Equilibrium and Kinetics of Copper(II) Extraction from Aqueous Solution by 1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone Doped Mesoporous Silica

Amarawan Intasiri* and Tuanjai Yubolpas

Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

ABSTRACT: The Cu(II) extraction properties of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP) doped mesoporous silica, prepared by a template-tailored sol-gel process were investigated through batch and column methods. The Cu(II) sorption capacity of the modified sorbent, as determined by batch experiments, appeared to be governed not only by the pH of the metal solution but also by the presence of alkali salts. The adsorption rate on the modified silica was entirely consistent with pseudo-second order rate kinetics. The principal parameters affecting the Cu(II) desorption efficiency of the sorbent in the column method was determined using a 2^3 factorial design. The significant factors found were the amount of Cu(II) loaded and the concentration of HNO_3. The analysis of the adsorption equilibrium data obtained from the column experiments revealed that the adsorption process followed a Langmuir isotherm. The Cu(II) sorption capacity of the modified silica, determined by the column process, was found to be 5.74 mg g^{-1} and copper(II) ions were successfully preconcentrated from aqueous solution by a factor of 40. The sorbent was reusable without considerable loss of adsorption capacity. The method has been successfully applied to the extraction and recovery of Cu(II) ions from real samples.

Key words: Sorption, batch, column, kinetic order, factorial design

INTRODUCTION

Solid-phase extraction (SPE) is a preconcentration method with rapidly growing importance in various analytical fields and especially for the extraction and separation of metal salts from environmental matrices.(1-3) This technique is superior to conventional liquid-liquid extraction in terms of simplicity, speed and high enrichment factor. However, the method still needs development to increase its efficiency. The development of a novel modified silica as a sorbent for metal extraction has been of growing interest in SPE research. A variety of functionalization methods, such as grafting,(4-7) impregnation(8,9) and doping,(10-17) have been studied fairly extensively for the modification of the sorbent. Among these methods, the doping technique is gaining popularity especially for its high versatility and simplicity. In this method, metal-binding organic ligands are incorporated in silica through a sol-gel process, which reduces the leaching of organic molecules and controls the physicochemical properties of the resulting materials.

To this end, there have been numerous studies on the modification of silica using a doping technique and the application of these modified materials for the extraction and determination of metal ions. Examples of doping molecules are: ethylenediaminetetraacetic acid (EDTA) for the extraction of Cu(II), Ni(II), Fe(III), Cr(III), Co(II), Mn(II), Pd(II) and Ir(IV);(10) dimethylglyoxime (DMG) for Ni(II);(11) 1-(2-thiazolylazo)-2-naphthol (TAN) for Zn(II);(13) 1-(2-pyridylazo)-2-napthol (PAN) for Cd(II)(14) and 1,5-diphenylcarbazide (DPC) for Hg(II).(15) Nevertheless, the application of the doped materials to the extraction of Cu(II) ions from aqueous solution has been limited.

Correspondence to : e-mail: amarawan.i@chula.ac.th

The use of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP) (Figure 1) as an extractant molecule has been reported extensively in liquid-liquid extraction, due to its excellent potential to form stable complexes with various metal ions.(18-21) However, relatively few studies have reported on the use of HPMSP as a complexing agent for the much more efficient SPE technique. Tong and coworkers(22,23) prepared a microporous silica impregnated with HPMSP for the extraction of metal ions including Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Mn(II), Zn(II) and Fe(III). They studied the conditions for effective adsorption in both batch and column methods and used the impregnated material for the preconcentration of metal ions in sodium chloride medium and from tap water. Our research team(12) recently introduced the use of HPMSP as a doping molecule to increase metal extraction properties of mesoporous silica and established the high availability of HPMSP to ions present in the aqueous phase and the excellent Cu(II) extraction capacity of the doped silica. Subsequently, the sorption of Cu(II) and Eu(III) by a mesostructured silica doped with one chelating head (HPMSP) and two chelating heads (1,12- bis(1′-phenyl-3′-methyl-5′-hydroxyl-4′-pyrazolyl, HL-10-LH) was studied,(16,17) revealing that the solid-liquid extraction occurred at a lower pH than in liquid-liquid extraction. The complexes formed in the doped silica are comparable to those obtained in solvent extraction.

