

Article

Novel Microwave-Synthesized Bimetallic Ce-Al-MOFs with Efficient Phosphate Removal from Aquaculture Effluent: Synthesis, Characterization and Applications

Jian Zeng ^{1,2}, Jiangnan Zhao ³, Zhenzhen Cai ^{1,2}, Jianshe Hu ³, Zesheng Zhuo ^{1,2} and Xiongping Miao ^{1,2,*} 

¹ School of Marine Biology, Xiamen Ocean Vocational College, Xiamen 361100, China; zengjian@xmoc.edu.cn (J.Z.); caizhenzhen@xmoc.edu.cn (Z.C.); zhuzesheng@xmoc.edu.cn (Z.Z.)

² Xiamen Key Laboratory of Intelligent Fishery, Xiamen 361100, China

³ Center for Molecular Science and Engineering, College of Science, Northeastern University, Shenyang 110819, China; jiangnanzhao@163.com (J.Z.); hujs@mail.neu.edu.cn (J.H.)

* Correspondence: szmzp2003@163.com

Abstract

The eutrophication of natural water is a severe environmental risk faced by coastal marine ecosystems, and the excess nitrogen and phosphorus in aquaculture effluent are one of the main sources of environmental pollution. Effectively reducing as well as controlling the phosphorus content in aquaculture effluent is of great importance for alleviating eutrophication and the governance of coastal environments. This study focuses on addressing phosphorus pollution by developing novel bimetallic Ce-Al-MOFs adsorbents via the microwave-assisted rapid synthesis method, among which the monomer Ce₃Al₃-BDC₃ exhibits excellent phosphate adsorption capacity (136.99 mg P g^{−1}) and great removal efficiency over a wide pH range (2~10). Batch experiments reveal that the adsorption is followed by pseudo-second-order kinetics and the Langmuir isotherm model, indicating monolayer chemisorption. The MOFs material shows high selectivity for phosphorus even under the interference of co-existing anions, as well as excellent reusability, retaining over 65% removal efficiency after six adsorption–desorption cycles. Field tests in coastal areas and indoor aquaculture systems both achieve over 97% phosphate removal, meeting discharge standards. A series of characterization methods identify ligand exchange, electrostatic interactions and surface complexation as key adsorption mechanisms. The Ce-Al-MOFs present a promising solution for mitigating eutrophication and managing aquaculture wastewater sustainably.

Keywords: bimetallic Ce-Al-MOFs; microwave-assisted synthesis; phosphorus removal; aquaculture effluent; eutrophication control



Academic Editors: Anastasios Zouboulis and Yuanrong Zhu

Received: 14 August 2025

Revised: 16 October 2025

Accepted: 17 October 2025

Published: 21 October 2025

Citation: Zeng, J.; Zhao, J.; Cai, Z.; Hu, J.; Zhuo, Z.; Miao, X. Novel Microwave-Synthesized Bimetallic Ce-Al-MOFs with Efficient Phosphate Removal from Aquaculture Effluent: Synthesis, Characterization and Applications. *Water* **2025**, *17*, 3019. <https://doi.org/10.3390/w17203019>

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1. Introduction

China is the world's leading aquaculture producer, with its farmed output consistently ranked first, accounting for more than 70% of the global production [1]. In 2023, the total aquatic products in China reached 71.163 million tons, of which 81.6% came from aquaculture [2]. Coastal aquaculture, as an important form of aquaculture, has continuously expanded in recent years, while the resulting eutrophication of water bodies has also become increasingly prominent [3–5]. In high-density coastal aquaculture models, there is often a large amount of feed input, and the nitrogen and phosphorus waste excreted by the metabolism of farmed aquatic products accounts for more than 70% of the total

feed input [3,6], thereby increasing and even exceeding the concentration of nitrogen and phosphorus elements in natural water of the aquaculture area. Although the eutrophication of seawater promotes the rapid growth of plankton, the resulting decrease in the dissolved oxygen concentration in seawater not only hinders the growth of aquatic economic animals and restricts the sustainable development of marine aquaculture [4,6] but also leads to “hypoxic” conditions in the water body, causing the death of fish, shellfish and other organisms as well as benthic aquatic plants, severely disrupting the balance and stability of the marine ecosystem [7,8]. Therefore, reducing the content of nitrogen and phosphorus in aquaculture effluent is crucial for alleviating the environmental pollution of nearshore marine areas.

Phosphorus, as one of the vital elements triggering eutrophication in water bodies, typically exists in aquaculture effluent in three forms: orthophosphate (PO_4^{3-} , HPO_4^{2-} and H_2PO_4^-), polyphosphates and organic phosphates. Since biological processes in water bodies generally convert complex forms of phosphorus into orthophosphate, the orthophosphate form is the most common target for recovery or removal. For wastewater treatment, typical phosphorus removal techniques include chemical precipitation, adsorption, biological transformation, reverse osmosis as well as membrane ion exchange. Among these methods, adsorption is considered the most economical and effective due to its simplicity, low cost, fast depletion rate and high removal efficiency and the recoverability of adsorbed pollutants [9–11]. However, the presence of co-existing ions and organic matters in water environments will interfere with the performance of traditional adsorbents for phosphate by competing for adsorption sites [12–14]. A practical way to overcome these shortcomings is to design highly selective porous sorbents that target phosphate. On the one hand, porous structures facilitate the diffusion of dissolved substances into the interior of the adsorbent for capture, ensuring the high adsorption capacity of phosphate. On the other hand, the surface of the adsorbent can be easily modified by introducing high-selectivity elements or functional groups to enhance adsorption performance.

Metal-based sorbents have attracted widespread attention due to their exceptional high affinity and adsorption property for phosphate. These sorbents primarily rely on metal atoms/ions (such as Mg, Ca, Fe, Al, Ce, etc.) to augment the number of adsorption sites on the adsorbent surface [10,11,15]. In recent years, metal–organic frameworks (MOFs) have emerged as a novel class of sorbing materials for water pollutants, drawing significant attention due to their structural stability, high porosity and specific surface area [16,17]. Meanwhile, the optimization of phosphorus adsorption performance through the modification of MOF materials has also become a research focus, with studies focusing on MIL-101(Fe) [18,19], Al-MOFs [20–22], UiO-66-NH₂ [23], ZIF-8 [24] and others. For instance, Li et al. (2021) [20] synthesized a series of Al-based MOFs using aluminum metal clusters as nodes and by altering the structure of organic linkers and investigated their phosphate adsorption performance. They found that different linkers can influence phosphate adsorption capacity by modulating the pore structure of MOFs. Férey et al. (2005) [25] discovered that the MIL-101 framework octahedral units synthesized from terephthalic acid groups and trivalent metals (Cr, Fe, Al) possess unsaturated metal sites and ideal porosity in the form of super-tetrahedral units. These units exhibit high chemical and thermal stability, making them strong candidates for phosphate adsorption through ligand exchange mechanisms. Additionally, cerium (Ce), as one of the high abundant rare earth elements, holds a broad range of applications, including as a catalyst, adsorbent, phosphor and magnetic material. The solubility constant (K_{sp}) of CePO_4 ($K_{\text{sp}} = 1.0 \times 10^{-23}$) indicates a strong binding affinity between Ce and phosphate, thus endowing Ce-based materials with good potential for phosphorus removal. To date, a variety of bimetallic MOFs have been developed for pollutant detection and removal [21], but only a few have been docu-

mented regarding the optimization and improvement of phosphorus removal performance from aquaculture effluent. It has been verified that bimetallic-doped frameworks not only retain the advantages of the parent monometallic MOFs but also exhibit the properties of the later-introduced metal, leading to the further enhancement of performance [26]. Especially for Al-containing bimetallic systems, the other metal or its oxide tends to shape fine, uniform and spherical particles and enlarge the specific surface area [27].

In view of the characteristics of the two metals mentioned above, it can be speculated that both high affinity for phosphate and improved pore structure will be endowed when integrating Ce and Al into a bimetallic MOF, thereby achieving the more efficient utilization of both elements. In this study, we employed a microwave-assisted rapid synthesis method for the first time to fabricate Ce-Al-MOFs materials for efficient phosphate removal from aquaculture effluent, using Ce and Al as the two metal sources and terephthalic acid (H_2BDC) as the organic linker. A series of adsorption experiments were conducted to investigate the effects of the precursor ratio, reaction time, solution pH, coexisting anions and initial phosphate concentration on the adsorption performance. Furthermore, the adsorption mechanisms were thoroughly explored through kinetic and thermodynamic tests as well as material characterization. Our synthesized adsorbents exhibit excellent phosphate adsorption performance both in laboratory tests and field practical applications. The materials show superior selectivity, stability, sustainability as well as environmental safety, which offers a novel and efficient strategy for eutrophication management from aquaculture wastewater.

2. Materials and Methods

2.1. Materials

AR grade aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), AR grade cerium chloride heptahydrate ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), AR grade terephthalic acid (H_2BDC ; Yuan Ye Chemical Technology Co., Ltd., Shanghai, China), AR grade N, N-dimethylformamide (DMF; Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), 36~38% hydrochloric (HCl; Xilong Chemical Co., Ltd., Shantou, China) and AR grade sodium hydroxide (NaOH; Xilong Chemical Co., Ltd., Shantou, China) were selected as reagents for MOFs synthesis. AR grade potassium dihydrogen phosphate (KH_2PO_4) was used for batch adsorption experiments. Ultrapure water was used for all batch experiments.

2.2. Preparation of Ce-Al-MOFs

The optimal microwave reaction time for the yield of the synthesized materials was initially investigated. Four different molar ratios of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}:\text{AlCl}_3 \cdot 6\text{H}_2\text{O}:\text{H}_2\text{BDC}$ (i.e., 1:3:3, 2:3:3, 3:3:3 and 3:3:1) were selected for the experiments. The reactants were placed in a polyethylene bottle, and 25 mL of DMF and 5 mL of deionized water were added to dissolve and mix the reactants. After stirring at room temperature (25 °C) for 30 min, the mixture was transferred to a 300 mL glass three-neck flask and subjected to magnetic stirring under microwave irradiation at 100 °C and 240 W. The synthesis proceeded thermostatically and under atmospheric pressure (1 atm) throughout the duration. The reaction time was set to 0.5 h, 1 h, 2 h, 3 h, 4 h and 5 h for comparison. After the synthesis reaction, the mixture was cooled to room temperature and then the product was collected via centrifugation. The product was rinsed three times with deionized water, DMF and anhydrous ethanol, sequentially, and then dried under vacuum at 80 °C to obtain a milky white Ce-Al-MOFs powder-like material. According to the molar amount of metal Ce, Al and the ligand H_2BDC in the reaction, the synthesized adsorbents are named $\text{Ce}_1\text{Al}_3\text{-BDC}_3$, $\text{Ce}_2\text{Al}_3\text{-BDC}_3$ and $\text{Ce}_3\text{Al}_3\text{-BDC}_3$, respectively. The prepared materials were sealed and

stored in a dry, room-temperature environment, and they were used directly for testing without further activation.

