

Preparation and application of an innovative integrated agent product for phosphorus control and oxygen release

Zhikang Zhou^a, Yulong Liu^a, Xiaogang Gu^b, Chaoxiang Yang^{IWA}^c and Shuguang Lyu^{IWA}^{a,*}

^a State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, China

^b Shanghai Urban Construction Design & Research Institute (Group) Co., Ltd, 3447 Dongfang Road, Shanghai 200125, China

^c Department of Industrial Design, East China University of Science and Technology, Shanghai 200237, China

*Corresponding author. E-mail: lvshuguang@ecust.edu.cn

ABSTRACT

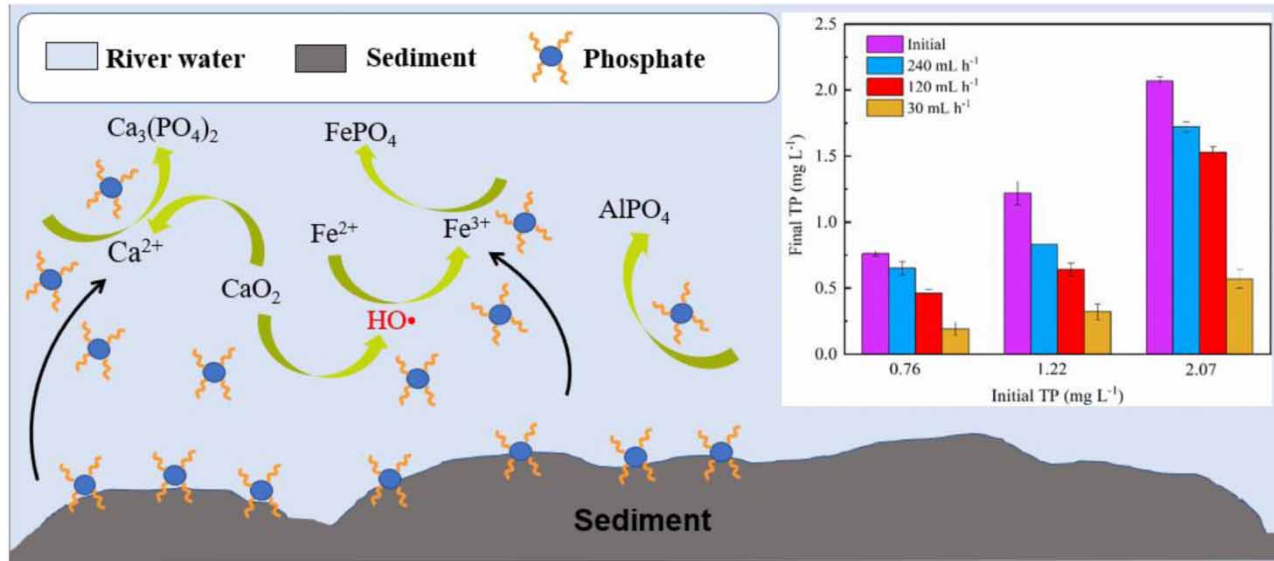
In this study, an oxygen-releasing and phosphorus-controlling agent (ORPC) consisting of calcium peroxide (CaO₂), bentonite, cement, stearic acid (SA), citric acid (CA) and fine sand was synthesized successfully and used to purify phosphorus-rich river water. The removal of phosphorus using ORPC was studied in actual river water and the results found that over 75.0% phosphorus was removed by adding ORPC at 30 mL h⁻¹ flow rate in initial phosphorus concentrations of 0.76 mg L⁻¹. The ORPC was further used to evaluate the changes of aluminum phosphate (Al-P), ferric phosphate (Fe-P) and calcium phosphate (Ca-P) in sediment. Fe-P, Al-P, and Ca-P in the sediment increased from 0.14, 0.196, and 1.63 mg g⁻¹ to 0.159, 0.372, and 2.74 mg g⁻¹ respectively within 28 days, indicating that the total dissolved phosphorus in the overlying water could be adsorbed by ORPC and further transformed into Al-P, Ca-P, and Fe-P in the sediment, thus inhibiting the release of endogenous phosphorus in sediment to the water. In addition, the performance of ORPC with various contents of SA and CaO₂ was investigated. In summary, ORPC can be employed to adsorb phosphorus in water and prevent phosphorus release from sediment, therefore achieving the purpose of controlling phosphorus and maintaining DO at a reasonable level.

Key words: calcium peroxide, oxygen release, phosphorus control, river water, sediment, water remediation

HIGHLIGHTS

- The presence of ORPC enhanced dissolved oxygen concentration and phosphorus removal.
- Purification effect on actual river water was elucidated.
- The effect of various CaO₂ and SA contents on ORPC was investigated.
- The dissolved phosphorus in the overlying water was not only transformed into Ca-P, but also into Al-P, Fe-P in sediment.
- The effect of ORPC on phosphorus removal in water with various flow rates was investigated.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Eutrophication is considered to be the most significant water quality problem in water bodies worldwide, although recently it has been improved to a certain extent (Smith & Schindler 2009; Zamparas & Zacharias 2014). Eutrophication has caused the rapid growth and reproduction of algae and other plankton, resulting in a decrease in the concentration of dissolved oxygen (DO) and the occurrence of black and malodorous problems. The phenomenon of eutrophication and black-odor are mainly related to the high concentration of phosphorus and low DO in the water body. Phosphorus is a main restrictive element that leads to the eutrophication of river water, therefore, controlling the concentration of phosphorus plays a key role in the governance of water resources (Schindler *et al.* 2008; Zhu *et al.* 2017). The practical implementation to control phosphorus in an actual river can be divided into the control of external phosphorus input and endogenous phosphorus release (Yu *et al.* 2019). Though numerous applications have been taken to control the loading of external phosphorus, black-odor is still one of the most vital problems. The reason is that the loading of internal phosphorus in sediment still maintains the high concentration, which delays the recovery of eutrophic water bodies (Cooke *et al.* 1993; Ding *et al.* 2018). The main method to control the phosphorus rebound in a river is to prevent the release of phosphorus from sediment. Remediation of river sediment can be classified into *in-situ* and *ex-situ* techniques. *In-situ* repair technology is widely used in engineering because it can avoid large-scale sediment excavation and subsequent treatment (Yin *et al.* 2018; Abel & Akkanen 2019; Lin *et al.* 2019). Solid-phase material capping technology in *in-situ* repair technology is mostly favored because of its moderate cost and simple operation (Fan *et al.* 2017; Wang *et al.* 2017; Zhou *et al.* 2018; Zhu *et al.* 2019).

Calcium peroxide (CaO_2) is an excellent oxidizing agent (Cassidy & Irvine 1999; Liu *et al.* 2006). On the one hand, CaO_2 can react with water to form H_2O_2 that can oxidize the organic matter in sediment (Equation (1)). At the same time, a physical barrier on the surface of sediment is formed by $\text{Ca}(\text{OH})_2$, thereby preventing the release of endogenous phosphorus in the sediment. On the other hand, CaO_2 releases oxygen to increase the level of DO at the sediment–water interface, and promote the conversion of endogenous phosphorus to stable-state phosphorus such as ferric phosphate (Fe-P) and calcium phosphate (Ca-P) in the sediment (Equations (2)–(5)) (Fonseca *et al.* 2011; Liu *et al.* 2012; Xu *et al.* 2018). However, because CaO_2 powder can be consumed quickly once it comes into contact with water, CaO_2 cannot exert a long-term effect and causes the pH of the water body to increase rapidly, therefore it is necessary to develop encapsulation of CaO_2 in order to provide a slow-release function (Kao *et al.* 2003). Embedding technology is an effective method for preparing sustained-release materials (Nykänen *et al.* 2012). Stearic acid (SA) is a familiar slow-release material often used as an embedding agent,

which is characterized by hydrophobic, non-toxic, and easily biodegradable properties (Wang *et al.* 2021).



