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Solid Phase Extraction of Cu(II) and Zn(II) Using Ligand Immobilized Silica Gel for the Removal, Recovery, Preconcentration vis-à-vis Separation from Mixture

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1. Introduction

In any component of an ecosystem, the occurrence and concentration of heavy metals depend largely on their sources. Generally seven major categories of sources of metal contamination of the terrestrial environment can be identified. These are (i) natural sources, such as surface weathering, volcanic out gassings, spontaneous combustion or forest fires, (ii) the use of metal containing agricultural sprays, soil amendments like sewage, active sludge and garbage (iii) the disposal of wastes from mines or mills, (iv) emissions from large industrial sources such as metal smelters and refineries, (v) emissions from moving sources, principally auto mobiles, (vi) emissions from municipal utilities, such as coal or oil fired electricity generating stations or municipal incinerators and (vii) other relatively minor sources of terrestrial contamination, such as smaller scale industries that process metals.

An ecosystem which has developed on a substrate rich in heavy metals the primary route of heavy metals to the ecosystem components is either via soil/water or water/soil system. As the contamination continues metal uptake by plants both from soil and water system occurs, but in different extent. Further, from environment point of view removal as well as recovery of heavy metals is of great significance considering the ever-increasing demand of water of high quality. Sometimes mutual separation of metal ions from bisolute composition becomes evident for precise analytical determinations.

Both copper and zinc find wide use in various industries and as a result huge amount of such metals are discharged into the environment destroying the natural balance of the ecosystem in various ways [1]. Copper is largely used in electrical machinery and for electroplating. The main use of zinc is for the manufacturing of several useful alloys and as the anode material in galvanic cells. Discharge of wastes from such industries increase the load of metal contamination, which in turn enter the different components of the ecosystem.

Copper is known to affect plant growth and may induce changes in metabolism. In human beings copper accumulates in liver, brain, kidney and cornea. Ingestion of excessive amounts of oral copper salts, most frequently copper sulphate, may produce death. Copper poisoning producing hemolytic anemia has been reported in case of burn treatment with copper compounds or as the result of using copper containing dialysis equipment. Zinc toxicity from excessive ingestion is uncommon but gastrointestinal distress and diarrhea has been known following ingestion of beverages standing in galvanized cans or from use of galvanized utensils. With regard to industrial exposure, metal fume fever resulting from inhalation of freshly formed fumes of zinc presents the most significant effect. In view of the load and degree of toxicity of Cu(II) and Zn(II) the minimization of toxicity becomes a prime requirement [2, 3]. Removal of metal toxicants from aqueous environment becomes critical as well as a challenging task to the chemists and environmentalists as they are non biodegradable and have long residence time in the environment. Sometimes the preconcentration from a large volume of aqueous samples becomes a primary step. Recent progress in chemical analysis of trace metal ions is mainly connected with the evaluation and improvement of various separation and trace concentration methods.

Liquid-liquid extraction has long been used for the removal of metal ions from aqueous samples but the large volume of solvent, tedious process and large through output led the scientists in search of alternative techniques. Solid phase extraction method using some solid extractants, as have some advantages over liquid-liquid extraction, is now gaining the popularity. The solid extractants range from the natural materials to synthetic materials as well as the biomaterials [4]. Ion exchange materials [5, 6], activated carbon [7, 8] and activated slag [9] are widely used for the purpose of metal ion separation and recovery. Chelate polymer impregnated over solid substances like polyurethane foam and cellulose [10÷12] show their marked potential. In our laboratory ligand immobilized over silica gel was successfully used for the enrichment of metal ions and decontamination or purification of alkali metal, alkaline earth metal and ammonium salts [13÷15]. Silica gel, as a solid support for ligand immobilization, has some special advantages like less swelling property, high resistance towards heat and acid treatment. For the synthesis of solid phase extractant silica gel surface can be modified with chelating ligands either via physical treatment [14], chemical reaction [16÷20]. The present communication deals with solid phase extraction of Cu(II) and Zn(II) using ligand immobilized silica gel for the removal, recovery, preconcentration vis-à-vis separation from bisolute composition.

