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Effect of ionic strength on phosphorus removal with modified sediments in lake: kinetics and equilibrium studies

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Phosphorus concentration in lakes is difficult to lower without adding extra materials, and modified lake sediments have the greatest environment-friendly potential for phosphorus removal. In this study, sediment samples were collected from the outlet of Yangtze River (the world's third longest river) in the Eastern part of Dongting Lake (OS) and the river estuary into Dongting Lake (ES) and subsequently modified with iron. Phosphorus-removal efficiency in different ionic strengths of the sediment samples were evaluated, and phosphorus sorption kinetics and isotherms were analyzed using pseudo-first- or pseudo-second-order models and Langmuir or Freundlich models, respectively. Results indicated that the modified sediment samples (MOS and MES) had higher removal efficiency (74.9%–89.2% for MOS and 58.9%–68.9% for MES) for phosphorus than the raw sediment samples (26.0%–34.3% for OS and 13.9%–20.1% for ES) in different ionic strengths. The pseudo-second-order model (R^2>0.95) better described the sorption kinetics than the pseudo-first-order one, and the sorption capacities of the sediment samples were highly influenced by ionic strength, with low ionic strength being favorable for phosphorus uptake. Modified Langmuir models well-described phosphorus sorption (R^2 = 0.9049–0.9996). MOS and MES had higher maximum phosphorus uptake amounts (3.350 and 1.569 mg g^{-1}, respectively) than the other modified phosphorus sorption materials and may thus be potential sorbents for the purification of wastewater containing phosphate.

Keywords: Sediment, Phosphorus, Sorption, Removal, Uptake amount

1. INTRODUCTION

Phosphorus (P), as one of the most significant elements for organism growth, exists in rivers, lakes, soil, sediments, and organisms [1, 2]. However, excessive phosphorus in rivers and lakes can cause eutrophication which is a serious environmental problem in the world [3]. Therefore, studying the effective, environment-friendly, and low-cost methods to remove phosphorus in lakes or rivers is becoming one of the most important tasks in wastewater treatment.

In previous studies, the phosphorus removal methods, such as constructed wetlands [4-6], sorption materials [7-9], and filter systems [10-12], have been introduced. Recently, cost-effective sorption materials have widely been used to remove phosphorus from the water. The sorption materials in constructed wetlands or filter systems are also important in phosphorus removal. In addition, the modified materials such as sand and burned clay coated with oxides of iron, aluminum, or manganese showed efficient removal of phosphorus [13, 14]. However, as increasing stringent regulations are being implemented in lake improvement, extra materials are banned from the lake for pollutant removal. Therefore, more attention should be paid to the method of phosphorus removal in lake.

Lake sediments can act as either phosphorus “sources” or “sink” to the overlying water column. Phosphorus concentration of the water is significantly correlated with sediments. Therefore, sediment treatment is one of the most important methods for controlling the phosphorus concentration in water. Sediment dredging [15, 16], landfilling [17, 18], and incineration or pyrolysis after dehydration [19] are commonly used to treat the sediments and reduce lake phosphorus levels. Although these methods have high removal efficiency for pollutants, the high implementation cost, the strong requirement of land, and the reuse of treatment products increase the difficulty of sediment treatment. Therefore, new methods of sediment treatment should be studied to control phosphorus concentration in lakes.

Dongting Lake, which is the second largest freshwater lake in China, is located in the Hunan Province (E 111°40’-113°10’, N 28°38’-29°45’). It is composed of a series of lakes and has three major lake districts, namely, Eastern, Southern, and Western. Yangtze River flows into Dongting Lake via two outfalls (Hudu and Ouchi), and water drains from the outlet in the Eastern Dongting Lake to Yangtze River [20, 21]. Environmental, hydrological, and hydraulic conditions from these places in Dongting Lake cause the sediments to have different physicochemical properties, which can affect the phosphorus sorption.

In this study, we collected the sediments from the outlet of Eastern Dongting Lake to Yangtze River and the river estuary into Dongting Lake, and used the raw sediment samples to prepare the modified sediment samples with iron. The objectives of this study are mainly to evaluate the phosphorus-removal efficiency of sorption using sediment samples, and to describe the sorption kinetics and isotherms in different ionic strengths using modified models. This study provides useful theoretical foundation for phosphorus removal using lake sediments.

2. EXPERIMENTAL METHOD AND MATERIALS

2.1 Sample collection and sorption materials

Figure 1 shows the sampling sites in Dongting Lake. One of the sampling sites is the outlet to Yangtze River in Eastern Dongting Lake, and the other sampling site is from the river estuary into Dongting Lake. These two raw sediment samples were immediately brought to the laboratory, where they were freeze-dried, ground, and sifted through a 100-mesh (0.15 mm) sieve to obtain a uniform size. The treated sediment samples from the outlet to Yangtze River and the river estuary into Dongting Lake were labeled OS and ES, respectively.

The OS and ES were used to prepare the modified sediment samples. The modified sediment samples were prepared by introducing 1 g of raw sediment samples into 100 mL of 0.2 mol L^{-1} iron solution made from $FeSO_4 \cdot 7H_2O$. The pH during iron loading was kept at 2.0. The mixtures were stirred continuously for 12 h at room temperature. The modified sediment samples were then obtained by filtration and drying, and the modified sediment samples from OS and ES were assigned as MOS and MES, respectively.

