Simulation study of phosphorus remediation using lanthanum chloride-modified fly ash and Mg-O modified biochar at the sediment water interface

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ABSTRACT

Water eutrophication is a significant environmental governance challenge faced by the world today, with nutrient overloading being a primary cause, while aquatic sediment serves as the main storage site for these nutrients and other pollutants. This study focused on the Guangfu Ancient City Moat in Handan City as the research subject, where lanthanummodified fly ash microspheres and Mg-O modified biochar, independently developed and processed, were employed in an in-situ remediation efficiency simulation within containment boxes. The study also investigated phosphorus recovery and utilization. The removal rates of total phosphorus in the containment boxes with fly ash microspheres, biochar, fly ash microspheres wrapped in non-woven fabric, and biochar wrapped in non-woven fabric were 51.91%, 66.67%, 84.52%, and 84.14% respectively, with removal effectiveness ranking as NO. $4'$ > NO. $4''$ > NO. 3 > NO. 2. The research indicated that both biochar and fly ash microspheres displayed outstanding performance in phosphorus adsorption, with fly ash microspheres being more cost-effective compared to activated carbon. The containment box experiments effectively demonstrated the significant impact of fly ash microspheres in the efficient recovery of phosphorus resources and the improvement of aquatic environments, offering essential insights for the integrated management of water quality and soil.

Keywords: Water eutrophication, fly ash microspheres, aquatic sediment, in-situ remediation, phosphorus

1. INTRODUCTION

Phosphorus, as a crucial element in ecosystems, plays a significant role in human production and influences nitrogen fixation in plants, subsequently affecting carbon cycling¹. Phosphorus finds widespread application in fields such as agricultural fertilizers, pesticides, food additives, and various chemical substances². Phosphorus from land flows into water bodies through leaching, leading to high phosphorus concentrations in water bodies, causing eutrophication and ecosystem imbalances³. Eutrophication severely impacts aquatic environments, posing threats to human life⁴. As external inputs are gradually controlled, the release of phosphorus from sediment becomes a critical source of phosphorus in water bodies, influenced by various environmental factors including pH, temperature, and dissolved oxygen, making it vital to delve into and control the release of phosphorus from sediment⁵.

In-situ sediment restoration techniques are categorized into physical, chemical, and biological methods. While physical techniques exhibit rapid and effective results, they are costly and not sustainable long-term, suitable for emergencies. Chemical methods are fast-acting and targeted but the addition of large amounts of chemicals increases costs and may cause secondary pollution. Biological methods are cost-effective, environmentally friendly, and capable of handling complex pollutants without adverse effects on existing ecosystems, but are greatly influenced by factors like temperature, leading to longer restoration periods⁶. Zhu⁷ investigated the adsorption performance of modified composite materials using modified sewage sludge, zeolite powder, and bentonite on nitrogen and phosphorus. Common techniques for controlling

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internal pollution include dredging, chemical passivation, sediment covering, and plant ecological restoration⁸.

Lanthanum, a rare earth element relatively abundant in the earth's crust, forms strong bonds with phosphates⁹, making it widely used for phosphorus removal in water bodies to reduce phosphorus levels. Lanthanum-based passivation materials are extensively employed in the remediation of phosphorus pollution in water bodies due to their excellent phosphate adsorption capacity¹⁰. However, standalone lanthanum-based passivation materials are costly and exhibit average adsorption capabilities, emphasizing the importance of providing carriers for lanthanum-based materials to enhance phosphorus removal from water bodies.

Fly ash is a byproduct of coal combustion widely utilized in construction and environmental engineering fields. Being rich in fine active pore channels and a large specific surface area, modified materials are extensively used to modify fly ash for water body restoration^{11,12}. Biochar (BC), a low-toxicity, low-cost, environmentally friendly material, is gaining attention and has been proven to be an excellent carrier^{13,14}. For instance, FeS-BC efficiently adsorbs Cr^{6+} (130.5 mg g^{-1} at pH 5.50)¹⁵, while Ca-Fe₃O₄-BC adsorbs As³⁺ and Cd²⁺. However, whether using lanthanum-modified fly ash microspheres or biochar, the materials are not effectively recycled. Failure to recover these materials will occupy space in water bodies.

