

PHOSPHATE AND NITRATE REMOVAL FROM DRINKING WATER SOURCES USING ACRYLAMIDE-FERRIHYDRITE GEL

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ABSTRAK

Telah dilakukan penyisihan ion fosfat dan nitrat dari air minum menggunakan gel akrilamid-ferrihidrit. Gel dibuat dengan mencampurkan pasta ferrihidrit dan larutan gel akrilamid kemudian dicetak pada suhu 42-46°C selama kurang lebih satu jam. Pengaruh pH dan konsentrasi fosfat serta nitrat diamati terhadap persen penyisihan. Efisiensi desorpsi diamati menggunakan asam sulfat pada berbagai konsentrasi. Hasil penelitian menunjukkan bahwa fosfat dan nitrat dapat disisihkan secara optimal pada pH 5. Konsentrasi larutan nitrat untuk penyisihan optimal adalah 10 mg NO₃⁻/L sementara fosfat dapat disisihkan secara optimal pada konsentrasi 0,3 mg PO₄³⁻/L. Analit dapat didesorpsi dari gel menggunakan H₂SO₄ 0,3 M. Pada aplikasinya, fosfat dan nitrat dalam air minum dapat disisihkan hingga 70%.

Kata kunci : gel akrilamid, ferrihidrit, fosfat, nitrat.

ABSTRACT

Phosphate and nitrate ions removal from drinking water has been conducted using acrylamide-ferrihydrite gel. The gel was prepared by mixing the ferrihydrite paste and acrylamide gel solution followed by casting at temperature 42-46°C for at least one hour. The effect of pH and concentration of phosphate and nitrates to the percent of removal were investigated. Desorption efficiency was also investigated using sulphuric acid at various concentration. As a result, phosphate and nitrate could be removed optimally at pH 5. The solution concentration of nitrate for optimum removal was 10 mg NO₃⁻/L, whilst phosphate could be removed optimally at concentration of 0.3 mg PO₄³⁻/L. The analytes could be desorbed from the gel using H₂SO₄ 0.3 M. In application, phosphate and nitrate in the drinking water sources could be removed up to 70 %.

Keywords : acrylamide gel, ferrihydrite, phosphate, nitrate.

INTRODUCTION

Increasing of population number and human activities caused the decreasing of drinking water sources quality. The sources could be contaminated by phosphate and nitrate from domestic waste and fertilizer. Phosphate and nitrate content in drinking water are as maximum as $0.2 \text{ mg PO}_4^{3-}/\text{L}$ and $50 \text{ mg NO}_3^-/\text{L}$, respectively. Excess phosphate and nitrate in drinking water may cause health problems. Bones and teeth calcium deficiency will occur as high level phosphate in blood [1]. Nitrate could be reduced to nitrosamine in gastrointestinal system [2] which causes intestine cancer [3, 4]. The reduction also changes blood hemoglobin to methaemoglobin so blood cannot bind oxygen. This phenomenon is called as "blue baby syndrome" [5, 6].

Adsorption technique has been approached for nitrate and phosphate removal. Some adsorbents have been used, for example wheat straw anionic sorbent [7] and chitosan hydrogel bead [8] for nitrate removal; amorphous aluminum, iron oxide [9] and aluminum-impregnated mesoporous silicates [10] for phosphate removal. Thick membrane of chitosan-ferrihydrite crosslinked by glutaraldehyde has also been used for phosphate sorption [11]. Ferrihydrite is a good adsorbent in aquatic systems because of its reactivity and large specific surface area ($> 200 \text{ m}^2/\text{g}$) [12]. However, only 42% of phosphate could be desorbed from the membrane by using 0.3 M of H_2SO_4 . It might be caused by weak embedding of ferrihydrite in the membrane.

In this study, acrylamide-ferrihydrite gel was used as an adsorbent to remove phosphate and nitrate from drinking water sources. The effect of pH and concentration of analytes to the percent of removal were investigated. H_2SO_4 eluent at various concentrations were used to desorb the retained phosphate and nitrate to assess the ability of the gel to be used for other cycle.

