



Metal-Modified Mussel Shell for Efficient Binding of Phosphorus in Eutrophic Waters

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Abstract

As phosphorus (P) exceeds 0.1 mg P L^{-1} , the water is usually considered high enough to cause eutrophication. Thermally treated mussel shell (TMS), a calcium-rich (36.76%) biological material, was an environmentally friendly and low-cost adsorbent for P removal. To achieve very low concentrations of P, composite agents of PAC–TMS, Fe–TMS and La–TMS were prepared with the optimum weight ratio of 0.4, 0.2 and 0.2 (g g^{-1}) [polyaluminium chloride (PAC), $\text{Fe}(\text{OH})_3$ or La_2O_3 to TMS] with the lower cost and high P adsorption efficiency, respectively, all of which had more than 80% of P removal rate after 12-h treatment of 5 mg L^{-1} P solution, much higher than that of TMS alone (50%). Isotherm experiment showed that these composite agents have maximum phosphate adsorption capacities of $91.74 \text{ mg P g}^{-1}$ (PAC–TMS), $101.42 \text{ mg P g}^{-1}$ (Fe–TMS) and $56.50 \text{ mg P g}^{-1}$ (La–TMS), respectively. Additionally, the metal-modified TMS was almost independent of pH. Long-term efficient removal of P ($< 0.1 \text{ mg L}^{-1}$) was achieved during a 3-month removal trial of P-contaminated water while using these metal-modified TMS. Since metal-modified TMS both had calcium and other multivalent metal (Al, La or Fe), the modification pathway was mainly dependent on both enhance adsorption/precipitation by a simultaneous effect of the calcium and other multivalent metal.

Article Highlights

- PAC–TMS, Fe–TMS and La–TMS with optimum ratio of 0.4, 0.2 and 0.2 for P removal
- P adsorption capacities of 91.74(PAC–TMS), 101.42(Fe–TMS) and 56.50 mg g^{-1} (La–TMS)
- Long-term efficient removal of P ($< 0.1 \text{ mg L}^{-1}$) via these metal-modified TMS

Keywords Phosphorus · Adsorption · Precipitation · Mussel shell · Aluminum · Lanthanum oxide

Introduction

Eutrophication is a global environmental problem that deteriorates water quality, damages ecosystems and threatens humans and animals health (Boeykens et al. 2017; Ruan et al. 2016; Deng et al. 2019). Phosphorous concentrations greater than 0.1 mg P L^{-1} are usually considered high enough to cause eutrophication (Kumar et al. 2019). In

recent years, significant attention has been paid to phosphorus adsorption using biomass materials due to their low-cost and environmental-friendly properties, such as biochar from cellulosic material, biological shell material and so on (Dai et al. 2017; Micháleková-Richveisová et al. 2017; Paradelo et al. 2016; Roy 2017; Xiong et al. 2011; Zheng et al. 2019). These studies also showed that biomass adsorbents modified via physical pyrolysis and chemical treatment were commonly used in obtaining effective phosphorus adsorption to achieve very low concentrations of P. Biochar pyrolyzed from cellulosic materials has been modified by chemical compounds of aluminum (Novais et al. 2018), iron (Micháleková-Richveisová et al. 2017) and lanthanum modification (Qiu et al. 2017). There was little multivalent metal in cellulosic material, while biological shells are calcium-rich materials. Considering these, the direct modification

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of biological shell is more practical as low-cost adsorbent for achieving very low concentrations of P. Biological shell modification via pyrolysis was applied in most cases (Dai et al. 2017; Paradelo et al. 2016; Xiong et al. 2011), while chemical agents were seldom used (Arulvel et al. 2017). To improve the phosphorus removal performance of shells, more modification methods are demanded.

Waste mussel shells are abundant in shellfish aquaculture and the canning industries. Several studies have attempted to turn mussel shell into phosphorus adsorbents (Paradelo et al. 2016; Romar-Gasalla et al. 2016; Xiong et al. 2011; Zapater-Pereyra et al. 2014). The raw powdered mussel shell was reported to have the maximum adsorption capacity 6.95 mg P g^{-1} and $18.23 \text{ mg P g}^{-1}$ for phosphate, respectively (Xiong et al. 2011; Paradelo et al. 2016). A thermally treatment could increase the maximum adsorption capacity of mussel shell from 18.23 to $38.75 \text{ mg P g}^{-1}$ for phosphate, and adsorption and precipitation both contributed to phosphate removal (Paradelo et al. 2016). However, the modification of thermally treated mussel shell is still needed to achieve very low concentrations of P. In this study, three metal-modified methods were attempted to improve the phosphorus removal performance of pyrolyzed mussel shell: polyaluminium chloride, iron and lanthanum oxide. In addition, lanthanum oxide has high phosphate affinity and often requires support materials such as activated carbon fiber (Zhang et al. 2011) and mesoporous silicate (Huang et al. 2015) to disperse the lanthanum. The pyrolyzed mussel shell powder could provide a much cheaper alternative support material for lanthanum.

