Optimization of Phosphate Oxygen Isotope Pretreatment Measurement Method Based on Phosphate In-situ Enrichment Blanket

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Abstract

Phosphate oxygen isotope analysis is an effective tool for investigating phosphorus migration and transformation in water bodies. However, existing pretreatment methods for this technology are severely restricted by large sample requirements, cumbersome operation, and poor applicability. To optimize the pretreatment method, hydrated zirconia was prepared by liquid-phase precipitation. Zeolite, D001 macroporous resin, activated carbon, and ceramsite were selected as potential support materials. The optimum zirconium support material was selected after field enrichment and laboratory elution experiments. The optimum in situ enrichment time, material dose, and elution time were determined using response surface methodology. The D001 resin provided the best selective adsorption and elution capacity for phosphate. The optimum parameters for an in situ phosphate-enrichment blanket were obtained by response surface optimization as a zirconium-loaded D001 resin mass of 13 g, enrichment time of 360 min, and elution time of 853 min. After purification, a bright yellow Ag_3PO_4 solid was obtained. The results showed that the optimization method was reliable. These results provide a foundation for the application of phosphate oxygen isotope analysis in freshwater bodies.

Introduction

Phosphorus is an important biogenic element but excess dissolved phosphate in water bodies contributes to eutrophication (Davies et al. 2014). Investigations of the source of phosphorus and cycling process in freshwater bodies are difficult and limited by methodology. Some studies have indirectly investigated the sources, migration, and transformation of phosphorus in water bodies using sediment fingerprinting (Lübeck et al. 2020), microbial community fingerprinting (Heathwaite and Johnes 2015), and spatio-temporal variation in phosphorus speciation (Heathwaite and Johnes 2015). However, challenges remain with quantitative analysis of phosphorus sources and the phosphorus cycle.

Stable isotope analysis is an effective tool for tracing the sources and cycles of elements in nature. Carbon and nitrogen are widely used in the stable isotope analysis of sources and cycles (Huang et al. 2019). Because there is only one stable isotope of phosphorus, it is impossible to use the stable isotope of phosphorus to trace its sources and cycle (Liu et al. 2021). However, most phosphorus in nature exists in the form of orthophosphate (PO_4^{3-}), and oxygen has three stable isotopes (^{16}O , ^{17}O , and ^{18}O) (Jaisi and Blake 2014). Therefore, the phosphate oxygen isotope ($\delta^{18}\text{O}_\text{p}$) can be used to trace phosphorus sources and the phosphorus cycle. Research in this area is currently in a stage of rapid development. This technology involves enriching phosphate in environmental samples, separation, and purification to obtain a bright yellow Ag_3PO_4 solid. The phosphorus stable isotope ratio is then measured by high temperature pyrolysis-stable isotope ratio mass spectrometry (Gross et al. 2013). The main issues hindering wide application of this technology are the cumbersome pretreatment method, large sample requirements, and poor method adaptability. Phosphate-selective adsorption materials could be used to achieve in situ phosphate enrichment and highly efficient laboratory elution to optimize the pretreatment method (Tcaci et al. 2019). This will avoid the need for collection of a large number of samples and simplify the

subsequent purification steps (Liu et al. 2020). When optimizing the phosphate oxygen isotope pretreatment method, phosphate-selective adsorption materials could be used to prepare an efficient in situ enrichment device to achieve rapid enrichment and efficient laboratory elution of phosphate.

Hydrated zirconia is a phosphate-selective adsorption material that has promising application prospects (Liu et al. 2018). The metal-based inner layer of this material can provide selective adsorption of phosphate (Li et al. 2020). To date, many studies have investigated preparation methods and the adsorption performance of hydrated zirconia (Feng et al. 2021; Wang and Wei 2021; Li et al. 2019; Bui et al. 2021). However, because hydrated zirconia is a powder, it is not suitable for release and recovery in rivers. To solve these issues, hydrated zirconium oxide loaded on the surface of a porous granular material could be used as a selective adsorption material for phosphate. Various studies have investigated the preparation and adsorption performance of zirconium support materials, such as a hydrated zirconium oxide support resin (Sowmya and Meenakshi 2014), natural zeolite (Vera-Puerto et al. 2020; Mosa et al. 2020), activated carbon (Almanassra. et al. 2021; Velu et al. 2020), ceramsite (Deng et al. 2019; Qiu et al. 2012), oyster shells (Lee et al. 2005; Tran et al. 2020), activated carbon fibers (Sakamoto et al. 2021), and bentonite (Xi et al. 2021; Angkawijaya et al. 2020). The maximum adsorption capacity range for these materials is 4.43–26.12 mg·g⁻¹. Most of these materials have been tested in highly concentrated phosphate solutions with the aim of obtaining high-performance phosphate-selective adsorbents for remediation of eutrophic water bodies. Little attention has been paid to phosphate elution from the support materials. In addition, the maximum adsorption capacity and time to reach adsorption equilibrium are not important when evaluating the enrichment effect for use in freshwater with a low phosphate concentration.