This study is based on self-made lanthanum-modified fly ash microspheres and modified biochar for simulating in-situ restoration of phosphorus pollution release in water body sediment, with food-grade non-woven fabric tea bags used to encapsulate the modified materials for recovery. The recovered microspheres and biochar adsorbed with phosphates can be applied to production and daily life after desorption, enabling multiple reuses of adsorbent materials. This experimental approach can significantly reduce costs in future practical applications, while the food-grade non-woven fabric tea bags prevent secondary pollution in water bodies. By comparing the adsorption performance of the two modified materials, this study provides a scientific basis and application guidance for broadening the recovery and utilization of adsorbent materials in actual water body restoration efforts.

2. MATERIALS AND METHODS

2.1 Sample collection

The sediments and water samples were collected from the moat surrounding the ancient city of Guangfu in the northeast of Handan City, Hebei Province, China. Guangfu Ancient City, a water city, is surrounded by thousands of acres of marshland and vast reed beds, with water on all sides, bordered by the 46,000-acre Yongnian marshland. Renowned for its significant architectural and historical value as well as aesthetic appreciation, Guangfu Ancient City holds a prominent position among ancient city wall remnants in China. Due to external factors, the moat's water has experienced severe eutrophication,Its water quality indicators are shown in Table 1.

	Water quality indicators							
			$\left TP\left(mg/L\right)\right TN\left(mg/L\right)$ $NH_3-N\left(mg/L\right)$ $ PO_4^3$ $(mg/L)\left DO\left(mg/L\right)\right ORP\left(mg/L\right)$ pH					T
NO. 1	0.19108	2.35094	0.55786	0.02789	6.08	-55.833	7.8	28.9
	NO. 2 0.24874	1.94521	0.47949	0.08948	5.72667	-61.067	7.9	28.7
	NO. 3 0.20156	2.29339	0.52459	0.08674	5.83333	-66.668	8.0	28.7
NO. 4	0.37324	0.12412	0.45976	0.07169	5.43	-68.733	8.0	28.7

Table1. Basic physicochemical indicators of water and sediment samples.

2.2 Experimental design

2.2.1 Preparation of chlorine-modified fly ash spheres. Initially, 10 grams of fly ash were placed in a 250-milliliter conical flask, followed by adding 11.1411 grams of lanthanum chloride heptahydrate (LaCl₃ 7H₂O) to the flask along with 200 milliliters of deionized water to obtain a 0.15 mol/L lanthanum chloride solution. The solution was then shaken for 24 hours at 180 revolutions per minute in a constant-temperature shaker at 25 °C. After shaking, the flask was rinsed with deionized water to neutralize and dried in an oven at 110℃ to obtain the lanthanum-modified fly ash. Montmorillonite was mixed with fly ash in a 7:3 ratio and added with a suitable amount of sodium silicate (water glass binder) for uniform bonding. The resulting material was rolled into cylindrical rods with a diameter of 3 millimeters and then compressed into spheres with a diameter less than or equal to 3 millimeters using a pelletizer. These spheres were then fired in a muffle

furnace at $850 \, \text{C}$ for 4 hours to obtain shaped pellets. The production process of fly ash pellets is depicted in Figure1. To investigate the optimal adsorption conditions, simulated experiments were conducted based on the phosphorus concentration in the bottom layer of the box, referencing the study by $Pan¹$.

Figure 1. Production process diagram of fly ash spheres adapted¹.

2.2.2 MgO-biochar composite material. The biochar used in this study was obtained from fallen leaves of Azalea, while the MgO-biochar composite material was prepared according to the method¹³. The resulting biochar was washed with high-purity water, precipitated, and dried to obtain the final product. The production process of MgO-biochar composite material is illustrated in Figure 2. The production process of activated carbon is depicted in Figure 3. After determining the optimal adsorption conditions of the composite material for phosphate concentrations, in situ remediation experiments were conducted in the sorted boxes under the best adsorption conditions¹⁵.

Figure 2. Production process diagram of biochar adapted¹⁶.

Figure 3. Simulation experiment diagram of the settling tank.