Therefore, in this work, SA was selected to embed CaO_2 powder to prepare a phosphorus-controlling and oxygen-releasing agent which has a strong mechanical strength. The addition of cement, fine sand, and bentonite during the preparation of the innovative phosphorus-controlling and oxygen-releasing agent (ORPC) can remarkably increase the efficiency of oxygen oxygen-release utilization and phosphorus removal. Furthermore, compared with other phosphorus-removal agents which exceeded 3 \$ kg^{-1} created by Chen *et al.* (2016), the 0.5 \$ kg^{-1} ORPC exceeded in this study was cheaper. The lifespan of ORPC surpassed over 28 days, whereas the material prepared by Zhang *et al.* (2018) and Liang *et al.* (2018) was merely maintained for about seven days. For the above reasons, therefore, the objectives of this work are to: (a) prepare and characterize the innovative ORPC; (b) investigate the effects of various mass fractions of CaO_2 and SA on phosphorus removal and oxygen-release performance; (c) elucidate the effect of ORPC in removing phosphorus from actual river water; (d) evaluate the inhibitive effect of ORPC on phosphorus release from river sediment and analyze the transformation of various forms of phosphorus in sediment.

2. MATERIALS AND METHODS

2.1. Material preparation and characterization

The supplies of the chemicals and other materials used in this study are available in the Supplementary Materials (Text S1).

The ORPC was prepared by the following procedure: first, 2.33 g of SA was added to a sufficient amount of ethanol under magnetic stirring until all SA was dissolved ($T = 60^\circ\text{C}$). Second, CaO_2 powder, bentonite, cement, fine sand, and citric acid (CA) with a mass ratio of 7:1.5:14:10:0.6 were simultaneously added and thoroughly mixed. Then, cylinder-shaped ORPC was manufactured by a tablet press machine. Finally, the ORPC was placed in an oven at 30°C for 12 h drying. Some researchers have prepared oxygen-releasing material by embedding CaO_2 . However, in all of the studies above, a certain amount of water was added to the CaO_2 during material preparation, leading to the loss of available oxygen in advance (Nykänen *et al.* 2012; Lee *et al.* 2014). The solvent in the whole preparation process of ORPC in this study was ethanol, which could not react with CaO_2 . Since the other chemicals in the ORPC were unable to react with CaO_2 , the content of CaO_2 in the prepared ORPC was greatly maintained in the whole preparation process. All the materials were stored in a desiccator at room temperature. A scanning electron microscope (Hitachi S-4800 FE-SEM, Japan) was used to characterize the surface microstructure of the CaO_2 powder and ORPC. Infrared spectra were detected by using Fourier transform infrared spectroscopy (Thermo Nicolet 6700, USA). A rotating anode X-ray powder diffractometer (Rigaku Denki Dmax2550, Japan) was used to analyze the structure of the substances.

2.2. Batch experimental procedures

The phosphorus solution was prepared by dissolving 0.2207 g solid potassium dihydrogen phosphate with 1 L ultrapure water which was then stored in a cabinet at 25°C . All batch tests were carried out in a 1 L glass reactor. The perforated sealing membrane was used to allow the oxygen in the reactor to escape, but prevent the outside oxygen from entering. The temperature was held at 25°C through being kept in a closed and dark cabinet. Phosphorus-containing water of 1.91 mg L^{-1} was prepared by adding 10 mL stock phosphorus solution to the 990 mL ultrapure water. In order to assess ORPC performance for oxygen release more intuitively, the DO of the phosphorus-containing water was set as 0 mg L^{-1} by nitrogen-stripping initially. A mass of 15 g of ORPC was added to the phosphorus-containing water. At the predetermined time, the samples were taken and filtered by $0.45 \mu\text{m}$ millipore membrane for measuring changes in phosphorus concentration. DO and pH were continuously monitored within 28 days. DO was measured by using a portable DO meter (model HQ40d, Hach, USA) and pH was recorded by a digital pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland). All experiments were carried out three times, and the average values were reported.

2.3. Test for the actual river water body in flowing pattern

A mass of 500 g of ORPC was evenly added above 5 centimetres of thick fine sand at the bottom of the reactor loaded at $3,200 \text{ g m}^{-2}$ to simulate the actual river flowing pattern (Figures S1(a) and S1(b)). The river water used in the experiment was obtained from the upstream of the Qingchun River that flows through the Xuhui campus of East China University of Science and Technology (ECUST), Shanghai, China. Potassium dihydrogen phosphate was added to the actual river water to prepare phosphorus-containing river water with three different concentrations, i.e. 0.76, 1.22, and 2.07 mg L^{-1} , respectively. Then, the river water flowed through the three closed reactors individually at flow rates of 30 mL h^{-1} , 120 mL h^{-1} , and 240 mL h^{-1} , respectively. The changes of TP, DO and pH of the river water and effluent after flowing through the reactor were measured and compared. All experiments were repeated three times, and the average values were reported.

2.4. Test for the actual river water body in flowing pattern with the river sediment on the bottom of the reactor

The river sediment was put on the bottom of the reactor with a height of five to six centimetres that simulated an actual flowing river (Figure S1(c)). A mass of 210 g of ORPC was paved evenly on the surface of the sediment. The sediment and river water used in the experiment were obtained from the Dongshangao pond and the Qingchun River that flowed through the Xuhui campus of ECUST, respectively. River water was pumped through the closed reactor. The changes of TP, DO and pH in the influent and effluent were measured and compared within 28 days. The changes of the various forms of phosphorus on top of the sediments and in the ORPC were measured.

2.5. Analytical methods

The active inorganic phosphorus in the water was analyzed with ammonium molybdate spectrophotometry. The active inorganic phosphorus in the sediment was analyzed with the alkali fusion–molybdenum antimony colorimetric method. In accordance with the Lake Eutrophication Investigation Specification, various inorganic forms of phosphorus were extracted and separated from the sediment, and the contents were determined by an ultraviolet spectrophotometer. Details for the determination of the various inorganic forms of phosphorus in this study are available in the Supplementary Materials (Text S2).

3. RESULTS AND DISCUSSION

3.1. Characterization of the prepared ORPC

The surface morphology of the calcium peroxide powder and the prepared ORPC in this study were measured by scanning electron microscope. Figure 1(a) shows the surface of the CaO_2 powder has a rough surface and many protrusions. After being embedded with SA, the surface of the ORPC is regular and smooth (Figure 1(b)). When the CaO_2 reacted with water, the CaO_2 was consumed and decomposed, then causing the ORPC slightly to crack (Figures S2(a) and S2(b)). Compared with the infrared spectra of CaO_2 powder and ORPC (Figure 2(a)), the O-O bond appeared in the CaO_2 at 869 cm^{-1} and the O-O bond appeared at 875 cm^{-1} in the ORPC, which would contribute to releasing oxygen (Zegliński *et al.* 2006). After exhaustion, the peak of the O-O bond in the ORPC became markedly attenuated due to oxygen release caused by the reaction between the ORPC and water. Meanwhile, the peak intensities at $1,474 \text{ cm}^{-1}$ and $1,423 \text{ cm}^{-1}$ in the ORPC decreased, reflecting the reduction in the amount of O-Ca-O (Yan *et al.* 2009). The characteristic peak at $2,850 \text{ cm}^{-1}$ in the ORPC was a long carbon chain structure that was derived from the SA, indicating the surface of CaO_2 was covered by organic layers. XRD patterns of CaO_2 powder and ORPC are provided in Figure 2(b). Typical peaks corresponding to CaO_2 and ORPC were at 2θ values of 30.09° , 35.44° , and 47.15° (JCPDS No. 03-0865), which also demonstrated CaO_2 was successfully embedded.

