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Analysis of Phosphate Adsorption Using Ferrihydrite with Diffusive Gradient in Thin Films Method

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Abstract

The high input of phosphate into the aquatic system results in eutrophication which leads to algae blooming. Therefore, it is necessary to measure the concentrations of phosphate pollutants that occur in surface waters. Conventional analysis techniques so far only provide an overview of the pollution situation through instant sampling, so it may not represent the current water conditions. Pollutant concentrations fluctuate due to dynamic interactions of phosphate species in natural systems, hence species concentrations may change during sample storage, making accurate analysis difficult unless performed in situ. In this study, the Diffusive gradient in thin films (DGT) method was investigated using a ferrihydrite binding gel assembly on a polyacrylamide gel sheet. The ferrihydrite gel was eluted using 0.25 N H_2SO_4 to release the adsorbed phosphate. The performance test of the method on the absorption of phosphate by ferrihydrite was assessed by testing the effect of pH, contact time, and variation of initial concentration. Determination of the concentration of adsorbed phosphate using the phosphomolidenium blue method with a UV-Visible Spectrophotometer. Characterization of functional groups in polyacrylamide diffusing gel and ferrihydrite adsorbent gel using Fourier Transform Infra Red while the surface morphology of each gel was analyzed by Scanning Electron Microscope.

INTRODUCTION

Phosphate (PO43-) is an anionic compound that enters water bodies through resident waste water, agricultural and industrial waste that uses detergents such as the washing industry, metal industry and so on. Disposal of excess phosphate waste into water bodies can inhibit the decomposition of biological processes and the occurrence of eutrophication. Phosphate is also persistent so that it accumulates which can cause irritation, while at high concentrations it can damage the liver and kidneys in humans [1]. In agricultural soil, phosphorus is a very important element because it plays a role in promoting root growth and development, and can also trigger flowering and fruit ripening in plants. However, if it is excessive, it can cause environmental pollution, therefore a method is needed that can measure phosphate levels in agricultural soil [2].

The most widely used phosphate measurement technique today is the adsorption technique because it is more effective, easy to prepare, and relatively inexpensive in cost compared to other methods. Phosphate adsorption is carried out with various inorganic and organic materials. Adsorbents with organic matter are very abundant in nature which come from various wastes that are not reused.

Various studies have been carried out to measure phosphate levels in aquatic samples. Methods that can be used to measure phosphate levels, one of which is the DGT (Diffusive Gradient in Thin Film) method. The DGT method is an excellent and easy in situ method for measuring unstable species in the aquatic environment. The basic principle of this method is the binding of analyte species to a binding gel or adsorbent after diffusion through a hydrogel and then eluted with an acid to determine its concentration. In the DGT technique, the average solute concentration measured over a certain time can be known, sample contamination can be reduced, and it is possible to perform preconcentration without damaging the sample. The concentration of analyte species bound by binding gel in DGT can be considered the same as the concentration that may diffuse from water to aquatic biota so that this method can be used to predict the bioavailability of a labile metal, sulfate, and phosphate [3].

The method used in this study is the DGT (Diffusive Gradient in Thin Film) method. The DGT method itself is one method that can be used to measure phosphate levels. This DGT method is an excellent and easy in situ method for measuring unstable species in the aquatic environment. The basic principle of the DGT method is the binding of analyte species to an adsorbent after diffusion through a hydrogel and then eluted with an acid to determine its concentration. The advantages of this method include that the average solute concentration measured can be known within a certain time, preconcentration without damaging the sample and also reducing sample contamination. The concentration of analyte species bound by binding gel in DGT can be considered the same as the concentration that may diffuse from water to aquatic biota so that this method can be used to predict the bioavailability of a labile metal, sulfate, and phosphate [4].

In this study, ferrihydrite was used as a binding gel (adsorbent). Ferrihydrite is a metal oxide that is abundant in soil formed by protonation and release of Fe that comes out of primary or secondary minerals due to oxidation processes. The mechanism of absorption of anion (Phosphate) by iron oxide is through the replacement of one phosphate ion by two surface hydroxyl ions (or water molecules) of the iron oxide. Then the two oxygen atoms of the phosphate ion will coordinate with each of the Fe(3+) ions to produce complex bonds on the surface of the material. Ferrihydrite is found in almost all types of soil. In most soils, iron oxide is found in low concentrations because most of it is in the form of secondary minerals. The hydroxide form with a high specific surface area is an adsorbent complex that is highly reactive to various forms of agricultural chemicals and is a very important component in the soil environment. The ferrihydrite form has a high specific surface area, its presence as a soil component is a highly reactive adsorbent component to various ions in the soil [5].