2.2.3 Simulation experiment setup. The experimental design included four sorted boxes as shown in Figure 4. Initially, sediment and water collected in a 1:4 volumetric ratio were placed in the sorted boxes: 15 liters of sediment were spread in each box, followed by adding 60 liters of surface water from the same site. After the suspended sediment was settled, water environmental parameters and water quality indicators were tested. A release experiment was first conducted, followed by a remediation experiment after the phosphates in the bottom layer of water reached equilibrium. The sorted boxes consisted of a blank box labeled NO. 1, where fly ash spheres were scattered at the sediment interface; box NO. 2 with an application of 33.00 g, a food-grade non-woven fabric tea bag with biochar was laid on the sediment surface designated as box NO. 3 with an application of 6.90 g; and the last box was divided into two parts, with non-woven fabric tea bags containing fly ash spheres and biochar labeled as NO. 4' and NO. 4", applying 36.36 g and 12 g respectively. A needle connected with a fine tube was used to regularly monitor changes in water quality indicators at the sediment-water interface in the boxes.

Figure 4. Experimental images of fly ash spheres.

Data Grabbing Technology (DGT) plates were placed on the first day (start of phosphate release), 50 days later (phosphate release equilibrium reached), and 120 days later (phosphate remediation completed) to test the concentration distribution patterns of Fe, S, and P at the sediment-water interface and in the interstitial water of the sediment.

2.2 Testing method

Water samples were analyzed for pH, temperature (T), dissolved oxygen (DO), and oxidation-reduction potential (ORP) using the HACH HQD Field Case portable water quality analyzer (Cat. NO.58258-00). Standard water quality parameters, including nitrate nitrogen (NO_3-N) , ammonia nitrogen (NH_3-N) , total nitrogen (TN) , and total phosphorus (TP), were measured according to the "Standard Methods for the Examination of Water and Wastewater (Fourth Edition)". Methods utilized included UV spectrophotometry, Nessler's reagent spectrophotometry, alkaline potassium persulfate digestion UV spectrophotometry, and ammonium molybdate spectrophotometry, with samples analyzed using a UV-26001 spectrophotometer (Shimadzu).

3. RESULTS

Figure 5 illustrates changes in the Water Environment Index under different conditions (NO. 1 box represents static conditions; NO. 2 box shows the introduction of a moderate amount of small balls; NO. 3 box indicates the addition of a suitable amount of biochar; NO. 4' box depicts small balls wrapped in non-woven fabric; and NO. 4" box represents biochar wrapped in non-woven fabric).

Figure 5. Compilation of monitoring indicator box changes, concentration variation graphs for each indicator, and removal efficiency images post incorporation of remediation materials

Analysis of the four major parameters, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and temperature

(T) in the water, revealed consistent temperature variations across all experimental groups. Throughout the experiments, the pH of the water fluctuated between 7.2 and 8.3, maintaining a slightly alkaline condition. Dissolved oxygen levels fluctuated between 1 and 9, with the lowest values observed in Box NO. 2. The oxidation-reduction potential in the settling tanks remained negative, fluctuating between -15 and -80.

The parameters of water quality are closely related to the form of phosphorus present in the sediment. After 50 days of observation, all five settling tanks reached phosphorus release equilibrium. Specifically, when reaching phosphorus release equilibrium:

Phosphate concentrations in different settling tanks were as follows: NO. 1: 0.1045 mg/L, NO. 2: 0.1037 mg/L, NO. 3: 0.1493 mg/L, NO. 4': 0.02557 mg/L, NO. 4": 0.01252 mg/L.

Total phosphorus concentrations were: NO. 1: 0.067 mg/L, NO. 2: 0.067 mg/L, NO. 3: 0.085 mg/L, NO. 4': 0.07 mg/L, NO. 4": 0.013 mg/L.

Ammonia nitrogen concentrations were: NO. 1: 0.0768 mg/L, NO. 2: 0.051 mg/L, NO. 3: 0.028 mg/L, NO. 4': 0.002 mg/L, NO. 4": 0.011 mg/L.

Lastly, total nitrogen concentrations were: NO. 1: 0.11 mg/L, NO. 2: 0.031 mg/L, NO. 3: 0.015 mg/L, NO. 4': 0.059 mg/L, NO. 4": 0.035 mg/L.

Observations after 110 days indicated that the removal rates of phosphate in boxes with spheres wrapped in non-woven fabric and biochar wrapped in non-woven fabric were 97.39% and 97.34%, respectively, demonstrating optimal removal efficiency. Furthermore, after 120 days of experimentation, the box with an appropriate amount of spherical fly ash reached a peak removal rate of 95% for phosphate after 99 days; the box with an appropriate amount of biochar reached a maximum removal rate of 88.65% for phosphate; the control group achieved a maximum phosphate removal rate of 82.18% in the same time frame. The removal efficiency for NH3-N ranked from highest to lowest as follows: NO. $4'$ > NO. $4''$ > NO. 3 $>$ NO. 2 $>$ NO. 1.