3.2. Composition effect on the performance of ORPC

3.2.1. Effect of CaO_2 content on ORPC performance

The content of various compositions is an important factor that can significantly affect ORPC performance. The content of CaO_2 was investigated for masses of 1.5 g bentonite, 14 g cement, 10 g fine sand, 0.6 g CA and 2.33 g SA in the ORPC (a bentonite/cement/fine sand/CA/SA mass ratio of 1.5:14:10:0.6:2.33). The mass of CaO_2 was changed from 2.5 g to 4.3 g, 6.2 and 9 g, respectively. The effect of ORPC with various contents of CaO_2 on DO in the glass reactor was monitored within 28 days in which the reactor was shaken regularly ($T = 25^\circ \text{C}$). The result showed that the DO concentration increased with the CaO_2 content (Figure 3(a)). During the first 15 days, ORPC with various contents of CaO_2 slowly increased the concentration of DO in the water. When the content of CaO_2 in the ORPC increased, the oxygen released from the ORPC in the water increased. After the 15th day, the DO in the water began to decrease for the reactors with 2.5 g and 4.3 g CaO_2 in ORPC. However, ORPC with 6.2

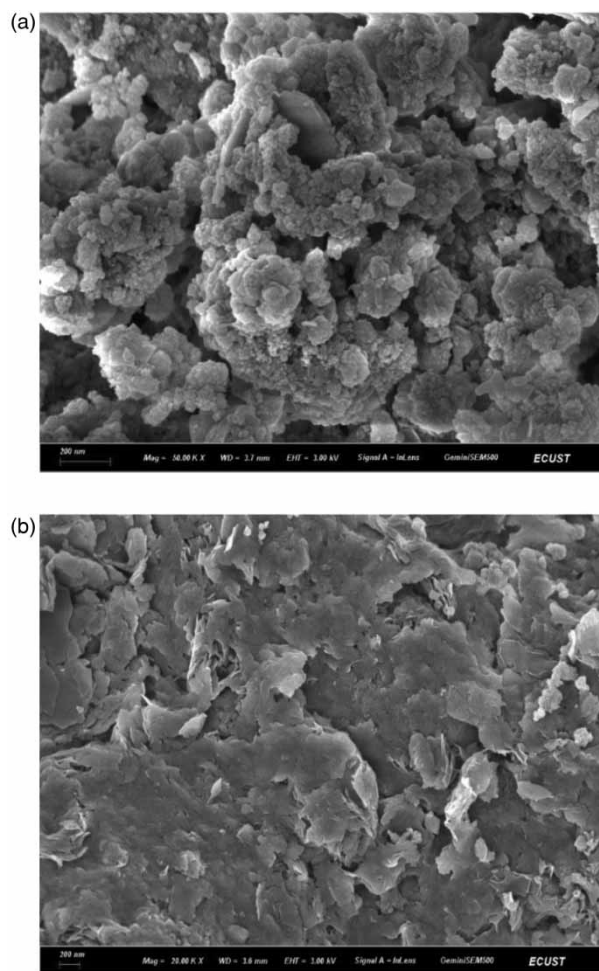


Figure 1 | SEM images: (a) CaO_2 powder, (b) ORPC.

and 9 g CaO_2 still increased DO in the water, suggesting that a high content of CaO_2 could increase the concentration of DO in the water much longer. [Figure 3\(b\)](#) shows that various contents of CaO_2 coming from the ORPC could also continuously reduce phosphorus concentration in the water. As the content of CaO_2 increased, the phosphorus removal increased. When the content of CaO_2 in the ORPC was 2.5 g, 4.3 g, 6.2 g, and 9 g individually, the final phosphorus removal reached 78.6%, 82.0%, 84.8%, and 87.2% within 28 days. The phosphorus removal increased with CaO_2 content in the batch reactor, and the alkalinity in the water also increased with CaO_2 content ([Figure 3\(c\)](#)). The pH of the effluent was increased from 7.94 to 8.2 and 8.41 with the flow rate decreasing from 240 mL h^{-1} to 120 mL h^{-1} and 30 mL h^{-1} at the initial phosphorus concentration of 1.22 mg L^{-1} , respectively, which were only minor changes compared with the influent pH of 7.62. The same elevation of pH value was also observed at the initial phosphorus concentrations of 0.76 mg L^{-1} and 2.07 mg L^{-1} . Compared with the influent, the effluent pH in the flowing pattern did not change significantly (see section 3.3, [Figure 5\(c\)](#)). The removal of phosphorus could satisfy the requirement to meet the practical demands by varying the content of CaO_2 .

3.2.2. Effect of SA content on ORPC performance

In this section, the performance of ORPC with various SA contents was tested. The content of SA was investigated for the fixed masses of 1.5 g bentonite, 14 g cement, 10 g fine sand, 0.6 g CA and 6.2 g CaO_2 in the ORPC (a bentonite/cement/fine sand/CA/ CaO_2 mass ratio of 1.5:14:10:0.6:6.2), while the mass of SA was changed from 0.53 g to 1.06 g, 2.13 g and 3.20 g. [Figure 4\(a\)](#) shows the effect of SA content on the oxygen-releasing performance of ORPC. As the content of SA increased, the oxygen-releasing rate decreased in the first 15 days. Because the cement and fine sand on the surface of the ORPC fell off slowly, the oxygen-releasing rate of ORPC which had a high content of SA was increased after 15 days. [Figure 4\(b\)](#) shows the effect of various contents of SA on the phosphorus removal performance of ORPC. When the content

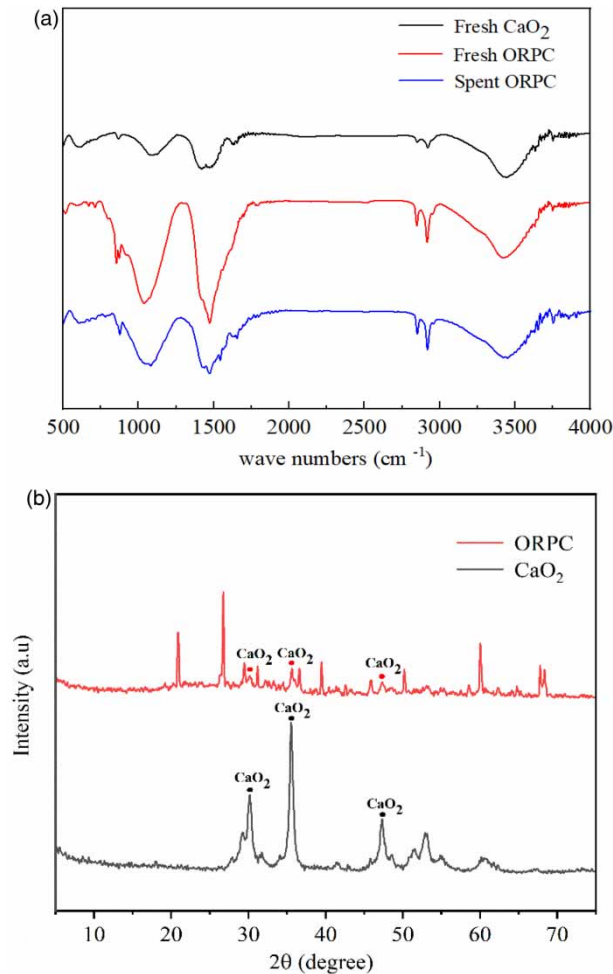


Figure 2 | Characteristics of ORPC and CaO₂ powder: (a) infrared spectra, (b) X-ray diffraction (XRD) images.

of SA in the ORPC was 0.53 g, 1.06 g, 2.13 g, and 3.20 g, respectively, the final phosphorus removal was 82.2%, 79.1%, 74.9%, and 73.3% within 28 days. As the content of SA decreased, the greater was the removal of phosphorus achieved, which clarified that the increase of SA content reduced the rate of ORPC oxygen release (Northup & Cassidy 2008).