To address these issues, we used hydrated zirconia as a phosphate-selective adsorption material, and comprehensively investigated the macroporous adsorption, mechanical strength, economics, and availability. We evaluated zeolite, D001 macroporous resin, activated carbon, and ceramsite as potential support materials. The optimum support material was selected after laboratory experiments, and an in situ phosphate-enrichment blanket was prepared using this material. Response surface methodology was used to determine the optimum in situ enrichment time, material dose, and elution time for rapid in situ enrichment and highly efficient elution of phosphate in the pretreatment method. This method could help promote the application of phosphate oxygen isotope analysis in freshwater bodies.

Materials And Methods

Preparation and optimization of the phosphate-enrichment materials

Preparation of the phosphate-enrichment materials

First, a zirconium solution was prepared by dissolving 150 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 500 mL of a mixture of 10% HCl, 17% NaCl, 10% ethanol and ultrapure water. Four groups of mixed solutions by this method were prepared. Next, 150 g of support material was added to the solution. The support material was either macroporous D001 resin, activated carbon, natural zeolite, or ceramsite. The solutions were then heated at 60°C for 24 h before filtration. After filtration, the D001 resin, activated carbon, natural zeolite, or ceramsite loaded with zirconium was added to 500 mL of 1 M NaOH. The samples were heated again at 60°C for 24 h. Subsequently, the enrichment material were filtered out and the samples were washed with deionized water until the pH of the eluate was close to neutral. The material was then dried at 60°C for 24 h to obtain zirconium supported on D001 resin, activated carbon, natural zeolite, or ceramsite (Li et al. 2020).

Optimization of the phosphate-enrichment materials

To evaluate the adsorption effect, the Langmuir adsorption isotherm model was used to determine the maximum adsorption capacities of the enrichment materials as follows:

$$q_t = \frac{K_l q_{\max} C}{1 + K_l C} \quad (1)$$

where q_t is the phosphorus equilibrium adsorption capacity of the phosphate-enrichment material ($\text{mg} \cdot \text{g}^{-1}$), $q_{\max}$ is the maximum adsorption capacity of the phosphate-enrichment material ($\text{mg} \cdot \text{g}^{-1}$), C is the equilibrium phosphorus concentration in the solution, ($\text{mg} \cdot \text{L}^{-1}$), and K_l is a constant.

A sample (10 g) of each phosphate-enrichment material was weighed into a 100-mL conical flask, and 100 mL of phosphate solution (10, 30, 50, 100, 150, 200, 250, or 300 $\text{mg} \cdot \text{L}^{-1}$) was added. After shaking at 25°C for 24 h (150r/min), the concentration of phosphorus (C in Eq. 1) in the supernatant was determined by the molybdenum–antimony anti-colorimetric method. The value of q_t was calculated from the difference between the mass of added phosphorus and the mass of residual phosphorus in the solution. The values of C and q_t were input into Eq. 1 to obtain K_l and $q_{\max}$ by fitting.

To evaluate the elution effect, the phosphate-enrichment material obtained after the adsorption effect experiments was added to 100 mL of 1 M NaOH. The solution was shaken at 25°C for 24 h and then filtered to obtain the phosphate-containing eluate. Next, 5 mL of the eluate was added to 5 mL of 1 M HNO_3 , and the molybdenum–antimony anti-colorimetric method was used to determine the mass of phosphate. The phosphate elution rate was calculated using the following equations:

$$m_x = (5 + 5) \times C_{\text{测}} \times \frac{100}{5}, \quad (2)$$

$$\eta = \frac{m_x}{m} \times 100, \quad (3)$$

where m_x is the total mass of phosphate removed from the enrichment material (mg); C is the concentration of phosphate in the eluate ($\text{mg}\cdot\text{mL}^{-1}$), η is the elution rate of the phosphate-enrichment material (%), and m is the mass of phosphate adsorbed on the enrichment material (mg).

The enrichment and elution experiments were carried out in three groups in parallel and the average for the three groups was used for analysis.

Placement and recovery of the in situ enrichment blankets

The in situ phosphate-enrichment blanket was composed of nylon mesh, foam, the enrichment material, and an iron plate (Fig. 1). We determined that the optimum enrichment material was zirconium-loaded resin (Section 1.1), and this was used as the phosphate-enrichment material in the in situ enrichment blanket. To ensure the blanket was easy to use, we gave it dimensions of 5 cm × 14 cm. The blanket was divided every 2 cm so that the material would be in full contact with the water. An iron plate was added to the bottom of the enrichment blanket to weigh it down and ensure it would be completely immersed in the water and not float on the surface. Foam was placed on top of the enrichment blanket to stop the entire device from sinking into the water. The phosphate-enrichment material was placed in between the foam and the iron plate in five layers. To prevent weeds on the water surface and waves from affecting the measurements, the enrichment blanket was used to enrich phosphate in water from at least 2 cm below the surface. The nylon mesh allowed for full contact between the enrichment material and the water, and stopped loss of the material into the water. Enrichment of PO_4^{3-} was conducted in Taiji Lake (Hebei, China) using the in situ phosphate-enrichment blanket. After enrichment, the device was recovered and the support material was removed and placed in a 250-mL Erlenmeyer flask. Then, 200 mL of 1 M NaOH solution was added and the flask was shaken continuously for several hours. Finally, the mixture was filtered through a 0.45- μm filter membrane and the phosphate-containing eluate was retained.

