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Adsorption of Cu(II) onto novel silica gel-immobilized bithiophene tripodal receptor

Said Tighadouini[1], Smaail Radi[*1,2], Mohamed El Massaoudi[1], Maryse Bacquet[3], Mustapha Zaghiroui[4]

[1]*LCAE, (URAC-25) Faculté des Sciences, Université Mohamed I, 60 000 Oujda, Morocco.*
[2]*Centre de l'Oriental des Sciences et Technologies de l'Eau (COSTE), Université Mohamed I, Oujda, Morocco.*
[3]*Université des Sciences et Technologies de Lille, UMET: Unité Matériaux et Transformations UMR8207, Equipe Ingénierie des Systèmes Polymères, 59655 Villeneuve d'Ascq, France.*
[4]*Laboratoire GREMAN CNRS-UMR 7347 IUT de BLOIS, Université François-Rabelais de Tours, 15 rue de la Chocolatrie 41029 Blois, France.*

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**Corresponding Author. E-mail*: radi_smaail@yahoo.fr

Abstract

A novel inorganic-organic hybrid material based on silica chemically modified with *N,C*-bis(thiophen-1-ylmethyl)amine (SiNTh) was synthesized and characterized by elemental analysis, FT-IR, ^{13}C NMR of the solid state, nitrogen adsorption-desorption isotherm, BET surface area, BJH pore sizes and scanning electron microscopy (SEM). The new surface exhibits good chemical and thermal stability determined by thermogravimetry curves (TGA). SiNTh has been used for Cu(II) sorption from aqueous solution using batch method. The influences of contact time, pH, concentration, and temperature for sorption on SiNTh were investigated. Studies show that the adsorption follow Langmuir isotherm model. The thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) reveal that the process was endothermic and spontaneous in nature, and the adsorption process was found to follow pseudo-second order kinetics.

Keywords: Cu(II) removal; Selective adsorbent, Synthesis, Characterization, Adsorption

Introduction

Copper is one of the essential elements that are required to maintain the normal structure, function and proliferation of cells, but excess Cu(II) produces many toxic and harmful effects in living organisms [1-3]. The high Cu(II) concentration not only endangers the growth of the aquatic animals and plants, but also exerts a deleterious effect on the human's health. The World Health Organization (WHO) has recommended a maximum acceptable concentration of 1.5 mg L^{-1} of Cu(II) in drinking water [4].

Therefore, in recent years, extensive research works have been focused on the development of effective and cheaper methods for the scavenging heavy metals from wastewaters such as cloud point extraction [5], electro-analytical techniques [6], liquid-liquid extraction [7], membrane filtration [8], ion exchange [9], solid phase extraction (SPE) [10], coprecipitation [11], resin chelation [12] and foam-flotation [13].

Recently solid-phase extraction (SPE) technique has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes [14-17]. The SPE has several major advantage that include (i) higher enrichment factor, (ii) simple operation, (iii) safety with respect to hazardous samples, (iv) high selectivity, (v) lower cost and (vi) ability to combine with different modern detection techniques [18]. Silica gel has been widely used for metal extraction in the SPE technique due to its high porosity, hydrophilicity, good mechanical and thermal stability, lower susceptibility to swelling and shrinking, and its easy modification.

For this reason, much chemically modified silica has been developed [19-23]. Hence, many authors reported the use of chelating ligands functionalized onto silica for metal ion extraction and preconcentration; for example 6-((2-(2-hydroxy-1-naphthoyl) hydrazono)-methyl) benzoic acid [24], 2-[(phosphonomethyl)-amino]acetic acid [25], amino-bearing calixcrown [26], ethylene-diaminetetraacetic acid [27], 2,2'-dipyridylamine [28] and 1-{4-

[(2-hydroxy-benzylidene) amino]phenyl}ethanone [29], etc. Their potential applications are due essentially to the nature of the grafted ligands. Indeed, the most commonly attached chelate ability for this purpose is devoted for donor atoms, such as oxygen, nitrogen and sulphur which have a large capability in forming complexes with a series of metal ions, forcing in some cases, a distinguishable selective extraction property.

In this context, the ability of thiophene and its derivatives to act as ligands with sulphur donors have been the research subjects of many preconcentration and coordination chemists. This is evident from the large number of articles on this topic [30, 31].

In continuation of our work in this field [32-38], this paper describes the synthesis and the characterization of a new hybrid material obtained by covalent modification of silica with a new synthesized bithiophene tripodal. The adsorbent showed great affinity, high adsorption capacity, high selectivity and less equilibrium time for binding Cu(II). Parameters that can affect the sorption efficiency of the metal ions were studied.