Thus, pyrolyzed mussel shell powder was prepared and modified via three multivalent metal chemicals (Al, La or Fe), the phosphorus removal characteristics of which were examined via batch experiments, and the long-term performance of treating phosphorous-contaminated water was further investigated.

Materials and methods

Materials

Marine mussel shell was collected from a local mussel breeding plant in Zhoushan City in China. Polyaluminium chloride (PAC), lanthanum oxide (La_2O_3) and pure ferric chloride (FeCl_3) were used as chemical modification agents for phosphorus removal in the study, respectively. The phosphate synthetic solution was prepared by dissolving potassium dihydrogen orthophosphate in deionized water. The real environmental water was collected from local contaminated river in Zhoushan city of China.

TMS preparation and modification

The mussel shell was washed to remove impurities and pulverized by grinder after drying in the oven. TMS was then obtained via pyrolyzing at $600 \text{ }^\circ\text{C}$ for 2 h in muffle furnace. Modification agents of PAC, La_2O_3 and $\text{Fe}(\text{OH})_3$ were mixed with TMS at different weight ratios to obtain composite phosphorus binding agents of PAC–TMS, La–TMS and Fe–TMS in the study. The weight ratio refers to the ratio of $\text{Fe}(\text{OH})_3$, La_2O_3 and PAC to TMS. La_2O_3 and TMS were physically mixed evenly with various weight ratios of 0.2, 0.4 and 0.8 to obtain aLa–TMS, bLa–TMS and cLa–TMS, respectively, and the same method was used to acquire aPAC–TMS, bPAC–TMS as well as cPAC–TMS. Fe–TMS was a mixture of TMS and the floc $\text{Fe}(\text{OH})_3$, and the floc was obtained via the reaction of FeCl_3 (1 M) and NaOH (1 M) solution. Next, the floc was dried to a constant weight and then physically mixed evenly with of TMS at various weight ratios of 0.2, 0.4 and 0.8 to achieve the composite phosphorus binding agents of Fe–TMS. Phosphorus removal characteristics were all observed for different types of Fe–TMS, La–TMS and PAC–TMS. The La_2O_3 and PAC used in the form of a solid powder. The optimum mass ratio of the three composited phosphorus binding agents was ascertained via the phosphorus removal performance after 12-h treatment of 5 mg P L^{-1} synthetic solution under the same dosage (20 g L^{-1}).

Batch experiments

Phosphorus (P) removal characteristics of Fe–TMS, La–TMS and PAC–TMS were further examined through the batch experiments of isotherm experiment, kinetics of P removal, the effect of adsorbents dosage, other ions and pH conditions. The batch experiments were conducted in a 250-mL conical flask inside a rotary mixer for 12 h (100 rpm and $25 \text{ }^\circ\text{C}$) with initial P concentration of 50 mg L^{-1} and P binding agent dosage of 20 g L^{-1} (excluding isotherm experiments). The initial pH of batch experiments was all adjusted to 7.0 ± 0.2 except for the effect of pH experiment.

- isotherm experiment: 100-mL solutions containing known concentrations of P ($2\text{--}500 \text{ mg P L}^{-1}$) were added to 0.1 g (1 g L^{-1}) of composite agent in 250-mL conical flask in oscillator for 12 h.
- kinetics of P removal: the sample was shaken for 0, 10, 20, 30, 60, 90, 150 and 210 min in a rotary mixer.
- the effect of adsorbents dosage: the experiment was observed with various dosages of P binding agent (2, 5, 10, 20, 40, 60, 80 and 100 g L^{-1}).

- the effect of other ions: different concentrations of ammonia nitrogen, nitrate nitrogen and nitrite nitrogen (0, 2, 5, 10, 20 and 50 mg L⁻¹) were added in P solution to examine the effect of other ions to optimum dosage of each mussel shell type in 500-mL conical flask with rotary mixer for 12 h.
- the effect of pH: according to environmental water quality, different solution pH conditions of 6, 7 and 9 were further considered.

Application of composite phosphorus binding agents for contaminated environmental water

The real environmental water was collected from a local contaminated river Jingguan in Zhoushan of China. The phosphate (PO₄³⁻-P) concentration of real water was 0.2 mg L⁻¹. To further highlight the phosphorus pollution, PO₄³⁻-P concentration in the real water was increased to 1.5 mg L⁻¹ with the addition of monopotassium phosphate. To study the performance of binding phosphorus characteristics of optimum Fe-TMS, La-TMS and PAC-TMS during phosphorus-contaminated water treatment, seven white plastic rectangle devices (dimensions by 32 × 24 × 19 cm) with working volume of 10 L were developed with different optimum composite phosphorus binding agents and hydrodynamic condition simulated via aeration (Table 1). Each device was filled with 10 L of phosphorus contaminated water with the initial PO₄³⁻-P concentration of 1.5 mg L⁻¹. Except control device W₁, the rest devices W₂–W₇ were filled with the same dosage of composite phosphorus binding agents. The phosphorus was added in the devices on about 1-month and 2-month operation time for the further study of long-term performances, respectively. The distilled water was added into the devices W₁–W₇ to replenish the evaporation of water every day. The PO₄³⁻-P concentration variations in the devices W₁–W₇ were all examined every day.

