THE EFFECT OF PHOSPHATE CONCENTRATION AND MIXING TIME TO PHOSPHATE ADSORPTION BY DIFFUSIVE GRADIENT IN THIN-FILM (DGT) BASED IRON METAL-ORGANIC FRAMEWORK (FE-MOF) AS A BINDING AGENT

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ABSTRACT

In this experiment, it would be developed Fe-Metal Organic Frameworks basis (MOFs) as a binding agent in Diffusive Gradient in Thin Film (DGT) to discover the capacity of phosphate adsorption that is influenced by phosphate concentration and mixing time. Phosphorus (P) is one of the materials that are common used by industrial can induced eutrophication phenomenon. This study will evaluate the effect of mixing time and phosphate concentration in phosphate loading capacity. These parameters can be considered for measuring the capacity of phosphate adsorption. The results of phosphate analysis showed that the % recovery value of Fe-MOFs in the DGT system was 81.29%. The diffusion coefficient of DGT Fe-MOF was $4.74 \times 10^{-7} \text{ cm}^2/\text{s}$. The accumulated phosphate will be increased in a row with time increasing. The capacity of phosphate adsorption optimum in 10 mg/l phosphate concentration. In the final result, it can be concluded that phosphate will be adsorbed optimally using Fe-MOF in DGT.

Keywords: Phosphate, DGT, MOF, Binding Agent, Iron

RASĀYAN J. Chem., Vol. 14, No.3, 2021

INTRODUCTION

Phosphate is one of the materials used in some industry especially in agriculture.¹ The large amount of phosphate can remain the residual that will become phosphate waste¹. Phosphate waste had to be a concern due to cause environmental pollution especially decrease water quality and eutrophication phenomenon.¹ Eutrophication phenomenon is a phenomenon of enrichment nutrition to the ecosystem and one of the major elements from phosphate.² In addition to, phosphate waste cause oxygen to decrease due to acidification and increase of oxygen demand.² For sampling the phosphate, there are some techniques sampling and one of common technique using Diffusive Gradient Technique (DGT).³ DGT technique utilizes the permeable diffusive gel layer and a binding agent that is suitable for phosphate adsorption.³ The principle of the DGT technique is measuring the concentration of average time during diffusion time and applying Ficks First Diffusion Law.⁴

The critical point to maximize the adsorption and selectivity of the analyte is to determine the suitable binding agent. Li et al 2016 and Xie et al, 2017 studies, stated that one of the binding agents for phosphate is iron (Fe) and it was combined with MOFs can increase the capacity of phosphate adsorption because it had high phosphate selectivity compared with another anion (Cl, Br, N, and S). Iron (Fe) is available in an environment so it can be easy to do this modification.^{5,6}

Latest, there is a new model to develops the porous of material. The model is Metal-Organic Frameworks (MOFs) that have some advantages to increase the capacity of phosphate adsorption due to they have high porosity and large surface area.^{8,9} MOFs characterizations can be adjusted by metal ions selection and organic bridging ligands.⁸⁻¹⁰ Another of MOFs advantages is they have good stability and adsorption of water pollutant.⁷⁻⁹ Beside that, MOFs also has another advantage become a new role model in photocatalytic research.¹¹ So, in the final result, we can evaluate how the effect of phosphate concentration and mixing time on phosphate adsorption by optimizing modification of Fe-MOF in the DGT technique.

EXPERIMENTAL

Material

Ferric Chloride Hexahydrate, Terephthalic Acid, N,N-dimethylformamide, Acrylamide 40%, N,N'-methylenebisacrilamide 1%, N,N,N',N'-tetramethylethylenediamine 99%, Persulphate, membrane filter (cellulose nitrate), Potassium phosphate monobasic, Sodium Hydroxide, Sodium Nitrate, Sodium Hydrogen Carbonate, Sodium Sulphate, Sulphuric acid, Vitamin C, potassium antimonyl tartrate, ammonium heptamolybdate tetrahydrate, purified water.

Methods

This modification utilizes the solvothermal method. Mix 1.35 gram of Ferric Chloride Hexahydrate and 0.412 gram of Terephthalic Acid were dissolved in 60 ml N,N-dimethylformamide and stir for 30 minutes. The solution was transferred into Teflon lined autoclave and heated up to 120°C for 20 hours. The product washed using N,N-dimethylformamide. And then the solid was collected by centrifuge and dried at 60 °C. Then, the 10 mg of Fe-MOF crystals mix with 20 µL of N,N,N',N'-tetramethylethylenediamine 99% and 70 µL of persulphate 10% and mold in a square glass then heated in 60 °C for 45 minutes. After binding gel synthesized, continue with diffusive gel synthesized. Firstly, synthesize the solution gel by mixing Acrylamide 40% and N,N'-methylenebisacrilamide 1%. Then, take 10 ml of solution gel, 20 µL of N,N,N',N'-tetramethylethylenediamine 99% and 70 µL of persulphate 10% and mold in a square glass then heated in 60°C for 45 minutes to synthesize diffusive gel.

