Removal of low-concentration phosphorus by efficient phosphorus removal composite-based ecological floating beds
Yan Liu, Juanjuan Lv and Rajendra Prasad Singh

ABSTRACT
In order to strengthen the effect of ecological floating beds on the removal of low-concentration phosphorus (P) in water, the efficient P removal composite (EPRC), which is a high-efficiency P removal material developed in the current work as the substrate for the Ipomoea aquatica floating beds, was introduced into the solar chamber. The EPRC dosage (2 g/L) and the optimal number of Ipomoea aquatica plants (6 plants/10 L) suitable for the floating beds were determined experimentally. Results revealed that EPRC and Ipomoea aquatica composite floating beds had the best P removal effect among the three floating beds. Moreover, the root growth ratio of Ipomoea aquatica in the composite floating bed and the plant-only floating bed was 1.90 and 1.25, respectively. The stem growth ratio of Ipomoea aquatica in the composite floating bed and plant-only floating beds was 1.54 and 1.21, respectively. The leaching experiments showed that the leaching of heavy metals from the EPRC was negligible.

Key words | efficient P removal composite (EPRC), floating bed, Ipomoea aquatica, matrix, P removal

INTRODUCTION
Due to the rapid economic development, the problem of eutrophication of water bodies has become critical. The excess nutrients discharged into the water bodies seriously affected the self-purification ability of the lake, resulting in algal blooms (Mehner & Benndorf 1995; Yang et al. 2008). Eutrophication leads to the sharp decline of dissolved oxygen in water and the deterioration of water quality, which destroy the freshwater ecosystems. Prominent methods widely used in practical engineering to control the eutrophication mainly include: physical methods, chemical methods, biological methods, and adsorption methods (Li et al. 2014; Santiago Sampaio et al. 2015; Liu et al. 2016a, 2016b; Hamzah et al. 2018; Tian et al. 2018; Wang et al. 2019).

As one of the key biological measures, ecological floating beds have been widely used in the pollution control and ecological restoration of surface water bodies due to easy to construct, simple, and cost-effective characteristics (Yeh et al. 2015; Chang et al. 2017). Performance, however, is unavoidably restricted by the growth rate and limited stand biomass of the plant. Therefore, improving the ability of artificial floating beds to remove pollutants is one of the research focus in studies related to the control of eutrophication (Lu et al. 2015). Liu et al. (2016a, 2016b) reported a novel artificial floating island which was equipped with an aerator device powered by a solar power. Their findings revealed that the artificial floating island can effectively break down the stratified water into homogenized water and inhibit the growth of algae. Li et al. (2010) introduced a novel approach to enhance the performance of traditional planted floating bed by the introduction of filter-feeding bivalve and biofilm.
carrier. Therefore, ecological floating beds are a good development direction in the future.

However, most of the previous studies focused on the removal effect of ecological floating beds on the water bodies with higher pollutant concentration (Chang et al. 2017), and there were few studies on the lower pollutant concentration (P concentration is less than 0.8 mg/L) (Chang et al. 2014; Wu et al. 2016). The previous study showed that for mildly eutrophic water bodies, due to their inability to provide sufficient nitrogen (N) and phosphorus (P) for plant growth, the biomass was relatively low and the purification capacity was correspondingly decreased (Ge et al. 1999). In addition, other studies revealed that the focus must be on reducing the inputs of P to control the eutrophication (Schindler et al. 2013; Schindler 2015).

Therefore, in order to solve the problem of poor P removal efficiency of traditional floating beds under low P concentration (Zhang et al. 2014), this study used the efficient P removal composite (EPRC) as the growth substrate of the ecological floating island for the first time. Through the enrichment of P by the EPRC, the uptake rate of P by plants in the ecological floating islands at low P concentration was improved. The main components of the EPRC were fly ash and steel slag, which were developed previously as a part of this research work (Liu et al. 2015). Industrial waste slags were recovered which also contribute to reducing environmental pollution. The roots of Ipomoea aquatica were buried in the EPRC particles. When the dissolved P in the water was low, the P absorbed by the EPRC was released through chemical equilibrium and the acidic substance secreted by the roots caused the hydroxyapatite precipitate to be converted into soluble P which was easily absorbed by the plant, thereby continuously transporting P to the plant. Therefore, the influence of the EPRC particle dosage on P removal was studied to determine the amount of EPRC particles used in the floating bed. The removal efficiency of low-concentration P in actual water bodies by the EPRC-based ecological floating bed was also conducted. The heavy metal leaching test was conducted after an absorption efficiency test.

