Development study of iron-based metal organic frameworks (Fe-based MOFs) as a binding agent in diffusive gradient in thin film method (DGT) for phosphate adsorption

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Abstract. In this study, Fe-based Metal Organic Frameworks (MOFs) will be developed as a binding agent in Diffusive Gradient in Thin Film (DGT) for phosphate adsorption, where it will be evaluated for the effect of pH, adsorbent concentration and mixing time in phosphate loading capacity of Fe-based MOFs in DGT because these parameters can influence the capacity of phosphate adsorption. Fe-based MOFs were synthesized using ferrichloride as a binding agent and terephthalic acid as a linker in solvothermal conditions. Fe-based MOFs will be characterized by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), Brunauer-Emmelt-Tellers (BET). The XRD peaks correspond to MIL-101 for 2θ around 9° and 17°. FTIR analysis indicated the broadening peak at 1595 cm⁻¹ for C=O and 1395 cm⁻¹ for C-C vibrational. The SEM analysis showed the morphology was rhombus. The BET analysis showed the surface area of Fe-based MOFs was 61.33 m²g⁻¹. Fe-based MOFs have been successfully synthesized by the solvothermal method and then will be applied as binding agent in DGT. Furthermore, Fe-based MOFs in DGT will be used for phosphate adsorption and measured using Spectrophotometer UV-Vis.

Keywords: Fe-based MOFs, DGT, adsorption, phosphate

1. Introduction
Phosphate is a material, often used in agricultural and industrial fields including for fertilizers, detergents, water softening, beverages, and metallurgy, etc. The use of phosphate in large quantities can cause high waste containing phosphate. The release of phosphate to the surface of water is an environmental concern because it can cause a eutrophication phenomenon that has an impact on water quality degradation [1].

Eutrophication is a process which causes the ecosystem to have a nutrition enhancement from the outside. Phosphorus can be a major element causing the eutrophication which leads to an increase of aquatic plants, algae growth, some of them are toxic and can interfere with the presence of organisms in the water. This can cause a decrease in oxygen due to an increase in biological oxygen demand and acidification [2].

DGT technique is a passive sampling for metal trace. The DGT device consists of a permeable diffusive gel layer for labile contaminant species (as a substitute for aquatic organisms), and a binding
gel layer containing binding agent with both layers embedded in the inside of a plastic container. The DGT technique measures the concentration of average time or flux solute during the deployment time. This measurement depends on the solute diffusion control flux from the surface of the DGT device to the binding phase of the device based on Fick’s First Diffusion Law [3, 4].

The selection of binding agent is crucial because it will affect the ability of the analyte ion absorption and affect the selectivity of an analyte species. One binding agent that has a function to absorb phosphate is iron (Fe). In the studies of Li et al. 2016 and Xie et al. showed that iron (Fe) combined with MOFs could play an effective role in phosphate adsorption [5-7]. The interaction between the phosphate and the Fe side of Fe-MOFs is a major factor in the calculation of phosphate adsorption. These Fe-MOFs also show a high selectivity toward phosphates among other anions such as Cl, Br, N, and S. Iron (Fe) is also relatively easy to obtain because of their relatively high availability in the environment [6].

In recent years, the Metal Organic Framework (MOFs) has become a new model in the development of porous materials because of their high porosity, morphology and large surface area [8-10]. The characteristics of MOFs can be easily adjusted with the selection of different metal ions and organic bridging ligands and MOFs have developed a new role as a solid adsorbent [10]. MOFs are stable materials and have a good adsorption to remove various pollutants in water [9].

In this study, Fe-MOFs will be developed as a binding agent in DGT for measuring the dissolved reactive phosphate in water which will be studied and evaluated for the influence of pH, adsorbent concentration, mixing time, diffusion coefficient and phosphate loading capacity in Fe-MOFs-DGT.

2. Materials and method

2.1. Materials

Material used in this study were in analytical grade and without any further purification step. FeCl₃·6H₂O, terephthalic acid (H₂BDC), N,N-dimethylformamide (DMF), Acrylamide 40 %, N,N’-methylenebisacrylamide 1 %, N,N,N’,N’- tetramethyl ethylenediamine (TEMED) 99 %, cellulose nitrate membrane filter, KH₂PO₄, NaOH, H₂SO₄, ascorbic acid, potassium antimonyl tartrate, ammonium heptamolybdate tetrahydrate, deionized water.