2. Experimental

2.1. Apparatus

Batch experiment was performed in glass container with 1g of the solid extractant. A glass column (160 x 6 mm i.d) with a coarse sintered glass disc and a tap at the bottom was used for the column study.

The absorbance spectra of the solution were registered with a UV-VIS Spectrophotometer (Shimadzu PC 1401). The IR spectra were registered with an IR spectrophotometer (Perkin Elmer L120-000A), samples being prepared as thin films between KBr windows. A Systronics pH meter (Model 324) with glass electrode was used for pH measurements. Voltammetric experiments of the metal solutions were performed with an electrochemistry apparatus (PAR Model 173). Atomic absorption measurement was recorded on an atomic absorption spectrometer (Perkin Elmer AA 1407) equipped with a standard burner with an air-acetylene flame. Standard hollow cathode lamps were used as a line source. The operating characteristics of the instrument for the metal ion estimation are as follows:

Metal ion	Lamp current (mA)	Wavelength (nm)	Slit width (mm)
Cu(II)	4.0	324.8	0.5
Zn(II)	5.0	213.9	1.0

2.2. Materials

All chemicals were of analytical reagent grade. Silica gel H 4267 of particle size 60 μm, specific surface area 420 m^2g^{-1} and pore size 120°A was obtained from Sigma. Stock solutions of copper and zinc (200 $mgdm^{-3}$) were prepared by dissolving respective metal chloride in doubly distilled water. pH of the experimental solution in the range 3.5÷6.0 was maintained by acetate buffer by mixing the required volumes of 0.2 $moldm^{-3}$ acetic acid and sodium acetate. pH below 3.5 was maintained by HCl while pH above 6.0 was maintained by NaOH solution.

For the preparation of the solid extractant silica gel was first refluxed with 6.0 $moldm^{-3}$ HCl for about 3 hours to remove contaminating metals such as iron. It was then washed with deionised water and dried under reduced pressure at 150°C. The dried silica gel was refluxed with salicylaldoxime in ethanol

(10% w/w) at 70÷80°C for 4 hours. The solid thus obtained was filtered and dried under vacuum.

2.3. Retention procedure

2.3.1 Batch Experiment

Batch experiments were performed to obtain rate and equilibrium data. The flask containing 20 cm^3 of metal solution (20÷200 $mgdm^{-3}$) maintained at definite pH was agitated with 1.0 g of prepared extractant in a mechanical shaker for the attainment of the equilibrium. The remaining metal ion in the supernatant was determined by atomic absorption spectrometry. The amount of metal ion retained by the extractant was determined by the equation,

$$N_f = (X-Y)/Z$$

where, X is the initial amount of metal ion added (μg), Y the equilibrium amount of metal ion remained in supernatant (μg), Z the mass of the extractant (g) and N_f the equilibrium amount of metal ion (μg) retained per gram of the extractant.

2.3.2. Column Experiment

Column experiment was performed for elution of the metal. A funnel type glass tube was used as chromatographic column. The column was fitted with cotton at the end and packed with the extractant [21]. Respective metal ion solution at a definite pH (2.0 to 8.0) was percolated at a definite flow rate of 5.0 cm^3min^{-1}. After washing the column with about 20 cm^3 of deionsed water, an eluting solution of definite composition (HNO_3 or $HClO_4$) was passed through at a flow rate of 3.0 cm^3min^{-1}. The metal ion concentration in the eluate, after diluting to the desired volume, was determined by AAS. Wet digestion of the samples with HNO_3 and H_2SO_4 was performed prior to estimate copper concentration by AAS following the standard procedure [22]. An air-acetylene flame was used with the observation at 10 mm above the burner at the respective wavelength of the metal ion.

3. Results and Discussion

3.1. Characterization of the solid phase extractant

The IR spectrum of the extractant show characteristic peaks of salicylaldoxime [23] suggesting that the ligand was immobilized as such without any structural change on the silica gel. In another experiment ethanol was passed through the column packed with a weighed quantity of the extractant to remove all the ligand immobilized with silica gel. The eluate gave identical absorption band of salicylaldoxime. Quantitative determination showed that the amount of sailylaldoxime in the extractant was 0.2 mmolg^{-1} of silica gel.

