Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.815585

52 (2014) 6530–6541
October

Taylor & Francis
Taylor & Francis Group

Synthesis, characterization, and sorption properties of silica gel-immobilized Schiff base derivatives

Esengül Kir[a,*], Murat Çelik[a], Gökhan Sevinç[b], Fatma Karipcin[c], Bülent Dede[a]

[a]*Faculty of Science and Art, Department of Chemistry, Suleyman Demirel University, Cunur Campus, Isparta 32260, Turkey*
Tel. +90 246 2114336; Fax: +90 246 2371106; email: esengulkir@sdu.edu.tr
[b]*Faculty of Science, Department of Chemistry, Ankara University, Ankara 06100, Turkey*
[c]*Faculty of Science and Art, Department of Chemistry, Nevsehir University, Nevsehir 50300, Turkey*

Received 12 February 2013; Accepted 7 June 2013

ABSTRACT

In this study, two Schiff base ligands were synthesized and characterized by Elemental analysis, infrared, spectroscopy and nuclear magnetic resonance, respectively. The silica gel surface was, respectively immobilized with Schiff base derivatives, 4-(4-(4-[1-methyl-3-oxobutidenamino]fenil] fenilimino)-2-pentanon (BAA) and 4-{5-[1-methyl-3-oxobutylideneamino]-1-naphthylimino}-2-pentanone (NAA), after surface modification by 3-aminopropyltrimethoxysilane (APTS) to prepare new adsorbents. Characterization of the surface modification was confirmed through elemental analysis, thermogravimetry and scanning electron microscopy. The immobilized silica gels (Si–APTS–BAA and Si–APTS–NAA) were used for sorption of Cu(II) ion in aqueous solution. The influence of the pH, amount of adsorbent, ion concentration, time, and temperature was investigated. The characteristics of the sorption process were evaluated by using the Langmuir and Freundlich sorption isotherms. The sorption of Cu(II) metal ion onto modified silica gels correlated well with the Langmuir type sorption isotherm and sorption capacities were found to be 28.57 mmol g^{-1} (BAA) and 25.31 mmol g^{-1} (NAA) for Cu(II) metal ion. Thermodynamic parameters such as the standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated to explain the nature of sorption process. Various kinetic models including pseudo-first-order and pseudo-second-order were investigated to determine the mechanism of sorptions. The experimental data fitted the pseudo-second-order well for both Schiff base ligands.

Keywords: Schiff base; Immobilization; Sorption; Cu(II); Isotherm

---

1. Introduction

In recent years, with the development of modern industry, the water and environment pollution caused by heavy metal ions are threat to human health and living species. Metals in waters may be of natural origin from the rocks and soil or from human activities, including industry, domestic wastewater, agricultural discharge and atmospheric deposition. Many metals are biologically essential but become toxic with increasing dosage. Heavy metal toxicity can cause several disorders and diseases [1]. Major

---

*Corresponding author.

sources of heavy metal release to the environment due to metal cleaning, plating facilities, mining, metal extraction, corrosion and electric devise manufactures [2,3].

Copper is an important element in most life forms as a micronutrient, but is also toxic at high concentrations [4]. Many separation techniques have been proposed for removal of metals in various environmental samples, including ion exchange, co-precipitation, solvent extraction, membrane processes and sorption [5–10]. Sorption is widely used in the removal of heavy metals from waste water and aqueous solutions through suitable sorbents [11,12]. Among the different adsorbents, silica gel immobilized with various organic compounds has especially received great attention [13–15]. The silica gel is a good solid support due to its thermal, chemical and mechanical stability for the reaction process [16,17]. Modification of silica gel can be achieved via chemisorptions of the desired organic functional groups onto the silica surface [18,19]. Modification of the surface is mostly carried out by using on the appropriate molecule (such as 3-aminopropyltrimethoxysilane, 3-chloropropyltrimethoxysilane) designated as precursor silylating agent. Thus a covalent bond can be formed between the silica gel surface and the silylating agent to give a new modified surface with various chelating ligands. Porous silica functionalized with various chelating agents is increasingly utilized as an adsorbent because of its excellent selectivity for a specific heavy metal ion [20]. A great number of chelating agents were immobilized on the silica gel surface such as Schiff base derivatives and oximes [21,22].

The purpose of the present paper is to develop new sorbents by immobilizing chemically the Schiff bases on the silica gel and to investigate the sorption capabilities of these new modified sorbents for removal of Cu(II) ion from aqueous solution.

This study was carried out in three basic steps. On the first step of the study, Schiff base ligands BAA and NAA were synthesized and characterized by elemental analysis, ^{1}H-NMR and IR spectroscopies. On the second step of the study, activated silica gel with dry nitrogen was modified by APTS. Schiff base ligands synthesized on the first step of the study were immobilized chemically to modificated silica structure. The modification and immobilization reactions were confirmed through elemental analysis, thermogravimetry and scanning electron microscope. The prepared sorbents were used to investigate the capability of removal of Cu(II) ion from aqueous solution. In addition, the sorption characteristics and thermodynamic properties of sorbents were examined.

2. Experimental

2.1. Chemicals

Powdered silica gel (Merck) was used as the support and the characteristics of the support are listed in Table 1.

Schiff base ligands, 4-(4-{4-[1-methyl-3-oxobutylideneamino]phenyl}phenylimino)-2-pentanone and 4-{5-[1-methyl-3-oxobutylideneamino]-1-naphthylimino}-2-pentanone were synthesized according to the method described in section 2.2. Benzidine, 1,5-diaminonaphthalene, ethanol and acetylacetone (Merck) were used for synthesis. 3-Aminopropyltrimethoxysilane (APTS, Aldrich) 97% was used for treatment of the silica supports. Toluene (Merck) was dried. Triethylamine (Merck) was used for immobilization. $Cu(NO_3)_2{\cdot}3H_2O$ (Merck) was used to prepare the metal ion solution.

2.2. Physical measurements

FT-IR spectra were obtained in the 400–4,000 cm^{-1} range by Shimadzu IR Prestige-21 FT-IR spectrometer. KBr pellets were used for solid samples. NMR spectra of Schiff base ligands were obtained on a Bruker, 300 MHz spectrometer at room temperature. Elemental analysis was performed by LECO 932 CHNS. TGA measurement was carried out on a Perkin Elmer Diamond thermogravimetric analyzer. The morphology of silica gel, Si–APTS, Si–APTS–BAA, and Si–APTS–NAA surfaces were assessed with TESCAN VEGA II LSU model SEM. The amount of the metal ions was determined by an AAS Perkin Elmer AA800. pH values were measured by a pH-meter model pH 221, Hanna instruments, Germany.

