Lanthanum based metal organic frameworks as a new binding agent material for diffusive gradient in thin film (DGT) technique in bioavailability of phosphate removal

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Abstract. High concentration of bioavailable phosphorus in aquatic system has been resulting in the eutrophication phenomenon that can trigger algae bloom. The measurement of bioavailable phosphorus in water body is needed. The diffusive gradient in thin film (DGT) is a well-developed in-situ analytical tool for separation and determination if bioavailable phosphorus or dissolver reactive phosphate (DRP). Using lanthanum based metal organic frameworks (La-MOF) with high surface area and tuneable pore might attribute the capacity of DRP adsorption in binding film. The surface area analysis of La-MOF powder was 84.957 m² g⁻¹. La-MOF then dispersed in gel solution to perform a binding film La-MOF then used in DGT tool for DRP uptake. The swelling activity of diffusive film was 2.24 and 1.93 for binding film La-MOF. The elution efficiency of DRP from binding film La-MOF was 95 % using HNO₃ 0.05 mol.L⁻¹ as an eluent. The diffusion coefficient of DRP from La-MOF DGT was 2.216 × 10⁻⁶ cm².s⁻¹. Optimum DRP uptake capacity was up to 37.83 µg P with optimum time of deployment of 24 h. This research shows that the DRP uptake on DGT La-MOF was depended on the time deployment and DRP solution concentration.

Keywords: Phosphorus, eutrophication, lanthanum, metal-organic, frameworks

1. Introduction
Eutrophication is a major case in freshwater ecosystem, water eutrophication conveys a global challenge in environment [1]. Eutrophication is defined as the over enrichment of water ecosystem with one or more limiting growth factors needed for photosynthesis such as phosphate and nitrate, conduces in the excess growth of phytoplankton and algae [2]. Based on the regulations set by Indonesia Ministry of Environment and Forestry no 51, year 2004, the threshold value of phosphate in natural waters is in the range of 0.016 to 1.19 mgL⁻¹.

Phosphorus (P) is the substance that most often limits the biological productivity in aquatic ecosystem. Spillover consumption of P in water body can result in an eutrophication [3]. Dibasic phosphate, dihydric phosphate (HPO₄²⁻ and H₂PO₄⁻) are the major species of P found in natural waters, which are believed as bioavailability species of P and considered to be measured as the dissolved organic phosphorus (DRP) [4]. Basic requirement is needed to reduce DRP concentration in order to counter the eutrophication and meets the government regulation. There are many measurement methods available
to determine the DRP concentration in natural waters, but most of them are expensive, require an intensive labor, time consuming process and low in sensitivity [5, 6]. Hereinafter, concentration of DRP measured may not show the real concentration within the natural water because the pre-treatment procedure before the measurement. Consequently, in situ sampling is preferable applied for a more accurate measurement of DRP concentration in natural waters [7, 8].

DGT technique is an in situ sampling approach which was developed for sampling the dissolved labile species in natural water, soils, and sediments [9]. The DGT sampler is consisted of a diffusive film, binding film and a filter membrane, analytes will infiltrated the diffusion film to the binding film and bound with binding agent material with intense affinity toward the analytes [10]. The measurement of analytes relies on the affinity of binding agent applied in DGT sampler, therefore the innovation of new binding agent material for DGT has increased in recent years.

Metal organic frameworks (MOF) is organic-inorganic framework that constructed by metal ion and organic linkers which have been utilized as an efficient adsorbent due to their high surface area, tuneable pore and predictable structure [11]. Lanthanum metal organic frameworks have strong Lewis acid properties, which can demonstrate strong ligand adsorption with phosphate which have Lewis basic properties and form lanthanum phosphate complex [12].

This research was aimed to synthesize La-MOFs as a new binding agent for DRP removal. The prepared binding agent La-MOF DGT exhibited a good performance for DRP removal. The La-MOF material characteristics were determined by XRD, surface area analysis, FTIR. The effect of different factors on the DRP removal by La-MOF DGT such as elution efficiency, DRP concentration and contact time were also studied.