MATERIAL AND METHODS

Water quality measuring methods and experimental equipment

The concentration of the PO\textsubscript{4}\textsuperscript{3–} P and total phosphorus (TP) was determined through a colorimetric ammonium molybdate method (State Environmental Protection Administration of the People’s Republic of China 2002). The amount of heavy metals leaching in beds was determined by inductively coupled plasma mass spectrometry. The main instruments used in the experiment are shown in Table 1.

The floating bed systems consist of a plastic pot (15 L in volume), and a foam board and a plastic mesh were designed and implemented in the current work as shown in Figure 1. Figure 2(a) shows the smallest unit of the

<table>
<thead>
<tr>
<th>Name of instruments</th>
<th>Model no.</th>
<th>Manufacturer</th>
</tr>
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<tbody>
<tr>
<td>Ultraviolet–Visible spectrophotometer</td>
<td>752</td>
<td>Shanghai Jinghua Technology Instrument Co., Ltd (China)</td>
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<tr>
<td>ICP-MS</td>
<td>Optima 5300DV</td>
<td>PerkinElmer (USA)</td>
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<tr>
<td>Electronic balance</td>
<td>AR124CN</td>
<td>Ohaus Instruments Co., Ltd (China)</td>
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<td>Portable stainless steel pressure steam sterilizer</td>
<td>YX280A</td>
<td>Shanghai Sanshen Medical Devices Co., Ltd (China)</td>
</tr>
<tr>
<td>pH meter</td>
<td>101-B</td>
<td>Jiangyan Guorui Analysis Instrument Co. (China)</td>
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![Figure 1](http://example.com/figure1.png)
Figure 2 | Floating bed model: (a) single experimental unit and (b) sectional view.
designed floating bed. The bed material used in the current work was polystyrene foam with the size of 0.7 m × 0.5 m × 0.05 m (length × width × height). It was perforated according to needs, and the diameter of the large hole was 8 cm and the diameter of the small hole was 4 cm. The EPRC particles and plants were placed in the plastic basket, and plant roots were grown in the EPRC. The plastic basket has an upper diameter of 10 cm, a lower diameter of 4 cm, and a total height of 15 cm, which was embedded in the large hole in the bed. Figure 2(b) shows a sectional view of the floating bed that has been placed in a plastic basket. The filler used in the current study was a bioelastic three-dimensional material. As a growth carrier of the microorganisms, the filler also facilitates the removal of nitrogen from the water. The upper end diameter of the filler and the diameter of the filling ring were 6 and 2 cm, respectively. The filler was suspended under the ring, and the length of the packing section was 15 cm. The fillers were embedded in the small holes of the floating bed.

**Preparation of matrix materials**

The principal component of the EPRC was fly ash, which is an industrial by-product from salt-refining by the chlorine-alkali process. According to the previous research, EPRC particles with a size of 5 mm were selected, and the optimum ratio of fly ash:steel slag:cement (mass ratio) was 12:2:1 (Liu et al. 2015). Foaming agent and water were added appropriately to the homogenator and mixed until the solution attains the consistency of the number of plants on the P removal effect

In the current study, four plastic pots numbered with 1, 2, 3, and 4 were utilized. All experimental pots were filled with 10 L of raw water collected from Jiulong Lake, Nanjing, China. The concentration P, total nitrogen (TN), and NH$_4$-N in the raw water was 0.13, 2.60, and 1.37 mg/L, respectively, and the pH value was 7.5. A foam board was placed in each of the plastic pots, and 2, 4, 6, and 8 plants of Ipomoea aquatica with similar length and growth conditions were sequentially planted. The TP concentration in the water was measured in 3-day intervals, and a certain amount of distilled water was added to the previously marked scale before each sampling to make up the evaporation amount. Following this process, the removal effect of

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

where $C_0$ (mg/L) is the initial concentration of a parameter in each group and $C_t$ (mg/L) is the concentration at time $t$ (days). All experiments were set up with three sets of parallel experiments. All figures were plotted by using the Origin 8.5 software. The data were analyzed by SPSS, version 12.0. Comparisons in pH, PO$_4^{3-}$, and TP concentrations, root growth ratio, and stem growth ratio between different groups of floating beds were evaluated using a one-way analysis of variance (ANOVA). *Post hoc* multiple comparisons were performed using Fisher's least significant difference (LSD) test. Differences between floating beds were deemed significant if $p < 0.05$.

