PHOSPHONATE MODIFIED SILICA FOR ADSORPTION OF Co(II), Ni(II), Cu(II), AND Zn(II)

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ABSTRACT

A new phosphonate modified silica (PMS) has been investigated for adsorption of Co(II), Ni(II), Cu(II), and Zn(II) in aqueous solution. The adsorbent was modified of silica by immobilizing aminoethyl dihydrogen phosphate (AEPH$_2$) on 1,4-dibromobutane grafted silica. The physicochemical of the adsorbent was investigated using Fourier Transform Infra-red (FTIR) spectroscopy, X-ray Fluorescence (XRF), and N$_2$ gas adsorption/desorption. The adsorption study was carried out in a batch system by mixing solution of metal ions at various pHs, contact times, and initial metal ion concentrations. The unadsorbed metals were determined by Flame Atomic Absorption Spectrophotometry (FAAS). Result of characterization showed that PMS has been successfully prepared. The product contained 45.99% (w/w) silica and 1.33% (w/w) phosphorous with surface area, pore volume, and pore size of 115.3 m^{2}g^{-1}; 0.7578 mLg^{-1}; and 131.44 Å, respectively. Adsorption of metal ions on PMS occurred quite fast, less than 30 min. Modification of phosphonate on silica increased the adsorption capability, up to 8 times higher than that of unmodified silica, depending on metal ion type and pH solution. The capacity order of the metals adsorption was Cu(II)>Co(II)>Ni(II)>Zn(II). Based on the adsorption characteristic, the adsorbent is promising to be applied as a material for solid phase extraction of transition metal ions.

Keywords: *modified silica; phosphonate; adsorption*

ABSTRAK

Suatu silika termodifikasi fosfonat (STF) baru telah dikaji sebagai adsorben larutan Co(II), Ni(II), Cu(II), dan Zn(II). STF disintesis dengan mengimobilisasi aminoetil dihidrogen fosfat (AEPH$_2$) pada 1,4-dibromobutana yang tergrafting pada silika gel. Fisikokimia STF dianalisis dengan Spektroskopi Infra-Merah, Fluoresensi Sinar-X, dan Adsorpsi/desorpsi gas N$_2$. Kajian adsorpsi dilakukan dengan sistem batch dengan mencampurkan larutan ion logam dalam pH, waktu kontak, dan konsentrasi ion logam awal yang bervariasi. Logam yang tidak teradsorpsi dianalisis dengan Spektrofotometri Serapan Atom. Hasil karakterisasi menunjukkan bahwa STF berhasil disintesis. Material ini mengandung Si dan P masing-masing sebesar 45,99% (b/b) dan 1,33% (b/b). Area permukaan, volume pori total dan jejari pori rerata STF masing masing sebesar 115,3 m^{2}g^{-1}; 0,7578 mLg^{-1}; and 131,44 Å. Adsorpsi ion logam berlangsung cepat, rata-rata kurang dari 30 menit. Modifikasi pada silika mampu meningkatkan kapasitas adsorpsi hingga 8 kali lipat daripada oleh silika, bergantung jenis ion dan pH larutan. Kapasitas adsorpsi STF memiliki urutan Cu(II)>Co(II)>Ni(II)>Zn(II). Berdasarkan karakteristik adsorpsinya, adsorben ini cukup memadai untuk diaplikasikan sebagai material dalam EFP

Kata Kunci: *silika termodifikasi; fosfonat; adsorpsi*

INTRODUCTION

The waste water of copper craft industries contains high amount of heavy metal ions, such as chromium, nickel, copper, and zinc. Although these metals are essential nutrient required by most living organism for healthy growth and enzyme function, it becomes toxic to human at elevated concentrations. Therefore, the maximum concentration in surface water, ground water and potable water are strictly regulated [1-4]. The removal of these heavy-metal ions is of highly importance.

Nowadays, there are various methods for the removal of these heavy metals from aqueous solution, such as deposition [5], ion exchange [6], filtration [7], membrane [8], solvent extraction [9], coagulation [10],

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and flotation [11]. However, adsorption is the most popular method applied pervasively in environmental chemistry and chemical industries. It presents convenience, easy operations, and simplicity of design. Further, this process can remove different type of pollutant and offers wide applications [12-13].

One of the most popular commercial adsorbent is silica gel which has been popularly used as desiccant due to its relatively weak bonds with water as well as its large pore volume [14]. However, to be used as metal ion adsorbent, silica gel must be modified due to limited capacity and selectivity of its presence and of silanol sites and porous structure.

Modification of silica gel could be done through increasing of surface area and/or decreasing pore diameter, i.e. ratio of silanol and siloxane concentration of particle surface (physical modification). This method usually includes media system adjustment [15] or thermal/hydrothermal treatment [16]. Another suitable method of modification of silica gel is through chemical modification. The latter method can be done through organofunctionalization using organic group as modifying agent or inorganofunctionalization using organometallic composite or metallic oxide in which the group is anchored on the surface [17].

The organofunctionalization of silica gel usually includes donor atoms such as carbon [18], nitrogen [19-20], sulphur [21], and phosphorous [22]. However, from three different types of phosphorus organo-functionalization: phosphate, phosphonic/phosphonate, and phosphinic, only phosphonate group can be successfully used because of poor hydrolytic or oxidative stability of phosphate and phosphinic. Phosphonate organofunctionalization of ion exchangers/adsorbents usually applied for trivalent or divalent cations [22]. While, the introduction of an amine (-NH_2) group into the phosphonate molecules to obtain -NH_2-C-$PO(OH)_2$ in such molecule as NTMP (nitrilostris(methhylene) phosphonate), EDTMP (ethylenediaminetetra (methylene)phosphonate) and DTPMP (diethylene-triaminepenta(methylene)phosphonate increases the metal binding abilities [23].