2.3. Synthesis of BAA and NAA

A modification of the method used by Shauib et al. was employed for the preparation of the ligands [23]. 0.01 mol benzidine(1.84 g) or 1,5-diaminonaphthalene(1.58 g) was dissolved in ethanol (30 mL) and 0.02 mol acetylacetone was added to this mixture. Over a period of 4 h, the reaction mixture was heated under reflux and then allowed to stand at room

Table 1
Properties of silica gel used as a support in this study

Particle size (mm)	0.063–0.200
Surface area (m^2/g)	480–540
Pore volume (cm^3/g)	0.74–0.84

temperature overnight. During this period, the dark green and brown precipitates were formed for BAA and NAA, respectively. These precipitates were filtered off, washed several times with diethyl ether and dried in a vacuum.

BAA: Dark green powder; yield: 81%; M. p. 132˚C. Anal. Calc. for $C_{22}H_{24}N_2O_2$: C, 75.84; H, 6.94; N, 8.04. Found: C, 75.62; H, 6.85; N, 8.31; FT-IR (υ, cm^{-1}): 2,993–3,032 m (Ar–H), 1,613 s (C = O), 1,557 s (C = N), 1,305 m (C–N). ^{1}H-NMR (δ, ppm): 2.15 (s, 4H, CH_2), 1.52–5.15 (s, 6H, CH_3), 6.68–7.49 (m, 8H, Ar–H). The molecular structure of this compound was shown in Fig. 1.

NAA: Brown powder; yield: 84%; M. p. 194 ˚C, Anal. Calc. for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.87; N, 8.69. Found: C, 74.88; H, 6.52; N, 8.48; FT-IR (υ, cm^{-1}): 1,610 (C = O), 1,570 (C = N), 2,996 ($C–H_{alip.}$), 3,045 (Ar–H). ^{1}H-NMR (δ, ppm): 1.18 (s, 6H, CH_3), 2.10 (s, 4H, CH_2), 4.06 (s, 6H, CH_3), 6.62–7.21 (m, 6H, Ar–H). The molecular structure of this compound was shown in Fig. 2.

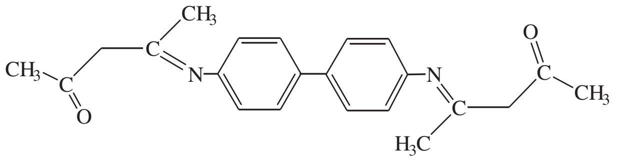

Fig. 1. 4-(4-{4-[1-methyl-3-oxobutylideneamino]phenyl} phenylimino)-2-pentanone (BAA).

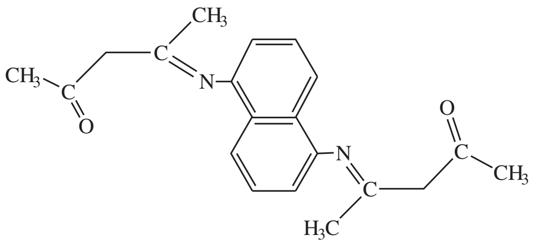

Fig. 2. 4-{5-[1-methyl-3-oxobutylideneamino]-1-naphthyl-imino}-2-pentanone (NAA).

2.4. Modification of silica gel by 3-aminopropyltrimethoxysilane

Silica gel was activated by heating for 10 h at 423 K in a stream of dry nitrogen [24]. A sample of 20.0 g activated silica gel was suspended in 100 mL of dry toluene and 10.66 mmol (2 mL) APTS was added to this suspension [25,19,26]. The mixture was refluxed under inert atmosphere for 72 h. The suspension was filtered and washed twice with toluene, and dried under vacuum. The product obtained was named Si–APTS (Fig. 3).

2.5. Immobilization of BAA and NAA on silica gel

A sample of 5.0 g modified silica gel (Si–APTS) and 1.31 g of BAA or 1.28 g of NAA(4 mmol) were added to 60 mL dry toluene, containing 4 mL of triethylamine in order to favor the reaction equilibrium [26]. The suspension was kept under reflux and mechanically stirred for 72 h at 90˚C. The final product which filtered, washed with toluene and ethanol and dried under vacuum for 24 h was named as Si–APTS–BAA (Fig. 4) and Si–APTS–NAA (Fig. 5).

2.6. Sorption studies for Cu(II) ion

The sorption studies were performed with batch technique in an aqueous solution for Cu(II) ion. Sorption experiments were studied with similar character ions such as Zn(II), Ni(II), Co(II), Pb(II) but Cu(II) ion selected for results to be better than other ions. 50 mg Si–APTS–BAA or Si–APTS–NAA was added into 10 mL of metal solution which has initial concentration of 1.0×10^{-3} mol/L for Cu(II). The samples were mechanically stirred for 2 h at 298 ± 1 K and the solid was separated by filtration. The experimental parameters studied are the amount of sorbent (10–90 mg), effect on pH (2–7), temperature (298–333 K), contact time (2–48 h) and ion concentration (5–200 ppm). The desired pH values were attained by adding 0.1 mol/L solutions of HCl and NaOH. After reaching sorption equilibrium, the sorbent was filtered and the concentration in the filtrate of the metal ion being investigated was determined by AAS.

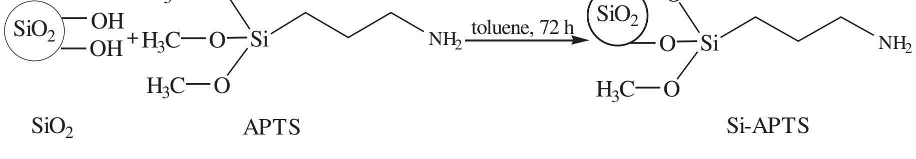

Fig. 3. Reaction for modification of silica gel with 3-aminopropyltrimethoxysilane.

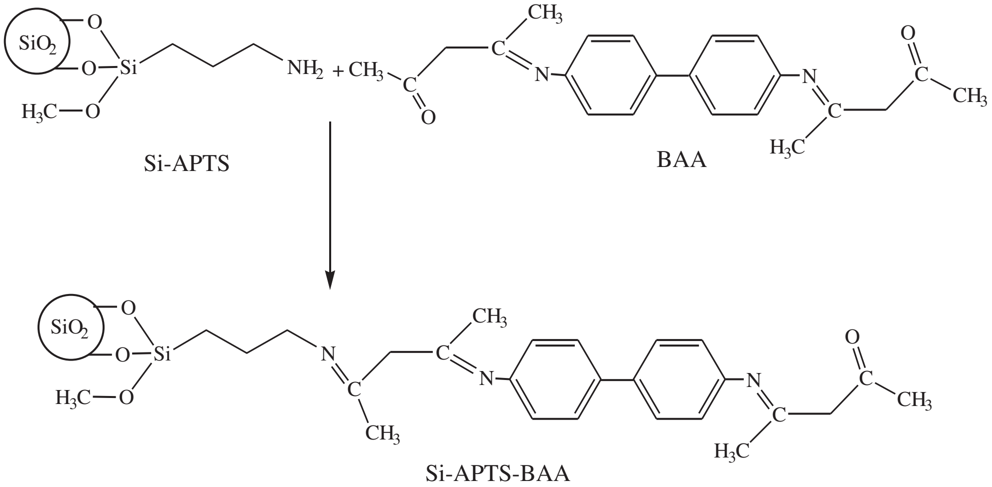

Fig. 4. Immobilization of BAA onto modified silica gel.

