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Use of clinoptilolite loaded with 1-(2-pyridylazo)-2-naphthol as a sorbent for preconcentration of Pb(II), Ni(II), Cd(II) and Cu(II) prior to their determination by flame atomic absorption spectroscopy

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Use of clinoptilolite loaded with 1-(2-pyridylazo)-2-naphthol as a sorbent for preconcentration of Pb(II), Ni(II), Cd(II) and Cu(II) prior to their determination by flame atomic absorption spectroscopy

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A solid phase extraction system for separation and preconcentration of trace amounts of Pb(II), Ni(II), Cd(II) and Cu(II) is proposed. The procedure is based on the adsorption of Pb²⁺, Ni²⁺, Cd²⁺ and Cu²⁺ ions on a column of 1-(2-pyridylazo)-2-naphthol (PAN) immobilised on surfactant-coated clinoptilolite prior to their determinations by Flame Atomic Absorption Spectroscopy (FAAS). The effective parameters including pH, sample volume, sample flow rate and eluent flow rate were also studied. The analytes collected on the column were eluted with 5 mL of 1 mol L⁻¹ nitric acid. A concentration factor of 180 can be achieved by passing 900 mL of sample through the column. The detection limits (3 s) for Cd, Cu, Pb and Ni were found to be 0.28, 0.12, 0.44 and 0.46 µg L⁻¹, respectively. The relative SDs at 10 µg L⁻¹ (*n* = 10) for analytes were in the range of 1.2–1.4%. The method was applied to the determination of Pb, Ni, Cd and Cu in water samples.

Keywords: flame atomic absorption spectroscopy; clinoptilolite; solid phase extraction; 1-(2-pyridylazo)-2-naphthol; preconcentration

1. Introduction

Trace heavy metal determinations are receiving at present particular attention due to their strong environmental impact. Flame atomic absorption spectroscopy (FAAS) has been widely used for the determination of trace metals, because of low costs and easy applications. However, the direct determination of metal ions by FAAS is limited due to their low concentration and matrix interferences. In order to solve the problems, a preconcentration/separation step is frequently necessary for their determination by FAAS. Several methods have been employed for separation and preconcentration of trace elements according to the nature of the samples, the concentration of the analytes and the measurement techniques. These include coprecipitation [1], flotation [2], solvent extraction [3], cloud point extraction [4] and solid phase extraction [5–14]. Among them, solid phase extraction is one of the most effective preconcentration methods because of simplicity, rapidity and ability to attain a high preconcentration factor.

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A variety of solid materials such as activated carbon [7], Amberlite XAD resins [8,9], microcrystalline naphthalene [10], silica gel [11], chitosan [12], chromosorb resins [13] and zeolites [14] have been used for preconcentration of trace metals. Zeolites are highly crystalline aluminosilicate frameworks comprising $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral units. The aluminium ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, and isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is neutralised by the exchangeable cations e.g. Na^+ , K^+ , Ca^{2+} and Mg^{2+} . Zeolites have been used for the removal of some heavy metals from wastewater [15]. Zeolites have also been used in the preparation of composite adsorbent for removal of UO_2^{2+} and Th(IV) in aqueous sample [16]. Clinoptilolite is the most abundant natural zeolite with relatively high cation exchange capacity. Clinoptilolite exhibits a high selectivity for NH_4^+ and is effective in removing ammonia from wastewater [17]. The quaternary amine methyltriethylammonium is a cationic surfactant that possesses a permanent positive charge. When brought into contact with clinoptilolite, the cationic surfactant selectively exchanges with the inorganic cations on the surfaces of the zeolite particles and forms hemi-micelles or ad-micelles.

Ionic surfactants adsorb on solid surfaces such as alumina [18], silica [19], clays [20], hydrated iron(III) oxide [21] and Amberlite XAD-2 resin [22] forming aggregates termed hemi-micelles and ad-micelles, which present a high potential to be used as sorbent materials in solid phase extraction (SPE). Modification of the clinoptilolite with cationic surfactant is similar to the modification of clay and produces a product which sorbs sparingly soluble organic substances [23].

1-(2-Pyridylazo)-2-naphthol (PAN) is a well-known reagent for the spectrophotometric determination of a variety of transition metal ions. It acts as a tridentate ligand complexing with metals through the hydroxyl oxygen atom, pyridine nitrogen atom and one of the azo group nitrogen atoms. It has also been used for the separation and preconcentration of trace heavy metals in various media [24–26]. In this work, PAN is immobilised on methyltriethylammonium-coated clinoptilolite. Then, the sorbent is used for separation and preconcentration of trace amounts of lead(II), nickel(II), cadmium(II) and copper(II) in water samples prior to their determinations by FAAS.