For a better understanding of the physico-chemical properties of HPMSP doped mesoporous silica, we scrutinized the Cu(II) adsorption rate and capacity of the modified sorbent using different kinetic models and sorption isotherms. We also examined the parameters affecting the Cu(II) sorption properties, for example, pH, salts and concentration of eluent and demonstrated the potential application of the HPMSP doped material as a sorbent for Cu(II) extraction from environmental samples.

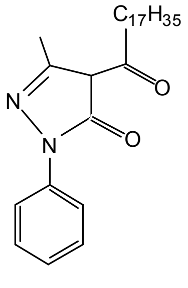

Figure 1. Chemical structure of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP, $C_{28}H_{44}N_2O_2$).

EXPERIMENTAL

Apparatus

A Perkin Elmer AAnalyst 100 atomic absorption spectrometer equipped with a hollow cathode lamp at a wavelength of 324.7 nm using an air-acetylene flame was used for the determination of Cu(II) concentration. The flow of liquid through the column was controlled by a Millipore® Waters Model 510 HPLC pump. A Denver pH-meter calibrated against two standard solutions of pH 4.0 and 7.0 was used for pH measurements.

Reagents

Tetraethoxysilane (TEOS) and cetyltrimethylammonium bromide (CTAB) were obtained from Fluka. Solvents, salts and other reagents in analytical grade were purchased from Merck and used directly without further purification. HPMSP was prepared and purified according to Jensen.(24) The HPMSP doped mesoporous silica was synthesized and characterized according to the published procedure.(12) The synthesis begins with the solubilization of the extractant molecule in a micellar media followed by the precipitation of silica around micelles. A standard solution of copper was prepared by dissolving requisite amounts of $Cu(NO_3)_2{\cdot}3H_2O$ in 0.01 M HNO_3. The solution used throughout the experiment was prepared using water purified by a Milli-Q Water System from Millipore. All containers and glassware were soaked in 3.0 M HNO_3 for 24 hours and rinsed three times with deionized water before use.

Analytical procedures

The sorption behaviors of HPMSP doped mesoporous silica towards Cu(II) were investigated in both batch and column methods as detailed below. Each extraction experiment was performed in triplicate unless stated otherwise.

Batch adsorption experiment

Two hundred milligrams of sorbents was added to 25 mL of a 200 ppm metal solution and stirred at 25°C in an isothermal bath. Samples were removed at known time intervals to investigate the kinetics of the adsorption process ensuring some were left long enough to reach equilibrium. Although kinetic experiments showed that the equilibrium was established within 5 h, to ensure equilibrium all experiments were carried out for 24 h. The solid was then separated by centrifugation and the amount of metal in the supernatant solution was determined by flame atomic absorption spectrometry. The metal extraction (mg g^{-1}) was calculated by $N_f = (n_i - n_e)/m$, where N_f is the amount of metal extracted by the sorbent; n_i is the initial amount of metal ions in solution; n_e is the amount of metal ions in solution at equilibrium; and m is the mass of the silica.

Column method

Seven hundred milligrams of silica were packed in a column (30 x 9.5 mm i.d.), which was then washed with water and conditioned with 0.01 M HNO_3. An aliquot of 40 ppm Cu(II) solution (unless stated otherwise) was passed through the packed column at a flow rate of 1 mL min^{-1} and the column was then washed with deionized water to remove the unextracted metal ions. For the desorption process, the adsorbed metal on the HPMSP doped silica was eluted with 1.0 or 3.0 M HNO_3 solution. The concentration of Cu(II) in the solution after passing the packed column and that in the eluent were determined by flame atomic absorption spectrometry.

