



Adsorption of Phosphate by Surface Precipitation on Lanthanum Carbonate Through *In Situ* Anion Substitution Reactions

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Specialty section:

This article was submitted to
Biogeochemical Dynamics,
a section of the journal
Frontiers in Environmental Science

Received: 19 January 2022

Accepted: 25 February 2022

Published: 06 April 2022

Citation:

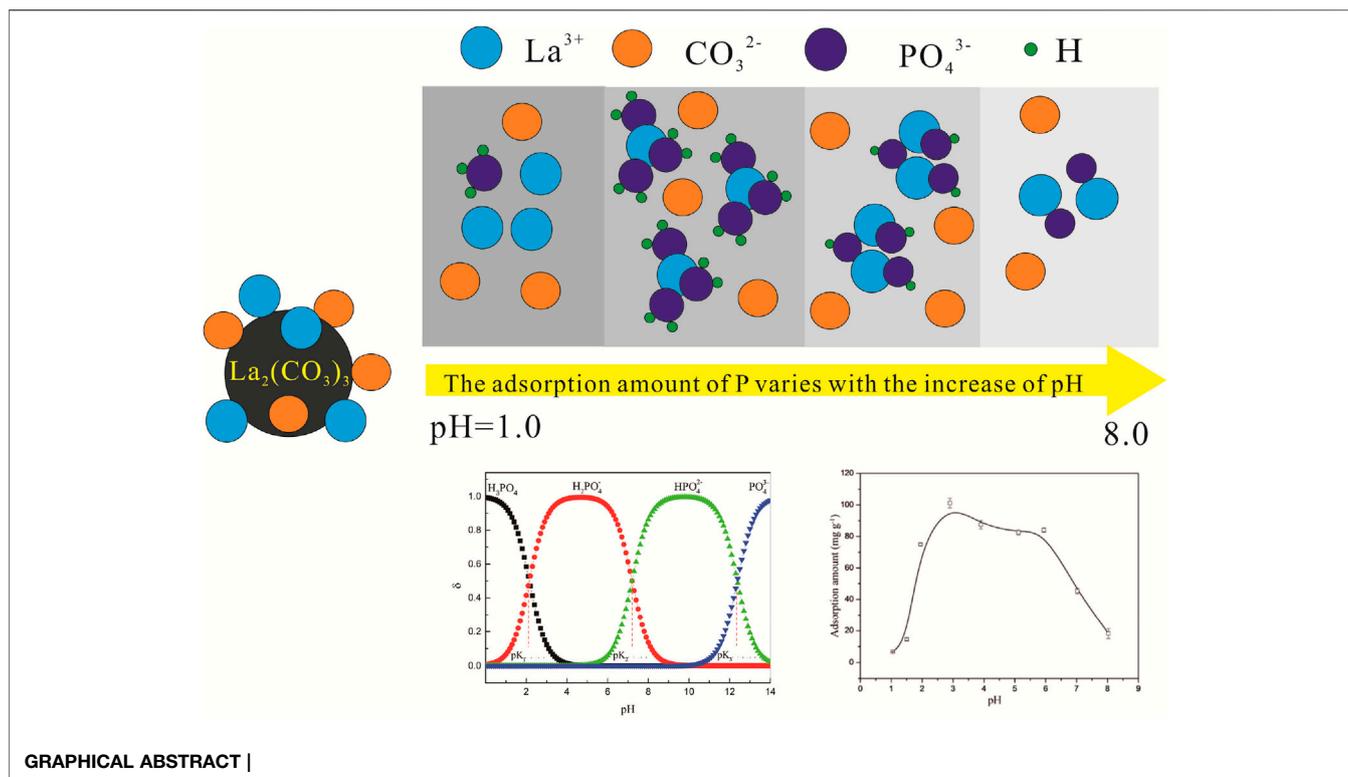
Zhang SY, Xie FZ, Tang Z, Zhao TH,
Fang MY and Giesy JP (2022)
Adsorption of Phosphate by Surface
Precipitation on Lanthanum Carbonate
Through *In Situ* Anion
Substitution Reactions.
Front. Environ. Sci. 10:858258.
doi: 10.3389/fenvs.2022.858258

Efficient removal of phosphate (PO_4^{3-}) is the main solution to control eutrophication. In this study, lanthanum carbonate ($\text{La}_2(\text{CO}_3)_3$) was the adsorbent of choice for the removal of PO_4^{3-} . Both adsorption isotherm and thermodynamic were investigated. $\text{La}_2(\text{CO}_3)_3$ was an effective adsorbent for the removal of phosphate (PO_4^{3-} or H_2PO_4^-) under weak acidic conditions ($\text{pH} = 2.0\text{--}6.0$); the maximum adsorption amount was 106.6 mg g^{-1} at $\text{pH} 2.9$. The pH_{zpc} of $\text{La}_2(\text{CO}_3)_3$ changed from 2.1 to 6.5 prior to and after adsorption of PO_4^{3-} . The adsorption of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$ was an endothermic process. With the increase of anions, the adsorption efficiency of PO_4^{3-} decreased. The presence of natural organic matter also inhibited the adsorption of PO_4^{3-} , but the interference was weaker than that of anions. The mechanisms of adsorption were investigated by various techniques including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Based on the results obtained using XPS, during the adsorption process of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$, La^{3+} was released and could precipitate with PO_4^{3-} or H_2PO_4^- under weak acidic conditions ($\text{pH} = 2.0\text{--}4.0$). Adsorption was dominated by *in situ* substitution reactions between CO_3^{2-} and H_2PO_4^- or HPO_4^{2-} . This study provides a useful reference and potential material for the removal of PO_4^{3-} in aquatic environments.

