
Development Study of Binding Agent in Diffusive Gradient In Thin Films (DGT) Technique for Absorption of Phosphate Compounds using Nano-La₂O₃

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Abstract

The abundance of phosphate is a concern because it causes problems in aquatic ecosystems. The diffusive gradient in thin films (DGT) technique is a promising method for phosphate absorption because it can be used in situ. The DGT device consists of a membrane filter, a diffusive gel, and a binding gel. The presence of a binding agent in the binding gel makes the specific analyte bound to the binding gel. One of the binding agents that can be used for phosphate absorption is La₂O₃. Binding gel La₂O₃ was successfully synthesized that proven by the similarity of FTIR peaks of the diffusive gel and binding gel. The typical absorption of La-O also proves it from the binding gel at 642 cm⁻¹ and 423 cm⁻¹. La₂O₃ binding gel was made of *N,N'*-methylenebisacrylamide as a cross-linker with an elution factor of 97.4%. DGT-La₂O₃ proved capable of adsorption for 72 hours, with phosphate absorbed at 1.91 x 10⁵ ng. DGT-La₂O₃ also has the optimum ability to absorb phosphate at pH 3 of 1.93 x 10⁵ ng.

Keywords: DGT, eutrophication, La₂O₃, *N,N'*-methylenebisacrylamide, phosphate.

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1. INTRODUCTION

Eutrophication has developed into one of the most discussed problems because of its effects which can damage the ecosystem function of water body. Eutrophication is a process of enrichment of soil and water by several nutrients, which is characterized by the excessive growth of algae due to the supply of nutrients to the aquatic system (Kitsiou & Karydis, 2011; Kobetičová & Černý, 2019). Eutrophication encourages cyanobacteria's growth, resulting in poor water quality, causing oxygen depletion and fish death in the waters (García, 2021). Excess phosphorus is one of the triggers for eutrophication. The use of phosphorus-containing fertilizers, along with soil erosion and wastewater discharges, has a more significant influence on the global phosphorus cycle to watersheds than naturally available phosphorus. Rapid population growth and living standards are the main driving

factors changing the global phosphorus cycle (Tao *et al.*, 2019).

Excess phosphorus occurs due to anthropogenic activities and its bioavailability. The efficiency of phosphorus utilization is relatively low, accompanied by the still feeble recovery of phosphorus, causing an almost one-way flow of phosphorus from mining to natural waters where excess phosphorus causes a decrease in the quality of water (Alam *et al.*, 2021). Phosphorus is trapped in bedrock, soil, and sediment. The conversion of unavailable forms to available forms, especially soluble orthophosphate, occurs through geochemical and biochemical reactions at various stages in the global phosphorus cycle (Ruttenberg, 2019). In general, phosphorus can be divided into inorganic phosphorus and organic phosphorus. The main form of phosphorus in soil is inorganic phosphorus (Zhao *et al.*, 2021). Thus, a method is needed to monitor the presence of phosphorus in water bodies, one of

which is the diffusive gradient in thin films (DGT).

The diffusive gradient in thin films (DGT) is a new approach for adsorbing phosphorus in the environment. The DGT technique has been applied to the in situ measurement of dissolved phosphorus in natural waters. The phosphorus species can change when the sample is stored because it has dynamic interactions in natural water. Thus, this technique allows in situ measurement of reactive phosphorus (Pichette *et al.*, 2009). DGT has practical advantages because it can be used directly in the field, identify multi-element samples, and measure integrated time (Yabuki *et al.*, 2014). DGT measurements are calculated based on the linear flux of solute to the DGT device, which is referred to as the average concentration on the surface of the DGT device during application. DGT has been used to measure various labile species in soil, sediment and air, depending on the type of binding gel used with a binding agent specific to a particular analyte (Wang *et al.*, 2016).