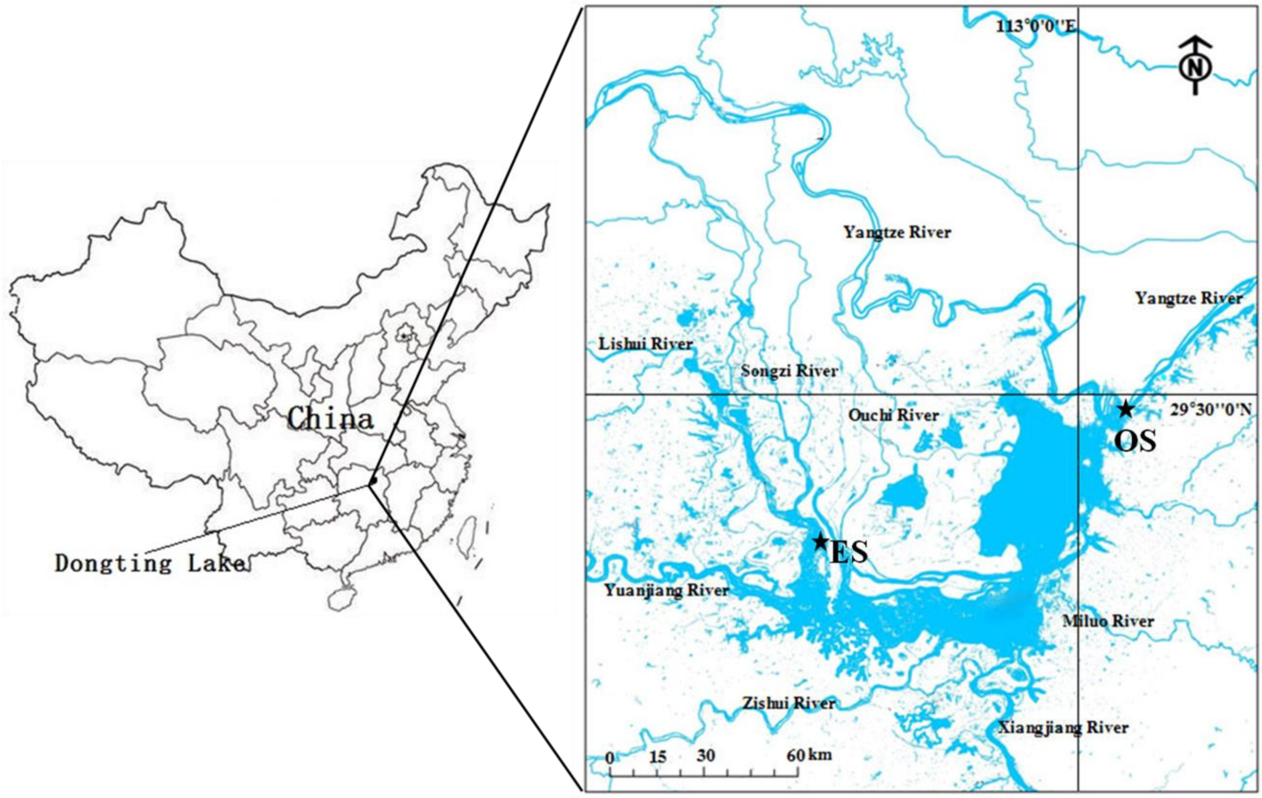


Figure 1. Location of sampling sites in Dongting Lake, China

2.2 Characterization of the sediment samples

The surface morphology and structure of the sediment samples were examined using scanning electron microscope (SEM, Philips XL 30). Surface area and pore volume measurements were obtained using Micrometritics Tristar 3000 Surface Analyzer. Oxide contents of the sediment samples were determined by X-ray fluorescence (XRF) analyzer (S4 Explorer, Germany). The mineralogy of the sediment samples was studied by X-ray diffraction (XRD) analysis (D8 Advance, Germany). The surface functional groups were identified by transmission infrared spectra obtained from a Fourier transform (FTIR) spectrophotometer (Nicolet 6700, USA). Zeta potentials were determined using zeta potential analyzer (Zetasizer Nano ZS90). Organic matter (OM) content was determined by the loss of ignition to constant mass (4 h) at the temperature of 550 °C. The pH of the sediment was measured in a

1:2.5 (w/v) mixture of sediment with deionized water [22].

2.3 Study of sorption kinetics and isotherms

Batch experiments were done to evaluate the kinetics of phosphorus sorption at four ionic strengths of 0, 0.001, 0.01 and 0.1 M KCl. The stock solution was obtained by dissolving the salt KH_2PO_4 in deionized water. Samples (1 g in triplicate) were added into phosphorus solution (50 mL, 20 mg L^{-1}) with different ionic strengths (0, 0.001, 0.01, and 0.1 M). Samples were constantly agitated in a shaker in batches with a speed of 220 rpm and a constant temperature of 25 ± 2 °C. At 9 different time intervals (1, 2, 5, 10, 20, 40, 60, 120, and 240 min), suspensions were obtained from each flask, centrifuged, filtered (0.45 μm), and analyzed to determine the phosphorus content by the molybdenum blue method [23].

Batch experiments were conducted to obtain the sorption isotherms of phosphorus. Sediment samples (1 g in triplicate) were added into 50 mL phosphorus solution at different initial phosphorus concentrations (0, 0.5, 1, 2, 5, 10, 20, and 50 mg L^{-1} as KH_2PO_4). The conical flasks were shocked in a shaker with a speed of 220 rpm and a constant temperature of 25 ± 2 °C for a 240 min. The suspensions were centrifuged, filtered (0.45 μm), and analyzed to determine the phosphorus content.

2.4 Data analysis

Phosphorus-removal efficiency, η (%), was calculated by the equation as follows:

$$\eta=\frac{C_0-C_t}{C_0}\times100\% \qquad (1)$$

Phosphorus uptake amount in the different sediment samples at each time, Q_t (mg g^{-1}), was calculated by using a mass balance relationship as follows:

$$Q_t=(C_0-C_t)\frac{V}{W}, \qquad (2)$$

where C_0 (mg L^{-1}) is the initial liquid-phase phosphorus concentration, C_t (mg L^{-1}) is the blank corrected concentration of phosphorus at time t, V (L) is the volume of the solution, and W (g) is the mass of dried sediment.

Sorption kinetics is described by pseudo first- and second-order models, and the models are expressed as follows [24-26]:

$$Q_t = Q_e(1 - e^{-K_1 t}), \qquad (3)$$

$$\frac{t}{Q_t}=\frac{1}{K_2Q_e^2}+\frac{t}{Q_e}, \qquad (4)$$

where Q_t and Q_e are the uptake amounts (mg g^{-1}) of phosphorus adsorbed at time point t and equilibrium (mg g^{-1}), respectively. K_1 (h^{-1}) is the first-order kinetic rate constant, and K_2 is the sorption rate constant of the pseudo-second-order kinetic model (g mg^{-1} h^{-1}).