Keywords: lanthanum carbonate, removal, natural organic matter, anion substitution reaction, eutrophication

HIGHLIGHTS

- Lanthanum carbonate was an effective adsorbent for phosphate under weak acidic conditions, with the maximum adsorption being 106.6 mg/g at $\text{pH} 2.9$.
- The presence of either inorganic anions or natural organic matter would inhibit the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$.
- Because of the longer adsorption path and weaker competition in the adsorption process, the influence of natural organic matter was weaker than that of inorganic anions
- The mechanism is the combined result of physisorption and chemisorption according to the characterization, in which LaPO_4 is formed when PO_4^{3-} is adsorbed on the surfaces of $\text{La}_2(\text{CO}_3)_3$



INTRODUCTION

Eutrophication has become one of the most pressing environmental issues that harm the quality of water. It produces undesirable color, taste, odor, and turbidity. Eutrophication reduces biodiversity, destroys aquatic habitats, and also poses significant public health risk (Wu et al., 2007; Gao et al., 2013; Su et al., 2013). Nutrient enrichment disturbs the natural ecological balance in lakes and rivers. One of the most important factors that drive the eutrophication in rivers and lakes is excess of phosphorus. Phosphate enters the environment not only through effluents of wastewater treatment plants (WWTPs) but also due to surface runoff of urban and agricultural areas. The development of a rapid and efficient method for the removal of PO_4^{3-} is a highly sensitive and very interesting topic for the scientific community.

Various techniques have been developed for the removal of PO_4^{3-} , including chemical precipitation (Chouyyok et al., 2010), biological processes such as harvesting biomass (Yao et al., 2011), and adsorption (Pan et al., 2014). Adsorption is a promising method because it has many advantages, including efficiency, greater speed, adaptability, easy to operate, and does not pollute the environment. In general, the adsorption, and therefore removal capacity, is directly conditioned by the physical and chemical properties of the adsorbent. In this regard, there has been a great interest in the field of environmental engineering, in advancing the development of efficient and cost-effective adsorbents. Recently, some scientific studies have reported on the removal of PO_4^{3-} using different types of adsorbent, such as

layered double hydroxide (Das et al., 2006; Chitrakar et al., 2010; Mandel et al., 2013), Fe–Mn binary oxide (Zhang et al., 2009), fly ashes (Chen et al., 2007), activated carbon fibers (Zhang et al., 2011; Liu et al., 2013), silica materials (Hamoudi and Belkacemi, 2013), ferrihydrite (Mallet et al., 2013), or goethite (Belelli et al., 2014). Once PO_4^{3-} is adsorbed, the complex is often removed from the suspension by flocculation, facilitated either by polymeric materials (amphoteric chitosan) or by alum (Sherman et al., 2000; Agbovi and Wilson, 2018). On the other hand, flocculants such as alum can cause toxic effects, especially when it is released during flocculation. A few adsorbents can maintain a maximum adsorption capacity of PO_4^{3-} under a broad range of pH, especially under acidic conditions (Lurling et al., 2014; Xie et al., 2014).

The lanthanum-based material has a great adsorption capacity and chemical stability. The lanthanum-based adsorbent contains the trivalent lanthanum ion (La^{3+}) that has a strong affinity for PO_4^{3-} even at trace levels. Once La^{3+} is released, it can bind with PO_4^{3-} and generate an insoluble complex under acidic conditions, lanthanum-phosphate ($\text{La}^{3+}\text{-PO}_4^{3-}$), which is nonabsorbable (Samy et al., 2010; Yang et al., 2013). Among the new lanthanum-based adsorbents that have been developed for the removal of PO_4^{3-} , $\text{NaLa}(\text{CO}_3)_2/\text{Fe}_3\text{O}_4$ (Hao, et al., 2019), $\text{La}(\text{OH})_3$ (He et al., 2015), $\text{La}^{3+}/\text{La}(\text{OH})_3$ (Dong et al., 2017), and La-201 (Zhang et al., 2016) are worth noting. Using such materials, adsorption of PO_4^{3-} is favored over a wide range of pH, and the adsorption mechanism involves the electrical interaction and ligand-exchange between lanthanum and PO_4^{3-} (Hao et al., 2019). The main concern of the

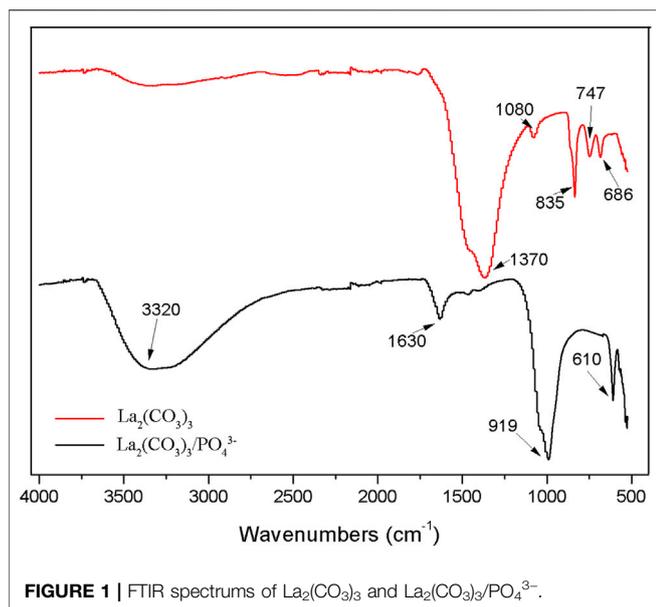


FIGURE 1 | FTIR spectrums of $\text{La}_2(\text{CO}_3)_3$ and $\text{La}_2(\text{CO}_3)_3/\text{PO}_4^{3-}$.

adsorbent was related to two basic factors—how to control phosphorus in the waters and the safety of chemicals used for this processing. $\text{La}_2(\text{CO}_3)_3$ was developed in recent years, and since then, its application in the pharmaceutical industry has been extensive (Persy et al., 2006). $\text{La}_2(\text{CO}_3)_3$ contains La^{+3} and has a very strong binding capacity to PO_4^{3-} . Furthermore, $\text{La}_2(\text{CO}_3)_3$ does not contain aluminum or calcium and does not contaminate the environment. Despite the lanthanum-based material was considered, by many, as a potent agent for the removal of PO_4^{3-} from water, few scientific articles have reported a systematic study concerning the removal of PO_4^{3-} by $\text{La}_2(\text{CO}_3)_3$. Therefore, the removal of phosphorus from water by $\text{La}_2(\text{CO}_3)_3$ was systematically studied in this study, and it provided an effective method for the removal of PO_4^{3-} in the aquatic environment.