In recent years, various fields of study have shown great interest in applying nanotechnology, one of which is environmental remediation. Oxides and hydroxides based on rare earth metals have been extensively studied to remove and restore water bodies. One of the rare earth metals that had considerable potential in the recovery of water bodies is lanthanum. The availability of lanthanum is relatively abundant, thus providing great potential as a promising adsorbent in phosphorus uptake (Zhi *et al.*, 2020). La naturally has a strong affinity for phosphate, and La^{3+} ions can attract oxygen donor atoms from phosphates through the anion-ligand exchange process (Razanajatovo *et al.*, 2021). In this research, a binding agent was developed using the diffusive gradient in thin films (DGT) technique for the adsorption of phosphate compounds using La_2O_3 . This study aimed to modify the binding agent components on the diffusive gradient in thin films (DGT) devices using La_2O_3 and to test the binding agent La_2O_3 on phosphate uptake. This research provides information regarding the synthesis of DGT- La_2O_3 , polyacrylamide polymerization, and the role of *N,N'*-methylene bisacrylamide (MBA) crosslinkers. It can be used to monitor phosphate concentrations in

water bodies to prevent eutrophication and control water pollution.

2. MATERIALS AND METHODS

Materials

The materials used in this work were lanthanum(III) nitrate hexahydrate 99.9% (Merck), starch soluble (Merck), acrylamide (Merck), methylenebisacrylamide (MBA) (Sigma-Aldrich), *N,N,N',N'*-Tetramethylethylenediamine (TEMED) 99% (Sigma-Aldrich), ammonium peroxodisulfate (Merck), cellulose membrane nitrate 0.45 μm (Whatman), potassium dihydrogen phosphate (Merck), sodium hydroxide (Merck), sodium nitrate (Merck), sulfuric acid 98% (Merck), ammonium heptamolybdate (Merck), L-ascorbic acid (Merck), potassium antimony tartrate (Merck), aqua demineralized.

Instrumentations

The instrumentation used in this work was Fourier Transform Infrared (FT-IR) Shimadzu IR Prestige 21, X-Ray Powder Diffraction (XRD) PANalytical, Field Emission Scanning Electron Microscopes Energy Dispersive X-Ray Spectroscopy (FESEM EDS) Jeol JIB-4610F, Ultraviolet-visible Spectrophotometry (UV-Vis) Shimadzu UV-2450. Characterization was carried out at the Department of Chemistry and Physics, University of Indonesia, and the National Research and Innovation Agency (BRIN)

Fabricated of La_2O_3

As much as 2.5 g of starch was dissolved in 100 mL water. Then 0.1 M lanthanum nitrate was added to the starch solution with a ratio of starch and lanthanum nitrate is 1:1. The resulting solution was stirred for 30 minutes, evaporated at 100 °C and calcined at 750 °C for 2 hours. Furthermore, obtained La_2O_3 was characterized by FTIR, XRD, and FESEM-EDS.

Preparation of *N,N'*-methylenebisacrylamide

0.3 g of solid *N,N'*-methylene bisacrylamide (MBA) was dissolved in 100 mL of demineralized water.

Fabricated of Diffusive Gel

This diffusive gel consisted of 1.9 mL of 40% acrylamide, 0.75 mL of 0.3% *N,N'*-

methylenebisacrylamide, and 2.35 mL of demineralized aqua, which was then added with 35 μL ammonium persulfate solution and 12.5 μL *N,N,N',N'*-tetramethylethylenediamine (TEMED). The mixture was stirred until homogeneous for 10-15 seconds and pipetted into a glass mould cleaned with 0.05 M HNO_3 solution, ensuring no bubbles formed. Then the solution in the mould was heated at 42-46 $^\circ\text{C}$ for 1 hour until a gel was formed. The formed gel was cut using a DGT cutter with a diameter of 2.5 cm, washed with demineralized water, and soaked for 24 hours for hydration. Aquademineralization was replaced 3-4 times during 24 hours. Then the gel was stored in 0.01 M NaNO_3 solution until it was used.