2.3. Material Characterization

For investigating the performance of synthesized Ce-Al-MOFs, a series of characterization methods were used to analyze. The Zeta potentials were detected in the various pH ranges between 2 and 10 using Zetasizer Nano-Z (Malvern, UK). The surface morphology was viewed by scanning electron microscopy (SEM, Su8020, Tianmei Scientific Instruments Co., Ltd., Zhongshan, China). X-ray diffraction (XRD) was utilized to judge the crystal structure of synthesized MOFs before and after phosphate adsorption using a SmartLab SE X-ray diffractometer (Rigaku, Tokyo, Japan) with a scanning speed of $5^{\circ} \text{ min}^{-1}$ and a scanning angle from 5° to 90° . The functional groups composition of synthesized Ce-Al-MOFs as well as the structural transformation after adsorption treatment were analyzed via Fourier transformation infrared (FT-IR, iS5, Thermo Fisher Scientific, Waltham, MA, USA). Thermogravimetric analysis (TGA) was conducted by an STA 449 F5 Jupiter thermal analyzer (Netzsch, Selb, Germany) to heat the materials to 800°C at a rate of $10^{\circ} \text{C min}^{-1}$ under air atmosphere.

2.4. Batch Experiments of Adsorption

A series of adsorption experiments were conducted to deeply explore the removal performance of phosphate by selected Ce-Al-MOFs.

First, under the condition of pH 6.0, 20 mL of various initial concentrations ($10\sim 500 \text{ mg L}^{-1}$) of phosphate solutions were placed in 50 mL polytetrafluoroethylene centrifuge tubes, and 20 mg of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ were added. The mixtures were magnetically stirred at 25°C for 6 h. Subsequently, the supernatant was collected by high-speed centrifugation (9800 rpm), and the residual concentration of phosphate was measured.

When studying adsorption kinetics, 100 and 200 mg P L^{-1} of phosphate concentrations were set, which are commonly adopted in previous reports [18–21]. The reaction temperature was controlled at 25°C , the solution pH was set at 6.0 and 20 mg of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ were added. Experiments were carried out at different time intervals. Specifically, samples were taken every 15 min in the first 3 h, while they were taken every 30 min in 4–6 h.

In the thermodynamics experiments, 20 mL of different concentrations ($10\sim 500 \text{ mg L}^{-1}$) of phosphate solutions were placed using 50 mL polytetrafluoroethylene centrifuge tubes. The solution pH was controlled at around 6.0, and 20 mg of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ was added. The mixtures were magnetically stirred at 298 K, 308 K, 318 K and 328 K for 6 h, respectively. The supernatant was subsequently collected by high-speed centrifugation (9800 rpm), and then the residual phosphorus concentration was measured.

When investigating the effect of pH on phosphate removal, the pH of solutions was adjusted to the range between 2 and 10 using HCl and NaOH. In total, 20 mg of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ was added to 20 mL of 100 mg P L^{-1} solution and stirred at 25°C for 6 h. After centrifugation, the residual PO_4^{3-} in the supernatant was measured. A PHSJ-4A pH meter was applied to detect the solution pH before and after adsorption during the experiment.

In the interference experiments, SO_4^{2-} , Cl^{-} , CO_3^{2-} and NO_3^{-} were introduced to the solution containing 100 mg P L^{-1} of phosphate. The solution pH was controlled at 6.0, and the dosage of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ was 20 mg. The procedure was the same as that used in the pH effect study.

For the adsorbent regeneration and phosphorus recovery tests, 20 mg of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ was adopted with a phosphate solution of 50 mg P L^{-1} . After magnetic stirring at 25°C for 3 h, the phosphorus concentration in the supernatant was measured. The phosphorus-loaded adsorbent was collected and then placed in $0.5 \text{ mol L}^{-1} \text{ NaHCO}_3$ solution. The

desorption treatment was carried out at 50 °C and 500 rpm for 6 h. Subsequently, the suspension was centrifuged to separate the adsorbent, and the residual phosphate concentration within the supernatant was determined. The above steps were repeated, and the phosphorus adsorption performance was tested again using the regenerated adsorbent. A total of six adsorption–desorption cycles were conducted in the entire experiment.

All the residual phosphate concentrations within supernatant mentioned above were measured spectrophotometrically by the molybdenum blue method with a UV-1800PC-DS2 spectrophotometer (MAPADA, Shanghai, China) at a wavelength of 710 nm. The adsorption capacity and efficiency of the adsorbent for phosphorus were calculated using Equations (1) and (2), respectively:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

$$\text{Re} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where C_0 (mg P L^{−1}) is the initial concentration of phosphate; C_e (mg P L^{−1}) is the residual concentration of phosphate at adsorption equilibrium; q_e (mg P g^{−1}) is the phosphorus adsorption capacity; m (g) is the dosage of the sorbent; V (L) is the solution volume; and Re represents the removal efficiency of phosphate.

3. Results and Discussion

3.1. Effect of Microwave Reaction Time on Materials Yield

The materials yield under different precursor molar ratio conditions as of the microwave reaction time are shown in Figure 1. The results indicate that the yields of the synthesized materials tend to stabilize when the reaction time reaches 3 h, suggesting that microwave-heating provides a rapid pathway for the preparation of MOFs. Therefore, a reaction time of 3 h was selected as the optimal condition in our study for preparing the Ce-Al-MOFs for adsorption performance and characterization tests. During the microwave synthesis, the product yield showed only slightly fluctuation at each time point. While under the same reaction condition, the yields of Ce₃-Al₃-BDC₁ were lower than for the other three precursor-ratio materials.

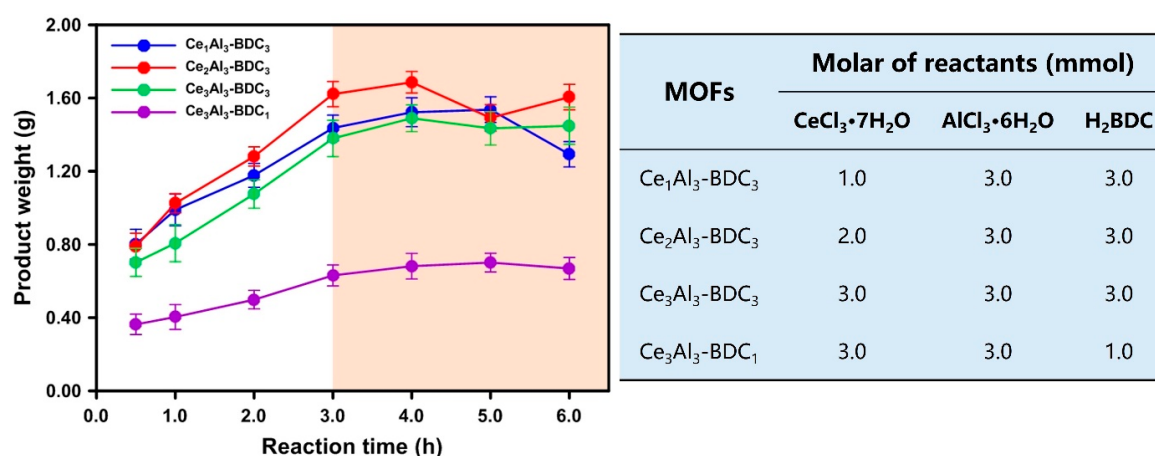


Figure 1. Regulation of microwave reaction time on material yield. (The microwave irradiation was 240 W, and the reaction temperature was 100 °C).

3.2. Adsorption Behavior of Phosphate

3.2.1. Effect of the Precursor-Ratios

The effect of various molar ratios of Ce:Al:H₂BDC on the phosphate removal capacity of the synthesized MOFs was subsequently investigated, with the results presented in Figure 2a. The comparative experiments with various molar ratios of Ce:Al:H₂BDC (i.e., 1:3:3, 2:3:3, 3:1:3, 3:2:3, 3:3:1, 3:3:2, 3:3:3, 3:3:4, 3:3:5 and 3:3:6) were conducted. The synthesized materials were used to measure the adsorption capacity (q_e) and removal efficiency (Re) for phosphate. The results indicated that both q_e and Re initially increased and then decreased with the increasing Ce:Al ratio, while they gradually increased with the increasing molar fraction of H₂BDC. Considering the characterization of XRD intensity (see Section 3.4.1), the MOF synthesized with a Ce:Al:H₂BDC molar ratio of 3:3:3 was finally chosen for subsequent adsorption experiments.

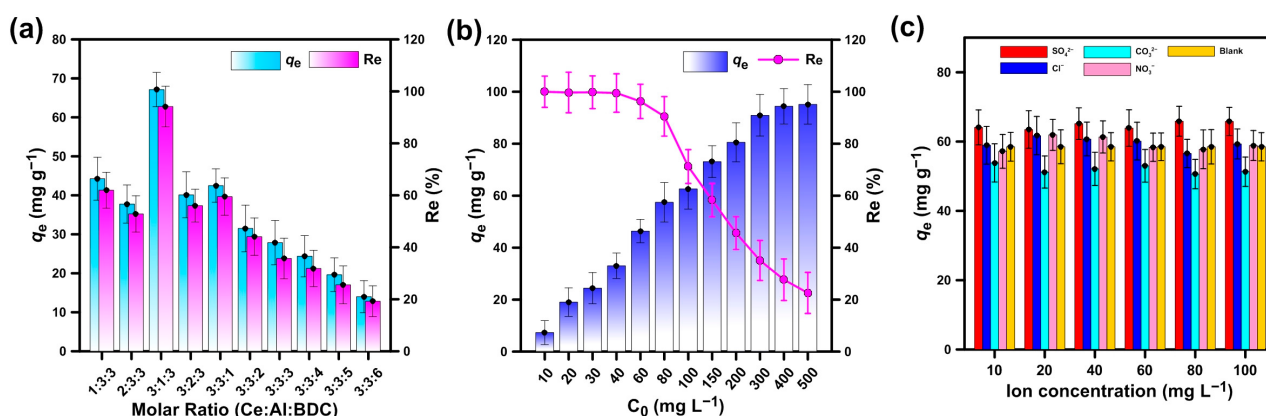


Figure 2. Effect on phosphate removal of the (a) precursor-ratios, (b) initial phosphate concentration and (c) interfered co-existing anions. (pH = 6.0, the dosage was 1 g L⁻¹, the mixing time was 6 h and the temperature was 25 °C; for (a,c), the concentrations were 70 mg P L⁻¹ and 100 mg P L⁻¹, respectively).

3.2.2. Effect of Initial Phosphate Concentration

The effect of various initial concentrations on phosphate removal is shown in Figure 2b. Under the conditions of a pH of 6.0, a temperature of 25 °C and a dosage of Ce₃Al₃-BDC₃ of 20 mg, the adsorption capacity gradually elevated with the initial phosphate concentration. This could be attributed to the higher phosphate concentration at the solid–liquid interface generating sufficient driving force to overcome the mass transfer resistance in the aqueous solution and then facilitating the rapid migration of ions and fully occupying the active sites of the adsorbent [28], thereby enhancing the adsorption capacity. When the phosphate concentration increased to 300–500 mg P L⁻¹, the sorbing performance tended to level off, indicating that the adsorption was approaching saturation. From another perspective, the decrease in phosphate removal efficiency can also be interpreted as the limited adsorption sites occupied by the initial adsorption of phosphate, hindering the further adsorption of the remaining ions [29].

