Synthesis of Silica Gel Supported Amidoxime Ligand for Adsorption of Copper and Iron from Aqueous Media

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Organic-inorganic hybrid polymers have been demonstrated to be an efficient technique for the adsorption of pollutants present in water. Silica gel adsorbent has been applied in this field due to promising characters, such as thermally stable, reusability and high metal ion adsorption capacities. Here, silica gel supported acrylonitrile functional group (silica-APTS-DPN) was reacted with hydroxylamine to yield silica gel supported amidoxime ligand (SBA). All the functionalized silica gel adsorbents were characterized by FTIR. In terms of metal ions adsorption, SBA revealed good absorption capacities towards both copper (Cu^{2+}) (172 mg g^{-1}) and iron (Fe^{3+}) (168 mg g^{-1}) ions at pH 6 and followed the order of $Cu^{2+} > Fe^{3+}$. Increased pH condition was beneficial for both metal ions adsorption. The adsorption kinetics of both ions followed the pseudo-first-order model within 0-60 min of adsorption time. Langmuir and Freundlich isotherm models were both applied to study the adsorption behaviour, Freundlich isotherm model ($R^2 > 0.99$) proved to be a better fit, which propose that multilayer adsorption occurred on the silica gel grafted with amidoxime ligand. Finally, this study proved that the silica gel supported amidoxime ligand was successfully applied as an absorbent for the removal of both copper and iron from aqueous media.

Keywords: Silica gel, Amidoxime, Acrylonitrile, Heavy metals, Adsorption.

INTRODUCTION

Metals have contributed immensely to the rapid development in information technology, telecommunications, construction, health care and many other sectors of industries. However, their presence in the environment may cause adverse health risks and hazards toward living organisms [1]. As reported by World Health Organization (WHO), heavy metals like mercury, copper, nickel, chromium, manganese, zinc and lead, are considered as high priority concern internationally [2]. These toxic metal ions able to pollute water resources, eventually accumulated in the human body through the food chain, and caused a series of diseases and disorders [3]. Thus, it is crucial to remove these metal ions from industrial wastewater. Conventional wastewater treatment techniques for heavy metal removal, such as evaporations, carbon adsorption, ultra-filtration, ion exchange and chemical treatment are insufficient to remove pollutants in order to achieve water pollution control limits [2,4,5].

To overcome these problems, recently, inorganic-organic hybrid composites have been introduced as a new type of chelating

adsorbent for the removal of toxic contaminants from wastewater [3]. The advantage of inorganic-organic hybrid composites come from the functional variation of organic materials incorporated with a robust and thermally stable inorganic substrate, resulting in strong binding affinities toward heavy metal ions with high adsorption capacities [6]. Some adsorbents were synthesized by a chelating agent (organic) and an inorganic particle like silica gel [7], bentonite [8] and smectite [9].

Silica gel with a glass-like character and porous structure of SiO_2, plays an important role as an adsorbent in material chemistry due to its inertness, non-toxic, high surface area, high purity content, excellent mechanical and thermal stability and modifiable surface properties [6]. Yin *et al.* [10] reported a silica sorbent functionalized with amidoxime groups prepared using co-condensation method. The functionalized silica sorbent able to remove uranium from saline lake brine with a maximum uranium extraction capacity of 3.36-3.94 mg g^{-1}. Amidoxime functionalized mesoporous silica was recently synthesized and examined the adsorption of uranium under seawater conditions and amidoxime group able to chelates uranium with high affinity [11].

In present work, silica gel grafted with amidoxime group (-CH₂-CH-C(NH₂)=NOH) was prepared by introducing acrylonitrile onto the surface of silica gel. The adsorbents were used for the removal of Cu^{2+} and Fe^{3+} ions in aqueous media. The silica-based amidoxime was used to study the metals ions (Cu^{2+} and Fe^{3+}) adsorption. Adsorption kinetics and isotherms were also investigated.

EXPERIMENTAL

Silica gel, (3-aminopropyl)triethoxysilane (APTS), toluene, acrylonitrile were procured from Sigma-Aldrich, while hydroxylamine hydrochloride (Sigma), sodium hydroxide (Fischer Scientific), methanol (Fischer Scientific), Cu(0) catalyst, copper sulphate pentahydrate (Sigma), iron chloride (RDH), *etc.* were used as received.