3.2. Retention behavior of metal ions on the extractant

3.2.1 Batch experiment

Effect of initial metal ion concentration and shaking time: The retention of metal ion on the extractant in a batch process is found to depend on both initial metal concentration and the agitation period. The time at which equilibrium is attained is considered as the equilibrium time and the corresponding concentration in the solution is the equilibrium concentration. The dependence of the Cu(II) retention (with different initial concentrations) on agitation time is shown in Fig.1. It is evident from the figure that the uptake of Cu(II) increases with lapse of time and reaches the saturation time in 30 minutes for each initial Cu(II) concentration. The maximum retention of 98% Cu(II) was observed at an initial concentration of 20 mgdm^{-3} which decreases to 63.5% for an initial concentration 100 mgdm^{-3} and further decreases to 46.7% when the initial concentration increases to 200 mgdm^{-3}. Similar nature of retention behavior was observed for Zn(II) but with different extent. A maximum retention of 96.0% was observed at 45 minutes for Zn(II) at an initial concentration 20 mgdm^{-3} that decreases to 78.0% for an initial concentration 100 mgdm^{-3} and further decreases to 60.9% when the initial concentration increases to 200 mgdm^{-3}.

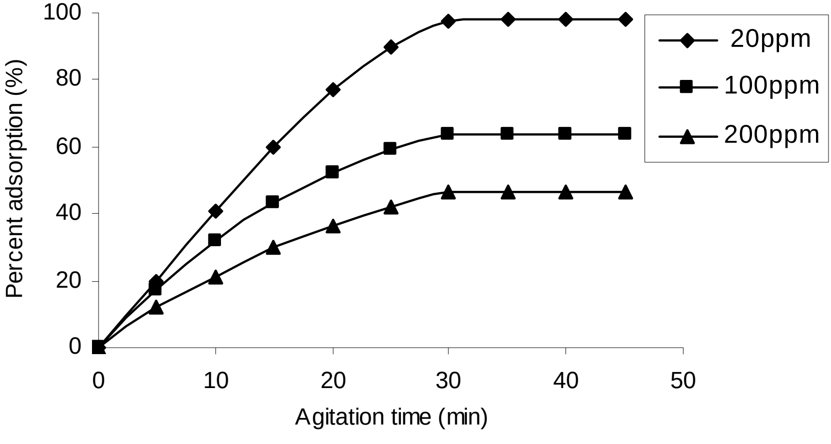

Fig. 1. Influence of agitation time and initial Cu(II) concentration on adsorption
Rys. 1. Wpływ czasu mieszania i początkowego stężenia Cu(II) na adsorpcję

The percent retention of each metal ion is thus increases as the initial metal ion concentration decreased. It may be thought that with higher metal ion concentration for a fixed amount of extractant, the available retention sites relative to the metal ions load becomes fewer. A comparison of adsorption behavior indicates that both the equilibrium time and the extent of metal retention follow the order Cu(II)> Zn(II).

Effect of agitation speed: The agitation rate was varied from 100 to 400 rpm keeping the initial metal concentration 20 mgdm^{-3}. The effect of agitation speed on the retention of Cu(II) ion on the extractant is presented in Fig. 2. The results indicate that the uptake increases from 61 to 98% with increase in agitation speed. For a similar situation the uptake of Zn(II) increases from to 56.0 to 96.0%. As the agitation speed increases, resistance to mass transfer in the bulk solution decreases resulting in the increased driving force and hence the increased retention of metal ion on the extractant [24].