Application to environmental samples

Tap and river water samples, collected from Chulalongkorn University and Chaophraya River, respectively, were filtered through a 0.45 µm cellulose membrane to remove particulate matter and then acidified to pH 2.0 with 1.0 M HNO_3 to optimize the extraction of Cu(II). Prior to use, the water samples were spiked with 5 mL of different concentrations of Cu(II) solution. The copper extraction was then performed using the column method as described above.

RESULTS AND DISCUSSION

Extraction of Cu(II) ion by batch method

Effect of pH

The degree of complexation was expected to be sensitive to the pH. Therefore the influence of pH on the Cu(II) extraction efficiency of HPMSP doped mesoporous silica was investigated within the pH range of 0.4 - 2.5 using 1.0 M HNO_3 for pH adjustment. However, since the addition of 0.1 M $NaNO_3$ into the metal solution has been reported to increase the metal extraction capacity of the sorbent,(12) all current Cu(II) extraction experiments were, therefore, performed using Cu(II) solution containing 0.1 M $NaNO_3$. The amount of Cu(II) extracted (mg g^{-1}) plotted against the initial pH of metal solution reveals that essentially no extraction of Cu(II) was observed at a pH $\leq$ 0.6, but above this pH the Cu(II) extractability increased with increasing pH values and reached its maximum around pH 1.2 (Figure 2). The lack of sorption capacity of the modified sorbent at pH $\leq$ 0.6 is probably due to the competition between the metal ions and the much larger amount of protons present in the solution. It should also be noted that when complexation took place, the pH of the solution changed during the equilibrium to a pH of ~4, which is the pKa value of the acidic chelating ligand.(12)

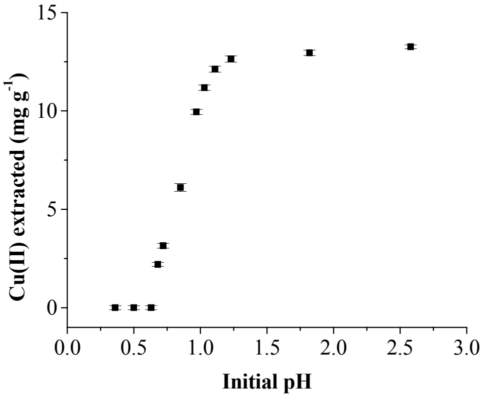

Figure 2. The effect of pH on Cu(II) extractability of HPMSP doped mesoporous silica by the batch method.

Effect of salts

Sorbents are used primarily to extract metal from various aqueous sources including natural water, seawater and industrial wastewater. These waters contain not only the metal ions of interest but also various interfering ions such as Na^+, K^+, Ca^{2+} and NO_3^-. In this work, the influence of nitrate salts on the Cu(II) extraction efficiency of mesoporous silica was examined. The experiments were performed in duplicate at pH 2 using a Cu(II) solution containing 0.1 M of nitrate salt from one of the three sources: $NaNO_3$, KNO_3 or $Ca(NO_3)_2$. The uptake of Cu(II) in mg g^{-1} increased in the presence of salts, as depicted in Figure 3. This phenomenon could be due to the replacement of the cetyltrimethylammonium ion (CTA^+) on the surface of the silica by the cations, which may decrease the surface steric hindrance and promote the sorption capacity. This improvement in metal extractability should benefit the extraction of metal ions from any environmental sample containing several nitrate salts.

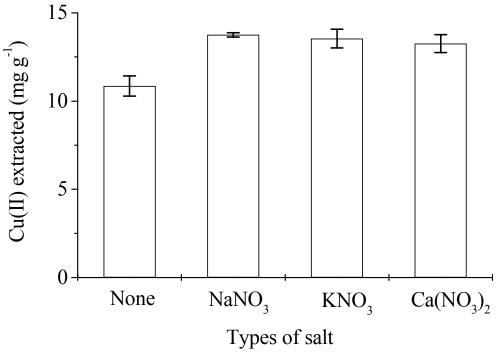

Figure 3. The effect of solvated salts on the Cu(II) extraction efficiency of the HPMSP doped mesoporous silica by the batch method.

