

Article

Adsorption Behavior of Inorganic and Organic Phosphate by Iron Manganese Plaques on Reed Roots in Wetlands

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Abstract: Inorganic and organic phosphate adsorption by iron–manganese (Fe–Mn) plaques extracted from reed roots was investigated. Scanning electron microscopy indicated the roots had rough surfaces and fine particles attached. X-ray photoelectron spectra indicated that Fe and Mn in the Fe–Mn plaques were mainly in the +III and +IV oxidation states, respectively. The contact time, initial phosphate concentration, and temperature effects on inorganic and organic phosphate adsorption were investigated by performing batch tests. Pseudo-second-order model described inorganic and organic phosphate adsorption, indicating the chemisorption was the dominant adsorption process. Langmuir and Freundlich isotherm models were fitted to the equilibrium data, and the Langmuir model fitted best. The maximum inorganic and organic phosphate adsorption capacities at 298 K were 7.69 and 3.66 mg/g, respectively. The inorganic and organic phosphate adsorption processes were spontaneous and exothermic. The inorganic phosphate adsorption capacity was higher than the organic phosphate adsorption capacity, and the presence of organic phosphate did not negatively affect adsorption at inorganic to organic phosphate molar ratios between 1:1 and 3:1. Fourier-transform infrared spectra before and after adsorption showed abundant functional groups on Fe–Mn plaques and that phosphate was probably adsorbed via replacement of hydroxyl groups and inner-sphere surface complexation.

Keywords: iron and manganese plaque; inorganic phosphate; organic phosphate; adsorption; reed roots; wetland

1. Introduction

Discharges of domestic sewage and agricultural wastewater containing phosphorus-rich chemicals, such as detergents and chemical fertilizers, into lakes and rivers can cause nutrient enrichment, excess algal growth, and eutrophication [1–3]. Dissolved phosphorus in wastewater is normally present as organic phosphates, inorganic phosphates, and polyphosphates. Inorganic and organic phosphates are generally the main species in wastewater and should be removed simultaneously.

In China, phosphorus residues in wastewater treatment plants effluent are generally removed primarily using a wetland system before the effluent is discharged into a water body. In such wetland systems, phosphorus is removed by plant uptake, media adsorption, and microorganism assimilation [4–6]. Media adsorption is usually limited because much of the solid matter is inert and has a poor adsorption capacity [7,8]. Assimilation by microorganisms contributes little to the removal of total phosphorus because the phosphorus will be released back to the water once the microorganisms die. Plant uptake is normally considered to affect phosphorus removal little until

the plants are harvested [9,10]. However, oxygen can be released from the dense root networks of plants in wetlands, creating an oxidizing rhizosphere environment. This can cause Fe^{2+} and Mn^{2+} in the rhizosphere soil or media to become oxidized to Fe^{3+} and Mn^{4+} , respectively. The Fe^{3+} and Mn^{4+} can precipitate and accumulate on the root surfaces, to form features called iron–manganese (Fe–Mn) plaques [11]. Iron–Mn plaques on hydrophyte root surfaces can immobilize various nutrients and metalloids [12,13]. Wang et al. [14] found *Arundo donax* Linn and *Typha latifolia* roots had higher phosphorus contents when iron plaques were presented than when iron–plaques were not present. Chong et al. [15] found that amorphous iron oxide on root surfaces caused phosphorus to accumulate in the rhizosphere. It has been shown the phosphorus adsorption behaviors and mechanisms by Fe–Mn plaques are not clearly stated, and the influence between inorganic and organic phosphate is ignored. Therefore, the contributions of Fe–Mn plaques to the removal of inorganic and organic phosphates in wetland systems need to be assessed to improve our understanding of how wetland system habitats may be managed to promote Fe–Mn plaques formation to effectively and sustainably remove phosphorus from water.

In this study, Fe–Mn plaques were extracted from reed roots from a long-established wetland, and the abilities of the plaques to adsorb inorganic and organic phosphates were assessed. The surface morphology and structure of the roots were assessed by scanning electron microscopy (SEM), and the electron binding energies and the oxidation states of Fe and Mn in plaques were investigated by X-ray photoelectron spectroscopy (XPS). The functional groups in Fe–Mn plaques were investigated by Fourier-transform infrared (FTIR) spectroscopy. The kinetics, isotherms, and thermodynamics of inorganic and organic phosphate adsorption by Fe–Mn plaques were also assessed.