However, direct bonding of organofunctional groups to inorganic surfaces such silica gel is difficult due to relative inertness of the surface in its ground state. While, there are three main methods in which functional groups are attached to the silica gel surface: (i) through reaction between organosilanes or organic molecules and silica gel surface reaction, (ii) chlorination of the silica gel surface followed by reaction of the Si-Cl with an appropriate functional molecule/reactant, and (iii) incorporation of functional group via sol-gel method followed by post modification, where necessary [15].

In the present work, silica gel was modified with aminoethyl dihydrogenphospate ($AEPH_2$) via 1,4-dibromobutane as linker. The adsorbent was applied for Co(II), Ni(II), Cu(II), and Zn(II) in aqueous solution in both single and multiple metals system. The presence of $AEPH_2$ as modifier agent is predicted to increase the adsorption capacity of PMS since lone pair electrons of amine group will complex the hydrated metal ion. The thermodynamics and kinetics parameters of adsorbent were evaluated with varying the contact time and concentration at optimum pH. From those parameters, the effect of modification toward silica on metal ions adsorption was evaluated as well.

EXPERIMENTAL SECTION

Materials

Chemicals used for the synthesis of phosphonate modified silica gel were silica gel (*kieselgel* 60) and aminoethyl dihydrogenphospate ($AEPH_2$) 98%. Nitrate salt of Co(II), Ni(II), Cu(II), and Zn(II) were used to prepare the solution of Co(II), Ni(II), Cu(II), and Zn(II) respectively. All chemicals were supplied from Merck without further purification.

Instrumentation

Fourier-transform infra-red (FTIR) spectrophotometer (Shimadzu 8201 PC) was used for identification of functional groups and active sites. X-ray fluorescence (XRF) of JEOL JSX-3211 and Flame Atomic Absorption Spectrophotometry (FAAS) of AA-6650 Shimadzu were used to determine elemental compositions of adsorbents and unadsorbed metals, respectively. N_2 gas adsorption/desorption (NOVA 1000 h) was used to analyze surface area, pore, and diameter size. Scanning Electron Microscope (SEM) of JEOL JSM-6360 LA was used to observe the surface morphology of particles.

Procedure

Synthesis of phosphonate modified silica

Synthesis of phosphonate modified silica was carried out according to the procedure reported by Jal et al. [15] and Garcia-Valls et al. [24] with a little modification. Silica gel (15 g) firstly was activated by stirring the powder with 1M NaOH for 3 h. The resulted residue was filtered, washed with high purity deionized water until free from base and dried. Then, the activated silica gel/ASG (10 g) was reacted with 1.5 mL 1,4-dibromobutane in 150 mL of dry toluene and then stirred for 8 h. The slurry was filtered and washed successively with toluene and dried at 70 °C for 3 h to obtain dibromobutane modified silica (DBMS).

Immobilization of phosphonate was conducted via mixing DBMS (10 g) with 1 g of $AEPH_2$ for 24 h, and then the resulted residue was washed with deionized water and dried at 70 °C for 3 h to obtain phosphonate modified silica (PMS). The material then was characterized with FTIR spectroscopy, XRF, and N_2 gas adsorption-desorption.

Adsorption of metal ions

Adsorption of Co(II), Ni(II), Cu(II), and Zn(II) on adsorbents was carried out according to the procedure reported by Mishra et al. [25] with little modification. Aqueous solution of Cu(II) containing 20 ppm was shacked with 0.025 g adsorbent for 30 min at various pHs (5-8). The optimum pH was used to evaluate the thermodynamics parameter by varying the contact time and kinetics parameter by varying the concentration (5, 10, 20, 50, 100, and 200 ppm). The solution was filtered with a filter paper and the concentration of unadsorbed metal ion was detected by FAAS. To study the adsorption for multiple metal systems, the work was carried out according to the procedure reported by Shoaib et al. [26]. A solution of metal ion mixture was prepared with the concentration of each metal ions equal to 20 ppm. The adsorption experiment was carried out analog to that for single metal system.

RESULT AND DISCUSSION

The physicochemical of adsorbent is affected by several factors, such as technique of synthesis and chemical modifications. While, the metal adsorption is affected by several operating parameters, such as pHs, contact times and initial metal concentrations. In present study, all these have been explored in order to evaluate treatment technology for Co(II), Ni(II), Cu(II), and Zn(II) removal from synthetic solutions.

Physical and Chemical Characteristic of Adsorbent

In present study, adsorbent has been synthesized with surface modification of inorganic substrate (grafting technique) [27]. The inorganic substrate used was silica gel. $AEPH_2$ and 1,4-dibromobutane were used as organic polymer and coupling agent, respectively.

The synthesis of PMS was done initially by activation of silica gel with NaOH [28], followed by grafting of 1,4-dibromobutane onto silica gel surface [18] and finally by grafting of phosphonate onto 1,4-dibromobutane previously grafted onto silica. As an adsorbent, the resulting material has been analyzed its physical and chemical character, such as active sites and pores properties [29].