MATERIALS AND METHODS

1. Materials

The materials used for the preparation of DGT gel were acrylamide (Sigma–Aldrich), ammonium persulfate (Sigma–Aldrich), tetramethylethylenediamine (Sigma–Aldrich), N,N'-methylenebisacrylamide (Sigma– Aldrich), membrane filter (Whatman). DGT probe (DGT Research, Lancaster University, UK), pH meter, Fourier Transform Infra Red Spectrophotometer (Prestige-21 Shimadzu), Scanning Electron Microscope. The other materials used were deionized water, sulfuric acid, ammoniummolybdate, potassium antimonyl tartrate, ascorbic acid. sodium nitrate. potassium dihydrogen phosphate, and iron nitrate.

2. Methods

2. 1 Preparation of N,N'-methylenebisacrylamide

A total of 2 grams of N,N'-methylenebisacrylamide was dissolved in methanol:water (1:9) in a 100 mL volumetric flask and then stir for ± 30 minutes.

2. 2 Ferrihydrite Gel Preparation

Solution of 0.1 M $Fe(NO_3)3.9H_20$ was added with 1 M NaOH while stirring and ensured that the pH was not more than 7. Water on top of the surface was removed using a pipette. The precipitate was washed two to three times and placed in the dark room at 4°C.

2. 3 Diffusive Gel Preparation

The diffusive gel was made by adding acrylamide, aquademineral, 2% N,N' methylenebisacrylamide. Then added with ammonium persulfate and tetramethylethylenediamine (TEMED) in a container, and stirred until homogeneous (± 15 – 20 seconds). Soon the solution was pipetted to a glass mold that had been cleaned with HNO_3. The gel solution that has been put in the glass mold is then heated into an oven at a temperature of 42 - 45°C for up to one hour until the gel is formed (not liquid). Gels that has been formed is washed with aquademineral and then soaked for 24 hours and replaced with water 3-4 times. The gel was then stored in 0.01 M $NaNO_3$ until it was used.

2. 4 *Binding Gel Preparation*

For the manufacture of ferrihydrite gel, ferrihydrite was added acrylamide, aquademineral, 2% N,N' methylenebisacrylamide. Then added with Ammonium persulfate and TEMED in a container, and stirred until homogeneous (±15 – 20 seconds). Soon the solution was pipetted in a glass mold that had been cleaned with HNO_3. The gel solution that has been put in the glass mold is then heated in an oven at a temperature of 42-45 C for up to an hour until a gel is formed (not liquid). The gel that has been formed is washed with aquademineralization and then soaked for 24 hours and replaced with water 3-4 times. The gel is then stored in aquademineral until it is used.

2. 5 *Assembly of DGT Components and Testing in Phosphate Solution.*

For the use of the DGT device, a diameter of 25 mm of the diffusive and binding layer were cut using a DGT mold, and the Whatman filter membrane was immersed in aquademineralized. The DGT device was washed and rinsed with aquademineralized. The binding gel layer were placed first on the DGT probe with the ferrihydrite binding side facing up, then followed by placing the diffusive layer and filter membrane. DGT is closed properly.

2. 6 *Effect of pH on Phosphate Adsorption Experiments*

Experiments of pH variation of phosphate solution was carried out by contacting the DGT device into a 3 mg/L phosphate solution with a pH variation of 3, 5, 7 and 9 for 4 hours, then eluted to determine the concentration.

2. 7 *Effect of Contact Time*

The modified ferrihydrite and cellulose samples were used to adsorb 25 mL of 100 ppm phosphate solution at the optimum pH with various contact times of 15 minutes, 30 minutes, 45 minutes, 60 minutes, 120 minutes, 180 minutes and 240 minutes at a temperature of 25°C. The amount of phosphate ion that was not adsorbed was measured using a UV-Vis spectrophotometer at a wavelength of 828 nm.

2. 8 *Effect of Concentration*

The modified ferrihydrite and cellulose samples were used to adsorb 25 mL of phosphate solution with various concentrations of 50 ppm, 75 ppm, 100 ppm, 125 ppm, 150 ppm, 175 ppm and 200 ppm. The process was carried out using a shaker at the optimum pH and time at a temperature of 25°C. The amount of phosphate ion that was not adsorbed was measured using a UVVis spectrophotometer at a wavelength of 828 nm.