2. Materials and Methods

2.1. Chemicals

All chemicals were of analytical reagent grade and were purchased from Beijing Chemical Co. (Beijing, China). Solutions of inorganic and organic phosphates for use in the adsorption tests were prepared by dissolving potassium dihydrogen phosphate (KH_2PO_4) and adenosine-5'-monophosphate ($\text{C}_{10}\text{H}_{14}\text{N}_5\text{O}_7\text{P}$), respectively, in ultrapure water. The ultrapure water ($18.2 \text{ }\Omega\text{M}\cdot\text{cm}^{-1}$) used throughout the study was prepared using a Millipore system (Merck, Darmstadt, Germany).

2.2. Fe–Mn Plaque Collection

Reeds with roots were collected from a wetland at the Beijing University of Civil Engineering and Architecture (Beijing, China). The wetland is used to treat effluent from a sewage treatment plant. The roots were cut from the reeds and washed thoroughly with ultrapure water. The roots were then placed in a beaker containing ultrapure water and ultrasonicated for 5 h using a KQ-500B instrument (Kun Shan Ultrasonic Instruments Co., Ltd., Kun Shan, China). This caused the Fe–Mn plaques to separate from the root surfaces and become suspended in the water. The process was repeated until sufficient suspension was obtained to perform the planned tests. The suspended plaques were reddish brown. The suspension was evaporated and freeze-dried to give dry Fe–Mn powder, which was stored in a desiccator. The iron and manganese contents of the Fe–Mn plaque powder were determined by acid digesting and then analyzing the solution using a Hitachi Z-2010 atomic absorption spectrometer (Hitachi High-Technologies, Tokyo, Japan). The total phosphorus and inorganic phosphorus contents of the Fe–Mn plaque powder were determined and used as the background concentrations (i.e., before adsorption experiments were performed). The weights of the roots were determined before the ultrasonic extraction process was performed.

2.3. Characterization

The reed roots with and without Fe–Mn plaques attached were examined by SEM using an S-3500N instrument (Hitachi High-Technologies). Before being examined, the samples were sputtering

coated with gold and palladium for 45 s using a Quorum Polaron SC7620 mini-sputter coater (Quorum Technologies Ltd., East Sussex, UK) to decrease charging effects inside the microscope [16].

The electron binding energies and the oxidation states of iron and manganese in the plaques were determined by XPS using a Shimadzu ESCA-lab-220i-XL instrument (Shimadzu, Kyoto, Japan) using monochromatized AlK α X-rays at 1486.4 eV.

Freeze dried Fe–Mn plaque samples before and after inorganic and organic phosphate had been adsorbed by plaques were analyzed by FTIR. Each sample was mixed with spectral grade KBr at a weight ratio of 100:1 and pressed to form a disk. The disks were analyzed using a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The FTIR spectra over the range 4000–500 cm^{−1} were acquired and the functional groups in the samples were identified.

2.4. Adsorption Kinetics

Tests were performed to investigate the kinetics of inorganic and organic phosphate adsorption by the Fe–Mn plaque powder. First, 0.1 g Fe–Mn plaque powder was added to 200 mL solutions containing 6 mg/L inorganic or organic phosphate at pH 7.0 in a 250 mL conical flask. The conical flasks were agitated at 120–130 rpm using a mechanical orbital shaker at 298 K. An aliquot of the solution in each test was sampled at each specified time intervals (5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 4 h, 8 h, 16 h, and 24 h) and passed through a 0.45 μ m polycarbonate membrane filter, then the inorganic phosphorus concentration was determined using an ammonium molybdate spectrophotometric method and the total phosphorus concentration was determined using an alkaline potassium persulfate digestion spectrophotometric method, using a Sunny Hengping Instrument 752 ultraviolet visible spectrophotometer (Sunny Hengping Instrument, Shanghai, China) at wavelength of 700 nm. The organic phosphorus concentration was defined as the difference between the total phosphorus and inorganic phosphorus.