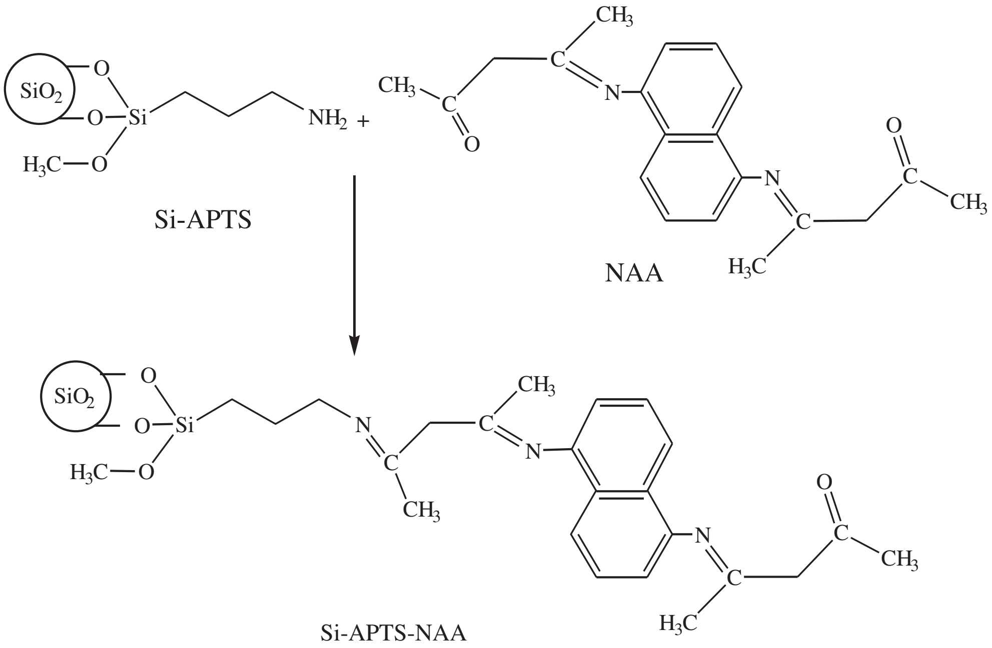

Fig. 5. Immobilization of NAA onto modified silica gel.

The amount of metal ions sorbed by sorbents was calculated as it was shown in below equation:

$$q = (C_0 - C)\ V/W \tag{1}$$

where q is the amount of metal ion sorbed onto the unit amount of the sorbent (mmol/g), C_0 and C are the concentrations of metal ions in the initial and equilibrium concentrations of the metal ions in aqueous phase (mol/L), V is the volume of the aqueous phase (L), and W is the dry weight of the sorbent (g).

In the sorption study, the effect of Cu(II) ion concentration on the sorption capacities was examined using the batch procedure. 50 mg of the sorbent was stirred with 10.0 mL of various concentrations of metal ion for 2 h. In order to evaluate the sorption characteristics of metal ion on the Si–APTS–BAA and Si–APTS–NAA, experimental data were fitted to sorption isotherm models of Freundlich and Langmuir.

The effect of temperature on the sorption of Cu(II) metal ion onto Si–APTS–BAA and Si–APTS–NAA is given as the plot of the distribution coefficient values (K_D) as a function of temperature. Thermodynamic parameters, free energy change (ΔH°), and entropy change (ΔS°) were calculated using temperature data. In addition, kinetic of sorption of Cu(II) metal ion was examined using sorption data.

3. Results and discussion

3.1. Characterization

In this study, BAA and NAA were immobilized on the silica surface after modification by 3-aminopropyltrimethoxysilane. Immobilization of Schiff base ligands onto silica gel followed a sequence of three steps. On the first step Schiff bases were synthesized and characterized by using elemental analysis, FT-IR and ^{1}H-NMR. The free Schiff bases exhibit bands at 1613, 1610 (vs.) and 1557, 1570 s cm^{-1} due to υC = O and υC = N, respectively. The low energy position of these bands could be attributed to its involvement in conjugation with the aromatic system [23].

On the second step silica gel was modified by APTS (Si–APTS) and then Schiff base ligands were immobilized onto modified silica structure. The modification and immobilization reactions were characterized through elemental analysis, thermogravimetry and SEM. Modification and immobilization procedures were shown in Figs. 3–5. The degree of immobilization on the surface was determined by considering the elemental analysis data. The percentage amount of carbon was 11.41 and 14.34 for Si–APTS and Si–APTS–BAA, respectively. The percentage amounts of carbon, nitrogen and hydrogen were shown in Table 2 for SiO_2, Si–APTS, Si–APTS–BAA, and Si–APTS–NAA compounds. These values showed that APTS, BAA and NAA were covalently bonded on activated silica gel.

The thermogravimetric curves reflect the thermal stability of anchored surface and also the confirmation of the amount of the compounds immobilized as shown Figs. 6 and 7. The curves showed distinct mass losses of the organic groups covalently bonded to inorganic phase. The activated silica gel presented a loss of adsorbed water mass of 5% from 303 to 373 K, assigned to physical adsorbed water (a). A curve involving Si–APTS (b) gave a mass loss of 19% in the 473–973 K interval of temperature. This loss is related to the decomposition of the attached APTS silylant chain and also included the condensation of the remaining silanol groups. As expected, the immobilized Si–APTS–BAA (c) surface presented two distinct stages of mass loss. The first mass loss of 10% in the 373–573 K range is assigned to adsorbed water [27]. The second mass loss of 26% between 573 and 973 K is attributed to the organic groups immobilized on the surface and the condensation of the remaining silanol groups. As parallel, mass loss of 23% in TGA curve (Fig. 7) of Si–APTS–NAA was indicated detaching of organic groups from silica surface. These results in mass loss are in agreement with a lot of works [18,28].