Fabricated of La_2O_3 Binding Gel

Binding Gel La_2O_3 consists of 2 g of La_2O_3 , acrylamide, *N,N'*-methylene bisacrylamide, and aquademineralization, which is added with ammonium persulfate solution and *N,N,N',N'*-tetramethylethylenediamine (TEMED). The mixture was stirred until homogeneous for 10-15 seconds and pipetted into a glass mold with 0.05 M HNO_3 solution, ensuring no bubbles formed. Then the solution in the mould was heated at 42-46 $^\circ\text{C}$ for 1 hour until a gel (not liquid) was formed. The formed gel was cut using a DGT cutter with a diameter of 2.5 cm, washed with demineralized water, and soaked for 24 hours for hydration. Aquademineralization was replaced 3-4 times during 24 hours. Then the gel was stored in 0.01 M NaNO_3 solution until it was used.

La_2O_3 Binding Gel Elution Factor Test

La_2O_3 binding gel was soaked in 20 mL of 10 ppm KH_2PO_4 solution for 24 hours. Next, the binding gel was washed with aquademin. Then the binding gel was eluted for 24 hours to determine the eluted concentration. La_2O_3 binding gel was eluted with 10 mL of NaOH solution at a concentration of 0.5-1.5 M each.

Installation of DGT Devices

DGT devices were washed and rinsed with aquademin. The filter membrane was soaked in aquademin for 5 minutes. The first order is the binding gel, followed by placing the diffusive gel and membrane filter. DGT closed tightly and firmly.

Diffusion Coefficient Test

The diffusion coefficient test was carried out by immersing the DGT La_2O_3 device in 30 mL of 10 ppm KH_2PO_4 solution. The solution was stirred for 2, 4, 6, 8, 12 and 24 hours of DGT immersion.

Soaking Time Variation Test

Immersing the DGT La_2O_3 device in 30 mL of 10 ppm KH_2PO_4 solution was tested for variations in immersion time. The solution was stirred for 2, 4, 6, 8, 12, 24, 48, and 72 hours of DGT immersion.

Phosphate Concentration Variation Test

The concentration variation test was carried out by immersing the DGT La_2O_3 device in 30 mL of KH_2PO_4 solution. The concentration of KH_2PO_4 was varied from 0.5, 1, 2, 3, 4, 5 and 10 ppm with soaking time for 24 hours with stirring.

Phosphate Solution pH Variation Test

Testing for pH variations was observed by immersing the DGT La_2O_3 device in 25 mL of 10 ppm KH_2PO_4 solution with pH variations of 3, 5, 7, 9 and 11 for 24 hours with stirring. The pH was adjusted with 0.1 M NaOH and 0.1 M HCl .

Sample Analysis

Phosphate concentration was determined using the elution solution, whose concentration was determined by the molybdenum blue method using a Uv-Vis spectrophotometer. The formation of a phosphomolybdenum blue complex observed the absorbance value.

3. RESULTS AND DISCUSSION

La_2O_3

La_2O_3 was fabricated using the Moothedan and Sherly (2016) method. La_2O_3 synthesis was carried out by reacting starch with 0.1 M lanthanum nitrate with a volume ratio of 1:1. The choice of starch as a capping agent is due to its environmental friendliness, non-toxicity, and unlimited sources in nature (Moothedan & Sherly, 2016). When the capping agent surrounds the lanthanum nitrate core, it inhibits its growth, thereby preventing agglomeration. When the concentration of the capping agent is insufficient to cover the core completely, the capping agent's crystal growth can be inhibited partially. Hence, the resulting particles are large (Kabir *et al.*, 2019).

The mixture was stirred for 30 minutes and evaporated at 100 °C. After that, the mixture was calcined at 750 °C. Calcination temperature affects the La₂O₃ crystal size growth. The average particle size increases with increasing calcination temperature. Growth is relatively slow when the temperature is low and increases rapidly when the temperature exceeds 750 °C. Pure La₂O₃ is obtained when the calcination temperature reaches 750 °C (Wang *et al.*, 2006).