3.2.3. Effect of temperature on ORPC performance

In this section, the influence of various temperatures on ORPC (a bentonite/cement/fine sand/CA/SA/CaO₂ mass ratio of 1.5:14:10:0.6:1.06:6.2) performance was tested. The batch experiment was carried out in a 1 L glass reactor. The different temperatures were fixed from 15 °C to 35 °C through the regulating thermostat of the solution. Nitrogen was used to blow off the oxygen of the phosphorus-containing water to 0 mg L⁻¹ before the beginning of the test, so that the influence of different temperatures on the ORPC could be compared clearly. As demonstrated in Figure S3(a), with the increasing of temperature from 15 °C to 25 °C and 35 °C at the initial phosphorus concentration of the 1.91 mg L⁻¹, the phosphorus concentration of the water was slightly decreased from 0.38 mg L⁻¹ to 0.34 mg L⁻¹ and 0.29 mg L⁻¹, respectively. This could be explained by the activity product of Ca²⁺ and PO₄³⁻ becoming larger which promoted the precipitation reaction of calcium phosphate with the increasing of temperature, thus slightly improving phosphorus removal (Song *et al.* 2002). The change of DO was inconspicuous with the temperature increase (Figure S3(b)). Wang & Wang (2006) also found that the behavior of CaO₂ for phosphorus removal in river water was only slightly affected by the climatic conditions.

3.3. ORPC purification test for the actual river water

A river simulation test was conducted to evaluate the feasibility of ORPC (the bentonite/cement/fine sand/CA/SA/CaO₂ mass ratio of 1.5:14:10:0.6:1.06:6.2) when putting 500 g ORPC evenly at the bottom of the reactor at the loading of

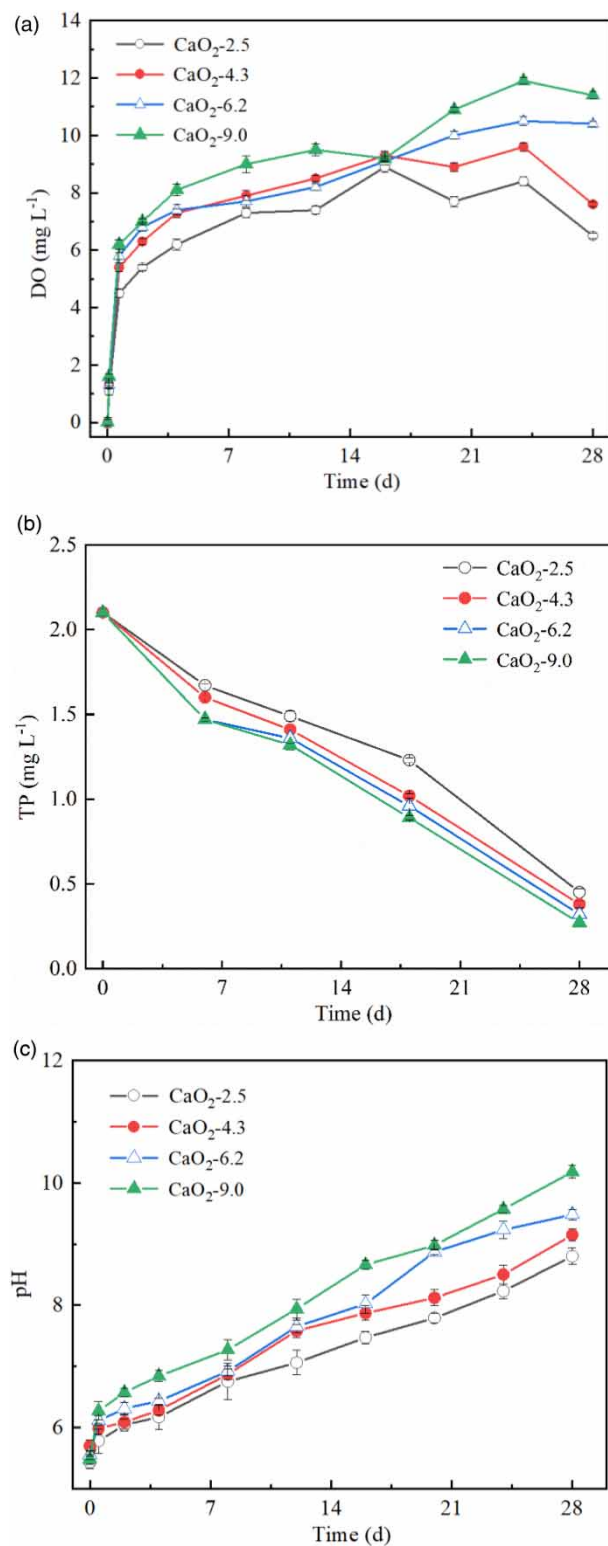


Figure 3 | Effect of ORPC with various CaO_2 contents on (a) DO, (b) the removal of phosphorus, and (c) pH.

$3,200 \text{ g m}^{-2}$ to remove phosphorus from the actual river water and to assess the effect on oxygen-release performance. Potassium dihydrogen phosphate was added to the actual river water to prepare phosphorus-containing river water with concentrations of 0.76 mg L^{-1} , 1.22 mg L^{-1} , and 2.07 mg L^{-1} , respectively. As illustrated in Figure 5(a), the effluent

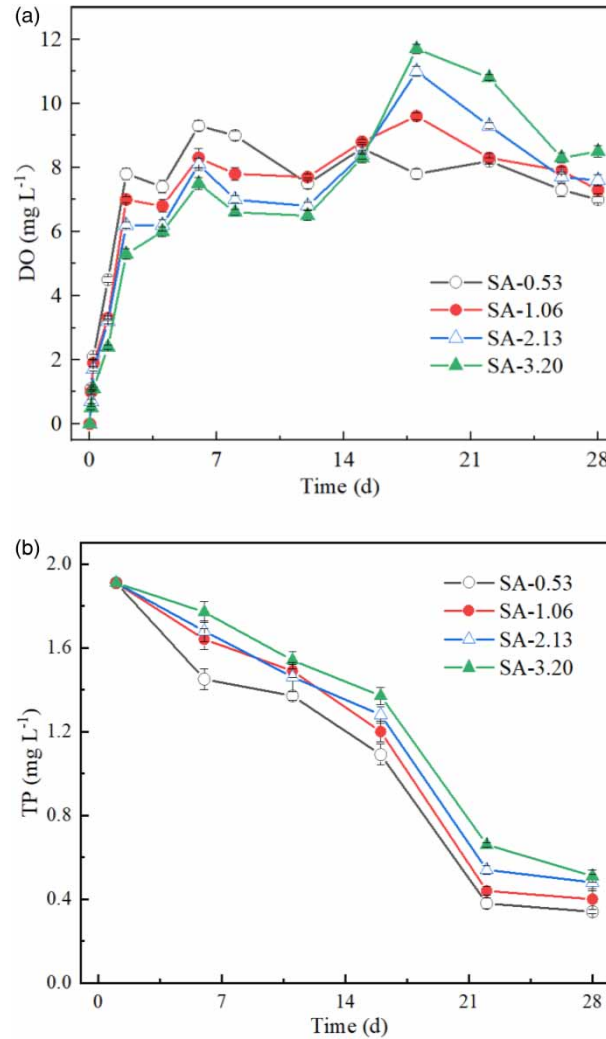


Figure 4 | Effect of ORPC with various SA contents on (a) DO, and (b) the removal of phosphorus.

concentration of phosphorus was 0.19 mg L^{-1} , 0.32 mg L^{-1} and 0.57 mg L^{-1} , respectively, after flowing through the reactor at a flow rate of 30 mL h^{-1} , and in accordance with the phosphorus removal efficiency of 75.0%, 73.8%, and 72.5%, respectively (Table 1). It can be seen that the ORPC displayed a great effect on phosphorus removal in the actual river water. In addition, after flowing through the reactor at the above three different phosphorus concentrations of the actual river water with an initial DO concentration of 5.3 mg L^{-1} , the concentration of DO in the effluent was raised to 7.0 mg L^{-1} , 8.3 mg L^{-1} , and 8.5 mg L^{-1} , respectively (Figure 5(b)). Moreover, it is well known that high pH will inhibit the activities of aquatic organisms (Wang *et al.* 2019). As shown in Table 2, when ORPC was applied, the pH of the above three different phosphorus concentrations of actual river water were increased from 8.03, 7.62, and 7.57 to 9.31, 8.41, and 8.69, respectively, which was similar to the pH change observed by Zhang *et al.* (2012). During the oxygen-releasing process, the change of the raised pH was caused by the formation of $\text{Ca}(\text{OH})_2$ via the reaction between CaO_2 and water. Compared with CaO_2 powder in Figure S4, OH^- was generated by ORPC more slowly due to the slower reactive rate of ORPC, resulting in the slow increase in pH. This was similar to the results obtained by Noyma *et al.* (2016) and Zhou *et al.* (2020). The above results suggested that ORPC has a great ability to remove phosphorus in actual river water and significantly increase the concentration of DO under complex river conditions.