Single-factor and response surface methodology optimization of phosphorus adsorption on the in situ enrichment blanket

Single-factor experiments

In preliminary experiments, we found that the phosphate enrichment effect was poor when the mass of the enrichment material was too low. However, when the mass of the enrichment material was too high, the enrichment effect was not obvious. These results might be related to the specific hydrodynamic conditions of Taiji Lake. To determine the optimum mass of enrichment material to add to a single enrichment blanket, zirconium-loaded blankets were prepared with different masses (5, 10, 15, 20, 25, and 30 g) of the enrichment material. The blankets were placed in Taiji Lake for 24 h. The optimum mass of the material was determined from the phosphate concentration measured in the eluate obtained after elution with 100 mL of 1 M NaOH solution for 24 h.

If the enrichment time is too short, the phosphate is not sufficiently enriched. However, if it is too long, isotope fractionation of the enriched phosphate occurs under the action of microorganisms. To investigate the enrichment time, we prepared eight zirconium-loaded enrichment blankets containing the optimum mass of enrichment material and placed them in Taiji Lake at the same time. The blankets were removed at 15, 30, 60, 120, 240, 360, 540, and 1440 min, and then eluted with 100 mL of 1 M NaOH for 24 h. The optimum enrichment time was determined after calculating the concentration of phosphate in the eluate.

To investigate the elution time, seven zirconium-loaded enrichment blankets were prepared, placed in Taiji Lake, and removed after the optimum enrichment time. Then, 100 mL of 1 M NaOH was used for elution for 30, 60, 120, 240, 360, 540, or 1440 min. The optimum elution time was determined after calculating the concentration of phosphate in the eluate.

Response surface optimization

Three variables, the mass of enrichment material (X_1), phosphate enrichment time (X_2), and phosphate elution time (X_3), were investigated in single-factor experiments. The phosphate elution volume (Y) was the response value. Seventeen sets of optimization conditions for in situ enrichment experiments were automatically generated by Design Expert 8.0 software. A response regression model was established and a response surface curve was constructed (Tran et al. 2021). The results were used to obtain the optimum parameters for the in situ enrichment blanket.

Optimization of purification process

Taking into consideration of the water quality of Taiji Lake, and results from preliminary experiments, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was replaced with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to avoid the introduction of Cl^- and prevent precipitation of AgCl (Tamburini et al. 2010), thus affecting the formation of the final product Ag_3PO_4 precipitation, on the basis of the traditional purification process of ammonium phosphomdate + magnesium ammonium phosphate.. We replaced NH_4NO_3 with HNO_3 and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution to make the experiments safer. The purification process is shown in Figure 2.

Reliability test

There is a lack of isotope fractionation during conventional adsorption and desorption of phosphate (Longinelli et al. 1976; Jaisi and Blake 2010), which means that isotope fractionation will not occur in the present purification method (Liu et al. 2021). Consequently, the reliability tests focused on whether high-purity Ag_3PO_4 could be generated because all current phosphate oxygen isotope pretreatment methods have Ag_3PO_4 as the end point (Jaisi et al. 2017; Yuan et al. 2019; Lei et al. 2019). We selected five sampling points in Taiji Lake for testing, and evaluated the reliability of the method for generation of bright yellow Ag_3PO_4 , which was detected by X-ray crystallography after purification.

Results

Optimization of the enrichment material

Adsorption effect of the phosphate-enrichment material

The Langmuir model provided a good fit for the adsorption effects of the various materials (Table 1). Among the four materials, zirconium-loaded resin had the highest adsorption capacity at $19.547 \text{ mg}\cdot\text{g}^{-1}$. Consequently, this material was selected for phosphate enrichment.

Table 1
Adsorption isotherm parameters of phosphate for four materials

材料	Langmuir		
	$q_{\max}$	K_L	r^2
	($\text{mg}\cdot\text{g}^{-1}$)	($\text{L}\cdot\text{mg}^{-1}$)	
Zirconium modified resin	19.547	0.488	0.999
Zirconium modified activated carbon	4.213	0.011	0.986
Zirconium modified zeolite	0.358	0.123	0.986
Zirconium modified ceramsite	0.608	0.024	0.991

Elution of the phosphate-enrichment material

Elution was investigated for the four in situ phosphate-enrichment materials (Fig. 3). The elution rates of zirconium-loaded activated carbon, zeolite, and ceramsite were more than 100%, which indicated that these three materials contained phosphate. Although the elution rate of zirconium-loaded D001 resin increased slowly with increases in the phosphate concentration, the mass of phosphate eluted was not larger than that adsorbed.

