Development study of Diffusive Gradient in Thin Film (DGT) method with binding agent Fe–Ca complex for phosphate measurement

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Abstract The inclusion of phosphorus as a phosphate compound into the aquatic system causes environmental problems, for which monitoring is required in particular on waste treatment. The Diffusive Gradient in Thin Film (DGT) technique with ferrihydrite as binding gel is commonly used for in situ phosphate measurement. Studies on Fe–Mn binary oxide adsorbent have been performed but are only able to absorb phosphate optimally at pH 3–5. In addition to ferric salts, calcium salt is an effective chemical reagent in absorbing phosphate. This research develops new technology by combining both reagent into Fe–Ca complex. The result of this study show that Fe–Ca complex has an antagonistic effect in absorbing phosphate at molar ratio of Fe–Ca 1: 1.5 to 1: 5 and has a synergistic effect when the molar ratio of Fe is increased from 1: 1 to 5: 1. The Optimum absorption occurs in the molar ratio of Fe–Ca complex 3: 1. The measurement of phosphate by spectrophotometric method of molybdenum blue known that Fe–Ca complex has wide working area that is in pH range 2.0–10.0 with optimum contact time 24 hours. Based on the results obtained Fe–Ca complex can be one alternative binding gel on phosphate measurement with DGT technique.

Keywords: diffusive Gradient in Thin Film, Fe–Ca complex

1. Introduction
Phosphorus is an important macronutrient for plants, animals and a crucial component of DNA, RNA, ATP, and phospholipids [1]. Phosphorus contained in natural waters mostly found as phosphates. The compounds are categorised as orthophosphates, condensed phosphates and phosphate which bound organically. Various anthropogenic and natural origins - namely, agricultural activity, drain water, waste from farming, and the degradation of organic compounds - lead to the diverse phosphate forms. Accelerated eutrophication may occur as a result of the phosphorus content of detergents or fertilizer in natural waters. Thus, the combined effects of excessive concentrations of phosphate in natural waters may reduce oxygen concentrations, a change in watercolour, increased turbidity and sedimentation, and a decrease in biological activity [2].

Some quantitative methods are available to determine the phosphate content in the natural water by colorimetric, inorganic phosphate by acid hydrolysis and total phosphate by per sulfate digestion [3]. In consequence of the phosphate’s dynamic interaction in natural water, during storage the concentration of each individual species might be changed. The method applied to determine the in situ of the dissolved phosphate in natural water is Diffusive Gradient in Thin film (DGT) with ferrihydrite as binding agent. [4].

A simultaneous oxidation and co-precipitation technique were employed in the synthesize process of Fe-Mn binary oxide absorbent with Fe/Mn molar ratio of 6:1 to remove the phosphate. Some tests were performed to examine the kinetic and equilibrium of adsorption in batch mode. The maximal...
adsorption capacity was found to be 36 mg·g$^{-1}$ at pH 5.6. It was discovered that adsorption of phosphate was greatly depended on pH [5]. Precipitants of Ferric–calcium complex is a cost effective option for phosphate removal, the study show that removal phosphate using Ferric–calcium complex (Fe–Ca Complex) increased up to 29.77% compared with the traditional technology using ferric salt as sole precipitant. The aim of study is to develop the alternative-binding agent with Fe–Ca Complex to applied on DGT Technique [6].

2. Material and methods

2.1. Material
N,N Methylenebisacrylamide preparation, Ferrihydrite slurry preparation, Fe–Ca complex slurry preparation, Diffusive gel preparation, Ferrihydrite binding gel preparation, Fe–Ca complex binding gel preparation

2.2. Method

2.2.1. Performance test of binding agent to optimize ratio concentration of Fe–Ca Complex. All variant of Fe–Ca complex binding gel were loaded with a known amount of phosphate by placing them in 10 ml KHPO. (100 µg/L of phosphate) solution for 8 hours. Phosphate on binding gel was eluting with 10 ml of H$_2$SO$_4$. 0.25 M for 16 hours. The concentration of phosphate is usually quantified by spectrophotometric determination using phosphomolybdenum method.