The flow rate of the actual river water was another important factor that could significantly affect the performance of the ORPC. Therefore, the effect of various flow rates on phosphorus removal in river water was investigated. The results showed that the removal of phosphorus increased with the decrease in flow rate (Figure 5(a)). The phosphorus removal efficiency of

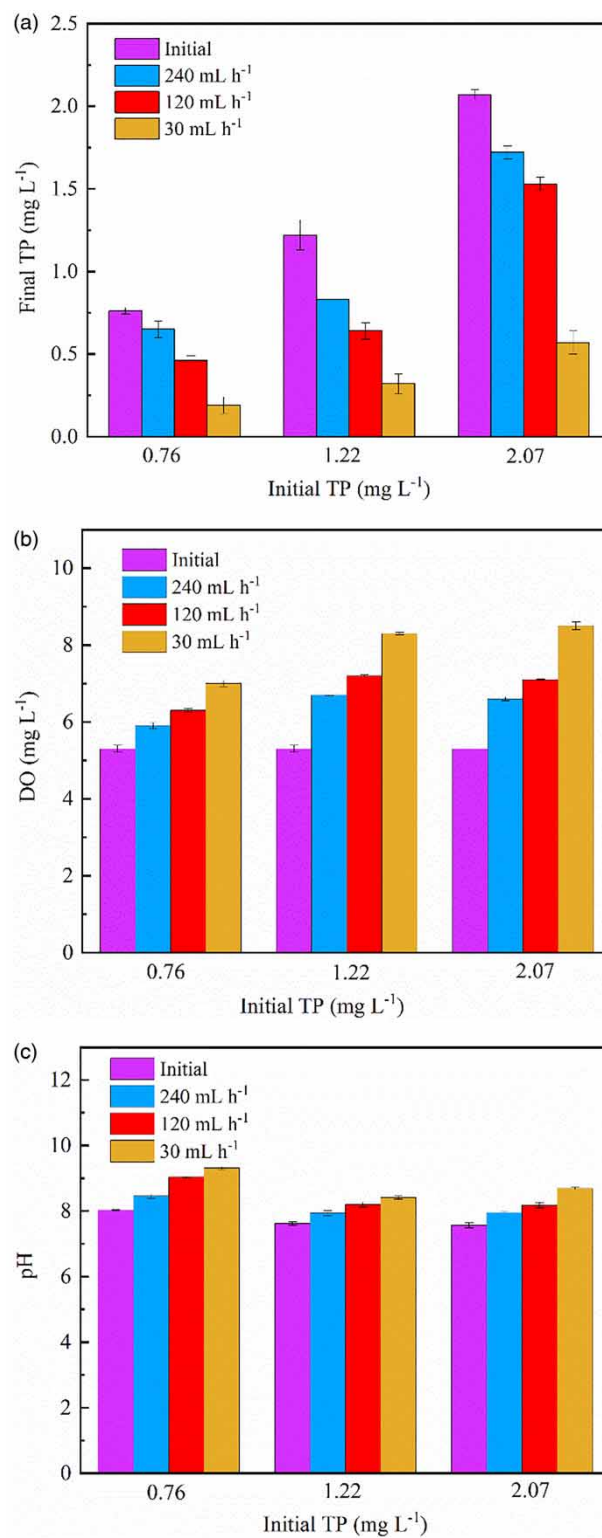


Figure 5 | Effect of different initial phosphorus concentrations and different flow velocities on (a) the removal of phosphorus, (b) DO of actual river water under the presence of ORPC, (c) pH value of actual river water under the presence of ORPC.

river water decreased from 75.0% to 40.0% and 14.5% with the flow rate increase from 30 mL h⁻¹ to 120 mL h⁻¹ and 240 mL h⁻¹ at the initial phosphorus concentration of 0.76 mg L⁻¹, respectively. The same trend was found at the initial phosphorus concentrations of 1.22 mg L⁻¹ and 2.07 mg L⁻¹ (Table 2). These results could be explained by the following reasons.

Table 1 | ORPC effect on the actual river water with different TP concentrations

TP (initial/final) (mg L ⁻¹)	TP removal (%)	DO (initial/final) (mg L ⁻¹)	pH (initial/final)
2.07/0.57	72.5	5.3/8.5	7.57/8.69
1.22/0.32	73.8	5.3/8.3	7.62/8.41
0.76/0.19	75.0	5.3/7.0	8.03/9.31

The flow rate of the river was 30 mL h⁻¹.

Table 2 | ORPC effect on the actual river water with different flow rates

Flow rate (mL h ⁻¹)	TP (initial/final) (mg L ⁻¹)	TP removal (%)	DO (initial/final) (mg L ⁻¹)	pH (initial/final)
30	2.07/0.57	72.5	5.3/8.5	7.57/8.69
120	2.07/1.53	26.1	5.3/7.1	7.57/8.18
240	2.07/1.72	17.0	5.3/6.6	7.57/7.95
30	1.22/0.32	73.8	5.3/8.3	7.62/8.41
120	1.22/0.64	47.6	5.3/7.2	7.62/8.2
240	1.22/0.83	32.0	5.3/6.7	7.62/7.94
30	0.76/0.19	75.0	5.3/7.0	8.03/9.31
120	0.76/0.46	40.0	5.3/6.3	8.03/9.04
240	0.76/0.65	14.5	5.3/5.9	8.03/8.46

The hydraulic retention time decreased with the increase of flow rate and then the contact time of the ORPC with the river water was reduced, thus causing the decrease of phosphorus reaction with ORPC and resulting in less removal of phosphorus. In addition, the DO of river water in the effluent was determined and the results are shown in [Figure 5\(b\)](#). The DO of river water was increased from 5.9 mg L⁻¹ to 6.3 mg L⁻¹ and 7.0 mg L⁻¹ with the flow rate decrease from 240 mL h⁻¹ to 120 mL h⁻¹ and 30 mL h⁻¹ at the initial phosphorus concentration of 0.76 mg L⁻¹, respectively, and all DO values increased when compared with the initial influent DO of 5.3 mg L⁻¹. The same elevation of DO level was also observed at the initial phosphorus concentrations of 1.22 mg L⁻¹ and 2.07 mg L⁻¹, confirming that the flow rate of the actual river performed an important role for ORPC on effluent phosphorus concentration and effluent DO level with an inverse correlation. Therefore, the phosphorus removal and DO level in river water could be adjusted to meet practical demands by varying the flow rate of the actual river water.

3.4. ORPC impact on DO level and the total soluble phosphorus in overlying water

The river simulation experiment was conducted to evaluate the feasibility of using ORPC (a bentonite/cement/fine sand/CA/SA/CaO₂ mass ratio of 1.5:14:10:0.6:1.06:6.2) when putting 210 g ORPC evenly at the bottom of the reactor under a loading of 4,000 g m⁻² to remove phosphorus in the actual river water. In this test, the sediment collected from the actual river was added to a height of 5–6 cm in the reactor to simulate a river and the actual river water flowed through the reactor with a flow rate of 180 mL h⁻¹. As shown in [Figure 6\(a\)](#), the initial DO was 4.7 mg L⁻¹ without ORPC in the blank control. After flowing through the reactor, the DO concentration in the effluent was less than 1 mg L⁻¹ for the whole 28 days, confirming that it was basically in an anoxic condition ([Sugiura et al. 2004](#)). When ORPC was added as an oxygen source, the DO concentration in the effluent was maintained from 2.0 to 3.5 mg L⁻¹ with less change of DO level in the tested condition. It was noted that ORPC could release oxygen for a longer period of time with a slow rate in the water. Even after 28 days, the DO in the effluent was still kept around 3 mg L⁻¹, indicating that the ORPC was beneficial to providing an oxic environment and therefore would inhibit the endogenous release of phosphorus in sediment, as discussed later ([Jiang et al. 2008](#)).