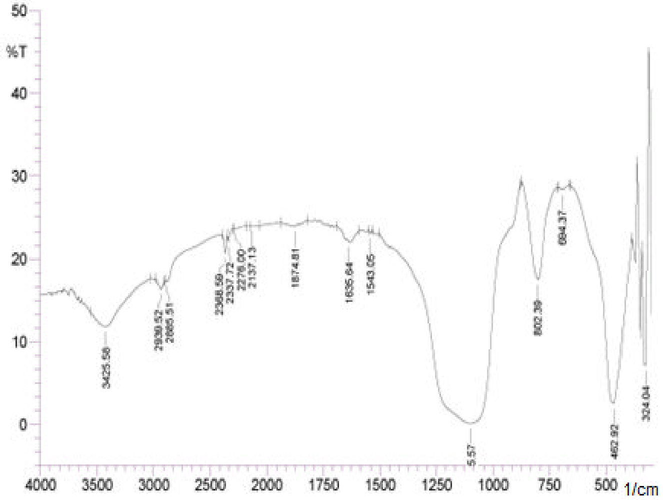

Fig 1. FTIR spectra of PMS

Fig. 1 shows infrared spectra of PMS. The presence of silica gel is identified with the existence of siloxane, Si-O-Si, and silanol, Si-OH. Siloxane is indicated with the band at 1087 cm^{-1} of Si-O asymmetric stretching vibration [30-31] and bands at 802 cm^{-1} and 455 cm^{-1} due to Si-O stretching and bending vibration, respectively [32]. Silanol is indicated with the band at 972 cm^{-1} due to Si-O stretching vibration on silanol group [29]. Phosphonate is identified with band at 1257 cm^{-1} of P=O and band at 1028 cm^{-1} of P-O stretching vibration of organic phosphate [33]. Hydrocarbon is indicated with band at 2939 cm^{-1} due to CH asymmetric stretching vibration in CH_2 aliphatic group and band at 2885 cm^{-1} due to CH symmetric stretching vibration in CH_2 group of hydrocarbon [30]. The presence of hydrocarbon is also indicated by the band at 1435 cm^{-1} due to CH asymmetric bending vibration of CH_2 and band at 1285 cm^{-1} of CH_2 stretching vibration on $Si\text{-}CH_2\text{-}R$ group [30]. The infrared spectra of PMS suggest that it consist of silica, phosphonate, and hydrocarbon.

Moreover, infrared spectra (Fig. 1) revealed the anchored of organic groups onto inorganic surface. The grafting of hydrocarbon onto silica surface is indicated with the broadening band at around 1000-1250 cm^{-1}, since the band of Si-O silica gel overlapped with the CH band of hydrocarbon. The grafting is also indicated with the presence of weak absorbance at wave number of 563.21 cm^{-1} due to the presence of C-Br stretching vibration. In the present study, 1,4-dibromobutane was used for coupling agent as surface modifier bearing non-reactive organic group. This surface modification allows the formation of stable bonds between the organic polymer and silica gel [32]. The immobilizing of phosphonate onto hydrocarbon chain is indicated by the band at 3400-3500 cm^{-1} correlated with the stretching vibration of N-H group, amine primary aliphatic and bending vibration of amine primary. Moreover, the immobilizing of phosphonate is also

Table 1. Summary of the infrared spectra assignment of PMS

Material	Functional Group	Frequency (cm^{-1})	Type of Vibration	Description	
Silica gel	Si-O	1087.85	Stretching	Asymmetric (Si-O-Si)	[30-31]
	Si-O	972.12	Stretching	Si-OH	[33]
	Si-O	802.39	Wagging	Symmetric (Si-O-Si)	[32]
	Si-O	455.20	Bending	Si-O-Si	[32]
	O-H	3425.85	Stretching	Water molecule adsorbed	[33]
1,4-dibomobutane	CH_2	1265.30	Stretching	Si-CH_2-R	[32]
	C-H	1435.04	Scissoring	Asymmetric (CH_2, R-CH_2-CH_2(SiOR))	[32]
	C-H	2892.22	Stretching	Symmetric CH_2	[32]
	C-H	2952.66	Stretching	Asymmetric CH_2	[32]
$AEPH_2$	P=O	1257		Aliphatic	[33]
	POH	900-1050			[33]
		2400			[33]
		2600			[33]

Table 2. Textural characteristic of materials

Material	Surface Area (m^2/g)	Total Pore Volume (mL/g)	Pore Size (Å)
SG	101.50	0.664	130.70
PMS	115.30	0.758	131.40

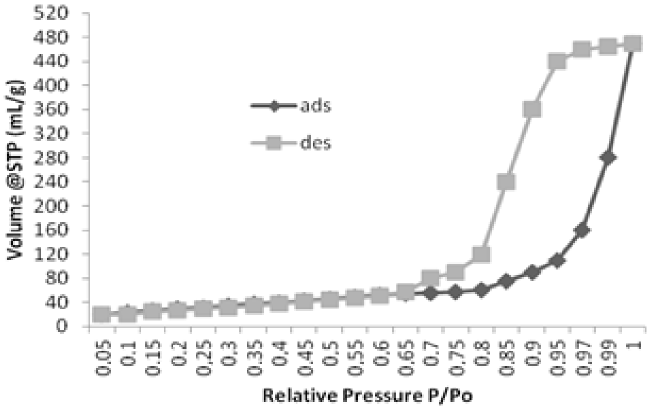

Fig 2. N_2 adsorption/desorption isotherm for PMS

indicated with band broadening at around 1000-1250 cm^{-1} due to the band of P=O and P-O of $AEPH_2$ overlapped with the band of silanol and siloxane and hydrocarbon previously described. In the same time band at 563.21 cm^{-1} disappearance since the C-Br groups mobilized while phosphonate immobilized. The result suggests that phosphonate parts grafting onto silica surface linked by hydrocarbon chain.