Table 1 Reactors operating parameters

Reactor	P binding agent	Dosage(g L ⁻¹)	Aeration intensity (L/h)
W ₁	0	0	0
W ₂	bPAC-TMS	7	0
W ₃	bPAC-TMS	7	150
W ₄	aLa-TMS	7	0
W ₅	aLa-TMS	7	150
W ₆	aFe-TMS	7	0
W ₇	aFe-TMS	7	150

Letter a refers to 0.2 of the mass ratio of modifying agent and TMS; letter b refers to 0.4 of the mass ratio of modifying agent and TMS

Analytical method

The total carbon (TC), hydrogen (H) and calcium (Ca) contents were estimated between thermally treated mussel shell (TMS) and unmodified mussel shell (UMS). The content of Ca was measured by inductively coupled plasma mass spectrometry (PerkinElmer, USA) and the content of C and H was analyzed using an Element Analyzer (PerkinElmer, USA). Water quality indexes including Permanganate Index (COD_{Mn}), ammonium nitrogen (NH₄⁺-N), nitrite nitrogen (NO₂⁻-N), nitrate nitrogen (NO₃⁻-N) and phosphate (PO₄³⁻-P) were measured according to standard method (SEPA 2002). pH was determined using a Delta320 precise pH meter.

All the data were statistically analyzed by OriginPro 8 (OriginLab, USA), with a p value less than 0.05 (p < 0.05) indicating statistically significant differences.

Results and discussion

Characteristics of TMS

The contents of TC and H in untreated mussel shell (UMS) were 14.42% and 0.71%, which were decreased to 12.99% (TC) and 0.08% (H), respectively, via the pyrolysis treatment in TMS. The decrease of TC in TMS was mainly attributed to the transformation of organic carbon in mussel shell to carbon oxide via the pyrolysis treatment. The content of Ca increased from 34.78 to 36.76% in TMS. The phosphorus removal efficiency and organics leaching levels of UMS and TMS were further determined following after 12-h treatment of 5 mg P L⁻¹ synthetic solution at the same dosage (20 g L⁻¹). The results showed that UMS and TMS both had approximately 50% P removal efficiency (0.125 mg P g⁻¹). A similar pyrolyzed mussel shell achieved P removal efficiency of 77% and 89% after 24-h treatment of 15.5 mg P L⁻¹ and 46.5 mg P L⁻¹ synthetic solution, respectively (Paradelo et al. 2016). The P removal efficiency largely depends on the contact time, initial P concentration, pH and absorbents dosage (Xiong et al. 2011). In addition, the organics leaching level (COD_{Mn}) of UMS (2.82 mg L⁻¹) was significantly higher than that of TMS (0.47 mg L⁻¹). It was suggested that calcination at the high temperature of 600 °C was advantageous to remove organic matter, which avoided secondary organic pollution during water treatment.

A study has reported that crab shell (CaCO₃-rich biomaterials) prepared at temperature 700–900 °C was lime-based biochar; while, CRB prepared at lower temperature of 300–600 °C was calcite-based biochar (Dai et al. 2017). Since CaCO₃ is also the abundant component of mussel shell, TMS prepared at temperature 600 °C was seemed to be calcite-based biochar in this study. The calcite was almost

insoluble in neutral or alkaline environment, and there was very limited Ca^{2+} dissolved in the solution. Thus, adsorption is vital for P removal via TMS in neutral or alkaline environment. It was reported that phosphate was adsorbed by calcite electrostatic and chemical interactions for pH between 7 and 8.2, and chemically adsorbed onto calcite for pH values greater than 8.2 (Karageorgiou et al. 2007). In addition, chemical precipitation between Ca^{2+} and phosphate can occur at low pH environment. A study has demonstrated P removal efficiency of mussel shell achieved the highest level at low pH of 1.5, which was related to the dissolution of Ca^{2+} ions from adsorbent (Xiong et al. 2011).

Screening of the optimum ratio of TMS and modifying agent for phosphorus removal

The P removal efficiency largely depends on the contact time, initial P concentration, pH and adsorbents dosage. TMS had only 50% P removal efficiency after 12-h treatment of 5 mg P L^{-1} synthetic solution at the same dosage (20 g L^{-1}). It was seemed that adsorbent TMS was not efficient to achieve very low concentration of P after 12-h treatment in the neutral environment, which was necessary to be further modified by other agents. The P removal efficiency of individual modifying agents of La_2O_3 , PAC and $\text{Fe}(\text{OH})_3$ was examined after 12-h treatment of 5 mg P L^{-1} synthetic solution at the same dosage (20 g L^{-1}). Results showed that La_2O_3 alone had P removal rate of 92.5%, and the water color was brown and not acceptable both for the PAC and $\text{Fe}(\text{OH})_3$ alone for P removal. Thus, the optimum ratio of TMS and modifying agent is essential for efficient phosphorus removal. The weight ratios of the modified agents to TMS of 0.2, 0.4 and 0.8 were further examined at 12 h of 5 mg P L^{-1} synthetic solution with the same dosage of 20 g L^{-1} . The P removal performance is shown in Fig. 1.

