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# Quantification of phosphate ions by diffusive gradients in thin films technique using ferrihydrite as a binding gel and application to marine sediments

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**Abstract.** A diffusive gradient in thin films (DGT) is a newly developed analytical technique that can isolate and quantify the phosphate ions. A DGT unit comprises two components: the diffusion and binding layers. The diffusion layer comprises polyacrylamide hydrogel, whereas the binding layer from the oxide gel of ferrihydrite is impregnated with polyacrylamide gel. The technique employs a thin film of diffusive hydrogel in contact with a binding phase (ferrihydrite) that can bind phosphate ions. The diffusive and binding gels were characterized via infrared spectroscopy. The main peaks of the diffusive gel were observed at 3336 and 1636  $\text{cm}^{-1}$ , whereas those of the binding gel were observed at 3332 and 1638  $\text{cm}^{-1}$ . The DGT technique was evaluated as a way to quantify the amount of phosphate ions present in an aqueous  $\text{KH}_2\text{PO}_4$  solution. After a contact time of 24 h, ferrihydrite exhibited a high affinity for phosphate, with an uptake efficiency of 98.17%. A linear relationship ( $R^2 = 0.9938$ ) was found to exist between the contact time (3–24 h) and uptake efficiency. Within the 0.2–1.2- $\text{mgL}^{-1}$   $\text{KH}_2\text{PO}_4$  concentration range, a linear relationship existed between analyte concentration and the mass of phosphate salt accumulated in the binding gel ( $R^2 = 0.9748$ ). The phosphate ion was eluted from the ferrihydrite hydrogel using 0.25-M  $\text{H}_2\text{SO}_4$  over 30 min. The DGT unit was used to measure the phosphate level in six marine sediment samples from Jakarta Bay. The results revealed mass accumulation of P-containing compounds in the 1.009–2.4676- $\mu\text{g}$  range.

**Keywords:** phosphate, DGT, ferrihydrite, marine sediment

## 1. Introduction

A diffusive gradient in thin films (DGT) serves as a passive sampling method, which was primarily promoted as an instrument to examine the species of trace metal contained in water, sediments, and soil. This technique enables us to determine the solute content diffuses in an established concentration gradient of hydrogel layer isolated from the analyte solution by a protective filter membrane [1]. Lately, the DGT method was employed for measuring the dissolved P content in environmental samples. DGT is an *in situ* passive sampling technique that enables to measure the time-weighted average concentration of an analyte in surface and interstitial water. This technique has been applied to the measurement of the concentration of phosphate [2], trace metals [3], radionuclides [4,5], sulfide [6], and nitrate [7].

DGT instrument comprises two sections: a diffusion layer and a binding layer. Regardless of the analyte being measured, the diffusion layer has been reported to comprise the diffusive gel of



polyacrylamide and cover membrane, which individually characterized by a specified thickness [8]. In the DGT-based approach, a solute diffuses through a diffusive layer and is immobilized within a binding layer (often hydrogel-based) containing a high affinity-binding agent against a specified analyte. The analyte content in the bulk solution is measured by analyte's mass accumulated in the binding layer [9]. The DGT instrument is a layer set, which with a sink (iron oxide layer) -where P is contained- serve as diffusive medium simultaneously. The device is characterized by a diffusion-driven analyte resupply from a kinetically unstable solid-phase in respect to the formed concentration gradient in the solution by DGT [10]. Acrylamide gel combined with agarose-derived cross-linker (patented by DGT Research), allow the target analyte present in solution to diffuse across the membrane and reach the binding gel [11]. The analyte thus binds to the binding phase and is removed from the liquid. The analyte content accumulated in the binding-phase in the described form is regarded as equal toward the one passed thru the diffusive layer. In our study, ferrihydrite was used as the analyte-binding species in the binding layer because it has a strong adsorption capacity for phosphorus-containing compounds. These compounds are some of the most important nutrients for biological growth. Additionally, they are nutrients, which mostly limit the biological productivity in the land and marine environments [12]. Observing the concentration of phosphate is considerably important to avoid and manage the eutrophication, which has a serious ecological impact, as it decreases species biodiversity and abundance [13]. The study aimed to determine phosphate concentration in analyte samples using a DGT device having ferrihydrite as a binding gel.