In the boxes with spheres wrapped in non-woven fabric and biochar wrapped in non-woven fabric, the removal rates for total phosphorus reached their peaks at 110 days, achieving 84.52% and 84.14% respectively. Boxes with an appropriate amount of spheres and an appropriate amount of biochar reached peak removal rates for total phosphorus at 120 days, reaching 51.91% and 66.67% respectively; the control group only achieved a removal rate of 37.41% for total phosphorus in the same time frame. The removal efficiency for total phosphorus ranked from highest to lowest as follows: NO. 4 ' > NO. 4" > NO. 3 > NO. 2 > NO. 1.

Analysis of Figure 5 indicates a close correlation between the trends of phosphate and total phosphorus. The total phosphorus removal rate with the addition of spheres was 51.91%, 1.38 times higher than the control group, but exhibited poorer adsorption efficiency for phosphate. In contrast, the non-woven fabric-wrapped spheres had a 97.39% removal rate for phosphate, 1.19 times that of the control group. Furthermore, their total phosphorus removal rate was 84.52%, 2.25 times that of the control group, demonstrating outstanding performance in removing total phosphorus from water. Biochar exhibited a total phosphorus removal rate of 66.67%, 1.78 times that of the control group, and a phosphate removal rate of 88.65%, 1.07 times that of the control group. Non-woven fabric-wrapped biochar had an 84.14% removal rate for phosphate, 2.24 times that of the control group, and a 97.34% removal rate for phosphate, 1.18 times that of the control group.

These results illustrate that the addition of spheres and biochar has a positive impact on improving phosphate removal efficiency, particularly exhibiting significant advantages in total phosphorus removal. The boxes with spheres wrapped in non-woven fabric and biochar wrapped in non-woven fabric showed the highest removal rates for ammonia nitrogen at 110 days, reaching 93.58% and 94% respectively. Similarly, the removal rates for boxes with an appropriate amount of spheres and an appropriate amount of biochar reached their peaks for ammonia nitrogen at 110 days, achieving 67.32% and 91.6% respectively; whereas the control group reached a maximum removal rate of 12.93% for ammonia nitrogen after 120 days. The removal efficiency for NH3-N ranked from highest to lowest as follows: NO. $4" >$ NO. $4' >$ NO. 3 $>$ NO. 2 > NO. 1.

Additionally, the removal rates for total nitrogen with spheres wrapped in non-woven fabric and biochar wrapped in nonwoven fabric reached their peaks at 110 days, achieving 60.75% and 55.65% respectively. Boxes with an appropriate amount of spheres and an appropriate amount of biochar reached their peak removal rates for total nitrogen at 120 days, reaching 17.01% and 40.14% respectively; the control group only achieved a removal rate of 7.56% for total nitrogen after

110 days. The removal efficiency for total nitrogen ranked from highest to lowest as follows: NO. 4" > NO. 4" > NO. 3 > NO. 2 > NO. 1.

Figure 6 displays the one-dimensional vertical distribution patterns of biological NH^{4+} , NO^3 , Fe, and P in sediment samples from September 2023 to January 2024. A depth of 0 mm indicates the sediment-water interface (SWI). (Groups A to D represent measurements taken on September 5th; groups E to H correspond to October 25th measurements; and groups I to H denote indicators measured on January 8th).

Figure 6. One-Dimensional Longitudinal Distribution Patterns of Biogenic NO4+, NO3-, Fe, and P in Sediment Samples from September 2023 to January 2024.(At a depth of 0 mm, denoting the sediment-water interface (SWI), the longitudinal distribution patterns of biogenic NO4+, NO3-, Fe, and P in sediment samples collected from September 2023 to January 2024 were analyzed. Measurements obtained on September 5 are represented by groups A to D, those on October 25 by groups E to H, and those on January 8 by groups I to H)