PAC–TMS with the ratio of 0.2 (marked as aPAC–TMS), 0.4 (marked as bPAC–TMS) and 0.8 (marked as cPAC–TMS) had P removal rates of 86.4% ($0.216 \text{ mg P g}^{-1}$), 95.4% ($0.238 \text{ mg P g}^{-1}$) and 95.8% ($0.239 \text{ mg P g}^{-1}$), respectively. These results demonstrated that the P removal rate significantly increased to the highest level when the proportion of PAC and TMS increased from 0.2 to 0.4. Since PAC material is cheap, the optimum ratio of 0.4 was recommended. Phosphate exhibits different ionization forms in different pH condition. The main forms of phosphate were H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} at the varying pH conditions of 2.1–7.2, 7.2–12.3 and above 12.3, respectively (Pan et al. 2009). This experiment was conducted in neutral environment (pH = 7.0). TMS as CaCO_3 -rich materials, the CaCO_3 solubility was around 15 mg L^{-1} in neutral water, which theoretically could only bind 2.79 mg P L^{-1} with Ca^{2+} ions according to Eq. 1 (Rietra et al. 2001; Yin et al. 2017). However, abundant Al^{3+} ions could release from PAC in neutral

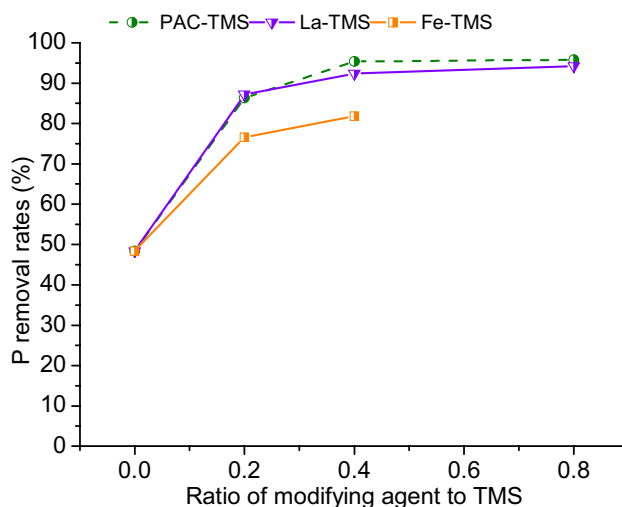
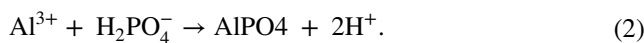
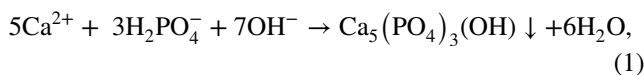


Fig. 1 P removal performance of P binding agents with various ratios of modifying agent to TMS

environment, which could efficiently bind with PO_4^{3-} to form the AlPO_4 in neutral environment (Eq. 2) (Toor and Kim 2019), which was the pathway to modify the TMS.



Composite P binding agents aLa–TMS, bLa–TMS and cLa–TMS with ratios of La_2O_3 to TMS of 0.2, 0.4 and 0.8, respectively, achieved P removal rates of 87.2% ($0.218 \text{ mg P g}^{-1}$), 92.4% ($0.231 \text{ mg P g}^{-1}$) and 94.2% ($0.236 \text{ mg P g}^{-1}$), respectively. La_2O_3 had a P removal rate of only 92.5% ($0.231 \text{ mg P g}^{-1}$), which was similar to that of bLa–TMS. The results showed that the P removal rate significantly increased by 5.2% and 1.8% when the proportions of La_2O_3 and TMS were increased from 0.2 to 0.4 and from 0.4 to 0.8, respectively. Considering the high cost of La_2O_3 , aLa–TMS with a ratio of 0.2 was the optimal composite P binding agent. Lanthanum has a good affinity towards phosphorus and has an especially strong anti-interference ability in complex systems containing phosphorus (Chen et al. 2012; Lin et al. 2018). These contribute to an efficient removal of phosphorus by La–TMS. Qiu et al. (2017) also reported that $\text{LaPO}_4 \cdot x\text{H}_2\text{O}$ is demonstrated to be the dominant pathway for specific adsorption by La_2O_3 .