The mechanisms and steps controlling adsorption were analyzed by fitting the pseudo-first-order and pseudo-second-order models expressed in the Equations (1) and (2) [17,18], respectively, to the kinetics data.

$$\ln (Q_e - Q_t) = \ln Q_e - K_1 t \quad (1)$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2} \quad (2)$$

where t (min) is the contact time, Q_e (mg/g), and Q_t (mg/g) are the amounts of phosphate adsorbed at equilibrium time and time t , and K_1 (1/min) and K_2 (g/mg/min) are the pseudo-first-order and pseudo-second-order adsorption rate constants, respectively.

2.5. Adsorption Isotherms

Tests were performed to investigate the isotherms for the inorganic and organic phosphate adsorption by the Fe–Mn plaque powder. In each test, 0.1 g Fe–Mn plaque powder was added to 200 mL solution containing inorganic or organic phosphate in a 250 mL conical flask. Tests were performed using initial phosphorus concentrations between 0.1 mg/L and 6 mg/L at pH 7.0. The conical flasks were agitated at 120–130 rpm using a mechanical orbital shaker at 298 K. After 24 h, each solution was passed through a 0.45 μ m polycarbonate membrane filter and the residual inorganic and organic phosphorus concentrations were determined.

The Langmuir and Freundlich models, shown in Equations (3) and (4), were used to describe the adsorption isotherms data [19,20].

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (3)$$

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (4)$$

where Q_m (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the equilibrium concentration of phosphate, K_L is the Langmuir constant related to the affinity of phosphate for the binding sites, K_F is the Freundlich constant related to the adsorption capacity, and n is a heterogeneity factor related to the heterogeneous surfaces of the absorbent.

2.6. Adsorption Thermodynamics

Tests were performed to investigate the thermodynamics of the inorganic and organic phosphate adsorption by the Fe–Mn plaque powder. In each test, 0.1 g Fe–Mn plaque powder was added to 200 mL solution containing inorganic or organic phosphate with an initial phosphorus concentration of 6 mg/L at pH 7.0 in a 250 mL conical flask. The conical flasks were agitated at 120–130 rpm in a mechanical orbital shaker at 293, 298, 303, 308, and 313 K for 24 h, then each solution was passed through a 0.45 μ m polycarbonate membrane filter and the residual inorganic and organic phosphorus concentrations were determined.

The effects of temperature on inorganic and organic phosphate adsorption by the Fe–Mn plaques were investigated by calculating the Gibbs free energy (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) using Equations (5)–(7).

$$\Delta G^0 = -RT \ln K_d \quad (5)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

where K_d is the adsorption distribution coefficient calculated from the ratio between the amounts of inorganic or organic phosphate adsorbed (Q_e) and the phosphorus concentration (C_e) at equilibrium, R (8.314 J/mol/K) is the ideal gas constant and T (K) is the temperature in Kelvin.

2.7. Competitive Adsorption

Competitive adsorption between inorganic and organic phosphate was investigated by performing a series of tests. In each test, 0.1 g Fe–Mn plaque powder and 200 mL solution containing 6 mg/L inorganic phosphate at pH 7.0 were added to a 250 mL conical flasks. Organic phosphate was added to different flasks to give inorganic to organic phosphate molar ratios of 1:1, 2:1, and 3:1. The flasks were agitated for 24 h at 120–130 rpm using a mechanical orbital shaker at 298 K, then each solution was passed through a 0.45 μ m polycarbonate membrane filter and the residual inorganic and organic phosphorus concentrations were determined.

Each test described above was performed in triplicate to minimize errors, and the mean inorganic and organic phosphate concentrations were used in the calculations.

3. Results and Discussion

3.1. Characterization

3.1.1. SEM Analysis

The reed roots with and without Fe–Mn plaques attached were photographed, as shown in Figure 1a,b. The surface morphology of the reed roots with and without Fe–Mn plaques attached were examined by SEM, as shown in Figure 1c,d.