Synthesis of 3,3′-[(3-iminaopropyl)triethoxysilane]-dipropanenitrile (APTS-DPN): To a round bottom flask (100 mL), (3-aminopropyl)triethoxysilane (10.0 g, 45.24 mmol) and acrylonitrile (4.798 g, 90.5 mmol) were added in methanol (50 mL) in the presence of copper catalyst (Cu(0)@PA, 0.1 mol %) [12]. The resultant mixture was stirred for 3 h at room temperature. The mixture was filtered and copper catalyst was removed. About 98 % yield of APTS-DPN was observed without any solvent used in the reaction. The APTS-DPN was directly used for the next reaction without purification (**Scheme-I**).

Synthesis of silica-3,3′-[(3-iminopropyl)triethoxysilane]dipropanenitrile (silica-APTS-DPN): Silica gel was dried overnight at 60 ℃. After drying, silica gel (50 g, 100-200 mesh) was added to a toluene (50 mL). Then APTS-DPN (10 g, 30.58 mmol) was added to the mixture and heated at 105 ℃ for 12 h with constant stirring. The resulting mixture was then filtered on a glass filter and washed with methanol followed by dichloromethane. The product was dried at 70 ℃ for 6 h (**Scheme-I**).

Synthesis of silica-based amidoxime ligand (SBA): Hydroxylamine hydrochloride (40 g) was dissolved in methanol (200 mL) with distilled water (50 mL). Then, NaOH solution (50 %) was added to the mixture until pH 9 achieved. The precipitate of NaCl was removed by filtration and clear solution of hydroxylamine was added to silica-APTS-DPN (20 g). The mixture was stirred with heated at 75 ℃ for 6 h. The solid product was collected by filtration and 0.1M of HCl (100 mL) in methanol with equal amount of distilled water was added. The resulting product was filtered on a glass filter and washed
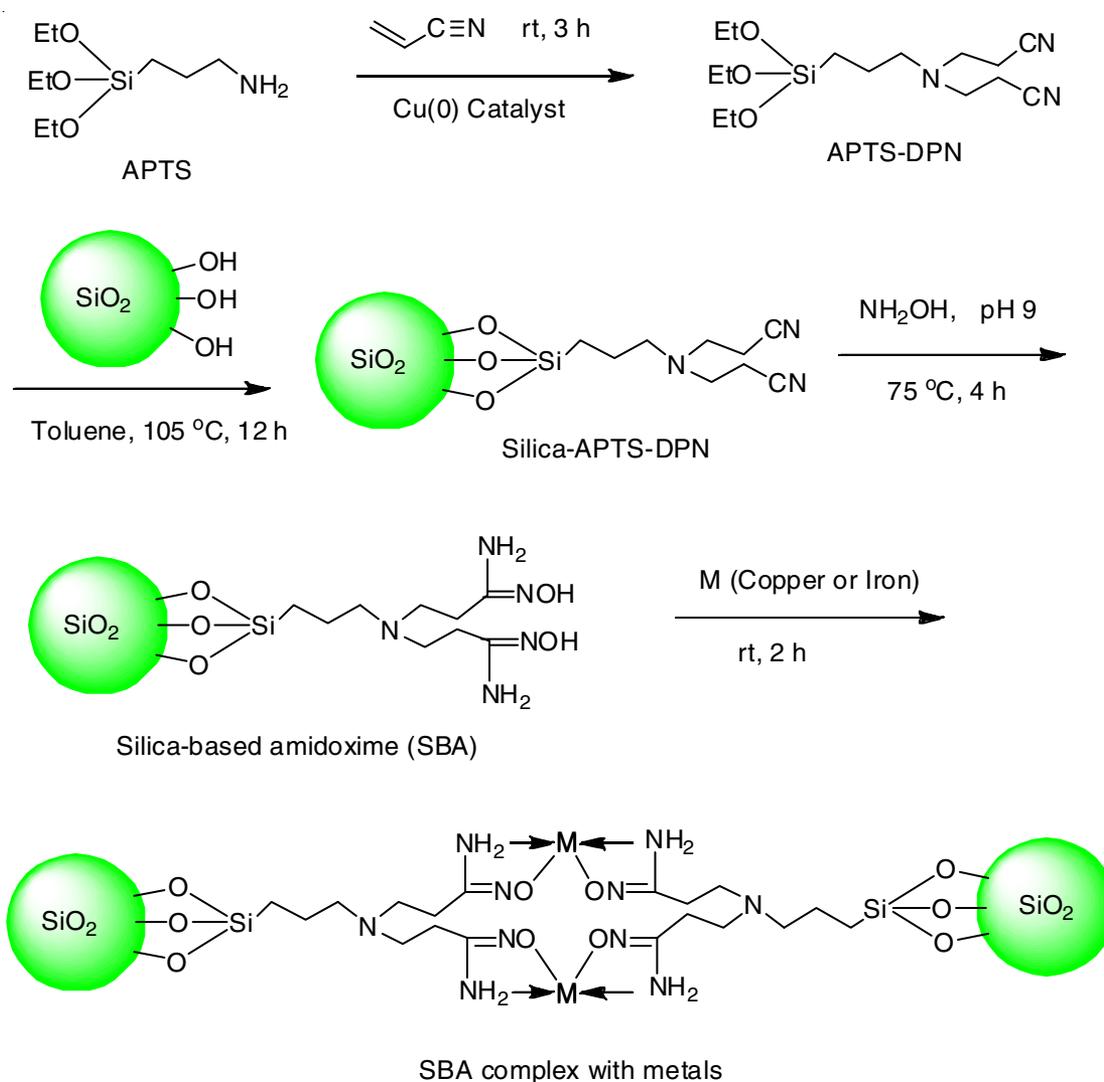
Scheme-I: Synthesis of silica gel based amidoxime ligand for metal ions complex formation