3.2.3. Effect of Interfered Co-Existing Anions

Various anions presented in water can either promote or inhibit the adsorption capacity of phosphate. In this study, the effects of co-existing Cl⁻, SO₄²⁻, CO₃²⁻ and NO₃⁻ (at concentrations of 10 mg L⁻¹, 20 mg L⁻¹, 40 mg L⁻¹, 60 mg L⁻¹, 80 mg L⁻¹ and 100 mg L⁻¹) on phosphate removal were investigated. As shown in Figure 2c, the existence of Cl⁻ and NO₃⁻ had little effect on the phosphorus adsorption capacity of Ce₃Al₃-BDC₃, while CO₃²⁻ exhibited a slight inhibition. It could be attributed to the hydrolysis of CO₃²⁻ in the solution, which easily generates -OH and competes with phosphate for Ce or Al active sites.

Intriguingly, among the interfering ions, SO_4^{2-} had improved phosphorus adsorption, with an enhancement of 8.5~12.6%. This phenomenon could be related to the formation of unique Al-O-P or Ce-O-P inner-sphere complexes through ligand exchange by the adsorbent [30,31]. When interfering ions have a hydrated radius close to that of phosphate ions, those with higher hydration energy are more likely to compete with phosphate. As the ion concentration increases, the distance between molecules decreases and electrostatic attraction intensifies, which may be an alternative explanation for promoting phosphorus adsorption [32]. Overall, the influence of co-existing ions on the phosphorus adsorption efficiency of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ examined in this study is consistent with the documented results of analogous phosphorus-removal materials [21,32–34].

We also simulated Cl^- and SO_4^{2-} concentrations at the natural seawater level to assess their interference with phosphate removal. It is found that the adsorption capacity of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ declined by 10~15% under high Cl^- and SO_4^{2-} contents (Table S1). The discrepancy between the two levels of experiments reflects competition for adsorption sites by Cl^- and SO_4^{2-} ions under a high concentration. But even so, the removal efficiency could remain about 60%, indicating a potential application for phosphorus removal of our Ce-Al-MOFs in coastal aquaculture effluent.

3.2.4. Influence of pH Conditions

Another key factor influencing phosphate adsorption is the pH condition. The influence of pH among the range of 2~10 on the adsorption performance of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ was tested. The experimental results of the pH effect on phosphorus removal, with other parameters kept optimal, are shown in Figure 3a. Both the adsorption capacity and removal efficiency originally increased and then decreased with pH, with the maximum q_e and R_e occurring at pH 6.0. This may be due to the competition between phosphate and OH^- under acidic or alkaline conditions [35,36]. As depicted by the Visual Miniteq model, the speciation of phosphate in the solution varies with pH levels (Figure 3b). When the acidic condition is dominated, the adsorption is weak since phosphate mainly exists in the form of H_3PO_4 [37]. While in the moderate pH range (2.15 to 7.20), H_2PO_4^- becomes the dominant form in phosphate. Because H_2PO_4^- is easily adsorbed by MOFs under strong electrostatic interaction [34], $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ exhibits good adsorption performance under this condition. As pH increases higher than 7, the adsorption capacity decreases because phosphate exists as HPO_4^{2-} . Ligand exchange will be facilitated by Ce(III)-induced hydrolysis, with the outer sphere of the adsorbent occupied by OH^- [38], which leads to a competitive relationship between OH^- and phosphorus anions for adsorption active sites and declining phosphate removal performance under high pH conditions [39,40]. Nevertheless, the adsorbent in our study maintained high performance for phosphorus adsorption over a wide pH range, with an adsorption capacity and efficiency of 65.9 mg g^{-1} and 60.3% even at a pH of 10.

The zeta potential measurements demonstrated the phosphate sorption by the $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ framework to be pH-dependent (Figure 3c). The point of zero charge (pH_{zpc}) is calculated as 7.62. This suggests that when the solution pH is below pH_{zpc} , $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ adsorbent is positively charged with H_2PO_4^- as the main form, and electrostatic attraction therefore plays a major role in the phosphate removal process, while with a pH between 7.62 and 10.0, the MOF material is negatively charged, with HPO_4^{2-} being the dominant species, and both of them have electrostatic repulsion. Additionally, -OH coordinated with Ce or Al under weak alkaline conditions will form a Ce-O-P or Al-O-P inner-sphere complex through ligand exchange.

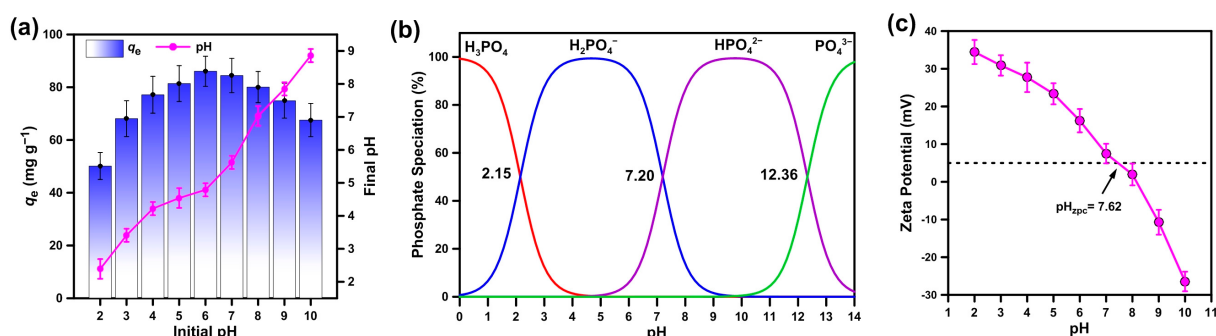


Figure 3. (a) Influence of pH on the phosphate removal; (b) Distribution of phosphate species; (c) Analysis of the zero-point charge (pH_{zpc}). (The dosage was 1 g L^{-1} , the stirred time was 6 h, the temperature was 25°C and the concentrations was 100 mg P L^{-1}).

3.3. Regeneration and Phosphorus Recovery of Adsorbents

Considering both the reuse of phosphorus resources and the cost of removal, the regeneration and recycle potential of the $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ material were also tested. As shown in Figure 4a,b, the removal efficiency by the Ce/Al bimetallic material slightly decreased after each adsorption–recovery cycle. However, even after six cycles, the removal efficiency of phosphorus remained above 65%. Recovery experiments indicated that 0.5 mol L^{-1} sodium bicarbonate (NaHCO_3) solution could effectively recover phosphate ions from the adsorbent, with the recovery yield exceeding 45.5 mg g^{-1} and 70% in each cycle, respectively. These results demonstrate that the Ce/Al bimetallic MOF material has superior adsorption and desorption performance, showing great potential for applications in eutrophication control and the recovery of excess phosphorus resources. In consideration of environmental safety, Al and Ce leaching in each adsorption–desorption cycle were also detected by ICP-MS. The measured concentrations of Ce and Al remaining in eluate were almost below detection limits (Table S2). However, we must emphasize that the large-scale application of this MOF adsorbent for P removal in natural aquaculture waters is still a long way off, and the uncertainties regarding its potential long-term risks in closed or semi-closed marine aquaculture systems require a more cautious assessment.

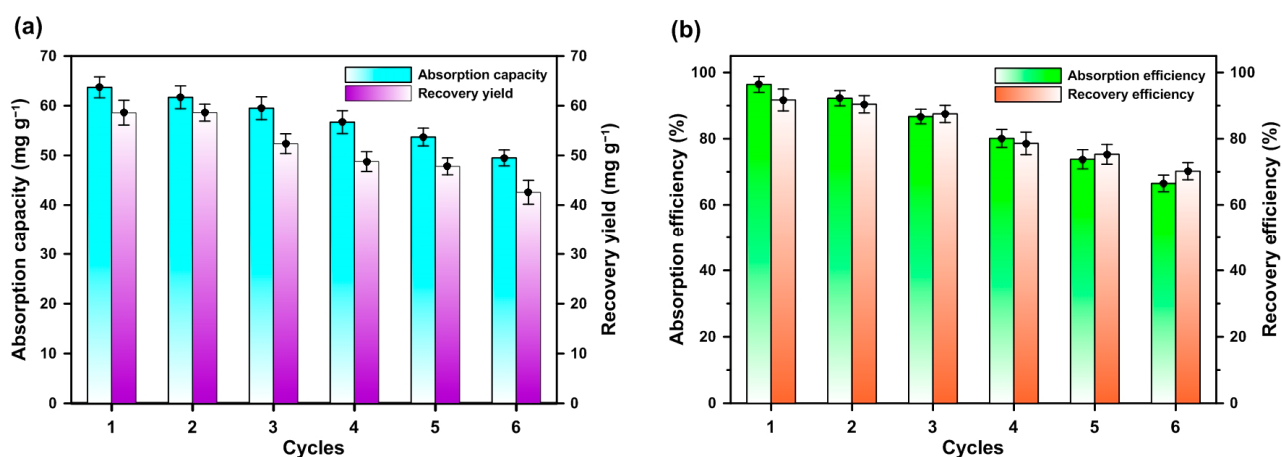


Figure 4. Regeneration of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ material with (a) adsorption capacity and recovery yield; (b) adsorption efficiency and recovery efficiency. (The dosage was 0.8 g L^{-1} , the phosphate concentration was 50 mg P L^{-1} , the NaHCO_3 was 0.5 mol L^{-1} , the recovery temperature was 50°C , the mixing speed was 500 rpm and the adsorption time was 6 h).

3.4. Characterization

3.4.1. XRD Analysis

The crystallinity of Ce-Al-MOFs was characterized by XRD. As presented in Figure 5a, the XRD patterns of MOFs synthesized under different molar ratios show consistent diffraction peak positions with significant intensities, indicating high crystallinity of the materials [28]. Among them, the peak intensities reached the strongest when the molar ratio of Ce:Al:BDC is 3:3:3. Based on the adsorption performance for phosphate in the solution, this precursor-ratio was selected as the optimal synthesis ratio for subsequent characterization tests. Before phosphate adsorption, the $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ exhibited sharp diffraction peaks, with the main characteristic peaks appearing at $2\theta = 9.04^\circ$, 16.61° , 23.71° , 29.09° and 33.68° . Comparison analysis revealed that these diffraction peaks highly matched the characteristic peaks of standard cerium acetate ($\text{Ce}(\text{COOH})_3$) (PDF#80-1503) and aluminum isopropoxide ($\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$) (PDF#30-1508). The corresponding crystal planes of these diffraction peaks are summarized in Table S3. The positions of the main peaks in the XRD spectrum were also consistent with the documented pattern of Ce-BDC [40,41] and Al-BDC [20,32] frameworks from literature reports, therefore confirming the successful synthesis of the Ce-Al-MOFs. After phosphate adsorption, the intensities of these peaks weakened or even disappeared, indicating that the metal active sites participated in the removal of phosphate and achieved adsorption through electrostatic interactions [20,22,31].