## 2. Materials and methods

### 2.1. Reagents and materials

Plastic wares were washed in 5% HNO<sub>3</sub>, followed by rinsing thoroughly with deionized water prior to use. Reagents were analytical grade. A stock solution (100 mgL<sup>-1</sup>) of phosphate was prepared by dissolving the relevant amount of KH<sub>2</sub>PO<sub>4</sub> in deionized water. The concentrated solution was kept at 4 °C and immediately added with solvent to the desired concentration before use. The DGT samples were purchased from DGT Research.

### 2.2. Characterization of the diffusive and binding gels

The functional groups of the binding and oxide gels were analyzed via Fourier transform infrared (FTIR) spectroscopy.

### 2.3. Analyte uptake and elution

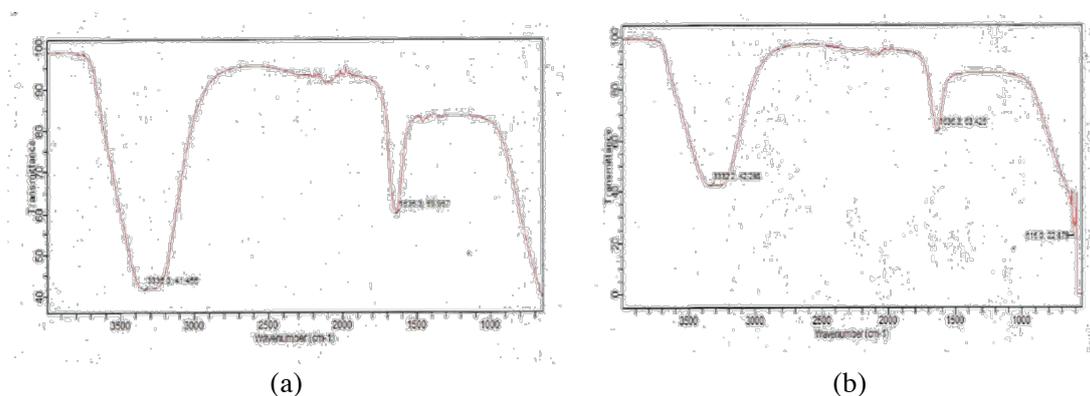
Triplicate experiments were conducted wherein ferrihydrite binding gel discs were exposed to known volumes of phosphate solutions for varying contact time and with varying phosphate concentration. The samples of the solution were collected before and after the solution's exposure to the binding gel discs for colorimetric analysis to determine the mass of phosphate accumulated on the binding gel. The elution of the phosphate ions from the binding gels was performed using H<sub>2</sub>SO<sub>4</sub>. The eluent thus obtained was diluted and analyzed via UV-Vis spectrophotometry to determine the efficiency of the elution procedure.