2. Experimental

2.1 Apparatus

A Buck Scientific atomic absorption spectrometer (model 210 VGP, USA) was used for the analysis. The hollow cathode lamps of lead, nickel, cadmium and copper were run under the conditions suggested by the manufacturer and air-acetylene flame was used for all measurements. A Metrohm model 691 pH meter with a combined glass electrode was employed for measuring the pH of solutions.

2.2 Reagents

Doubly-distilled deionised water and analytical reagent grade chemicals (E. Merck, Darmstadt, Germany) were used throughout. Cadmium, copper, nickel and lead standard stock solutions (1000 mg L^{-1}) were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$. Working solutions were prepared daily from the stock solution by appropriate dilution with water. A 0.025% of PAN was prepared by dissolving

Table 1. The chemical composition of clinoptilolite.

Chemical constituent	Amount (wt%)
SiO ₂	68.96
Al ₂ O ₃	11.96
CaO	2.32
Na ₂ O	1.87
MgO	1.31
TiO ₂	0.21
Fe ₂ O ₃	1.40
Loss on ignition	9.78

0.025 mg of PAN in 100 mL of ethanol. The natural zeolite used in this work is clinoptilolite from the Semnan region in the centre of Iran. The chemical composition of the clinoptilolite used in this study was given in Table 1 [27].

2.3 Preparation of surfactant-coated clinoptilolite

The clinoptilolite was ground and sieved to a size range of 0.125–0.140 mm. The ammonium ion has a high affinity for clinoptilolite. Therefore, it can be used to replace exchangeable cations. Thus, H-clinoptilolite was prepared from the ammonium form of clinoptilolite by calcinations at 660 K for 2.5 h. The quaternary amine, methyltriocetylammmonium chloride, was used for modifying the zeolite surface as follows: 250 mL of methyltriocetylammmonium chloride solution (50 mmol L⁻¹) was added to clinoptilolite, the resulting suspension shaken for 12 h and then the adsorbent dried at room temperature.

2.4 Preparation of PAN-coated clinoptilolite column

The surfactant coated clinoptilolite (1.00 g) was added to a glass column (500 mm height × 5 mm internal diameter). Then, 5 mL of 0.025% PAN solution in ethanol was passed through the column at a flow rate of 0.5 mL min⁻¹. Afterwards it was washed with water until excess reagent was eliminated from column.

2.5 Analytical procedure

The pH of sample (not more than 900 mL) was adjusted to ~8.5 by addition of ammonium hydroxide solution and was passed through the PAN-coated clinoptilolite column at a flow rate 5 mL min⁻¹. After passing the sample, the adsorbed metal ions were eluted with 5 mL of 1 mol L⁻¹ nitric acid at a flow rate of 1 mL min⁻¹. The concentration of metal ions in the eluate was determined by FAAS.

3. Results and discussion

3.1 Optimisation of variables

The optimised conditions for the enrichment procedure were established using 50 mL of aqueous solutions containing 10 µg of each element and submitting these solutions to the

preconcentration procedure. Various parameters such as pH, sample volume, sample flow rate and eluent flow rate were investigated. The percentage of metal retained was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the column.

The effect of pH on the retentions of Cu^{2+} , Cd^{2+} , Ni^{2+} and Pb^{2+} on the column was examined. Metal ions were enriched on the PAN-coated clinoptilolite column in the pH ranges 3.0–9.0, keeping the other parameters constant. The optimum pH range for quantitative recoveries of Pb, Ni, Cd and Cu is 8.0–9.0. The progressive decrease in the retention of analytes at a low pH is due to the competition of the hydrogen ion with the analytes for reaction with PAN. To achieve high efficiency, all subsequent studies were carried out at pH \sim 8.5.

The desorption of the analytes from the PAN-coated clinoptilolite column was studied using 5 mL of nitric acid solutions at concentration of 0.25–2 mol L⁻¹, as eluent. The recoveries of analytes increased with nitric acid concentration up to 0.8 mol L⁻¹ and then levelled off at higher concentration. A concentration of 1 mol L⁻¹ of nitric acid was selected for further studies.

The flow rate of the sample solution affects the retention of cations on the sorbent and on the duration of complete analysis. Therefore, the effect of the flow rate of sample solution was examined in the range of 1–7 mL min⁻¹. It was found that the retention of the analytes was practically not changed up to a flow rate of 5 mL min⁻¹. The adsorption of the analytes decreases slightly when the flow rate is over 5 mL min⁻¹. Therefore, a flow rate of 5 mL min⁻¹ was selected for subsequent work. The effect of eluent flow rate on the recoveries of analytes was also investigated. With 5 mL of 1 mol L⁻¹ nitric acid solution, quantitative elution of analytes from the column was achieved in a flow rate of 0.5–3 mL min⁻¹.