**Effect of the EPRC particle dosage on P removal**

EPRC particles with a size of 5 mm were selected, and EPRC particles of 2, 3, 4, 5, and 6 g quantity were added, respectively, to five beakers with a specification of 1 L capacity. Subsequently, the simulated solution with a concentration of 0.5 mg/L of P in deionized water was added to five beakers with the additional amount of 1 L capacity, oscillated in an oscillator at constant temperature, and sampled at regular intervals. The P concentration of the supernatant was measured by a 752 UV spectrophotometer (Shanghai jinghua Technology Instrument Co., Ltd, China). Through this, the influence of different EPRC particle dosages on the P removal effect was investigated.

**Influence of the number of plants on the P removal effect**

In the current study, four plastic pots numbered with 1, 2, 3, and 4 were utilized. All experimental pots were filled with 10 L of raw water collected from Jiulong Lake, Nanjing, China. The concentration P, total nitrogen (TN), and NH$_4$-N in the raw water was 0.13, 2.60, and 1.37 mg/L, respectively, and the pH value was 7.5. A foam board was placed in each of the plastic pots, and 2, 4, 6, and 8 plants of Ipomoea aquatica with similar length and growth conditions were sequentially planted. The TP concentration in the water was measured in 3-day intervals, and a certain amount of distilled water was added to the previously marked scale before each sampling to make up the evaporation amount. Following this process, the removal effect of
different numbers of *Ipomoea aquatica* on low concentration of P was investigated.

**P removal effect of the composite plant floating bed with EPRC and *Ipomoea aquatica***

In the current study, 15 plastic pots were selected and divided into three groups, numbered A, B, and C, and were utilized to investigate the P removal effect of the composite plant floating bed with EPRC and *Ipomoea aquatica*. The five pots of each group were numbered sequentially from 1 to 5. Raw water (10 L) was added (which was taken from Jiulong Lake) to each pot. The P concentration was 0.10 mg/L, the TN concentration was 3.22 mg/L, the ammonia nitrogen concentration was 1.53 mg/L, and the pH value was 7.8 in the raw water of Jiulong Lake. Since the time of the water sampling in the current work differs from the time of the sampling of the above water samples by nearly 1 month, there was a certain difference in the TP concentration of the two water samples. Considering the difference of P concentration under different water systems, the current experiment was designed for a certain gradient of P concentration. As the current study mainly focused on water with low P concentration, the designed concentration gradient was 0.1, 0.2, 0.4, 0.6, and 0.8 mg/L. A certain amount of KH₂PO₄ particles were added to the pots numbered 1 to 5 of groups A, B, and C, respectively, to ensure the P concentrations in the No. 1 to No. 5 experimental pots were 0.1, 0.2, 0.4, 0.6, and 0.8 mg/L, respectively. Then, a floating bed was placed in each of the plastic pots. Group A was a planted floating bed, and the number of *Ipomoea aquatica* plants selected were 6 based on the previous study. Group B consists of the plant + EPRC particles floating bed, and the number of plants was 6 and the amount of EPRC particles was 20 g. Group C consists of a floating bed with only EPRC particles, and the amount of EPRC particles was 20 g. The concentration of TP and PO₄³⁻-P in the water was monitored every 3 days. A certain amount of distilled water was added to the previously marked scale before sampling to compensate for the evaporation, and the test period was 18 days. Through this process, the P removal effect of the composite floating bed by EPRC and plants was investigated.