4. DISCUSSION

4.1 Impact of water environment parameters on phosphorus release and remediation in sediments

The analysis of temperature, pH, oxidation-reduction potential, and dissolved oxygen provides insights into the predominant factors influencing P in the aquatic environment, leading to the exploration of optimal water conditions for phosphorus removal. It was observed that the blank group exhibited a removal effect of phosphorus, preliminarily

attributed to variations in water environment parameters such as temperature and pH. Throughout the experiment, significant overlap in temperatures was noted in each of the five treatment tanks, showcasing temperature's notable influence on the adsorption and release of phosphorus in sediments. Increasing temperature shortened the overall reaction process raised the rate of phosphorus release from sediments, and increased phosphorus adsorption by the sediment. Existing literature suggests that under high temperature conditions, total phosphorus (TP) content in the overlying water is higher, resulting in increased phosphorus release from sediments¹⁷. In contrast, under low temperature conditions, phosphorus release from sediments is suppressed, leading to lowered TP content in the overlying water¹⁸. Analysis revealed that as pH decreased from 8.0 to 7.5, concentrations of TP and PO43- decreased in all treatment tanks, showing a consistent trend with pH variations. Moreover, studies indicate that in weakly alkaline water with lower pH, phosphorus release from sediments is inhibited, promoting phosphorus attachment to sediments¹⁹. Additionally, with changes in the pH of the overlying water, the negative charge on colloidal particles in surface sediments increases, resulting in a gradual decrease in phosphorus adsorption²⁰.

Furthermore, under anaerobic conditions, an increase in oxidation-reduction potential leads to a decrease in TP content in the treatment tanks. Hence, higher oxidation-reduction potential correlates with lower TP concentrations, while lower oxidation-reduction potential corresponds to higher TP concentrations. Research indicates that a low ORP value signifies a high content of reducing substances or organic pollutants in wastewater treatment systems, and low dissolved oxygen concentrations, indicating a reducing environment. Conversely, a high ORP value indicates high dissolved oxygen or oxidizing substance concentrations, suggesting an oxidizing environment. In conditions with high ORP values, elevated dissolved oxygen concentrations facilitate phosphorus release, resulting in increased TP and PO⁴³⁻ concentrations. Conversely, under low ORP values, low dissolved oxygen concentrations inhibit phosphorus release, leading to decreased TP and PO^{43} - concentrations^{21,22}.

4.2 Impact of different materials on the adsorption of phosphorus in sediments

4.2.1 Influence of remediation materials on water quality indicators. Upon analysis as depicted in Figure 5, both fly ash beads and biochar showed promising effects compared to the blank control group. These materials demonstrated effective phosphorus control in the water. In the experiments with five arranged boxes, it was observed that the boxes containing fly ash beads and biochar wrapped in non-woven fabric exhibited higher removal rates for phosphate compared to the blank control group, albeit with minimal removal of total phosphorus. This might be attributed to the transformation of phosphate in the water to other phosphorus forms. In the composition of orthophosphate, there are three hydroxyl groups and one oxygen bond. Upon dissociation of one hydrogen ion, a negative monovalent H_2PO^4 is formed, while dissociation of two hydrogen ions results in a divalent $H_2PO_4^{2-23,24}$. Hence, with a moderate total phosphorus removal rate, phosphate ions transform into more readily released phosphorus forms. Fly ash beads exhibited a slightly better removal efficiency for phosphate ions compared to biochar, albeit with a lower total phosphorus removal rate. However, non-woven fabricwrapped fly ash beads and biochar showed higher removal efficiencies for both total phosphorus and phosphate ions. Nonwoven fabric exerts a catalytic effect during the reaction process of complex pollutants and possesses considerable adsorption potential²⁵. Therefore, the impact of non-woven fabric on phosphorus cannot be overlooked.

Ammonia nitrogen in water is labile and significantly influenced by changes in dissolved oxygen in the water column. Under conditions of sufficient dissolved oxygen, ammonia nitrogen readily oxidizes to nitrate or nitrite²⁶. By analyzing the trends in ammonia nitrogen and total phosphorus, a remarkable similarity was observed between their variations, with fly ash beads demonstrating significant removal efficiency for ammonia nitrogen. Total nitrogen comprises inorganic nitrogen such as nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen, as well as organic nitrogen components like amino acids, proteins, and organic amines²⁷. As a crucial indicator of water quality, the content of total nitrogen is closely linked to water pollution^{28,29}. Analysis of the total nitrogen concentrations in the five arranged boxes revealed almost negligible removal rates of total nitrogen in natural water bodies. Specifically, fly ash beads exhibited a maximum removal rate of 17.01% for total nitrogen, while biochar showed a maximum removal rate of 40.14%. Moreover, non-woven fabric-wrapped fly ash beads achieved a removal rate of 60.75% for total nitrogen, while non-woven fabric-wrapped biochar attained a removal rate of 55.65%. Evidently, non-woven fabric exhibits significant adsorption capabilities for total nitrogen³⁰. Biochar, with its large surface area, strong ion exchange properties, and rich functional groups, is considered an environmentally friendly multifunctional carbon material suitable for the adsorption of organic and inorganic substances in water, or for environmental restoration through catalytic oxidation processes^{31,32}. A comparison between the adsorption effects of fly ash beads and activated carbon revealed that individual fly ash beads had a lower removal efficiency for total phosphorus than biochar, but non-woven fabric-wrapped fly ash beads exhibited a slightly higher removal efficiency for total phosphorus than non-woven fabric-wrapped biochar. From a cost perspective, fly ash is more cost-effective compared to biochar.