In addition to the characterization, the images of the sorbent surfaces were examined by scanning electron microscopy. SEM images of activated silica

Table 2
Percentages (%) of hydrogen (H), carbon (C), and nitrogen (N) for the matrices SiO_2, Si–APTS, Si–APTS–BAA, and Si–APTS–NAA

Surface	Carbon (%)	Hydrogen (%)	Nitrogen (%)
SiO_2	0	0	0
Si-APTS	11.41	2.44	3.75
Si-APTS-BAA	14.34	2.67	5.07
Si-APTS-NAA	14.01	2.13	5.03

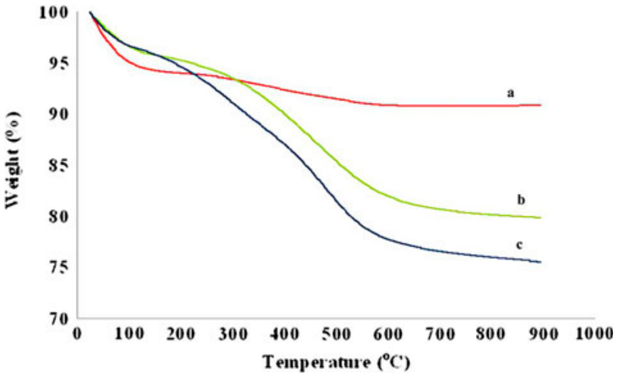

Fig. 6. Thermogravimetric diagrams of: (a) SiO_2, (b) Si-APTS, and (c) Si-APTS-BAA.

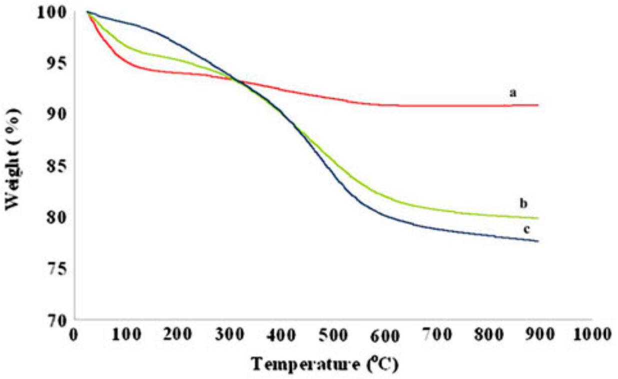

Fig. 7. Thermogravimetric diagrams of: (a) SiO_2, (b) Si-APTS, and (c) Si-APTS-NAA.

gel, Si–APTS, Si–APTS–BAA, and Si–APTS–NAA were recorded and representative images of these surfaces are presented in Figs. 8–11. The surface of the activated silica gel is composed of a macro particle structure (Fig. 8). After the modification of APTS on silica gel, the surface was changed (Fig. 9). Figs. 10 and 11 presented SEM of the surfaces of BAA and NAA immobilized onto silica [29]. It can be seen that Si–APTS–BAA and Si–APTS–NAA surfaces could have large surface area with immobilization.

3.2. Optimum conditions for sorption

3.2.1. Effect of pH

The pH of the aqueous solutions is an important variable, which controls the sorption between the adsorbent and water interface. The sorption of Cu(II) ions on sorbents was studied at different pH values ranging from 2 to 7. The results are presented in Fig. 12, which reveals that the sorption of Cu(II) is maximum at pH 5 for both sorbents. It can be seen

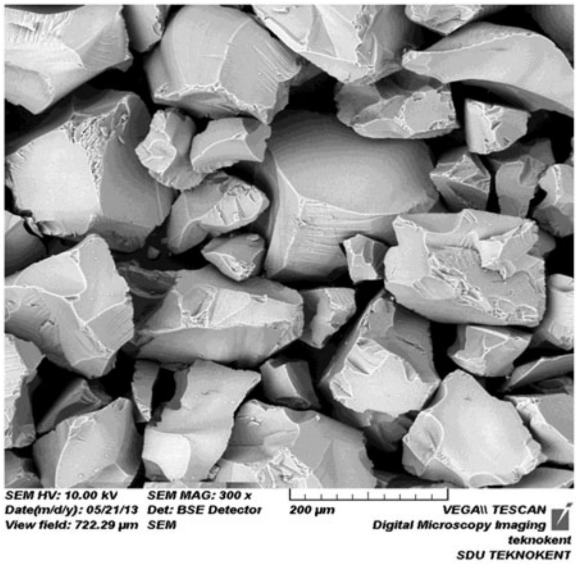

Fig. 8. SEM of the surface of activated silica gel.

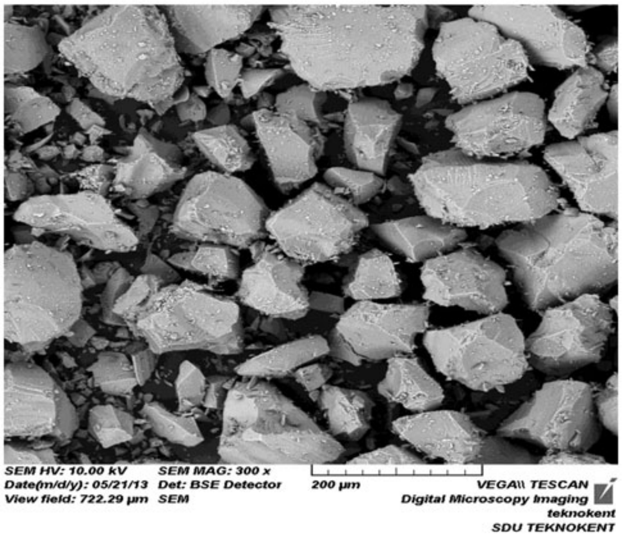

Fig. 9. SEM of the surface of APTS modified silica gel.

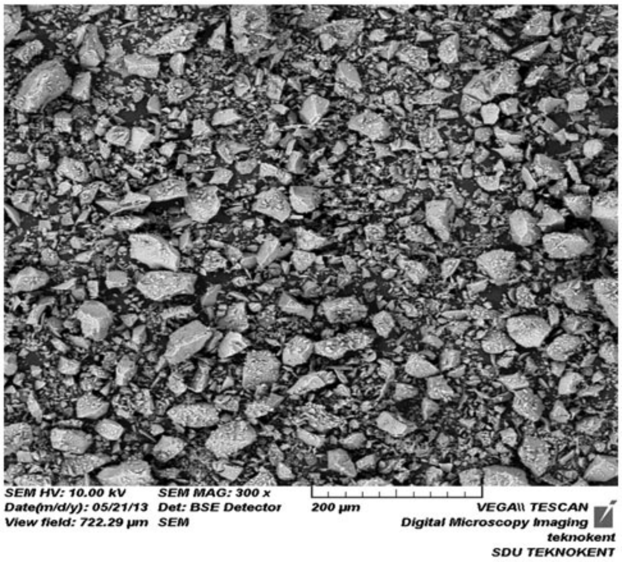

Fig. 10. SEM of the surface of BAA immobilized silica gel.

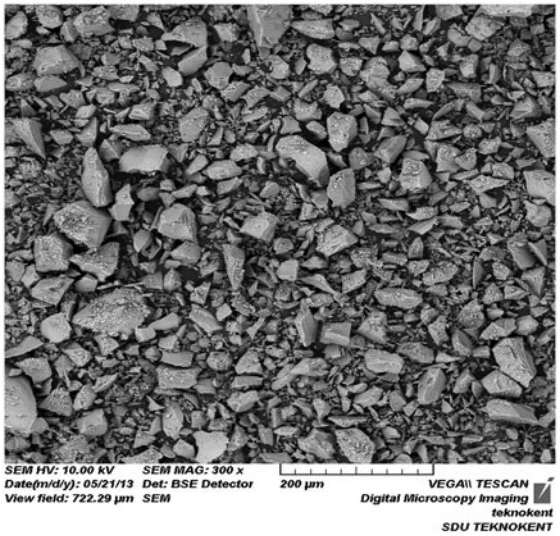

Fig. 11. SEM of the surface of NAA immobilized silica gel.