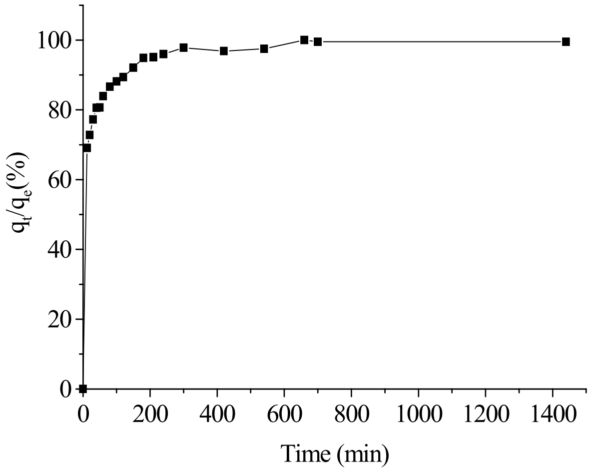

Figure 4. A plot of q_t/q_e versus time showing the fast adsorption of Cu(II) on the HPMSP doped silica in the presence of 0.1 M $NaNO_3$ at pH 2.
q_t and q_e are the amounts of sorbed metal ions (mg g^{-1}) on the sorbent at time t and at equilibrium, respectively.

Kinetics of metal sorption

The kinetics of the extraction was evaluated using a Cu(II) solution containing 0.1 M $NaNO_3$ at pH 2. As shown in Figure 4, the extraction of Cu(II) ions was extremely rapid in the beginning, attained the equilibrium after approximately 200 min and then remained constant, presumably due to the saturation of active sites on the modified silica and a possible monolayer coverage of Cu(II) ion on the sorbent surface. The time for 50% sorption ($t_{1/2}$) was less than 10 min, indicating the excellent kinetic sorption of HPMSP doped mesoporous silica.

To investigate the controlling mechanism of the metal sorption onto the HPMSP modified sorbent, different kinetic models were considered: the intraparticle diffusion model proposed by Weber and Morris,(25) the pseudo-first order equation of Lagergren(26) and the pseudo-second order model of Ho and McKay(27) (correlation coefficients are given in Table 1).

The intraparticle diffusion model is formalized as:

$$q_t = k_i t^{1/2} \qquad \ldots (1)$$

where q_t is the amount of sorbed metal ions (mg g^{-1}) on the sorbent at time t and k_i is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$). From this, the k_i value was calculated from the plot of q_t versus $t^{1/2}$. No plot for the intraparticle diffusion model is shown due to the low correlation coefficient.

The pseudo-first order kinetic model of Lagergren is represented as:

$$\ln\frac{q_e - q_t}{q_e} = -k_1 t \qquad \ldots (2)$$

where q_e is the amount of sorbed metal ions (mg g^{-1}) on the sorbent at equilibrium and k_1 is the rate

Table 1. Intraparticle diffusion, pseudo-first order and pseudo-second order kinetic parameters for the sorption of Cu(II) by HPMSP doped silica.

Intraparticle diffusion model	Pseudo-first order	Pseudo-second order			$q_{e,\mathrm{exp.}}$ (mg g^{-1})
r_i^2	r_1^2	r_2^2	k_2 (g mg^{-1} min^{-1})	$q_{e,\mathrm{th.}}$ (mg g^{-1})	
0.410	0.768	0.999	0.00753	13.30	13.26

$q_{e,\mathrm{th.}}$ and $q_{e,\mathrm{exp.}}$ represent theoretical and experimental values of q_e, respectively.

constant of the first-order sorption model (min^{-1}). The value of k_1 was calculated from the slope of the plot of ln $[(q_e-q_t)/q_e]$ versus t. The plot obtained for the pseudo-first order model is not shown due to its relatively low correlation coefficient.