by methanol-water mixture until litmus paper turns to natural. The mesoporous silica-based amidoxime ligand (SBA) was dried in oven at 60 °C (**Scheme-I**).

Batch adsorption: The metal ion binding capacity of SBA was determined by using a batch equilibrium technique under different pH conditions (pH 3 to 6). For typical removal of transition metal ions (iron and copper), exactly 150 mg of dried SBA was placed into a set of plastic bottles, subsequently, 10 mL of distilled water was added and the equilibration of ligand was performed for 2 h. Sodium acetate buffer solution (5 mL, 0.1 M) ranging from pH 3 to 6 was adding to each bottle for 1 h. After that, 5 mL of 0.1 M of metal ion solution was added and the mixture shaked in a temperature controlled shaker machine for 2 h at a constant agitation speed of 180 rpm. After the reaction reached equilibrium, ligand was separated by filtration and the metal ions concentration are determining by ICP-OES. The initial and final values of the metal ions concentration were calculated based on the following eqn. 1:

$$q_e = \frac{(C_o - C_e)V}{L} \quad (1)$$

where q_e value is the adsorption amount (mg/g) at equilibrium; C_o represents the concentration of metal ion solution (ppm) at initial stage and C_e represents the concentration of metal ion solution (ppm) at equilibrium. V and L represent the volume of metal ions solution (mL) and the mass of polymeric ligand used (g), respectively.

Sorption isotherms study: In order to determine the isothermal behaviour, batch adsorption experiment was performed through the traditional bottle point method at constant temperature (30 °C) and agitation speed (180 rpm). Exactly, 150 mg of dried SBA placed into a set of plastic bottles with 10 mL of distilled water and the equilibration of ligand was performed for 2 h. Next, 5 mL of 0.1 M of sodium acetate buffer solution at pH 6 is added to each bottle for another 1 h. Then, exactly 5 mL of different concentration of metal ion solution (5 ppm to 1500 ppm) was added and the mixture was shaken in a temperature controlled shaker machine for 2 h with a constant agitation speed (180 rpm). After the reaction reached equilibrium, the ligand was separated by filtration and the metal ions concentration was analyzed using ICP-OES.