From XRF analysis, PMS contains Si of about 45.69% (w/w) and P of about 1.33% (w/w). It reveals that modification of silica gel increases the content of phosphorous significantly.

Infrared techniques are also useful in studying the nature of the active sites for adsorption, through the use of water molecules adsorbed as probes. The active sites of material was indicated by the presence of water molecules adsorbed (Fig.1). The band at 3425 cm^{-1} due to the OH stretching vibration of silanol and OH stretching vibration of water molecules [33]. The band of OH stretching vibration correlates to silanol active sites at band of 3745 cm^{-1}. The band at 972.12 cm^{-1} is overtone of silanol. The band correlates to the Si-O stretching vibration of silanol Si-OH group. The water adsorbed onto material surface correlates with the presence of silanol active sites, since oxygen atom of water molecules interact with hydrogen atom of PMS to form hydrogen bonding [34]. The metal adsorption may occur through coordinately bonded or protonated species, i.e. P-O or P=O [34]. Table 1 summarizes the assignment for the infrared spectrum of PMS. The result suggests that PMS contains active sites which attracted polar molecule.

Porosity

The N_2 adsorption-desorption isotherm of PMS is depicted in Fig. 2 showing typical isotherm of type IV. This type of isotherm is commonly associated with mesoporous materials. Mesopores are the pores which give rise to the phenomenon of capillary condensation with the adsorption/desorption isotherm, which is observed by the existence of an inherent hysteresis loop. The mesopores fill in the final stages of the isotherm by multilayer formation. The pore diameters are so large that at low relative pressures monolayer coverage occurs followed by further layers and the adsorbed film acts as a nucleus upon which capillary condensation may take place. This mechanism gives rise to hysteresis, as there are differences in the pore filling and emptying processes. Capillary condensation give rises to a hysteresis loop and the isotherm also exhibit a limited uptake at higher relative pressure. The N_2 adsorption-desorption isotherm of PMS is similar with silica gel. The results indicate that modification of silica has no significant effect on the pore structure.

From Table 2, it can be seen that modification process increases surface area and total pore volume.

Surface area and total pore volume of product are 115.30 m^2g^{-1} and 0.758 mLg^{-1}, respectively. However, surface area and total pore volume of silica gel are 101.5 $m^{-2}g^{-1}$ and 0.664 mLg^{-1}, respectively. This phenomenon is due to grafting of modifier to surface of silica. In the grafting step of hydrocarbon chain to silica, the surface area of modified silica expand to 111.85 m^2g^{-1}. In the grafting step of phosphonate to modified silica with hydrocarbon chain, surface area, pore volume, and pore diameter increase to 115.30 m^2g^{-1}, 0.758 mLg^{-1}, and 131.40 Å respectively. It indicates that the grafting of hydrocarbon chain and phosphonate molecules are on the surface and inside of the silica pores. The phenomenon are similar to those investigated by Jal et al. [18].

According to the surface area of 115.30 m^2g^{-1} (Table 2) the experimental P analysis of 1.33% (w/w) corresponds to a grafting density close to 2 μmol m^{-2} [35]. Within the experimental errors, the elemental analyses of P were agreement with the chemical structure.

Morphology

SEM image of PMS prepared by grafting technique are presented in Fig.3. The images suggest that the amorph particles of PMS is likely covered by grafted molecules and a significant change could be observed compared to silica. It indicates the synthesis of PMS by immobilizing phosphonate on DBMS has been successfully done.

Adsorption of Metal Ions

Effect of pH

The effect of pH on metal ions adsorption was studied at a pH range of 5–8 since pH of waste water released to the environment should over 5 [1-4] and the investigated metal ions tend to form solid complex hydroxo metal $M(OH)_2$ at higher pH. Therefore, the adsorption study was performed only at pH of 5 and 6 (Table 3). It can be seen that phosphonate modification on silica increases its capability and the capability in pH of 6 is bigger than that of 5.

Table 3. Parameter result of the adsorption study

Metal-ion	Adsorbent	Adsorption(mg/g)	
		pH 5	pH 6
Co(II)	Silica	0.38	4.43
	PMS	3.23	7.43
Ni(II)	Silica	2.52	2.22
	PMS	6.13	12.47
Cu(II)	Silica	8.68	19.20
	PMS	8.76	21.02
Zn(II)	Silica	7.41	4.70
	PMS	16.43	8.26

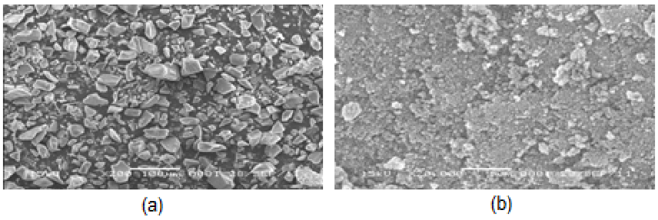
(a) (b)

Fig 3. SEM image of PMS 200x (a) PMS 20000x (b)

The metal ions adsorption on PMS has similar pattern to that on silica gel. From Table 3, it can be seen that in both pH, 5 and 6, the amount of metal ions adsorbed on PMS are bigger that of silica. The bigger capability of PMS is performed by the existence of active sites of phosphonate, i.e. P-OH group on the surface of PMS. These active sites could interact with metal ion by forming hydrogen bridging. However, the other active sites, i.e. P=O group still in the same form due to the pH of solution in the range of pH 5.4–11. These active sites could interact with metal ions by forming complex. The presence of other active sites, i.e. amin since has lone pair electrons as oxygen of P=O could interact with metal ions by forming complex. The active sites mentioned above perform more effective than the adsorption of silanol active sites.