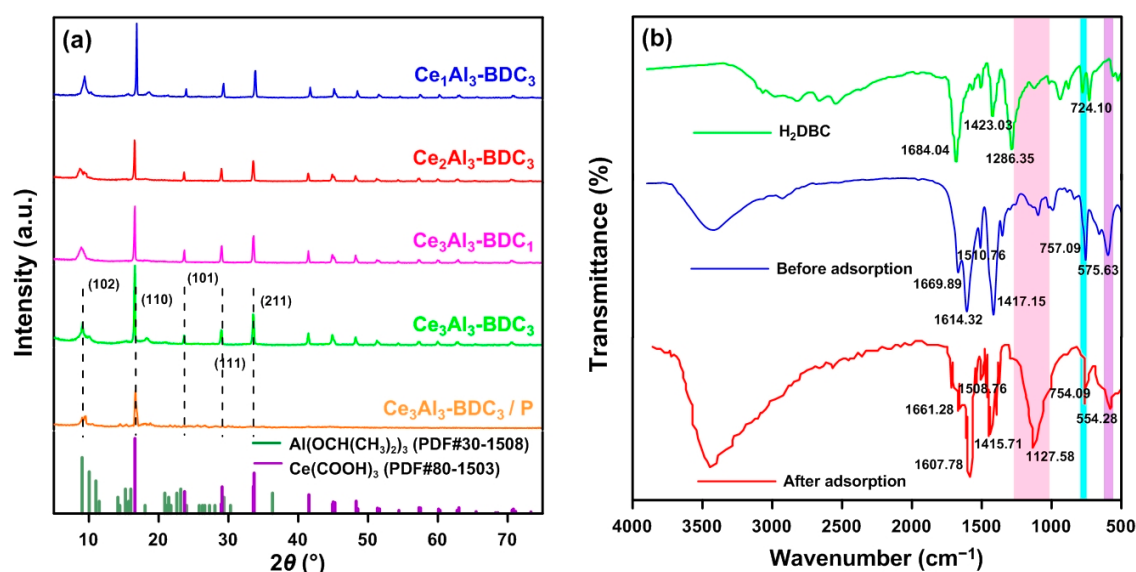


Figure 5. (a) XRD patterns at different molar ratios and Ce-Al-MOFs after phosphate adsorption compared with standard Ce- and Al-compounds; (b) FT-IR spectra of H_2BDC and $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ before and after phosphate removal.

3.4.2. FT-IR Analysis

To elucidate the phosphate adsorption mechanism of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$, FT-IR was utilized to analyze the transformation in functional groups of the sorbent before and after phosphate adsorption (Figure 5b). For the ligand H_2BDC , the characteristic symmetric and asymmetric stretching vibration frequency of the carboxyl carbonyl group ($-\text{COOH}$) appeared at 1684.04 cm^{-1} and 1423.03 cm^{-1} , respectively, and the bending vibration peak of the hydroxyl group ($-\text{OH}$) was located at 1286.35 cm^{-1} , all within the typical vibrational frequency ranges [42]. After the ligand coordinates with the Ce and Al, the asymmetric and symmetric stretching vibration peaks of the $\text{C}=\text{O}$ group in $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ red-shifted to 1417.15 cm^{-1} and 1669.89 cm^{-1} , respectively, and the adsorption peak at 1286.35 cm^{-1} for the ligand disappeared, indicating that Ce and Al coordinated with the carboxyl oxy-

gen atoms to form the target compound and partially replaced the -OH group [43–45]. It could also be inferred that the carboxylate was involved in the adsorbing process, on the basis of its diminished strength post-phosphate adsorption [32,43]. This provides robust evidence for the simultaneous introduction of Ce and Al into the prepared MOF. Additionally, distinct adsorption peaks were observed in the synthesized MOF at 1607.78 cm^{-1} , 757.09 cm^{-1} and 575.63 cm^{-1} . The peak at 1607.78 cm^{-1} can be attributed to the stretching vibration of the carboxylate and carbonyl groups in the MOFs [22]. Based on previous literature reports, the peaks at 757.09 cm^{-1} and 575.63 cm^{-1} are typical adsorption peaks of Al-OH and Ce-OH, respectively [20,22]. Compared to that before adsorption, a new broad and strong peak appeared at 1127.58 cm^{-1} after phosphate adsorption, corresponding to the asymmetric and bending vibrations of P-O [20,33]. Meanwhile, the characteristic adsorption peaks of the Al-O and Ce-O bonds red-shifted to 754.12 cm^{-1} and 554.28 cm^{-1} , respectively, reflecting the coordination between Ce, Al and P [22,32,46]. Because of the more significant red-shift of the Ce-O adsorption peak compared to the Al-O peak, it might suggest a stronger coordination between Ce and P. A similar inference can also be made based on the literature reporting a difference between the Ce-O peak and Al-O peak after P loading [20,32]. The FT-IR spectra indicates that the synthesized MOFs provide plentiful metal adsorption sites, enabling them to exhibit ligand exchange and chemical adsorption capabilities [33].

3.4.3. SEM and Energy-Dispersive Spectroscopy (EDS) Analyses

SEM was conducted to analyze the morphological characteristics of the bimetallic $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ framework. As shown in Figure 6a–d, the synthesized material does not have a fixed shape, with some particles appearing as rough, spherical granules and others as smooth, prismatic shapes. The diameter of the granules is approximately $0.3\text{--}0.5\text{ }\mu\text{m}$, while the length of the prismatic shapes ranges from $10\text{ to }20\text{ }\mu\text{m}$ with a cross-sectional width of about $1\text{--}3\text{ }\mu\text{m}$. According to previous reports, the MOF monomers formed by the coordination of metals Ce and Al with H_2BDC are porous rod-like and flake-like structures, respectively [20,22]. Therefore, the $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ observed in this study can exclude the possibility of being a mixture of Ce-MOFs or Al-MOFs. It has also been reported that for bimetallic MOFs, the morphology of the material would undergo transitional polymorphic changes with different molar ratios of the two metals [21,31].

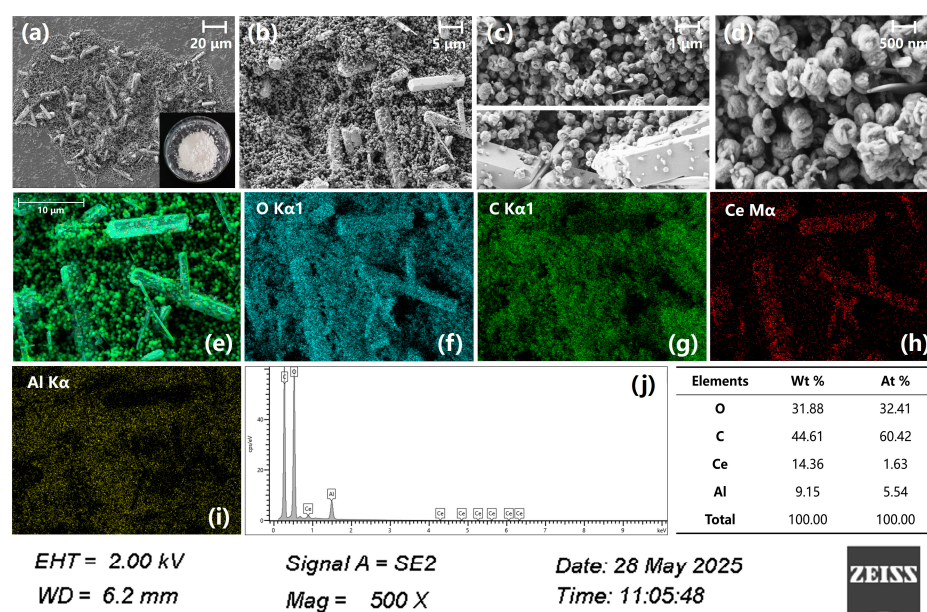


Figure 6. (a–d) SEM scanning and (e–j) EDS mapping of the $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ framework.

To further determine the elements; presence in $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ and analyze their distribution, EDS elemental distribution analysis was conducted (Figure 6e–j). The results clearly show that elements of O, C, Ce and Al are uniformly distributed on the surface of the adsorbent, indicating a rich and even distribution of active sites, which lays the structural foundation for the good adsorption performance of materials.

In addition, other Ce–Al–MOFs materials with different precursor molar combinations, also have similar morphological and elemental distribution characteristics according to SEM and EDS analyses, which are shown in Figures S1–S3 (Supplementary Materials).

3.4.4. N_2 Adsorption–Desorption Tests

The BET surface area and pore sizes of the adsorbent are vital factors in determining the adsorption performance. In this study, the pore size of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ was determined by N_2 adsorption–desorption tests. As presented in Figure 7a, the amount of captured N_2 gradually increased with the increase in relative pressure (P/P_0), and the adsorption amount sharply elevated when P/P_0 reached 0.9. As defined by the International Union of Pure and Applied Chemistry (IUPAC), this adsorption curve belongs to the Type-IV isotherm, featuring the typical H_3 hysteresis loop characteristic of mesoporous materials [47]. The BET surface area and average pore size of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ were $414.28 \text{ m}^2 \text{ g}^{-1}$ and 6.9 nm , respectively, with a higher BET surface area than other documented monometallic Ce–MOFs [48]. The high BET surface area and larger pore size compared to the phosphate ion diameter indicate a favorable advantage of this Ce–Al–MOF material for phosphorus adsorption.

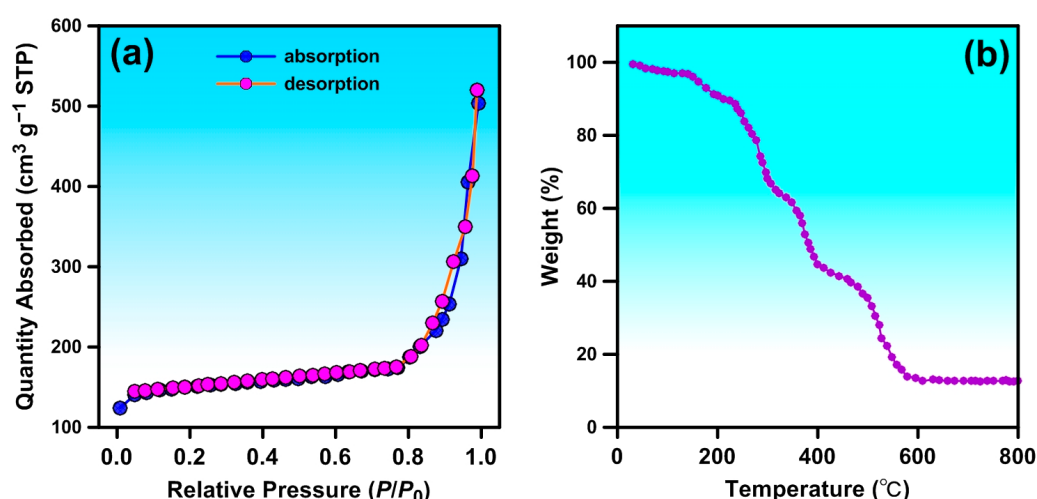


Figure 7. (a) N_2 adsorption–desorption isotherms; (b) TGA curve of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ (heating at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ under air atmosphere).

3.4.5. TGA

The thermal stability of the material was investigated using TGA analysis [49]. As presented in Figure 7b, the material experienced a series of mass losses as the temperature increased from $150 \text{ }^\circ\text{C}$ to $578 \text{ }^\circ\text{C}$. Below $150 \text{ }^\circ\text{C}$, the mass loss was negligible, indicating that $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ are thermally stable within this temperature range. Between 150 and $235 \text{ }^\circ\text{C}$, the material lost approximately 11.3% due to the removal of coordinated water, free water and DMF solvent [50]. When the temperature rose from $235 \text{ }^\circ\text{C}$ to $578 \text{ }^\circ\text{C}$, the material underwent three stages of sharp mass reduction, with the loss rate increasing to 86.1%, which should be associated with vigorous decomposition of the organic ligand. During this phase, the $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ thermal stability declined, indicating a collapse of structure. After the temperature exceeded $578 \text{ }^\circ\text{C}$, the material was almost completely decomposed,

with no further significant mass loss. In summary, the material exhibited good thermal stability before decomposition, demonstrating potential for practical applications.