Kinetic study: A kinetic adsorption study is carrying out with 150 mg of SBA using the similar method as described above. However, mixtures were shaken by a temperature controlled shaker machine at various time intervals such as 5, 15, 30, 60 and 120 min at a constant agitation speed (180 rpm). The concentration of metal ions in the solution was then analyzed by ICP-OES. The amount number of metal ions that adsorbed by SBA was calculated [13] as follows:

$$q_t = \frac{(C_o - C_t)V}{L} \quad (2)$$

where q_t is the amount of metal ions adsorbed by ligand at time t (mg/g); C_o represents the concentration of metal ions (ppm) at initial stage and C_t represent the concentration of metal ions solution at equilibrium. Similarly, V and L represent the volume of metal ions solution (mL) and the mass of polymeric ligand used (g), respectively.

RESULTS AND DISCUSSION

3,3′-[(3-Iminaopropyl)triethoxysilane]dipropanenitrile (APTS-DPN) was synthesized from (3-aminopropyl)triethoxysilane and acrylonitrile monomer in methanol in the presence of copper catalyst Cu(0)@PA with mild conditions [12]. The product (APTS-DPN) was high yield 98 % without any solvent used in the reaction. The APTS-DPN was directly used for the next reaction without further purification.

Silica-3,3′-[(3-iminaopropyl)triethoxysilane]dipropanenitrile (silica-APTS-DPN) was synthesized from dried silica gel and APTS-DPN with toluene and the mixture was heated at 105 °C for 12 h with constant stirring. The work-up procedure was very simple as the product was collected by filtration on a glass filter and washed with methanol and dichloromethane, yielded pure silica-APTS-DPN.

Silica-based amidoxime ligand (SBA) was synthesized from silica-APTS-DPN under oximation with hydroxylamine in slightly alkaline medium. The work-up procedure was followed according to reported previous work [13]. The mesoporous silica-based amidoxime ligand (SBA) was dried in oven before adsorption studies.

FT-IR analysis: FT-IR spectra of APTS-DPN, silica-APTS-DPN and SBA are shown in Fig. 1. For APTS-DPN, the characteristic of both APTS and acrylonitrile were observed at 2974 and 2888 cm^{-1}, which signified the absorption bands of the asymmetric and symmetric -CH$_2$ group. A low intensity new peak at 2928 cm^{-1} resembled to C-H stretching while another new peak appeared in the range of 1450-1300 cm^{-1} due to aminopropyl group's bending vibrations [14,15]. A new absorption peak characterized the nitrile vibration band appeared at 2248 cm^{-1}. In the IR spectrum of functionalized silica gel , the peaks at 1083 and 800 cm^{-1} are due to the asymmetric and symmetric stretching of Si-O-Si, while the peak at 467 cm^{-1} is attributed due to the Si-O stretching of Si-OH and Si-O groups on the surface of silica gel. These bands showed the typical functional group of silica backbone [16]. The mesoporous silica network was confirmed by the symmetric and bending vibrations of Si-O-Si at peak 467 cm^{-1} [17]. The broaden stretching band of silica gel at 3508 cm^{-1} due to the O-H stretching of
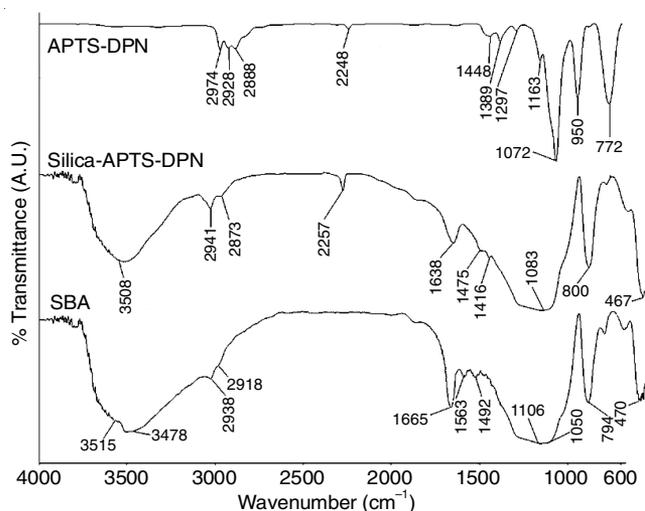