The pseudo-second order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \ldots (3)$$

where k_2 is the observed pseudo-second order rate constant of adsorption (g mg^{-1} min^{-1}). Values of q_e and k_2 were calculated from the slope and intercept of the plot of t/q_t versus t (Figure 5).

The correlation coefficients: r_i^2, r_1^2 and r_2^2, determined from the plots of q_t versus $t^{1/2}$ for the intraparticle diffusion, of ln $[(q_e-q_t)/q_e]$ versus t for the pseudo-first order model and of t/q_t versus t for the pseudo-second order model, respectively, are given in Table 1. The Cu(II) sorption on the HPMSP doped silica follows the pseudo-second order kinetic model, as evidenced by a close-to-one value of r^2 and the excellent agreement of q_e values from the model and the experiment (13.30 vs. 13.26 mg g^{-1}, Table 1).

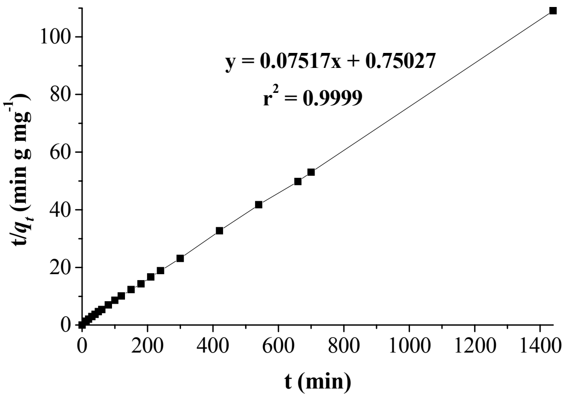

Figure 5. Pseudo-second order kinetics of Cu(II) sorption by HPMSP doped mesoporous silica. q_t is the amounts of sorbed metal ions (mg g^{-1}) on the sorbent at time t.

Table 2. Experimental variables, levels, design matrix and results (amounts of Cu(II) desorbed) in the 2^3 factorial design for Cu(II) desorption.

Variables	Codes	Level	
		Low (-)	High (+)
Amount of Cu(II) loaded (μmol)	A	94.4	188.8
Concentration of HNO_3 (M)	E	1	3
Volume of HNO_3 (mL)	V	20	40

Run	A	E	V	Amounts of Cu(II) desorbed (mg g^{-1}) ± SE
1	-	-	-	1.96 ± 0.08
2	+	-	-	2.08 ± 0.06
3	-	+	-	2.18 ± 0.25
4	+	+	-	2.55 ± 0.02
5	-	-	+	1.62 ± 0.19
6	+	-	+	2.20 ± 0.10
7	-	+	+	2.13 ± 0.11
8	+	+	+	2.43 ± 0.13

Table 3. The estimated effects of the variables and their interactions.

Variables/Interactions	Estimated effects ± SE
<u>Main</u>	
Amounts of Cu(II) loaded, A	0.341 ± 0.055
Concentration of HNO_3, E	0.359 ± 0.055
Volume of HNO_3, V	-0.102 ± 0.055
<u>Two-factor interaction</u>	
AE	-0.005 ± 0.055
AV	0.097 ± 0.055
EV	0.012 ± 0.055
<u>Three-factor interaction</u>	
AEV	-0.135 ± 0.055

Table 4. Analysis of variance for the Cu(II) desorption efficiency of HPMSP doped mesoporous silica.

Source of variance	Sum of square[a]	Degree of freedom	Mean square[b]	F-ratio[c]	P-value
A	0.6979	1	0.6979	37.71	<0.0001
E	0.7735	1	0.7735	41.80	<0.0001
V	0.0620	1	0.0620	3.35	0.0858
AE	0.0002	1	0.0002	0.01	0.9252
AV	0.0570	1	0.0570	3.08	0.0985
EV	0.0008	1	0.0008	0.04	0.8365
AEV	0.1086	1	0.1086	5.87	0.0277
Error	0.2961	16	0.0185		
Total	1.9961	23			