2. Materials and method

2.1. Materials
Lanthanum(III)nitrate hexahydrate 99.9 % (Merck), N,N-dimethylformamide (DMF) 99.8 % (Merck), terephthalic acid (BDC) 98 % (Merck), acetone (Merck), acrylamide (Sigma-Aldrich), N,N-methylenebisacrylamide (MBA) (Sigma-Aldrich), N,N,N’-tetramethylenediamine (TEMED) 99 % (Sigma-Aldrich), cellulose membrane nitrate 0.45 μm (Whatman), kalium dihydrogenephosphate (Merck), ascorbic acid (Merck), kalium antimonyltartrate (Merck), ammonium molybdate (Merck), sulfuric acid 98 % (Merck), natrium nitrate (Merck), ethanol 99.9 % (Merck), aqua demineralized.

2.2. Preparation of La-MOFs
Preparation of La-MOFs by solvothermal. 0.437 g LaNO₃.12H₂O and 0.254 g terephthalic acid (BDC) was mixed in DMF/water solvent for 30 min then placed into a Teflon-lined autoclave and heated at 120 °C for 20 h. The filtrate then washed using ethanol and acetone three times. The solid of La-MOF was collected and dried at 60 °C for 24 h.

2.3. Preparation of diffusive and binding gel
A polyacrylamide hydrogel 40 % and 1 % MBA was used as gel solution. For diffusive film, 10 mL of gel solution was added with 70 μL of persulfate 10 % and 20 μL TEMED. For binding film, 10 mg of La-MOF powder was dispersed in gel solution. The solution was casted into mould then set to temperature 42–46 °C for 60 min. Diffusive film was stored in sodium nitrate solution and binding film stored in aqua demineralized.

2.4. La-MOF DGT assembly
A membrane cellulose nitrate with pore diameter 0.45 μm was placed at the bottom of DGT disk cap followed by diffusive film and binding film, then DGT piston spacer was fixed and the DGT disk was tightened securely.
2.5. Determination of swelling ratio
The swelling ratio of diffusive and binding film were determined by deploying the diffusive and binding film with diameter 25 mm in aqua demineralized for 2 to 60 h. Then, the weight of diffusive and binding film were measured every hour.

2.6. Determination of elution coefficient
La-MOF binding gel with diameter 25 mm was dispersed in 5 mgL\(^{-1}\) of P solution for 24 h then eluted with eluent for 24 h. Elution efficiency is described as factor elution was determined using different concentration of HNO\(_3\) (0.025 to 1 molL\(^{-1}\)) as an eluent then neutralized with NaOH 0.1 mol L\(^{-1}\).

2.7. Performance test on variation of P concentration
La-MOF DGT was placed in 250 mL P solution with the concentration ranged from 1 to 10 mgL\(^{-1}\), the DGT was set in the middle of a beaker glass by binding with a string. P solution was stirred for 24 h. Phosphate was eluted from La-MOF binding gel using HNO\(_3\) 0.05 M.

2.8. Performance test on variation of time deployment
La-MOF DGT was placed in 250 mL P solution, the DGT was set in the middle of a beaker glass by binding with a string. P solution was stirred for 2 to 96 h. Phosphate was eluted from La-MOF binding gel using HNO\(_3\) 0.05 M.

2.9. Analytical method and DRP concentration calculation
Concentration of P captured by La-MOF DGT was analyzed by the molybdenum blue spectroscopy method. The mass (M) of DRP trapped in binding gel La-MOF was calculated according to the equation:

\[
M = C_e \times (V_{\text{binding gel}} + V_{\text{HNO3}})/f_e
\]

\(C_e\) is the concentration of DRP in eluent, \(V\) binding gel is volume of binding film, \(V_{\text{HNO3}}\) is volume of eluent HNO\(_3\) and \(f_e\) is the elution efficiency.

The accumulated DRP in the binding gel La-MOF then can be related to its solution concentration (\(C_{\text{DGT}}\)) by using this equation:

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

where \(\Delta g\) is the thickness of diffusive gel and membrane filter, \(D\) is diffusion coefficient of DRP, \(A\) is area of sampling window that directly contacted with P solution and \(t\) is time of deployment.

3. Results and discussion
3.1. Structural characterization of La-MOF
The La-MOF crystal was examined by XRD. Figure 1a shows the pattern of La-MOF, the first peak at 9.50° suggesting that the pattern corresponded to the structure of MIL-53 material [12]. This peak was also observed on La-MOFs (figure 1a) at 9.5371, the position of peak signal is slightly shifted which may due to the unreacted terephthalic acid (BDC) in the reaction or residual of unreacted acetone during the washing process that trapped in La-MOF pore. Other important XRD pattern of La MOF such as 16.70°, 18.56° and 26.49° were also found in the synthesized La-MOF which corresponded with previous findings by Liu et al. [12].