2. 9 *Analysis of Phosphate*

Measurement of the concentration of phosphate as P (P-PO_4) using a UV-Visible Spectrophotometer at a wavelength of 880 nm. The absorbance value was observed based on the formation of a phosphomolybdenum blue complex. Diffusive and binding layer were characterized using Shimadzu's Prestige-21 FTIR. The surface morphology of ferrihydrite gel was characterized by SEM.

RESULTS AND DISCUSSION

1. Assembly of diffusive gel and binding gel

A total of 2 grams of N,N'-methylenebisacrylamide was dissolved with methanol:water (1:9) in a 100 mL volumetric flask and then stirred with a magnetic stirrer for ± 30 minutes. Acrylamide, distilled water, N,N' Methylenebisacrylamide 2%. Ammonium persulfate and tetramethylethylenediamine (TEMED) were stirred until homogeneous (±15–20 seconds). Immediately the solution was pipetted into a glass plate mold that had been cleaned with HNO3. The solution that has been put in the mold is then heated in an oven at a temperature of 42-45 C for up to one hour to form a gel. The gel that has been formed is washed with distilled water and then soaked for 24 hours for hydration and replaced with water 3-4 times. The gel was then stored in 0.01 M $NaNO_3$ until it was used Ferrihydrite synthesis was carried out by reacting a 0.1 M Fe^{3+} solution with 1 M NaOH added while stirring and ensuring that the pH was not more than 7. The water on the surface was removed using a pipette. The precipitate was washed two to three times and stored in the dark at 7°C. The measurement of the pH of ferrihydrite which produces a slurry is pH 6.5. Separate the water from the ferrihydrite precipitate, then wash it with distilled water and store it in the refrigerator for 4 days. The synthesis of ferrihydrite begins with weighing, titration, until the formation of a precipitate The formation of diffusive gels and binding gels is based on reactions of free radical polymerization. Acrylamide act as monomer, N,N'-methylenebisacrylamide as a crosslinker, ammonium persulfate as an initiator, and TEMED as a catalyst. The concentration of crosslinker used is 0.5% [3]. The DGT-Ferrihydrite test was carried out using the synthesized ferrihydrite. Ferrihydrite was synthesized by precipitation of $Fe(NO_3)_3.9H_20$ which was titrated with 1 M NaOH. Controlled precipitation during the preparation of ferrihydrite (FeOOH) from $Fe(NO_3)_3.9H_20$ and NaOH to avoid the formation of other iron oxides, such as geotite (α-FeOOH) and haematite (α-Fe_2O_3) [6]. The ferrihydrite binding gel was eluted using 0.25 M H2SO4 in order to release the phosphate anions bound to the ferrihydrite binding gel. The phosphate bonded to the iron atom will be replaced by SO_4^{-2}. The assembly of diffusive and binding gels must begin with the preparation of a gel solution first. To make a diffusive gel or binding gel mold, 5 mL of gel solution is needed. Each gel consists of a cross-linker, water, and acrylamide. After the gel solution is homogeneously mixed, the initiator is added. The initiator for this reaction is a 10% solution of ammonium persulfate. After the addition of the initiator, the catalyst was added. The catalyst used for this reaction is TEMED (N,N,N'N'Tetramethylethylenediamine). Stirring after adding TEMED is approximately 15-20 seconds. Stirring will cause collisions to accelerate polymerization. The diffusive gel solution that has been prepared is immediately inserted into the mold carefully until the mold is completely filled with gel, and no bubbles form. If bubbles form the pipetting is paused until the bubbles disappear so that all parts are equal. Transfer to the mold must be carried out immediately after stirring because polymerization proceeds very rapidly. If the stirring is too long and is not immediately inserted into the mold, the mixture will thicken so that it can no longer be pipette into the mold. If this has happened, then the mixture can no longer be used for the manufacture of diffusive gels.

2. Gel characterization with SEM

The characterization of ferrihydrite gel using a Scanning Electron Microscopy (SEM) tool aims to see the morphological appearance of the diffusive and binding gels. Binding surface of the ferrihydrite gel can be seen in figure 1.