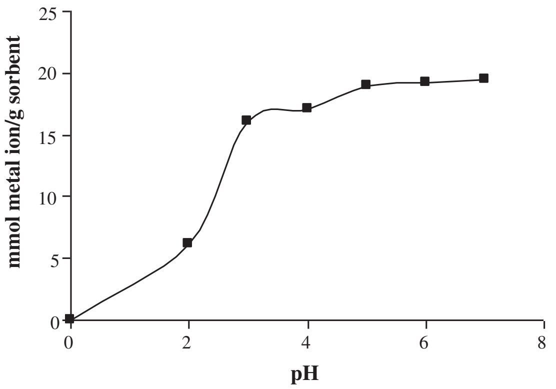

Fig. 12. The effect of pH on the sorption of Cu(II) ion (Cu: 1.0×10^{-3} mol/L, t: 120 min m(sorbent): 0.05 g, temperature: 25˚C).

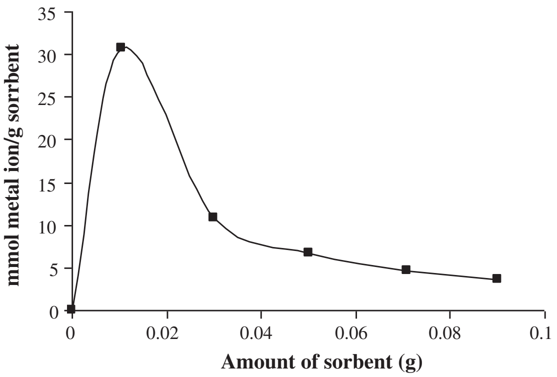

Fig. 13. Effect of sorbent amount (0.01–0.09 g) on the sorption of Cu(II) on immobilized silica at pH 5. Cu(II) solution: 1.0×10^{-3} mol/L, temperature: 25˚C.

from Fig. 12 that the sorption capacity of Cu(II) increases with the raise in pH values. As the pH increased, the sorbent surface becomes less positive and therefore electrostatic attraction between the metal ions and sorbent surface is likely to be increased. Sorption is also not favor in the acidic range; this may be as a result of the sorption of [H_3O^+] ions on the same active sorption site instead of metal ions [13,19].

3.2.2. Effect of sorbent amount on sorption

The effect of sorbent amount's variation on the sorption of Cu(II) by sorbents is shown in Fig. 13. Sorbent amount varied from 0.01 to 0.09 g and equilibrated for 2 h at on initial Cu(II) concentration of 1.0×10^{-3} mol/L. As it can be seen from Fig. 13, the percent sorption of Cu(II) ions increased with the raise in amount of sorbent up to a certain level, and then leveled off. The required minimum sorbent amount for the quantitative sorption of 1.0×10^{-3} mol/L Cu(II) in 25 mL was found 0.05 g of sorbents. As expected, an increase in the sorption with the amount of added sorbent can be attributed to greater surface area and the availability of more sorption sites.

3.2.3. Effect of time on the sorption

Cu(II) ion sorption capacity was determined as a function of time to determine an optimum contact time for the sorption of metal ion on sorbents. Fig. 14 illustrates the sorption of Cu(II) by sorbent as time functions. An initial concentration of Cu(II) 1.0×10^{-3} mol/L was tried and the concentration of Cu(II) in equilibrium on sorbent was plotted as a function of the equilibrium period for the sorbent. The

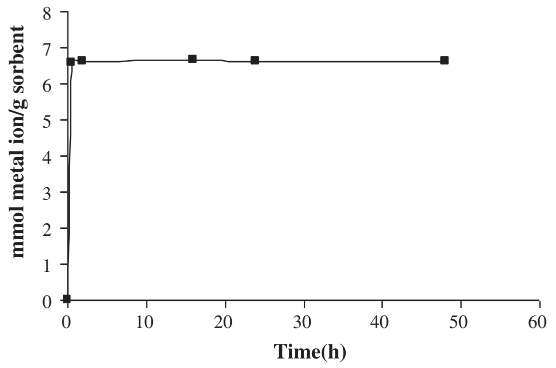

Fig. 14. Sorption of Cu(II) by sorbent as a function of time at pH 5. Sorption conditions; initial concentration of Cu(II): 1.0×10^{-3} mol/L, amount of sorbent: 0.05 g, sorption time: 30 min-48 h, temperature: 25˚C.

sorption equilibrium time is attained within 120 min for Cu(II) ion.

3.2.4. Temperature dependence of sorption

The isotherms for sorption of Cu(II) ions at pH 5 for four different temperatures (25, 35, 50, 60) are presented in Figs. 15 and 16. The effect of temperature on the equilibrium constant (K) or the sorption of Cu(II) ion onto sorbents was investigated at this stage. The equilibrium constant for Cu(II) was low and sorption decreased with increasing temperature for Si–APTS–BAA. This is due to the exothermic sorption reactions of Cu(II) ion with sorbent. The equilibrium constants for such reactions slightly decrease with temperature. In contrast to Si–APTS–BAA, sorption increased with increasing temperature for Si–APTS–NAA. The sorption reaction is endhotermic for this sorbent. As seen from Figs. 15 and 16, maximum sorption capacity was obtained at 25˚C.

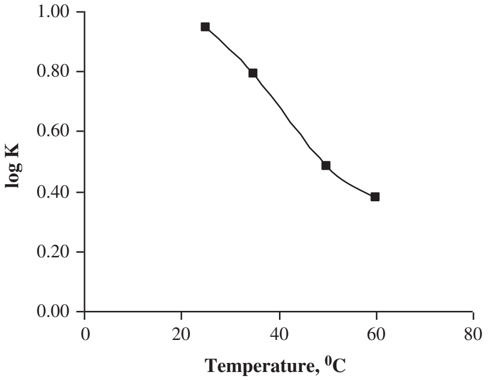

Fig. 15. The equilibrium constant for Cu(II) on the BAA sorbent as a function of temperature at pH 5. Amount of sorbent: 0.05 g, Cu(II) solution: 1.0×10^{-3} mol/L.