Next, we investigated whether zirconium-supported on activated carbon, zeolite, or ceramsite would precipitate phosphate. Samples (5, 10, and 20 g) of zirconium-supported resin, activated carbon, zeolite, and ceramsite were added to 100 mL of 1 M NaOH with shaking at 25°C for 30, 60, 120, 240, 360, 540, or 1440 min. The samples were then filtered and the eluate (5 mL) was neutralized with 5 mL of 1 M HNO_3 . The molybdenum–antimony anti-colorimetric method (Sinopharm Group Chemical Reagent Co., Ltd., 2007) was used to determine the phosphate mass to establish whether the enriched materials themselves contained phosphate. The phosphate elution rate was calculated using Eqs. 2 and 3. The results for phosphate elution from the four enrichment materials are shown in Figure 4. Phosphate was detected in the eluate for activated carbon, zeolite, and ceramsite loaded with zirconium, which indicated that these three materials themselves contained some phosphate. Mixing of phosphate from the enrichment material with that in the water will affect the oxygen isotope analysis results. Considering these results in combination with those for the adsorption effect, we decided that zirconium-loaded resin was the optimum material for use in the in situ phosphate-enrichment blanket.

Single-factor experiments

Figure 5(a) shows the effect of the mass of zirconium-loaded resin on the mass of phosphate eluted. The mass of phosphate eluted was 0.127 mg when the zirconium-loaded resin dose was 5 g, and 0.196 mg when the zirconium-loaded resin dose was more than 10 g. With increases in the mass of zirconium-loaded resin, the number of adsorption active sites will increase. However, too much material will slow phosphorus exchange between the inner material and the water body. This phenomenon will be more obvious in still or slow water bodies. The optimum dose of zirconium-loaded resin was set at 10 g on the basis of the experimental results and in consideration of the economics.

Figure 5(b) shows the effect of the enrichment time on phosphate elution. As the enrichment time increased, the mass of phosphate eluted from the zirconium-loaded resin increased first quickly and then slowly, and then stabilized at 540 min. The mass of phosphate eluted from the zirconium-loaded resin reached saturation at 540 min. Accordingly, 540 min was selected as the optimum enrichment time for phosphate.

Figure 5(c) shows the effect of the phosphate elution time on the mass of phosphate eluted. The mass of phosphate eluted from the zirconium-loaded resin increased linearly with increases in the elution time, and stabilized after 600 min when the phosphate was fully released. The optimum phosphate elution time was set at 540 min.

Response surface results

Follow-up experiments were performed using the 17 orthogonal experimental groups generated by Design Expert. Phosphate elution was compared for the experimental groups (Table 2). The significance of the quadratic model was evaluated by analysis of variance. The F value of the model was 71.50 and P was < 0.0001 , which indicated that the fit of the regression model was significant. The corrected coefficient of determination of the model was $r_{adj}^2 = 0.98$, which indicated that approximately 98.00% of the response value could be explained by this model. The lack of fit term $P = 0.6950$ (> 0.05) was not significant, which further illustrated the significance of the model. The precision was 21.855 (> 4), which indicated that the model had high precision. The F values of the phosphate-enrichment materials A and B were 53.94 and 46.25, respectively. Both of the P values were < 0.0001 , which indicated that the two materials had a significant impact on the response value.

Table 2
Experimental design and experimental results of response surface analysis

Material dosage X1(g)	Enrichment time X2(min)	Elution time X3(min)	Lease quality Y(mg)
17.50	15.00	30.00	0.18
5.00	727.50	1440.00	0.08
17.50	1440.00	1440.00	0.30
17.50	15.00	1440.00	0.08
17.50	1440.00	30.00	0.21
17.50	727.50	735.00	0.30
30.00	727.50	30.00	0.18
30.00	727.50	1440.00	0.30
17.50	727.50	735.00	0.28
5.00	1440.00	735.00	0.10
17.50	727.50	735.00	0.28
5.00	15.00	735.00	0.07
17.50	727.50	735.00	0.30
30.00	1440.00	735.00	0.30
17.50	727.50	735.00	0.28
5.00	727.50	30.00	0.07
30.00	15.00	735.00	0.08

To understand the interaction of each factor and its influence on the response value, a contour map and three-dimensional response surface map were constructed using the regression equation (Juwar and Rathod 2021). The shape of the contour map can reflect the interaction of two factors. If the contour line is close to elliptical, the interaction of the two factors is stronger, whereas if the contour line is close to circular, the interaction of the two factors is weaker (Jensen 2017). The interactions of three factors in the preparation and application of the phosphate in situ enrichment blanket and the effects on the response value are shown in Fig. 6–8.

The slope of the response surface in Figure 6 was low and the contour was circular, which meant that the phosphate elution time and quality of the enrichment material had no effect on each other. The contours in Figures 7 and 8 were close to elliptical, which indicated that the phosphate enrichment time had an obvious interaction with the quality of the phosphate-enrichment material, and the phosphate enrichment time had an obvious interaction with the phosphate elution time. The slope of the phosphate-enrichment material quality was greater than that of the phosphate enrichment time, which indicated that the

phosphate-enrichment material quality had a stronger influence on the phosphate elution volume than the enrichment time. The phosphate enrichment time slope was greater than that of the elution time, which indicated that the phosphate enrichment time had a stronger influence on the elution volume of phosphate than the elution time. Therefore, the quality of the phosphate-enrichment material has the most obvious influence on the phosphate elution volume, followed by the phosphate enrichment time, and finally the phosphate elution time.