[a] Sum of square = N X (estimated effect)^2/4

[b] Mean square = sum of square/degree of freedom

[c] F-ratio = mean square of factor/mean square of error. Critical value of $F_{1,16}$ = 6.115 (P = 0.05).(28)

Extraction of Cu(II) ion using column method

Optimization of metal desorption

To attain the most suitable condition for Cu(II) desorption properties of HPMSP doped mesoporous silica, three parameters were optimized experimentally. The parameters were the amount of Cu(II) loaded into column, the concentration of HNO_3 used as eluent and the volume of the eluent (a 2^3 factorial design). Each variable contained two levels and each experimental run was performed in triplicate. The experimental variables, codes, levels, design matrix and results are summarized in Table 2.

From the amounts of Cu(II) desorbed, the influence of each variable (and its interactions) could be determined by calculating the estimated effects. The results and their standard errors (SE) were presented in Table 3. The influence of factors or interactions is considered significant if their estimated effect is higher than the standard error. Thus, from Table 3, the significant factors were the amounts of Cu(II) loaded (A), the concentration of HNO_3 (E), the volume of HNO_3 (V), the AV interaction and the three-factor interaction (AEV). However, among these significant factors, the concentration of HNO_3 and the amounts of Cu(II) loaded were more important than other variables/interactions. The positive sign of these estimated effects indicated the increasing of Cu(II) desorption when high concentrations of HNO_3 and large amounts of Cu(II) loaded were used.

In addition, support for the most significant factor affecting the Cu(II) desorption was attained by the analysis of variance (ANOVA) (Table 4), where the main two factors found were the concentration of HNO_3 and the amounts of Cu(II) loaded. Thus, to obtain the high Cu(II) desorption efficiency of the sorbent, the optimum condition used should be the high concentration of nitric acid and the large amounts of Cu(II) loaded into column, although of course the latter is practically determined by the environmental samples available for extraction of depletion.

Determination of column capacity

The maximum extraction capacity of the material is an important characteristic of the sorbent. In this work, the column capacity of HPMSP doped mesoporous silica was evaluated using Cu(II) solution containing 5 x 10^{-3} M $NaNO_3$ at pH 2 with a Cu(II) concentration of 64, 85, 99, 152, 200 and 296 ppm in a fixed volume of 60 mL each. The Cu(II) extraction capacity of the sorbent estimated from the breakthrough curve was 5.74 mg g^{-1} (Figure 6). This value is superior to the Cu(II) extraction capacity of other functionalized sorbents reported elsewhere (i.e. 4.96 mg g^{-1} for the Cu(II) sorption capacity of zirconium phosphate functionalized silica(29) and 0.40 mg g^{-1} for Schiff's base modified octadecyl silica membrane disk).(30)

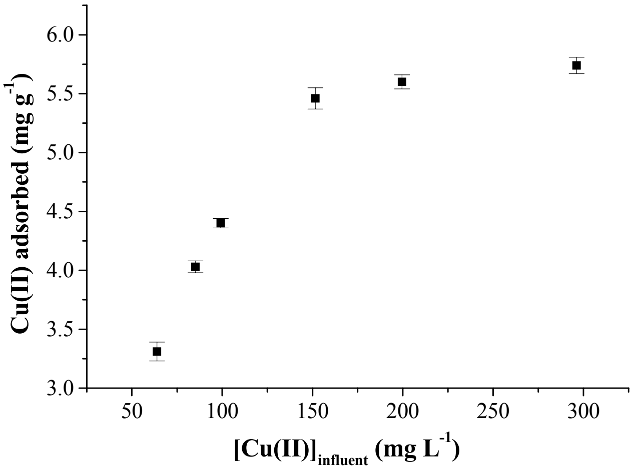

Figure 6. Cu(II) adsorption on HPMSP doped mesoporous silica as a function of influent Cu(II) concentration.

Table 5. Effect of sample volume on the Cu(II) desorption efficiency of HPMSP doped mesoporous silica.