In terms of the composite P binding agents Fe–TMS, P removal rates of 76.6% ($0.191 \text{ mg P g}^{-1}$) and 81.8% ($0.204 \text{ mg P g}^{-1}$) were achieved for aFe–TMS and bFe–TMS with ratios of 0.2 and 0.4, respectively. As the ratio of Fe–TMS increased to more than 0.8, the color of the water was brown, which was not acceptable for applications in natural waters. In consideration of the water color and P

removal rates, composite P binding agent aFe–TMS with a proportion of 0.2 was recommended. Ferric hydroxide is an efficient method for P removal mainly by ion exchange adsorption in neutral water environment (Ren et al. 2015), but it easily caused high treatment cost. The combination of TMS and ferric hydroxide in this study could largely decrease the cost. As Fe^{3+} ions dissolved in acid solution, precipitation between $\text{Fe}^{3+}/\text{Ca}^{2+}$ and phosphate (FePO_4) could simultaneously occur. A similar study has reported that a synergistic effect for P removal was examined at Fe/Ca molar ratio of 7:3–4:1 (Qiu et al. 2015). In addition, the batch results demonstrated there was still residual P concentration in solution ($> 0.1 \text{ mg L}^{-1}$) after 12-h treatment of TMS-based composite phosphorus binding agents, which might be mainly attributed to the insufficient contact time to achieve very low concentration of P.

Composite P binding agents bPAC–TMS, aLa–TMS and aFe–TMS were all low-cost adsorbent for P removal, because TMS was still the major component, accounting for 60%, 80% and 80%, respectively. P retention on TMS was mainly attributed to adsorption of phosphate on the surface of adsorbent in neutral environment, which was also the major pathway for P removal via bPAC–TMS, aLa–TMS and aFe–TMS in neutral environment. In addition, phosphate can be partially bound by the released Ca^{2+} , Fe^{3+} , Al^{3+} and La^{3+} cations on the surface of adsorbent. Thus, composite P binding agents bPAC–TMS, aLa–TMS and aFe–TMS all had two metal cations, which could both bind phosphate resulting in phosphate adsorption/precipitation. Thus, PAC, $\text{Fe}(\text{OH})_3$ and La_2O_3 all modified TMS for phosphate removal in this study.

Phosphorus removal characteristics of TMS-based composite phosphorus binding agents

Efficient composite P binding agents bPAC–TMS, aLa–TMS and aFe–TMS were obtained based on TMS. The phosphorus removal characteristics of the three composite P binding agents was further examined via the various tests of adsorption isotherms, adsorption kinetics of P removal, effect of dosage, and the effect of other ions and different solution pH conditions.

Adsorption isotherms

The results of the adsorption isotherm experiments are shown in Fig. 2 and Table 2. At a dosage of 20 g L^{-1} , the adsorption capacities of bPAC–TMS, aLa–TMS and aFe–TMS were correlated with the concentration of P in the solution. The adsorption capacity of phosphorus increased with an increase in the phosphorus concentration. The linear equations for Langmuir isotherm adsorption and Freundlich

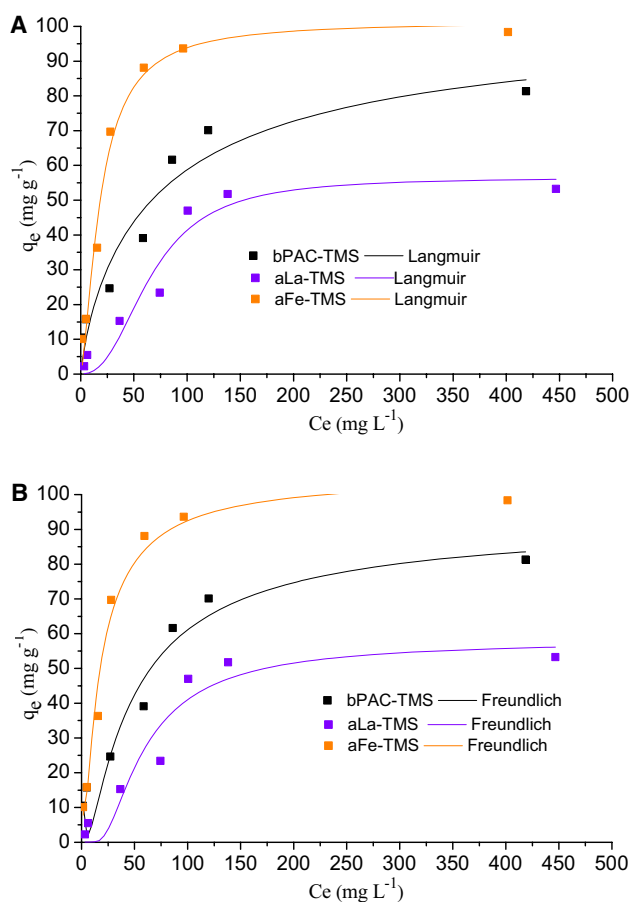


Fig. 2 Adsorption isotherms of P adsorption on composite P binding agents

isotherm adsorption were used to fit the data. The governing equations of these models are written as follows:

$$\text{Langmuir isotherm adsorption: } \frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}},$$

$$\text{Freundlich isotherm adsorption: } \ln q_e = \ln K_F + \frac{1}{N} \ln c_e,$$

where q_e and q_{\max} are the amount of adsorption and maximum adsorption, c_e is the concentration, and K_L and K_F are the Langmuir and Freundlich adsorption equilibrium constants.