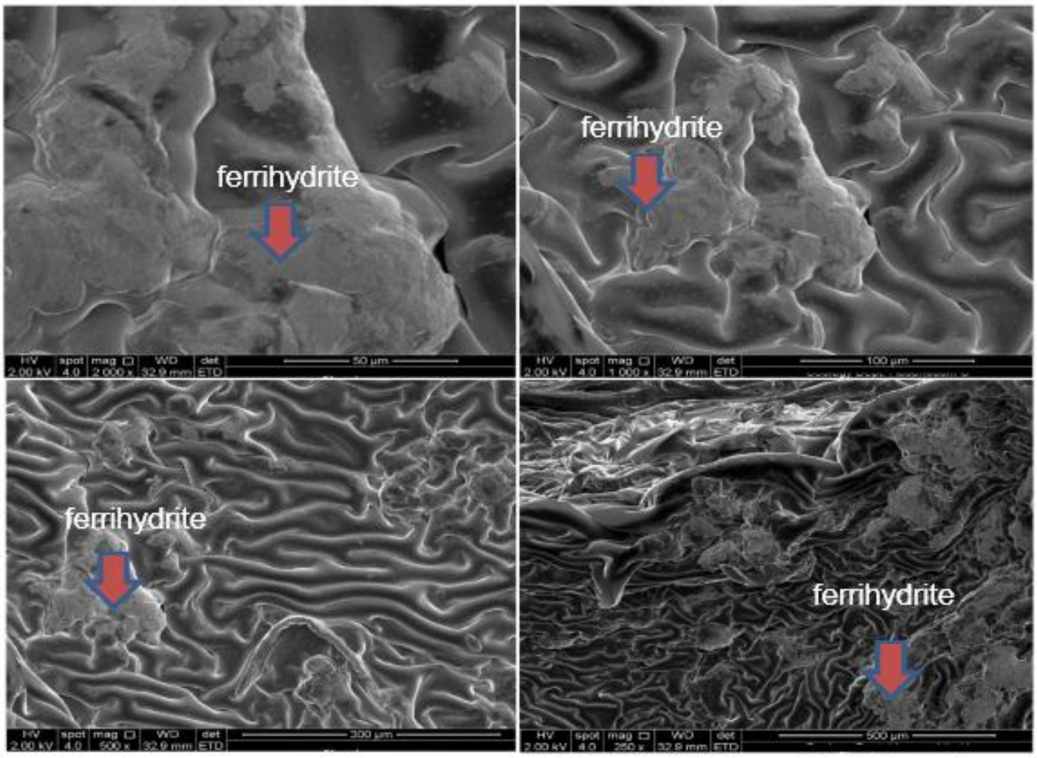

Figure 1. Surface morphology of ferrihydrite in binding gel

From the SEM image with magnification of 50 and 100 microns, it shows that the homogeneity of ferrihydrite binds well to the polyacrylamide matrix so that the concentration of each constituent compound in the manufacture of ferrihydrite gel by attaching it to the polyacrylamide gel is correct and the gel can be formed properly. The surface morphology image of the ferrihydrite gel with SEM showed that there was no chemical interaction between the ferrihydrite compound and the polyacrylamide compound and there was only physical mixing and there was no change in the structure of the acrylamide or ferrihydrite polymers [7].

3. Gel characterization by FTIR

To determine the functional groups contained in the diffusive and binding gels with FTIR characterization was carried out. FTIR spectrum of ferrihydrite and polyacrylamyde gels can be seen in figure 2.