Modified Langmuir and Freundlich models were used to describe the sorption isotherms. The modified Langmuir model was obtained from previous studies [27, 28], and the isotherm parameters are expressed as follows:

$$\text{Langmuir: } Q_e = \frac{Q_m KC_e}{1+KC_e} - \frac{Q_m KC_e^0}{1+KC_e^0} - Q_e^0. \qquad (5)$$

Freundlich: $Q_e = K_f C_e^m - K_f (C_e^0)^m - Q_e^0$, (6)

where Q_m is the maximum phosphorus uptake amount (mg g^{-1}). C_e is the phosphorus concentration in the aqueous phase at equilibrium (mg L^{-1}), and K is the affinity parameter (L mg^{-1}). K_f is the sorption coefficient (L g^{-1}) and m is a constant utilized to measure sorption intensity or surface heterogeneity. C_e^0 and Q_e^0 are the equilibrium concentration (mg L^{-1}) and uptake amount (mg g^{-1}), respectively

3. RESULT

3.1 Characterization of the sediments

3.1.1 Physicochemical properties

Physicochemical properties including surface property, oxide content, and physical property are shown in Table 1. The raw sediments of OS and ES had the lower surface areas than modified sediments, which were 3.87 and 2.26 m^2 g^{-1}, respectively. Iron-doped samples (MOS and MES) had higher specific surface areas (19.45 and 10.36 m^2 g^{-1}, respectively) and total pore volumes (5.34×10^{-2} and 3.67×10^{-2} cm^3 g^{-1}, respectively) than raw sediments. In addition, SiO_2 was the main oxide in the samples, and the modified sediment had high Fe_2O_3 content than the raw sediments. The modified sediment samples shows zeta potential values higher than +40 mV or lower than -30 mV. Furthermore, OS and MOS had the higher OM contents than ES and MES, and pH was similar value among the four samples.

Table 1. Physicochemical properties of four sediment samples

	Surface Property		Oxide Content (%)					Physical Property		
Samples	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	SiO_2	Fe_2O_3	Al_2O_3	MgO	CaO	OM (%)	pH	Zeta potential (mV)
OS	3.87	7.74×10^{-3}	62.50	7.11	17.90	1.56	0.87	7.84	7.35	-35.4
MOS	19.45	5.34×10^{-2}	58.00	15.20	17.10	1.69	0.39	7.84	7.35	+48.7
ES	2.26	3.46×10^{-3}	62.60	5.12	17.40	1.42	0.62	5.89	7.39	-32.3
MES	10.36	3.67×10^{-2}	59.80	13.16	17.50	1.74	0.17	5.89	7.39	+41.2

3.1.2 Morphology analysis

The SEM images of the raw and modified sediment materials are shown in Figure 2 which shows the surface structure and morphology of sediment samples. The raw sediment samples of OS and ES had smooth and flat surfaces, shown in Figs. 2(a) and (c). The porosity of the sample surface was one of the main reasons for phosphorus sorption, and the surface structures of OS and ES have caused the low sorption efficiency of phosphorus. On the surface of MOS and MES (Figs. 2(b) and (d)), amounts of pores were observed and MOS had more pores on the sediment surface than MES. These pores could increase the surface area and pore volume, thereby increasing phosphorus sorption [29]. In addition, MOS had the more pores than MES, which was one of the main reasons that MOS had the higher phosphorus sorption efficiency.

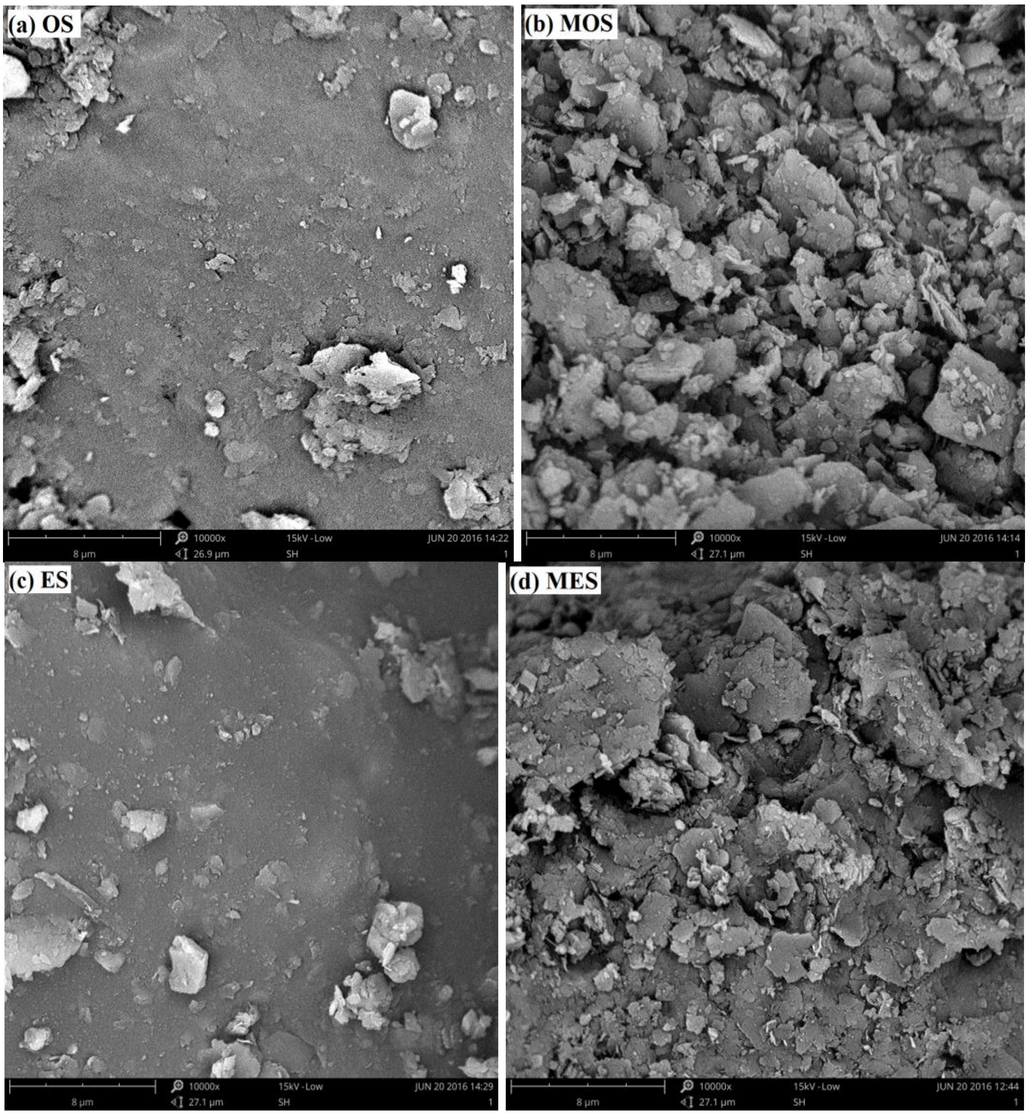


Figure 2. SEM images of sediment samples ((a) for OS, (b) for MOS, (c) for ES, and (d) for MES)

3.1.3 XRD analysis

The XRD diagrams are shown in Figure 3. The four diagrams obtained for OS, MOS, ES, and MES were almost identical, which indicated that modifying the sediments with iron could not change the mineralogy of the samples, or maybe also because of the very low concentration of adsorbed iron.