Fig. 1.   IR spectra of APTS-DPN, silica-based APTS-DPN and silica-based amidoxime ligand

silanol group and the adsorbed water, which shows a peak at 1638 cm^{-1} for stretching vibration of water. Due to the over-lapping of bending vibrations of physisorb water and C=N stretching vibration by imine group, peak appears at 1638 cm^{-1} cannot dependably qualified the C=N stretching vibration [18]. However, in case of SBA, a notable shift of peak intensity at 1665 cm^{-1} may be assigned to C=N stretching mode [18], which belongs to amidoxime groups. When silica-APTS-DPN reacted with hydroxylamine hydrochloride, a peak at 2257 cm^{-1} disappears as the nitrile group is converted into amidoxine group, where a new band of NH$_2$ bond vibration in the amidoxine group was observed at 3478 cm^{-1} [6].

Adsorption of metal ions

Effect of pH: The effect of pH on the metal ions adsorption by SBA is shown in Fig. 2. The pH condition ranges from 3 to 6 was evaluated and adjusted using sodium acetate buffer solution. Hence, the adsorption behaviour of SBA under different pH conditions were revealed by the binding of transition metal ions. As expected, metal ions adsorption capacities of SBA towards both Cu^{2+} and Fe^{3+} ions were increased by elevating the pH condition from 3 to 6. According to the previous study [13], ligand has been reported to possess high affinity towards Cu^{2+} ion at neutral pH range and also showed higher affinity towards other common transition metals at pH 6 . The findings here revealed that at pH 6, binding capacities of SBA towards Cu^{2+} and Fe^{3+} reached 172 and 168 mg g^{-1}, respectively. The results also suggested that metal ions absorption by SBA depended on the pH condition and in the order of Cu^{2+} > Fe^{3+}. The purpose of SBA is to work actively with metal ions to form complexation for removal from water [19-21].
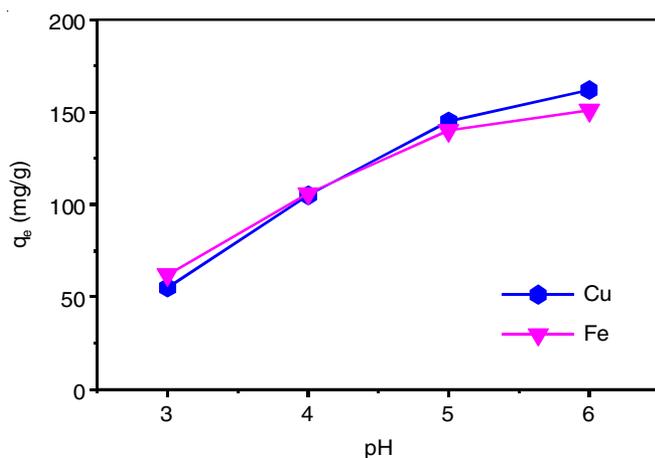

Fig. 2. Effect of pH on the metal ions absorption capacity on silica-based amidoxime ligand (SBA): other parameters were fixed: SBA ligand dosage = 150 mg, volume of metal ions solution (0.1 M) = 10 mL, volume of sodium acetate buffer solution (0.1 M) = 10 mL and shaken for 2 h

Adsorption kinetic study: The metal ions sorption by SBA ligand was studied according to the time depending factor, where the filtrate solution was analyzed by ICP-OES. The rate of adsorption for both cupper and iron were determined at pH 6 in buffer solution. To uncover the adsorption mechanism between the ligand and metal ion, the kinetic data were evaluated by pseudo-first order and pseudo-second order kinetic models.