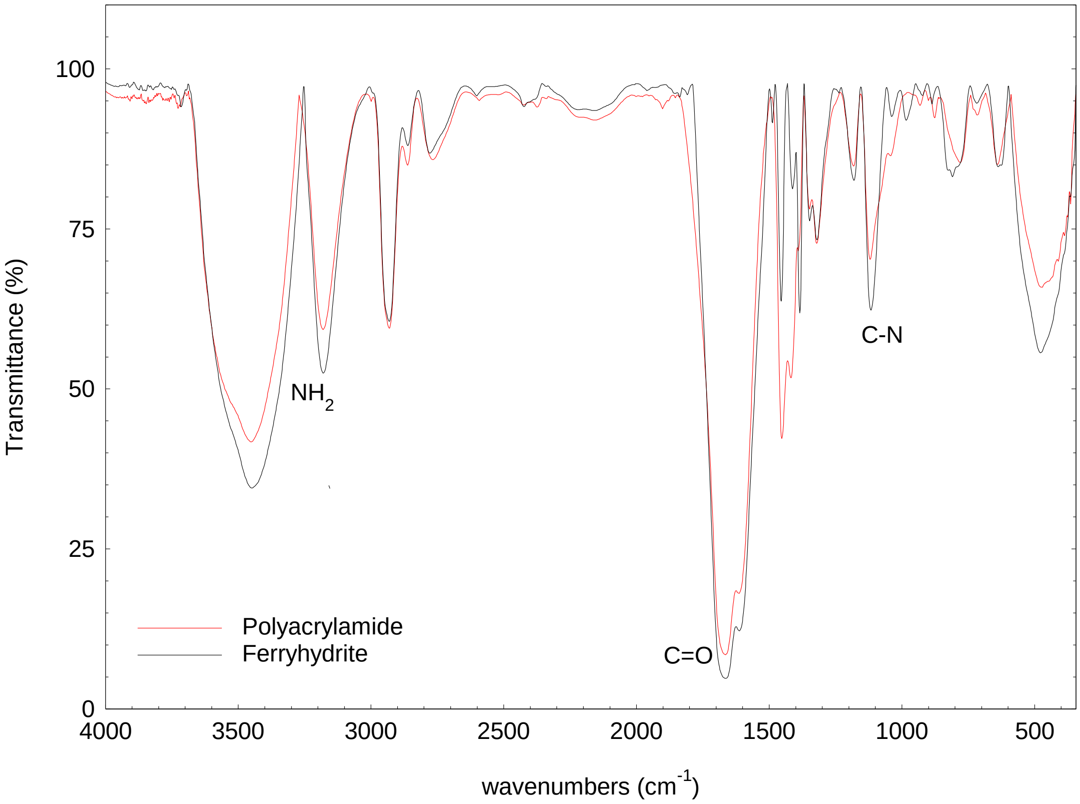

Figure 2. FTIR Spectrum of binding gel and diffusive gel

Characterization with the FTIR instrument was used to ensure that polyacrylamide was successfully synthesized. There are two peaks at wave numbers 3450 cm^{-1} and 3180 cm^{-1} for the polyacrylamide gel sample, while also for the ferhydrite gel sample there are two peaks at wave numbers 3448 and 3178 cm^{-1}. This absorption wave number is typical for primary amines (–NH$_2$) in the wave number 3300–3600 cm^{-1} with a moderate intensity peaks form. Peaks at wave numbers of 1664 cm^{-1} for the polyacrylamide gel and 1662 cm^{-1} for the ferrihydrite revealed the absorption of carbonyl amide (-CONH-), usually found in the wave number 1690-1650 cm^{-1} with strong intensity forms. The peak at wave number 1182 cm^{-1} for the diffusion gel sample and 1180 cm^{-1} for the ferrihydrite sample indicates the absorption of aliphatic amines (C–N) is usually found at wave number 1250 cm^{-1} with moderate intensity peaks. The functional groups that appears is the polyacrylamide, so it can be reported that the polyacrylamide has been successfully synthesized. The functional groups that appear in the polyacrylamide and ferrihydrite are not too different, so there is no change in the polymer structure in the presence of ferrihydrite [8]. The SEM data also show that the interaction between ferrihydrite and polyacrylamide is a physical interaction.

4. Effect of pH variation on phosphate adsorption

This pH variation test aims to calculate the effect of pH on phosphate measurements. pH variations are carried out by adding HNO_3 to make an acidic pH or adding NaOH to make an alkaline pH. The phosphate ion concentration is determined after previously measuring the standard solution series so that a calibration curve is obtained as shown in the figure 3, and the concentration of phosphate absorbed by binding gel (CDGT) is calculated using the following equation (1) bellow:

$$C_{DGT} = M \, \Delta g / (D.t.A)$$

Wherw C_{DGT} concentration of phosphate absorbed by binding gel, M mass of phosphate absorbed by binding gel, Δg the thickness of the diffusive gel plus the thickness of the filter membrane, D = diffusion coefficient of phosphate in the gel, t = deployment time, A exposure area.