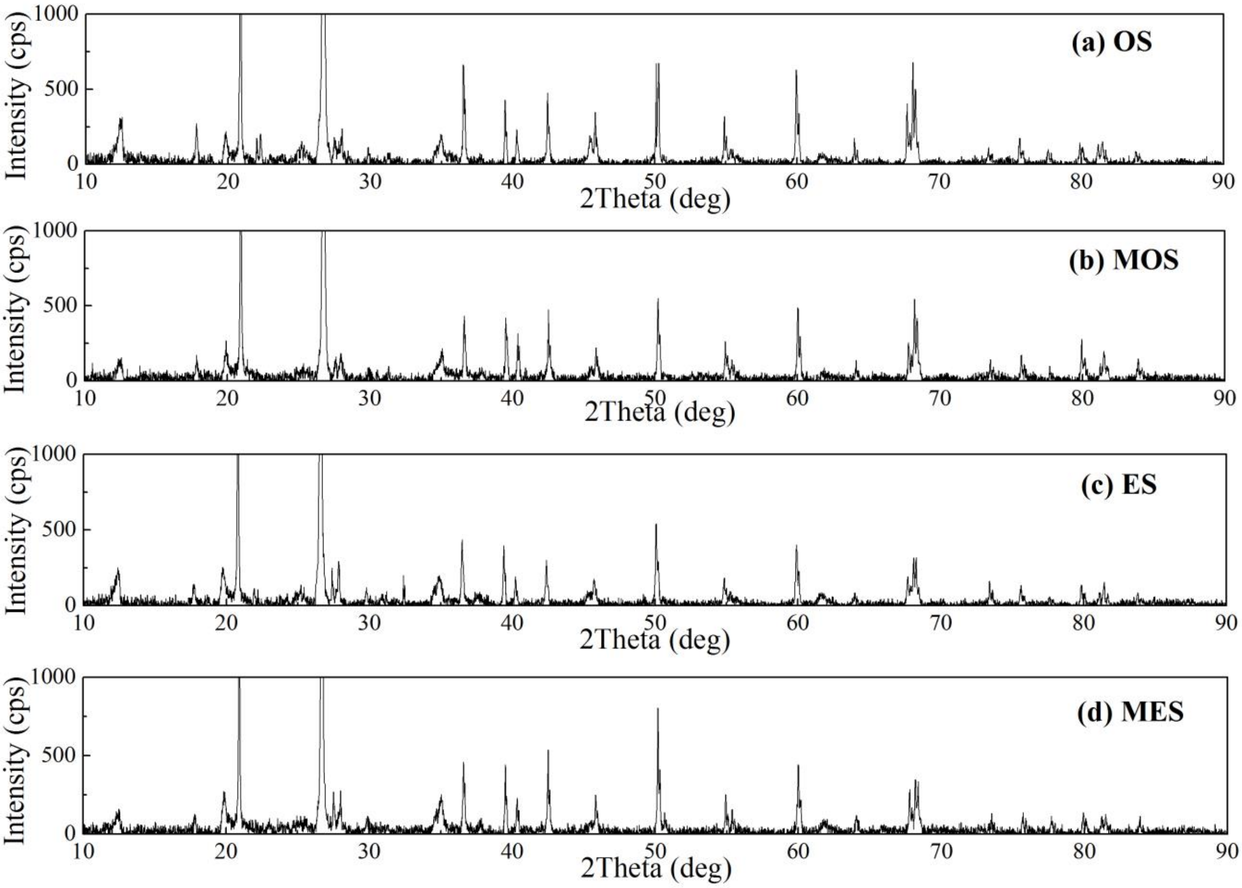


Figure 3. XRD patterns of sediment samples ((a) for OS, (b) for MOS, (c) for ES, and (d) for MES)

3.1.4 FTIR analysis

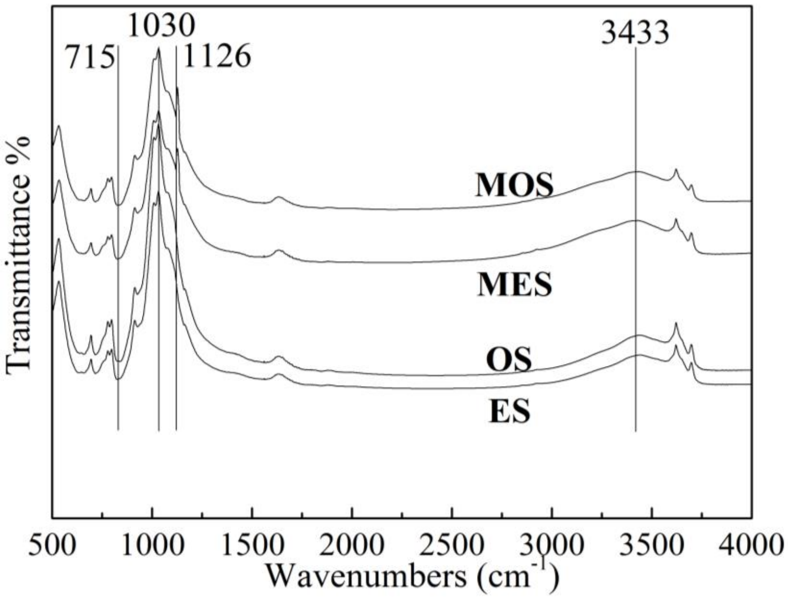


Figure 4. FTIR spectra of sediment samples

The FTIR spectra of sediment samples are shown in Figure 4. Some distinctions were observed in the FTIR spectra of the four sediment samples. The treatment process on raw sediments (OS and ES) might have caused the hydroxyl stretching band at 3433 cm^{-1} [30]. The peak at approximately 1126 cm^{-1} (in MOS and MES) might be assigned to the Si-O-Fe that were modified with iron, and no peak existed in OS and ES[31]. A strong Si-O-Si at 1030 cm^{-1} existed in four sediment samples. Additionally, the peaks at 715 cm^{-1} corresponded to the Fe-OH [32]. These four samples were all from lake sediments, with SiO_2 as the main composition, because it is common in these four sediment samples. The bond around 1126 cm^{-1} in MOS and MES revealed that these two modified sediments were a complexes of Fe and Si, and had relatively high contents of Fe compared with raw sediment samples.