For the preconcentration of trace metal ions in liquid samples, the method used must have high preconcentration factor. To obtain a high preconcentration factor, sample volume is an important factor. The effect of sample volume on the recoveries of analyte ions was investigated in the range of 100–1200 mL. The adsorption of metal ions was not affected by sample volume below 900 mL. At the higher volumes, the recoveries for analytes decreased. Consequently, a preconcentration factor of 180 can be achieved by using 900 mL of the sample volume and 5.0 mL of final elution volume.

3.2 Adsorption capacity

Adsorption capacity is an important factor to evaluate the sorbent, as it determines how much solid phase is required for a given solution. In order to study the adsorption capacity of sorbent, the batch method was used. To 1.0 g PAN-coated clinoptilolite was added 50 mL of solution containing 2 mg of analyte ion at pH 8.5. After shaking for 1 h, the mixture was filtered. Ten millilitres of the supernatant solution was diluted to 100 mL and determined by FAAS. The capacity of the sorbent was found to be 3.82, 3.02, 6.04 and 5.18 $\mu\text{mol g}^{-1}$ of PAN-coated clinoptilolite for Cd(II), Pb(II), Cu(II) and Ni(II), respectively.

3.3 Interferences

In order to examine the effect of possible matrix ions in natural water samples on the determination of cadmium, lead, copper and nickel with the proposed procedure,

Table 2. Effect of matrix ions of natural waters on the recoveries of the analytes ($N=3$).

Ion	Added as	Concentration (mg L^{-1})	Recovery (%)			
			Cd	Cu	Pb	Ni
Na^+	NaCl	10,000	95.2 ± 1.3	96.3 ± 0.8	96.4 ± 1.6	96.7 ± 3.2
K^+	KCl	1000	98.7 ± 2.1	97.3 ± 1.4	95.2 ± 2.6	96.4 ± 2.0
Ca^{2+}	CaCl_2	800	98.2 ± 1.5	99.6 ± 1.2	96.6 ± 3.1	97.8 ± 0.7
Mg^{2+}	MgCl_2	1000	97.4 ± 1.8	97.2 ± 2.8	98.4 ± 2.9	96.2 ± 2.9
Cl^-	NH_4Cl	15,000	98.6 ± 3.1	97.2 ± 3.3	97.8 ± 1.3	97.1 ± 1.5
SO_4^{2-}	$(\text{NH}_4)_2\text{SO}_4$	1000	97.1 ± 2.3	98.9 ± 1.6	98.3 ± 1.8	98.0 ± 2.4

fixed amounts of analytes ($5 \mu\text{g}$) were taken with various amounts of matrix ions and the procedure was followed. A relative error of less than 5% was considered to be within the range of experimental error. The results were summarised and tabulated in Table 2. It can be mentioned that the major ions normally present in water do not interfere. Also, the effect of some transition metal ions (Al^{3+} , Fe^{3+} , Zn^{2+} , Mn^{2+} and Co^{2+}) on the recovery of $5 \mu\text{g}$ of cadmium, lead, copper and nickel from 500 mL of sample solution was investigated. These transition metals at 500 ng mL^{-1} did not interfere with the recovery of the analyte ions. These results show that the recommended separation/preconcentration method can be used for the determination of analytes in different water samples.

3.4 Analytical characteristics

Under the optimum conditions above, the calibration curves were obtained by using 500 mL of preconcentration volumes at $\text{pH} \sim 8.5$. Calibration curves were linear in the concentration range of $1.0\text{--}60 \mu\text{g L}^{-1}$ Cd, $0.5\text{--}50 \mu\text{g L}^{-1}$ Cu, $5\text{--}50 \mu\text{g L}^{-1}$ Pb and $5\text{--}70 \mu\text{g L}^{-1}$ Ni.

The limit of detection (LOD) of Cd, Cu, Pb and Ni for 500 mL volumes as three times the SD of the blank (3s) was found to be 0.28, 0.12, 0.44 and $0.46 \mu\text{g L}^{-1}$, respectively.

The precisions for six determinations of $10 \mu\text{g L}^{-1}$ of Cd, Cu, Pb and Ni (sampling volume 500 mL) were 1.3, 2.4, 1.2 and 1.8%, respectively.