### 2.4. Contact time and concentration dependence of phosphate uptake by ferrihydrite

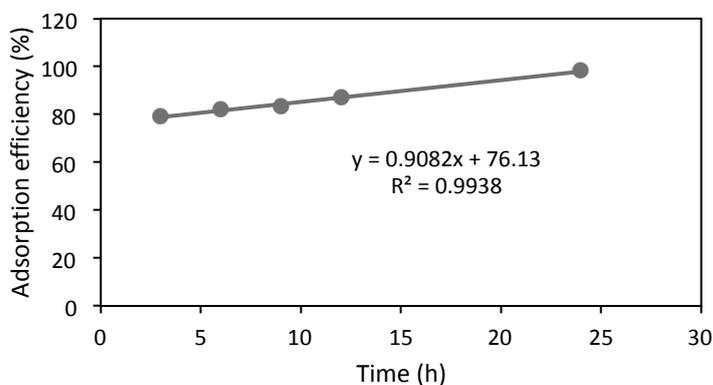
To determine whether the sorption capacity of phosphorus by ferrihydrite was linear, three sets of triplicate oxide gel were exposed to a well-stirred solution containing 0.2 mgL<sup>-1</sup> of KH<sub>2</sub>PO<sub>4</sub> for 3, 6, 9, 12, and 24 h. In particular, the oxide gel containing ferrihydrite was exposed to a 10-mL solution of 0.2 mgL<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>. The phosphate ion accumulated in the binding gels was eluted with 10 mL of H<sub>2</sub>SO<sub>4</sub> 0.25 M. The amount of phosphate ion eluted was determined through the spectrophotometric method. To study the concentration dependence of the adsorption efficiency (sorption capacity) of the oxide gel, KH<sub>2</sub>PO<sub>4</sub> solutions with concentrations ranging between 0.2 and 1.2 mgL<sup>-1</sup> were utilized. In these experiments, three sets of triplicate oxide gel were exposed to a well-stirred KH<sub>2</sub>PO<sub>4</sub> solution for 24 h. Phosphorus in the binding gel was eluted with 10 mL of H<sub>2</sub>SO<sub>4</sub> 0.25 M, and its amount determined through the spectrophotometric method.

### 2.5. Acid concentrations used to effect phosphate elution

Sulfuric acid concentrations used for the elution of the phosphate salt from the binding gel were 0.05,



**Figure 1.** Fourier transform infrared (FTIR) spectra of (a) the diffusive gel and (b) the binding gel.



**Figure 2.** Effect of contact time on the uptake of phosphate ions by ferrihydrite

0.10, 0.15, 0.20, 0.25, and 0.30 M. The eluent was then analyzed using the spectrophotometric method.

### 3. Results and discussion

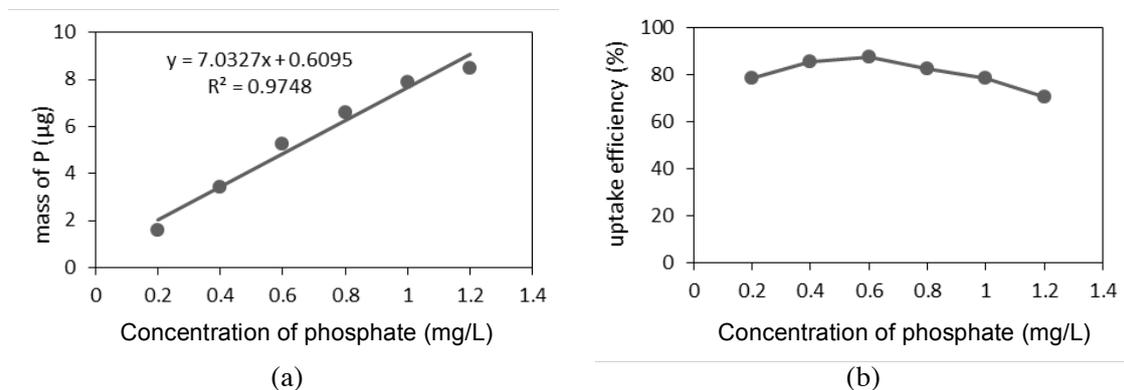
#### 3.1. Infrared analysis

The characteristics of the diffusive and binding gels were analyzed via infrared spectroscopy. In particular, the FTIR spectra of the diffusive gel and the ferrihydrite-containing binding gel are shown in figure 1.

