Removal of PO_4^{3-} and Cu^{2+} Using Ferrihidrite-Chelex 100 Gel by Adsorption Column

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Received 23 July 2013; Accepted 28 November 2013; Final revision completed 30 May 2014
Published online for edition May-Augus 2014

ABSTRACT

There is an global issue of contaminated drinking water sources with a heavy metals and nutrient that harm to human health, such as phosphate and Cu^{2+}. It occurs as the byproduct or waste material from sewage population, industry and agricultural. Indonesian Government Regulation No 82 in 2001 declared maximum quantity 0.2 mg PO_4^{3-}/L and 2 mg Cu/L contain in the drinking water. Resins chelex 100 and ferrihydrite reported can be applied to adsorpt PO_4^{3-} and Cu^{2+}. The adsorbent composition of ferrihydrite-chelex 100 was 1:1. This was able to displaced PO_4^{3-} and Cu^{2+} optimally at 7.5 mL with percentage of analyte 97.66% PO_4^{3-} and 96.33% Cu^{2+}. The highest desorption percentage for PO_4^{3-} and Cu^{2+} was achieved at 86.61% and 60.87% when H_2SO_4 0.3 M was used. In the sample of drinking water, this adsorbent was able to removed PO_4^{3-} and Cu^{2+} between 71 and 81% and meanwhile from water tap sample around 84-98% at pH 5, respectivelly.

Key word: adsorption, PO_4^{3-}, Cu^{2+}, ferrihydrite-chelex 100

INTRODUCTION

Water is an essential chemical for living survival. So that drinking water supply for living must be healthy and hygienic. However, it was found often contaminated with several dangerous heavy metals particularly phosphate and Cu^{2+}. The source contamination can be from house hold, industrial and agricultural waste. The excess phosphate contains in drinking water may cause a health problems. Bones and teeth calcium deficiency can occur as high level phosphate in the blood and also the adults will be more prone to osteoporosis [1]. While Cu(II) is highly toxic and able to cause diseases if over the limit, it will affect almost of every organ of the body, such as kidney, gastrointestinal irritation, and damage to the liver [2].

Separation of phosphate and heavy metals in water can be undertaken using a liquids adsorption method, filtration using a membrane, co-precipitation and solid phase adsorption [3]. Some advantages of the solid phase adsorption method such as a simple procedure, a quick process, safe, less a harmful side effect to the health, and have high concentration factor and thus requires less solvent [4] often was chosen. Several types of adsorbents have been applied such as amberlite XAD-4 resin coated with ammonium pyrolidine dithiocarbamate (APDC) and C_{18}-silica gel chelated with 4-(2-pyridylazo)-resorcinol (PAR) [5]. Another type adsorbent is Chelex-100 resin with polystyrene-divinyl benzene embedded in the acrylamide gel. This resin is reported able to binding Cu^{2+} ions by a chelate formation with iminodiacetic acid (IDA) as active group. This functional group act as a cation exchanger on its negative charged ($-CH_2COO^-$) [6]. Meanwhile for removal of phosphate ions, an clay commonly have been used [7], and also sludge of alum [8], however the process of the adsorption required complicated conditions. Ferrihydrite is an alternative for adsorbent in aqueous system. It has a high reactivity and large specific surface area (>200 m^2/g). It was applied as an anion exchanger with its positive charged on (OH_2^+) [9]. Moreover, other type of adsorbent model commonly used is plastic or glass from tube. It has a small area and requires a low flow rate of the analytes. Beside that, the diverse of adsorbent particle size in the column causes a channeling process, and reduces a capacity of the retained analyte in the adsorbent [10]. This paper discloses ferrihydrite-chelex 100 gel as adsorbent for removal of phosphate and Cu(II) ion from the drinking water sources. The effect of volume of analytes were also displayed.

EXPERIMENT

Chemicals and instrumentation

Chemicals

All chemicals used as bought from the manufacturer, including acrylamide 40% (Merck), bis-acrylamide, ammonium persulfate 98% (Merck), N,N,N',N'-tetramethylethylene diamine (TEMED) 99% (Merck), potassium dihydrogen phosphate (Merck), copper sulfate pentahydrate (Merck), hexaammonium molibdate tetrahydrate (Merck), sulfuric acid 96% (Merck), tin chloride dihydrate (Merck), nitric acid 65% (Merck), and aquadest.