**Heavy metal leaching test**

The purpose of the composite floating island was to control P in water source, so the safety of materials was required. Considering that the heavy metals contained in fly ash and steel slag of matrix materials were mainly Zn and Cu, the test mainly measured these two indexes. The optimal EPRC dosage (2 g/L) taken as an example to determine the EPRC with a particle size of 0.5 cm about 2 g was taken and placed into 1 L of KH₂PO₄ solution with a concentration of 0.5 mg/L. The heavy metal leaching test was conducted after absorption equilibrium and analyzed for heavy metals using inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, USA).

**RESULTS AND DISCUSSION**

**Effect of the EPRC particle dosage and *Ipomoea aquatica* floating bed on P removal**

As shown in Figure 3(a), results revealed that with the increase of the dosage of EPRC particles, the P removal rate increased sequentially, while the P removal amount per unit mass of particles decreased in a sequential manner. When the EPRC dosage was increased, the usable surface area of the EPRC was increased. More adsorption sites for P exist, and the P was more easily combined with the active sites and hence removed. When the dose was low, the removal rate of P increased rapidly. The removal rate continued to increase with gradually decreased dosage until P was completely removed. For example, the P removal rate was the highest when the dose was 6 g, which was 69.8%, but the P removal amount per unit mass of particles was only 0.058 mg/g, which was the lowest value of the five groups. While at the 2 g dose, the P removal amount per unit mass of particles was 0.157 mg/g and the P removal rate was 62.6%. Therefore, considering the P removal rate and the P removal amount per unit mass of particles, from an economic point of view, the 2 g/L dosage was selected in the subsequent experiments as the most economical.

The P removal rate of different quantities of *Ipomoea aquatica* is shown in Figure 3(b). Under the condition of different numbers of plants ranging between 2 and 8, the P
concentration of the four devices decreased from the initial 0.13 to 0.030, 0.021, 0.013, and 0.012 mg/L, respectively. The P removal rates were 76.6%, 84.1%, 90.0%, and 90.8%, respectively. The P removal rate did not show further increase with increase of plant numbers due to the limited total amount of P in the solution. Therefore, 6 plants/10 L were selected as the optimal number of plants in this experiment when influent P concentration was 0.13 mg/L.

The comparison of the removal rates of PO$_4^{3-}$ and TP of three floating beds under different P concentrations is shown in Figure 4. Results revealed that the composite floating bed with EPRC particles and plants had the best P removal effect, followed by the EPRC-only floating bed and finally plant-only floating bed. There was no significant difference in TP and PO$_4^{3-}$ concentration between three groups of floating beds when initial P concentration was 0.1 mg/L ($p > 0.05$). There was a significant difference in TP and PO$_4^{3-}$ concentration between the plant-only floating bed and other floating beds when initial P concentration was 0.2 mg/L ($p < 0.05$). The TP and PO$_4^{3-}$ concentration in the EPRC + plant floating bed was significantly lower than that of other floating beds ($p < 0.05$) when initial P concentration was 0.4, 0.6, and 0.8 mg/L. It is indicated that the EPRC can significantly improve the P removal efficiency of plant-only floating beds. The removal pathways of P in the plant-only floating bed mainly include plant absorption, precipitation, adsorption, and the fixation of microorganisms in roots of plants (Wu et al. 2016; Li et al. 2009). The mechanism of the EPRC-only floating bed for the removal of P is mainly manifested in the joint process of physical adsorption and chemical adsorption (Oguz 2005). The large specific surface area and many active sites which are easy to react with ions in water (such as silicon and aluminum) determine the strong adsorption capacity of steel slag and fly ash. The
physical adsorption effect mainly depends on the porosity and specific surface area of fly ash, which is positively correlated with the specific surface area (Zeng et al. 2015). The adsorption of P by the EPRC is mainly chemical adsorption, which is an exothermic process. It is mainly achieved by chemical precipitation and ligand exchange (Blanco et al. 2016). Studies have shown that P immobilization by fly ash and steel slag was governed by Ca ingredient (especially CaO) and Fe ingredient (especially Fe2O3) (Chen et al. 2014; Bowden et al. 2009). When the EPRC was mixed with the P solution, calcium ions and phosphate ions form calcium phosphate precipitation (Blanco et al. 2016) which can be expressed as shown in Equation (2):

$$3Ca^{2+} + 2OH^- + 2HPO_4^{2-} = Ca_3(PO_4)_2 + 2H_2O$$  \hspace{1cm} (2)