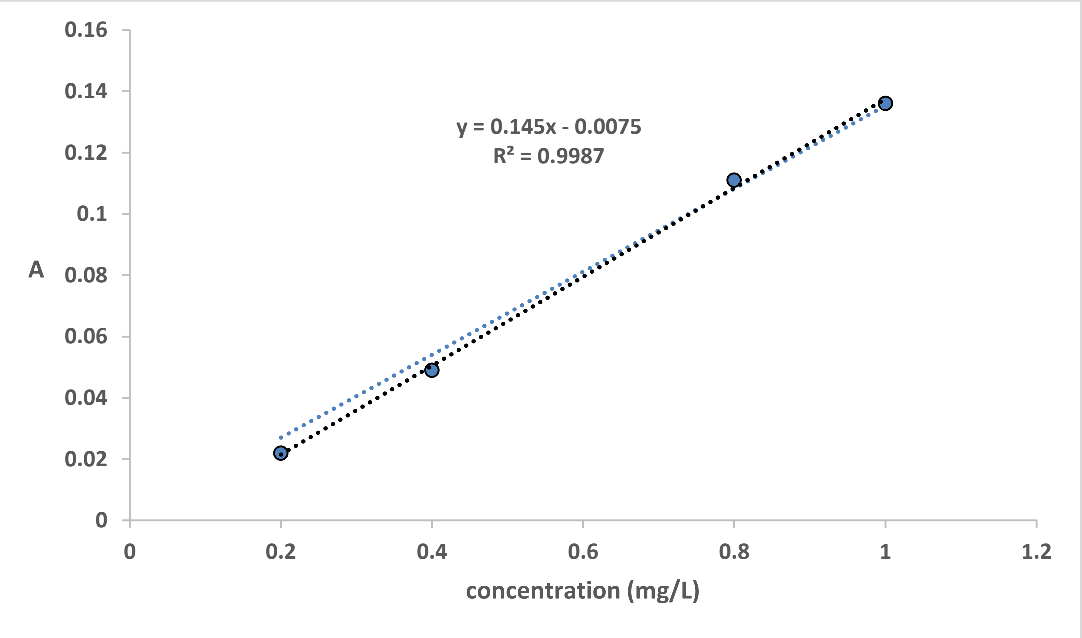

Figure 3. Phosphate standard solution calibration curve

The results of pH effect variation on phosphate adsorption obtained data as shown in the figure 4.

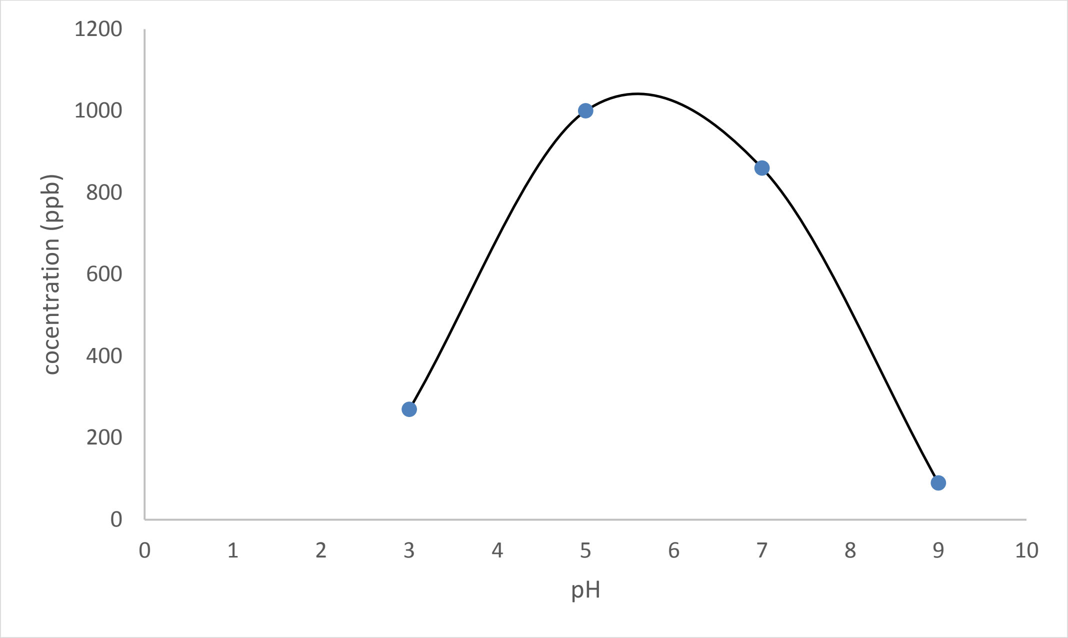

Figure 4. The effect of pH variations on the concentration of adsorbed phosphate.