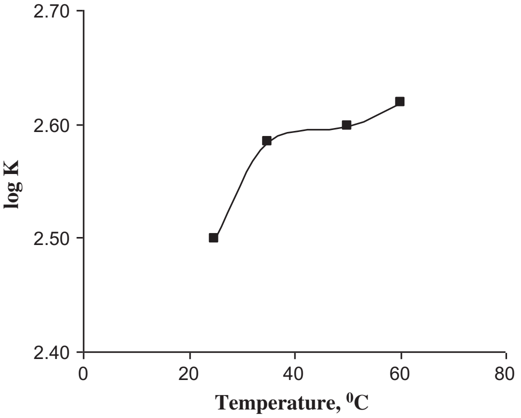

Fig. 16. The equilibrium constant for Cu(II) on the NAA sorbent as a function of temperature at pH 5. Amount of sorbent: 0.05 g, Cu(II) solution: 1.0×10^{-3} mol/L.

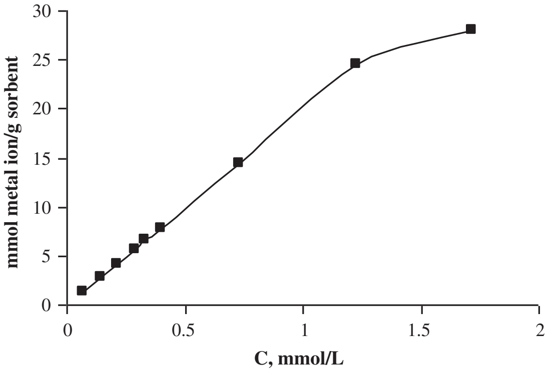

Fig. 17. Effect of initial concentration for metal ion sorption on Si-APTS-BAA sorbent. Cu(II) pH 5; t: 120 min, m: 0.05 g, temperature: 25˚C.

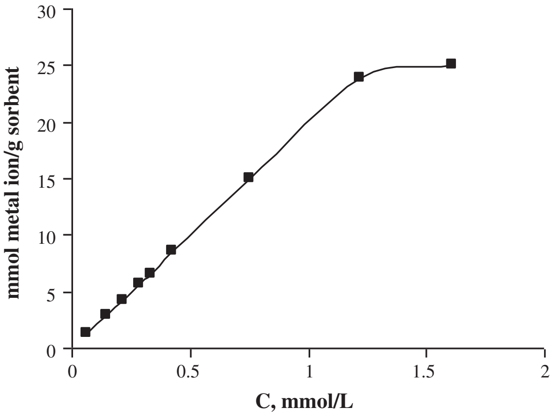

Fig. 18. Effect of initial concentration for metal ion sorption on Si-APTS-NAA sorbent. Cu(II) pH 5; t: 120 min, m: 0.05 g, temperature: 25˚C.

3.2.5. The effect of initial concentration and sorption isotherms

The effect of initial concentrations on metal ion sorption was investigated by varying the initial concentrations of the metal ion at optimum pH value. The obtained results were presented in Figs. 17 and 18. The sorption amount of metal ion was increased with increasing initial concentration, then the line leveled off after 1.71 mmol metal ion concentration for BAA. However, this value was found to be 1.61 mmol metal ion concentration for NAA.

The equilibrium isotherms are very important for understanding the sorption systems. There are several isotherm equations available for analyzing experimental sorption equilibrium data. The most frequently used for sorption are the Langmuir and Freundlich isotherm equations. Experimental data obtained from the effect of initial concentration on sorption capacity were fitted to Langmuir and Freundlich sorption isotherms.

3.2.5.1. Langmuir isotherm. The Langmuir isotherm applies to sorption on a completely homogenous surface with negligible interaction between adsorbed molecules [28]. It is valid for monolayer sorption onto a surface containing a finite number of identical sites.

The linear form of the Langmuir equation can be represented as follows:

$$C/q = 1/(A_s\,K_b) + C/A_s \tag{2}$$

where C ($\mathrm{mmol\,L^{-1}}$) is the concentration of the ion solution at equilibrium and q ($\mathrm{mmol\,g^{-1}}$) is the amount of sorption at equilibrium. A_s is the maximum surface density of monolayer coverage and K_b is the

Langmuir sorption constant ($\mathrm{L\,mmol^{-1}}$) when C/q is plotted against C, a straight line with slope $1/A_s$ and intercept $1/K_b\ A_s$ is obtained. The Langmuir parameters for Cu(II) metal ion, A_s and K_b are calculated from the slope and intercept of the graph are given in Table 3.

3.2.5.2. Freundlich isotherm. The Freundlich isotherm is based on the assumption that the sorption occurs on heterogeneous surfaces with non-uniform distribution of energy levels [30].

The linear form of the Freundlich equation is written as:

$$\ln q = \ln k + 1/n \ln C \tag{3}$$

where C ($\mathrm{mmol\,L^{-1}}$) is the concentration of the ion solution at equilibrium and q ($\mathrm{mmol\,g^{-1}}$) is the amount of sorption at equilibrium. K is the Freundlich constant ($\mathrm{mmol\,g^{-1}}$) which indicates the sorption capacity and n is the heterogeneity factor which represents the bond distribution. When ln q is plotted against ln C, a straight line with slope $1/n$ and intercepts ln K is obtained. The Freundlich parameters for the sorption of Cu(II) ion are given in Table 4. On the comparison of the R^2 (correlation coefficient) values given for Freundlich and Langmuir, Langmuir isotherm represents an excellent fit to the experimental data ($R^2 = 0.9967$) than the Freundlich isotherm for sorbents. It can be concluded that, the metal ion sorption on the immobilized silica gel surface with sorbents can be occurred on homogeneous surface. This result also confirms that the image of SEM is a homogeneous structure of immobilized Schiff base ligands on the silica gel (Figs. 10 and 11).

Table 3
Langmuir constants

Langmuir sorption isotherm				
Metal	Sorbents	Kb	As	R^2
Cu(II)	Si–APTS–BAA	38.8	28.57	0.9967
	Si–APTS–NAA	65.83	25.31	0.9997

Table 4
Freundlich constants

Freundlich sorption isotherm					
Metal	Sorbents	K_f	n	R^2	$1/n$
Cu(II)	Si–APTS–BAA	13.18	2.43	0.8280	0.41
	Si–APTS–NAA	11.015	3.17	0.5185	0.315

3.3. Thermodynamic parameters

Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were determined by following Eqs:

$$\Delta G^\circ = -RT \ln K \tag{4}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

$$\log K = (\Delta S^\circ/2.303R) - (\Delta H^\circ/2.303RT) \tag{6}$$

where ΔG° is the change in free energy ($\mathrm{kj\,mol^{-1}}$), ΔH° is the change in enthalpy ($\mathrm{kj\,mol^{-1}}$), ΔS° is the change in entropy ($\mathrm{kj\,mol\,K^{-1}}$), T is the absolute temperature (K), R is the gas constant (8.314×10^{-3}), and K is the equilibrium constant. The thermodynamics of Cu(II) ion sorption onto sorbents from aqueous solution were studied between 25 and 60℃, when log K is plotted against $1/T$, a straight line with slope $\Delta H^\circ/$ 2.303 RT and intercept $\Delta S^\circ/2.303\ R$ is obtained (Figs. 15 and 16) and the values of ΔH° and ΔS° were obtained from the slope and intercept of the Van't