As shown in Figure 1a, the reed roots with Fe–Mn plaques had reddish surface coatings but the reed roots without Fe–Mn plaques attached, shown in Figure 1b, did not. This indicated that long-term flooding could cause Fe–Mn plaques to form on hydrophyte root surfaces. As shown in Figure 1c,d, that the root surfaces with and without Fe–Mn plaques were distinctly different. The surfaces of roots without Fe–Mn plaques present were smooth and had no fine particles adhering. In contrast,

the surfaces of roots with Fe–Mn plaques present were rough with irregular structures and particles attached. The deposited iron and manganese on the roots' surface can provide high specific surface areas, which would promote the adsorption of inorganic and organic phosphates.

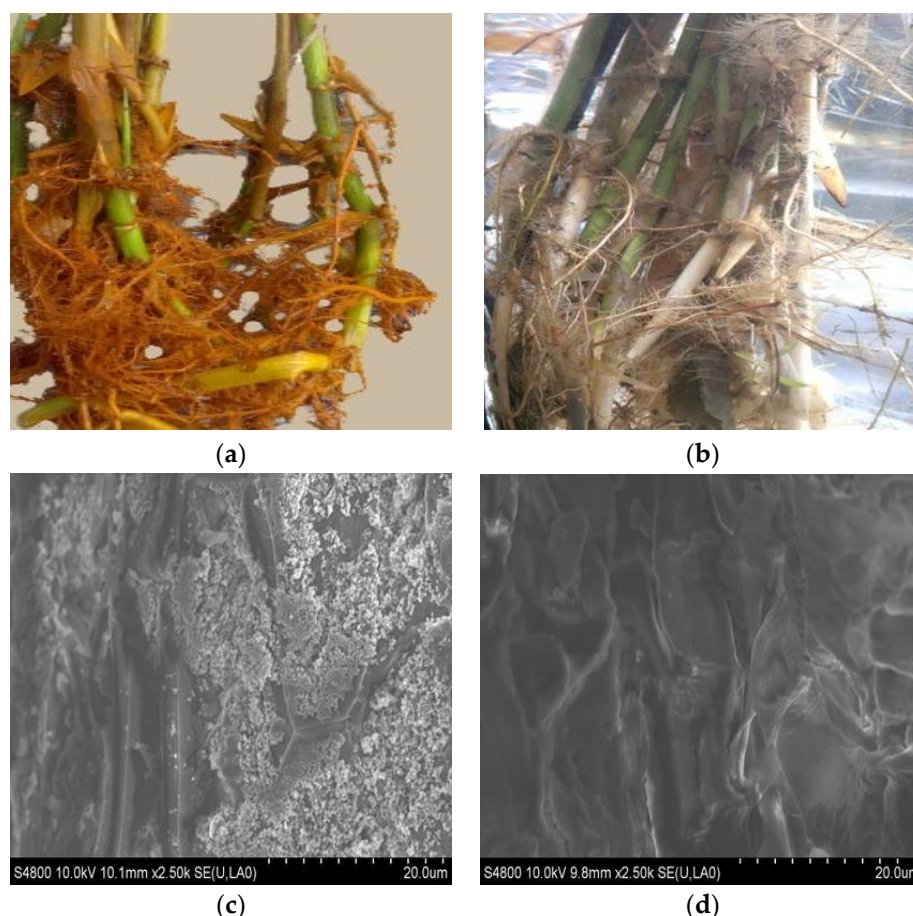


Figure 1. The reed roots (a) with Fe–Mn plaques, (b) without Fe–Mn plaques; SEM images of the reed root surfaces (c) with Fe–Mn plaques, (d) without Fe–Mn plaques.

The iron and manganese contents of the Fe–Mn plaque were 11,867.34 and 21.55 mg/kg, respectively. These results were consistent with the result of the study by Yang [21] and Liu [22] in which the iron and manganese contents of the root of different cultivars were 2330–13125 and 8.73–17.59 mg/kg, respectively. The background inorganic and organic phosphorus contents were 1.01 mg/g and 0.29 mg/g, respectively. The inorganic and organic phosphorus contents of plant roots will depend on the phosphorus concentrations of the water and the environmental conditions in the wetlands [23,24].

3.1.2. XPS Analysis

The detailed XPS scans of Fe2p and Mn2p regions are shown in Figure 2.