2.2.2. Performance test of binding agent to optimize weight of slurry. All variant of Fe–Ca complex binding gel were loaded with a known amount of phosphate by placing them in 10 mL KHPO. (100 µg/L of phosphate) solution for 8 hours. Phosphate on binding gel was eluting with 10 mL of H$_2$SO$_4$. 0.25 M for 16 hours.

2.2.3. Preparation of DGT devices, diffusive gel and binding gel. DGT devices, diffusive gel and binding gel cut with diameter 25 mm using DGT cutter, and the filter membrane soaked on aqua demineralization. Binding gel was placed first on moulding, and then followed for the diffusive gel and membrane filters. Front cap was pressed down tightly until a good seal was formed.

2.2.4. DGT response as a function of contact time. DGT was exposed to a phosphate solution of 5 ppm for different time periods 4 – 36 hours. Then, to eluate from binding layer, the layer was placed in a clean plastic tube, after peeled off the diffusive gel, and added with 10 mL 0.025 M H$_2$SO$_4$.

2.2.5. DGT response as a function of pH. DGT was exposed to a phosphate solution of 5 ppm for variation of pH 2–10. Then, the same procedure with section 2.2.4 was performed.

3. Results and discussion

3.1. Performance test for binding agent
Manufacture of diffusive gels and bindings gel based on radical polymerization reactions free. Acrylamide as monomer, N, N-methylenebisacrylamide as a crosslinker, ammonium per sulfate as initiator, and TEMED as catalyst (figure 1). The concentration of crosslinkers used is 0.05% [7].

Performance test of binding gel is to ensure that binding gel have ability for phosphate adsorption. Fe–Ca complex was made from combination of Fe(SO$_4$)$_2$ 0.1 M and Ca(OH)$_2$. 0.1 M solution. Determinations of ratio concentration of Fe–Ca complex were conducted to study Fe-Ca ratio influence on the adsorption of phosphate. The synergetic effect was defined if the phosphate adsorption, using ferric-calcium complex as binding agent, is higher than that using ferrihydrite as binding agent. On the contrary, antagonistic effect was defined when the phosphate adsorption using ferrihydrite was higher.

In experiment, the total concentration of the mixture was 0.10 M, it shows that when the concentration of Ca(OH)$_2$. 0.1 M the solution does not contain Fe$_3$(SO$_4$)$_2$. otherwise when the concentration of Fe$_3$(SO$_4$)$_2$. 0.1 M then the solution does not contain Ca(OH)$_2$. According the data on
Figure 1. Polyacrylamide polymerization reaction [7].

Figure 2. Variation concentration of Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2} and Ca(OH)\textsubscript{2} versus phosphate concentration

Figure 3. Optimization graph of the Fe–Ca complex ratio concentration test

Figure 4. Variation ratio Fe–Ca and Ferricydrite

Figure 5. Variation of ratio Fe and Ratio Ca–Ferricydrite

Figure 6. Variation concentration of Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2} and Ca(OH)\textsubscript{2} versus phosphate concentration

When the volume of Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2} reaches 100%, the phosphate absorption around 75 µg/L but when the volume of Ca(OH)\textsubscript{2} reaches 100%, the phosphate absorption only around 52 µg/L. The ratio of the optimum concentration occurs when the solution of Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2} is in the concentration of 0.08 M and Ca(OH)\textsubscript{2} 0.02 M. Through the above graph there is a tendency of high phosphate absorption when the binding gel is dominated by Fe\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}, and phosphate uptake a significant decrease when the presence of Ca(OH)\textsubscript{2} predominates. Along with testing of ferricydrite composite binding gel-calcium sulphate was also absorbed by binding gel of ferricydrite obtained from Fe(NO\textsubscript{3})\textsubscript{3} 0.1 M solution, based on the test known that phosphate absorption by ferricydrite binding gel ranges from 70–72 µg/L.

According the data shown in figure 3 the effect of Fe–Ca complex binding agent on the phosphate adsorption compared ferricydrite binding agent was antagonistic when the proportion of Ferric was below 50%, while the effect of Fe–Ca complex binding agent on the phosphate adsorption compared ferricydrite binding agent was synergist when the proportion of Ferric was over 50%. The data on graph show the optimal ratio of Fe–Ca complex was 3:1 or for instance, total volume consist of 75% Ferric solution and 25% calcium solution.