Further confirmation of the La-MOF structure was defined by FTIR. In figure 1b, bands at 1563 and 1397 cm\(^{-1}\) are identified as asymmetric and symmetric stretching –COO from BDC. No bands observed at 1716 cm\(^{-1}\) for –C=O vibration from BDC indicates that the carboxyl has coordinated with lanthanum
ions. Bands at 3059, 827, 675 and 753 cm\(^{-1}\) were the characteristic vibration from the aromatic frameworks of benzene ring from BDC which includes \(\gamma(=C-H)\) and \(\delta(=C-H)\) from the face of benzene ring. Bands at 2938 and 1660 cm\(^{-1}\) is the characteristic vibration of asymmetric stretching from methyl groups and stretching from \(\gamma(C=O)\) of DMF which has shifted from 1685 cm\(^{-1}\) due to the amine release and ligation of DMF molecules with lanthanum ions by coordination of oxygen atom of the carbonyl group. The bands at 3482 cm\(^{-1}\) is the characteristic vibration from water molecules.

Surface area of La-MOF were analyzed by multi-point BET method was 84.957 m\(^2\)g\(^{-1}\). The surface area found for La-MOF synthesized using solvent DMF/water was higher than the surface area of La-MOF synthesized using only DMF as solvent which is only 5.47 m\(^2\)g\(^{-1}\) [13]. By adding water to DMF, it gives a breathing effect and improve the flexibility of La-MOF structure as well for increasing the surface area of La-MOF.

3.2. Swelling activity of diffusive and binding film

The swelling activity of diffusive film and binding film La-MOF need to be determined. The film was cured in an oven at 42–46 °C for one hour, disassembled from the mould and stored in aqua demineralized for hydration treatment. Based on the properties of diffusive and binding film (figure 2), it shows that the film had to be stored for at least 3 h in aqua demineralized to swell into a dimensionally stable form. During the hydration process, excess of ammonium persulfate and TEMED were removed.

![Figure 1. (a) XRD pattern of La-MOF and (b) FTIR spectra of La-MOF (top line) and BDC (bottom line).](image1)

![Figure 2. Swelling ratio of diffusive and binding film.](image2)
The swelling ratio of diffusive film was 2.24 and 1.93 for binding film. It showed that by adding La-MOF powder to binding film can reduce the swelling ratio because the polymeric structure in binding film became more rigid than in diffusive film. The swelling ratio in this study for diffusive film was lower than the result found by Zhang et al. This corresponded due to the different cross linker used in hydrogel formation, Zhang et al. [14] used acrylamide agarose as cross linker and this research used MBA. The different type of cross linker will affect the porosity of hydrogel which affecting the swelling ability.

### 3.3. Performance of elution efficiency

Elution is an extraction process of a material by washing it with an appropriate solvent. The higher the elution factor corresponded to the higher recovery value. HNO₃ was used as eluent to release phosphate ion from binding film La-MOF by ion exchange process. Ion phosphate that bound in binding film La-MOF will exchange with nitrate ion from HNO₃, hence there will be anion exchange. After eluted for 24 h, the eluent was then neutralized by 0.1 mol.L⁻¹ NaOH to prevent the excess acidic condition while it analyzed by molybdenum blue method to determine the phosphate concentration. Based on the table 1, it shows that 0.05 mol.L⁻¹ HNO₃ displays a higher elution factor value than 0.1 and 0.025 mol.L⁻¹ HNO₃, therefore 0.05 mol.L⁻¹ HNO₃ was chosen as an eluent for binding film La-MOF.

### 3.4. Diffusion coefficient

The diffusion coefficient (D) of DRP was measured by connecting graph of deployment time and mass of DRP adsorbed in La-MOF DGT. La-MOF DGT was deployed in 5 mg L⁻¹ DRP solution for 2 to 24 h. The graph shows linear uptake of DRP in La-MOF DGT with \( R^2 = 0.9982 \) (figure 3).

The diffusion coefficient is calculated by intercept and slope of the linear line. The D value was \( 2.216 \times 10^{-6} \) cm²s⁻¹, which was lower than the previous diffusion coefficient found by Zhang et al. [14] which is \( 7.39 \times 10^{-6} \) cm²s⁻¹. This difference could be corresponded to the different cross linker used for hydrogel film which affect the porosity of diffusive film. This recent report was using MBA as cross linker while Zhang et al. [14] was reported to use Lancaster patent agarose as cross linker.

