 2. Each of the species was considered as interference when the signal exhibits a deviation more than $\pm 5\%$ in the presence of it. Moreover, the SIR has shown a high tolerance limit for the alkali and the alkaline earth metal ions as the electrolytes including NaCl, $NaNO_3$, K_2SO_4, and KNO_3, with the concentration of 1×10^{-3} mol dm^{-3}. This is particularly useful for the analysis of the metal ions in natural samples.

Analysis of Real Samples

In order to investigate the validity of the proposed method, a synthetic water sample was prepared adapting to composition of SRM 1643d, by following the literature considerations (41). The results of the expected and found values of the interested metal ions concentrations are shown in Table 3. Satisfactory recoveries, being in the range of 94.7 to 104.3%, were

Table 2. Effect of interfering ions with concentration of 1.0×10^{-4} mol dm^{-3} on the determination of the interested metal ions with equal concentrations of 1.0×10^{-7} mol dm^{-3} in 1000 ml aliquots of the solutions[a]

Interfering ion	Zn recovery (%)	Cd recovery (%)	Cu recovery (%)	Ni recovery (%)
Al^{3+}	98.78 ± 0.11	94.25 ± 0.12	92.35 ± 0.10	91.41 ± 0.11
Pb^{2+}[b]	99.87 ± 0.12	95.6 ± 0.10	93.21 ± 0.11	90.38 ± 0.12
Mg^{2+}	100.10 ± 0.10	96.23 ± 0.11	89.58 ± 0.11	90.25 ± 0.10
Mn^{2+}[b]	101.24 ± 0.12	97.65 ± 0.12	91.27 ± 0.10	90.37 ± 0.11
Co^{2+}	98.86± 0.10	95.52 ± 0.11	92.05 ± 0.10	90.31 ± 0.10
Ca^{2+}	102.00 ± 0.10	97.59 ± 0.10	92.18 ± 0.10	89.91 ± 0.11
Ba^{2+}	99.17 ± 0.10	96.25 ± 0.10	—	89.58 ± 0.12
Hg^{2+}	100.86 ± 0.12	95.01 ± 0.11	90.05 ± 0.12	88.76 ± 0.11
Cd^{2+}	69.80 ± 0.10	—	92.61 ± 0.11	51.48 ± 0.11
Cu^{2+}	76.75 ± 0.10	65.25 ± 0.10	50.21 ± 0.11	54.55 ± 0.12
Ni^{2+}	78.56 ± 0.10	74.82 ± 0.12	55.85 ± 0.12	—
Zn^{2+}	—	45.38 ± 0.10	41.87 ± 0.11	40.57 ± 0.11

[a]Average and standard deviation of three determinations.

[b]The major contents of these ions were precipitated and separated by filtering the solution before the sorption process.

Table 3. Determination of Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} in 1000 ml aliquots of the synthetic certified sample of SRM 1643d

	Concentration ($\mu g\ dm^{-3}$)		
Metal ion	Expected	Found (n = 3)	Recovery (%)
Cd^{2+}	6.47	6.35 ± 0.13	98.1
Cu^{2+}	20.5	19.58 ± 0.42	95.6
Ni^{2+}	58.1	55.04 ± 1.21	94.7
Zn^{2+}	72.48	75.62 ± 1.47	104.3

obtained. The agreement between found and expected values of the metal ions concentrations demonstrated that the described method was accurate for trace analysis of such metal ions in the complex matrices. The proposed method was also applied to determine the above metal ions in several natural water samples collected from water sources of Birjand

Table 4. The chemical composition of the natural water samples that were collected from the water sources of Birjand city and used for investigation of applicability of the proposed method

Measurand	Drinking water	Tap water	Well water
Alkalinity, Total (as CaCO3)	16.7	185	92.7
Ammonia (as N)	0.004	0.02	0.045
Boron	0.006	0.064	0.025
Calcium	26.1	91.2	42.8
Chloride	6.18	105.6	64.5
Dissolved inorganic Carbon	25.1	45.7	24.9
Dissolved organic Carbon	1.7	4.9	1.7
Fluoride	0.16	0.07	0.05
Hardness, total (as CaCO3)	96.4	338	163
Magnesium	7.36	27.5	11.8
Nitrate + Nitrite	0.252	4.3	2.56
pH	7.83	8.32	8.00
Potassium	0.97	4.2	2.7
Silica (as Si)	0.482	2.27	1.16
Sodium	4.85	48.5	38
Sulfate (as SO4)	14.8	112	46
Total Kjeldahl Nitrogen (TKN)	0.09	0.13	0.35

Table 5. Determination of the investigated metal ions in aliquots of 1000-ml of the natural water samples

	Spiked (μmol)°				Found[a] (μmol) ± s (nmol)				Recovery (%)			
Sample	Zn^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Ni^{2+}
Drinking	—	—	—	—	—	—	—	—	—	—	—	—
water	0.0360	0.0360	0.360	0.360	0.0370 ± 0.0021	0.0355 ± 0.0021	0.355 ± 0.017	0.351 ± 0.012	102.8	98.6	98.6	97.5
Tap water	—	—	—	—	0.309 ± 0.019	—	—	0.042 ± 0.010	—	—	—	—
	0.0360	0.0360	0.360	0.360	0.347 ± 0.021	0.0356 ± 0.016	0.357 ± 0.019	0.391 ± 0.015	105.6	98.9	99.2	96.9
Well	—	—	—	—	0.519 ± 0.023	—	0.062 ± 0.012	0.037 ± 0.013	—	—	—	—
water	0.0360	0.0360	0.360	0.360	0.555 ± 0.022	0.354 ± 0.019	0.417 ± 0.015	0.388 ± 0.017	100.0	98.3	98.6	97.5

[a]Average and standard deviation of three determinations.

city. The chemical composition of these water samples are detailed in Table 4. Before the treatment, they were filtered through a membrane filter with a pore size of 0.45 μm before the determinations. The analysis process was carried out according to the recommended procedure using 1000-ml aliquots of the samples. The accuracy of the determinations was investigated using the spiked water samples with these metal ions at the various concentrations. The obtained results are summarized in Table 5. As observed from the results, the recoveries for the added amounts were found to be 96.9–105.6%, which confirmed satisfactorily applicability of the proposed method for complicated environmental samples.

CONCLUSION

The results of the present work proved that the SIR containing QNZ, which were easily prepared, presents a good potential for the selective separation and preconcentration of the recommended metal ions. It benefits from a high capacity, selectivity, and good stability in high acidic and basic media. It is also stable against sorption/desorption processes without significant mass loss effect during the employment for a long time. These behaviors can be considered as the advantages of the above SIR system on some other SIRs that suffer from these limitations (25, 42–46). Furthermore, in comparison with the synthetic functional resins, the important advantages of the above SIR system are including the high capacity and fast reactivity factors (47, 48). One of the characteristic features of the present work is its high preconcentration capability for the metal ions under investigation, especially when the concentrations are usually very low in the water samples. The method benefits from a low detection limit and high preconcentration factor. More investigation about this type of SIR is now under examination in our lab.

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