The data from step 1 used for variation weight for applied at binding agent. For all result compared with binding agent of ferricydrite. The conclusion is same with the step one, If the phosphate adsorption using weight test of ferric–calcium complex as binding agent is higher than phosphate adsorption using ferricydrite as binding agent, it is defined as synergistic effect. On the contrary, If the phosphate adsorption using weight test of ferric–calcium complex as binding agent is less than phosphate adsorption using ferricydrite as binding agent, it is defined as antagonistic effect. According the data shown in figure 4 the effect of Fe–Ca complex binding agent on the phosphate adsorption compared ferricydrite binding agent was antagonistic when the proportion of slurry Fe–Ca complex ratio 3:1 below 1.5 g while the effect of Fe–Ca complex binding agent on the phosphate adsorption compared ferricydrite binding agent was synergist when the proportion of slurry Fe–Ca complex ratio 3:1 over 1.5 g. The data on graph show the optimal weight of Fe–Ca complex ratio 3:1 was 2 g.
3.2. Performance test for DGT device

The DGT method is built upon a common instrument, in which the solute is accumulated on a binder through a hydrogel, serves as a well-defined diffusion layer. The method depends on the formation of concentration gradient of a steady-state form, from solution to the binder. The solution’s concentration was measured by Fick’s first diffusion law and the solutes’ mass accumulated on the binder in a known deployment time was calculated.

For phosphate adsorption, Δr thickness of a binding gel layer is impregnated in a binder. This binding gel is isolated from the solution using Δg thickness of an ion-permeable diffusive gel membrane (figure 5). Diffusive Boundary Layer (DBL) in a thickness of d lies between the diffusive gel layer and the bulk solution, where only molecular diffusion plays a role in transporting the ions. The DGT instrument is disseminated into the aqua system to determine the reactive phosphate in situ’s concentration. Investigation effect contact times of DGT with Fe–Ca complex ratio 3:1 were conducted to estimate the maximum deployment time for test in real condition of environment. According the data on figure 6 show the DGT device using Fe–Ca complex as binding agent can be used to measure phosphate. The data show phosphate adsorption of DGT device using ferrihydrite as binding agent was increased until 18 hours (64800 s) and stable until 36 hours (129600 s) for DGT. While phosphorate adsorption of DGT device using Fe–Ca complex ratio 3:1 as binding agent was increased until 24 hours (86400 s) and stable until 36 hours (129600 s). Contact time of DGT with Fe–Ca complex ratio 3:1 as binding agent is longer than DGT with ferrihydrite as binding agent but the capacity of DGT with Fe–Ca complex as binding agent is bigger than DGT with ferrihydrite as binding agent.

The diffusion rate depends on both the concentration gradient and the solution pH. While the pH of natural water is around pH 4–9, industrial effluents may produce higher pH. Therefore, the pH dependence of the DGT was examined. The DGT was placed inside the phosphate solution with range pH 2–10. pH solution arrange by NaOH 1M or H2SO4 1M solutions. According the data on figure 7 show the DGT device using Fe–Ca complex as binding agent can be used to measure phosphate in
large of pH range. The data show phosphate adsorption of DGT device using ferrihydrite as binding agent was stable over 60% in range pH 2–8, on pH 9–11 adsorption of phosphate decreased below 50%. While phosphate adsorption of DGT device using Fe–Ca complex ratio 3:1 as binding agent was stable over 60% in range pH 2-10, on pH 11 adsorption of phosphate decreased below 60%. The data show that the adsorption phosphate with DGT using Fe–Ca complex ratio 3:1 as binding agent was optimal in pH 2-10.

4. Conclusions
Fe–Ca complex can act as binding agent, and effective for applied as binding agent on DGT technique. Adsorption phosphate using DGT technique with Fe–Ca complex was gave the strongest synergistic effect at ratio 3:1 with mass of slurry 2 g. Phosphate adsorption using DGT device with Fe–Ca complex ratio 3:1 is optimize at 24 h contact and that the adsorption phosphate with DGT using Fe–Ca complex ratio 3:1 as binding agent was optimal in pH 2-10.

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