FT-IR, XRD, and FESEM-EDS then characterized the synthesized La₂O₃. FT-IR characterization is used to see the functional groups contained in La₂O₃. The FT-IR spectrum of La₂O₃ is shown in **Figure 1**. The FTIR spectrum of La₂O₃ shows absorption at 3611 cm⁻¹, indicating O-H stretching vibrations due to air absorption in the La₂O₃ compound. Absorption peaks of 1480 cm⁻¹ and 1400 cm⁻¹ appear, indicating the presence of asymmetric and symmetric COO⁻ stretching vibrations. Other absorptions also appear at 988 cm⁻¹ and 856 cm⁻¹ indicating the presence of C-O stretching and C-O bending vibrations. Absorption of La-O stretching appears at wave number 643 cm⁻¹, and La-O bending appears at 414 cm⁻¹ (Kabir *et al.*, 2019).

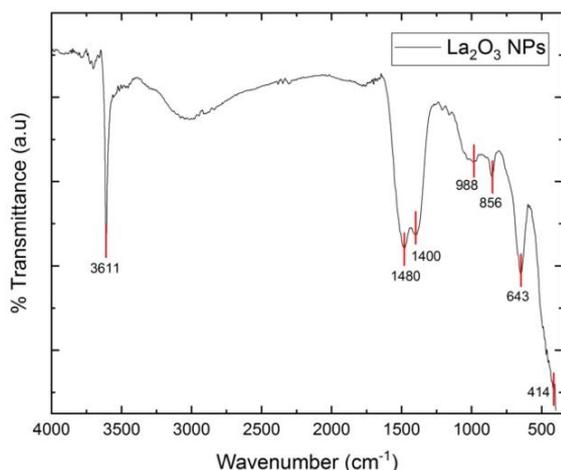


Figure 1. FT-IR spectrum of La₂O₃

XRD then identified the La₂O₃ diffraction pattern. The XRD results are shown in **Figure 2**, where a peak appears at 2θ = 15.65°; 27.30°; 27.98°; 39.50°; 48.65°. These peaks have similarities with previous literature indicating that La₂O₃ was successfully synthesized (Sulaiman *et al.*, 2018). These peaks also resemble JCPDS data from La₂O₃ no. 04-0856 (Mustofa *et al.*, 2020). Furthermore, the crystal size of La₂O₃ is calculated by the Debye-Scherrer equation 1.

$$D = \frac{0.9\lambda}{FWHM \cos \theta} \dots\dots\dots(1)$$

Where, D is the crystal size, λ is wavelength (1.54 Å), FWHM is the full width at half maximum, and θ is peak position (Ravi *et al.*, 2019). Based on the calculation results, the average crystal size of La₂O₃ is 28.51 nm.