2. Materials and methods

All solvents and other chemicals (Aldrich, purity 99.5%) were of analytical grade and used without further purification. Silica gel (E. Merch) with particle size in the range of 70-230 mesh, median pore diameter 60 Å, was activated before use by heating it at 160°C during 24h. The silylating agent 3-aminopropyltrimethoxtsilane (Janssen Chimica) was used without purification. All metal ions determined by atomic adsorption measurements were performed by Spectra Varian A.A. 400 spectrophotometer. The pH value was controlled by a pH 2006, J. P. Selecta; s. a. Elemental analyses were performed by Microanalysis Centre Service (CNRS). FT-IR spectra were obtained with Perkin Elmer System 2000. SEM image were obtained on an FEI-Quanta 200. The mass loss determinations were performed in 90:10 oxygen/nitrogen atmospheres on a Perkin Elmer Diamond TG/DTA, at a heating rate of 10°C min-1. The ^{13}C NMR spectrum of the solid state was obtained with a CP MAX CXP 300MHz. A specific area of modified silica was determined by using the BET equation. The nitrogen adsorption-desorption was obtained by means of a Thermoquest Sorpsomatic 1990 analyzer, after the material had been purged in a stream of dry nitrogen.

2.1. Synthesis of 3-aminopropylsilica ($SiNH_2$)

Activated silica (5g) suspended in 150 ml of dried toluene was refluxed and mechanically stirred under nitrogen atmosphere for 2h. To this suspension, 10ml of aminopropyltrimethoxysilane was added dropwise and the mixture was kept under reflux for 24h. The solid was filtered, washed with toluene and ethanol. It was then Soxhlet extracted with a mixture of ethanol and dichloromethane (1/1) for 12h to remove the silylating reagent residue. The immobilized silica gel, named $SiNH_2$, was dried in vacuum at room temperature.

2.2. Synthesis of bithiophene-substituted silica (SiNTh)

For the synthesis of SiNTh, the mixture of 3-aminopropylsilica ($SiNH_2$) (3g), 2-(chloromethyl)thiophene (6.16g, 23.34mmol) and sodium carbonate (3.29g, 31.12mmol) in 70ml of dry acetonitrile was stirred and refluxed under nitrogen for 5 days. Then the substituted silica was filtered off and washed with hot distillated water to eliminate sodium carbonate. The product was transferred to the Soxhlet extraction apparatus for reflux-extraction in acetonitrile, methanol and dichloromethane for 12h, respectively. The product was dried under vacuum at 70°C over 24h.

2.3. Batch experiments

The applicability of SiNTh to remove Cu(II) was performed by adding 10 mg of adsorbent in 10 ml of metal ion solution with concentration ranging from 15 to 150 mg L^{-1} at 25°C. The effect of pH was studied in the range of 1-7. The solutions were mechanically stirred at room temperature for 5 min to 40 min at 25°C and under various pH. After extraction, the solid phase was separated by filtration. Residual metal concentration of the supernatant was determined by atomic absorption measurements. The amount of metal ions adsorbed by the synthesized material SiNTh from aqueous solution was calculated using the following equations [39]:

$$Q_M = (C_0 - Ce) \times V / W$$

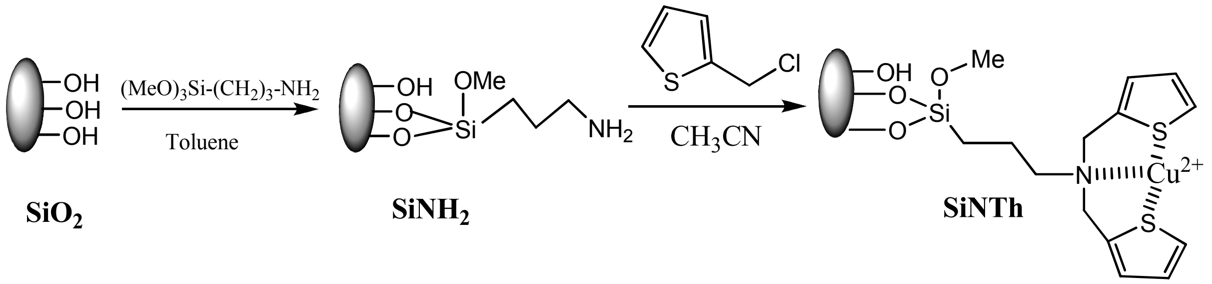
$$Q_W = Q_M \times M$$

where Q_M is the amount of the metal ion adsorbed (mmol/g), Q_W the amount of the metal ion adsorbed (mg/g), V is the volume of the aqueous solution (l), W is the weight of the adsorbent (g), C_0 the initial concentration of metal ion (mmol/L), Ce the equilibrium metal ion concentration in solution (mmol/L) and M the atomic weight of metals (g/mol). Analyses were performed in duplicate for each sample and the mean data are reported.

3. Result s and discussion

3.1. Linker synthesis

The synthetic procedure for the new chelating material can be summarized in scheme1. The preparation involves reacting the activated silica gel with 3-aminopropyltrimethoxysilane in toluene to from the amino groups attached to the silica surface [40]. These NH_2-groups onto the silica surface were then reacted with bis(2-(chloromethyl)thiophene under refluxing at 80°C for 5 days using anhydrous acetonitrile as solvent and sodium carbonate to trap the hydrochloric acid formed during the reaction which leaded to the new chelating sorbent SiNTh.