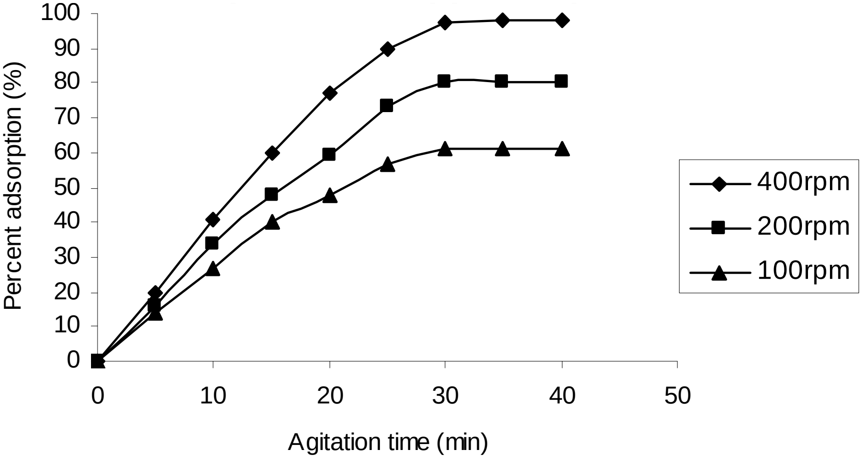

Fig. 2. Influence of agitation time and speed on Cu(II) adsorption
Rys. 2. Wpływ czasu oraz prędkości mieszania na adsorpcję Cu(II)

Effect of the amount of the extractant: The effect of the amount of the extractant on the percent retention of metal ions was studied (Fig. 3) varying the amount of extractant from 0.1 to 1.0 g for 20 cm^3 metal solution at pH 2.2 for Cu(II) and at pH 5.5 for Zn(II).

Effect of pH: The retention behavior of the metal ions on the modified silica gel (m), the extractant, at different pH values was investigated and compared with the unmodified silica gel (u). It is found that Cu(II) retains quantitatively at pH 2.2 and Zn(II) at pH 5.5 (Fig 4). However, for the control measurement with unmodified silica gel, different behavior for each metal was observed.

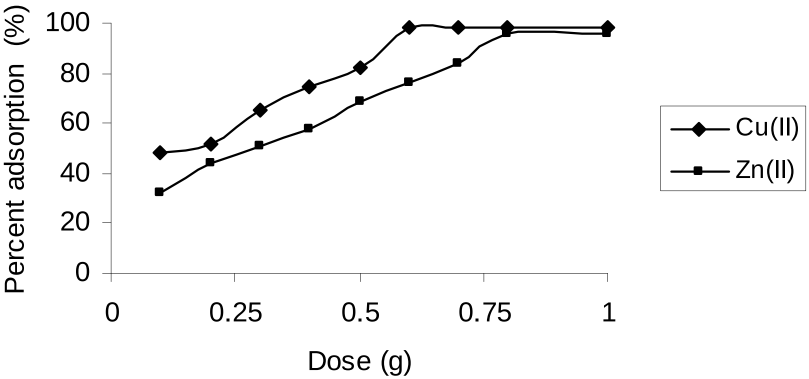

Fig. 3. Influence of dose on adsorption of metals
Rys. 3. Wpływ dawki na adsorpcję metali

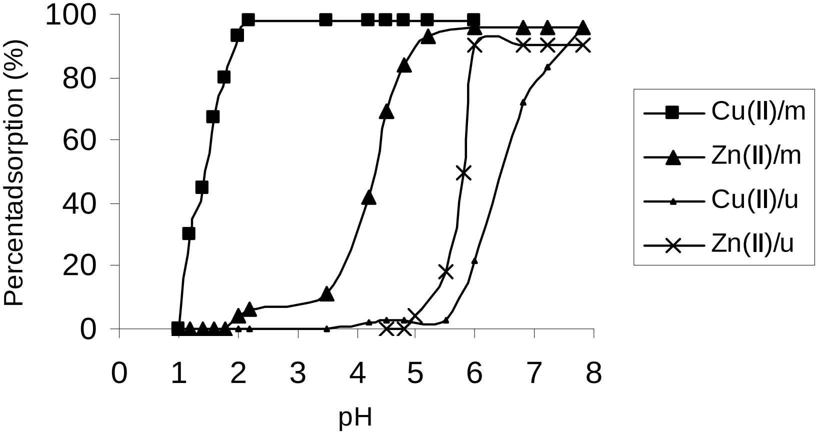

Fig. 4. Influence of pH on adsorption of metals
Rys. 4. Wpływ pH na adsorpcję metali

Effect of temperature: The temperature has an influence on the metal retention. It is found that retention of both Cu(II) and Zn(II) on the extractant increases with increase in temperature. Figure 5 represents the retention behavior of Cu(II) ion at different temperatures. The retention pattern of Zn(II) is found similar; although the extent of increase is different. It is found that for an initial metal concentration of 200 mgdm^{-3} and temperature increase from 298 to 318 K, the percent retention of Cu(II) increases from 46.7 to 56% and that of Zn(II) from 60.9 to 78%.