EXPERIMENTAL SECTION

Materials

Ferrihydrite paste was produced through precipitation process between NaOH (Merck) 1 M and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 0.2 M . Gel

solution was prepared by mixing acrylamide 40% and cross-linker 2% (an olefinic derivatives agarose supplied by DGT Research Ltd, UK) and aquadest. Ammonium persulfate (Merck) 10% was used for polymerization initiator, and N,N,N',N'-tetramethylethylenediamine (TEMED) (Merck, 99%) was used as a catalyst. Synthetic sample of phosphate was prepared from KH_2PO_4 while synthetic sample of nitrate was prepared from NaNO_3 . Reactive phosphate was detected as phosphomolybdenum blue complex which was produced by mixing the colouring reagents of ammonium pentamolybdate tetrahydrate in acidic solution (H_2SO_4 , 95-97%) and reducing agent of SnCl_2 . Nitrate was analyzed as nitrophenol sulphate by mixing 1,3 disulphonic acid and concentrated ammonia 25%.

Instrumentation

Volumetric glasses were used for preparing reagents, gel solution and ferrihydrite (FeOOH) paste. Acrylamide-ferrihydrite gel was drying mounted in an oven. Phosphomolybdate blue complex absorbance was measured by UV-Vis 1601 Shimadzu spectrophotometer. Nitrate absorption was measured by Educator spectronic. The pH of phosphate and nitrate solution was measured by Schott Gerate CG 820 pH meter.

Procedure

Preparation of acrylamide-ferrihydrite gel

Ferrihydrite paste was synthesized by precipitation process between 25 mL FeCl_3 0.2 M and NaOH 1 M while stirring up to pH 8. Water was decanted and the excess of water on the surface ferrihydrite paste was removed using tissue layers. Meanwhile, 100 mL gel solution was formed by mixing 47.5 mL and 15 mL DGT crosslinker 2% accompanied by stirring, then the gel was added by 37.5 mL acrylamide 40% until homogen. Afterwards, the acrylamide-ferrihydrite gel was produced by mixing 2 g ferrihydrite paste and 10 mL of gel solution, then it was added by $60 \mu\text{L}$ ammonium persulfate 10% and $16 \mu\text{L}$ TEMED 99%, then stirred up until homogen. The solution was pipetted to glass mold smoothly to prevent bubbles inside the mold. The gel then was casted by drying in oven at $42-46^\circ\text{C}$ during for one hour. The gel was hydrated before use.

Removal of Nitrate and Phosphate

Phosphate and nitrate removal was conducted using two mini columns. Column 1 mL was attached to column 5 mL. An acrylamide-ferrihydrite gel disc was arranged between whatman paper discs and was placed inside the column 5 mL. The columns were then positioned inside the vacuum erlenmeyer which have been arranged with vacuum pump. 5 mL nitrate or phosphate solution with various pH and concentration was flowed to the column. Nitrate solution was prepared at various pH 3, 4, 5, 6, 7, and 8 with concentration of 0, 5, 10, 15, 20, 25, and 30 mg NO_3^-/L . Phosphate solution were prepared at pH 3, 4, 5, 6, and 7 with concentration of 0; 0.1; 0.3; 0.6; and 0.9 mg $\text{PO}_4^{3-}/\text{L}$. The effluent would be analyzed spectrophotometrically as blue complex of phosphomolybdate and nitrate phenol sulphate complex based on standard procedure [13,14].

Elution experiments

The gel that has retained phosphate or nitrate was eluted using H_2SO_4 with concentration of 0.2; 0.25; 0.3 M. The effluent would be analyzed spectrophotometrically for nitrate and phosphate concentrations.