3.5. Adsorption Kinetics

To further explore the complete absorbing process, the experimental data were fitted to the pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra-particle diffusion model, respectively. The mathematical expressions for these three kinetic models are described by Equations (3)–(5) [10,51].

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = K_p t^{\frac{1}{2}} + C \quad (5)$$

In the above equations, q_t and q_e represent the adsorption amount at time t (mg g^{-1}) and the equilibrium adsorption amount (mg g^{-1}), respectively; K_1 and K_2 are the rate constants for the pseudo-first-order and pseudo-second-order models (min^{-1}), respectively; K_p is the intra-particle diffusion constant ($\text{mg (g} \cdot \text{min}^{1/2})^{-1}$); and C is a constant.

Experimental tests were conducted under 100 mg L^{-1} and 200 mg L^{-1} of phosphate initial concentrations. The fitting results are shown in Figure 8, and the model parameters are listed in Tables 1 and 2. The coefficient of regression R^2 reflects the correlation between the experimental data and the kinetic model, with a higher R^2 value indicating a stronger correlation [22,33]. By comparing the fitting parameters and model curves, it is shown that the behavior of adsorption kinetic is more consistent with the Pseudo-second-order kinetic model (Table 1). In the case of intra-particle diffusion, since the plots of q_t versus $t^{1/2}$ are non-linear over the whole-time range (Figure 8d), it implies that more than one process affected the adsorption. Although it shows a linear pattern at the initial stage, the Weber–Morris intercepts (i.e., constant C in Equation (5)) reach 10.9 and 7.8 under 100 mg P L^{-1} and 200 mg P L^{-1} tests, respectively (Table 2), which indicate film diffusion across the boundary layer would play an important role, except for pore diffusion. To better elucidate the adsorbing process, the Boyd kinetic model [52] is further applied to differentiate the two diffusion methods:

$$B_t = -\ln \left[\frac{6}{\pi^2} \times (1 - F) \right] \quad (6)$$

$$F = \frac{q_t}{q_e} \quad (7)$$

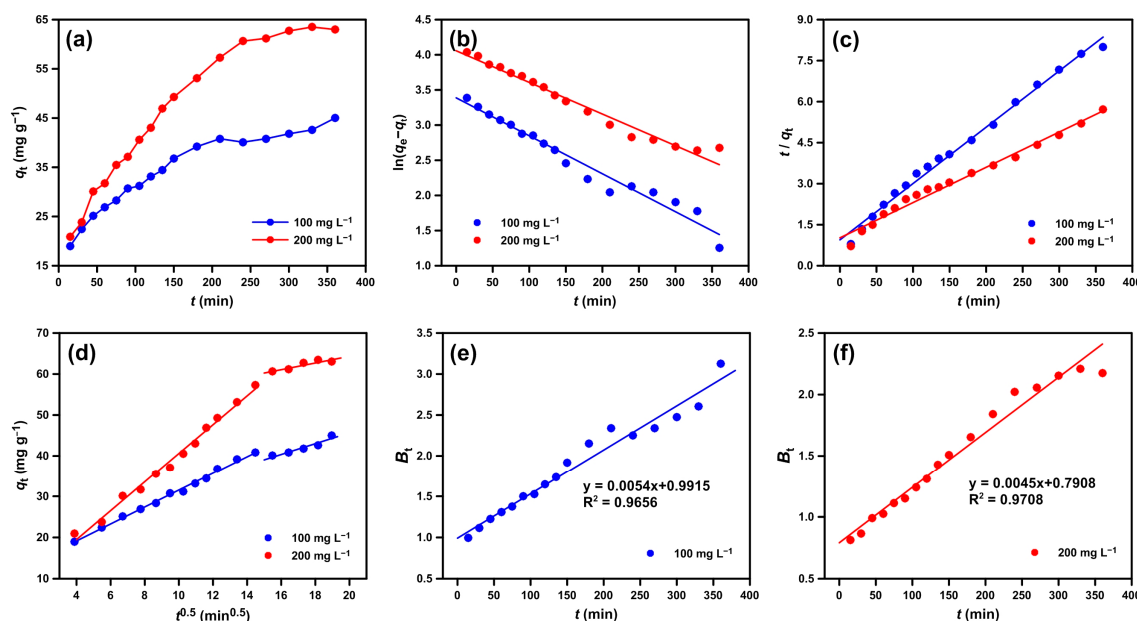
As shown in Figure 8e,f, the relations between B_t and t are linear ($R^2 = 0.965$ and 0.971) for both concentration scenarios but do not pass through the origin. This result confirms that surface film diffusion accounts for the rate limiting step where the external transport of phosphate is more dominant than internal transport [53,54].

Table 1. Fitted parameters of the pseudo-first order and pseudo-second order models.

Models	C_0 (mg L^{-1})	K_1	K_2	q_e (mg g^{-1})	R^2
Pseudo-first order	100	$(5.4 \pm 0.3) \times 10^{-3}$	-	29.61 ± 1.50	0.9656
	200	$(4.5 \pm 0.2) \times 10^{-3}$	-	57.81 ± 2.21	0.9708
Pseudo-second order	100	-	$(4.5 \pm 15) \times 10^{-4}$	48.54 ± 1.18	0.9920
	200	-	$(1.6 \pm 5.3) \times 10^{-4}$	77.52 ± 2.41	0.9831

Table 2. Fitted data of the intra-particle diffusion model.

C_0 (mg L ⁻¹)	Equation	R ²
100	$y = 10.9077 + 2.0622x$	0.9952
	$y = 19.1953 + 1.3234x$	0.9189
200	$y = 7.7802 + 3.1840x$	0.9939
	$y = 23.1588 + 2.1424x$	0.8092

**Figure 8.** (a) Adsorption amount at time t ; (b) pseudo-first-order model; (c) pseudo-second-order model; (d) intra-particle diffusion model; (e,f) Boyd kinetic model for phosphate removal of $Ce_3Al_3-BDC_3$. (pH = 6.0, the dosage was 1 g L⁻¹, the temperature was 25 °C and the concentrations were 100 mg P L⁻¹ and 200 mg P L⁻¹, respectively).

3.6. Thermodynamic and Isothermal Explorations

The exploration of thermodynamics and related parameters is crucial for understanding the sorbing process. In this study, the thermodynamic parameters ΔG° , ΔH° and ΔS° were calculated according to Equations (8) and (9) [21].

$$\Delta G^\circ = -RT \times \ln K_C \quad (8)$$

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

where K_C is the dimensionless Langmuir equilibrium constant; ΔG° , ΔS° and ΔH° represent the Gibbs free energy (kJ mol⁻¹), entropy change (J·(mol·K)⁻¹) and enthalpy change (kJ mol⁻¹), respectively; T is the thermodynamic temperature (K); and R is the gas constant, taken as 8.314 J·(mol·K)⁻¹.

The calculated results of these parameters are listed in Table 3. The positive value of ΔH° indicates that the entire adsorption process is endothermic. Combined with Figure 9b, it is observed that increasing the temperature is favorable for the adsorption process. The positive value of ΔS° implies an increase in the disorder of the system during the adsorption process, while the negative ΔG° across all tested temperatures and its increasing absolute value with temperature suggest a spontaneous and irreversible process of the adsorption reaction, and high temperatures can intensify the driving force of the adsorption process.

Therefore, it is inferred that the adsorption of phosphate by $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ is the result of the synergistic action of physical and chemical adsorption.

Table 3. Thermodynamic parameters of phosphate adsorption by $\text{Ce}_3\text{Al}_3\text{-BDC}_3$.

T (K)	ΔG^0 (kJ mol $^{-1}$)	ΔH^0 (kJ mol $^{-1}$)	ΔS^0 (J (mol·K) $^{-1}$)
298	-8.46 ± 0.24	23.196 ± 1.929	106.087 ± 6.186
308	-9.41 ± 0.24		
318	-10.72 ± 0.50		
328	-11.55 ± 0.41		

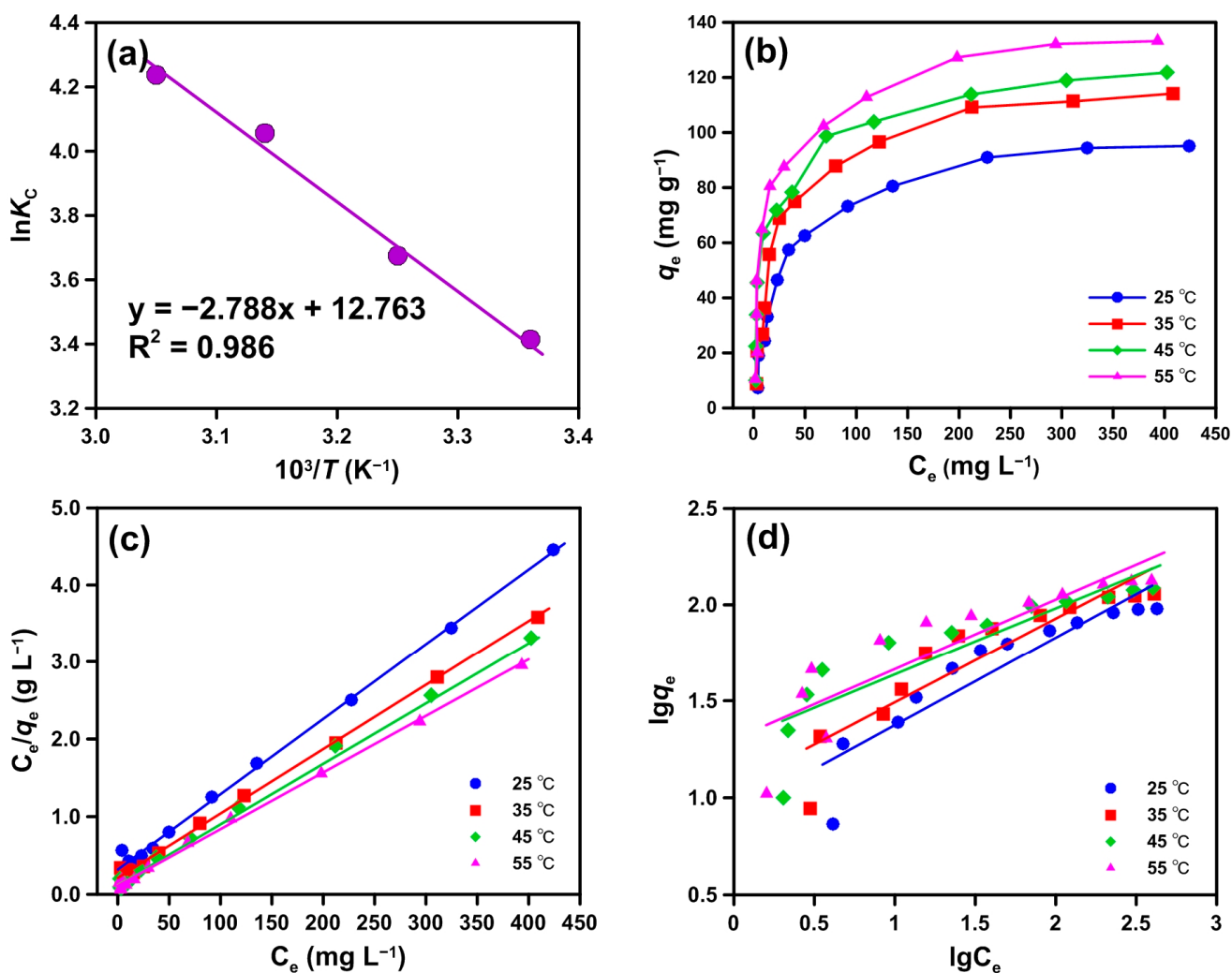


Figure 9. (a) Plotted $\ln K_c$ against $10^3 T^{-1}$; (b) adsorption thermodynamics; (c) Langmuir model; and (d) Freundlich model. (pH = 6.0, the dosage was 1 g L $^{-1}$ and the temperature was 25 °C).