The removal of phosphorus by using ORPC in the above tested condition was also monitored. As shown in [Figure 6\(b\)](#), around 0.05 mg L⁻¹ phosphorus in the blank was the increase in the effluent compared with the influent, whereas the concentration of phosphorus decreased by 0.07–0.29 mg L⁻¹ in the presence of ORPC, indicating that ORPC had the ability to

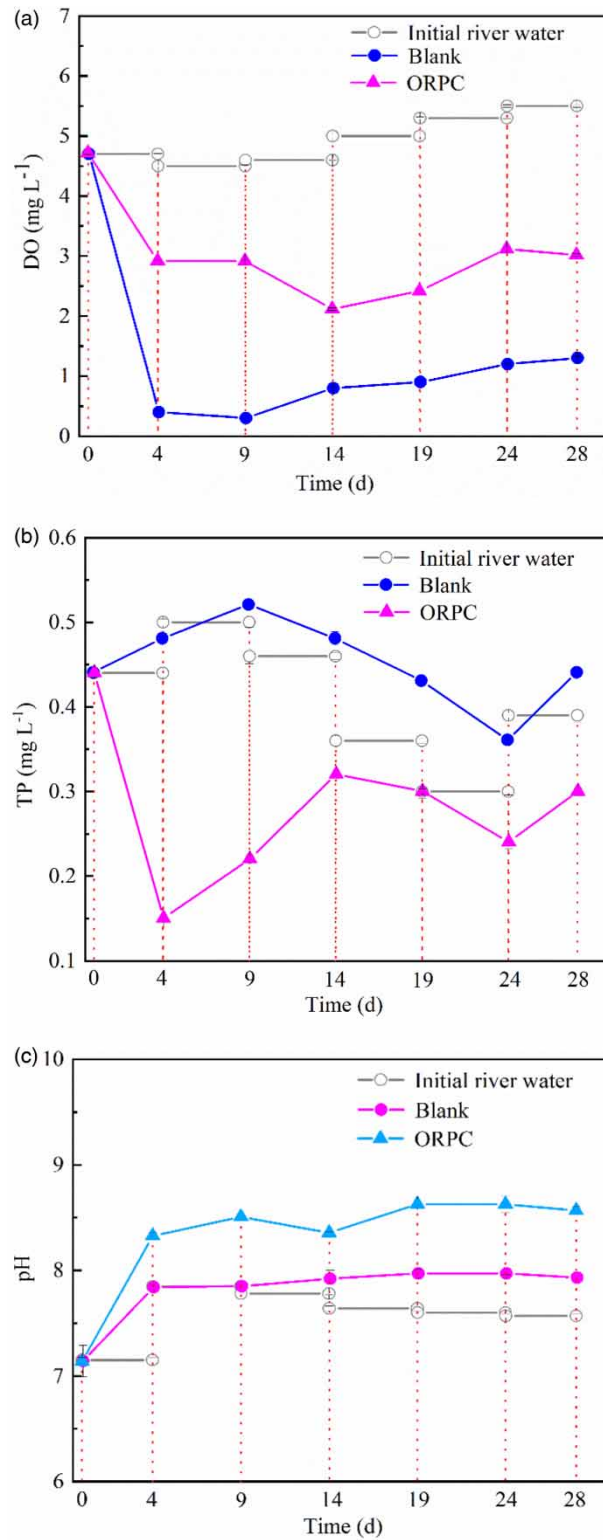


Figure 6 | Effect of ORPC on (a) DO, (b) the removal of phosphorus, and (c) pH in overlying water.

solidate phosphorus from water and sediment. The solution pH was also evaluated and the result is provided in Figure 6(c). The pH in the blank was steadily kept between 7 and 8, while the effluent pH was only increased to 8–9 after adding ORPC in 28 days, although the ORPC could generate $\text{Ca}(\text{OH})_2$ during oxygen release (Equation (1)). The slight and reasonable

elevation of effluent pH might be due to the sustained and slow release of oxygen by the ORPC that was suitable for the survival and aerobic respiration of microorganisms in the sediment, in which the microorganisms could consume organic matter to produce CO_2 that decreased the pH of the water (Zhou *et al.* 2017). In addition, SA and CA were also beneficial to inhibiting an excessive rise of pH due to their buffering capacity. Therefore, ORPC was suitable to be applied in removing phosphorus and, at the same time, releasing oxygen with little effect on the pH elevation in the actual river water.

3.5. ORPC effect on the species of inorganic phosphorus in sediment

The changes of various species of inorganic phosphorus in the sediment were compared between blank and ORPC groups and the results are shown in Figure 7. In Figure 7(a), only a little difference of Al-P mass concentration was found in the blank group within 28 days, indicating the low conversion efficiency of Al-P to other species of phosphorus. However, the Al-P mass concentration in the sediment was significantly increased from 0.196 mg g^{-1} to 0.372 mg g^{-1} with the addition of ORPC (Figure 7(b)). Further, the mass concentration of Al-P in the ORPC which was on the top of the sediment for 28 days evidently increased to 1.040 mg g^{-1} (Figure 8) due to the adsorption of ORPC to the phosphorus in the water phase which later converted it into Al-P. The reasons for the above results were as follows: (a) Other species of phosphorus such as Cl-P and Fe-P in the sediment could be transformed into Al-P. In the mobile phosphorus fractions, Cl-P and Fe-P were the dominant fractions. Cl-P and the soluble phosphorus were easily desorbed and competitively adsorbed by other ions such as Fe and Al ions (Lin *et al.* 2017; Song *et al.* 2020). However, $\text{Al}(\text{OH})_3$ was formed due to the reaction of Al wrapped

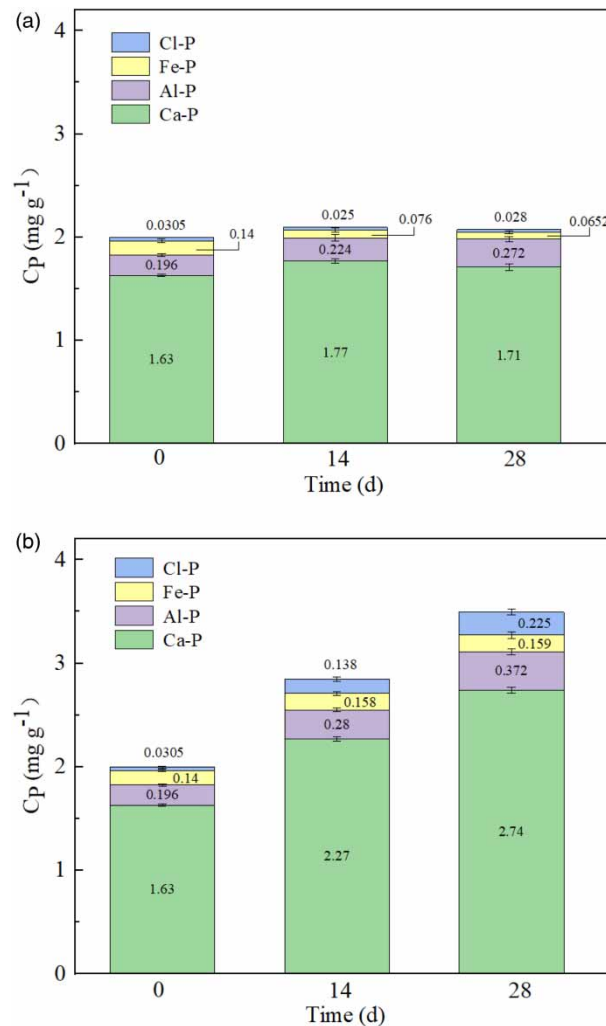


Figure 7 | Changes in the species of inorganic phosphorus in sediment: (a) blank group, (b) ORPC group.