3.2 Effects of ionic strength on phosphorus-removal efficiency

Effects of ionic strength on phosphorus-removal efficiency are shown in Figure 5. The results indicated that the sediment samples from the outlet of Yangtze River (OS) had higher phosphorus-removal efficiency (average value, 30.9%) than the samples from the estuary of Dongting Lake (ES) (average value, 17.7%). In addition, the modified sediments, MOS and MES, had the higher removal efficiencies than raw sediments (OS and ES), and the removal efficiency reached 89.2% and 68.9% with an ionic strength of 0 M. As the ionic strength increased to 0.01 M, there was little change in removal efficiency, and the removal efficiencies decreased slowly from 34.3% to 31.0% (OS), 89.2% to 83.8% (MOS), 20.1% to 18.0% (ES), and 68.9% to 65.9% (MES). However, when the ionic strength increased to 0.1 M, the removal efficiencies decreased rapidly to 26.0% (OS), 74.9% (MOS), 13.9% (ES), and 58.9% (MES).

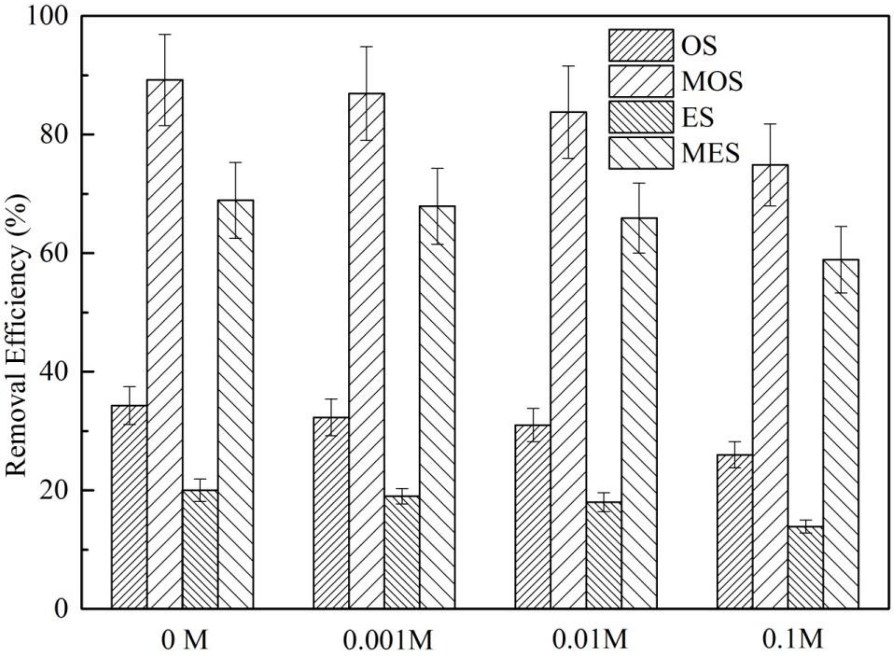


Figure 5. Effects of ionic strength on phosphorus removal efficiency

3.3 Phosphorus sorption kinetics

The kinetics curves of phosphorus sorption on these four sediments using pseudo-first and –second-order models were shown in Figure 6. The results indicated that the phosphorus sorption on the four sediment samples were initially fast (20 min), and the sorption rate decreased after the initial sorption. Then the phosphorus uptake amounts of these sediment samples trended to equilibrium at approximately 240 min. Two kinds of modified sediment samples (MOS and MES) had higher values of Q_e than raw sediment samples (OS and ES), and the value of Qe had little change when the ionic strength increased from 0 to 0.01 M. As the ionic strength increased to 0.1 M, Q_e decreased greatly to approximately 0.76 mg g^{-1}, which is shown in Figure 6(d).