Studies of the adsorption isotherm are also important for interpreting the removal mechanism of phosphate [11,13,18,21], as they elucidate the interactions between the adsorbate and the adsorbent, providing a theoretical basis for optimizing the performance of adsorption materials. In this study, the experimental data were fitted according to the Langmuir and Freundlich models, and the goodness of fit was assessed by the correlation coefficient.

The Langmuir model is described by the nonlinear Equation (10) and the linear Equation (11) as follows:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (10)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (11)$$

And the Freundlich model is defined by the nonlinear Equation (12) and the linear Equation (13):

$$q_e = K_f C_e^{\frac{1}{n}} \quad (12)$$

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \quad (13)$$

where q_e (mg g^{-1}) and q_m (mg g^{-1}) represent the equilibrium adsorption capacity and the theoretical maximum adsorption capacity, respectively; C_e is the equilibrium concentration of phosphate in the solution (mg L^{-1}); K_L is the Langmuir adsorption equilibrium constant (L mg^{-1}); K_f is the Freundlich constant, reflecting the adsorption capacity (L g^{-1}); and n is the adsorption intensity constant, indicating the strength of the adsorption force.

The experiments were repeated within the temperature range of 298–318 K, and the fitting features of the models are shown in Figure 9c,d and Table 4. It suggests that the Langmuir model was highly consistent with the experimental data, with a coefficient of regression $R^2 = 0.9974$, which was better than that from the Freundlich model. Consequently, the Langmuir model is more suitable for interpreting the thermodynamic adsorption process, indicating that the removal mechanism of phosphate is dominated by monolayer adsorption.

Table 4. Fitted parameters of the Langmuir and Freundlich models.

T (K)	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_f (L g^{-1})	n	R^2
298	103.09 ± 2.12	0.0304 ± 0.0030	0.9967	8.32 ± 2.08	2.204 ± 0.298	0.8451
308	120.48 ± 1.45	0.0394 ± 0.0037	0.9980	11.40 ± 2.65	2.297 ± 0.313	0.8435
318	123.46 ± 1.56	0.0577 ± 0.0110	0.9978	14.64 ± 3.13	2.578 ± 0.367	0.8317
328	136.99 ± 1.88	0.0692 ± 0.0103	0.9978	20.04 ± 4.51	2.757 ± 0.465	0.7790

3.7. A Brief Summary of the Adsorption Mechanism

The study of adsorption mechanisms usually requires a comprehensive examination of the adsorbent characteristics (including surface properties, charge states, crystal structure and chemical bonding characteristics), adsorption kinetics and thermodynamic behavior, as well as the specific interactions between the adsorbent and phosphate ions. Through characterization analysis and studies on adsorption thermodynamics and kinetics, it is revealed that the -OH groups on the surface of the adsorbent form a Ce/Al-O-P complex with phosphate in the solution through ligand exchange. Ce^{3+} and Al^{3+} , as hard acids, can facilely react with phosphate via electrostatic attraction as well as surface complexation (Figure 10), thereby achieving the efficient removal of phosphate. In addition, the kinetic and thermodynamic experiments indicated that the pseudo-second-order model and the Langmuir model fitted the experimental data well, suggesting a monolayer chemisorption of the adsorption process. In summary, the $\text{Ce}_3\text{-Al}_3\text{-BDC}_3$ synthesized in this study follows a phosphate adsorption mechanism of Ce-based or Al-based MOFs that is essentially similar to those previously documented [20,32,34,48].

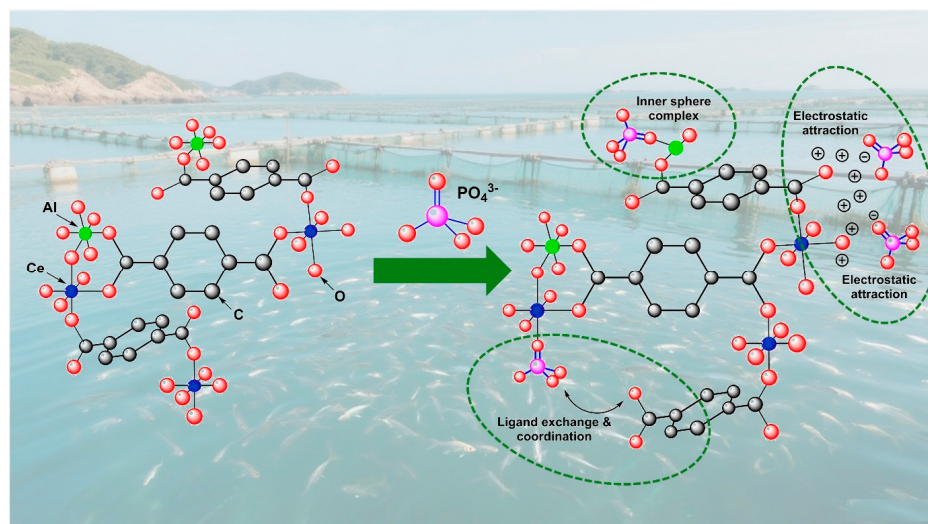


Figure 10. Mechanism schematic of bimetallic Ce-Al-MOFs for phosphate removal.

3.8. Performance Comparison of MOFs Adsorbents for Phosphate Removal

Meanwhile, the phosphorus removal performance of $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ synthesized in our study was compared with that of the reported MOFs-based adsorbents (Table 5). The results indicated that $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ exhibited excellent adsorption performance for phosphate among similar materials, confirming its significant application potential in the field of phosphorus removal from marine aquaculture effluents or environmental wastewater. Notably, as discussed in Section 3.2.3, the ionic strength of seawater systems would interfere with the phosphorus adsorption by the adsorbent. Therefore, the performance of this Ce-Al-MOF material in natural mariculture water requires further evaluation.

Table 5. Comparison of phosphate adsorption capacity with documented MOFs adsorbents.

Adsorbents	pH	Adsorption Capacity (mg P g ^{−1})	References
$\text{CuFe}_2\text{O}_4/\text{MIL-101(Fe)}$	2~10	3~30	[19]
Al-BDC	7.0	97.5	[20]
Al-PMA	7.0	42.25	
La/Al-BTC	7.0~8.0	85.2~210.3	[21]
F-Al/La MOFs	7.0	94.77~46.67	[31]
UiO-66-NH ₂	6.0~7.0	50.5	[23]
ZIF-8	2.8	38.22	[24]
Fe-Al-MOF	7.0	38.33	[32]
NH ₂ -MIL-101(Fe)	5.0~7.0	94.34	
NH ₂ -MIL-101(Al)	5.0~7.0	87.85	[33]
UiO-66	N.A.	85.0	
UiO-66-NH ₂	N.A.	92.0	[55]
La-MOFs	6.3	142.04	[56]
$\text{Fe}_3\text{O}_4/\text{NH}_2\text{-La-MOF}$	8.0	111.22	[57]
$\text{Ce}_3\text{Al}_3\text{-BDC}_3$	6.0	136.99	This study

3.9. Field Practical Application

To evaluate the adsorption performance of the $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ synthesized in our study in actual aquaculture seawater environments, the effluent seawater from the coastal aquaculture area in Ningde City, Fujian Province, and the indoor recycled aquaculture simulated (RAS) pond in Xiamen City were selected as the treatment targets (Figure 11). The seawater quality parameters of these two different environments are shown in Table S4. Briefly, 20 mg of synthesized $\text{Ce}_3\text{Al}_3\text{-BDC}_3$ was added into a polytetrafluoroethylene centrifuge

tube containing 50 mL of aquaculture seawater, and the mixture was magnetically stirred at 25 °C for 120 min. It showed that the concentration of reactive phosphate in the seawater from the coastal area decreased from 1.573 mg L⁻¹ to 0.046 mg L⁻¹ after adsorption, while the phosphate concentration in the indoor RAS pond decreased from 4.694 mg L⁻¹ to 0.084 mg L⁻¹, corresponding to the phosphorus removal efficiencies of 97.1% and 98.2%, respectively. The treated aquaculture seawater met the secondary discharge standard of reactive phosphate in aquaculture effluent seawater (<0.1 mg L⁻¹) specified in the “Discharge Requirements for Aquaculture Effluent” (SC/T9103-2007) [58]. To the best of our knowledge, the trial of MOF-based adsorbents for removing phosphorus from marine aquaculture wastewater has only been documented a few times so far. Comparing our field-test results with documented Ce-based and Al-based MOFs applications to natural waters, we find that the bimetallic Ce-Al-MOF exhibits a remarkable performance of phosphate removal under high-salinity conditions (Table S5). It indicates that the Ce₃Al₃-BDC₃ framework has an excellent effect on the removal of reactive phosphate from aquaculture effluent and highlights the potential application prospects of the sorbent in actual aquaculture seawater environments.