2.2. Method

2.2.1. Synthesis and characterization of Fe-MOF. Fe-MOF was synthesized by solvothermal method. In this study, 0.675 g of FeCl₃·6H₂O and 0.206 g of H₂BDC were dissolved in 30 mL DMF then stirred for 30 min. The solution was then transferred into a Teflon-lined autoclave and heated at 120 °C for 20 h [6]. The product was washed using DMF. The solid was collected by centrifugation and dried at 60 °C. The crystal phases of Fe-MOF were examined by X-Ray diffraction. The morphology, surface area and functional group were characterized using SEM, Brunauer-Emmet-Teller (BET) analysis, and Fourier Transform Infrared.

2.2.2. DGT assembly and deployment. Acrylamide 40 % and N,N’-methylenebisacrylamide 1 % was mixed to form the solution gel. Diffusive gel was then synthesized by mixing 10 mL of solution gel, 20 µL of TEMED and 70 µL of persulphate 10 % then printed in a glass mold and heated in 60 °C for 45 min. The step of binding gel synthesis was the same with diffusive gel by adding 10 mg of Fe-MOF. Binding gel was added into the base of DGT mold, then followed by diffusive gel and cellulose nitrate membrane on the top of the gasket. DGT cap was tightened securely then deployed in DRP solution to determine the DRP concentration.

2.2.3. Determination of elution coefficient. Fe-MOF binding gel with diameter 25 mm was dispersed in 10 mg L⁻¹ of P solution for 24 h then eluted with eluent for 24 h. Elution efficiency, described as factor
elution was determined using different concentration of H\textsubscript{2}SO\textsubscript{4} (0.25–1 mol L\textsuperscript{-1}) as an eluent then neutralized with NaOH 0.1 mol L\textsuperscript{-1}.

2.2.4. Analytical method and DRP concentration calculation. Concentration of synthetic DRP adsorbed in binding gel were analyzed by the ammonium molybdate spectrophotometric method, the concentration of DRP solution was measured by UV-Visible spectrophotometer (Shimadzu UV-2450) at the wavelength 713.50 nm. Before analysis, the DRP adsorbed inside Fe-MOF binding gel was eluted by 10 mL H\textsubscript{2}SO\textsubscript{4} 1 mol L\textsuperscript{-1} for 20 h and neutralized by NaOH 1 mol L\textsuperscript{-1}. The mass (M) DRP inside Fe-MOF binding gel was calculated by equation 1:

\[
M = Ce \times (VFe - MOF + VH_{2}SO_{4} + VNaOH) / Fe
\]  

where Ce is the concentration of DRP in eluent solution, VFe-MOF is volume of binding gel FeMOF, VH\textsubscript{2}SO\textsubscript{4} is volume of eluent used, VNaOH is the volume NaOH added into eluent, and Fe is the factor of elution. Factor of elution was obtained by using different concentration of H\textsubscript{2}SO\textsubscript{4} from 0.025–1 mol L\textsuperscript{-1}. The concentration of DRP measured by DGT was calculated by equation 2:

\[
C_{DGT} = \frac{M \times \Delta g}{D \times A \times t}
\]  

where M was calculated by equation 1, \Delta g is cellulose membrane and diffusive gel thickness, A is exposure area of binding gel which directly contact with DRP solution, t is deployment time in second unit.

3. Results and discussion

3.1. Characterization of Fe-MOF

After the solids are dried, the identification of Fe-MOF powder is carried out using a bioimaging microscope, XRD, and FTIR. The FTIR results shows in figure 1a the IR spectrum of Fe-MOF which is characterized by the presence of a benzene-carboxylic main group which is attributed to C=O bond in the carboxylic group shown at a wavenumber of 1604 cm\textsuperscript{-1} and at a wavenumber of 1396 cm\textsuperscript{-1} indicating the presence of aromatic carbon group C-C vibrational mode. The XRD results of Fe-MOF in figure 1b show that the MOF crystal structure is formed and can be seen from the formation of the same crystal structure with certainty and repetition in the 2 theta position at 5.0–10.9 degree and 15.0–20 degree. The sharp peak with high intensity in XRD result shows that MOF have a high crystallinity. The BET examination results obtained the surface area of 61.33 m\textsuperscript{2}/g. The BET result is lower because the structure of FeCl\textsubscript{3}.6H\textsubscript{2}O is amorph. The distribution of binding agent can be seen in figure 1c using the bioimaging microscope and the figure shows the distribution are homogeneous. The SEM analysis shows the morphology is prism-like with rude surface in figure 1d.