RESULTS AND DISCUSSION

Properties of Ferrihydrite-Acrylamide Gel

The ferrihydrite-acrylamide gel was red brownish with 0.09 cm in thickness. Hydration of the gel up to three hours in water gave 2.08 of expansion factor and the swelling was not preceded afterward. The gel consisted of approximately 95% water inside. Therefore, unlike resin adsorbent, the use of the gel as an adsorbent was feasible without precondition.

The synthesis of ferrihydrite through precipitation between FeCl_3 and NaOH needs controlled precipitation and cool storage to avoid the formation of other iron oxides, such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) or goetite ($\alpha\text{-FeOOH}$). The ferrihydrite had to be stored in dark bottle to prevent reduction Fe^{3+} into Fe^{2+} . Fe^{2+} had low affinity to phosphate and nitrate ions, so the performance of ferrihydrite could be bad. Therefore, in this research, ferrihydrite paste was stored approximately at 4°C through controlled precipitation of synthesis.

Ferrihydrite which was embedded in acrylamide gel matrix was functioned as an adsorbent for phosphate and nitrate. pH solution will change the surface charge of the adsorbent. Even though the polyacrylamide gel reported has positive charge [15] so it could attract anions but then Warnken *et al.* [16] showed that the gel has a charge close to zero at low ionic strength. Hence, only the ferrihydrite sites will responsible in the phosphate and nitrate sorption.

Phosphate and Nitrate Removal

Figure 1 shows the percent of phosphate removal at pH from 3 to 7 at initial phosphate concentration from 0.1 to 0.9 mg $\text{PO}_4^{3-}/\text{L}$. It can be seen from the figure that phosphate in solution could be removed up to 85% at pH 5 and at initial concentration of 0.3 mg $\text{PO}_4^{3-}/\text{L}$. In addition, it can be seen from Figure 2 that nitrate in the solution could be removed up to 88% at pH 5 with initial nitrate concentration that was 10 mg NO_3^-/L .

pH has a significant role in the adsorption process. It changes nature of surface site groups of the acrylamide-ferrihydrite gel and the species of analytes in solution. Ferrihydrite has point of zero charge (pzc) at pH 7.8-7.9 [17]. Ferrihydrite will have positive charge of FeOH_2^+ at below pzc while FeO^- groups will be dominant on the surface of ferrihydrite at pH above pzc. As depicted on Figure 1 and Figure 2, the pH optimum for phosphate and nitrate adsorption was at pH 5. At pH 5.0, phosphate was mostly in form of H_2PO_4^- while nitrate was as NO_3^- . Both cations could have high affinity to cationic hydroxyl sites of ferrihydrite through electrostatic interaction at pH 5, giving high percentage of removal. At pH solution less or more than 5, the percent removal of phosphate and nitrate was lower. It might be occurred due to enhancing of ferric iron dissolution at pH less than 4. Additionally, the formation and storage of ferrihydrite paste might be not controlled well so there was reduction of ferric iron into ferrous iron which is generally relatively soluble up to near pH 8. Moreover, the presence of ferrous iron will facilitate reduction of nitrate to nitrite or ammonia. Thus, it leads to continuously decreasing of phosphate and nitrate removal at pH more than 5.

As for concentration, it determines the capacity factor of the adsorption. Phosphate and nitrate removal was higher at relatively low concentration. At higher concentration than 0.3 mg $\text{PO}_4^{3-}/\text{L}$ or 10 mg NO_3^-/L , the interaction amongst the ions could be occurred so decreasing affinity of the ions to be sorbed.

By using the optimum pH, the percent removal of phosphate and nitrate in the water samples is shown in Table.1. It is shown that the ferrihydrite is effective to remove phosphate and nitrate in the water samples of 70% in average. This process has brought the concentration of phosphate and nitrate in the samples below than the recommendation of maximum concentration of the analytes.

Elution of Phosphate and Nitrate

For desorption investigation, H_2SO_4 has been used for an eluent solution. Number of % desorption is determined by the amount of phosphate and nitrate are desorbed in acidic conditions. A variety of acids can lower the pH so that cause anion desorption which represent competition between protons and target ions to bind to the active sites [18]. Electrostatic interactions FeOH_2^+ against SO_4^{2-} is stronger than to ion H_2PO_4^- and NO_3^- . Therefore, phosphates and nitrates could be desorbed.