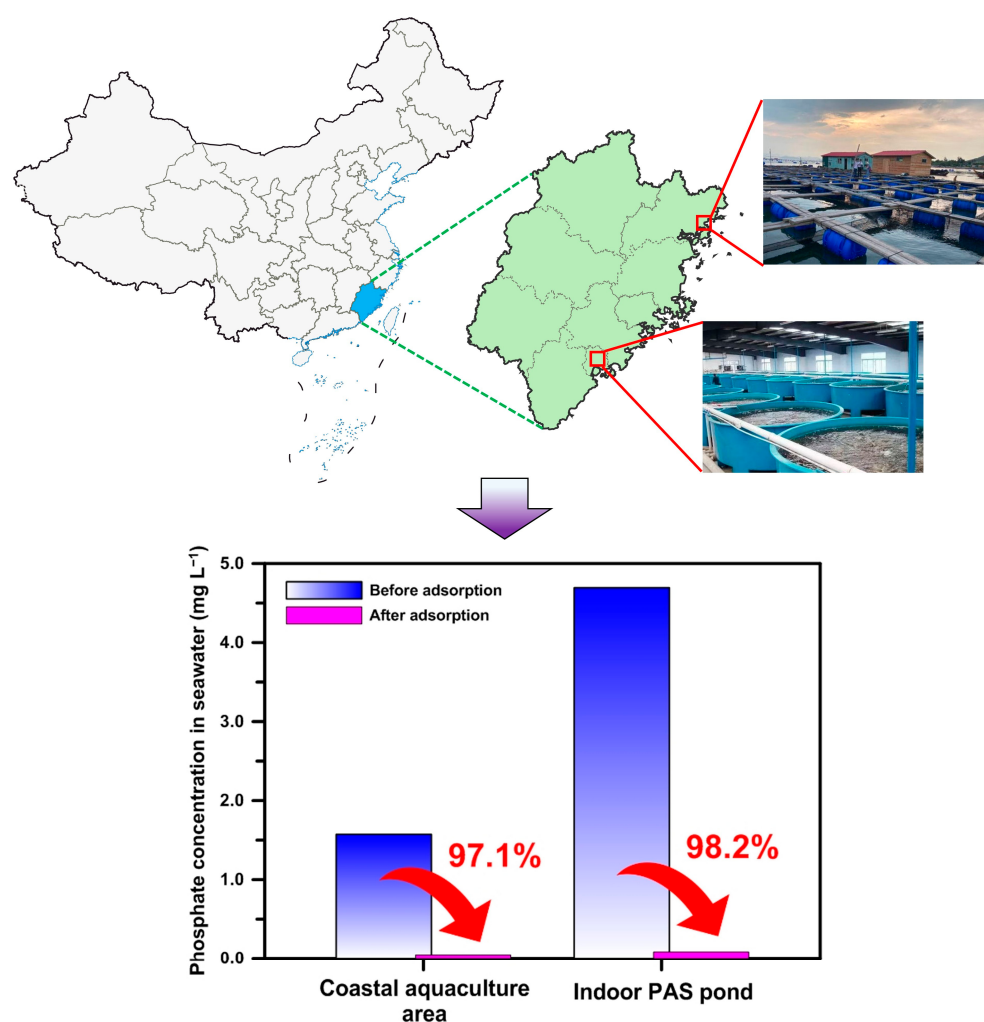


Figure 11. Field application of the Ce₃Al₃-BDC₃ framework on phosphate removal in the aquacultural coastal area and RAS pond. (The dosage was 0.4 g L⁻¹, the temperature was 25 °C, the mixing speed was 500 rpm and the mixing time was 2 h).

4. Conclusions

In this study, a series of novel bimetallic frameworks of Ce-Al-MOFs with H₂BDC as an organic ligand were synthesized via the rapid microwave heating method for the first time. These materials exhibit excellent adsorption performance with superior phosphorus removal capacity and efficiency over a wide pH range (2~10). Mechanism analysis indicated that physisorption, ligand exchange and electrostatic interactions together account for the phosphate adsorption from water. Moreover, the Ce-Al-MOFs show good selectivity, reusability and environmental safety. Meanwhile, the synthesized adsorbents can be effectively applied to the treatment of actual aquaculture effluents, which provides a promising technological solution for the management of eutrophication and the prevention of risks from aquaculture wastewater. For future work, there remains a lot to be explored regarding how to further improve these framework materials to enhance their phosphorus adsorption performance, reduce the industrial production costs, as well as evaluate the long-term stability and ecotoxicology in marine environments.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w17203019/s1>. Table S1. Effect of Cl[−] and SO₄^{2−} ions on phosphate adsorption under seawater level. Table S2. Detection of Ce and Al concentrations in the desorption eluate by ICP-MS. Table S3. Corresponding crystal planes of main diffraction peaks in the Ce₃Al₃-BDC₃. Table S4. Field trial results of Ce₃Al₃-BDC₃ material. Table S5. Comparison of phosphorus removal in natural waters by Ce-based and Al-based MOFs adsorbents. Figure S1. (a–d) SEM scanning and (e–j) EDS mapping of Ce₃Al₃-BDC₃ framework. Figure S2. (a–d) SEM scanning and (e–j) EDS mapping of Ce₁Al₃-BDC₃ framework. Figure S3. (a–d) SEM scanning and (e–j) EDS mapping of Ce₃Al₃-BDC₁ framework.

Author Contributions: Conceptualization, J.H. and X.M.; Data curation, Z.Z.; Formal analysis, J.Z. (Jiangnan Zhao) and Z.Z.; Funding acquisition, J.H.; Investigation, J.Z. (Jian Zeng) and J.Z. (Jiangnan Zhao); Methodology, J.Z. (Jian Zeng) and J.Z. (Jiangnan Zhao); Project administration, Z.C. and X.M.; Resources, J.H. and X.M.; Software, Z.Z.; Supervision, Z.C. and J.H.; Validation, Z.C.; Visualization, J.Z. (Jian Zeng); Writing—original draft, J.Z. (Jian Zeng); Writing—review and editing, J.Z. (Jian Zeng) and J.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Xiamen Key Laboratory of Intelligent Fishery (XMKLIF-OP-202302 and XMKLIF-ZR-202407) and the Fujian Provincial Education Research Project for Young and Middle-aged Teachers (Category: Science and Technology) (JAT210802).

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors acknowledge the valuable comments from the reviewers, which led to the significant improvement of the paper.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. FAO. *The State of World Fisheries and Aquaculture. Sustainability in Action*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2021. Available online: <https://coillink.org/20.500.12592/x69pbvz> (accessed on 16 October 2025).
2. Deng, X.; Song, M.; Li, Z.; Zhang, F.; Liu, Y. Renewable and Common Resources: Marine Fishery Resources. In *Environmental and Natural Resources Economics*; Springer: Singapore, 2024. [CrossRef]
3. Du, J.; Zhao, H.; Wang, Y.; Xie, H.; Zhu, M.; Chen, J. Presence and environmental risk assessment of selected antibiotics in coastal water adjacent to mariculture areas in the Bohai Sea. *Ecotoxicol. Environ. Saf.* **2019**, *177*, 117–123. [CrossRef]
4. Li, H.; Li, X.; Li, Q.; Liu, Y.; Song, J.; Zhang, Y. Environmental response to long-term mariculture activities in the Weihai coastal area, China. *Sci. Total Environ.* **2017**, *601–602*, 22–31. [CrossRef]
5. Lao, Q.; Chen, F.; Liu, G.; Chen, C.; Jin, G.; Zhu, Q.; Wei, C.; Zhang, C. Isotopic evidence for the shift of nitrate sources and active biological transformation on the western coast of Guangdong provinces, south China. *Mar. Pollut. Bull.* **2019**, *142*, 603–612. [CrossRef] [PubMed]

6. Li, M.; Liu, W.; Jiang, J. Analysis of spatial-temporal variation and nutritional status of environmental quality in the mariculture zone at the Yueqing Bay. *Mar. Environ. Sci.* **2021**, *40*, 724–731. [\[CrossRef\]](#)
7. Burkholder, J.M.; Noga, E.J.; Hobbs, C.H.; Glasgow, H.B., Jr. New phantom dinoflagellate is the causative agent of major estuarine fish kills. *Nature* **1992**, *360*, 768–769. [\[CrossRef\]](#)
8. Rabalais, N.N.; Turner, R.E.; Justic, D.; Dortch, Q.; Wiseman, W.J.; Sen Gupta, B.K. Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. *Estuaries* **1996**, *19*, 386–407. [\[CrossRef\]](#)
9. Indeewari, K.M.; Dunuweera, S.P.; Dunuweera, A.N.; Rajapakse, R.M.G. Synthesis and characterization of 2D magnesium oxide nanoflakes: A potential nanomaterial for effective phosphate removal from wastewater. *ChemistrySelect* **2022**, *7*, e202103973. [\[CrossRef\]](#)
10. Chen, D.; Yu, Y.; Cheng, P.; Arbid, Y.; Liu, H.; Zou, X.; Chen, T. Utilization of Waste Adsorbent Generated after Ca/Al-LDH Adsorption of High-Concentration Phosphate: Fluorine Removal. *J. Environ. Eng.* **2023**, *149*, 04022090. [\[CrossRef\]](#)
11. An, W.; Wang, Q.; Chen, H.; Liu, Y.; Hu, X.; Di, J. Efficient recovery of phosphate from water media by iron-magnesium functionalized lignite: Adsorption evaluation, mechanism revelation and potential application exploration. *Molecules* **2024**, *29*, 1252. [\[CrossRef\]](#)
12. Wu, B.; Fang, L.; Fortner, J.D.; Guan, X.; Lo, I.M.C. Highly efficient and selective phosphate removal from wastewater by magnetically recoverable La(OH)₃/Fe₃O₄ nanocomposites. *Water Res.* **2017**, *126*, 179–188. [\[CrossRef\]](#)
13. Wan, J.; Wu, B.; Lo, I.M.C. Development of FeO/Fe₃O₄ composites with tunable properties facilitated by Fe²⁺ for phosphate removal from river water. *Chem. Eng. J.* **2020**, *388*, 124242. [\[CrossRef\]](#)
14. Ma, P.; Zhu, J.; Du, X.; Yang, Y.; Hao, X.; An, X.; Hao, X.; Prestigiacomo, C. Specific separation and recovery of phosphate anions by a novel NiFe-LDH/rGO hybrid film based on electroactivity-variable valence. *J. Colloid Interface Sci.* **2022**, *626*, 47–58. [\[CrossRef\]](#)
15. Di, J.; Ruan, Z.; Zhang, S.; Dong, Y.; Fu, S.; Li, H.; Jiang, G. Adsorption behaviors and mechanisms of Cu²⁺, Zn²⁺ and Pb²⁺ by magnetically modified lignite. *Sci. Rep.* **2022**, *12*, 1394. [\[CrossRef\]](#)
16. Mon, M.; Bruno, R.; Ferrando-Soria, J.; Armentano, D.; Pardo, E. Metal-organic framework technologies for water remediation: Towards a sustainable ecosystem. *J. Mater. Chem. A* **2018**, *12*, 4912–4947. [\[CrossRef\]](#)
17. Fang, X.; Zhang, D.; Chang, Z.; Li, R.; Meng, S. Phosphorus removal from water by the metal-organic frameworks (MOFs)-based adsorbents: A review for structure, mechanism, and current progress. *Environ. Res.* **2024**, *243*, 117816. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Xie, Q.; Li, Y.; Lv, Z.; Zhou, H.; Yang, X.; Chen, J.; Guo, H. Effective adsorption and removal of phosphate from aqueous solutions and eutrophic water by Fe-based MOFs of MIL-101. *Sci. Rep.* **2017**, *7*, 3316. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Liu, Q.; Lin, S.; Khan, S.; Zhao, Y.; Guan, Q.; Geng, Z.; Guo, Y.; Chen, L.; Yang, X. Rapid removal and mechanism investigation of low concentration phosphate from wastewater by CuFe₂O₄/MIL-101(Fe) composite. *J. Nanostructure Chem.* **2022**, *12*, 117–127. [\[CrossRef\]](#)
20. Li, S.; Zhang, Q.; Yin, C.; Chen, J.; Yang, X.; Wang, S. Tuning microscopic structure of Al-based metal-organic frameworks by changing organic linkers for efficient phosphorus removal. *J. Clean. Prod.* **2021**, *292*, 125998. [\[CrossRef\]](#)
21. Zhu, Z.; Qin, L.; Liu, Y.; Zhang, Q.; Cheng, P.; Liang, W. Fabrication and mechanism of La/Al bimetallic organic frameworks for phosphate removal. *Chem. Eng. J.* **2023**, *479*, 147081. [\[CrossRef\]](#)
22. Song, J.; Yang, W.; Han, X.; Jiang, S.; Zhang, C.; Pan, W.; Jian, S.; Hu, J. Performance of Rod-Shaped Ce Metal-Organic Frameworks for Defluoridation. *Molecules* **2023**, *28*, 3492. [\[CrossRef\]](#)
23. Zhang, X.; Liu, M.; Han, R. Adsorption of phosphate on UiO-66-NH₂ prepared by a green synthesis method. *J. Environ. Chem. Eng.* **2021**, *9*, 106672. [\[CrossRef\]](#)
24. Shams, M.; Dehghani, M.H.; Nabizadeh, R.; Mesdaghinia, A.; Alimohammadi, M.; Najafpoor, A.A. Adsorption of phosphorus from aqueous solution by cubic zeolitic imidazolate framework-8: Modeling, mechanical agitation versus sonication. *J. Mol. Liq.* **2016**, *224*, 151–157. [\[CrossRef\]](#)
25. Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area. *Science* **2005**, *309*, 2040–2042. [\[CrossRef\]](#)
26. Moumen, E.; Bazzi, L.; El Hankari, S. Metal-organic frameworks and their composites for the adsorption and sensing of phosphate. *Coord. Chem. Rev.* **2022**, *455*, 214376. [\[CrossRef\]](#)
27. Lien, H.-L.; Yu, C.-H.; Kamali, S.; Sahu, R.S. Bimetallic Fe/Al system: An all-in-one solid-phase Fenton reagent for generation of hydroxyl radicals under oxic conditions. *Sci. Total Environ.* **2019**, *673*, 480–488. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Jeyaseelan, A.; Viswanathan, N. Design of Amino-Functionalized Benzene-1,4-Dicarboxylic Acid-Fabricated Lanthanum-Based Metal–Organic Frameworks for Defluoridation of Water. *J. Environ. Chem. Eng.* **2020**, *65*, 5328–5340. [\[CrossRef\]](#)
29. Haghighat, G.A.; Saghi, M.H.; Anastopoulos, I.; Javid, A.; Roudbari, A.; Talebi, S.S.; Ghadiri, S.K.; Giannakoudakis, D.A.; Shams, M. Aminated graphitic carbon derived from corn stover biomass as adsorbent against antibiotic tetracycline: Optimizing the physicochemical parameters. *J. Mol. Liq.* **2020**, *313*, 113523. [\[CrossRef\]](#)
30. He, J.; Xu, Y.; Xiong, Z.; Lai, B.; Sun, Y.; Yang, Y.; Yang, L. The enhanced removal of phosphate by structural defects and competitive fluoride adsorption on cerium-based adsorbent. *Chemosphere* **2020**, *256*, 127056. [\[CrossRef\]](#)