Figure 4 shows that the concentration measured by DGT at pH 5 is 1.003 mg/L (1003 ppb), which is the optimum pH, while at pH 7 the phosphate concentration is 0.859 mg/L (859 ppb). At pH 3; 0.272mg/L (272 ppb) was obtained and the lowest was 0.093 mg/L (93 ppb) at pH 9. The low phosphate concentration at pH 9 was probably due to the presence of some Fe^{3+} ions forming $Fe(OH)_3$ precipitate. This phenomenon is caused by the presence of OH^- ions from the NaOH solution which is added when adjusting the pH of the solution to become more alkaline. It can be seen from the presence of a fine yellowish solid that is formed. This precipitation occurs because the K_{sp} value of $Fe(OH)_3$ is 6.3 x 10^{38}. At pH 7-9, the solubility product value of the ions is greater than the K_{sp} value, so a precipitate of $Fe(OH)_3$ is formed. This causes the phosphate ion that can diffuse into the resin to decrease due to the larger size of $Fe(OH)_3$ compared to the size of the membrane pores, so that it cannot diffuse through the diffusive layer and into the gel layer binder. Phosphate adsorption on FeOOH is influenced by pH because of the contribution of H_2O and OH^- in the exchange of ligands. At high pH the ligand exchange is weak due to the presence of OH^-, which is known to be the strongest monovalent Lewis base. Therefore, phosphate is well absorbed by ferrihydrite at low pH. The ferrihydrite surface has the same amount of $FeOH^{2+}$ and FeO^- at high pH, while at low pH the ferrihydrite surface has a more positive charge and is easy to bind to phosphate [9].

5. Effect of Contact Time on phosphate ion adsorption

This test aims to determine the amount of phosphate that can be bound to ferrihydrite. In addition, it can also be determined the maximum ability of ferrihydrite in binding phosphate. The phosphate concentration tested was 0.5-5 ppm. The results obtained are as follows:

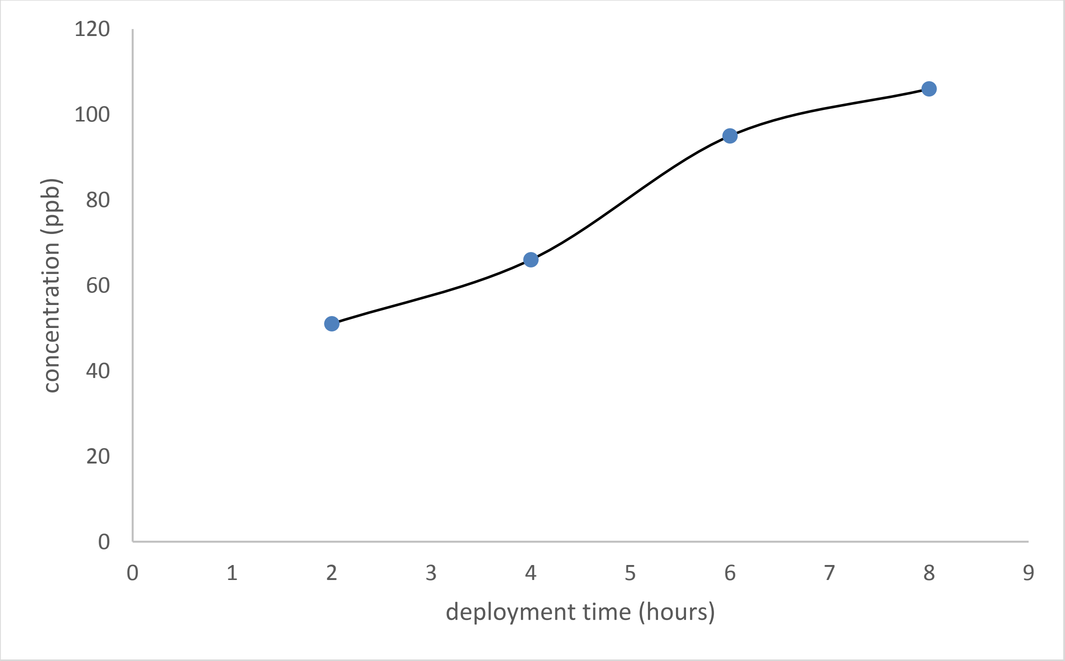

Figure 5. Effect of contact time variation on the concentration of adsorbed phosphate.