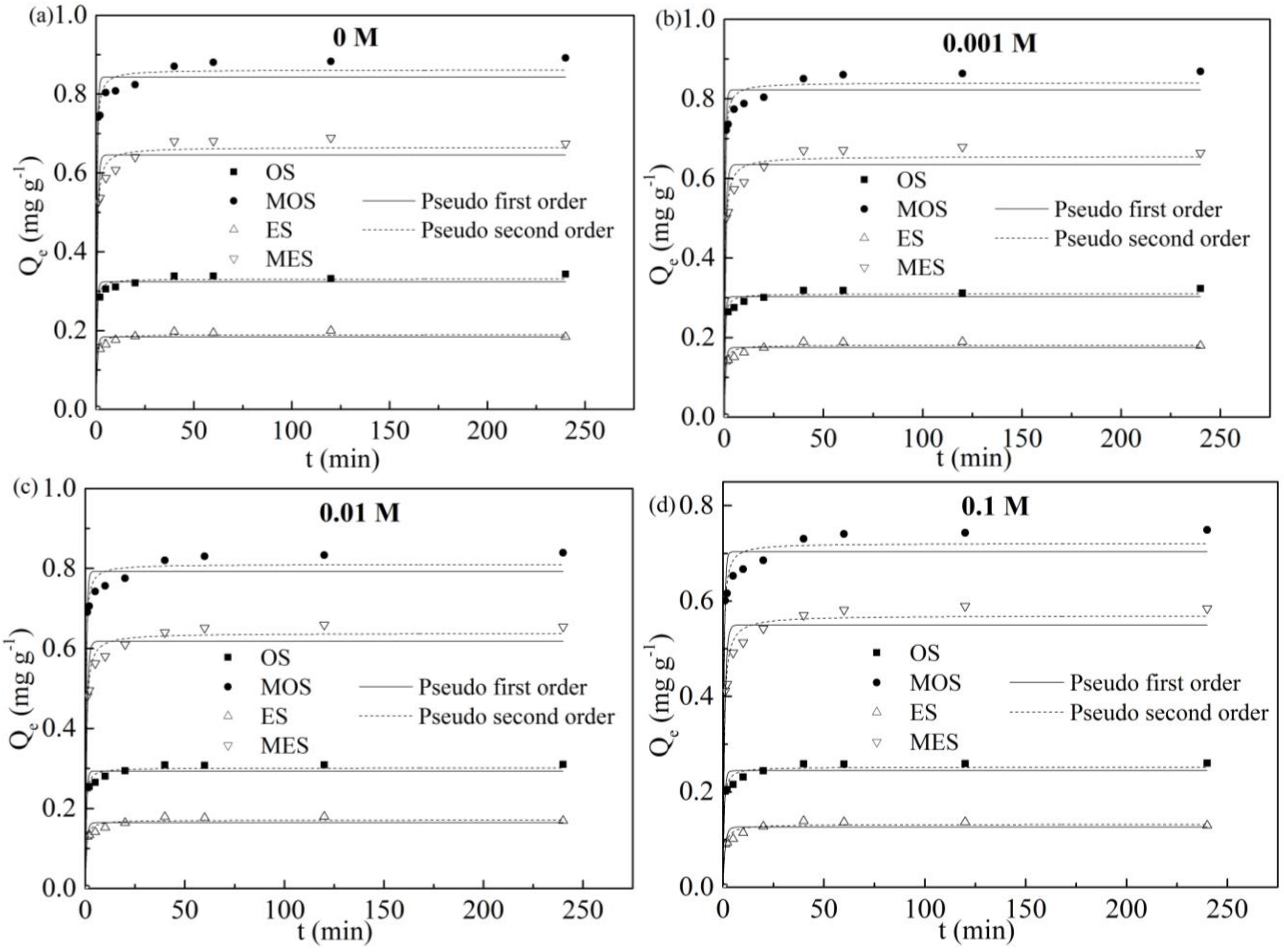


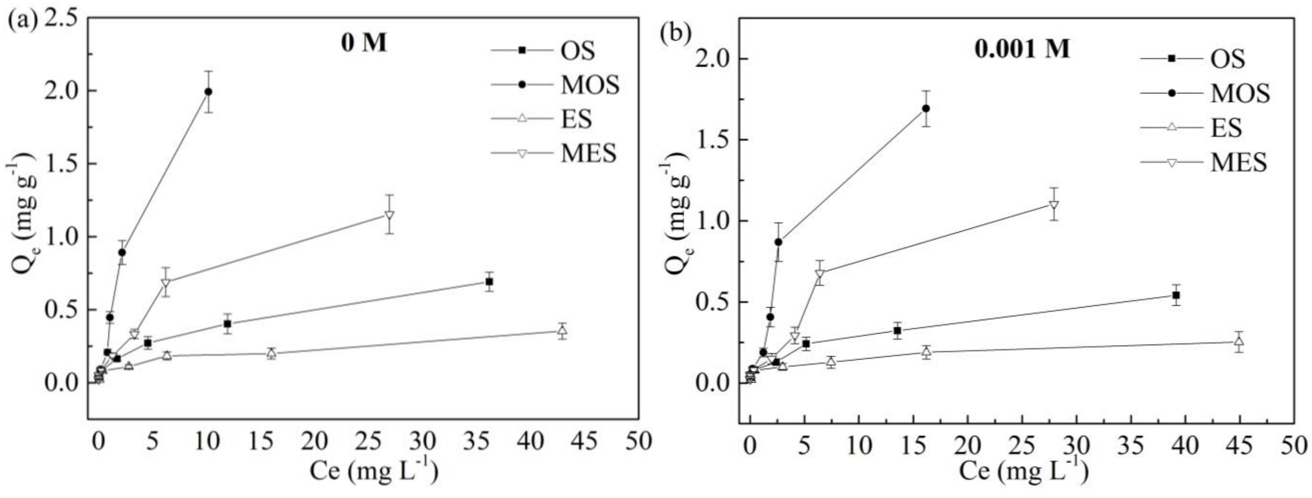
Figure 6. Sorption kinetics of phosphorus onto sediment samples in four different ionic strengths.

The kinetic parameters were obtained according to nonlinear regression (Eqs. (3) and (4)), which were shown in Table 2. Pseudo-second-order model (R^2>0.95) can describe the sorption kinetic better than pseudo-first-order model. The modified sediment samples, MOS and MES, had higher values of Q_e and K_2 than the raw sediment samples (OS and ES); and the highest value of Q_e was 0.862 mg g^{-1} when the ionic strength was 0 M using the sediment samples of MOS. The sediment samples from the outlet of Yangtze River (OS) had higher phosphorus uptake amount than the samples from the estuary of Dongting Lake (ES); and the modified sediment samples had the same tendency. In addition, Q_e and K_2 decreased when the ionic strength increased from 0 to 0.01 M, and the values changed marginally. The highest ionic strength (0.1 M) decreased the Q_e and K_2 values of sediment samples.

Table 2. Parameters for pseudo-first and -second-order

Ionic strength	Sample	Pseudo-first-order modes			Pseudo-second-order modes		
		Q_e	K_1	R^2	Q_e	K_2	R^2
0 M	OS	0.324±0.006	1.903±0.380	0.9705	0.331±0.005	13.900±3.354	0.9877
	MOS	0.844±0.016	1.898±0.367	0.9720	0.862±0.012	5.409±1.291	0.9882
	ES	0.184±0.005	1.506±0.335	0.9454	0.190±0.004	15.905±4.169	0.9755
	MES	0.646±0.017	1.430±0.287	0.9518	0.665±0.012	4.264±0.928	0.9818
0.001 M	OS	0.302±0.007	1.861±0.420	0.9607	0.310±0.005	13.535±3.740	0.9818
	MOS	0.822±0.016	1.905±0.368	0.9723	0.841±0.012	5.572±1.346	0.9879
	ES	0.175±0.006	1.344±0.320	0.9282	0.181±0.004	13.483±3.690	0.9669
	MES	0.634±0.018	1.294±0.259	0.9460	0.656±0.012	3.722±0.781	0.9802
0.01 M	OS	0.294±0.007	1.710±0.364	0.9588	0.302±0.005	12.197±3.016	0.9827
	MOS	0.793±0.016	1.863±0.366	0.9700	0.811±0.012	5.509±1.343	0.9869
	ES	0.165±0.006	1.282±0.307	0.9236	0.171±0.004	13.282±3.596	0.9653
	MES	0.618±0.017	1.239±0.233	0.9497	0.638±0.011	3.656±0.684	0.9836
0.1 M	OS	0.244±0.007	1.481±0.331	0.9437	0.252±0.005	11.360±2.838	0.9764
	MOS	0.703±0.016	1.719±0.348	0.9631	0.721±0.012	5.320±1.306	0.9838
	ES	0.126±0.005	0.943±0.235	0.8953	0.132±0.004	11.148±2.914	0.9550
	MES	0.550±0.016	1.097±0.585	0.9414	0.570±0.011	3.417±0.631	0.9812