31. Song, Q.-X.; Xu, Y.-X.; Fang, N.; Liu, J.; Zhu, H.-L. Novel aluminum/lanthanum-based metal organic frameworks for phosphate removal from water. *J. Environ. Chem. Eng.* **2023**, *11*, 111418. [\[CrossRef\]](#)
32. Yang, Z.; Zhu, T.; Xiong, M.; Sun, A.; Xu, Y.; Wu, Y.; Shu, W.; Xu, Z. Tuning adsorption capacity of metal-organic frameworks with Al^{3+} for phosphorus removal: Kinetics, isotherm and regeneration. *Inorg. Chem. Commun.* **2021**, *132*, 108804. [\[CrossRef\]](#)
33. Liu, R.; Chi, L.; Wang, X.; Wang, Y.; Sui, Y.; Xie, T.; Arandiyán, H. Effective and selective adsorption of phosphate from aqueous solution via trivalent-metals-based amino-MIL-101 MOFs. *Chem. Eng. J.* **2019**, *357*, 159–168. [\[CrossRef\]](#)
34. Gao, Z.; Wei, Y.; Tian, X.; Liu, Y.; Lan, X.; Zhang, D.; Han, S.; Huo, P. A novel Ce/Fe bimetallic metal-organic framework with ortho-dodecahedral multilevel structure for enhanced phosphate adsorption. *Chem. Eng. J.* **2024**, *486*, 150284. [\[CrossRef\]](#)
35. Pandi, K.; Viswanathan, N. A facile synthesis of metal ion-imprinted graphene oxide/alginate hybrid biopolymeric beads for enhanced fluoride sorption. *RSC Adv.* **2016**, *6*, 75905–75915. [\[CrossRef\]](#)
36. Han, M.; Zhang, J.; Hu, Y.; Han, R. Preparation of Novel Magnetic Microspheres with the La and Ce-Bimetal Oxide Shell for Excellent Adsorption of Fluoride and Phosphate from Solution. *J. Environ. Chem. Eng.* **2019**, *64*, 3641–3651. [\[CrossRef\]](#)
37. Huo, Y.; Ding, W.; Huang, X.; Xu, J.; Zhao, M. Fluoride Removal by Lanthanum Alginate Bead: Adsorbent Characterization and Adsorption Mechanism. *Chin. J. Environ. Chem. Eng.* **2011**, *19*, 365–370. [\[CrossRef\]](#)
38. Li, M.; Liu, J.; Xu, Y.; Qian, G. Phosphate adsorption on metal oxides and metal hydroxides: A comparative review. *Environ. Rev.* **2016**, *24*, 319–332. [\[CrossRef\]](#)
39. Jeyaseelan, A.; Kumar, I.A.; Naushad, M.; Viswanathan, N. Fabrication of hydroxyapatite embedded cerium-organic frameworks for fluoride capture from water. *J. Mol. Liq.* **2022**, *354*, 118830. [\[CrossRef\]](#)
40. Han, X.; Liu, Z.; Bakhtari, M.F.; Luo, J.; Deng, L. Preparation of novel Ce (IV)-based MOF/GO composite and its highly effective phosphate removal from aqueous solution. *Environ. Eng. Res.* **2023**, *28*, 220647. [\[CrossRef\]](#)
41. Zhu, M.; Fu, W.; Zou, G. Urothermal synthesis of an unprecedented pillar-layered metal-organic framework. *J. Coord. Chem.* **2012**, *65*, 4108–4114. [\[CrossRef\]](#)
42. Wei, F.; Ren, Q.; Liang, Z.; Chen, D. Synthesis of Graphene Oxide/Metal-Organic Frameworks Composite Materials for Removal of Congo Red from Wastewater. *ChemistrySelect* **2019**, *19*, 5755–5762. [\[CrossRef\]](#)
43. Wei, F.; Chen, D.; Liang, Z.; Zhao, S.; Luo, Y. Synthesis and characterization of metal-organic frameworks fabricated by microwave-assisted ball milling for adsorptive removal of Congo red from aqueous solutions. *RSC Adv.* **2017**, *7*, 46520–46528. [\[CrossRef\]](#)
44. Wei, F.; Ren, Q.; Zhang, H.; Yang, L.; Chen, H.; Liang, Z.; Chen, D. Removal of tetracycline hydrochloride from wastewater by Zr/Fe-MOFs/GO composites. *RSC Adv.* **2021**, *11*, 9977–9984. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Yu, D.; Wu, M.; Hu, Q.; Wang, L.; Lv, C.; Zhang, L. Iron-based metal-organic frameworks as novel platforms for catalytic ozonation of organic pollutant: Efficiency and mechanism. *J. Hazard. Mater.* **2019**, *367*, 456–464. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Tan, Y.; Sun, Z.; Meng, H.; Han, Y.; Wu, J.; Xu, J.; Xu, Y.; Zhang, X. A new MOFs/polymer hybrid membrane: MIL-68(Al)/PVDF, fabrication and application in high-efficient removal of p-nitrophenol and methylene blue. *Sep. Purif. Technol.* **2019**, *215*, 217–226. [\[CrossRef\]](#)
47. Farrag, M. In situ preparation of palladium nanoclusters in cerium metal-organic frameworks Ce-MOF-808, Ce-Uio-66 and Ce-BTC as nanoreactors for room temperature Suzuki cross-coupling reaction. *Microporous Mesoporous Mater.* **2021**, *312*, 110783. [\[CrossRef\]](#)
48. Zhang, L.; Mao, D.; Qu, Y.; Chen, X.; Zhang, J.; Huang, M.; Wang, J. Facile Synthesis of Ce-MOF for the Removal of Phosphate. *Fluoride Arsen. Nanomater.* **2023**, *13*, 3048. [\[CrossRef\]](#)
49. Yao, Z.-Q.; Li, G.-Y.; Xu, J.; Hu, T.-L.; Bu, X.-H. A Water-Stable Luminescent Zn-II Metal-Organic Framework as Chemosensor for High-Efficiency Detection of Cr-VI-Anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) in Aqueous Solution. *Chem. A Eur. J.* **2018**, *24*, 3192–3198. [\[CrossRef\]](#)
50. Zhang, N.; Sun, L.-X.; Xing, Y.-H.; Bai, F.-Y. A Double-Walled Thorium-Based Metal-Organic Framework as a Promising Dual-Function Adsorbent for Efficiently Capturing Iodine and Dyes. *Cryst. Growth Des.* **2019**, *19*, 5686–5695. [\[CrossRef\]](#)
51. Zhuang, H.; Yan, G.; Wang, J.; Hu, Z.; Yan, S.; Sun, Y.; Guo, T.; Hu, J.; Rehemán, A. Efficient Adsorption of Hg(II) Ions Benefits from the Synergistic Effect between Sulfur-Containing MOF-808 and C_3N_4 . *J. Environ. Eng.* **2024**, *150*, 04024050. [\[CrossRef\]](#)
52. Boyd, G.E.; Adamson, A.W.; Myers, L.S., Jr. The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. II. Kinetics. *J. Am. Chem. Soc.* **1947**, *69*, 2836–2848. [\[CrossRef\]](#)
53. Mittal, A.; Kurup, L.; Mittal, J. Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers. *J. Hazard. Mater.* **2007**, *146*, 243–248. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Banerjee, S.; Chattopadhyaya, M.C. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. *Arab. J. Chem.* **2017**, *10*, S1629–S1638. [\[CrossRef\]](#)
55. Lin, K.-Y.A.; Chen, S.-Y.; Jochems, A.P. Zirconium-based metal organic frameworks: Highly selective adsorbents for removal of phosphate from water and urine. *Mater. Chem. Phys.* **2015**, *160*, 168–176. [\[CrossRef\]](#)
56. Liu, H.; Guo, W.; Liu, Z.; Li, X.; Wang, R. Effective adsorption of phosphate from aqueous solution by La-based metal-organic frameworks. *RSC Adv.* **2016**, *6*, 105282–105287. [\[CrossRef\]](#)

57. Luo, F.; Feng, X.; Li, Y.; Zheng, G.; Zhou, A.; Xie, P.; Wang, Z.; Tao, T.; Long, X.; Wan, J. Magnetic amino-functionalized lanthanum metal-organic framework for selective phosphate removal from water. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *611*, 125906. [[CrossRef](#)]
58. SC/T 9103-2007; Water Drainage Standard for Sea Water Mariculture. Ministry of Agriculture of the People's Republic of China: Beijing, China, 2007. Available online: https://www.cssn.net.cn/cssn/list?sub_type=ST_N_CSIC&orderby=-a101 (accessed on 16 October 2025).

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