The pseudo-first-order kinetic equation is usually applied for the adsorption of solute from solution, which is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 \times t}{2.303} \tag{3}$$

where q_t and q_e are the adsorption capacity at time t and at equilibrium (mg g^{-1}), respectively. The rate constant of pseudo-first-order adsorption process (min^{-1}) is presented by k_1. The values of q_e and k_1 can be calculated from the intercept and slope of plots of log ($q_e - q_t$) *versus* t (Fig. 3) and calculated values are given in Table-1. Furthermore, the values of correlation coefficient R^2 showed well fitted for copper and iron ions, however, the experimental values of adsorption capacity (q_m) indicate no significant difference, as compared to the calculated values (q_e) based on the first-order plot. These results demonstrated that the experimental data showed best fit to the pseudo-first-order model.
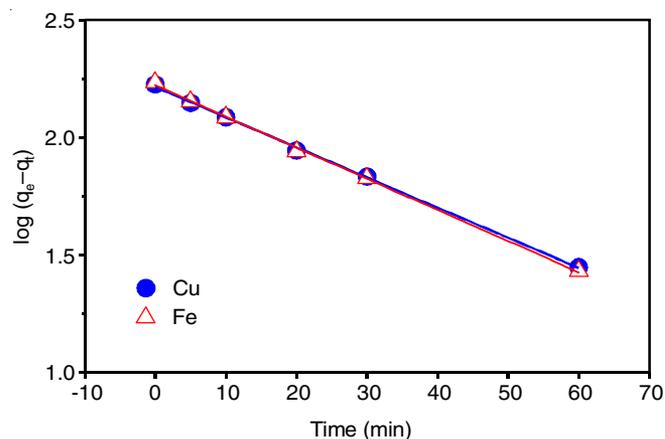

Fig. 3. Kinetic plots of transition metals on SBA ligand using pseudo-first-order model, other parameters were fixed: SBA ligand dosage = 150 mg, volume of metal ions solution (0.1 M) = 10 mL and volume of sodium acetate buffer solution (0.1 M) = 10 mL

TABLE-1
PARAMETERS OF THE PSEUDO-FIRST-ORDER
MODEL FOR Cu(II) AND Fe(II) ON SBA LIGAND

Adsorbate	Pseudo-first-order			Experimental
	q_e (mg g^{-1})	K_1 (min^{-1})	R^2	q_m (mg g^{-1})
Cu	164	0.0128	0.998	172
Fe	166	0.0132	0.998	168

The pseudo-second-order model equation explains the relationship of adsorption rate under difference adsorption capacities at different contact times and at equilibrium, which can be represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where the rate constant of the pseudo-second-order sorption (g mg^{-1} min^{-1}) is represented by k_2. The q_e and q_t are the amount of metals adsorbed (mg g^{-1}) at equilibrium and at any time t, respectively. The values of k_2 and q_e can be determined from a plot of t/q$_t$ *versus* t. The values of q_e, k_2 and coefficient R^2 are given in Table-2. It is clearly seen that the experimental values of adsorption capacity (q_m) possess a significant difference as

TABLE-2
PARAMETERS OF THE PSEUDO-SECOND-ORDER MODEL
FOR Cu(II) AND Fe(II) ON THE SBA LIGAND

Adsorbate	Pseudo-second-order			Experimental
	q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1}) × 10^{-3}	R^2	q_m (mg g^{-1})
Cu	243	0.1544	0.996	172
Fe	244	0.1693	0.995	168

compared to the calculated values (q_e) for the pseudo-second-order. Furthermore, correlation coefficient R^2 for the pseudo-second-order is lower than the pseudo-first-order. These results demonstrated that the predominant kinetic mechanism is through first-order model, where the chemical activity depends on the adsorption mechanism. This can be explained by the sharing or exchanging electrons through valance forces between the amidoxime group grafted on SBA ligand and the transition metal ions [22,23].