The condition optimization function of Design Expert 8.0 software was used to optimize the parameters of the phosphate-enrichment material. The optimum mass of the enrichment material was 13.150 g, the optimum enrichment time was 360.000 min, and the optimum elution time was 852.550 min. The predicted mass of phosphate eluted with these parameters was 0.240 mg. To ensure the in situ phosphate-enrichment blanket was easy to prepare, we rounded the parameters to 13 g for the enrichment material mass, 360 min for the enrichment time, and 853 min for the elution time. The average mass of phosphate eluted was 0.215 mg with these parameters. The actual value was close to the predicted value, which showed that the predicted result was credible.

Reliability verification

The reliability of the optimized pretreatment method was verified using its ability to generate bright yellow Ag_3PO_4 . An in situ phosphate-enrichment blanket was prepared using 13 g of zirconia-loaded D001 resin. After enrichment for 360 min, the resin was eluted for 853 min in the laboratory. The eluate was further purified by the optimized purification process. Finally, a bright yellow solid was obtained. The X-ray crystallography pattern of the bright yellow solid showed it was Ag_3PO_4 (Fig. 9). Therefore, the method is reliable.

Discussion

Phosphate oxygen isotope analysis is challenging because of large sample requirements, cumbersome pretreatment methods, and poor method adaptability. These issues hinder wider application of this method in lakes and rivers. In addition to conventional adjustment of test parameters, optimization of the reagent dose, the use of selective adsorption materials for in situ phosphate enrichment, laboratory elution, and purification have been investigated as promising pretreatment methods. On the basis of the diffusive gradient in thin-films technique (DGT) principle, some studies have used an internal zirconium oxide selective adsorption membrane (DGT binding phase) as the enrichment material, and used in situ enrichment, elution, and purification steps to optimize the method (Liu et al. 2020). The phosphate oxygen isotope analysis pretreatment method constructed in this paper has the following characteristics: (1) The preparation and use parameters of the in situ phosphate-enrichment blanket are optimized for the target water body, and they could be adjusted for water bodies where the water quality varies. The construction of enrichment blankets with different parameters will allow for accurate control of the specific material dose, enrichment time, and elution time, which will avoid problems with excessive material consumption, and over lengthy enrichment and elution time. (2) The in situ phosphate-

enrichment blanket is a modular device. Consequently, multiple enrichment blankets could be placed the same point to clarify the results obtained with a single enrichment blanket. The results could be used to improve the method. This could also prevent failure of the experiment caused by operational errors with a single enrichment blanket. (3) The key material in the in situ enrichment blanket is D001 resin loaded with hydrated zirconia. This is combined with a nylon mesh outer layer, which gives the device high mechanical strength. Consequently, the device can be readily transported, placed for sampling, and recycled. Even when crushed, the integrity of the device is maintained. The mechanical strength of the device is higher than that of a conventional zirconium oxide selective adsorption membrane (Liu et al.,2020). Therefore, the in situ phosphate-enrichment blanket is beneficial in terms of its adaptability, convenience, and stability.

Currently, the application of phosphate oxygen isotope analysis in water bodies is limited by the complexity of the water matrix. Optimization of the present method provides effective support for the application of phosphate oxygen isotope analysis in freshwater bodies. The source of phosphorus pollution in freshwater bodies in China cannot be effectively identified using existing methods. These methods mainly rely on sediment fingerprinting, characterization of the form of phosphorus, and phosphorus balancing (Lslam 2005). Phosphate oxygen isotope analysis can be used for quantitation of phosphorus sources in freshwater bodies. A database of phosphate oxygen isotope ratios for different sources could be used to establish a way to identify phosphorus sources. Because sewage plants are continuously undergoing upgrades in China, it is questionable whether point source pollution is the main source of phosphorus in specific water bodies. Phosphate oxygen isotope analysis has very broad application prospects for exploring phosphorus migration and transformation in freshwater bodies. To date, research on the migration and transformation of phosphorus in freshwater bodies has mainly used nuclear magnetic resonance spectroscopy (Jin et al. 2019), X-ray diffraction (Rivard et al. 2016), and Raman spectroscopy (Furer et al. 2006). Phosphate oxygen isotope analysis can be used to explore the relationship between different forms of phosphorus in various environmental media. This method provides a new tool for evaluation of the phosphorus cycle in freshwater bodies and will have great application value.