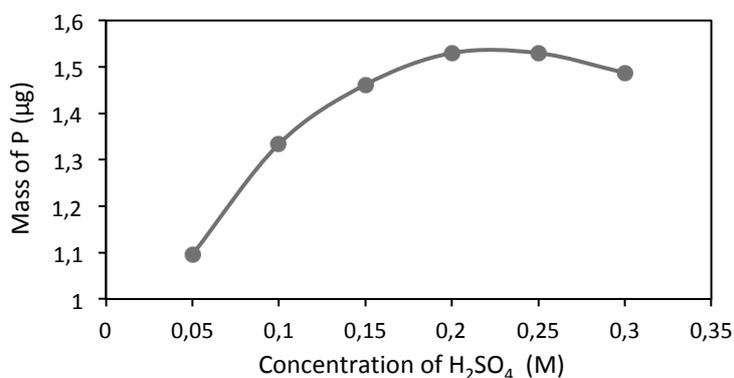
The FTIR spectrum of the diffusive gel is characterized by the presence of two main peaks at wavenumbers of 3336 and 1638  $\text{cm}^{-1}$ . The peak at 3336  $\text{cm}^{-1}$  is related to the content of a primary amine ( $-\text{NH}_2$ ), whereas that at 1638  $\text{cm}^{-1}$  is attributed to the presence of a C–N bond. The peak at 615  $\text{cm}^{-1}$  is because of the presence of ferrihydrite. The functional groups in the diffusive and binding gels were similar and the process of impregnation of the hydrogel with ferrihydrite did not cause substantial changes in the structure of the hydrogel. Based on these spectra, we showed that the interactions between ferrihydrite and polyacrylamide gel are physical in nature and do not involve any reactivity.

#### 3.2. Phosphate ion uptake and elution

The optimization of the binding gel to ferrihydrite was performed to show the ability of ferrihydrite gel into phosphorus ( $\text{KH}_2\text{PO}_4$ ) with a concentration of 0.2  $\text{mgL}^{-1}$ . Figure 2 shows that increasing the contact time between the phosphate-containing solution and the ferrihydrite binding gel increases the



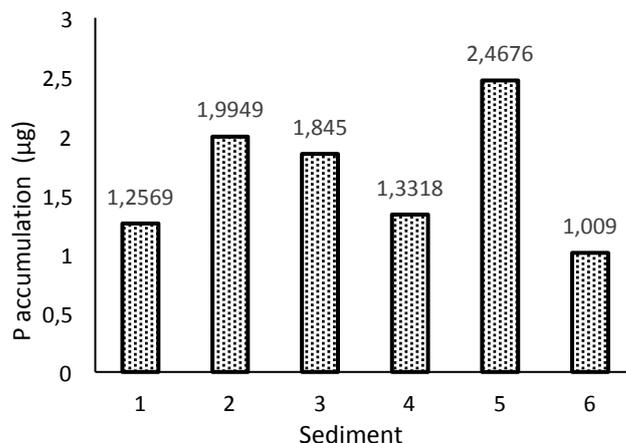
**Figure 3.** (a) Effect of the phosphate concentration on the accumulated mass of  $\text{KH}_2\text{PO}_4$  and (b) the efficiency of the uptake of phosphate ferrihydrite



**Figure 4.** Effect of eluent concentration on the removal of analyte ions from the binding phase

efficiency of phosphate absorption. In particular, a linear correlation was observed between the uptake of phosphate ions and the contact time between the analyte solution and the oxide gel, with an  $R^2$  value of 0.9938. The efficiency of the uptake of phosphate ions by ferrihydrite was 79.31 % over 3 h, an observation that provided the initial verification of the the high affinity of ferrihydrite binding gels against phosphate, hence compatible to be applied in further experiment. The binding phase's affinity for the target ion and its binding capacity were sufficiently high for the solute to accumulate within the oxide gel, thereby maintaining the solute concentration to be zero on the gel's surface contacted with the diffusive layer [14]. The accumulation of the phosphate ion on ferrihydrite was tested by the deployment samples of each type in triplicates for 3, 6, 9, 12, and 24 h. As can be seen in the graph reported in figure 2, the P uptake rapidly increased across the chosen contact time interval. The P uptake efficiency after a contact time of 24 h displayed its maximum value, i.e., 98.17%.