4.2.2 Analysis of the correlation between iron, phosphorus, and sulfur. Iron is a trace element and limiting factor essential for aquatic plants and phytoplankton in photosynthesis and nitrogen fixation processes^{33,34}. Phosphorus is a key factor in the eutrophication of lakes. Iron serves as an electron donor and energy source in denitrification processes, directly or indirectly impacting phosphorus transformations through its influence on nitrogen conversion³⁵. According to Figure 6, the concentration trends of iron and phosphorus exhibit significant similarities at the sediment-water interface, showing a pronounced positive correlation. Research by Yang³⁶ indicates that iron in sediment significantly influences phosphorus forms. Sulfur, as a redox-sensitive element at water-environment interfaces, contributes uniquely to the causes of black water and odorous conditions³⁷.

Analyzing the sulfur two-dimensional graph in Figure 6, in the control group, sulfur gradually migrates from sediment to overlaying water; after the addition of fly ash pellets in NO. 2 box, only a small amount of sulfur covers the water surface, significantly reducing overall sulfur content. With the introduction of biochar in NO. 3 box, the migration of phosphorus from sediment to water is inhibited, with continued adsorption in the sediment. In NO. 4' box, covering the fly ash pellets with non-woven fabric results in a thorough removal of sulfur from the sediment, though a small fraction migrates to the overlaying water. In the NO. 4" box, covering the biochar with non-woven fabric leads to a more comprehensive removal of phosphorus with some residual presence. Comparing the two-dimensional graphs, it is evident that non-woven fabricwrapped fly ash pellets show significant effectiveness in inhibiting sulfur diffusion to the overlaying water and in sulfur adsorption. The non-woven fabric itself also exhibits a certain adsorption capacity for sulfur.

5. CONCLUSION

This study conducted a comprehensive analysis and in-depth exploration of the phosphorus adsorption effects and recycling of lanthanum-modified fly ash pellets processed through independent design in settling tank experiments. The following conclusions were drawn:

In the settling tank, internal phosphorus in sediment reached a phosphorus release equilibrium after 50 days, with total nitrogen content also reaching relatively low levels.

Within 15 days of adding the remediation materials, their effects became apparent as both total phosphorus and total nitrogen in the water showed a decreasing trend. Non-woven fabric encasing fly ash pellets and biochar exhibited similar phosphorus adsorption effects in the water, but with a more pronounced performance, achieving 84.52% and 84.14% removal rates, respectively.

Fly ash pellets outperformed biochar in phosphorus adsorption and offered a more cost-effective solution; however, they slightly lagged biochar in ammonia-nitrogen and total nitrogen adsorption. Thus, under specific conditions, fly ash microspheres present certain advantages.

As environmentally friendly multifunctional materials, independently designed and processed fly ash pellets and biochar displayed effective adsorption capabilities for total phosphorus and total nitrogen in eutrophic water bodies, along with phosphorus recycling potential. These features can further be applied in water and soil management in saline-alkali lands, achieving the goal of integrated water and soil governance.