3.4 Sorption isotherm fitting



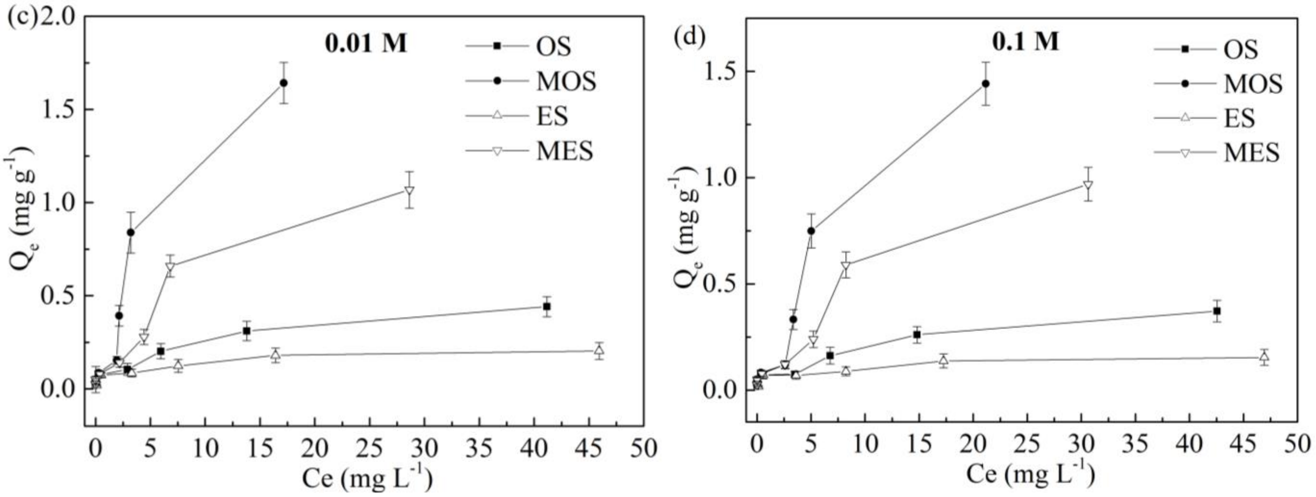


Figure 7. Sorption isotherms of phosphorus in four different ionic strengths

Figure 7 shows the sorption isotherm of phosphorus using four sediment samples in different ionic strengths. The phosphorus uptake amounts were MOS>MES>OS>ES in different ionic strengths. When the ionic strength increased from 0 to 0.01 M, the phosphorus uptake amount was not statistically significant (Figs. 7(a)-(c)); whereas in the 0.1 M, the phosphorus uptake was relatively lower, as shown in Figure 7(d). Furthermore, the phosphorus uptake increased with increasing initial phosphorus concentration, and the increased rate slowed as the equilibrium concentration increased.

In this study, the isotherm data were fitted using two modified Langmuir and Freundlich models. Table 3 shows the fitting results using the modified Langmuir and Freundlich model. The values of R^2 indicated that the modified Langmuir model (0.9049-0.9996) describe the phosphorus sorption isotherm better than modified Freundlich model (0.8206-0.9756). For the modified Langmuir isotherm, the maximum phosphorus uptake (Q_m) of MOS (3.35 mg g^{-1}) was higher than other sediment samples, and ES had the lowest Q_m value of 0.13 mg g^{-1} in 0.1 M ionic strength. The fitting results also indicated that Q_m also decreased as the ionic strength increased, especially in 0.1 M ionic strength; Q_m reached the lowest value in four sediment samples. In addition, Table 3 shows that the values of n ranged from 0 to 1, which indicated that the experimental condition benefitted the phosphorus sorption.

Table 3. Modified Langmuir and Freundlich models parameters for phosphorus sorption

Ionic strength	Sediment sample	Langmuir: $Q_e=\frac{Q_m K C_e}{1+KC_e}-\frac{Q_m K C_e^0}{1+KC_e^0}-Q_e^0$			Freundlich: $Q_e=K_f C_e^n-K_f (C_e^0)^n-Q_e^0$		
		Fitting results			Fitting results		
		Q_m	K	R^2	n	K_f	R^2
0 M	OS	0.870±0.119	0.095±0.033	0.9823	0.449±0.054	0.143±0.027	0.9756
	MOS	3.350±0.383	0.147±0.033	0.9970	0.652±0.071	0.450±0.070	0.9748
	ES	0.383±0.079	0.126±0.076	0.9860	0.361±0.050	0.087±0.014	0.8260
	MES	1.569±0.140	0.106±0.022	0.9822	0.515±0.061	0.216±0.039	0.9652

0.001 M	OS	0.665±0.096	0.095±0.036	0.9996	0.438±0.067	0.113±0.027	0.9399
	MOS	2.454±0.383	0.142±0.049	0.9842	0.572±0.101	0.355±0.094	0.9326
	ES	0.270±0.053	0.173±0.111	0.9544	0.261±0.060	0.100±0.024	0.8548
	MES	1.631±0.272	0.078±0.028	0.9832	0.566±0.094	0.172±0.048	0.9311
0.01 M	OS	0.554±0.072	0.096±0.032	0.9871	0.424±0.080	0.099±0.028	0.9381
	MOS	2.738±0.677	0.089±0.043	0.9732	0.643±0.122	0.270±0.088	0.9183
	ES	0.215±0.038	0.257±0.085	0.9406	0.194±0.0074	0.119±0.044	0.9002
	MES	1.602±0.302	0.070±0.027	0.9886	0.581±0.102	0.157±0.049	0.9273
0.1 M	OS	0.501±0.091	0.071±0.031	0.9668	0.441±0.101	0.076±0.028	0.9156
	MOS	2.925±0.987	0.047±0.027	0.9877	0.717±0.129	0.165±0.061	0.9260
	ES	0.134±0.024	0.320±0.114	0.9049	0.132±0.115	0.136±0.047	0.8611
	MES	1.476±0.365	0.049±0.021	0.9885	0.628±0.108	0.116±0.039	0.9317