In this study, $\text{La}_2(\text{CO}_3)_3$ was synthesized and evaluated for its phosphate adsorption capacity. The effect of solution pH, adsorbent dosage, coexist inorganic ions, and natural organic matter on the removal of PO_4^{3-} by $\text{La}_2(\text{CO}_3)_3$ was investigated. The adsorption kinetics and isotherms were determined to compare their adsorption capacity and understand adsorption mechanisms. The X-ray photo-electron spectroscopy (XPS), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) were used to explore the mechanisms of adsorption.

MATERIALS AND METHODS

Materials and Chemicals

$\text{La}_2(\text{CO}_3)_3$ was obtained from Guangfu Institute of Fine Chemicals, China. All other chemicals used (KH_2PO_4 , $\text{Na}_2\text{SiO}_4 \cdot 9\text{H}_2\text{O}$, NaCl , NaNO_3 , Na_2CO_3 , and Na_2SO_4) were of analytical grade. The measurements of pH were carried out using a PHS-3C pH-meter (Dapu instrumentation Corp., Ltd.

Shanghai, China). All glassware used in experiments was carefully cleaned and rinsed with deionized water. The samples of natural organic matter (HA and FA) were collected from the soils of Jiufeng Mountain (Beijing) (Lin et al., 2011).

Batch Adsorption Experiments

$\text{La}_2(\text{CO}_3)_3$ was equilibrated with a suitable amount of PO_4^{3-} solution ($10\text{--}100\text{ mg L}^{-1}$) using magnetic stirring for 20 h. Once the adsorbent was recovered by centrifugation, the concentration of PO_4^{3-} in the supernatant was measured using the ammonium molybdate blue method. The adsorption amount of PO_4^{3-} was calculated based on the difference between the balance and total amount. The influence of temperature was evaluated by setting the concentration of PO_4^{3-} from 10 to 40 mg L^{-1} and applying a temperature which ranged from 303.15 to 323.15 K. To determine the concentration effect, the weight from 20 to 100 mg was added to 50 ml of PO_4^{3-} solution (200 mg L^{-1}), and then the suspension was agitated on a shaker for 24 h.

Interference Study

To study the influence of coexisting inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , and SiO_3^{2-}), 40 mg of $\text{La}_2(\text{CO}_3)_3$ was mixed with PO_4^{3-} solution (100 mg L^{-1}) and various competing ions. The effects of natural organic matter including HA and FA were also investigated, by combining 40 mg of $\text{La}_2(\text{CO}_3)_3$ with 100 mg L^{-1} of PO_4^{3-} solution and HA and FA at the concentrations of 10, 30, or 50 mg L^{-1} . The mixture was shaken for 24 h, and the suspension was filtered through a $0.45\text{-}\mu\text{m}$ fiber membrane. The concentration of PO_4^{3-} in the solution was measured using the ammonium molybdate blue method.

pH_{zpc} Determination

The pH_{zpc} of $\text{La}_2(\text{CO}_3)_3$ was estimated according to the ΔpH method (Kinniburgh et al., 1975; Zhang et al., 2014), for which 50 mg of $\text{La}_2(\text{CO}_3)_3$ or PO_4^{3-} -saturated $\text{La}_2(\text{CO}_3)_3$ was mixed with 50 ml of NaNO_3 (0.01 mol L^{-1}). These mixtures were shaken at room temperature for 20 h on an automatic shaker and then adjusted to various values of pH by additions of NaOH or HNO_3 . After 60 min of equilibrium, pH was measured and defined as $\text{pH}_{(\text{initial})}$. Then, 1 g of NaNO_3 was added to each suspension. After shaking for 1 hour, the $\text{pH}_{(\text{final})}$ was measured, and the change in pH (ΔpH) was calculated as follows: $\text{pH}_{(\text{final})} - \text{pH}_{(\text{initial})}$.

Characterization of the Adsorbent Before and After Adsorption

A JEOL JSM-6700F scanning electron microscope (SEM) was used to measure surface morphology. The energy dispersive spectrometer (EDS, Oxford X-MAX-20) associated with the SEM system and FTIR (Nicolet 6,700, United States) was utilized to examine chemical compounds on the surface and shape of the adsorbent before and after adsorption. Powder X-ray diffraction (XRD, Bruker D8 Advance, Germany) was also used to characterize the adsorbent. The chemical composition of $\text{La}_2(\text{CO}_3)_3$ after adsorption was determined by XPS (ESCALAB250 Thermo-VG Scientific, United States). The

release of CO_3^{2-} and HCO_3^- from $\text{La}_2(\text{CO}_3)_3$, during adsorption was detected by acid–base titration.

RESULTS AND DISCUSSION

Characterization of $\text{La}_2(\text{CO}_3)_3$ Prior to and After Adsorption of Phosphorus

The FTIR spectrums of $\text{La}_2(\text{CO}_3)_3$ prior to and after adsorption of PO_4^{3-} are shown in **Figure 1**. Compared with the spectrum of $\text{La}_2(\text{CO}_3)_3$, some vibration peaks corresponding to CO_3^{2-} at 1,420, 878, and 713 cm^{-1} almost disappeared, while other peaks at 1,054, 616, and 542 cm^{-1} were observed after the adsorption of PO_4^{3-} . Furthermore, the peak at 1,054 cm^{-1} was assigned to the asymmetric stretching vibration of P-O of the PO_4^{3-} group, and the peaks at 616 and 542 cm^{-1} were assigned to the bending vibration of O-P-O (Li et al., 2014; Wang et al., 2016), which indicated that the adsorption mechanism of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$ included a ligand exchange process.