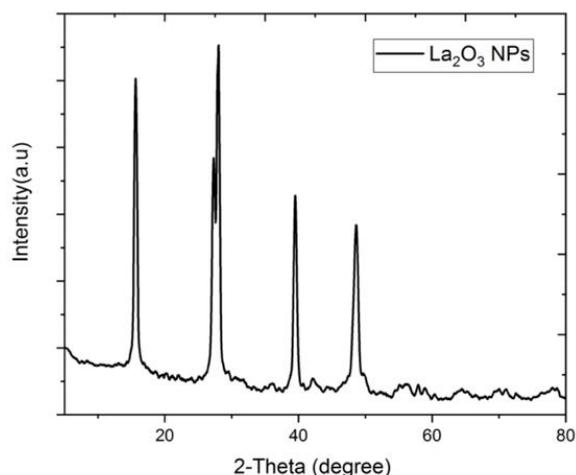
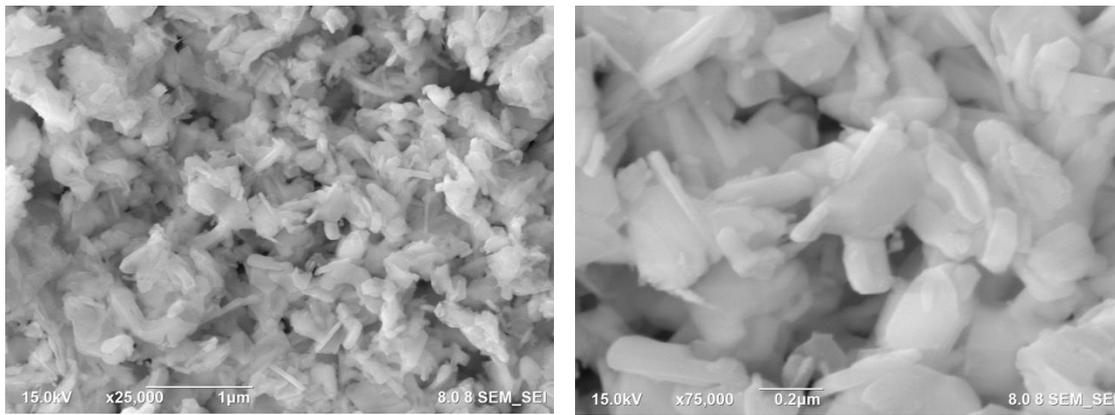


Figure 2. Diffraction pattern of La₂O₃

FESEM-EDS then identified the morphology and composition of La₂O₃ can be seen in **Figure 3**. Based on **Figure 3b**, the EDX results show the composition of the elements of La₂O₃, namely La and O. La₂O₃ (Kabir *et al.*, 2019).



(b)

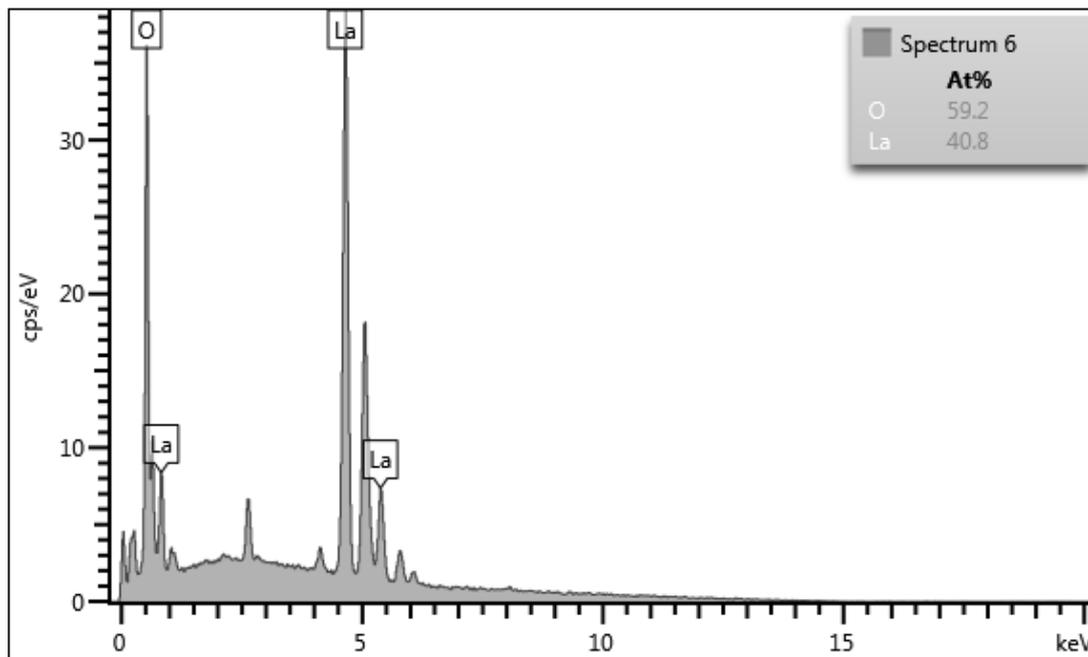


Figure 3. (a) FESEM La_2O_3 results with a magnification of 25,000x; (b) 75,000x magnification; and (c) The EDX spectrum of La_2O_3 shows the presence of La and O