Scheme 1. The synthesis route of modified chelating material

3.2. Elemental analysis

The elemental analysis of carbon and nitrogen (not present in the starting activated silica) of aminopropylsilica ($SiNH_2$) makes it possible to characterize and highlight the organic introduced group on surface of silica. The microanalysis (%C = 4.46 and %N =1.66) suggests that two methoxy groups were substituted by silanol. The final material SiNTh showed also an increase in the percentage of %C =4.83 and %N =1.45 which means that 2-(chloromethyl)thiophene ligand was immobilized on the silica surface.

3.3. FT-IR Characterization

To confirm the presence of functional groups in the material, FT-IR spectra were performed for free silica, $SiNH_2$, and SiNTh materials (Figure 1). Compared to free silica gel, $SiNH_2$ spectrum exhibits some new peaks such as the CH_2 vibration band at 2941 cm^{-1} and NH_2 vibration at 1560 cm^{-1} [41-43]. The characterization features of SiNTh compared with $SiNH_2$ were the disappearance of the adsorption band at 1560 cm^{-1} due to the reaction of primary amine ($-NH_2$) and the appearance of new characteristic bond around 1545 cm^{-1} resulted from C=C vibration, which confirms the anchoring of the organic molecule onto the silica surface.

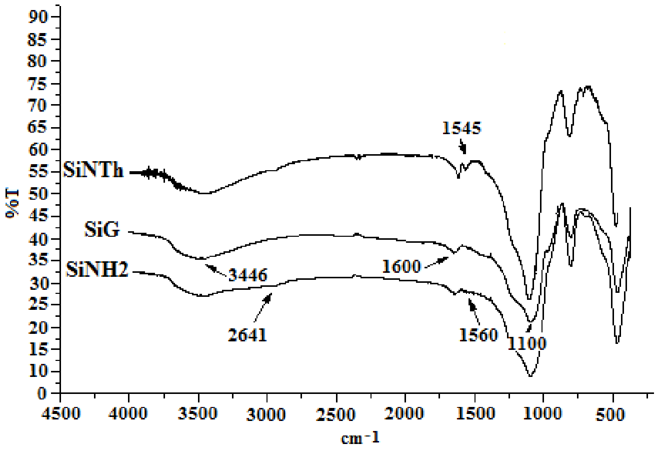


Figure 1. FT-IR Spectra of free silica (SiG), 3-aminopropylsilica ($SiNH_2$) and (SiNTh).

3.4. Scanning Electron Micrographs

Scanning electron micrographs (SEM) were obtained on the free silica and chemically modified silicas in order to detect differences in their surfaces. SEM of silica gel, SiNH2, and SiNFn in Figure 2 were obtained at 300 and 1200 magnification. The SEM was displayed to clarify the un-agglomeration of the silica after treatment to support the claiming of regular distribution of the functional group on the whole surface. It was evident that the loaded functional groups were distributed on the whole surface of SiNTh that made it rough.

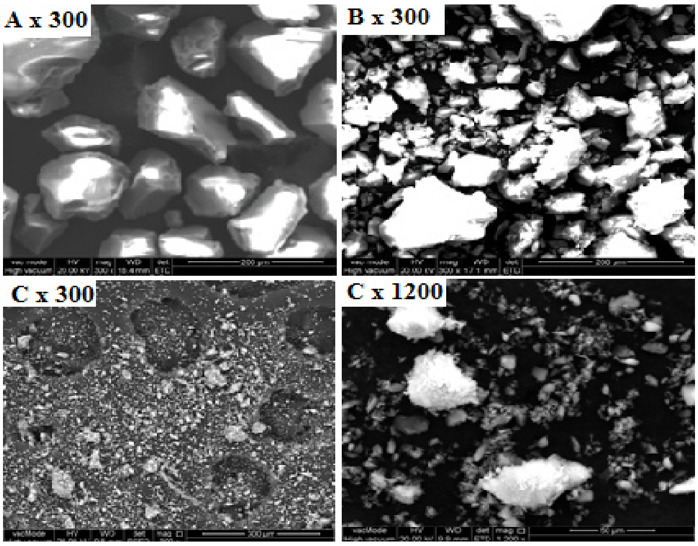


Figure 2. SEM images of free silica (A), $SiNH_2$ (B) and SiNTh (C)

3.5. TGA analysis and thermal stability

The thermogravimetric curves for all surfaces indicate a degradation process between 116 and 800°C which confirms the high thermal stability of the prepared material (Figure 3). The free silica presents a first mass loss stage of 3.15% at 25-110°C interval assigned to physically adsorbed water and a second loss of 5.85% at 110-800°C allotted to the condensation of the free silanol groups [44,45]. Again two distinct mass loss steps were detected for SiNH2 sample. Thus, for the first one, a small mass loss of 1.56% from 25 to 100°C rang was attributed to the remaining silanol hydration water, as a consequence of the use of these groups on immobilization process. On the other hand, a pronounced increase of 9.77% in masse loss was observed for the second step, between 208 and 800°C corresponded to the organic matter added onto surface during immobilization. The final SiNTh material presented two distinct mass loss stages. Following the preceding interpretation, the first mass loss of 1.51% in the 25–116°C range is assigned to adsorbed water, and other mass loss of 8.33% between 261 and 800°C is attributed to the decomposition of the thiophene fraction immobilized on the surface of silica gel, together with the condensation of the remaining silanol groups. The pronounced increase in mass loss reflects the higher amount of the anchored organic groups.