General Procedure

The experimental design to measure diffusion coefficient was to optimize Fe-MOF DGT disk in 100 mL of 10 mg/L P solution for 4 to 26 hours. The P uptake efficiency of Fe-MOF DGT also optimizes P solution concentration ranging from 1-10 mg/L. The effect of mixing time was designed for 4 to 26 hours. The effect of phosphate concentration was also investigated by optimize the phosphate loading capacity ranging from 5 mg/L to 15 mg/L.

Detection Method

The instrument used to detect the MOF formation was X-Ray diffraction (XRD). Then, to examine the surface area, morphology, and functional group is SEM-EDX, Brunauer-Emmet-Teller (BET) analysis, and Fourier Transform Infrared (FTIR) respectively. The capacity of phosphate adsorption in Fe-MOF DGT will be measured by Spectrophotometry Ultraviolet-Visible using ammonium molybdate at wavelength 713.5 nm.

RESULTS AND DISCUSSION

Identification of Fe-MOF Crystals

Firstly, Fe-MOF crystals are identified using a bioimaging microscope to know the distribution of crystals, then continue using XRD to examine the crystals phase, and lastly utilize the FTIR to ensure the functional group of MOF exists (Fig.-1).

Fig.-1: Identification of Fe-MOF: (a) FTIR Spectrum, (b) XRD Pattern, (c) Bioimaging Microscope Image and (d) SEM Image

In Fig.-1a (FTIR), there is a unique functional group of MOF. There is benzene-carboxylic main group attributed with C = O bond in the carboxylic group and aromatic carbon group C-C vibrational mode at 1604 cm^{-1} and 1396 cm^{-1} wavenumber respectively. In Fig.-1b (XRD) shows the formation of the crystals exists. It is evidenced by certainty and repetition of crystals structure in 2 theta position at $5.0\text{--}10.9$ degree and $15.0\text{--}20$ degree respectively. In XRD result also inform that MOF has high crystallinity due to there is a high-intensity sharp peak. The surface area is only $61.33\text{ m}^2/\text{g}$ examined by BET due to the characteristic of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is amorf. In Fig.-1c (bioimaging microscope), the distribution of Fe-MOF is homogeny and figure 1d (SEM) shows the morphology is like a prism with a rude surface.

Elution Value of Phosphate Adsorption

After identified the Fe-MOF crystals, measure the capacity of dissolved reactive phosphate in Fe-MOF binding gel. The binding gel was eluted using 10 ml of H_2SO_4 1 M for 20 hours then neutralized using NaOH 1 M. Firstly, perform the eluent optimization by varying the H_2SO_4 concentration from 0.025 M to 1 M. The results show the optimum eluent for phosphate analysis is H_2SO_4 1 M with 81.29 % elution value. This stage aims to define the capacity of phosphate adsorption.

Table-1 : Elution Value of Phosphate Adsorption

Eluent	Absorbance	Dilution Factor	C _{Elution} (ppm)	% Elution	Rata-rata
H_2SO_4 1 M (1)	0.016	20	1.037509976	81.25	81.29 %
H_2SO_4 1 M (2)	0.017	20	1.197126895	68.18	
H_2SO_4 1 M (3)	0.018	20	1.356743815	94.44	

Diffusion Coefficient

After the elution value was obtained, continue to measure the diffusion coefficient (D). The D value is obtained from linearity regression of time (second) and mass of accumulated P (ng) in Fe-MOF DGT. The design of this experiment was Fe-MOF DGT soak in 13 mg/L DRP solution for 4 to 26 hours. From linearity regression in Fig.-2 shows the R^2 value is 0.9921 so D value is obtained $4.74 \times 10^{-7}\text{ cm}^2\text{s}^{-1}$. This result lower than Zhang et al, 1998 due to the structure of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are amorf and low porosity. In Fig.-2 also inform the effect of increasing time leads to an increase in the capacity of loading phosphate. The optimum time for maximum accumulated phosphate is for 26 hours.

The Capacity of Loading Phosphate in Fe-MOF DGT

The phosphate adsorption from aqueous solution onto Fe-based MOF as a function of mixing time is shown in Fig.-3. The adsorption capacity increased in a row of increasing time. In the first 4 hours, the adsorption

of capacity Fe-MOF was reached 1.6 μg . The adsorption of capacity continued to increase with increasing time. In the 26 hours, the capacity of phosphate adsorption was 14.5 μg . This situation because the binding agent was in phosphate solution for a long time so it had a chance to adsorb more phosphate.

Fig.-2: Linearity Graph of Time and Accumulated Phosphate

In Fig.-4, we can also see the effect of phosphate concentration variation. In the first concentration 5 mg/L the adsorption of capacity Fe-MOF was reached 3.08 μg and then until concentration 10 mg/L had a constant value. This situation means that the capacity of Fe-MOF in phosphate adsorption optimum is 10 mg/L.

Fig.-3: The Effect of Mixing Time

Fig.-4: The Effect of Phosphate Concentration Variation

CONCLUSION

This experiment was successful to synthesize Fe-MOF by solvothermal methods in the DGT technique. Mixing time and phosphate concentration influence the capacity of loading phosphate. The final result was showed modification of Fe-MOF in the DGT technique had phosphate adsorption activity.

ACKNOWLEDGEMENT

We gratefully acknowledge funding by the University of Indonesia Competitive Research Grant (PITTA A 2019) for conducting research.

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[RJC-5756/2020]