La_2O_3 Binding Gel and Diffusive Gel

FT-IR characterized La_2O_3 binding gel and diffusive gel. Based on **Figure 4**, the two gels show peaks at 1119 cm^{-1} and 1123 cm^{-1} , which are absorptions from C-N stretching. Absorption from N-H stretching appears at 3335 cm^{-1} and 3197 cm^{-1} , and N-H bending absorption appears at 1664 cm^{-1} , 1610 cm^{-1} for La_2O_3 binding gel and 1650 cm^{-1} , 1601 cm^{-1} for diffusive gel. C-H stretching absorption appears at 2945 cm^{-1} and 2950 cm^{-1} , and C-H bending occurs at 1451 cm^{-1} and 1456 cm^{-1} (Li *et al.*, 2020; Sabbagh & Idayu, 2017). The characteristic absorption that most distinguishes between La_2O_3 binding gel and diffusive gel is absorption at 642 cm^{-1} , which indicates La-O stretching, and 423 cm^{-1} , which indicates La-O bending (Li *et al.*, 2020).

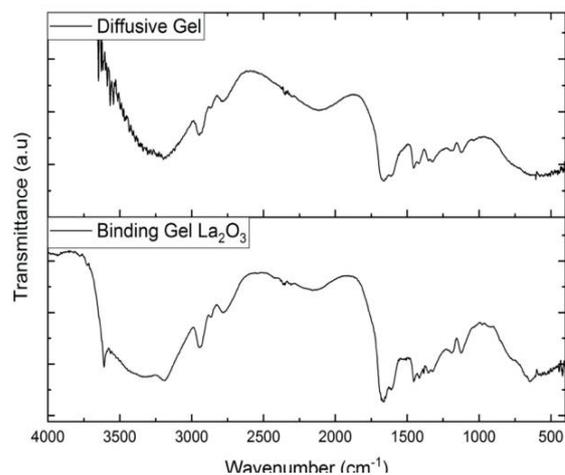


Figure 4. FT-IR spectrum of La_2O_3 binding gel and diffusive gel

Elution Factor Test Results

The elution factor is needed for the phosphate desorption process that a material has adsorbed. Eluent optimization was carried out with various concentrations of NaOH, namely 0.5 M; 1 M; and 1.5 M, for 24 hours. The optimum eluent concentration for eluting La₂O₃ binding gel was 1 M NaOH. Based on **Table 1**, 1 M NaOH was successful in eluting with an elution factor of 97.4%. 1 M NaOH will be used as the best eluent to desorb phosphate.

Diffusion Coefficient Test Results

The diffusion coefficient test was carried out by immersing the DGT device in 30 mL of 10 ppm KH₂PO₄ solution with a contact time of 2 to 24 hours with stirring at room temperature. In **Figure 5**, the resulting regression value is 0.98148, with a slope value of 2.1636. This slope value will be used in calculating the diffusion coefficient value for the La₂O₃ binding gel. Based on the calculations, the resulting value of the diffusion coefficient for La₂O₃ binding gel is 1.4542 x 10⁻⁵ cm²s⁻¹. The value of the diffusion coefficient affects the diffusion rate for analyte species, where a more excellent value of the diffusion coefficient will result in a greater diffusion rate (Kuntari *et al.*, 2019). The resulting diffusion coefficient value is greater than that of the previous experiment by Zhang *et al.* (1998), which is 7.39 x 10⁻⁶ cm²s⁻¹. It is due to the differences in the cross-linkers used in the gel manufacture, which give a different porosity effect to the diffusive gel.