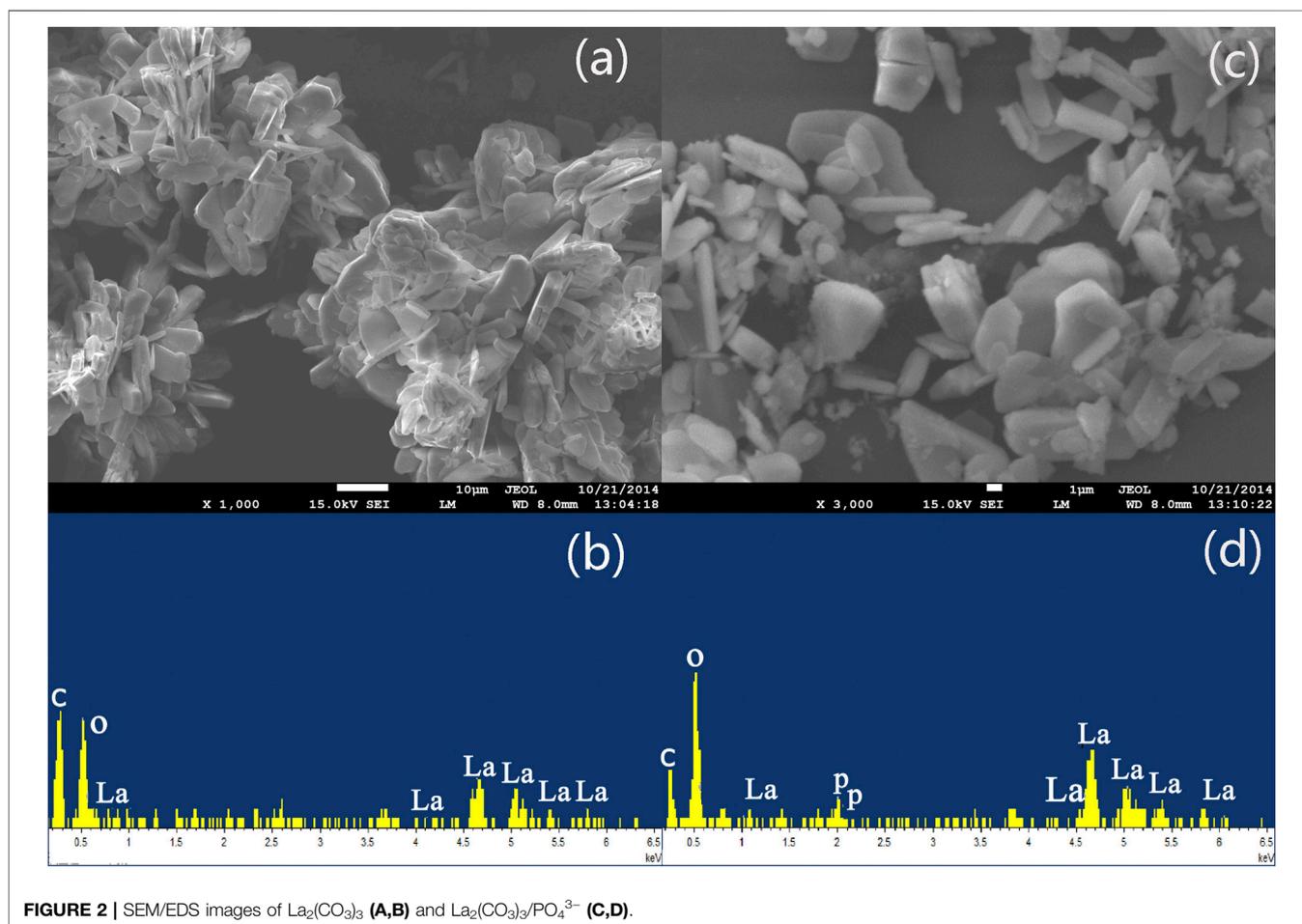
The typical SEM images of $\text{La}_2(\text{CO}_3)_3$ prior to and after adsorption of PO_4^{3-} are shown in **Figure 2**. $\text{La}_2(\text{CO}_3)_3$ exhibited a more regular surface and better particle dispersion after the adsorption of PO_4^{3-} . The adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ was confirmed by energy-dispersive spectroscopy

analysis. As shown in **Figure 2D**, the characteristic peaks of P appeared in the spectra of $\text{La}_2(\text{CO}_3)_3$ after the adsorption of PO_4^{3-} , which indicated that PO_4^{3-} was successfully adsorbed on the surfaces of $\text{La}_2(\text{CO}_3)_3$. Meanwhile, the characteristic peaks of C decreased significantly after the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$, evidencing that CO_3^{2-} was mostly replaced by PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$ (Huang et al., 2007).

The analysis of the powder X-ray diffractograms of the $\text{La}_2(\text{CO}_3)_3$ prior to and after adsorption of PO_4^{3-} was illustrated in Fig. S1, in which the XRD standard diffraction card was also presented. $\text{La}_2(\text{CO}_3)_3$ used as an adsorbent in this study can be indexed as $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ (JCPDS card NO.25-1,400) from the XRD patterns. The XRD pattern of $\text{La}_2(\text{CO}_3)_3$ after the adsorption of PO_4^{3-} was closely matched to $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$ (JCPDS card NO.46-1,439). These results demonstrated that a new substance was generated after PO_4^{3-} being adsorbed on the surfaces of $\text{La}_2(\text{CO}_3)_3$.