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REFERENCES

- [1] Pan, Y., Liu, G., Chai, B. B., et al., "Control of endogenous phosphorus release at the sediment–water interface by lanthanum-modified fly ash," Coatings, 12(6), 719 (2022).
- [2] Zhao, Y. M., Shan, X. C., An, Q. D., et al., "Interfacial integration of zirconium components with amino-modified lignin for selective and efficient phosphate capture," Chemical Engineering Journal, 398, (2020)
- [3] Liu, W., Qin, T., Wu, M. T., et al., "Analyzing the phosphorus flow characteristics in the largest freshwater lake (Poyang Lake) watershed of China from 1950 to 2020 through a bottom-up approach of watershed-scale phosphorus substance flow model," Water Research, 245, 120546-120546 (2023).
- [4] Daldorph, P. W. G., Spraggs, G. E., et al., "Integrated lake and catchment phosphorus model—a eutrophication management tool. I: model theory," Water and Environment Journal, 15(3), 174-181 (2001).
- [5] Xu, Y., [The Investigation on the Effect of Redox Condition on the Release of the Sediment Phosphorus in Lake], Guizhou University, (2015).
- [6] Li, T., Liu, Y., Chen, J. Z., et al., "Effectiveness of fixed activated sludge with different carriers to in-situ remediate mildly silted sediment," Municipal Technology, 42(02), 207-213 (2024). DOI: 10.19922/j.1009- 7767.2024.02.207.
- [7] Zhu, Z. L., Zou, J. L., Li, Q., et al., "The adsorption efficiency of nitrogen and phosphorus by in-situ remediation of modified sediment composite material," Water Science and Technology: A Journal of the International Association on Water Pollution Research, 83(4), 922-933 (2021).
- [8] Luo, Q. Y., Wei, J., Guo, Z., et al., "Adsorption and immobilization of phosphorus from water and sediments using: a lanthanum-modified natural zeolite: Performance, mechanism and effect," Separation and Purification Technology, 329, (2024).
- [9] Tang, Q., Shi, C.H., Shi, W. M., et al., "Preferable phosphate removal by nano-La(III) hydroxides modified mesoporous rice husk biochars: Role of the host pore structure and point of zero charge," Science of the Total Environment, 662, 511-520 (2019).
- [10]Liu, Z. W., Hu, J. R., Zhong P., et al., "Successful restoration of a tropical shallow eutrophic lake: Strong bottomup but weak top-down effects recorded," Water Research, 146, 88-97 (2018).
- [11]Li, F. H., Wu, W. H., Li, R. Y., et al., "Adsorption of phosphate by acid-modified fly ash and palygorskite in aqueous solution: Experimental and modeling," Applied Clay Science, 132-133, 343-352, 0169-1317 (2016).
- [12]Cui, J. X., Wang, L. Y., Zhang, K., et al., "Treatment of Nitrogen and Phosphorus Wastewater with Fly Ash-Based Zeolite [J]. Bulletin of the Chinese Ceramic Society," 40(08), 2622-2630 (2021). DOI: 10.16552/j.cnki.issn1001- 1625.20210629.002.
- [13]Li, R. H., Wang, J. J., Zhou, B. Y., et al., "Simultaneous capture removal of phosphate, ammonium and organic substances by MgO impregnated biochar and its potential use in swine wastewater treatment," Journal of Cleaner Production, 147, 96-107 (2017).
- [14]Luo, H. Y., Lin, Q. T., Zhang, X. F., et al., "New insights into the formation and transformation of active species in nZVI/BC activated persulfate in alkaline solutions," Chemical Engineering Journal, 359, 1215-1223 (2018).
- [15]Lyu, H. H., Tang, J. C., Huang, Y., et al., "Removal of hexavalent chromium from aqueous solutions by a novel biochar supported nanoscale iron sulfide composite," Chem. Eng. J. 322, 516-524 (2017).
- [16]Luo, H. Y., Wang, Y. J., Wen, X. Q., et al., "Key roles of the crystal structures of MgO-biochar nanocomposites for enhancing phosphate adsorption," Science of the Total Environment, 766 (prepublish), 142618 (2020).
- [17]Peng, W. H., [Phosphorus Adsorption and Release Characteristics of Sediments in the Xiaowan Reservoir, Lancang River], Yunnan University, (2021). DOI:10.27456/d.cnki.gyndu.2021.001450.
- [18]Li, S. G., [Phosphorus Adsorption and Release Characteristics and Coverage Control of Small Shallow Lakers in Urban Areas], East China Jiaotong University, (2019). DOI:10.27147/d.cnki.ghdju.2019.000457.