At the 10 ng mL^{-1} level of Cd(II), Pb(II), Cu(II) and Ni(II), the relative SD (10 replicate analysis) was 1.3, 1.2, 1.4 and 1.3%, respectively.

3.5 Applications

The method was applied for the determination of Cd, Pb, Cu and Ni in tap water, well water and river water samples. The reliability of procedure was checked by the spiking experiments and by comparing the results with data obtained by graphite furnace atomic absorption spectroscopy (GFAAS). The results given in Table 3 show that the recovery of the spiked sample is good and at 95% confidence level, there is no significant difference between the results and data obtained by GFAAS.

Table 3. Determination of analytes in water samples.^a

Element	Tap water (Yazd city)			River water (Zayandeh Rood)			Sea water (Caspian)			
	Added ($\mu\text{g L}^{-1}$)	Found ^b ($\mu\text{g L}^{-1}$)	GFAAS ^b ($\mu\text{g L}^{-1}$)	Recovery (%)	Found ^b ($\mu\text{g L}^{-1}$)	GFAAS ^b ($\mu\text{g L}^{-1}$)	Recovery (%)	Found ^b ($\mu\text{g L}^{-1}$)	GFAAS ^b ($\mu\text{g L}^{-1}$)	Recovery (%)
Cd	–	1.6±0.1	1.53±0.06	–	4.9±0.2	5.10±0.24	–	1.3±0.1	1.21±0.04	98
	10.0	11.4±0.2	–	98	14.5±0.1	–	96	11.1±0.3	–	–
Cu	–	5.6±0.1	5.72±0.24	–	6.7±0.2	6.78±0.33	–	8.1±0.3	7.94±0.41	98
	10.0	15.5±0.3	–	99	16.4±0.3	–	97	17.9±0.5	–	–
Pb	–	<LOQ ^c	0.39±0.02	–	6.1±0.1	6.12±0.25	–	10.2±0.3	9.94±0.45	101
	10.0	10.2±0.2	–	102	16.0±0.3	–	99	20.3±0.4	–	–
Ni	–	<LOQ	<LOQ	–	5.2±0.1	5.36±0.13	–	5.8±0.1	5.72±0.27	97
	10.0	9.9±0.2	–	99	15.5±0.3	–	103	15.5±0.2	–	–

Notes: ^aSample volume, 500 mL.^bMean and SD related to three determinations.^cLower than limit of quantification.

Table 4. Comparison of the proposed method with some previously solid phase extraction methods using PAN as a chelating agent.

Metals	Adsorbent	Technique	PF	DL ($\mu\text{g L}^{-1}$)	RSD (%)	Reference
Cd	Naphthalene	DPP	50	70	0.98	[10]
Pb	Naphthalene	FAAS	100	0.3	1.5	[24]
Cu, Ni, Cd, Pb, Cr, Co	Ambersorb 563	FAAS	125	0.21–1.4	<10	[25]
Cu, Cd, Pb	Amberlite XAD-2	FAAS	50	0.8–23.2	<5	[9]
Cu, Ni, Cd, Pb, Cr, Mn	Amberlite XAD-4	FAAS	200	0.16–0.45	–	[8]
Cd	Surfactant-coated alumina	FAAS	100	0.024	1.6	[26]
Pb, Cd	Chromosorb-106	FAAS	250	0.19–0.32	<8	[13]
Ni	Surfactant-coated alumina	FAAS	300	40	2.4	[18]
Cu, Cd, Pb, Ni	Surfactant-coated clinoptilolite	FAAS	180	0.12–0.46	<1.5	Present study

Notes: PF: Preconcentration, RSD: Relative SD, DL: Detection limit, DPP: Differential pulse polarography, FAAS: Flame atomic absorption spectroscopy.

4. Conclusions

A simple preconcentration method for the determination of Cd(II), Cu(II), Pb(II) and Ni(II) from aqueous solution at micrograms per litre levels by FAAS is presented. The trace elements are sorbed onto a column of PAN-coated clinoptilolite. The metals are quantitatively desorbed with 1 mol L⁻¹ nitric acid. The metals are quantitatively desorbed with 1 mol L⁻¹ nitric acid. The preparation of sorbent is easy and it can be used at least 10 times without any significant change in the recovery of metal ions. Comparative data from some literature on preconcentration studies using PAN are summarised in Table 4. A preconcentration factor of 180, which is achieved by this method, is superior to those of some solid phase extraction methods [9,10,24–26]. The detection limits of investigated elements (0.12–0.46) are also lower than some previously reported methods [9,10,18]. The method can be applied for determination of cadmium, copper, lead and nickel in a variety of water samples with low detection limit, high accuracy and high precision.

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