Effect of Solution pH

The pH can affect not only charges on the surfaces of $\text{La}_2(\text{CO}_3)_3$ but also dissociation and solubility of the adsorbent, which would influence the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ (Yang et al., 2013). The effect of solution pH in the range of 1.0–8.0 is shown in **Figure 3A**. The adsorption amount increased sharply when the



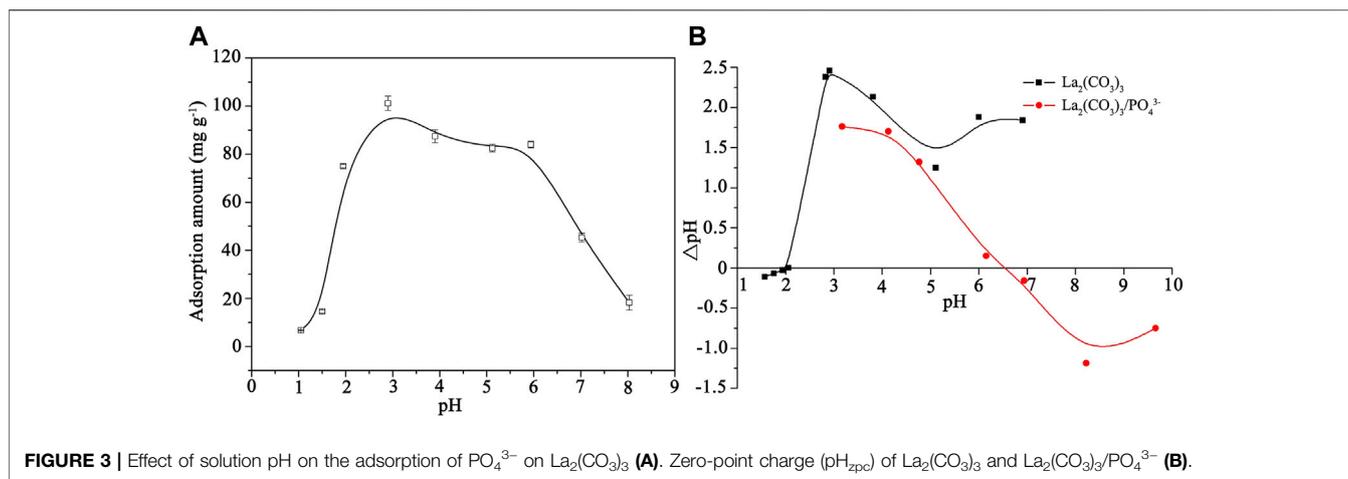


FIGURE 3 | Effect of solution pH on the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ (A). Zero-point charge (pH_{zpc}) of $\text{La}_2(\text{CO}_3)_3$ and $\text{La}_2(\text{CO}_3)_3/\text{PO}_4^{3-}$ (B).

TABLE 1 | Comparison of the maximum adsorption amount of phosphate on various adsorbents.

Adsorbent	Molar ratio	pH	q_m (mg g ⁻¹)	pH_{zpc}	Reference
ZrO ₂	—	6.9	29.7	4.90	Liu et al. (2008)
Red-mud	—	5.5	0.6	—	Huang et al. (2008)
La-Cu	1:1	—	63.9	—	Zhao et al. (2014)
Fe-Zr	1:2:16	4.0	13.7	3.24	Long et al. (2011)
Fe-Mn	6:1	5.6	36.0	6.6	Zhang et al. (2009)
Fe-Al-Mn	3:3:1	6.8	48.3	8.70	Lü et al. (2013)
$\text{La}_2(\text{CO}_3)_3$	—	3.0	101.6	2.1	This study

pH changed from 1.0 to 3.0 and then decreased slowly with an increase in pH. The maximum adsorption amount of PO_4^{3-} was obtained at pH 3.0 (101.6 mg g⁻¹), which is 15.6-fold greater than that at pH 1.1. It means that $\text{La}_2(\text{CO}_3)_3$ was an efficient adsorbent for the removal of PO_4^{3-} under acidic conditions. This is similar to the results of other research studies. Many researchers have studied the influence of the pH value on PO_4^{3-} adsorption capacity and found that the lanthanide adsorbent has a higher PO_4^{3-} removal efficiency only at a lower pH value (Lu et al., 2021). There have been many studies on the removal of PO_4^{3-} by various materials, including binary and ternary compounds, for e.g., ZrO₂, red-mud, La-Cu, Fe-Zr, Fe-Mn, and Fe-Al-Mn (Lü et al., 2013; Zhang et al., 2009; Liu et al., 2008; Huang et al., 2008; Zhao et al., 2014; Long et al., 2011). The adsorption amount of PO_4^{3-} on these materials was different and significantly affected by the solution pH (Table 1). The adsorption amount of binary materials (La-Cu) and ternary materials (Fe-Al-Mn) was significantly higher than that of other materials, and the adsorption capacity of $\text{La}_2(\text{CO}_3)_3$ was much greater than that of other materials. Meanwhile, the composition and synthesis method of $\text{La}_2(\text{CO}_3)_3$ was simple and better when applied to removal of PO_4^{3-} .

The isoelectric points of $\text{La}_2(\text{CO}_3)_3$ prior to and after adsorption were 2.1 and 6.5, respectively (Figure 3B), indicated that PO_4^{3-} neutralized the positive charge on the surface of $\text{La}_2(\text{CO}_3)_3$ and caused an increase in the isoelectric point. These findings revealed that in the surface of $\text{La}_2(\text{CO}_3)_3$,