The generated calcium phosphate precipitation can be further converted into stable hydroxyl calcium phosphate precipitation which can be expressed as shown in Equation (3):

$$5Ca^{2+} + 4OH^- + 3HPO_4^{2-} = Ca_5(OH)(PO_4)_3 + 3H_2O$$ \hspace{1cm} (3)

Iron oxides in the EPRC enter the solution and combine with coordinating water to form hydroxides or hydroxides of hydroalloys, resulted in a large number of -OH groups on the surface of the EPRC. An earlier study revealed that phosphate ions can be adsorbed by exchanging with the coordination groups of iron ions (Li et al. 2016). The specific reaction process is shown in Equations (4) and (5):

$$Fe_2O_3 + 3H_2O = 2Fe(OH)_3$$ \hspace{1cm} (4)

$$Fe(OH)_3 + H_2PO_4^- = FePO_4 + 2H_2O + OH^-$$ \hspace{1cm} (5)

In the composite floating bed, plants did not easily absorb the crystalline P formed by the chemisorption of the EPRC, and it was necessary to complete the absorption of P by plants through two pathways. Earlier studies (Lei et al. 2018; Cichy et al. 2019) considered that crystalline P was unstable, because it may form unstable colloids. The plant firstly absorbed the dissolved P in the water. When the dissolved P dropped to a certain concentration, the colloidal P was released to maintain the chemical balance between the solution and the solute in the water and the released P can be absorbed by the plant. The second pathway is that plant roots secreted acidic substances (such as citric acid) under the condition of P deficiency to promote the release of insoluble P (Lyu et al. 2016; Xing et al. 2016). Previous studies have shown that the adsorbed phosphate could be successfully recovered by 2% citric acid solution, which implied that recovered phosphate could be reused as a fertilizer (Jiang et al. 2014). The roots of Ipomoea aquatica were buried in the EPRC particles, with a small amount of soluble P. Under the P deficiency, the roots secreted acidic substances and dissolved the crystal P into dissolved P which was easily absorbed by plants. This was equivalent to increasing the concentration of dissolved P around the roots, promoting the absorption of P, and thus improving the P removal rate.

**Influences of three groups of floating beds on the pH of raw water**

The experiment also examined the influences of three groups of floating beds on the pH of the water. Figure 5 shows the changes in the pH of raw water of the three floating beds under different initial P concentrations (where the pH of the raw water at 24 °C was 7.8). It can be seen from Figure 5 that at the end of experiment, the pH of the floating bed of C was the highest, reaching to about 8.5. The floating bed of A had little change compared with the pH of raw water. The floating bed of B had a slight change compared with the original water, but it was also stable at around
8.0. There were significant differences in the pH values in different groups of the floating bed ($p < 0.005$). At the initial stage of the reaction in the floating bed of C, alkaline substances such as CaO in the EPRC precipitated into the solution and hydrolyzed:

$$\text{CaO} + \text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{OH}^-$$  \hspace{1cm} (6)

This reaction caused the pH of the solution to rise rapidly. As the reaction proceeded further, the pH of the solution dropped to some extent. The reason could be that Ca$^{2+}$ combined with phosphate ions to form stable precipitate, such as hydroxyl calcium phosphate, after the pH reached a certain value, which consumed a part of OH$^-$. When the reaction was completed in the later stage of adsorption, the pH began to stabilize. The specific reaction process is shown in Equations (7) and (8) (Khadhraoui et al. 2002):

$$5\text{Ca}^{2+} + 7\text{OH}^- + 3\text{H}_2\text{PO}_4^- = \text{Ca}_5(\text{OH})(\text{PO}_4)_3 + 6\text{H}_2\text{O}$$  \hspace{1cm} (7)

$$3\text{Ca}^{2+} + 4\text{OH}^- + 2\text{H}_2\text{PO}_4^- = \text{Ca}_3(\text{PO}_4)_2 + 4\text{H}_2\text{O}$$  \hspace{1cm} (8)

From the experimental results, the pH of the floating bed of group C was finally stabilized at around 8.5. Whereas in group B, the roots of the plants released acidic substances, neutralizing a part of the alkalinity (Wang et al. 2018), so that the pH had a certain degree of decline compared with the EPRC-only floating bed.