From Figure 5 above, it can be seen that the phosphate absorption increases with the increase in time used for contact immersion. The adsorption mechanism on ferrihydrite is generally dominated by ligand exchange in which two hydroxyl groups or water molecules are replaced by one phosphate anion to form a binuclear bidentate complex [10,11].

6. Effect of concentration variation on phosphate ion adsorption

This test aims to determine the amount of phosphate that can be bound to ferrihydrite. In addition, it can also be determined the maximum ability of ferrihydrite in binding phosphate. The phosphate concentration tested was 1-9 mg/L. The results obtained are as follows:

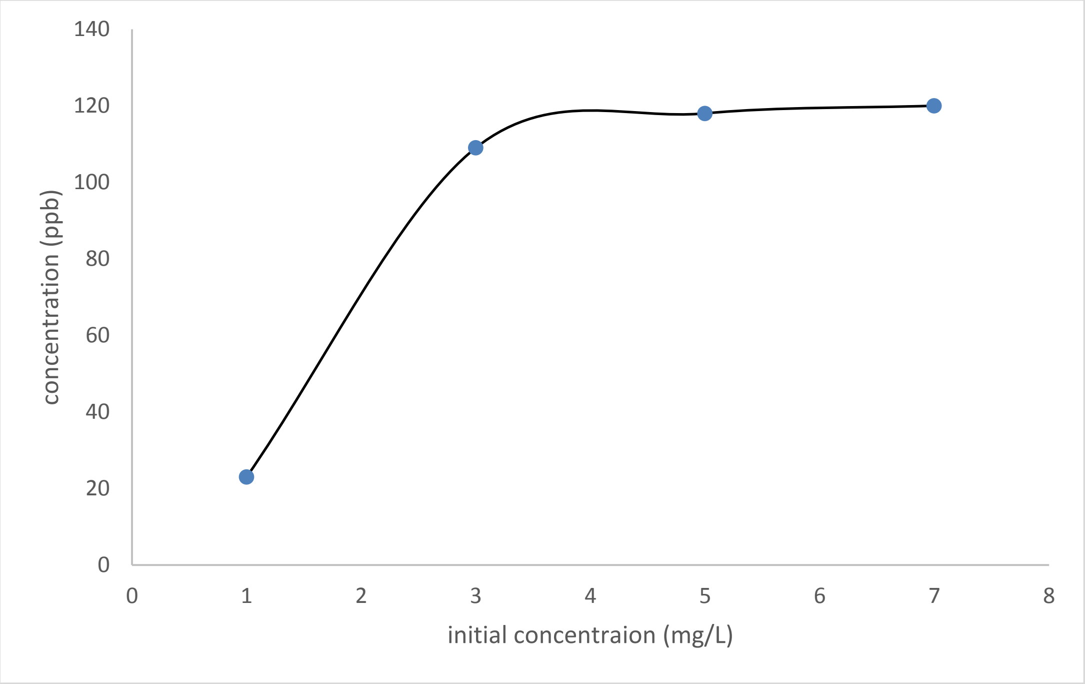

Figure 6. Effect of initial contact concentration on adsorbed phosphate concentration.

From Figure 6 regarding the test of the effect of concentration on the concentration of P above, it can be seen that with increasing phosphate concentration, the concentration of phosphate absorbed is higher. However, at a concentration of 3 – 7 mg/L, it has been sloping. This is probably caused by the binding capacity of ferrihydrite gel which has reached its maximum capacity so that its binding ability is no longer optimal. According to Khairuddin et al [12] that the greater the number of adsorbents used, the more adsorbate absorption, this happens because there are many empty spaces on the surface of the adsorbent and active groups that can bind ions. The results showed that the adsorbent dose given was not too large which could cause maximum absorption of the analyte that could be adsorbed. This is due to the large number of active groups capable of absorbing the adsorbate, especially in the treatment with a low adsorbent concentration while the higher number of active groups causes the adsorbents to not reach the equilibrium point.

CONCLUSION

Based on the experiments that have been carried out and the results of the analysis obtained, it is concluded that binding gel ferrihydrite can be used to adsorb phosphate ions. The ferrihydrite in the binding gel is uniformly dispersed. DGT using ferrihydrite binding gel was most effectively used in a solution with a pH of 5, deployment time of 8 hours, and initial concentration of 3 - 7 mg/L for phosphate measurement.

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