The MBA cross-linker was used in this work, while the previous experiment used agarose (Zhang *et al.*, 1998).

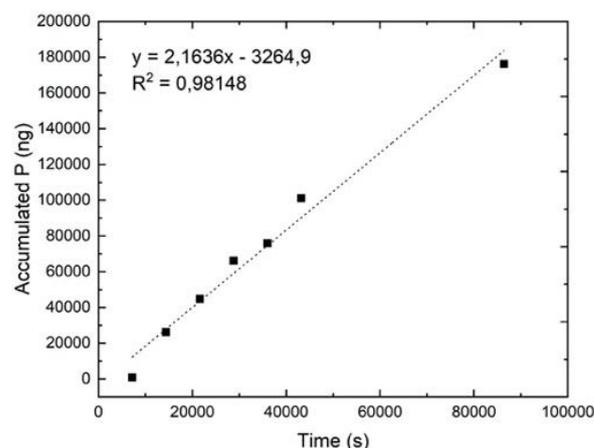


Figure 5. Diffusion Coefficient of La₂O₃

DGT-La₂O₃ Ability in Phosphate Absorption

The ability of DGT-La₂O₃ was tested by immersing DGT-La₂O₃ in 10 ppm KH₂PO₄ pH 7.4 within 2 to 72 hours with stirring. The ability of DGT-La₂O₃ to absorb phosphate can be seen in **Figure 6a**, where the absorbed phosphate increases with increasing time and becomes saturated when entering 24 hours to 72 hours. Therefore, 24 hours was chosen to test for pH variations and solution concentration variations. The highest phosphate value absorbed at 72 hours was 1.91 x 10⁵ ng.

Table 1. Results of the elution factor of NaOH

Eluent	Repetition	The mass of P in the eluent (µg) (B)	Adsorbed P mass (µg) (A)	Elution factor (A/B)
NaOH 0,5 M	1	83.920	106.658	78.681
	2	87.688	111.683	78.515
	3	75.754	99.749	75.945
	Average			77.714
NaOH 1 M	1	154.146	158.794	97.073
	2	149.121	151.256	98.588
	3	145.352	150.628	96.497
	Average			97.386
NaOH 1,5 M	1	78.266	202.136	38.720
	2	78.266	185.804	42.123
	3	70.729	205.905	34.350
	Average			38.398

DGT-La₂O₃ was also tested by varying the pH of the KH₂PO₄ solution from pH 3 to 11 to see its ability to absorb phosphate (**Figure 6b**). DGT-La₂O₃ decreased with increasing pH. It is because when the pH is acidic, the dominant orthophosphate species are H₃PO₄ and H₂PO₄⁻. Excess of H⁺ protonates the hydroxyl group from La, making it easier for the metal to bind to phosphate. However, at alkaline pH, the dominant orthophosphate species is PO₄³⁻ which will compete with OH⁻ so it can bind to metals (Zhang *et al.*, 2022). The pH condition that gave the best absorption was pH 3, with the amount of phosphate absorbed at 1.93 x 10⁵ ng.

The ability of DGT-La₂O₃ was also tested by varying the concentration of KH₂PO₄ solution from 0.5 to 10 ppm with a pH of 7.4. **Figure 6c**, as the concentration increases, the amount of phosphate absorbed in DGT-La₂O₃ increases with a value of 2.29 x 10⁵ ng. The increased phosphate concentration will cause the phosphate mass diffused and bound to the binding gel to increase.

The mechanism that occurs is that when the pH is acidic, the H⁺ ions in the solution will protonate the hydroxide groups from the surface so that they will be preferred by negatively charged phosphates (H₂PO₄⁻ and HPO₄²⁻) and increase the capability of phosphate absorption. When the pH is alkaline, the surface of the adsorbent is rich in negative charges due to OH⁻ in solution, resulting in electrostatic repulsion with HPO₄²⁻ and PO₄³⁻, thereby reducing the capability of phosphate absorption (Zhang *et al.*, 2022).