The effect of the concentration of the phosphate ion in solution on this ion's accumulation on ferrihydrite was studied by putting the binding gel into contact with  $\text{KH}_2\text{PO}_4$  aqueous solutions with concentrations ranging between 0.2 and 1.2  $\text{mgL}^{-1}$ . The contact time was 20 h, and the mixture was agitated at 150 rpm. The data reported in figure 3 indicate that there was a linear relationship between phosphate ion concentration in solution and the accumulated mass of the corresponding phosphate salt. In other words, an increase in the concentration of the phosphate ion in solution was associated with an increase in the amount of phosphate adsorbed onto the binding gel. Specifically, after a 20-h contact with a 1.2  $\text{mgL}^{-1}$  solution of  $\text{KH}_2\text{PO}_4$ , the amount of this salt accumulated in the binding gel was 8.5525 grams. The mass of P's linear regression accumulated by binding gel samples confirmed the linearity of the uptake process after sometimes and was characterized by an  $R^2$  value of 0.9748. On the other hand, data show that the relationship between phosphate ion concentration and binding efficiency was such that, as the  $\text{KH}_2\text{PO}_4$  concentration increased from 0.8 to 1.2  $\text{mgL}^{-1}$ , the binding



**Figure 5.** Results of the implementation of the DGT approach to perform the analysis of six marine sediment samples.

efficiency decreased from 83.85% to 71.72%. In particular, the highest binding efficiency was measured to be 87.37% at a  $\text{KH}_2\text{PO}_4$  concentration of  $0.6 \text{ mgL}^{-1}$ . Notably, the near-infinite sink no longer applies under the condition of accumulated analyte's amount is close to the binding layers' highest capacity.

Elution of the phosphate ion from the binding gel was investigated placing the oxide gel in sulfuric acid solutions at concentrations ranging from 0.05 to 0.3 M. The effect of the concentration of sulfuric acid on the mass of  $\text{KH}_2\text{PO}_4$  accumulated in ferrihydrite was studied after putting into contact with the ferrihydrite binding gel a 10-mL solution of  $0.2\text{-mgL}^{-1} \text{ KH}_2\text{PO}_4$ . This processes, with the amount of phosphorus of binding to oxide-gel was determined for the mass of P that was released from oxide gel. The mass of  $\text{KH}_2\text{PO}_4$  released from the binding gel increased with the concentration of  $\text{H}_2\text{SO}_4$ , up to a maximum at an acid concentration of 0.25 M. When the concentration of the acid increased further to 0.3 M, the mass of  $\text{KH}_2\text{PO}_4$  released decreased. The optimum concentration of sulfuric acid to elute of  $\text{KH}_2\text{PO}_4$  from the binding gel was thus determined to be 0.25 M (see figure 4), in which case mass of released  $\text{KH}_2\text{PO}_4$  was 5298 µg. Elution is an important step when performing a DGT measurement, as an efficient removal of analyte ions from the binding phase ensures the accuracy of the measurement.

### 3.3. Use of a DGT device to analyze marine sediments

In this study, DGT analysis was performed on marine sediments collected in six stations located in Teluk Jakarta (Jakarta Bay). In particular, DGT units were placed into sediments to observe the phosphate migration process from sediments to the ferrihydrite hydrogel. The DGT unit responds by binding to phosphate in the sediment. The results obtained indicated that the amount of phosphate accumulated ranged between 1.0090 and 2.4676 µg P (see figure 5). Evidence thus suggests that a DGT unit could be used to measure the amount of unstable phosphate in the sediments. Should it be deployed in sediment, DGT device might be applied for quantitative measurement, either porewater SRP concentration as well as resupply of kinetically unstable phosphate present in the sediment, as the porewater SRP has already depleted by the instrument. In the aquatic system, P bound to amorphous iron oxides (note that ferrihydrite is an amorphous iron oxide) are considered some of the most active inorganic phosphorous pools [15].

## 4. Conclusions

The isolation and quantification of phosphorus was performed by implementing the DGT technique using a ferrihydrite-based binding gel. The efficiency of ferrihydrite for the uptake of phosphate ions was measured to be 98.17% when the DGT device was kept in contact with the analyte solution for 24 h. The elution of the binding gel with 0.25-M  $\text{H}_2\text{SO}_4$  was determined to be optimal for the recovery of bound phosphate (1.5298 µg of isolated  $\text{KH}_2\text{PO}_4$ ). The performance of the DGT unit was found to depend on the time of deployment, the concentration of phosphate, and the concentration of acid used in the elution step.

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