3.2. Elusion factor of phosphate adsorption

Before analysis, the DRP adsorbed inside Fe-MOF binding gel was eluted by 10 mL H\textsubscript{2}SO\textsubscript{4} 1 mol L\textsuperscript{-1} for 20 h and neutralized by NaOH 1 mol L\textsuperscript{-1}. The optimization of eluent was performed by using different concentration of H\textsubscript{2}SO\textsubscript{4} from 0.025–1 mol L\textsuperscript{-1}. After the optimization of eluent is completed, it is obtained the good eluent for analyzing the phosphate in Fe-MOF is H\textsubscript{2}SO\textsubscript{4} 1 mol L\textsuperscript{-1} with elusion value 81.29 %. This elusion value is important because it will be affecting the phosphate adsorption.
Figure 1. Characterization of F-MOF; (a) FTIR spectra, (b) XRD pattern, (c) Bioimaging microscope image, and (d) SEM image.

Table 1. Results of elution factor from H$_2$SO$_4$ 1 molL$^{-1}$ as a eluent.

| Eluent     | Absorbance | Dilution factor | $C_{\text{elusion}}$ (ppm) | % elusion | Average |
|------------|------------|----------------|-----------------------------|-----------|---------|
| H$_2$SO$_4$ 1 M (1) | 0.016 | 20 | 1.037509976 | 81.25 |         |
| H$_2$SO$_4$ 1 M (2) | 0.017 | 20 | 1.197126895 | 68.18 | 81.29 % |
| H$_2$SO$_4$ 1 M (3) | 0.018 | 20 | 1.356743815 | 94.44 |         |

3.3. Diffusion coefficient
The diffusion coefficient (D) of DRP was measured by creating graph of time and mass DRP adsorbed in Fe-MOF DGT. Fe-MOF DGT was soaked in 13 mgL$^{-1}$ DRP solution for 4 to 26 h. From figure 2 we can see the diffusion coefficient calculated by the intercept and slope of the linear line that is obtained $R^2$ value is 0.9921. The D value was 4.74 x 10$^{-7}$ cm$^2$s$^{-1}$. The D value is lower than the experimental of Zhang et al. 1998 whereas it obtained 7.39 x 10$^{-6}$ cm$^2$s$^{-1}$ because of FeCl$_3$.6H$_2$O have amorph structure so the porosity is low. From figure 2, it can also be observed that increasing time can cause an increase in the capacity of loading phosphate. The good time to obtain the accumulated phosphate is 26 h.
3.4. Capacity of loading phosphate in Fe-MOF DGT
The uptake of DRP by Fe-MOF DGT was evaluated by deploying the Fe-MOF DGT in 13 mgL\(^{-1}\) for 4 to 26 h with variation of Fe-MOF concentration 10 to 80 mg and pH variation from 2 to 10. The capacity of loading phosphate will be affected by the concentration of binding gel and pH variation.

As seen from figure 3, the optimum Fe-MOF concentration of DRP uptake was 20 mg. Higher amount of binding agent will decrease the capacity of loading phosphate because it can cause the binding agent contains in gel to be rigid and the elasticity will decrease, so phosphate will be difficult to interact with material and the capacity of loading phosphate also decrease. The maximum DRP uptake was 9.30 μg P. From figure 4, it is noted that the optimum pH of DRP uptake was pH 2 with capacity 64.35 %. At the lower pH, the charge of Fe-MOF surface is more positive and easier for phosphate bonding, but at the higher pH, the charge will be more negative so it can cause an electrostatic repulsion to negative phosphate (PO\(_4^{3-}\)) which is available in alkali condition.

4. Conclusion
This experiment was successfully synthesized the Fe-MOF by solvothermal methods. Material was applied to DGT system for measuring the capacity of loading phosphate. The capacity of loading phosphate in DGT system will be affected by the mixing time, concentration of binding agent, and pH variation. The results revealed that Fe-MOF in DGT system had an activity in the phosphate adsorption.
Acknowledgments
This work was financially supported by Universitas Indonesia under research grant PITTA A.

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