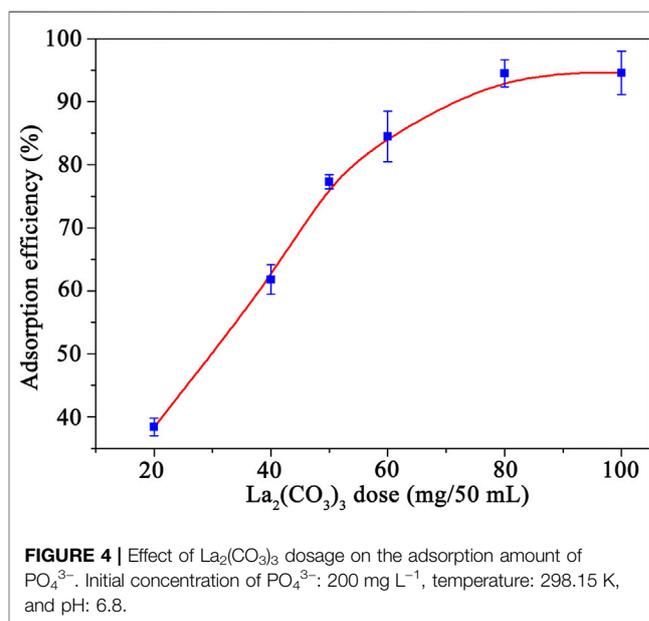
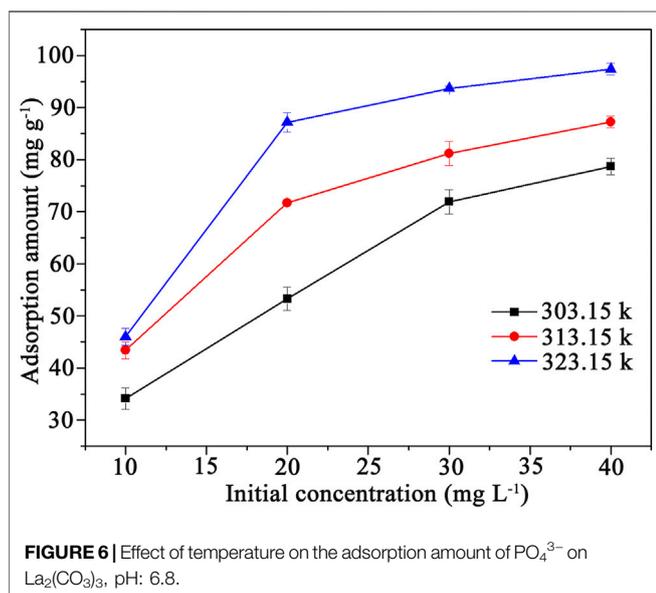
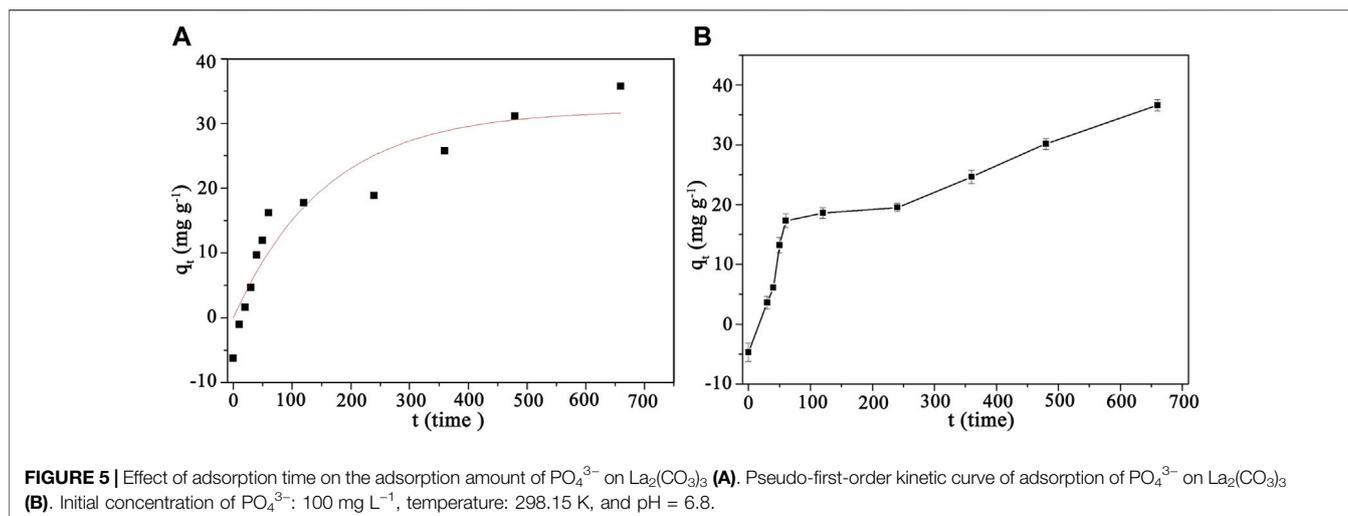


FIGURE 4 | Effect of $\text{La}_2(\text{CO}_3)_3$ dosage on the adsorption amount of PO_4^{3-} . Initial concentration of PO_4^{3-} : 200 mg L⁻¹, temperature: 298.15 K, and pH: 6.8.

there was a change from carbonate to PO_4^{3-} when the pH values were 2.0–6.0. The existence of PO_4^{3-} species mainly in the form of H_2PO_4^- is explained because the adsorbent gathered more positive charges on the surface under acidic conditions, which caused strong adsorption of PO_4^{3-} on the surface of $\text{La}_2(\text{CO}_3)_3$ by electrostatic attraction. Meanwhile, La^{3+} and CO_3^{2-} in $\text{La}_2(\text{CO}_3)_3$ were dissociated in weak acid solutions and could be replaced by H_2PO_4^- under acidic conditions (Haghseresht et al., 2009; Xie et al., 2014). When the pH was greater than 6.0, the adsorption amount of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ continue to decrease presumably due to the competition for the adsorption sites between PO_4^{3-} and other coexisting anions such as CO_3^{2-} or OH^- .

Effect of Adsorbent Dosage

The effect of dosage on the adsorption efficiency of PO_4^{3-} is shown in Figure 4. The adsorption efficiency varied from 38.4 to 94.6% for the range of concentrations of 20–80 mg ml⁻¹, which



suggested that the adsorption efficiency of PO_4^{3-} by $\text{La}_2(\text{CO}_3)_3$ was directly proportional to the dose of $\text{La}_2(\text{CO}_3)_3$. This is because there were more adsorption sites available for PO_4^{3-} as the dosage increased. When the concentration of $\text{La}_2(\text{CO}_3)_3$ was higher than $80 \text{ mg } 50 \text{ mL}^{-1}$, it had a negligible effect on the adsorption efficiency of PO_4^{3-} .