Except Zn(II), the metal ions adsorption at pH of 6 t is bigger than that at 5 (Table 3). On the other hand, the pH raising effect on metal ions speciation. The metal ions exist in the solution based on pH as M^{2+}, MOH^+, $M(OH)_2$, $M(OH)_3^-$, and $M(OH)_4^{2-}$ depend on its pH. When the initial pH was adjusted at 5, most metal ions tend in the form of free ion or as complex $[M(H_2O)_x^{n+}]$ [36-39]. At this low pH, repulsion force between metal ions in solutions is occurred. As long as raising the pH, the free metal ions decrease and tend to form as hydroxide metal species $[MOH(H_2O)_{x-1}^{+(n-1)}]$. The later species are much more easy to adsorp than its free complex ion [16]. In case of zinc metal ions, adsorption shows different trend especially at higher pH. As the pH increases from 6 to 12, zinc ion undergoes complex such as $[Zn(OH)_4]^{2-}$ where zinc can hydrolysis according to the general expression for divalent metal as

$Zn^{2+} + n\,H_2O \leftrightarrow Zn(OH)_n^{2-n} + n\,H^+$

This complex ions and negative functional group on the silica or PMS surface tend to have electrostatic repulsion. However, this complex forming more strongly bound “inner sphere” complexes (such as Si-O-Zn) or rather loosely bound “outer sphere” complexes via hydrogen bridges (Si-O..... H-O-Zn, Si-O ... HOHZn) [34].

The pH raising also effect on the protonation of functional group on the surface of adsorbents. When the initial pH was adjusted to 5, phosphonate active sites of PMS in the form of $–PO_3H^-$. With increasing pH,

Table 4. Kinetics of metal ion adsorption on PMS

Model kinetic	Co(II)		Ni(II)		Cu(II)		Zn(II)	
	K	R^2	K	R^2	K	R^2	K	R^2
1st Order	0.0121	0.9119	-0.0236	0.8166	0.0054	0.2551	0.0044	0.7837
2nd Order	0.0848	0.7881	-0.1088	0.5420	0.1304	0.5548	0.0427	0.7913
Pseudo 1st order	0.3832	0.9985	*0.0804*	*0.9835*	0.0544	0.1482	0.1124	0.8585
Pseudo 2nd order	*0.0489*	*0.9999*	0.0015	0.8692	*0.4012*	*0.9939*	*0.1590*	*0.9967*

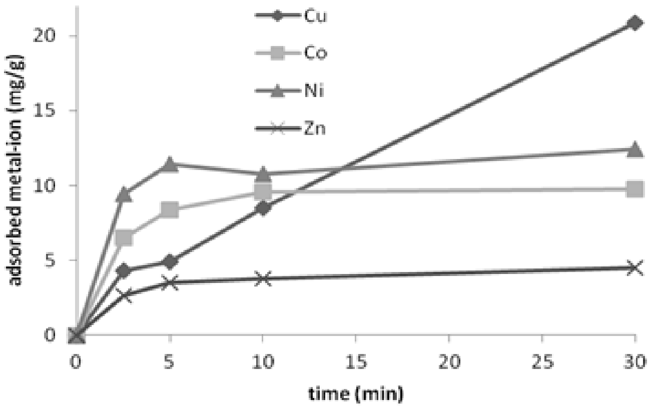

Fig 4. Adsorption curve of metal ion on PMS at various contact times

phosphonate active sites of PMS in the form of $–PO_3^{2-}$ inspite of its $pK_2 = 5.4$ and $pK_3 = 11$. The charge raising effect on the interaction force. The electrostatic interaction in the pH of 5 is big. However, the electrostatic interaction in the pH of 6 is bigger than that in of 5. At low pH, due to high positive charge density of protons on the surface sites, electrostatic repulsion will be high during uptake of metal ions resulting in lower removal efficiency. With increasing pH, electrostatic repulsion decrease due to the reduction of positive charge density on the sorption sites, thus resulting in an enhancement of metal adsorption. The above fact related to the effect of pH on adsorption was also supported by several earlier workers [15-16]

The adsorption of metal ions onto the surface of PMS as well as surface of silica gel can also by hydroxocomplexes that are inclined to the formation of polynuclear diamagnetic cluster as

$\equiv SiOH + M^{2+} \leftrightarrow \equiv SiOM^{+} + H^{+}$, $M^{2+} = Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$

and

$\equiv SiOH + M^{2+} \leftrightarrow \equiv SiOMOH + 2H^{+}$

The first reaction provides a positive surface charge, which yield a repulsion force between part of the adsorbed surface and the copper ions that exist freely in the solution. The second reaction takes place between the surface and the free Cu^{2+} in the solution leading to formation complex surface of SiOCuOH. It is cleared that an extra proton produced in the solution at the hydrolysis of adsorbed copper. This proton was released from water molecule in the coordination sphere of hydrated Cu^{2+} ions. The possibility of the formation of such complexes is confirmed by Vlasova and coworkers [40].

On the other hand, other active sites, i.e amin, not change its charge because its pKa >3. However these active sites could interact with metal ions by complexing. In case of silanol as other active sites of PMS, the pH raising has no effect on its charge. In both pH of 5 and 6, silanol active sites in the form of $\equiv Si\text{-}O^-$. This negative surface charge interacts effectively with M^{2+}.