Table 5
Thermodynamic parameters for the sorption of Cu(II) on sorbents

Metal Cu(II)	T (K)	$1/T$	ln K (kJ/mol)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
Si–APTS–BAA	298	0.003356	2.17838	−7.44934	−32.2251	−0.08314
	308	0.003247	1.825104	−6.61794		
	323	0.003096	1.107009	−5.37084		
	333	0.003003	0.869581	−4.53944		
Si–APTS–NAA	298	0.003356	5.754018	−14.3724	5.8198	0.067759
	308	0.003247	5.94964	−15.05		
	323	0.003096	5.980973	−16.0664		
	333	0.003003	6.029884	−16.744		

Table 6
The rate constants of sorption kinetic model for Cu(II) on sorbents

Metal	Sorbents	q (experimental)	Pseudo-first-order			Pseudo-second-order		
			k_1	q_e (calculated)	R^2	k_2	q_e (calculated)	R^2
Cu(II)	Si–APTS–NAA	0.3341	6.9×10^{-5}	4.1605	0.731	10.152	0.3349	1.000
	Si–APTS–BAA	0.3331	2.3×10^{-4}	3.6377	0.802	3.8463	0.3342	0.999

Hoff plots. The obtained parameters of the sorption process are given in Table 5. As it can be seen from Table 5, negative ΔG° values confirm the feasibility of the process and spontaneous nature of the sorption for the adsorbent. The negative values of ΔH° indicate the exothermic nature of the process while the negative ΔS° corresponds to a decrease in the degree of freedom of the adsorbed species [31].

3.4. Sorption kinetics

3.4.1. The pseudo-first-order kinetic model

Experiments were also performed to understand the kinetics of Cu(II) sorption by these sorbents. The kinetics of Cu(II) sorption on adsorbent followed the first-order kinetic model given by Lagergren:

$$\ln(q_e - q_t) = \ln\ q_e - k_1\ t \tag{7}$$

where q_t is the quantity of Cu(II) (mg/g) sorbed on the sorbent after various times t, q_e is the maximum sorption capacity (mg/g) and k_1 is the pseudo-first-order rate constant for the sorption process (min^{-1}) [32]. In order to calculate kinetic data, a plot of ln ($q_e - q_t$) against t was carried out. First-order constant (k_1) and q_e values were calculated from the slope and intercept, respectively (Table 6). It is clear that the R^2 value is relatively low and the experimental q_e value did not agree with the calculated q_e value from the linear plot. These results showed that the pseudo-first-order model did not satisfactorily predict the kinetic of Cu(II) sorption on to the sorbents.

3.4.2. The pseudo-second-order kinetic model

The sorption kinetic can also be given by a pseudo-second-order equation [33].

$$t/q_t = 1/k_2\ q^2 + (1/q_e)\ t \tag{8}$$

where q_t and q_e are the amount of Cu(II) (mg/g) sorbed on the sorbent after various times t and maximum sorption capacity (mg/g), respectively, and k_2 is the pseudo-second-order rate constant for the sorption (g/mg min). Figs. 19 and 20 show the curves obtained from the experimental data. The kinetic parameters were calculated from curves and are listed in Table 6. As it can be seen from Table 6, higher correlation coefficient was obtained for the pseudo-second-order model. Experimental q_e value also agrees with the calculated q_e value. It indicates that the

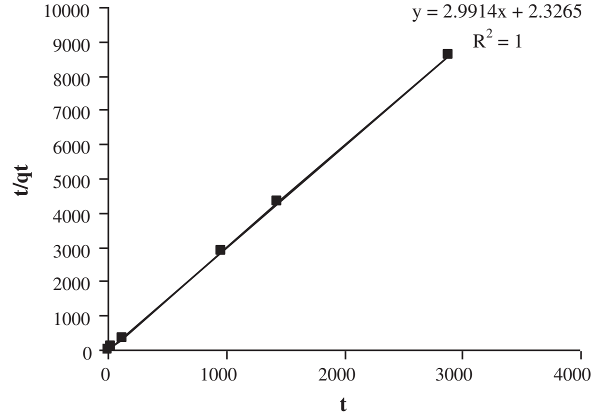

Fig. 19. The fitting of pseudo-second-order model for Cu (II) ion on Si-APTS-BAA(Cu(II): 1.0×10^{-3} mol/L, pH 5, m: 0.05 g).

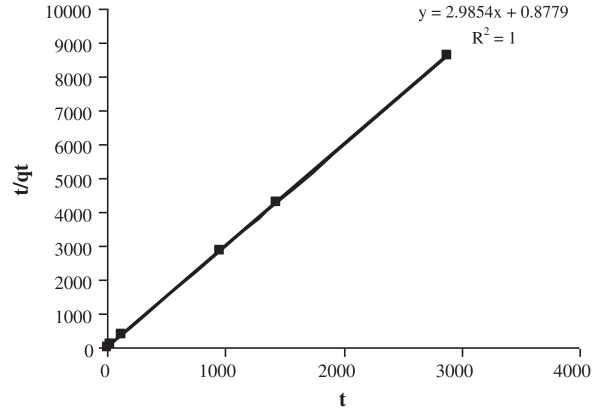

Fig. 20. The fitting of pseudo-second-order model for Cu (II) ion on Si-APTS-NAA(Cu(II): 1.0×10^{-3} mol/L, pH 5, m: 0.05 g).

sorption of Cu(II) on to sorbents can be more favorably approximated by a pseudo-second-order model than the pseudo-first-order one.

4. Conclusions

In the presented study, BAA and NAA were successfully bound on the silica surface after modification by 3-aminopropyltrimethoxysilane. Structural, chemical and metal ion sorption properties of this newly prepared sorbents were investigated. The sorbents showed a high sorption capacity towards Cu (II) ion. The removal of Cu(II) ion strongly depends on the solution pH. The maximum removal of Cu(II) was observed at an optimum pH of 5. Because the prepared materials have a good sorption capacity obtained at lower temperatures, Cu(II) ion sorption was significantly affected by the change of temperature.

Sorption of Cu(II) ion on the prepared sorbents can be expressed better with Langmuir type sorption isotherm which shows the homogenous characteristic of the sorption sites on sorbents.

This immobilized silica gel structure can be used as effective, lower cost material for the removal of Cu (II) ion from contaminated or waste water.

Acknowledgement

The authors are grateful for the financial support provided by the Suleyman Demirel University Unit of Scientific Research Project under Project 1917-YL-09.

References

[1] A.H. Chen, S.C. Liu, C.Y. Chen, C.Y. Chen, Comparative adsorption of Cu(II), Zn(II) and Pb (II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin, J. Hazard. Mater. 154 (2008) 184–191.

[2] S.H. Lin, S.L. Lai, H.G. Leu, Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process, J. Hazard. Mater. 76 (2000) 139–153.