The results showed that the Langmuir model had a higher correlation coefficient than the Freundlich model (Fig. 2 and Table 2), which indicated that a monolayer homogeneous adsorption process occurred during P adsorption via the composite agents. The maximum phosphate adsorption capacity of bPAC–TMS, aLa–TMS and aFe–TMS were 91.74 mg g^{-1} , 56.50 mg g^{-1} and 101.42 mg g^{-1} . The raw powdered mussel shell was reported to have the maximum

Table 2 P adsorption isotherm and kinetic parameters for phosphate adsorption on composite phosphorus binding agents

P binding agent	Model	Parameter 1	Parameter 2	R^2
bPAC–TMS	Langmuir	$K_L=0.019$	$q_{\max}=91.74$	0.9034
	Freundlich	$K_F=3.30$	$1/n=0.60$	0.8973
	Pseudo-first order	$K_1=0.14$	$q_e=2.51$	0.7927
	Pseudo-second order	$K_2=0.33$	$q_e=2.36$	0.9999
aLa–TMS	Langmuir	$K_L=0.008$	$q_{\max}=64.94$	0.9083
	Freundlich	$K_F=0.98$	$1/n=0.79$	0.8896
	Pseudo-first order	$K_1=0.05$	$q_e=1.06$	0.9582
	Pseudo-second order	$K_2=0.16$	$q_e=3.07$	0.9998
aFe–TMS	Langmuir	$K_L=0.045$	$q_{\max}=105.26$	0.9746
	Freundlich	$K_F=9.49$	$1/n=0.47$	0.9732
	Pseudo-first order	$K_1=0.03$	$q_e=2.00$	0.8374
	Pseudo-second order	$K_2=0.01$	$q_e=2.47$	0.9764

adsorption capacity of 6.95 mg P g^{-1} and $18.23 \text{ mg P g}^{-1}$ for phosphate, respectively (Xiong et al. 2011; Paradelo et al. 2016), and a higher value of $38.75 \text{ mg P g}^{-1}$ by TMS (Paradelo et al. 2016), which were all much lower than that of bPAC–TMS, aLa–TMS and aFe–TMS. This result suggested that the composite agents exhibited a high ability to remove phosphate.

Kinetics study

Figure 3a shows the results of adsorption kinetics. The P adsorption capacity and removal rates of the three kinds of P binding agents were enhanced with an increase in the contact time, which increased rapidly in the first 10 min and then slowly increased between 10 and 90 min. Adsorption equilibrium was obtained within 90 min. Linear equations of a pseudo-first-order reaction kinetic model and a pseudo-second-order reaction kinetic model were used to fit the kinetic data. The governing equations of these models are written as follows:

the pseudo - first - order reaction kinetic model : $\lg(q_e - q_t)$

$$= \lg q_e - \frac{k_1}{2.303} t,$$

the pseudo - second - order reactionkinetic model : $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t,$

where q_e and q_t are the amounts of adsorption at time t , and k_1 and k_2 are the pseudo-first-order and pseudo-second-order adsorption rate constants.

In terms of the fitting coefficient of determination (R^2) in Table 2, the adsorption kinetics of the three kinds of phosphorus binding agents was more satisfactory described by the pseudo-second-order reaction kinetic model ($R^2 > 0.97$), which indicated that the adsorption of P on biochars was

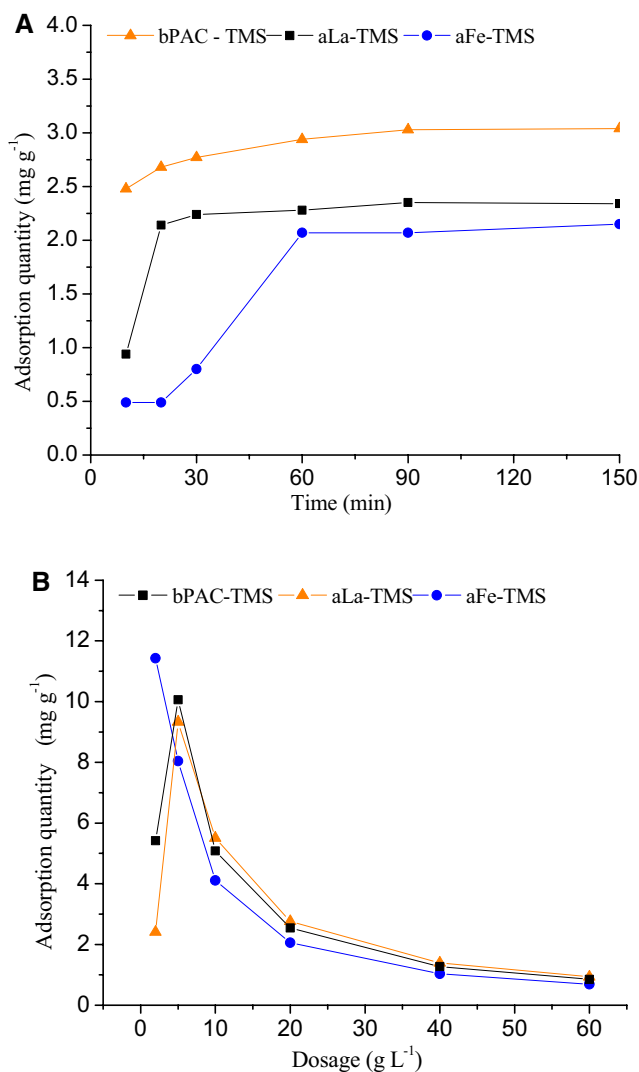


Fig. 3 Adsorption kinetics (a) and optimal dosage (b) of P adsorption on composite P binding agent

conducted through the inner sphere complex (Wang et al. 2011).