Conclusions

Liquid-phase precipitation was used to prepare hydrated zirconia. Zeolite, D001 macroporous resin, activated carbon, and ceramsite were evaluated as potential support materials in enrichment and elution experiments. Among the four materials, the D001 macroporous resin was the optimum zirconium support material. Single-factor experiments and response surface methodology were used to obtain the optimum parameters for an in situ enrichment blanket for application in Taiji Lake. These parameters were 13 g of zirconium-loaded D001 macroporous resin, an enrichment time of 360 min, and elution with 1 M NaOH for 853 min The phosphate in situ enrichment blanket performed well on application in Taiji Lake. All experimental groups gave bright yellow Ag_3PO_4 . The enrichment device could be used to promote the application of phosphate oxygen isotope analysis in freshwater bodies.

Declarations

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Author Contributions All authors contributed to the study conception and design. Sumei Li: Writing-original draft, visualization, sampling, experiment; Chengyu Du: Writing-original draft, visualization; Xin Jin: Conceptualization, Funding acquisition, writing-review & editing; Jing Yang: Conceptualization; Wei Zhang: Editing, fund support; Simin Li: Editing, fund support.

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Availability of data and materials The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Ethical Approval Not applicable.

Consent to Participate Not applicable.

Consent to Publish Not applicable.

Competing Interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Almanassra IW, Kochkodan V, McKay G, Atieh MA, Al-Ansari T (2021) Review of phosphate removal from water by carbonaceous sorbents. *Journal of Environmental Management*, 287, 112245. <https://doi.org/10.1016/j.jenvman.2021.112245>
2. Angkawijaya AE, Santoso SP, Bundjaja V, Soetaredjo FE, Gunarto C, Ayucitra A, Ismadji S (2020) Studies on the performance of bentonite and its composite as phosphate adsorbent and phosphate supplementation for plant. *Journal of Hazardous Materials*, 399, 123130. <https://doi.org/10.1016/j.jhazmat.2020.123130>
3. Bui TH, Hong SP, Kim C, Yoon J (2021) Performance analysis of hydrated Zr (IV) oxide nanoparticle-impregnated anion exchange resin for selective phosphate removal. *Journal of Colloid and Interface Science*, 586, 741-747. <https://doi.org/10.1016/j.jcis.2020.10.143>.
4. Davies CL, Surridge BW, Gooddy DC (2014) Phosphate oxygen isotopes within aquatic ecosystems: Global data synthesis and future research priorities[J]. *Science of the Total*

- Environment,2014,496:563-575. <https://doi.org/10.1016/j.scitotenv.2014.07.057>
5. Deng A, Li C, Yu Q, Wang H, Fan D (2019) Phosphate Removal from Swine Waste Waterwith Unburned Red Mud Ceramsite. In IOP Conference Series: Earth and Environmental Science (Vol. 252, No. 3, p. 032036). IOP Publishing. <https://doi.org/10.1088/1755-1315/252/3/032036>.
 6. Feng Y, Luo Y, He Q, Zhao D, Zhang K, Shen S, Wang F (2021) Performance and mechanism of a biochar-based Ca-La composite for the adsorption of phosphate from water. Journal of Environmental Chemical Engineering, 9(3), 105267.<https://doi.org/10.1016/j.jece.2021.105267>
 7. Furer VL, Vandukova II, Majoral JP, Caminade AM, Kovalenko VI (2007) Spectral additive properties of phosphorus-containing dendrimers. Vibrational spectroscopy, 43(2), 351-357. <https://doi.org/10.1016/j.vibspec.2006.04.021>.
 8. Gross A, Nishri A, Angert A (2013) Use of phosphate oxygen isotopes for identifying atmospheric-P sources: a case study at Lake Kinneret. Environmental science & technology, 47(6), 2721-2727. <https://doi.org/10.1021/es305306k>.
 9. Heathwaite AL, Johnes PJ (1996) Contribution of nitrogen species and phosphorus fractions to stream water quality in agricultural catchments. Hydrological processes, 10(7), 971-983.[https://doi.org/10.1002/\(SICI\)1099-1085\(199607\)10:7<971::AID-HYP351>3.0.CO;2-N](https://doi.org/10.1002/(SICI)1099-1085(199607)10:7<971::AID-HYP351>3.0.CO;2-N)
 10. Huang J, Norgbey E, Li G, Wang J, Rainizafy, M, Nkrumah, PN, Takyi-Annan, GE (2019) Unraveling the feeding dynamics of Chinese mitten crab-based ecosystems using carbon and nitrogen stable isotope techniques. Journal of Consumer Protection and Food Safety, 14(3), 251-261. <https://doi.org/10.1007/s00003-019-01220-w>.
 11. Jaisi DP, Blake RE (2010) Tracing sources and cycling of phosphorus in Peru Margin sediments using oxygen isotopes in authigenic and detrital phosphates. Geochimica et Cosmochimica Acta, 74(11), 3199-3212.<https://doi.org/10.1016/j.gca.2010.02.030>
 12. Jaisi DP , Blake RE (2014) Advances in Using Oxygen Isotope Ratios of Phosphate to Understand Phosphorus Cycling in the Environment[J]. Advances in Agronomy, 2014, 125:1-53. <https://doi.org/10.1016/B978-0-12-800137-0.00001-7>.
 13. Jaisi DP, Hou Y, Stout LM, Massoudieh A(2017)Modeling of biotic and abiotic processes affecting phosphate oxygen isotope ratios in a mineral-water-biota system. Water research, 126, 262-273.<https://doi.org/10.1016/j.watres.2017.09.025>.
 14. Jensen WA(2017) Response surface methodology: process and product optimization using designed experiments. Journal of Quality Technology, 49(2), 186.<https://doi.org/10.1080/00224065.2017.11917988>
 15. Jin X, Rong N, Zhang W, Meng X, Shan B (2019) Bioavailability of organic phosphorus in an eutrophic lake: insights from an in-situ experiment. Ecological Indicators, 107, 105622. <https://doi.org/10.1016/j.ecolind.2019.105622>.
 16. Juwar VA, Rathod AP (2021) Optimization and statistical analysis of sono-Fenton treated wastewater of food industry using reactor by response surface method. International Journal of Chemical Reactor Engineering, 19(9), 949-959. <https://doi.org/10.1515/ijcre-2021-0105>