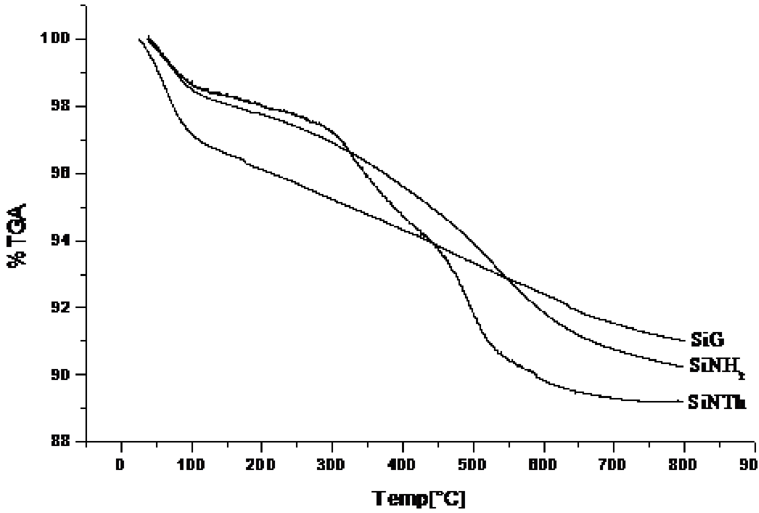


Figure 3. Thermogravimitric curves of free silica, $SiNH_2$ and SiNTh

3.6. ^{13}C NMR characterization

The presence of the organic spacer arm on the inorganic silica was asserted by ^{13}C solid state NMR spectroscopy (Figure 4). Three well-formed peaks, at 9.02, 24.79 and 42.62 ppm were attributed to the propyl carbon, Si-CH2, -CH2- and N-CH2, respectively. For the SiNTh, the spectrum reveals other signals at 60-160 ppm corresponding to specific carbons of *N,C*-bis(Thiophen-1-ylmethyl)amine.

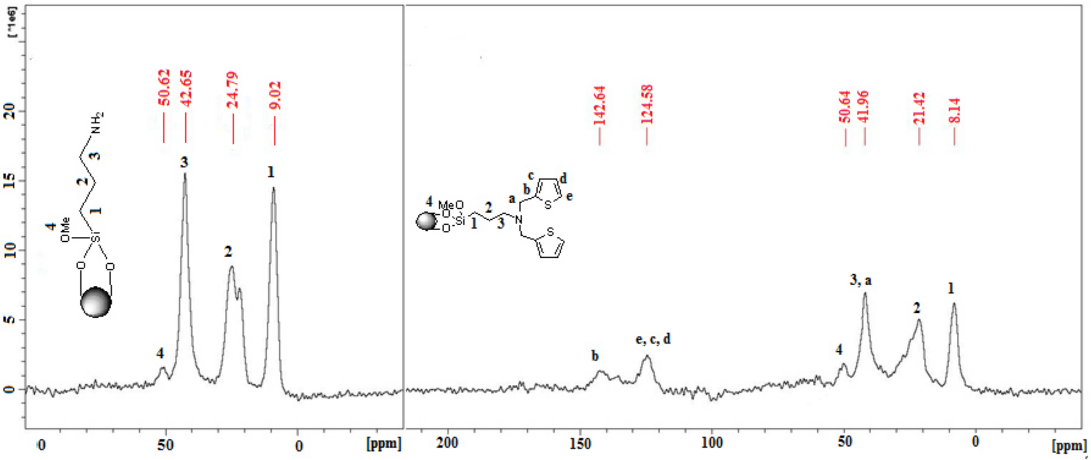


Figure 4. ^{13}C NMR spectra of (SiNH$_2$) and (SiNTh)

3.7. Chemical stability

Chemical stability of the newly synthesized material SiNTh was examined in various acidic and buffer solutions (pH 1-7). No change in the material structure was observed even after 24h of contact. The high stability exhibited by the attached organofunctional group is presumably due to the pendant group. It has been shown that when the length of the hydrocarbon bridge was more than two methylene groups, the rupture of Si–C bond did not occur in a mineral acid medium, due to the length of the chain; longer chains can no longer have a functional handle that can undergo beta-elimination of the Si cation [46, 47].

3.8. Surface properties

To show the porosity changes of the silica induced by the introduction of 3-aminopropyl and bithiophene unit, we measured the surface area S$_{BET}$ (Brunauer–Emmett–Teller), pore volumes, and pore diameters of both silica and its derivatives with nitrogen adsorption–desorption isotherms (Figure 5) and by Barrett–Joyner–Halenda (BJH) methods [48,49]. The anchoring of organic moieties onto the silica matrix obstructs the access of nitrogen gas molecules reducing thus its surface area. As a result, the BET surface area decreased after grafting, according to the sequence SG > SiNH2 > SiNTh.