Adsorption Kinetics

Figure 5A demonstrates the effect of time on the adsorption amount of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$. The adsorption amount of PO_4^{3-} increased rapidly during the first 50 min, probably due to a fast exchange of CO_3^{2-} and PO_4^{3-} on the surface of $\text{La}_2(\text{CO}_3)_3$ and occupancy of the sites by PO_4^{3-} . After that, the adsorption amount of PO_4^{3-} increased slowly over time. This implied mass transfer of CO_3^{2-} and PO_4^{3-} and subsequent exchange, predominant during the adsorption process. There was

no significant change in the adsorption amount of PO_4^{3-} on the surface of $\text{La}_2(\text{CO}_3)_3$ after 24 h.

A quantitative approach to determine adsorption is feasible using a kinetic model. The equation for pseudo-first-order kinetic was introduced by Lagergren (Eq. 1), which is used for the prediction of the physisorption of the adsorbate onto the adsorbent in a given system.

$$\ln[q_e - q_t] = \ln q_e - kt, \quad (1)$$

where q_e is the amount of the adsorbate at equilibrium (mg g^{-1}), q_t is the amount of the adsorbate (mg g^{-1}) at time t (min), and K (min^{-1}) is the rate constant for the pseudo-first-order sorption.

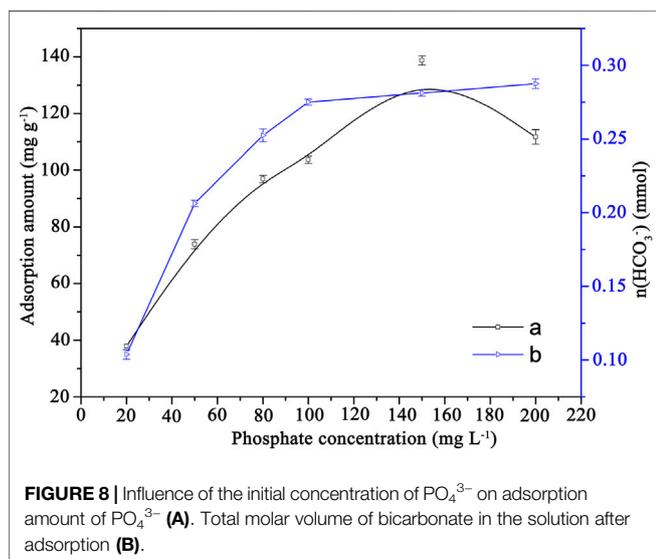
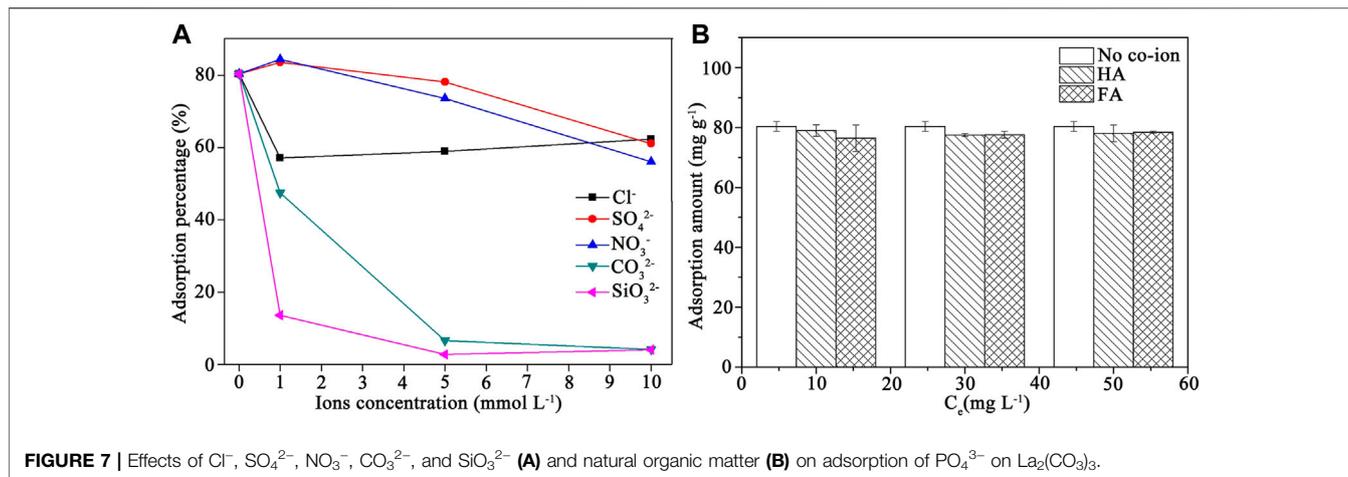
This equation can also be expressed by the following alternative equation:

$$q_t = q_e (1 - \exp^{-kt}). \quad (2)$$

The kinetic curve of pseudo-first-order corresponding to the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ is shown in Figure 5B. The q_e from the nonlinear optimization was 32.08 mg g^{-1} , the rate constant of the pseudo-first-order reaction was 6.3×10^{-3} , and the correlation coefficient (r) of the formula was 0.95. These results indicated the existence of a reversible interaction between PO_4^{3-} and $\text{La}_2(\text{CO}_3)_3$.

Adsorption Thermodynamics

Figure 6 displays the adsorption amount of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ at 303, 313, and 323 K. The adsorption amount of PO_4^{3-} increased gradually with the increase of temperature, significantly affecting the adsorption of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$, since more carbonate ions could be dissociated from the surfaces of the adsorbent. The exchange rate of ions between PO_4^{3-} and CO_3^{2-} also increased, which could accelerate the adsorption reaction. The increase of the adsorption amount indicated that the adsorption of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$ was an endothermic process (Mezener and Bensemali, 2009).