17. Lee CW, Kwon HB, Jeon HP, Koopman B (2005) Phosphate recovery from water as hydroxyapatite with activated oystershell. In Materials Science Forum (Vol. 486, pp. 177-180). Trans Tech Publications Ltd.<https://doi.org/10.4028/www.scientific.net/MSF.486-487.177>
18. Lei XT, Chen M, Guo L, Zhang XG, Jiang ZH, Chen ZG (2019) Diurnal variations in the content and oxygen isotope composition of phosphate pools in a subtropical agriculture soil. *Geoderma*, 337, 863-870.<https://doi.org/10.1016/J.GEODERMA.2018.10.039>.
19. Li X, Liu B, Hu Z, Liu P, Ye K, Pan J, Niu X (2020) Smartphone-assisted off– on photometric determination of phosphate ion based on target-promoted peroxidase-mimetic activity of porous $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x \geq 0.5$) nanocomposites. *Environmental Research*, 189, 109921.<https://doi.org/10.1016/j.envres.2020.109921>
20. Li X, Liu B, Ye K, Ni L, Xu X, Qiu F, Niu X (2019) Highly sensitive and specific colorimetric detection of phosphate by using Zr (O) to synergistically suppress the peroxidase-mimicking activity of hydrophilic Fe_3O_4 nanocubes. *Sensors and Actuators B: Chemical*, 297, 126822. <https://doi.org/10.1016/j.snb.2019.126822>.
21. Liu T, Feng J, Wan Y, Zheng S, Yang L (2018) ZrO_2 nanoparticles confined in metal organic frameworks for highly effective adsorption of phosphate. *Chemosphere*, 210, 907-916. <https://doi.org/10.1016/j.chemosphere.2018.07.085>
22. Liu Y, Wang J, Chen J, Jin Z, Ding S, Yang X (2020) Method for phosphate oxygen isotopes analysis in water based on in situ enrichment, elution, and purification. *Journal of Environmental Management*, 279, 111618. <https://doi.org/10.1016/j.jenvman.2020.111618>.
23. Liu Y, Wang J, Yang H, Jiang S, Jin Z, Chen, J (2021) Method for analyzing the oxygen isotope composition of HCl-extractable inorganic phosphate in sediments and soils. *Applied Geochemistry*, 130, 104978. <https://doi.org/10.1016/J.APGEOCHEM.2021.104978>.
24. Longinelli A, Bartelloni M, Cortecchi G (1976) The isotopic cycle of oceanic phosphate, I. *Earth and Planetary Science Letters*, 32(2), 389-392.[https://doi.org/10.1016/0012-821X\(76\)90079-0](https://doi.org/10.1016/0012-821X(76)90079-0)
25. Lübeck, Josephine S, Guilherme LA, Jan HC (2020) GC–HRMS nontarget fingerprinting of organic micropollutants in urban freshwater sediments. *Environmental Sciences Europe* 32.1 (2020): 1-16 <https://doi.org/10.1186/s12302-020-00353-2>.
26. Islam MS (2005) Nitrogen and phosphorus budget in coastal and marine cage aquaculture and impacts of effluent loading on ecosystem: review and analysis towards model development[J]. *Marine Pollution Bulletin*, 2005, 50(1): 48-61. <https://doi.org/10.1016/j.mar-polbul.2004.08.008>.
27. Mosa A, El-Ghamry A, Tolba M (2020) Biochar-supported natural zeolite composite for recovery and reuse of aqueous phosphate and humate: Batch sorption–desorption and bioassay investigations. *Environmental Technology & Innovation*, 19, 100807.<https://doi.org/10.1016/j.eti.2020.100807>
28. Qiu L, Wang G, Zhang S, Yang, Z, Li Y (2012) An approach for phosphate removal with quartz sand, ceramsite, blast furnace slag and steel slag as seed crystal. *Water Science and Technology*, 65(6), 1048-1053. <https://doi.org/10.2166/wst.2012.931>