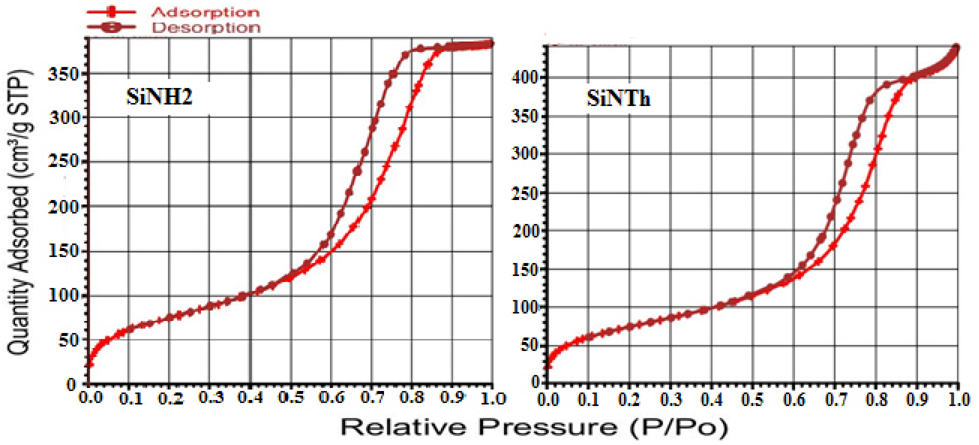


Figure 5. Nitrogen adsorption-desorption isotherm plots of SiNH$_2$ and SiNTh.

The reduction in surface area in this order confirms the functionalization of silica with 3-aminopropyl-trimethoxy silane to give SiNH$_2$, and its modification with bithiophene unit to yield a chelating sorbent SiNTh. Therefore, the total pore volume and pore diameter increased, which benefit to expose the active sites and also benefit to chemical sorption. It can be concluded that SiNTh presents an adequate chemical characteristic to adsorb metal ions. The physical properties of silica derivatives are shown in Table 1.

Table 1. Physical properties of silica derivatives

Silica derivatives	**Specific surface S_{BET} ($m^2 g^{-1}$)**	**Pore volume ($cm^3 g^{-1}$)**
Free silica	305.21	0.77
$SiNH_2$	283.08	0.69
SiNTh	275.16	0.75

3.9. Adsorption studies

3.9.1. Effect of pH

It is well-known that binding of metal ions to the chelate compounds is mainly dependent on several factors such as the nature of the metal ions, nature of the donor atoms and the buffering conditions [50-53]. Therefore, to evaluate the suitability of the newly synthesized SiNTh for copper ion extraction, we studied the effect of pH as one of the most significant controlling factors in such process.

The adsorption properties of SiNTh were investigated in the pH 1-7 range as shown in Figure 6. Results reveal that the metal ion uptake of the adsorbent varies significantly as the pH changes. At lower pH values, the retention of metal ions by the functionalized silica SiNTh is not significant since the ligand must be almost entirely in its protonated form. As the pH increases, the protonation becomes weak, which enhances the chelation and adsorption of metal ions. At pH > 7, the retention of metal ions decreased because of the hydrolysis of metal ions (leading to the hydroxides of M(II): $M(OH)^+$and $M(OH)_2$), this makes it difficult to distinguish between the hydrolyzed or adsorbed M(II). Therefore, the optimum pH for the maximum sorption of Cu(II), was at pH 6. The possible reason for such a high capacities for Cu(II) is mainly based on the Cu(II)-bithiophene complex which is probably stable.

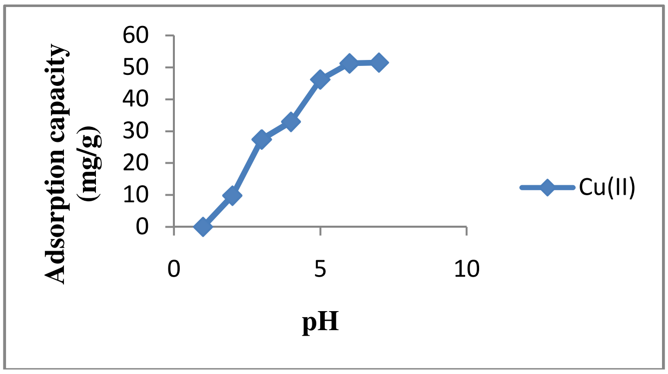


Figure 6. Effect of pH on the adsorption of metal ions on SiNTh, at optimum concentration, t = 40 min and Temp: 25°C.