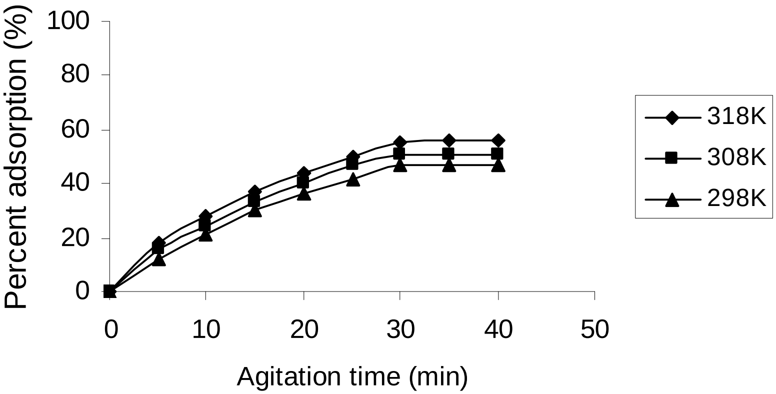

Fig. 5. Influence of agitation time and temperature on Cu(II) adsorption
Rys. 5. Wpływ czasu mieszania i temperatury na adsorpcję Cu(II)

Retention of metal ions on the solid extractants is generally decreases with increased temperature, although there are reports for increased retention with increase in temperature. Solid phase extraction of metal ions, in fact, is a complex process consisting of surface interactions like ion exchange, adsorption, surface complexation as well as the pore diffusion. The relative contribution of each of the interaction to the equilibrium determines the overall situation. In fact the overall equilibrium constant increases with temperature and as a result the retention of metal on the present extractant increases. Detailed mechanistic study using surface complexation model may be helpful in predicting the exact behavior. The equilibrium retention data when fitted to the Langmuir adsorption isotherm model, gives the adsorption capacity of respectively for Cu(II) and Zn(II). The process is favorable from thermodynamic view point, as evidenced from the negative G values of respectively for Cu(II) and Zn(II).

The metal ion retention, as studied above, varying the operational variables determines the conditions for highest retention. The optimum conditions for highest Cu(II) retention (6.17 μmolg^{-1}) are; agitation time: 30 minutes, agitation speed: 400 rpm, extractant dose: 1.0 g, pH: 2.2, temperature: 318 K. The optimum conditions for highest Zn(II) retention (5.91 μmolg^{-1}) are; agitation time: 45 minutes, agitation speed: 400 rpm, extractant dose: 1.0 g, pH: 5.5, temperature: 318 K.

Tolerance level of electrolytes, foreign ions: Different electrolytes such as sodium chloride, potassium nitrate and potassium chloride possess higher tolerance during metal retention. Other ions and salts show different levels of tolerance (Table 1). The efficiency of the extraction is evaluated with the synthetic and spiked samples and is presented in Table 2.

Table 1. Tolerance limit of different diverse ions
Tabela 1. Granice tolerancji dla różnorodnych jonów

Ion	Tolerance limit	
	Cu(II)	Zn(II)
KNO_3, NaCl, NH_4Cl, Na_2SO_4, KCl	1 g	1 g
$NaClO_4$	500 mg	500 mg
NH_4F	100 mg	150 mg
$K_2C_2O_4$,NaSCN	200 mg	200 mg
KI, KCN	100 μg	200 μg
EDTA	5 μg	5 μg
Mg(II), Ca(II), Mn(II), Al(III)	1 g	1 g

Cu(II): 20 μgcm^{-3}, pH 2.2; Zn(II): 20 μgcm^{-3}, pH 5.5

Table 2. Recovery of metal ions from synthetic and spiked samples
Tabela 2. Odzysk jonów metali z próbek syntetycznych wzorców wewnętrznych