Effect of dosage on P removal

The optimal dosage experiment for the three kinds of phosphorus binding agents is shown in Fig. 3b. In the case of a fixed initial phosphate concentration of 50 mg L^{-1} , the P removal rate of bPAC–TMS was significantly increased to 98.8% as the dosage added increased to 5 g L^{-1} , which was considered as the optimal dosage of bPAC–TMS. The removal rate of aLa–TMS rapidly increased within the dosage range of $0\text{--}5 \text{ g L}^{-1}$, and highly efficient removal of P (98.8%) was achieved as the dosage approached 10 g L^{-1} , indicative of the optimal dosage of aLa–TMS. Meanwhile, the optimal amount of aFe–TMS was 5 g L^{-1} with the effective P removal of 97.3%. Thus, the optimal dosages of bPAC–TMS, aLa–TMS, and aFe–TMS were 5 g L^{-1} , 10 g L^{-1} and 5 g L^{-1} , respectively. As the maximum phosphate adsorption capacity of bPAC–TMS, aLa–TMS and aFe–TMS was 91.74 mg g^{-1} , 56.50 mg g^{-1} and 101.42 mg g^{-1} , the dosage of 10 g L^{-1} and 5 g L^{-1} for 50 mg L^{-1} was enough. However, there was still residual P concentration detected in solution. It might be speculated that the contact time of 12 h was not enough to achieving the very low concentration of P.

Effect of inorganic nitrogen occurrence and pH on P removal

Since the occurrences of inorganic nitrogen (ammonia nitrogen, nitrate nitrogen and nitrite nitrogen) are very common in natural waters, the effect of varying concentrations of inorganic nitrogen ($0\text{--}50 \text{ mg L}^{-1}$) on P removal performance was observed using composite P binding agents of bPAC–TMS, aLa–TMS and aFe–TMS. Results demonstrated that efficient P removal ($> 90\%$) is obtained from bPAC–TMS, aLa–TMS and aFe–TMS with the coexistence of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and $\text{NO}_2^-\text{-N}$ in the range of $0\text{--}50 \text{ mg L}^{-1}$.

According to pH values in environmental water, the P removal by bPAC–TMS, aLa–TMS and aFe–TMS was investigated at varying pH values of 6, 7 and 9 (Fig. 4). Phosphate exhibits different ionization forms in different pH condition. The P removal rate of aLa–TMS was maintained at high levels of almost 100%, which was not affected by the pH dynamics. Efficient P removal (92.2–99.1%) using bPAC–TMS was also achieved in a pH range of 4–13. Additionally, aFe–TMS produced highly efficient P removal of (97.8–99.6%) in the pH range of 6–7 and was reduced to 83% at a pH value of 9, respectively. The modification agents of PAC and $\text{Fe}(\text{OH})_3$ mainly enhanced the precipitation of TMS, and the chemical precipitation also depended on pH. However, La had good affinity of P over wide range of pH.

In this respect, aLa–TMS was a good choice. However, three composite agents all achieved more than 80% of P removal efficiency at pH range of 6–9. Therefore, the modification agents all extended TMS to use in wider range of pH circumstances. The phosphorus removal using ferric, calcium salts or PAC was all dependent of pH change. However, the application of these composite P binding agents in this study could reduce the consumption of reagents for pH adjustment.

Application of composite phosphorus binding agents for contaminated environmental water

Figure 5 shows the long-term P removal performances of composite phosphorus binding agents for phosphorus contaminated water. The initial P concentration of systems $W_1\text{--}W_7$ was 1.52 mg L^{-1} . The results showed that P concentrations rapidly declined in the initial 3 days via addition of P binding agents, with removal rates of 0.66 (W_2), 0.42 (W_3), 0.56 (W_4), 0.68 (W_5), 0.69 (W_6) and 0.74 (W_7) (mg (Ld)^{-1}). To achieve very low concentration of P ($< 0.1 \text{ mg L}^{-1}$), more than 1 day was required. Results further suggested that the contact time of 12 h was one of the factors that caused residual P concentration during batch experiments in this study. In contrast, no significant decrease of P was observed in device W_1 without agent addition. After the secondary addition of phosphorus (on day 33), the rapid decrease in P concentrations were also detected in device $W_2\text{--}W_7$, with removal rates of 0.60 (W_2), 0.68 (W_3), 0.62 (W_4), 0.73 (W_5), 0.58 (W_6) and 0.74 (W_7) (mg (Ld)^{-1}) in the initial 3 days.