Sorption isotherms: The sorption isotherms of silica-based ligand were studied under various concentrations of metal ions, where the complete metal ions taken up by the absorbent were determined. Transition metal ions, like Cu^{2+} and Fe^{3+} were adsorbed by SBA ligand in a wide range of initial concentration from 226 to 4024 mg L^{-1}, while other experimental conditions were fixed (ligand dosage, pH condition and agitation period). The results demonstrated that increased initial concentration of metal ions lead to higher adsorption capacity as shown in Fig. 4.
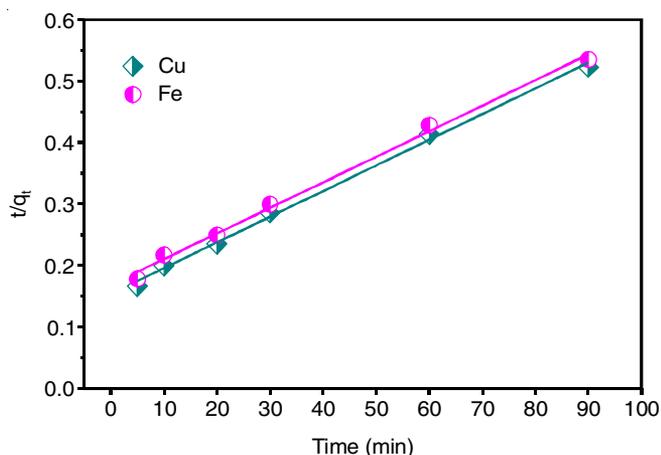

Fig. 4. Kinetic plots of transition metals on SBA ligand using pseudo-second-order model, other parameters were fixed: SBA ligand dosage = 150 mg, volume of metal ions solution (0.1 M) = 10 mL and volume of sodium acetate buffer solution (0.1 M) = 10 mL

Isotherm models: The best-known isotherms models used to explain and evaluate the equilibrium data of adsorption from aqueous solution are Langmuir and Freundlich isotherm models [24]. The Langmuir isotherm model is derived by assuming a monolayer adsorption condition with some identical active sites

or those active sites are allocated uniformly onto the adsorbent surface and without interaction among adsorbents [25]. The Langmuir isotherm equation (linear form) is represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (5)$$

where the values of C_e and q_e are similar to eqn. 1, whereas q_m and K_L symbolize the maximum adsorption capacity of adsorbents (mg g^{-1}) and the Langmuir adsorption constant (L mg^{-1}), respectively. The values of sorption coefficient (K_L) and the maximum sorption capacity (q_m) were determined from the intercept and slope of the linear plot as tabulated in Table-3. The data collected here clearly seen that correlation coefficient R^2 values are smaller than 0.99. Thus, these results demonstrated that the adsorption of both transition metals did not belong to monolayer adsorption.

In addition, adsorption isothermal capacity was further evaluated by Freundlich isotherm model, which is well known for adsorption on heterogeneous surfaces and multilayer adsorption in an adsorption system [22,23]. This model is represented in the form of eqn. 6 as follows:

$$\log q_e = \log K_F + \frac{\log C_e}{n} \qquad (6)$$

where K_F and n are the Freundlich constants, which represent the adsorption capacity and adsorption strength, respectively. The experimental data were utilized to Freundlich isotherm model and the parameters (K_F and n) are tabulated in Table-3. K_F and n were determined based on the intercept and the slope of linear plot of log q_e *versus* log C_e. The data suggested that no significant correlation coefficient ($R^2 > 0.99$) according to the Freundlich equation. Thus, these results demonstrate that the metal ions sorption onto the silica-based ligand were well fitted to a Freundlich isotherm model and also indicates that both copper and iron ions adsorption is a multilayer adsorption that taken place by the polymeric ligand.

Conclusion

In summary, silica gel supported amidoxime (SBA) was successfully prepared through the reaction between silica-APTS-DPN and hydroxylamine. The FT-IR studies suggested that organic groups successfully immobilized onto the surface of silica gel. The adsorption process of SBA towards Cu^{2+} and Fe^{3+} ions follows a pseudo-first-order pathway and obey a Freundlich isotherm model. Moreover, the efficiency adsorption process further increased by increasing the pH conditions (pH 3 to 6). This work could provide good insights for the preparation and development of highly effective silica gel based absorbent for removal of metal ions.

TABLE-3
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS ACQUIRED BY NONLINEAR FITTING FOR THE SBA LIGAND

Adsorbate	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L g^{-1})	R^2	n	K_F (L mg^{-1})	R^2
Cu	318	0.0128	0.981	1.22	0.254	0.993
Fe	349	0.0151	0.982	1.20	0.226	0.991

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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