### 3.5. Capacity of La-MOF DGT

La-MOF binding gel might be saturated when it was used for quantify the high concentration of DRP or used for a long period of deployment. The uptake of DRP by La-MOF DGT was evaluated by deploying La-MOF DGT in 5 mg L⁻¹ for 2 to 94 h (figure 4a). The evaluation of P uptake by

| Eluent | Replication | \( P_{abs.} \) in eluent | \( P_{concentration in eluent} \) (B) | \( P_{concentration adsorbed} \) (A) | Elution factor \((A/B)\) |
|--------|-------------|--------------------------|---------------------------------------|----------------------------------|------------------|
| HNO₃  | 1           | 0.748                    | 2.246                                 | 2.510                            | 0.895            |
|       | 2           | 0.747                    | 2.243                                 | 2.513                            | 0.892            |
|       | 3           | 0.745                    | 2.236                                 | 2.510                            | 0.891            |
|       | Average     |                          |                                       |                                  | 0.893            |
| 0.05 M| 1           | 0.876                    | 2.671                                 | 2.805                            | 0.952            |
| HNO₃  | 2           | 0.931                    | 2.853                                 | 2.706                            | 0.948            |
|       | 3           | 0.847                    | 2.575                                 | 2.706                            | 0.952            |
|       | Average     |                          |                                       |                                  | 0.951            |
| HNO₃  | 1           | 0.621                    | 1.825                                 | 2.139                            | 0.853            |
| 0.025 M| 2           | 0.632                    | 1.862                                 | 2.139                            | 0.871            |
|       | 3           | 0.627                    | 1.845                                 | 2.125                            | 0.868            |
|       | Average     |                          |                                       |                                  | 0.864            |
Figure 3. Diffusion coefficient of La-MOF DGT.

Figure 4. Accumulated DRP adsorbed by DGT La-MOF as a function of (a) time and (b) DRP concentration.

La-MOF DGT was also evaluated by deploying La-MOF DGT for 24 h with variation of DRP solution 1 to 10 mg L\(^{-1}\) (figure 4b).

Figure 5 reveals that the DRP uptake by DGT La-MOF was saturated after 24 h. Meanwhile, figure 4b shows the capacity of DRP uptake was saturated when the concentration of DRP solution was higher than 4 mg L\(^{-1}\) when the DGT La-MOF was deployed in DRP solution with range concentration of 1 to 10 mgL\(^{-1}\). The highest DRP uptake was 37.83 μg P which was 6 times higher than the capacity of binding agent based ion oxide which is only 6.7 μg P by using 2 g of ferrihydrite slurry as a binding film [14]. Nevertheless, this finding was lower than the Metsorb binding phase with capacity 40 μg P [15], Zr-oxide binding gel [16] and ZrO-Chelex [17]. This different binding capacity might be affected by the different of binding agent amount used in DGT devices. In this research, the amount of binding agent La-MOF used was 10 mg of La-MOF dispersed in 10 ml of gel solution, while Zr-oxide gel was prepared from the mixture of 1.8 g Zirconium oxide and 3.6 mL of gel solution [3]. This results reveal that by using little amount of La-MOF as binding gel (10 mg La-MOF powder in 10 mL of solution gel) will be able to remove DRP up to 37.83 μg P.

The probability mechanism of DRP adsorption of the binding agent La-MOF inside the binding gel La-MOF in DGT system was explained by the previous research by Liu [12]. Liu stated that the proposed
Figure 5. Probability mechanism of phosphate adsorption in binding gel La-MOF.

mechanism for phosphate removal by La-MOFs was by electrostatic attraction between La$^{3+}$ and phosphate to perform LaPO$_4$ white precipitation and ligand exchange between the OH group from La-MOF framework and phosphate ion [12]. BDC prefers to make complexes with La by performed La-O-La and C-O-La, where the hydroxyl groups were responsible for orthophosphate adsorption by ligand exchange.

4. Conclusion

A new binding agent based on lanthanum metal organic frameworks was successfully developed by a simple solvothermal method. By combining DMF/water as a solvent for La-MOF synthesis, a higher surface area was reached. With the high surface area and high affinity to remove the dissolved reactive phosphate (DRP), La-MOF was applied as a binding agent material for binding film in DGT technique. The DGT La-MOF was able to be deployed in a long period of time without any damage in both binding and diffusive film. Furthermore, DGT La-MOF was able to remove the DRP up to 37.83 µg P.

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