3.9.2. Effect of contact time and kinetic modeling

The kinetics of adsorption that describes the solute uptake rate governing the contact time of the sorption reaction is one of the important characteristics that define the efficiency of sorption. Hence, in the present study, the extraction time was varied from 5 to 40 min. A model solution consisting of 10 mL of 100 mgL^{-1} Cu(II) at pH 6.5 was used for all experiments. The extraction time required for reaching extraction equilibrium was rapid and the plateau was reached after about 25 min of contact. The fast extraction rate indicates that the sorbent is highly suitable for the preconcentration of trace Cu(II) from aqueous solution. This behavior indicates that Cu(II) ion has a good accessibility through the chelating sites on the modified silica and the binding constant between the metal ion and the bithiophene tripod immobilized on the silica surface is possibly high. According to this result, it is suitable for applying the sorbent in a flow system where shorter extraction time or faster adsorption is required. The results as shown in Figure 7

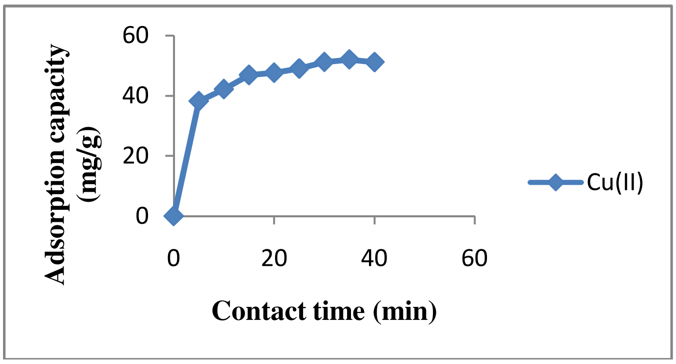


Figure 7. Effect of shaking time on the adsorption capacity of Cu(II) at optimum pH, optimum concentration and Temp: 25°C

Kinetic modeling was performed to find the adsorption rate of metal ions onto the SiNTh. Adsorption kinetics was conducted by using the pseudo-first-order [54, 55] and pseudo-second-order models [56, 57]. The linear equations for pseudo-first order and pseudo-second order kinetics are as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

where q_e and q_t are the amounts of metal ions adsorbed (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 is the rate constant of the first-order adsorption in min^{-1}.

Pseudo-second-order can be written in a linear form as the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where k2 (g/mg min) is the pseudo-second-order adsorption rate constant.

The values of kinetic parameters are summarized in Table 2. The results show that pseudo-second-order model has a better determination coefficient R^2 than pseudo-first-order model.

Table 2. Kinetics of copper removal onto SiNTh

Pseudo-first-order				Pseudo-second-order		
$q_{e(exp)}$(mg/g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
51.14	20.08	0.09	0.976	52.63	$13.52.10^{-3}$	0.996

The values of regression coefficient obtained by pseudo-second order model are much higher than that obtained from pseudo-first order kinetic model. The calculated value of qe by pseudo-second-order model is much closer to the experimental value, which also confirms the validity of the model. The fitted curve of linear pseudo-second order model is shown in Figure 8.

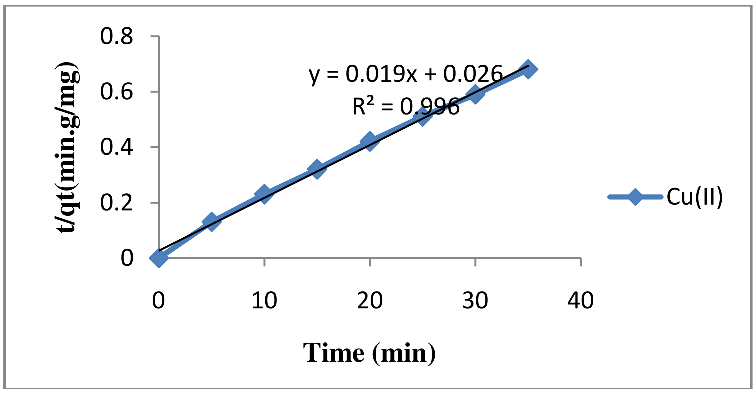


Figure 8. Pseudo-second-order model fit for the adsorption of Cu(II) by SiNTh

3.9.3. Adsorption isotherm

For a further understanding of the functionalized silica's adsorption behavior, the effect of the initial Cu(II) concentration on the adsorption ability was examined. Solutions with metal ion in the range of 15–150 mgL^{-1} were used in the batch containing 0.01 g/10 mL adsorbent at room temperature as shown in Figure 9. With the raise of initial metal concentration, the adsorption capacity, typically, showed a sharp increase, followed with a slow down to equilibrium state. The maximum adsorption capacity was obtained as 51.14 mg/g. This value was reached for the initial concentration of Cu(II) of 100 mg.L^{-1}.