The phenomenon above can be explained by considering the potential ionic of adsorbate. All metal ions are borderline cations (HSAB). Ionic radii of Cu(II), Co(II), Ni(II), and Zn(II) are (pm) 69, 74, 72, and 74 respectively. Therefore Cu(II) which has the smallest ionic radii has the biggest potential ionic. The above fact related to the effect of atomic radii on adsorption was also supported by several earlier workers [41,43-44]

Kinetics of adsorption

The effect of contact time on the adsorption of 50 mL 20 ppm metal ions at room temperature and initial pH 6 with 0.025 g adsorbent is shown in Fig. 4. It is obvious that the adsorption of metal ions on PMS is very fast and equilibrium is achieved within 5 min, except Cu(II), within 30 min. These patterns are similar to that on silica gel. However, the amount of metal ions adsorbed on silica is less than that on PMS (graphic is not shown). The nature of PMS and metal ions types governs the time needed to reach the equilibrium. The fast adsorption probable occurred due to the mesoporousity in PMS facilitating the transportation of metal ion to meet easily the active sites. Since Cu(II) is the smallest radii among metal ions, it leads to hydrate water molecules in a large number and to form bulky hydrated metal ions. As consequence, the mobility of that that ion is lower.

This kinetics of metal ions adsorption is evaluated from the curve of correlation between the amounts of metal ions adsorbed vs. contact time. The kinetics parameter of metal ions adsorption calculated using models of 1st order, 2nd order, pseudo-1st order, and pseudo-2nd order [42-44] are shown in Table 4.

According to the value of the correlation coefficient (R^2), the kinetics of Cu(II) adsorption on PMS

Table 5. Adsorption capacity of metal ions on PMS

Metal	Langmuir Model		Freundlich Model	
	Capacity (mmol/g)	R^2	Capacity (mmol/g)	R^2
Co(II)	*0.3332*	*0.9783*	0.2692	0.8091
Ni(II)	*0.5032*	*0.9996*	0.5565	0.5898
Cu(II)	0.4745	0.9524	*1.0049*	*0.9679*
Zn(II)	*0.0356*	*0.9269*	0.0624	0.2460

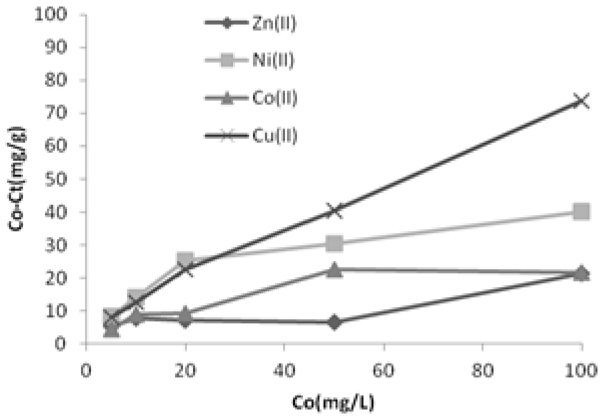

Fig 5. Curve of metal adsorption at the various metal ion concentration

was observed to follow the pseudo 1st order indicating that a large excess of one of the reactants ([adsorbent]>>[adsorbate]) so that, during adsorption occurs, only a small amount of the reactant (adsorbate) is consumed so the reaction rate depend on the concentration of adsorbate. It is supported by high capability PMS in adsorbing Cu(II) since silanol, amin, and phosphonate active sites have similar capability to interact with the ions. However, Co(II), Ni(II), and Zn(II) prefer to follow pseudo 2nd order indicating that the adsorbent does not contain a large excess amount available for those ions so that concentration of active sites on the adsorbent declines linearly to that of the adsorbate during adsorption. As mentioned above, phosphonate groups govern more in adsorbing those metals ions rather than silanol ones. In the case, the adsorption rate depends on the square concentration of adsorbate. A similar phenomenon has been reported in other studies The rate constants (k) for each system calculated from the linear least square method and presented in Table 4 give a good correlation coefficient (R^2 close to 1).

Capacity of adsorption

The adsorption capacity and also the performance of the PMS were usually predicted from equilibrium sorption isotherm. The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state.

The efficiency of metal ions removal is affected by metal ion concentration, with decreasing removal percentage as concentration increase from 5 to 100 mg/L at constant pH and room temperature. After maximum capability is achieved, the increase in adsorbate concentration result in decrease steadily in removal percentage of Co(II), Ni(II), Cu(II), and Zn(II). At 5 mg/L of Cu(II) solution the removal of metal ion was found to be between 34.4% (silica) and 67.9% (PMS). At 10 mg/L of Cu(II) solution the removal of metal ion from 28.1% (silica) and 50.3% (PMS). Cu(II) solution removal efficiency of 0.4% (silica) and 40.9% (PMS) were achieved at adsorbate dosage level of 20 mg/L. It is evident that for all adsorbents maximum removal efficiency was achieved at an adsorbate dosage level of 50 mg/L. The variation in sorption capacity between the various adsorbents could be related to the type and concentration of surface group responsible for adsorption of metal ions from solution. Increasing adsorbate dosage reduces the number of active sites in the surface available for adsorption.

To study of the extent and degree of favorability of adsorption, in this experiment with variation range from 5 to 200 ppm of metal ions was carried out and the isotherm data obtained were fitted with two well known models suggested by Langmuir and Freundlich which commonly used in solution model. The results are shown in Table 5.