- [19]Jiao, N. Z., "On the problem of phosphorus-release from the sediment," Transactions of Ocaenologu and Limnology, (02), 80-84 (1989). DOI:10.13984/j.cnki.cn37-1141.1989.02.016.
- [20]Jin, X. C., Jiang, X., Wang, Q., et al., "Seasonal changes of P adsorption/desorption characteristics at the watersediment interface in Meiliang Bay, Taihu Lake, China," Acta Scientiae Circumstantiae, (01), 24-30 (2008). DOI:10.13671/j.hjkxxb.2008.01.014.
- [21]Yue, Z. Q., Wang, Y., Yang, P. L., et al., "Effects of nitrate nitrogen concentration in overlying water on phosphorus release from sediments in landscape water," Environmental Pollution & Control, 45(07), 923-927+934 (2023). DOI:10.15985/j.cnki.1001-3865.2023.07.005.
- [22]Li, H., Song, C. L., Yang, L., et al., "Phosphorus supply pathways and mechanisms in shallow lakes with different regime," Water Research, 193, 116886-116886 (2021).
- [23]Xiang, S. L., Chu, M. H., Liu, L. Z., et al., "Characteristics and release risk of phosphorus fractions in sediments of Nanchang section of Ganjiang River, Lake Poyang Basin," Journal of Lake Sciences, 1-11 [2024-04-25]. http://kns.cnki.net/kcms/detail/32.1331.p.20240311.2228.002.html.
- [24]Xia, L. L., [Study on the Phosphorus Forms and Character of Phosphorus Adsorption and Release in Sediment of the Poyang Lake], Nanchang University, (2007).
- [25]Zhang, X. Q., [Study on the Adsorption and Catalytic Performance of Modified Polypropylene Non-woven Fabric Membrane on Sewage], Shanghai Normal University, (2021). DOI:10.27312/d.cnki.gshsu. 2021. 001034.
- [26]Chen, R., Zhou, W., Qiao, Y. M., et al., "Phosphorus speciations and its distribution characteristics in sediments of Xinfengjiang Reservoir," Journal of Hydroecology, 1-12 [2024-03-14]. https://doi.org/10.15928/j.1674- 3075.202211220470.
- [27]Yu, S. H., Zhang, X. T., Zhang, Y. X., et al., "Analysis of the sources of total nitrogen pollution and the causes of seasonal changes in typical rivers in the north of China: Take the Mihe River as an example," Research of Environmental Sciences, 1-16 [2024-03-14]. https://doi.org/10.13198/j.issn.1001-6929.2024.02.12.
- [28]Yang, M. D., "Improvement of pretreatment methods for total nitrogen analysis," Cleaning World, 39(10), 55-58 (2023).
- [29]Li, W. W., "Research on the Method for measuring total nitrogen in water quality HJ636-2012," Shanxi Chemical Industry, 43(10), 47-49 (2023). DOI:10.16525/j.cnki.cn14-1109/tq.2023.10.021.
- [30]Xing, R. L., [Experimental Study on Modified Non-woven Fabric-Cyclic Activated Sludge System for Ship Domestic Sewage Treatment], Harbin Engineering University, (2018). DOI: 10.27060/d.cnki.ghbcu.2018.000152.
- [31]Yang, T. M. and Wang, C., "Current status of biochar preparation and its application in water remediation," Agricultural Science Journal of Yanbian University, 45(03), 95-104 (2023). DOI:10.13478/j.cnki.jasyu.2023.03.014.
- [32]Chammi, A., Saman, R. D., Darshani, K., et al., "Flooding induced inorganic phosphorus transformations in two soils, with and without gypsum amendment," Journal of Environmental Quality, 51(1), 90-100 (2021).
- [33]Xie, F. Z., [Occurrence and Sorption Mechanisms of Nutritional Elements(P, Fe) in Lake Enviroments], University of Science and Technology of China, (2012).
- [34]Emily, V., Darshani, K., Geethani, A., et al., "Ferric chloride amendment reduces phosphorus losses from flooded soil monoliths to overlying floodwater," Canadian Journal of Soil Science, 102(3), 707-718 (2022).
- [35]Tong, Y. J., Wang, Y., Hua, Y. M., et al., "Transformation of phosphorus in sediments driven by nitrate and iron in the presence of organic electron donor," Ecology and Environmental Sciences, 32(07), 1263-1274 (2023). DOI:10.16258/j.cnki.1674-5906.2023.07.009.
- [36]Yang, H. W., "Influence of Iron in Yellow River Sediments on the Forms and Release of Phosphorus," Chinese Society for Environmental Sciences, 8, (2019).
- [37]Duan, W. S., Huang, G. C., Hao, M., et al., "Release characteristics of sulfur in black and odorous water in cities against the change of environmental factors," Science Technology and Engineering, 20(31), 13072-13078 (2020).