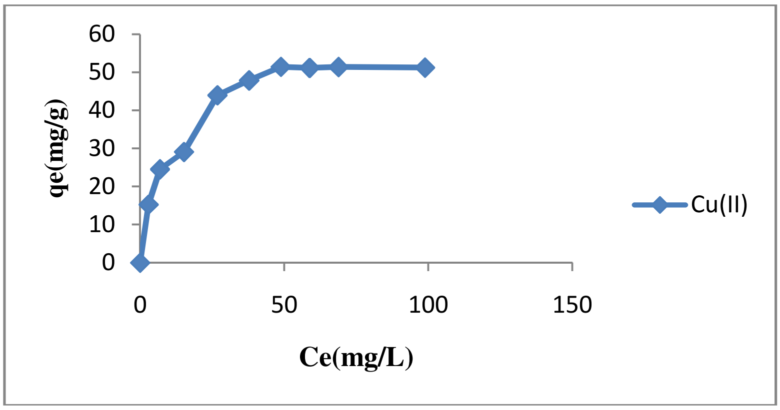


Figure 9. Concentration of copper on adsorption onto SiNTh. Adsorption dose: 10mg, V=10ml, Temp: 25°C and pH=6.5

The adsorption equilibrium data were fitted with Langmuir and Freundlich isotherm models for a comparative study of the sorption behavior. The Langmuir model represents the nonlinear sorption and suggests that metal uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed species. The linearised from of the Langmuir isotherm equation can be represented as [58-60]:

$$\frac{C_e}{q_e} = \frac{C_e}{q} + \frac{1}{qK_L}$$

where q_e is the amount of solute sorbed (mg.g^{-1}), C_e is the equilibrium ion concentration in the solution (mg.L^{-1}), q is the saturated adsorption capacity (mg.g^{-1}) and K_L is the Langmuir adsorption constant (L.mg^{-1}). The plot of C_e/q_e versus C_e for the sorption gives a straight line of slope $1/qK_L$ and intercepts 1/q.

Freundlich model describes the adsorption on a heterogeneous (multiple layer) surface with uniform energy, Linearised of the Freundlich isotherm equation: [61]

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n}$$

where q_e is the adsorption capacity (mg.g^{-1}), C_e is the equilibrium concentration of the solute (mg.L^{-1}), *n* is Freundlich constant and K_F is the binding energy constant reflecting the affinity of the adsorbents to metal ions (mg.g^{-1}). According to the equation the plot of the ln q_e versus ln C_e gives a straight line and K_F and n values can be calculated from the intercept and slope of this straight line.

The fitted parameters of the adsorption isotherm were shown in Table 3.

Table 3. Adsorption isotherm parameters for the removal of copper onto SiNTh

Metal	Langmuir isotherm model			Freundlich isotherm model		
	q (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
Cu(II)	54.94	0.180	0.993	11.36	2.71	0.943

In comparison, the adsorption behavior of Cu(II) was better fitted by Langmuir model with the coefficient (R^2) of 0.993. The maximum sorption capacity was calculated to be 54.94 mg/g, which was very close to the experimental data. The R^2 value (0.943) of Freundlich model indicated that the model was not able to adequately describe the adsorption behavior in our experiment. The fitted curve of linear Langmuir model was shown in Figure 10.

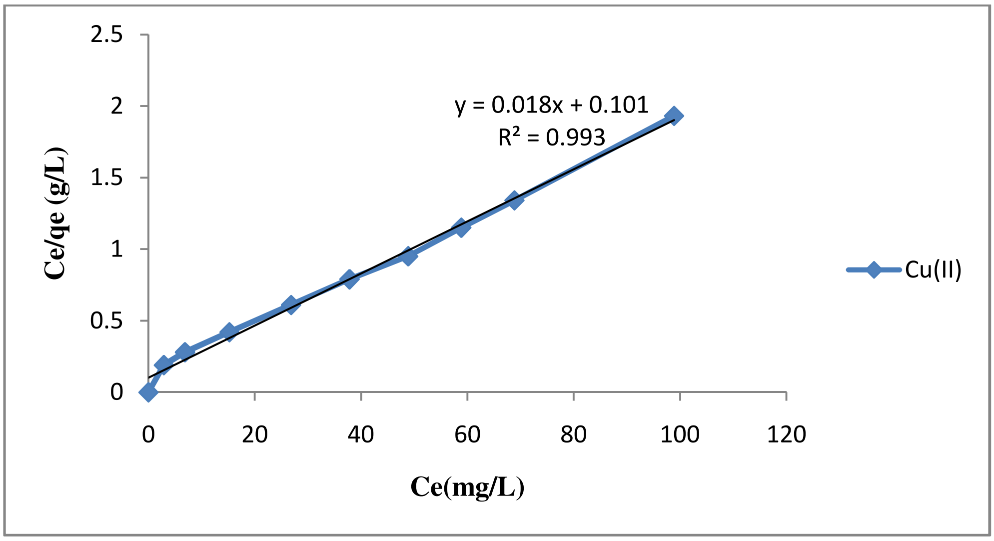


Figure 10. Langmuir adsorption model fit of Cu(II) on SiNTh

3.9.4. Thermodynamic studies

The thermodynamics of copper(II) sorption onto SiNTh from aqueous solution was studied between 25 and 45°C using 100mg/l of Cu(II). The effect of temperature on sorption is shown in Figure 11. The equilibrium constant K_d value and the thermodynamic parameters, Gibbs free energy change ΔG°, enthalpy change ΔH° and entropy change ΔS° were determined using the following equations [62-64]:

$$Kd = \frac{C_0 - C_e}{C_e}\frac{V}{m}$$

$$\ln Kd = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

where C_0(mg/L) is the initial concentration of metal solution, C_e(mg/L) is the equilibrium concentration, V(ml) is the volume of solution, m(g) is the dosage of sorbents, R is the universal gas constant (8.314J/mol/K) and T(K) is the absolute temperature. The ΔH° and ΔS° values were obtained from the slop and intercept of lnKd verses 1/T as shown in Figure 11 and summarized in Table 4.