From the coefficient linearity (R^2) of Table 4, adsorbents prefer to Langmuir model in adsorbing Cu(II). However adsorbents prefer to Freundlich model in adsorbing Co(II), Ni(II), and Zn(II). Therefore, in adsorption of Cu(II), the metal ion tend to form an adsorbed solute monolayer, with no side interactions between the adsorbed ions. It also assumes that the interactions take place by adsorption of one ion per binding site and that the sorbent surface is homogeneous and contains only one type of binding site. However, in adsorption of Co(II), Ni(II), and Zn(II), these metal ions tend to form multilayered structure. The result indicates that PMS prefer in trend adsorption capacity of Cu(II)>Ni(II)>Co(II)>Zn(II). Adsorption capacity of adsorbent depends on its surface area, pore diameter, solubility adsorbate, pH, and temperature.

Selectivity

A comparison of capability of PMS in adsorbing Co(II), Ni(II), Cu(II), and Zn(II) in individual, binary and quarternary metal ions system represented as selectivity coefficient is expressed in Table 6. While in individual metal ions, PMS prefer in trend selectivity of Cu(II)>Co(II)>Ni(II)>Zn(II). However, in binary and quartenary metal ions system PMS prefer in trend selectivity of Cu(II)>Ni(II)>Co(II)>Zn(II). It indicates that

Table 6. PMS selectivity of Cu(II) toward other metal ions

System	Selectivity Coefficient		
	Cu/Co	Cu/Ni	Cu/Zn
Individual	4.331	3.364	33.753
Binary	1.868	2.193	3.775
Tertiary	1.300	1.400	2.980

the trend selectivity of PMS is not too strong.

PMS selectivity toward individual metal ion system correlated with the decreasing strength of bond with soft ligand. It is similar to the adsorption of metal ions on silica. However, the presence of other ions which has similar properties change significantly the selectivity of PMS in adsorbing Co(II), Ni(II), Cu(II), and Zn(II). It is probably due to the absence of competitive process between metals and adsorbent in single component system. The most likely reason for the trend is the competition for adsorption site and screening effect by the competing metal ions.

Ionic radii and hydration energy is an important factor in adsorption process. The preferential adsorption behavior of adsorbent for metal ions acquired in present investigations could also explained in term of ionic radii (Å) of metal ions (Cu(II) 69, Co(II) 74, Ni(II) 72, and Zn(II) 74. Thus the element with larger ionic radius will compete faster for exchange sites than those of smaller ionic radius. Adsorption may be related to the loss of the entire hydration sphere that precedes hydrolysis. The smaller the ionic radius, the greater its tendency to hydrolyze leading to reduce sorption. The observed order indicates that Cu may have greater accessibility to the surface of certain pore than Ni(II), Co(II), and Zn(II) due to its larger ionic radius. Adsorption may relate to the loss of entire hydrogen sphere that proceeds hydrolysis. The smaller the ionic radius, the greater its tendency to hydrolyze leading to reduce adsorption [45].

CONCLUSION

Phosphonate modified silica (PMS) has been successfully prepared by covalently grafting technique in two-steps procedure. Namely attachment of a linker compound and immobilization of phosphonate functional groups. Adsorption of metal ions investigated on phosphonate modified silica follow a pseudo 1st order mechanism for Cu(II) and pseudo 2nd order for Co(II), Ni(II), and Zn(II). PMS gives the adsorption capacity of metal ions with the order: Cu(II)> Ni(II)> Co(II)> Zn(II) and the selectivity for adsorption of Cu(II) is higher toward Zn(II) than Co(II) and Ni(II). Further investigation is focused on the removal of metal ion from the potency adsorbent to analyze the capacity of the adsorbent to be applied as stationary phase in ion chromatography. Additionally, synthetic adsorbents immobilized with phosphonate open a broad spectrum of prospects for tailor-made application in the removal of different type of heavy metals ions for recovery and preconcentration.

REFERENCES

1. WHO, 2003, *Guidelines for Drinking-water Quality: Cu in Drinking Water*, World Health Organization.
2. WHO, 2006, *Concise international chemical assessment document; 69, Cobalt and Inorganic Cobalt Compounds*, World Health Organization.
3. WHO, 2005, *Guidelines for Drinking-water Quality: Nickel in Drinking Water*, World Health Organization.
4. WHO, 2003, *Guidelines for Drinking-water Quality: Zink in Drinking Water,* World Health Organization, Geneva.
5. Sampaio, R.M., Timmers, R.A., Xu, Y., Keesman, K.J., and Lens, P.N., 2009, *J. Hazard. Mater.*, 165 (1-3), 256–265.
6. Pohl, P., and Prusisz, B., 2004, *Anal. Chim. Acta*, 502 (1), 83–90.
7. Genç-Fuhrman, H., Wu, P., Zhou, Y., and Ledin, A., 2008, *Desalination,* 226 (1-3), 357–370.
8. Ulewicz, M., Walkowiak, W., Gega, J., and Pośpiech, B., 2003, *Ars Separatoria Acta*, 2, 47–55.
9. Sholkovits, E.R. and Copland, D., 1981, *Geochim. Chosmochim. Acta*, 45 (2), 181–189.
10. Koutlemani, M.M, Mavros, P., Zouboulis, A.I., and Matis, K.A., 1994, *Sep. Sci. Technol.*, 29 (7), 867–886.
11. Krajewska, B., 2001, *React. Funct. Polym.*, 47 (1), 37–47.
12. Georgaka, A., and Spanos, N., 2010, *Global NEST J.*, 12 (3), 239–247.
13. Bhatnagar, A., and Minocha, A.K., 2006, *Indian J. Chem. Technol.*, 13, 203–217.
14. Yang, R.T, 2003, *Adsorbents: Fundamentals and Applications*, John Willey and Sons.
15. Dash, S., Mishra, S., Patel, S., and Mishra, B.K., 2008, *Adv. Colloid Interface Sci.*, 140 (2), 77–94.
16. Foschiera, J.L., Pizzolato, T.M., and Benvenutti, E.V., 2001, *J. Braz. Chem. Soc.*, 12 (2), 159–164.
17. Bordelanne, O., and Dellvile, M-H., 2002, *Solid State Sci.*, 4 (6), 851–858.
18. Jal, P.K., Patel, S., and Mirsha, B.K., 2003, *Talanta*, 62 (5), 1005–1028.
19. Arakaki, L.N.H., and Airoldi, C., 2000, *Polyhedron*, 19 (4), 367–373.
20. Qu, R., Niu, Y., Sun, C., Ji, C., Wang, C., and Cheng, G., 2006, *Microporous Mesoporous Mater.,* 97 (1), 58–65.