Volume of Cu(II) solution (mL)	Volume of eluent (mL)	Preconcentration factor	Recovery (%)
100	20	5	96.2 ± 0.5
200	20	10	95.4 ± 0.5
300	20	15	92.3 ± 0.5
800	20	40	93.7 ± 0.5

Preconcentration factor

The preconcentration efficiency of HPMSP doped mesoporous silica was investigated using different volumes of 20 ppm Cu(II) solution loaded into the packed column. The extraction medium was 5x10^{-3} M $NaNO_3$ at pH 2 and 20 mL of 3 M HNO_3 was used as the eluent through the desorption process. The detection limit for Cu was 19 ng L^{-1} (data not shown). Table 5 shows the high (92 - 96%) recovery of Cu(II) obtained in all experiments with preconcentration factors varying from 5 - 40., suggesting the high adsorption and desorption efficiency of the HPMSP modified sorbent. The highest preconcentration factor was found to be 40. Though this value could be augmented by loading much more volume of metal solution, the experiment was not carried out since the analysis time appeared too long.

Table 6. The Cu(II) adsorbed and desorbed on HPMSP doped mesoporous silica, using 20 mL of 3 M HNO_3 as eluent in the column method.

Cycle	Amounts of Cu(II)	
	Adsorption (mg g^{-1})	Desorption (mg g^{-1})
1	5.05	4.96
2	5.06	4.75
3	4.66	4.06

Reusability of material

The potential reusability of HPMSP doped mesoporous silica was demonstrated by loading 60 mL of 150 ppm Cu(II) solution containing 5x10^{-3} M $NaNO_3$ at pH 2 into the column and eluting the adsorbed metal with 20 mL of 3 M HNO_3. The Cu(II) adsorption-desorption cycle was repeated three times. It is clearly seen from Table 6 that the adsorption capacity of the reused sorbent was slightly decreased after three cycles of adsorption and desorption.

Reproducibility of extraction

Reproducibility is one of the defining factors for an effective sorbent. In this work, the reproducibility of the modified material for Cu(II) extraction was investigated by loading 300 mL of 20 and 40 ppm Cu(II) solution containing 5 x 10^{-3} M $NaNO_3$ at pH 2 into the column of fresh sorbent. The results obtained from 16 replicate measurements revealed an RSD of 7% for both initial concentrations.

Table 7. The recovery of Cu(II) from tap water and river water.

Water samples	Cu(II) spiked (mg L^{-1})	Recovery (%)
Tap water	20.0	92.7 ± 0.3
	30.0	95.6 ± 0.3
	40.0	96.9 ± 0.3
River water	20.0	96.6 ± 0.3
	30.0	96.8 ± 0.3
	40.0	96.2 ± 0.3

Application

To assess its use with real samples, the synthesized sorbent was applied to the extraction of Cu(II) from tap water (Chulalongkorn University, taken after 15 min operation of the tap) and river water (taken from Chaophraya river near Siphraya Pier, Klongsan District, Bangkok). As shown in Table 7, the added Cu(II) was quantitatively recovered (92.7-96.9 %) which suggested that HPMSP doped mesoporous silica can be used with real samples without matrix effects.

CONCLUSIONS

The physicochemical properties of 1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone doped mesoporous silica were studied on the extraction and preconcentration of Cu(II) from aqueous solution using static and dynamic methods. The kinetic study of Cu(II) uptake revealed the speed in reaching equilibrium and showed the sorption process followed the pseudo-second order kinetic model. The adsorption is consistent with the Langmuir adsorption isotherm. The Cu(II) sorption capacity of the modified silica under optimum conditions was fairy high, 5.74 mg of copper per gram of sorbent. The application of HPMSP doped mesoporous silica to the preconcentration of Cu(II) from aqueous solution was achieved with the maximum preconcentration factor of 40. The high loading capacity for copper by the HPMSP doped silica in highly acidic medium suggested its promising application in the extraction of Cu(II) ions from aqueous solution.

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