Sample No.	Metal added		Cu(II)		Zn(II)	
	Mean	Spiked	Found (μgcm^{-3})	Recovery (%)	Found (μgcm^{-3})	Recovery (%)
	(μgcm^{-3})					
1	1.0	0.0	0.92±0.04	98.0	0.92±0.04	95.8
2	1.0	0.5	1.38±0.04	98.0	1.38±0.04	96.0
3	1.0	1.0	1.84±0.05	98.5	1.84±0.05	96.1
4	1.0	5.0	5.53±0.06	98.2	5.53±0.06	95.7
5	1.0	10.0	10.16±0.05	98.4	10.16±0.05	96.2
6	1.0	20.0	19.32±0.04	98.0	19.32 ±0.04	95.8

(n = 5; Standard deviation < 0.06; 95% confidence level)

3.2.2. Column experiment

The effect of flow rate of the solution through the column on the retention behavior of metal ion solution was studied over the range 1.0 to 10.0 cm^3min^{-1}. The extent of metal retention was found to remain unchanged up to the flow rate of 10.0 cm^3min^{-1} for Cu(II) and 8.0 cm^3min^{-1} for Zn(II). In the present study flow rate for metal ion retention was maintained at 5.0 cm^3min^{-1}. Again when the volume of the sample solution was varied no change in the extent of metal retention was observed up to a volume of 1000 cm^3.

3.2.2.1. Electroanalytical study

Voltammetric study was performed to characterize as well as to determine the metal concentration in the effluent from the column. Thus the effectiveness of removal in extractant column can be judged from the constructed voltammogram. The blank sample solution of Cu(II) and Zn(II) mixture put to the voltammetric determination shows the analytical peaks at -0.29 and -0.98 V corresponding to Cu(II) and Zn(II) respectively [13]. The same mixture of metals solution after passing through the extractant bed shows only the base line peak in the voltammogram. This indicates that the metal ions has retained in the column bed, effective quantitative removal of Cu(II) and Zn(II).

Table 3. Column behavior of metal ions
Tabela 3. Zachowanie się jonów metali w teście kolumnowym

Metal ion	Highest flow rate during retention (cm^3min^{-1})	Eluent strength ($moldm^{-3}$)		Elution Volume (cm^3)	Recovery (%)	P.F	Lower limit of detection (μgdm^{-3})
		HNO_3	$HClO_4$				
Cu(II)	10.0	1.4	0.4	15	98	66	1.0
Zn(II)	8.0	0.4	0.01	25	96	40	2.0

Influent sample volume: 1000 cm^3; P.F: Preconcentration factor;

3.2.2.2. Elution of the retained metals from mixture

In an aim to recover, preconcentrate or separate metal ions from aqueous samples elution of retained metals from the extractant was studied. Metal loaded extractant was subjected to interaction with a varying concentration of HNO_3 or $HClO_4$. The flow rate during elution was maintained at 3.0 cm^3min^{-1}. About 98.0% of retained Cu(II) was recovered when treated with either 1.4 $moldm^{-3}$ HNO_3 or 0.4 $moldm^{-3}$ $HClO_4$ within a small volume of 15 cm^3. The elution was found effective with either HNO_3 (0.4 $moldm^{-3}$) or $HClO_4$ (0.01 $moldm^{-3}$) and about 96.0% of the added Zn(II) was recovered within 25 cm^3 of the eluent. The preconcentration factor for Cu(II) and Zn(II) were evaluated as 66 and 40 respectively.

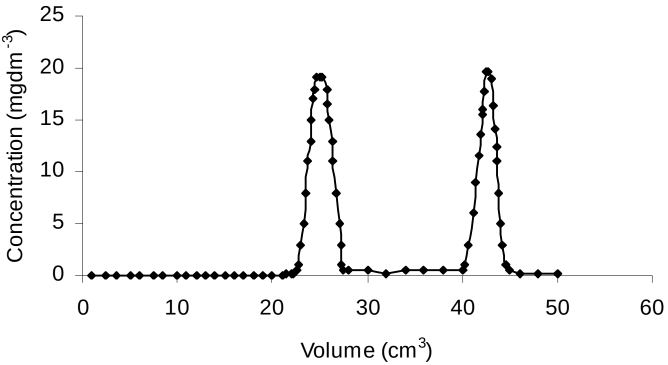

Fig. 6. Elution curve for metals
Rys. 6. Krzywe elucji metali

The separation of individual metal ions from their bisolute composition (each metal with 20 mgdm^{-3}) is done with gradient elution with HNO_3 (0.4 moldm^{-3} followed by 1.4 moldm^{-3}). Zn(II) appears first and Cu(II) the next (Fig 6). The band width corresponds to about 5.0 cm^3 and the resolution factor 2.0.