29. Rivard C, Lanson B, Cotte M (2016) Phosphorus speciation and micro-scale spatial distribution in North-American temperate agricultural soils from micro X-ray fluorescence and X-ray absorption near-edge spectroscopy. *Plant and soil*, 401(1-2), 7-22. <https://doi.org/10.1007/s11104-015-2494-5>.
30. Sakamoto T, Amano Y, Machida M (2021) Phosphate Ion Adsorption Properties of PAN-Based Activated Carbon Fiber Prepared with Na₂CO₃ Activation. *Journal of Water Chemistry and Technology*, 43(4), 298-304. <https://doi.org/10.1007/s42452-020-2465-1>
31. Sowmya A, Meenakshi S. (2014) Zr (IV) loaded cross-linked chitosan beads with enhanced surface area for the removal of nitrate and phosphate[J]. *International Journal of Biological Macromolecules*, 2014, 69: 336-343. <https://doi.org/10.1016/j.ijbiomac.2014.05.043>
32. Tamburini F, Bernasconi SM, Angert A, Weiner T, Frossard E (2010) A method for the analysis of the $\delta^{18}\text{O}$ of inorganic phosphate extracted from soils with HCl. *European Journal of Soil Science*, 61(6), 1025-1032. <https://doi.org/10.1111/j.1365-2389.2010.01290.x>
33. Tcaci M, Barbecot F, Hélie JF, Surridge BW, Gooddy DC (2019) A new technique to determine the phosphate oxygen isotope composition of freshwater samples at low ambient phosphate concentration. *Environmental science & technology*, 53(17), 10288-10294. <https://doi.org/10.1021/acs.est.9b00631>.
34. Tran TT, Tra, NNT, Sugiyama S, Liu JC (2021) Enhanced phosphate removal by thermally pretreated waste oyster shells. *Journal of Material Cycles and Waste Management*, 23(1), 177-185. <https://doi.org/10.1007/s10163-020-01112-4>
35. Tran TV, Nong LX, Nguyen HTT, Nguyen VH, Nguyen DTC, Nguyen TT, Nguyen TD (2021) Response surface methodology modeling for methylene blue removal by chemically modified porous carbon: Adsorption mechanism and role of surface functional groups. *Separation Science and Technology*, 56(13), 2232-2242. <https://doi.org/10.1080/01496395.2020.1820523>
36. Velu M, Balasubramanian B, Velmurugan P, Kamyab H, Ravi AV, Chelliapan S, Palaniyappan J (2021) Fabrication of nanocomposites mediated from aluminium nanoparticles/Moringa oleifera gum activated carbon for effective photocatalytic removal of nitrate and phosphate in aqueous solution. *Journal of Cleaner Production*, 281, 124553. <https://doi.org/10.1016/j.jclepro.2020.124553>
37. Vera-Puerto I, Saravia M, Olave J, Arias C, Alarcon E, Valdes H (2020) Potential Application of Chilean Natural Zeolite as a Support Medium in Treatment Wetlands for Removing Ammonium and Phosphate from Wastewater. *Water*, 12(4), 1156. <https://doi.org/10.3390/w12041156>
38. Wang J, Wei J (2021) Facile synthesis of Zr (IV)-crosslinked carboxymethyl cellulose/carboxymethyl chitosan hydrogel using PEG as pore-forming agent for enhanced phosphate removal[J]. *International Journal of Biological Macromolecules*, 2021, 176: 558-566. <https://doi.org/10.1016/J.IJBIOMAC.2021.02.106>
39. Xi H, Jiang H, Zhao D, Zhang AH, Fan B, Yang Y, Zhang J (2021) Highly selective adsorption of phosphate from high-salinity water environment using MgO-loaded and sodium alginate-immobilized bentonite beads. *Journal of Cleaner Production*, 127773. <https://doi.org/10.1016/j.jclepro.2021.127773>

40. Yuan H, Li Q, Kukkadapu RK, Liu E, Yu J, Fang H, Jaisi DP (2019) Identifying sources and cycling of phosphorus in the sediment of a shallow freshwater lake in China using phosphate oxygen isotopes. Science of the total environment, 676, 823-833. <https://doi.org/10.1016/j.sci-totenv.2019.04.322>

Figures

Figure 1

Phosphate in-situ enrichment blanket (PISEB Unit).

Figure 2

Experimental flow chart of optimization of pretreatment method of phosphate oxygen isotopes

Figure 3

Phosphate elution efficiency of four materials

Figure 4

Phosphate self elution amount of the four phosphate in-situ enrichment materials

Figure 5

Effects of different factors on phosphate elution amount: (a) resin dosage; (b) phosphate enrichment time; and (c) phosphate elution time

Figure 6

The contour and response surfaces for the interaction of phosphate elution time with in-situ enriched material amount

Figure 7

The contour and response surfaces for the interaction of phosphate enrichment time with in-situ enrichment material amount

Figure 8

Concontour and response surfaces for the interaction of phosphate enrichment time and elution time

Figure 9

XRD diagram of the pretreatment end product