Table 4. Adsorption models used in this work and their parameters

Metal	ΔH°(kJ mol^{-1})	ΔS°($Jk^{-1}mol^{-1}$)	T(K)	ΔG°($kJmol^{-1}$)
Cu(II)	14.62	49.29	299.15	-0.12
			309.15	-0.61
			319.15	-1.10

Results showed that the values of ΔG° are negative at all the studied temperatures indicating the spontaneous nature of adsorption process and more favorable at high temperature. The positive ΔH° value indicates the endothermic nature of adsorption process and the positive ΔS° reveals the increase in randomness at solid solution interface during the adsorption of Cu(II) onto SiNTh.

3.9.5. Comparison with alternative materials

Table 5 shows the adsorption of Cu(II), by other material reported in the literature. It is clear that the functionalized silica described in this work presents further improvement and shows better values and higher affinity for the effective adsorption for Cu(II).

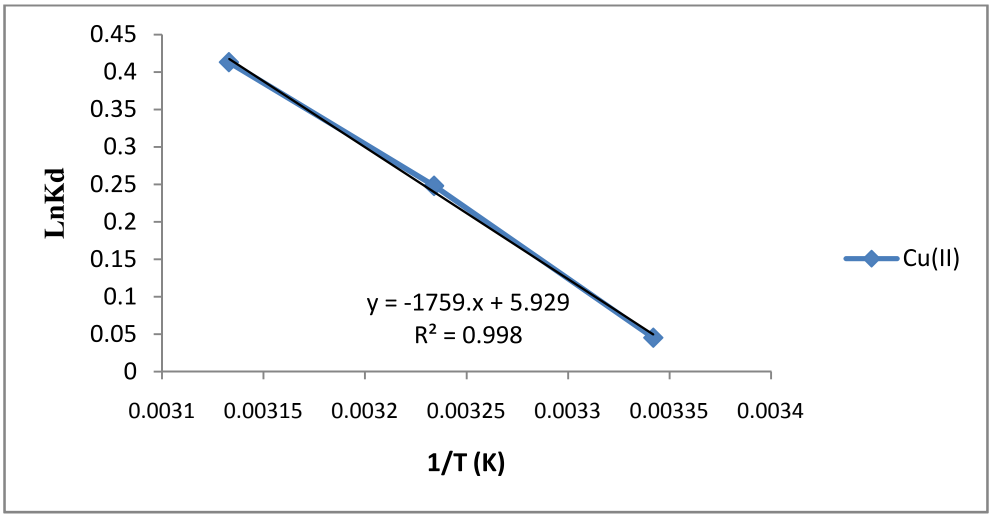


Figure 11. Effect of temperature for the sorption of Cu(II) onto SiNTh (shaking time 40 min, pH = 6.5, adsorption dose: V =10 cm^3, m =10mg of SiNTh at optimum concentration 100 mg/l.

Table 5. Comparison of SiNTh with other reported sorbents for Cu(II) absorption.

Support: Silica / ligand	**Reference**	**Capacity (mg of Cu^{2+} / g of silica)**
Bis(2-(chloromethyl)thiophene) (this work)	-	51.14
Gallic acid	[40]	15.38
3-amino-1,2,4-triazol-propyl	[65]	13.34
C,N-pyridylpyrazole	[66]	01.8
Acid red 88	[67]	0.76
Dithizone	[68]	06.07
Resacetophenone	[69]	11.80
Oxime	[70]	02.66
Amidoamidoxime	[71]	01.03

3.9.6. Regenerability of SiNTh

The sample was easily regenerated by soaking the sample in 6N HCl for a few minutes (5–10 mL of 6N HCl per g of support). After washing, the adsorption properties were measured again. No change was noticed when undergoing five cycles of adsorption/ regeneration. This new solid extractor has thus a good stability and can be reused without decreasing its extraction percentage.

Conclusion

In this study, hybrid material (SiNTh) was synthesized, well characterized and evaluated as an alternative low-cost adsorbent for selective removal of Cu(II) from aqueous solution. Optimum adsorption conditions were determined as a function of pH, contact time, initial metal ion concentration and temperature of solution. Langmuir adsorption isotherm model adequately described the adsorption of Cu(II) ion onto SiNTh. The pseudo-second order kinetic model better described the sorption kinetics with high correlation coefficients. The effect of temperature on sorption was also investigated and thermodynamic parameters were calculated. It was observed that the adsorption process was found to be endothermic and spontaneous.

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