Reactive phosphate was detected as phosphomolybdenum blue complex which was produced by mixing the coloring reagents of $(NH_4)_6Mo_7O_{24}.4H_2O$ (Merck) in acidic solution (H_2SO_4, 96% Merck) and reducing agent of $SnCl_2.2H_2O$(Merck). Cu was analyzed with the addition of HNO_3 (Merck, 65%).

Instrumentation

Phosphate absorbance was measured using UV-Vis 1601 Shimadzu spectrophotometer. Cu was analysed using AA-6200 Shimadzu Atomic Absorption Spectrophotometer. Solution was measured at pH 5 by Schott Gerate CG 820 pH meter and acrylic column as a place to removal analyte.

Procedure

Preparation of ferrihydrite-chelex 100 gel

Gel solution was formed by mixing 0.3 g bis-acrylamide and 37.5 mL acrylamide 40% and stirring to homogen, and it was added distilled water to a volume of 100 mL. Meawhile ferrihydrite paste was formed by precipitation process between 25 mL $FeCl_3$ 0.2 M and NaOH 1 M. It was stirred to pH 8 and the precipitate was stored in the dark bottles. Afterwards, the ferrihydrite-chelex 100 gel was produced by mixing of 1.0 g ferrihydrite paste and 1.0 g chelex-100 (wet weight) and 10 mL of gel solution. This mixture was added with 70 µL of ammonium persulfate 10% and 20 µL TEMED 99%. Then, it was stirred until homogen. The solution resulted was pipetted to glass mold smoothly to prevent bubbles inside the mold.

Removal of phosphate 0.3 mg PO_4^{3-}/L and Cu 1 mg Cu/L at pH 5

Phosphate and Cu(II) removal was conducted using acrylic columns. An ferrihydrite-chelex-100 gel disc was arranged between whatman paper discs, and the phosphate and Cu(II) solution in various volume was flown to the column. The analytes solution was prepared in volume variation such as 5.0; 7.5; 10; 15; 20; 25 and 30 mL. Then the effluent resulted was analyzed using spectrophotometer for phosphate and Cu(II) concentrations.

Elution experiments

The gel that has retained phosphate and Cu(II) was eluted using sulphuric acid 0.3 M or nitric acid 0.6 M with various volume 2.5; 3; 3.5; 4; 5; 6; 7; 8; 10 and 20 mL. The effluent resulted was analyzed using spectrophotometer.

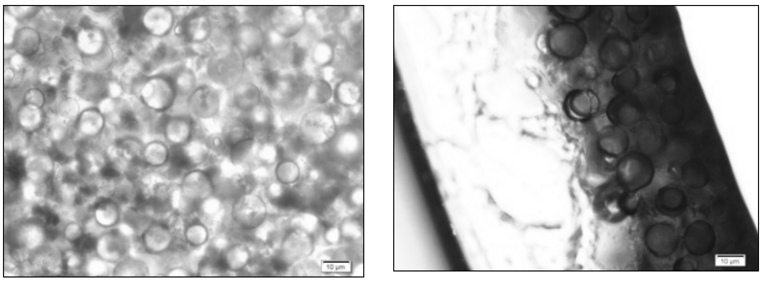
RESULT AND DISCUSSION

Characteristics of ferrihydrite-chelex 100 gel

Resin chelex-100 and ferrihydrite was embedded into the acrylamide gel has a high adsorption capacity to the analyte. It has stability at pH solution below 11 [11]. Ferrihydrite-chelex 100 gel showed expansion/swelling indication after immersion it in distilled water up to 3 h. The characteristic of the resulted of gel adsorbent are shown in Table1.

Table 1. Characteristics of ferrihydrite-chelex 100 gel

Parameter	Characteristics
Color	Red brownie
Initial size	l= 11 cm; w= 8.6 cm; h= 0.09 cm
Size after 3 hours	l =12.2 cm; w =9.4cm; h = 0.12 cm
Expansion factor	1.62
Porosity	0.38



(surface) (sliced)

Figure 1. Gel ferrihydrite-chelex 100

Expansion factor ferrihidrit gel-chelex 100 after hydration in distilled water was 1.62 and porosity value of 0.38. The porosity itself showed a blank space on the gel surface that can be filled by water. The greater the porosity gel shows the gel more easily to bind the water molecules. Gel formed has a pore size > 2 nm [12], meanwhile selectivity of the analyte adsorption toward the adsorbent is affected by the pore size of the gel. Visualization of the gel resulted by using Olympus DP72 BX53 microscope 100x expansions (Figure 1). It appears the distribution of resin chelex-100 in the gel. The sides of the gel show the resin chelex-100 and ferryhidrite on one surface. It occurs during the process of gel formation, ferryhidrite and resin chelex 100 which has a large molecular weight and tends to felt down due to its gravity influence.