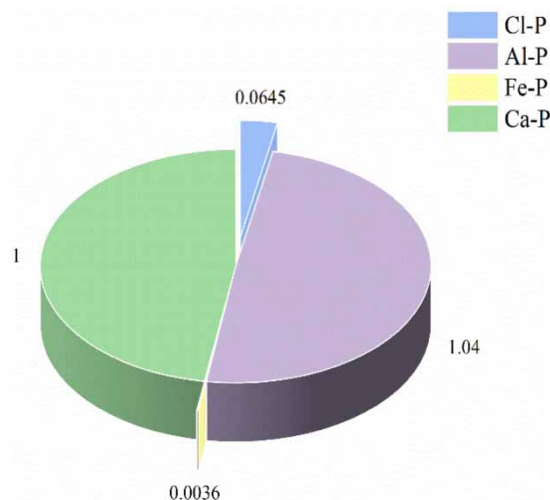


Figure 8 | The quantity of various species of inorganic phosphorus in ORPC.

in ORPC with water, and the settled Al oxyhydroxide flocs adsorbed phosphorus which was displaced from iron-carriers due to the preferential adsorption of phosphorus by Al rather than by Fe (Zhou *et al.* 2020). (b) The total soluble phosphorus in the overlying water was able to be transformed into Al-P in the sediment. (c) $\text{Al}(\text{OH})_3$ was not converted into meta-aluminate acid but could form colloids to further adsorb PO_4^{3-} in the water (Zhou *et al.* 2020). Therefore, the content of Al-P in the sediment kept rising due to the effect of the ORPC.

The mass concentration of Ca-P in the blank was maintained around 1.7 mg g^{-1} , demonstrating the low conversion of Ca-P to other species of phosphorus. After adding ORPC, the mass concentration of Ca-P in the sediment increased tardily and finally rose to 2.74 mg g^{-1} (Figure 7(b)). At the same time, the mass concentration of Ca-P in the ORPC apparently increased to 1.0 mg g^{-1} . These results were because the $\text{Ca}(\text{OH})_2$ as formed by Equation (1) could adsorb PO_4^{3-} in the overlying water, then formed stable Ca-P such as hydroxyapatite (Madsen *et al.* 1995). With the increase of Ca^{2+} concentration, other species of phosphorus such as iron phosphorus also could be converted to Ca-P (Hanh *et al.* 2005). It further showed that ORPC had achieved the ability of long-term phosphorus removal and the effect of sustained release after CaO_2 was embedded by SA.

In Figure 7(a), the mass concentration of Fe-P in the blank slightly decreased from 0.14 mg g^{-1} to 0.065 mg g^{-1} , whereas after the addition of ORPC, the mass concentration of Fe-P in the sediment finally rose to 0.159 mg g^{-1} (Figure 7(b)). The mass concentration of Fe-P in the ORPC slightly increased to 0.0036 mg g^{-1} . The reasons for the above results were as follows. On the one hand, Fe^{2+} in the sediment was transformed to Fe^{3+} owing to the slow release of oxygen by the ORPC, which could combine with PO_4^{3-} to form insoluble Fe-P (Zhou *et al.* 2012). On the other hand, CaO_2 formed an alkaline environment to produce $\text{Fe}(\text{OH})_3$ colloids. It adsorbed soluble total phosphorus and increased the Fe-P in the sediment.

4. CONCLUSIONS

In this study, an ORPC product was prepared with CaO_2 , bentonite, cement, SA, CA, and fine sand, and the prepared ORPC was proved to have the ability to control phosphorus and to release oxygen. The phosphorus removal by ORPC grew with the increase of CaO_2 content, while the removal of phosphorus decreased with increasing SA content during ORPC preparation. The effluent phosphorus concentration of the actual river water with initial phosphorus concentrations of 0.76, 1.22, and 2.07 mg L^{-1} could be reduced after flowing through the reactor with the presence of ORPC. Further, the hydraulic retention time was decreased with the increase of flow rate and then the contact time of the ORPC with the river water was reduced, thus causing the decrease of phosphorus reaction with ORPC and resulting in less removal of phosphorus. The total soluble phosphorus in the overlying water was adsorbed on the ORPC and later converted to Al-P, Ca-P, and Fe-P in the sediment, thus achieving the purpose of adsorbing phosphorus in the water body and preventing the release of phosphorus from sediment. In conclusion, ORPC can maintain DO at a reasonable level and control phosphorus in the water body, therefore displaying the potential for its application in the removal of phosphorus from the actual river and inhibiting phosphorus release from sediment while maintaining DO in the water body.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Abel, S. & Akkanen, J. 2019 Novel, activated carbon-based material for in-situ remediation of contaminated sediments. *Environmental Science & Technology* **53** (6), 3217–3224.
- Cassidy, D. P. & Irvine, R. L. 1999 Use of calcium peroxide to provide oxygen for contaminant biodegradation in a saturated soil. *Journal of Hazardous Materials* **69** (1), 25–39.
- Chen, X. Y., Liu, J. X., Su, Y. P., Zhang, C. W., Weng, Y., Lai, S. H. & Zhao, Y. J. 2016 Comparative study on the effect of two phosphorus locking agents. *Journal of Fujian Normal University* **32** (4), 56–60.
- Cooke, G. D., Welch, E. B., Martin, A. B., Fulmer, D. G., Hyde, J. B. & Schriever, G. D. 1993 Effectiveness of Al, Ca, and Fe salts for control of internal phosphorus loading in shallow and deep lakes. *Hydrobiologia* **253** (1–3), 323–335.
- Ding, S. M., Chen, M. S., Gong, M. D., Fan, X. F., Qin, B. Q., Xu, H., Gao, S. S., Jin, Z. F., Tsang, D. C. W. & Zhang, C. S. 2018 Internal phosphorus loading from sediments causes seasonal nitrogen limitation for harmful algal blooms. *Science of the Total Environment* **625**, 872–884.
- Fan, Y., Li, Y. W., Wu, D. Y., Li, C. J. & Kong, H. N. 2017 Application of zeolite/hydrous zirconia composite as a novel sediment capping material to immobilize phosphorus. *Water Research* **123**, 1–11.
- Fonseca, R., Canário, T., Morais, M. & Barriga, F. J. A. S. 2011 Phosphorus sequestration in Fe-rich sediments from two Brazilian tropical reservoirs. *Applied Geochemistry* **26** (9–10), 1607–1622.
- Hanh, D. N., Rajbhandari, B. K. & Annachhatre, A. P. 2005 Bioremediation of sediments from intensive aquaculture shrimp farms by using calcium peroxide as slow oxygen release agent. *Environmental Technology* **26** (5), 581–590.
- Jiang, X., Jin, X. C., Yao, Y., Li, L. H. & Wu, F. C. 2008 Effects of biological activity, light, temperature and oxygen on phosphorus release processes at the sediment and water interface of Taihu Lake, China. *Water Research* **42** (8–9), 2251–2259.
- Kao, C. M., Chen, S. C., Wang, J. Y., Chen, Y. L. & Lee, S. Z. 2003 Remediation of PCE-contaminated aquifer by an in situ two-layer biobarrier: laboratory batch and column studies. *Water Research* **37** (1), 27–38.
- Lee, C. S., Thanh, T. L., Kim, E. J., Gong, J. Y., Chang, Y. Y. & Chang, Y. S. 2014 Fabrication of novel oxygen-releasing alginate beads as an efficient oxygen carrier for the enhancement of aerobic bioremediation of 1,4-dioxane contaminated groundwater. *Bioresour. Technology* **171**, 59–65.
- Liang, Y. K., Zhang, Y. L., Su, X. S. & Dong, T. Z. 2018 Preparation of slow-releasing oxygen materials and study on their properties. *Water Supply* **18** (1), 23–31.
- Lin, J., Sun, Q., Ding, S. M., Wang, D., Wang, Y., Chen, M. S., Shi, L., Fan, X. F. & Tsang, D. C. W. 2017 Mobile phosphorus stratification in sediments by aluminum immobilization. *Chemosphere* **186**, 644–651.
- Lin, J. W., He, S. Q., Zhan, Y. H., Zhang, Z., Wu, X. L., Yu, Y., Zhao, Y. Y. & Wang, Y. 2019 Assessment of sediment capping with zirconium-modified bentonite to intercept phosphorus release from sediments. *Environmental Science and Pollution Research* **26** (4), 3501–3516.
- Liu, S. J., Jiang, B., Huang, G. Q. & Li, X. G. 2006 Laboratory column study for remediation of MTBE-contaminated groundwater using a biological two-layer permeable barrier. *Water Research* **40** (18), 3401–3408.
- Liu, Y., Sheng, X., Dong, Y. H. & Ma, Y. J. 2012 Removal of high-concentration phosphate by calcite: effect of sulfate and pH. *Desalination* **289**, 66–71.
- Madsen, H. E. L., Christensson, F., Polyak, L. E., Suvorova, E. I., Kliya, M. O. & Chernov, A. A. 1995 Calcium phosphate crystallization under terrestrial and microgravity conditions. *Journal of Crystal Growth* **152** (3), 191–202.
- Northup, A. & Cassidy, D. 2008 Calcium peroxide (CaO₂) for use in modified Fenton chemistry. *Journal of Hazardous Materials* **152** (3), 1164–1170.
- Noyma, N. P., de Magalhães, L., Furtado, L. L., Mucci, M., van Oosterhout, F., Huszar, V. L. M., Marinho, M. M. & Lüring, M. 2016 Controlling cyanobacterial blooms through effective flocculation and sedimentation with combined use of flocculants and phosphorus adsorbing natural soil and modified clay. *Water Research* **97**, 26–38.
- Nykänen, A., Kontio, H., Klutas, O., Penttinen, O.-P., Kostia, S., Mikola, J. & Romantschuk, M. 2012 Increasing lake water and sediment oxygen levels using slow-release peroxide. *Science of the Total Environment* **429**, 317–324.
- Schindler, D. W., Hecky, R. E., Findlay, D. L., Stainton, M. P., Parker, B. R., Paterson, M. J., Beaty, K. G., Lyng, M. & Kasian, S. E. M. 2008 Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proceedings of the National Academy of Sciences of the United States of America* **105** (32), 11254–11258.
- Smith, V. H. & Schindler, D. W. 2009 Eutrophication science: where do we go from here? *Trends in Ecology and Evolution* **24** (4), 201–207.
- Song, Y. H., Hahn, H. H. & Hoffmann, E. 2002 Effects of solution conditions on the precipitation of phosphate for recovery: a thermodynamic evaluation. *Chemosphere* **48** (10), 1029–1034.
- Song, X. J., Li, D. P., Zhao, Z. H., Zhou, J., Xu, C. T., Geng, X. & Huang, Y. 2020 The effect of microenvironment in the sediment on phosphorus immobilization under capping with ACPM and Phoslock. *Environmental Science and Pollution Research* **27** (13), 15440–15453.