[3] S. Karabulut, A. Karabakan, A. Denizli, Y. Yurum, Batch removal of copper (II) and zinc (II) from aqueous solutions with low-rank Turkish coals, Sep. Purif. Technol. 18 (2000) 177–184.

[4] J. Li, J. Hu, G. Sheng, G. Zhao, Q. Huan, Effect of pH, ionic strenght, foreign ions and temperature on the adsorption of Cu(II) from aqueous solution to GMZ bentonite, Colloids Surf. A. 349 (2009) 195–201.

[5] P.A. Sule, J.D. Ingle, Jr., Determination of the speciation of chromium with an automated two-column ion-exchange system, Anal. Chim. Acta 326 (1996) 85–93.

[6] X. Chen, G. Chen, P.L. Yue, Novel electrode system for electro flotation of wastewater, Environ. Sci. Technol. 36 (2002) 778–783.

[7] D.M. Adria-Cerezo, A.R. Llobat-Estelles, A.R. Mauri-Aucejo, Preconcentration and speciation of chromium in waters using solid-phase extraction and atomic absorption spectrometry, Talanta 51 (2000) 531–536.

[8] R.Y. Ning, Arsenic removed by reverse osmosis, Desalination 143 (2002) 237–241.

[9] M. Ersoz, Y. Cengeloglu, E. Kır, M. Koyuncu, Z. Yazıcıgil, Transport of Cu(II) ions through charged cation-exchange membranes, J. Appl. Polym. Sci. 81 (2001) 421–427.

[10] P.K. Roy, V. Swami, D. Kumar, C. Rajagopal, Removal of toxic metals using superabsorbent polyelectrolytic hydrogels, J. Appl. Polym. Sci. 122 (2011) 2415–2423.

[11] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metal uptake from contaminated water a review, J. Hazard. Mater. 97 (2003) 219–243.

[12] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye on crosslinked chitosan beads, J. Hazard. Mater. 93 (2002) 233–248.

[13] I.H. Gubbuk, R. Gup, H. Kara, M. Ersoz, Adsorption of Cu(II) onto silica gel-immobilized Schiff base derivative, Desalination 249 (2009) 1243–1248.

[14] P. Tzvetkova, P. Vassileva, R. Nickolov, Modified silica gel with 5-amino-1,3,4-thiadiazole-2-thiol for heavy metal ions removal, J. Porous Mater. 17 (2010) 459–463.

[15] S. Radi, A. Attayibat, Y. Lekchiri, A. Ramdani, M. Bacquet, Synthesis and characterization of a new material based on porous silica—Chemically immobilized C, N-pyridylpyrazole for heavy metals adsorption, Mater. Chem. Phys. 111 (2008) 296–300.

[16] Y. Cui, X. Chang, X. Zhu, H. Lou, Z. Hu, X. Zou, Q. He, Chemically modified silica gel with p-dimethylaminobenzaldehyde for selective solid-phase extraction and preconcentration of Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) by ICP-OES, Microchem. J. 87 (2007) 20–26.

[17] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, A. Imyim, Highly selective preconcentration of Cu(II) from seawater and water samples using amidoamidoxime silica, Talanta 78 (2009) 1004–1010.

[18] A.N. Kursunlu, E. Guler, H. Dumrul, O. Kocyigit, I.H. Gubbuk, Chemical modification of silica gel with synthesized new Schiff base derivatives and sorption studies of cobalt (II) and nickel (II), Appl. Surf. Sci. 255 (2009) 8798–8803.

[19] I.H. Gubbuk, I. Hatay, A. Coskun, M. Ersoz, Immobilization of oxime derivative on silica gel for the preparation of new adsorbent, J. Hazard. Mater. 172 (2009) 1532–1537.

[20] A. Goswami, A.K. Singh, Silica gel functionalized with resacetophenone: Synthesis of a new chelating matrix and its application as metal ion collector for their flame atomic absorption spectrometric determination, Anal. Chim. Acta 454 (2002) 229–240.

[21] I.H. Gubbuk, R. Gup, M. Ersoz, Synthesis, characterization, and sorption properties of silica gel-immobilized Schiff base derivative, J. Colloid Interface Sci. 320 (2008) 376–382.

[22] J.S. Kim, J. Yi, The removal of copper ions from aqueous solutions using silica supports immobilized with 2-hydroxy-5-nonylacetophenoneoxime, Sep. Sci. Technol. 34 (1999) 2957–2971.

[23] N.M. Shauib, A.Z.A. Elassar, A. El-Dissouky, Synthesis and spectroscopic characterization of copper(II) complexes with the polydentate chelating ligand 4,4-[1,4-phenylenedi(nitrilo) dipente-2-one, Spectrochim. Acta 63 (2006) 714–722.

[24] J.A.A. Sales, P.F. Faira, A.G.S. Prado, C. Airoldi, Attachment of 2- aminomethylpyrridine molecule onto grafted silica gel surface and its ability in chelating cations, Polyhedron 23 (2004) 719–725.

[25] J. Fan, C. Wu, Y. Wei, C. Peng, P. Peng, Preparation of xylenol orange functionalized silica gel as a selective solid phase extractor and its application for preconcentration-separation of mercury from waters, J. Hazard. Mater. 145 (2007) 323–330.

[26] A.G.S. Prado, C. Airoldi, The pesticide 3-(3,4-dicholorophenyl)-1,1-dimethylurea (Divron) immobilized on silica gel surface, J. Colloid Interface Sci. 236 (2001) 161–165.

[27] R.S.A. Machado, M.G. Fonseca, L.N.H. Arakaki, J.G.P. Espinola, S.F. Oliveira, Silica gel containing sulfur, nitrogen and oxygen as adsorbent centers on surface for removing copper from aqueous/ethanolic solutions, Talanta 63 (2004) 317–322.

[28] M. Puanngam, F. Unob, Preparation and use of chemically mosified MCM-41 and silica gel as selective adsorbents for Hg(II) ions, J. Hazard. Mater. 154 (2008) 578–587.

[29] F. Xi, J. Wu, Preparation of macroporous chitosan layer coated on silica gel and its application to affinity chromatography for rypsin inhibitör purification, React. Funct. Polym. 66 (2006) 682–688.

[30] Y.S. Ho, A.E. Ofomaja, Biosorption thermodynamics of cadmium on coconut copra metal as biosorbent, Biochem. Eng. J. 30 (2006) 117–123.

[31] D. Mohan, V.K. Gupta, S.K. Srivastava, S. Chander, Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste, Colloids Surf. A 177 (2000) 169–181.

[32] P. Antonio, K. Iha, M.E.V. Suárez-Iha, Kinetic modeling of adsorption of di-2-pyridylketone salicyloylhydrazone on silica gel, J. Colloid Interface Sci. 307 (2007) 24–28.

[33] Y.S. Ho, G. Mckay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2007) 735–742.