From figure 3, it can be concluded that the phosphate and nitrate were desorbed using H_2SO_4 eluent. Phosphate and nitrate could be desorbed from the gel by using H_2SO_4 with the percent of desorption were 81.5% and 77.5% for phosphate and nitrate, respectively.

CONCLUSION

Acrylamide-ferrihydrited gel has been produced for phosphate and nitrate removal. The removal was effective at pH 5 with initial concentration of phosphate and nitrate 0.3 mg $\text{PO}_4^{3-}/\text{L}$ and 10 mg NO_3^-/L , respectively. Electrostatic interaction between cationic hydroxo sites of ferrihydrite and anionic species occurred at this pH. By conditioning the drinking water sources at pH 5, the acrylamide-ferrihydrite gel could remove phosphate and nitrate in the drinking water as high as 70%. The phosphate and nitrate could be desorbed from the gel by using H_2SO_4 0.3 M as much as 88%. The desorption could occur due to high affinity of SO_4^{2-} ion to positive charge of ferrihydrite through electrostatic interaction.

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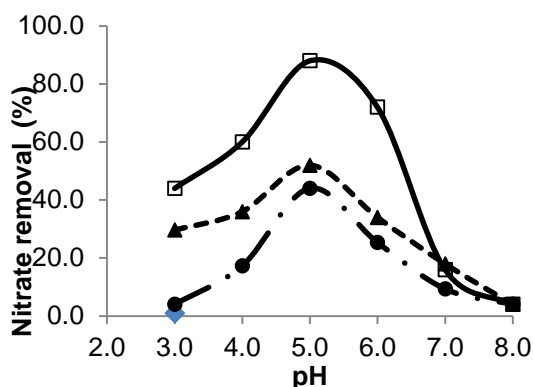


Figure 1. Removal of phosphate ion at various pH and concentration

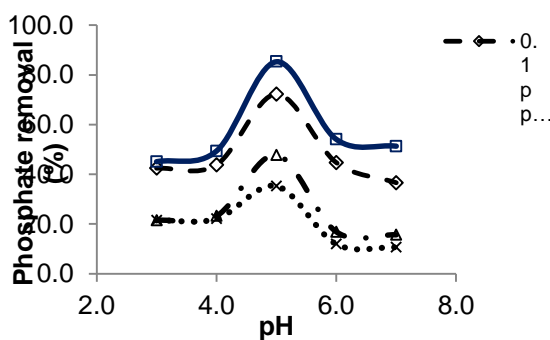


Figure 2. Removal of nitrate ion at various pH and concentration

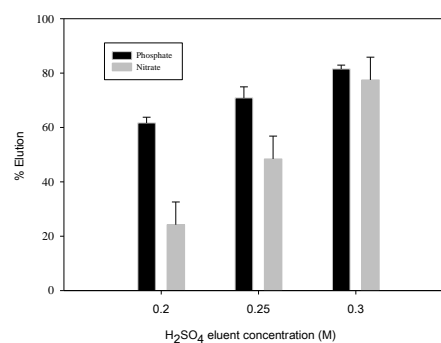


Figure 3. Elution of phosphate and nitrate from the acrylamide-ferrihydrite gel. The analyte solution was adjusted at pH 5. (Error bars represent $\pm 1s_{n-1}$ with $n = 3$).

Table 1. Removal percentage of phosphate and nitrate from drinking water sources

Analytes	PDAM water		Depo/refilling water	
	[Initial] (mg/l)	% Removal	[Initial]	% Removal
Phosphate	0,34	78,8 \pm 6,9	0,14	72,99 \pm 5,3
Nitrate	14,50	63,4 \pm 10,9	8,00	76,5 \pm 6,9