4. Conclusion

The present investigation shows that salicylaldoxime immobilized silica gel as a solid phase extractant can be employed for the removal, recovery, preconcentration vis-à-vis separation of Cu(II) and Zn(II) from bisolute composition. The removal was found to depend on time of contact, initial metal concentration, agitation speed, temperature and pH of the medium. The equilibrium data fits well the Langmuir adsorption isotherm model. The process is favorable both from kinetic and thermodynamic points. The high uptake rate represents significant advantage over those of conventional resin based ion exchange. In column extraction the quantitative recoveries of Cu(II) and Zn(II) (98 and 96%) makes the process comparable with other known methods viz., solvent extraction and ion exchange [25]. The lower detection limit calculated as the concentration of metal with a signal to noise ratio equal to 2 makes the process much effective. Considering the enrichment factor of 66 and 40 corresponding to Cu(II) and Zn(II) at least 1.0 and 2.0 μgdm^{-3} of Cu(II) and Zn(II) respectively can be detected by the proposed method. Moreover the separation of Cu(II) and Zn(II) from the mixture with high resolution makes the process viable for analytical work.

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Ekstrakcja SPE Cu(II) i Zn(II) przy zastosowaniu liganda immobilizującego silikażelu do usunięcia, odzysku, koncentracji przy separacji z mieszaniny

Streszczenie

Ekstrakcja ciecz-ciecz jest od dawna stosowana do usuwania jonów metali z próbek wodnych lecz duże objętości rozpuszczalników, długi proces i duży przerób zmusiła naukowców do poszukiwania alternatywnych metod. Metoda Solid Phase Extraction (SPE), używająca stałych ekstrahentów, posiadająca wiele zalet w porównaniu metodą ciecz-ciecz, zyskuje popularność. W laboratorium autorów ligand immobilizujący silikażelu z powodzeniem został zastosowany do wzbogacania jonów metali i oczyszczenia metali alkalicznych, metali ziem alkalicznych i soli amonowych. Silikażel, jako stały szkielet ligandu immobilizującego, posiada szczególne zalety, takie jak: mniejsze pęcznienie, duża odporność na działanie temperatury i kwasów. Do syntezy stałego extrahentu powierzchnia silikażelu może być modyfikowana ligandami chelatującymi albo poprzez obróbkę fizyczną jak i chemiczną.

Przedstawione wyniki badań pokazują, że aldoksym salicylowy immobilizujący silikażel jako stały ekstrahent może być stosowanym do usuwania, odzysku, koncentracji przy separacji Cu(II) i Zn(II) z roztworu dwuskładnikowego. Usunięcie zależy od czasu kontaktu, początkowego stężenia metalu, prędkości mieszania, temperatury i pH ośrodka. Dane równowagi dobrze pasują do modelu Langmuira izotermy adsorpcji. Proces jest korzystny zarówno z kinetycznego jak i termodynamicznego punktu widzenia. Wysoka szybkość adsorpcji stanowi znaczną przewagę nad konwencjonalnymi żywicami jonowymiennymi. W teście kolumnowym ilościowy odzysk Cu(II) i Zn(II) (98 i 96%) stawia ten proces na równi z innymi znanymi metodami, mianowicie: ekstrakcją rozpuszczalnikami i wymianą jonową. Niższy limit detekcji obliczony jako stężenie metalu ze stosunkiem sygnałem do tła równego 2 poprawia efektywność procesu. Biorąc po uwagę współczynniki wzbogacenia 66 dla Cu(II) i 40 dla Zn(II) co najmniej 1,0 $\mu g \cdot dm^{-3}$ Cu(II) i 2,0 $\mu g \cdot dm^{-3}$ Zn(II) może być oznaczony za pomocą proponowanej metody. Ponadto oddzielenie Cu(II) i Zn(II) z mieszanki z wysoką rozdzielczością sprawia, że proces jest przydatny do pracy analitycznej.