21. Machado Jr., R.S.A., da Fonseca, M.G., Arakaki, L.N.H., Espinola, J.G.P., and Oliveira, S.F., 2004, *Talanta,* 63 (2), 317–322.
22. Nesterenko, P.N., Zhukova, O.S., Shpigun, O.A., and Jones, P., 1998, Synthesis and Ion Exchange Properties, *J. Chromatogr., A*, 813 (1), 47–53.
23. Nowack, B., 2003, *Water Res*., 37 (11), 2533–2546.
24. Garcia-Valls, R., Hrdlicka, A., Perutka, J., Havel, J., Deorkar, N.V., Tavalides, L.L., Muñoz, M., and Valiente, M., 2001, *Anal. Chim. Acta,* 439 (2), 247–253.
25. Mishra, S.P., Achary, P.G.R., and Das, M., 2012, *J. Chem. Pharm. Res.*, 4 (2), 1207–1216.
26. Shoaib, A., Badar, T., and Aslam, N., 2011, *Pak. J. Bot.*, 43 (6), 2997–3000.
27. Mutin, P.H., Guerrero, G., and Vioux, A., 2005, *J. Mater. Chem.*, 15 (35-36), 3761–3768.
28. Wijnen, P.W.J.G., Beelen, T.P.M., de Haan, J.W., Rummens, C.P.J., van de Ven, L.J.M, and van Santen R.A., 1989, *J. Non-Cryst. Solids*, 109 (1), 85–89.
29. Mori, Y, and Pinnavaia, T.J., 2001, *Chem. Mater*., 13 (6), 2173–2178.
30. Jabbour, J., Calas, S., Gatti, S., Kribich, R.K., Myara, M., Pille, G., Ettienne, P., and Moreau, Y., 2008, *J. Non-Cryst. Solids*, 354 (2-9), 651–658.
31. Lisovskyy, I.P., Litovchenko, V.G., Mazunov, D.O., Kaschieva, S., Koprinarova, J., and Dmitriev, S.N., 2005, *J. Optoelectron. Adv. Mater*., 7 (1), 325–328.
32. Dawy, M., 2002, *Egypt. J. Sol*., 25 (1), 137–152.
33. Coates, J., 2000, *Interpretation of Infrared Spectra, A practical Approach, Encyclopedia of Analytical Chemistry*, Meyers ed., John Wiley & Sons Ltd, Chichester, 10815–10837.
34. Basila, M.R., *The Use of Infrared Spectroscopy to Study Surface Groups and Adsorbed Species on Catalysts*, Gulf Research & Development Company, Pittsburgh, Pennsylvania, 203–209.
35. Zhuravlev, L.T., 2000, *Colloids Surf., A*, 173 (1-3), 1–38.
36. Plyasunova, N.V., Zhang, Y., and Muhammed, M., 1998, *Hydrometallurgy*, 48 (2), 153–189
37. Mercê, A.L.R., Szpoganicz, B., Dutra, R.C., Khan, M.A., Thanh, X.D., and Bouet, G., 1998, *J. Inorg. Biochem.*, 71 (1-2), 87–91.
38. Schock, M.R., Lytle, D.A, and Clement, J.A., 1995, Effect of pH, DIC, *Orthophosphate and Sulfate on Drinking Water Cuprosolvency*, National Risk Management Research Laboratory Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati Ohio.
39. Weng, C-H., and Huang, C.P., 2004, *Colloids Surf., A*, 247 (1-3), 137–143.
40. Shawabkeh, R., Al-Harahsheh, A., and Al-Otoom, A., 2004, *Sep. Purif. Technol.*, 40 (3), 251–257.
41. Say, R., Birlik, E., Ersöz, A., Yilmaz, F., and Gedikbey, T., 2003, *Anal. Chim. Acta*, 480:251-258
42. Lee, B., Kim, Y., Lee, H., and Yi, J., 2001, *Microporous Mesoporous Mater.,* 50, 77–90.
43. Wang, H., Kang, J., Liu, H., and Qu, J., 2009, *J. Environ. Sci*., 21 (11), 1473–1479.
44. Terrada, K., Matsumoto, K., and Kimora, H., 1983, *Anal. Chim. Acta,* 153, 237–247.
45. Elbhiri, Z., Chevalier, Y., Chovelon, J-M., and Jeffrezic-Renault, N., 2000, *Talanta*, 52 (3), 495–507.