Removal of phosphate 0.3 mg PO_4^{3-}/L and Cu 1.0 mg Cu/L at pH 5

The adsorption of analyte volume affects the mass of the adsorbed analyte. The analyte amounts is adsorbed increases with the increasing of mass, and it causes the displacement of analytes from solution to the surface of the adsorbent. It occurs continuously until the mass of the analyte in equilibrium condition. Interaction of Cu^{2+} with the side active of adsorbent chelex 100 (CH_2COO^-) has formed a stable chelate complexes constant 2.65 [13], so that Cu^{2+} ions was adsorbed on the gel. Meanwhile, the phosphate ion have interaction to the cationic hydroxo ($FeOH_2^+$) sites from ferrihydrite through electrostatic interaction

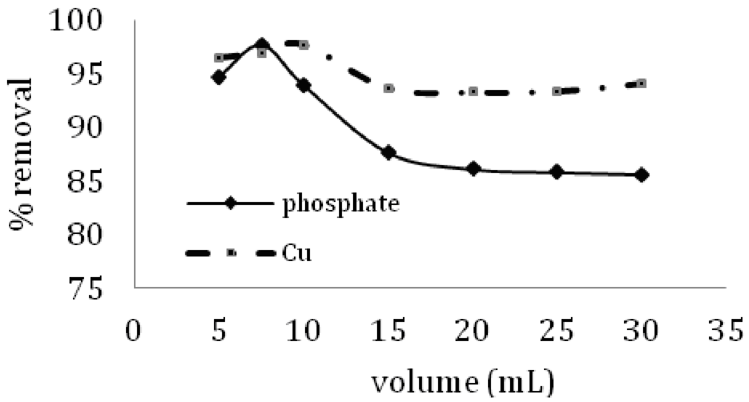


Figure 2.Removal of phosphate and Cu at various volume

Changing of the analyte volume from 5.0 to 30 mL increase the removal percentage of Cu^{2+} and phosphate ion. The optimum removal percentage of phosphate and Cu^{2+} is achieved at volume 7.5 mL. Increasing of the volumes analyte, the adsorbent was be saturated, then the ability to adsorb phosphate and Cu^{2+} ion decreased. The result, it was found that phosphate ion in solution can be displaced up to 97.66% meanwhile Cu^{2+} up to 96.93% using initial volume 7.5 mL with initial concentration 0.3 mg PO_4^{3-}/L and Cu 1 mg Cu/L at pH 5.

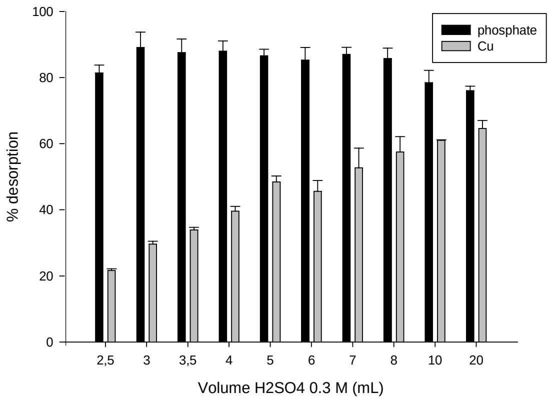


Figure 3. Desorption of phosphate and Cu(II) using H_2SO_4 0.3 M

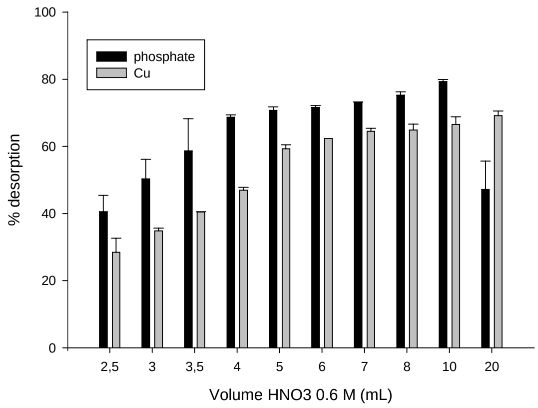


Figure 4. Desorption of phosphate and Cu(II) using HNO_3 0.6 M

Elution of phosphate and Cu(II)

The desorption was performed using nitric acid (0.6 M) and sulfuric acid (0.3 M). The desorption percentage was determined by calculating the amount of phosphate and Cu(II) desorbed by the acid. The results was displayed in Figure 3 and 4, respectively.