4. DISCUSSION

4.1 Effect of sample surface characterization on phosphorus sorption

The results indicated that the phosphorus-removal efficiency was MOS>MES>OS>ES, and the modified sediment samples had higher removal efficiency than the raw sediment. According to characterization, the raw sediment samples of OS and ES had poor internal volume, and the modified sediment samples of MOS and MES had the higher surface area and pore volume which caused the high phosphorus-removal efficiency of the modified sediment sample [33]. The previous study indicated that the high Fe, Al, Ca, and Mg oxides favored both the phosphorus uptake amount and velocity of sorption [34, 35]. Therefore, MOS and MES, which were iron-doped, have high Fe oxides to increase the phosphorus-removal efficiency. In addition, the comparison of phosphorus removal efficiencies for the raw sediment samples showed that OS had higher removal efficiency than ES, which could be explained OS having higher OM and Fe oxides [36].

The SEM images indicated that MOS and MES had more pore structures, and a large number of pores were observed on the surface of these sediment samples. Therefore, their surface structures were more conductive to sorption. The FTIR results indicated that the peaks in MOS and MES around 1126 cm^{-1} assigned to the Si-O-Fe might be among the main mechanisms of sorption and high phosphorus-removal efficiency. The modified sediment samples might supply new sites for phosphorus sorption.

4.2 Ionic strength effects on phosphorus sorption kinetics

Sorption kinetics indicated that three steps might be considered in kinetic models of these sediment samples: (1) the sorbate ions diffuse from the liquid phase to the liquid–solid boundary; (2) the sorbate ions move from the liquid–solid boundary to the solid surface; (3) the sorbate ions diffuse into the particles [37]. In the first few minutes, the sorbate ions occupied the active sorption sites rapidly. MOS and MES had more active sorption sites than OS and ES because of their high surface area and Fe oxides. As the ionic strength increased from 0 to 0.01 M, the introduction of cations (K^+) could increase the electrostatic potential (ψ) to facilitate phosphorus uptake capacity [38]. However, the chloride ions with low ionic strength would also compete with phosphorus ions (such as $H_2PO_4^-$ or HPO_4^{2-}) on the actives sites, which decreases of phosphorus uptake. Therefore, as the ionic strength increased from 0 to 0.01 M, the phosphorus uptake became statistically insignificant. The sorption kinetic results showed that as the ionic strength increased from 0.01 to 0.1 M, the phosphorus uptake amount considerably decreased. Although the introduction of K^+ could increase the electrostatic potential by making the plane potential less negative, the large amount of competing anions (Cl^- in this study) were introduced to compete with phosphorus ions. In the sorption processes, the ion exchange reaction was the main mechanism for phosphorus sorption[39]. The function of the competition between Cl^- and phosphorus ions on the active sites of the samples was larger than the increase of electrostatic potential by K^+ [40]. In addition, zeta potential of the raw sediment samples were lower than -30 mV and the modified sediment samples were higher than +40 mV. Zeta potential changed after the modification because of the introduction of Fe^{2+} or Fe^{3+} (the oxidation of Fe^{2+}). The change of zeta potential can also cause the electrostatic sorption between Fe ion and $H_2PO_4^-$ or HPO_4^{2-}.

4.3 Equilibrium sorption of phosphorus

The Langmuir and Freundlich models usually assume a homogeneous surface, uniform binding energy, and monolayer coverage. The model has been widely used to describe anion, cation, or compound sorption behaviors by different materials despite their heterogeneous natures [41-43]. However, for the sediments, the native adsorbed phosphorus (NAP) can immediately participate in the sorption or desorption to influence the phosphorus removal efficiency. Therefore, in this study, the modified Langmuir and Freundlich models were used to describe the isotherms of these four sediment samples.

The fitting results according to the modified models indicated that OS sediment samples had the higher maximum phosphorus uptake than ES because of the higher OM and Fe oxides contents. However, the maximum phosphorus uptake amount of the raw sediments was also relatively low compared with other natural phosphorus sorption materials such as ceramic sand (0.51 mg g^{-1}), zeolite (0.46 mg g^{-1}), and shale (0.65 mg g^{-1}) [44, 45]. In addition, some modified phosphorus sorption materials that contain iron or aluminum such as pyrrhotite (0.92 mg g^{-1}) and bauxite (0.65 mg g^{-1}), had higher phosphorus uptake amounts [46] than OS and ES. Therefore, the raw sediment samples may not be suitable as phosphorus removal materials. The maximum phosphorus uptake of modified sediment samples (MOS and MES) could reach 3.350 and 1.569 mg g^{-1}, respectively, and the values decreased as the ionic strength increased. However, as the ionic strength increased to 0.1 M, the maximum phosphorus uptake of MES decreased to 1.476 mg g^{-1}; the value was higher than the common modified materials of phosphorus sorption. This suggested that the modified sediment samples might be potential sorbents for purification of wastewater containing phosphate.

5. CONCLUSION

Sediment samples were characterized and subjected to analyses of phosphorus-removal efficiency, sorption kinetics, and sorption isotherms using modified models in different ionic strengths. Results suggested that the surface structures of modified sediment samples were conductive to phosphorus uptake according to characterization, and that modified sediment samples have better phosphorus-removal efficiency. The rate of sorption followed the pseudo-second-order models and the modified Langmuir models could describe the sorption isotherms better. Ionic strength influenced the phosphorus uptake of the sediment samples greatly, and low ionic strength was favorable for phosphorus uptake of the sediment samples. The removal of phosphorus in lake is difficult without adding extra materials. This study used lake sediments and modified them as phosphorus sorption materials, and the modified sediments are potential sorbents for phosphorus removal in lakes.

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