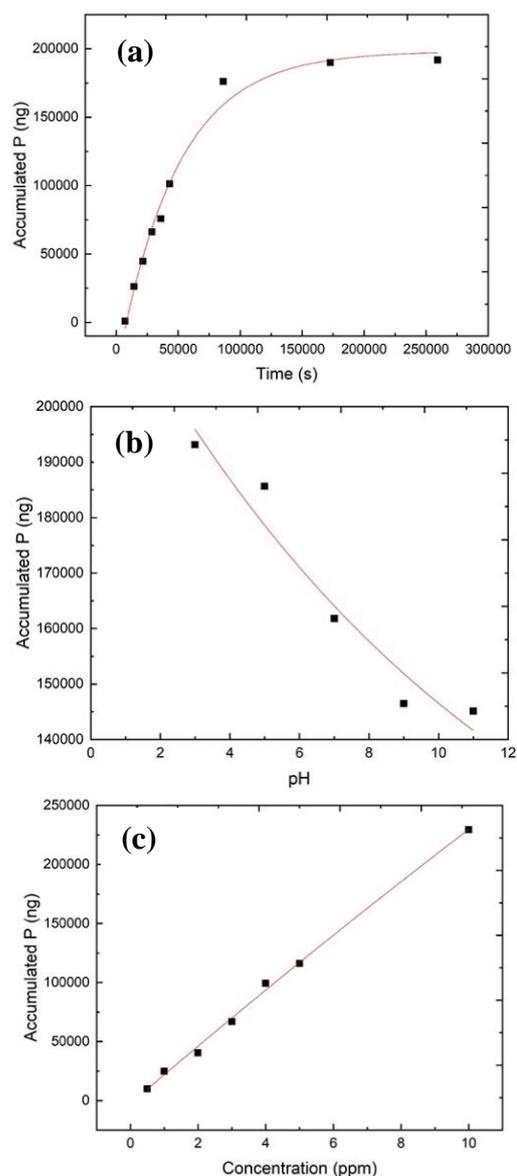


Figure 6. The ability of DGT-La₂O₃ to influence (a) contact time, (b) pH, and (c) concentration

Table 2. Research related to DGT

Binding agent	Targeted analyte	Conditions used	Result	Referensi
Ferrihydrite	Dissolved phosphate (ortophosphate)	immersion time: 24 hours pH optimum: -	86200-98300 ng	(Zhang <i>et al.</i> , 1998)
Fe-Al Oxide	Ortophosphate	immersion time: 24 hours, pH optimum: 3.3	5000 ng	(Saefumillah <i>et al.</i> , 2015)
Fe-MOF	Ortophosphate	immersion time: 26 hours, pH optimum: 2.0	9300 ng	(Sintya <i>et al.</i> , 2020)
La-MOF	Dissolved phosphate (ortophosphate)	immersion time: 24 hours, pH optimum: -	37830 ng	(Santikasari <i>et al.</i> , 2020)
La-MOF/chelex 100	Labile phosphate	immersion time: 24 hours, pH optimum: 4.5	330.2 ng	(Julianti <i>et al.</i> , 2022)

4. CONCLUSIONS

La₂O₃ was successfully synthesized and confirmed by FT-IR, XRD, and FESEM-EDX. La₂O₃ can be used as a binding agent in testing the DGT technique as an absorbent for phosphate compounds. DGT-La₂O₃ could absorb phosphate for 72 hours with accumulated phosphate of 1.91 x 10⁵ ng. DGT-La₂O₃ could also absorb phosphate at various concentrations with accumulated phosphate of 2.29 x 10⁵ ng at a concentration of 10 ppm. DGT-La₂O₃ has an optimum pH at pH 3 with accumulated phosphate of 1.93 x 10⁵ ng.

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