These results indicate that both nitric and sulfuric acid desorbed the phosphate retained on the gel-chelex ferrihidrit 100. It occur possibly electrostatic interaction between the phosphate and adsorbent getting weak when acidic condition or lower pH was applied. Increasing of volume of eluent increases of the desorbed phosphate, but when the volume 20 mL of phosphate likely to go down. It was predicted that Fe ions from ferrihidrite was desorpted by the acids. Fe ions in the solution could adsorb back the phosphate, so that it give negative interference during analysis of phosphate in solution [14]. Therefore, the optimum eluent was indicated in 10 mL H_2SO_4 0.3 M with desorption percentage of phosphate 86.61% and 79.74% for when using HNO_3 0.6 M.

Both figure 3 and 4 showed that not all of Cu^{2+} was desorpted from the adsorbent when using HNO_3 0.6 M and H_2SO_4 0.3 M. The number of Cu^{2+} ions can be separated from resin chelex-100 as eluent solution because of changing the charge on the adsorbent being total zero or positively charged, so that the formation of the metal chelate complex with iminodiacetic group will be disturbed and Cu^{2+} ions was desorpted.

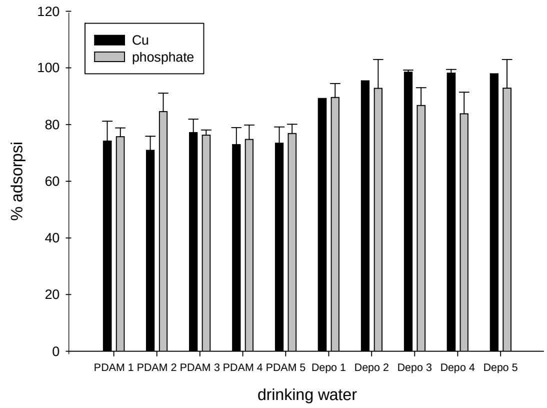


Figure 5. Removal of phosphate and Cu ions in drinking water

Applications the adsorbent in drinking water

Adsorption of phosphate and Cu(II) using gel disc ferryhidrite-chelex 100 was applied to the drinking water are adjusted to pH 5. It follows the optimum pH in previous study [15]. The result is showed in Figure 5. The adsorption percentage of phosphate and Cu^{2+} ions from drinking water using developed adsorbent was obtained in range between 84-98% for water tap sample, meanwhile for refills water sample around 71-81%.

The adsorption strongly depends on the amount of analyte to be adsorbs in drinking water. Figure 5 shows that the percentage analyte on tap water slightly lower than that in the refills water sample. This possibly due to many others metal cations and anions contains in the water tap sample such as Hg, Pb, As, Cd , Cr, Ni and nitrat [16]. These cations and anions compete to the Cu(II) and phosphate ions to be adsorbed by the gel ferrihidrit-chelex 100 adsorbent. Meanwhile, for the refills water sample generally has gone through the process of water purification before consumption such as fitration process so that having less cation and anions impurities.

CONCLUSION

Ferrihydrite-chelex 100 gel has been developed for phosphate and Cu^{2+} removal. Phosphate in solution could be removed up to 97.66% meanwhile Cu^{2+} up to 96.93% at volume 7.5 mL with initial concentration 0.3 mg PO_4^{3-}/L and 1.0 mg Cu/L at pH 5. Ion Cu^{2+} interact with IDA groups on the chelex 100 forms a chelate compound, while phosphate through electrostatic interaction with the active site on ferrihidrit $FeOH_2^{+}$. The phosphate and Cu^{2+} could be desorbed from the gel using H_2SO_4 0.3 M and HNO_3 0.6 M. Ferrihidrit-chelex 100 gel can be applied to removed Cu^{2+} and phosphate in the refilled drinking water approximately 71-81% and 84-98% in the taps water at pH 5.

ACKNOWLEDGMENT

Author thanks to Chemistry Post-Graduate Programe, Brawijaya University and BPKLN (Biro Perencanaan dan Kerjasama Luar Negeri) which has provided scholarships Fast Track.

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