The third addition of P was conducted after 2-month operation (on day 64). Device $W_2\text{--}W_7$ with different composite phosphorus binding agents (bPAC–TMS, aLa–TMS

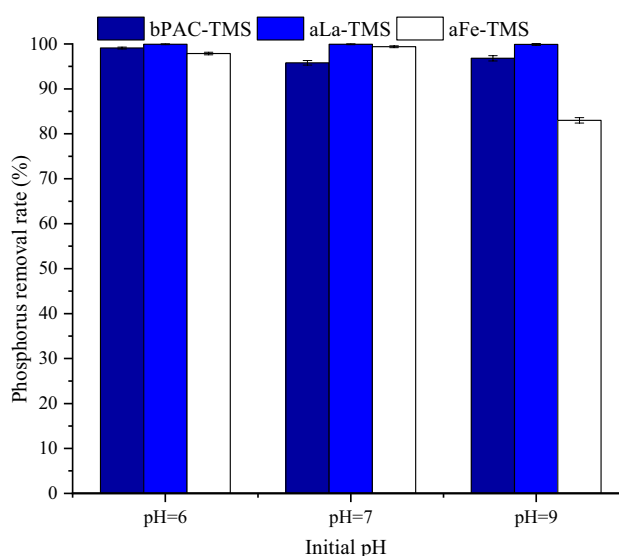


Fig. 4 The effects of pH on the performance of P binding agent

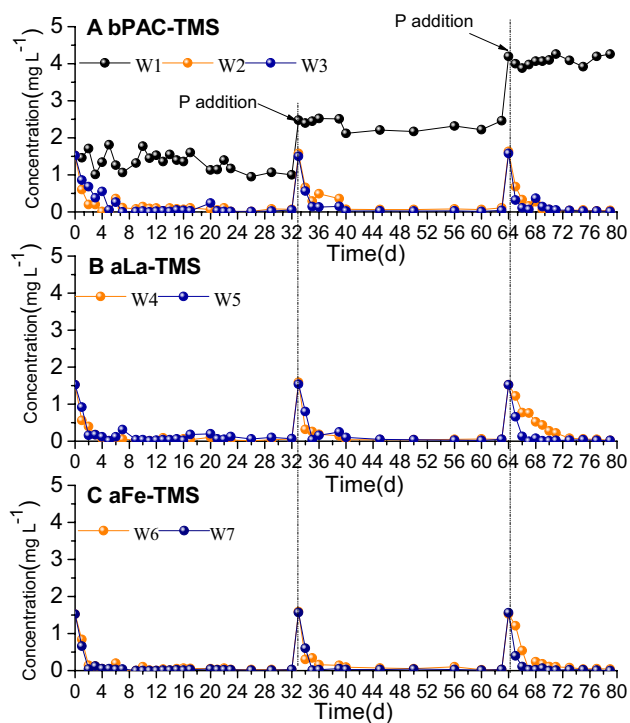


Fig. 5 P removal performance of P binding agents for phosphorous-contaminated water purification

and aFe-TMS) addition still achieved efficient P removal, having removal rates of 0.59 (W_2), 0.69 (W_3), 0.38 (W_4), 0.69 (W_5), 0.48 (W_6) and 0.7 mg (Ld)⁻¹ (W_7) in the initial 3 days. In addition, no P release was detected after efficient removal of P. The results indicated that the water disturbance via aeration might have advantageous to improve P removal, especially for P binding agents of aLa-TMS and aFe-TMS. Meanwhile, the P concentration in device W_1 increased to approximately 4.0 mg L⁻¹ after 2 months of operation. P eutrophication is a growing concern globally. Phosphorous concentrations greater than 0.1 mg P L⁻¹ are usually considered high enough to cause eutrophication (Kumar et al. 2019). Less than 0.1 mg L⁻¹ of P concentrations in devices W_2 – W_7 was all detected in approximately a week after each P addition. Thus, the three agents of bPAC-TMS, aLa-TMS and aFe-TMS adapted well to low P concentration of contaminated water and had long-term efficient removal of P. In addition, no P desorption was detected.

Conclusion

Calcium-rich biological material TMS was an environmentally friendly and low-cost adsorbent for P removal. A calcium-rich material of TMS was effectively metal modified via PAC, Fe(OH)₃ and La₂O₃ to remove P. Composite agents of PAC-TMS, Fe-TMS and La-TMS prepared at different

optimum weight ratios had the P removal rate more than 80% of after 12 h treatment of 5 mg L⁻¹ P solution, which was much higher than that of TMS alone (50%). These composite agents had maximum phosphate adsorption capacities of 91.74 mg P g⁻¹ (PAC-TMS), 101.42 mg P g⁻¹ (Fe-TMS) and 56.50 mg P g⁻¹ (La-TMS), respectively. The metal-modified TMS all extended the use of TMS in a wider range of pH conditions and achieved very low concentration of P in natural water. Composite P binding agents of PAC-TMS, La-TMS and Fe-TMS both had two metal cations, which could both bind phosphate via simultaneous adsorption/precipitation.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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