Effect of Coexisting Inorganic Ions

Inorganic ions such as Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , and SiO_3^{2-} are ubiquitous in environmental water. The influence of such anions on the adsorption of PO_4^{3-} is shown in **Figure 7A**. Compared with the control, all anions had a negative effect on the adsorption efficiency of PO_4^{3-} . In particular, the coexistence of CO_3^{2-} and SiO_3^{2-} reduced the adsorption efficiency of PO_4^{3-} from 54.1 to 14.2%–9.5 and 7.6%, respectively, when the concentration of CO_3^{2-} and SiO_3^{2-} increased from 1.0 to 10 mmol L^{-1} . The previous studies have also examined the effect of ions on adsorption efficiency of phosphorus of other materials, such as La-porous carbon composites (Koilaraj and Sasaki, 2017). The result was consistent with this study, and the adsorption capacity was disturbed by 20 mM CO_3^{2-} but not reduced in the presence 20 mM Cl^- and 20 mM SO_4^{2-} . To further study the mechanism involved, the change of pH was measured after adsorption in the presence of CO_3^{2-} and SiO_3^{2-} . The pH rose when the concentration was increased for CO_3^{2-} (pH = 7.1–10.2) and SiO_3^{2-} (pH = 7.7–11.9). This then entails a strong interfering

effect on the adsorption of PO_4^{3-} due to CO_3^{2-} and SiO_3^{2-} . On the one hand, the rise of pH would cause a decrease of positive charges on the surfaces of $\text{La}_2(\text{CO}_3)_3$, weakening the electrostatic attraction between PO_4^{3-} and $\text{La}_2(\text{CO}_3)_3$. On the other hand, the increase of anions could lead to stronger competitive adsorption with PO_4^{3-} , resulting in a decrease of adsorption amount of PO_4^{3-} .

Effect of Natural Organic Matter

HA and FA are the most important components in the natural organic matter, being ubiquitous in the aquatic environment. They are complex mixtures of heterogeneous compounds with a negative charge, originated from the decomposition of plant and animal residues (Valencia et al., 2012; McIntyre and Guéguen, 2013). The existence of HA and FA in environmental waters may cause interference in the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ through a competitive process. As shown in **Figure 7B**, with no coexisting ions in solution as a blank controller (no co-ion), both HA and FA had a weaker effect, as interference on the adsorption of PO_4^{3-} , than that observed for the anion. This is because the molecular weight of natural organic matter was larger than that of anion and requires a longer adsorption path. HA and FA were less competitive to PO_4^{3-} than inorganic anion, and FA, with a small molecular weight, had more influence on the adsorption than HA. Since HA and FA can be combined with PO_4^{3-} in aqueous solution, the complex of $\text{La}_2(\text{CO}_3)_3/\text{HA}$ (or FA) can still be combined with PO_4^{3-} , so the change in the adsorption amount of PO_4^{3-} was not perceivable in the presence of HA and FA.

Analysis of the Mechanism in the Adsorption of PO_4^{3-}

As shown in **Figure 8**, the adsorption amount of PO_4^{3-} increased with the concentration of PO_4^{3-} , reaching a maximum adsorption amount at 150 mg L^{-1} . When PO_4^{3-} concentration exceeded 150 mg L^{-1} , the adsorption amount decreased. The corresponding total molar volume of bicarbonate in the solution after adsorption is also shown in **Figure 8**, which

rose when the concentration of PO_4^{3-} increased and attained equilibrium at variable concentration. In addition, the change of the adsorption amount of PO_4^{3-} (the initial concentration of PO_4^{3-} was 100–200 mg L^{-1}) could be due to the coexistence of anions such as OH^- . Therefore, PO_4^{3-} in the solution would react with $\text{La}_2(\text{CO}_3)_3$, and HCO_3^- would be released.

The XPS spectra of $\text{La}_2(\text{CO}_3)_3$ after the adsorption of PO_4^{3-} is shown in Fig. S2(a). The content of C, O, La, and P at the surface of $\text{La}_2(\text{CO}_3)_3$ after adsorption were 13.7, 57.4, 18.0, and 10.8%, respectively. Fig. S2(b) and Fig. S2(c) show the fitted spectra corresponding to La_{3d} and P_{2p} , respectively. The peak at 835.10 eV corresponded to $\text{La}_{3d_{5/2}}$ of LaPO_4 (Jorgensen et al., 2002). The binding energy of P 2p was 133.89 and 132.89 eV, which contributed to LaPO_4 (Ivanova et al., 1996) and HPO_4^{2-} (Kurmaev et al., 1996), respectively. The XPS spectrum indicated that the adsorption of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$ might be the result of ion exchange between PO_4^{3-} and carbonate, according to the aforementioned results. Based on a previous study, the adsorption process of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$ could be mainly explained in terms of ion exchange (chemisorptions). A tentative adsorption mechanism is presented in Fig. S3, when HPO_4^{2-} reacted with $\text{La}_2(\text{CO}_3)_3$, and HCO_3^{2-} was released in the solution.

CONCLUSION

This study has enabled the exploration of the adsorption process of PO_4^{3-} on the surfaces of $\text{La}_2(\text{CO}_3)_3$ and its characterization in aqueous solution. It has been evidenced that the pH had a greater impact in the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$, and the adsorbent have an excellent adsorption ability under acidic conditions (pH = 2.0–6.0). On the other hand, the presence of either inorganic anions or natural organic matter would inhibit the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$. The influences of both CO_3^{2-} and $\text{Si}_2\text{O}_3^{2-}$ were far higher than those of other anions. Because of the longer adsorption path and weaker competition in the adsorption process,

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the influence of natural organic matter was weaker than that of inorganic anions. The mechanism involved in the adsorption of PO_4^{3-} on $\text{La}_2(\text{CO}_3)_3$ is the combined result of physisorption and chemisorption according to the characterization, in which LaPO_4 is formed when PO_4^{3-} is adsorbed on the surfaces of $\text{La}_2(\text{CO}_3)_3$. All these results prove that $\text{La}_2(\text{CO}_3)_3$ has a large adsorption capacity and useful for the removal of PO_4^{3-} from water.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

SZ, ZT, and FX: conceptualization, methodology, and software. SZ and ZT: data curation and writing-original draft preparation. MF and TZ: visualization and investigation. ZT and FX: supervision. MF and TZ: software and validation. SZ, ZT, and JPG: writing-reviewing and editing.

FUNDING

This research was financially supported by the National Science Foundation of China (21777001, 21107001, and 42077349) and Key Research and Development Project of Anhui Province, China (202004i07020006).

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvs.2022.858258/full#supplementary-material>

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