### Growth status of plants in groups A and B under different initial P concentrations

In the experiment, the growth of the roots and stems of the *Ipomoea aquatica* in the floating beds of groups A and B were also measured to verify that the EPRC can enhance the P removal of the *Ipomoea aquatica* floating beds. Figure 6 shows the comparison of roots and stems growth ratio of plants in the floating beds of groups A and B under different initial P concentrations. It can be seen from the figure that under the conditions of five different initial P concentrations, the root length and the stem length of group B floating bed (plants + EPRC) plants were larger than that of group A floating bed (plants-only). The root growth ratio and stem growth ratio in the EPRC + plant floating bed was significantly higher than that in the plant-only floating bed ($p < 0.05$).

This further demonstrated that EPRC particles promote the growth of plants. Deficiency in plant-available P is considered to be a major limiting factor to the growth of many plants (Arcand & Schneider 2006). A study conducted by Vidal-Beaudet et al. (2018) also indicated that available P content was sufficient for plant development. In this study, the enrichment of P by EPRC particles allowed the roots in contact with the particles to absorb P more effectively; therefore, the plants of group B obtained a larger root length and stem length better than group A. Besides, previous studies have shown that the EPRC can provide nutrients, such as Ca, Na, K, P, Mg, B, S, and Mo, which promote plant growth and also alleviate the condition of
nutrient deficiency in low P concentration (Sajwan et al. 2003; Kumpiene et al. 2007).

Heavy metal leaching test

The concentration of Cu was under the ICP-MS detection limit (0.001 mg/L) (<0.01 mg/L), which met the Class I water quality standard of Environmental Quality Standard for Surface Water (GB 3838-2002). The Zn leaching was 0.0314 mg/L (<0.05 mg/L), which was slightly higher than Cu but also met the Class I water quality standard of Environmental Quality Standard for Surface Water (GB 3838-2002). Although fly ash was reported leaching heavy metals, leaching rates of metals from fly ash were reduced using the cement of which the main components were limestone and clay (Bankowski et al. 2004; Liu et al. 2011; Li et al. 2017).

APPLICATIONS OF CURRENT WORK AND FUTURE RESEARCH

At present, EPRC particles have been used in the P reduction experiment in Taihu Lake, and the results showed that the EPRC has effective P removal efficiency. The test site was a river flowing into Taihu Lake in Yixing City. The width of the river surface was 4 m, the average depth was 0.6 m, and the velocity was 0.5 m/s. During the experiment, the EPRC was placed in nylon mesh bags with a length of 1 m and a diameter of 6 cm. The nylon bags were immersed in river water. The nylon mesh bag filled with the EPRC material weighed about 600 g per bag, totaling 40 strings, and the total dosage of the EPRC was 24 kg. Within 1 week of the initial implementation, the total P concentration in the channel into the lake decreased from 1.2 to less than 0.2 mg/L. It brings two kinds of environmental benefits: it allows the reuse of potentially hazardous waste and increases the removal of pollutants from the wastewater treatment systems. In the future, consideration should be given to increase the hardness of the EPRC. Moreover, the EPRC is a solid material, and only the surface layer and voidage are involved in P removal. Therefore, subsequent studies may consider increasing the specific surface area of the material, such as making it into fibers, so that the material has a higher P removal efficiency than granular materials. In addition, in future research, different plants can be selected for the experiment of composite floating beds, such as plants growing at low temperature, ornamental plants, or plants with high economic value, to provide a reference for a practical engineering application from multiple perspectives. Finally, fly ash, steel slag, and soil with different weight ratios can be considered as the growth matrix of plants in constructed wetlands, and the P removal performance of which can be studied.

CONCLUSION

Findings of the current study revealed that the composite floating bed can significantly enhance the P removal efficiency of the Ipomoea aquatica and promote its growth. The presence of the EPRC caused a slight increase in the pH, but the plant released the acidic substance and neutralized a part of the alkalinity. Therefore, the composite floating bed had a negligible effect on the pH of the raw water. In summary, the composite floating bed based on the EPRC can be used as a new way to strengthen P removal in actual water bodies.

REFERENCES


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