- Sugiura, N., Utsumi, M., Wei, B., Iwami, N., Okano, K., Kawauchi, Y. & Maekawa, T. 2004 Assessment for the complicated occurrence of nuisance odours from phytoplankton and environmental factors in a eutrophic lake. *Lakes and Reservoirs: Research and Management* **9** (3–4), 195–201.
- Wang, H. Z. & Wang, S. G. 2006 Study on phosphorus recovery by calcium phosphate precipitation from wastewater treatment plant. *China Water and Wastewater* **22** (9), 93–96 (in Chinese).
- Wang, Z., Lu, S. Y., Wu, D. Y. & Chen, F. X. 2017 Control of internal phosphorus loading in eutrophic lakes using lanthanum-modified zeolite. *Chemical Engineering Journal* **327**, 505–513.
- Wang, Y., Wang, W. H., Yan, F. L., Ding, Z., Feng, L. L. & Zhao, J. C. 2019 Effects and mechanisms of calcium peroxide on purification of severely eutrophic water. *Science of the Total Environment* **650**, 2796–2806.
- Wang, C. L., Yan, K., Lei, P. F., Li, H. Y. & Zheng, J. H. 2021 Preparation and characterization of CaCO₃ filler modified with double-site stearic acid for trademark fabric coated by polyamide. *The Journal of the Textile Institute* **112** (2), 333–340.
- Xu, Y., Han, F. E., Li, D. P., Zhou, J. & Huang, Y. 2018 Transformation of internal sedimentary phosphorus fractions by point injection of CaO₂. *Chemical Engineering Journal* **343**, 408–415.
- Yan, S. L., Kim, M., Salley, S. O. & Ng, K. Y. S. 2009 Oil transesterification over calcium oxides modified with lanthanum. *Applied Catalysis A: General* **360** (2), 163–170.
- Yin, H. B., Zhu, J. C. & Tang, W. Y. 2018 Management of nitrogen and phosphorus internal loading from polluted river sediment using Phoslock and modified zeolite with intensive tubificid oligochaetes bioturbation. *Chemical Engineering Journal* **353**, 46–55.
- Yu, P. P., Wang, J. F., Chen, J. G., Guo, J. Y., Yang, H. Q. & Chen, Q. 2019 Successful control of phosphorus release from sediments using oxygen nano-bubble-modified minerals. *Science of the Total Environment* **663**, 654–661.
- Zamparas, M. & Zacharias, I. 2014 Restoration of eutrophic freshwater by managing internal nutrient loads. A review. *Science of the Total Environment* **496**, 551–562.
- Żegliński, J., Piotrowski, G. P. & Piękoś, R. 2006 A study of interaction between hydrogen peroxide and silica gel by FTIR spectroscopy and quantum chemistry. *Journal of Molecular Structure* **794** (1–3), 83–91.
- Zhang, Y. X., Liang, J. K., Wang, R., Ren, Z. Y. & Jing, Q. 2012 Application of improving oxygen releasing material in situ polluted groundwater PRB bioremediation. *Chinese Journal of Environmental Engineering* **6** (11), 3910–3914 (in Chinese).
- Zhang, F., Zhang, M., Su, X., Zhang, S., Zhang, Q. & Zhong, S. 2018 Preparation and application of oxygen slow-releasing materials for in situ manganese removal from groundwater. *International Journal of Environmental Science and Technology* **16**, 5585–5594.
- Zhou, Y. B., Wang, Y. X., Zhou, Z. H., Li, Y. & Lu, J. 2012 Preparation and oxygen release properties of calcium peroxide-based oxygen slow-release composite. *China Water and Wastewater* **28** (7), 64–67 (in Chinese).
- Zhou, Y. B., Fang, X. B., Zhang, Z. Q., Hu, Y. H. & Lu, J. 2017 An oxygen slow-releasing material and its application in water remediation as oxygen supplier. *Environmental Technology* **38** (22), 2793–2799.
- Zhou, J., Li, D. P., Chen, S. T., Xu, Y., Geng, X., Guo, C. R. & Huang, Y. 2018 Sedimentary phosphorus immobilization with the addition of amended calcium peroxide material. *Chemical Engineering Journal* **357**, 288–297.
- Zhou, J., Li, D. P., Zhao, Z. H., Song, X. J., Huang, Y. & Yang, J. J. 2020 Phosphorus immobilization by the surface sediments under the capping with new calcium peroxide material. *Journal of Cleaner Production* **247**, 119135.
- Zhu, J., He, Y., Wang, J. H., Qiao, Z. C., Wang, Y., Li, Z. H. & Huang, M. S. 2017 Impact of aeration disturbances on endogenous phosphorus fractions and their algae growth potential from malodorous river sediment. *Environmental Science and Pollution Research* **24** (9), 8062–8070.
- Zhu, Y. Y., Tang, W. Z., Jin, X. & Shan, B. Q. 2019 Using biochar capping to reduce nitrogen release from sediments in eutrophic lakes. *Science of the Total Environment* **646**, 93–104.

First received 6 May 2021; accepted in revised form 5 August 2021. Available online 18 August 2021