The main elements in the Fe–Mn plaques were O, Fe, Mn, C, and S. The XPS spectra of the Fe2p_{1/2} and Fe2p_{3/2} regions contained peaks with binding energies of 724.98 and 711.08 eV, respectively, indicating that Fe(III) was the dominant Fe form in the Fe–Mn plaques [25]. Peaks with binding energies of 653.28 and 641.08 eV were assigned to the Mn2p_{1/2} and Mn2p_{3/2} regions, indicating that Mn(IV) was the dominant Mn form in the Fe–Mn plaques [26]. Both Fe(II) and Mn(II) are dominant in anoxic flooded environments, and these results indicated that the oxidation environment in the rhizosphere caused Fe(II) and Mn(II) to be converted into Fe(III) and Mn(IV), respectively [2].

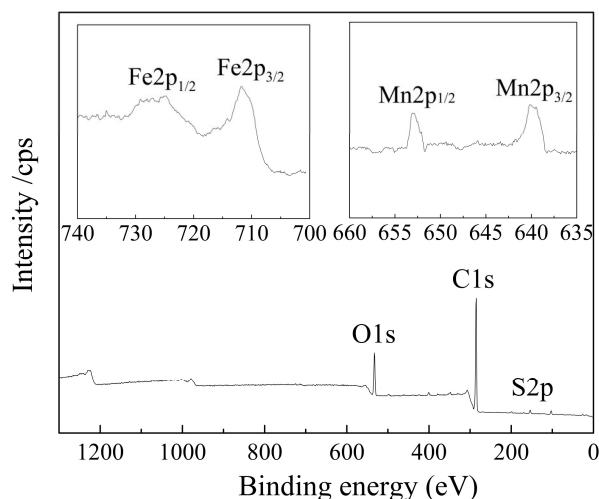


Figure 2. XPS of Fe–Mn plaque on roots' surface.

3.2. Adsorption Kinetics

As shown in Figure 3, the inorganic and organic phosphate adsorption process both exhibited a fast first stage, followed by a slow second stage. In the fast stage, 79% of the inorganic phosphate equilibrium adsorption capacity was reached in 240 min and 65% of the organic phosphate equilibrium adsorption capacity was reached in 60 min. This was attributed to abundant adsorption sites on Fe–Mn plaques and the high initial phosphate concentrations in the solutions. In the slow stage, equilibrium was achieved (i.e., the remaining 21% and 35% of the inorganic and organic phosphate equilibrium adsorption capacities, respectively, were achieved) in 1440 min. Larger amounts of inorganic phosphate than organic phosphate were adsorbed, indicating that inorganic phosphate was more easily absorbed than organic phosphate by the Fe–Mn plaques. Fast adsorption of phosphate (i.e., in the first 60 min of our tests) means that the hydraulic retention time (important for continuous operation of waterfront wetland system) will decrease greatly when effluent enter a wetland system.

The kinetic parameters for the pseudo-first-order and pseudo-second-order models are presented in Table 1. As shown in Table 1, the experimental data were better described by the pseudo-second-order model than the pseudo-first-order model. The R^2 values for inorganic and organic phosphates were 0.989 and 0.965, respectively. This indicated that both inorganic and organic phosphates may be adsorbed by Fe–Mn plaque through chemisorption involving covalent forces by sharing or exchanging of electrons between the Fe–Mn plaques and phosphate, as described by [26,27].

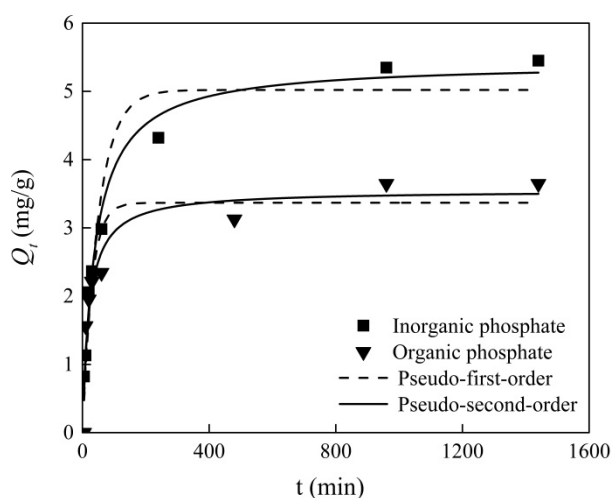


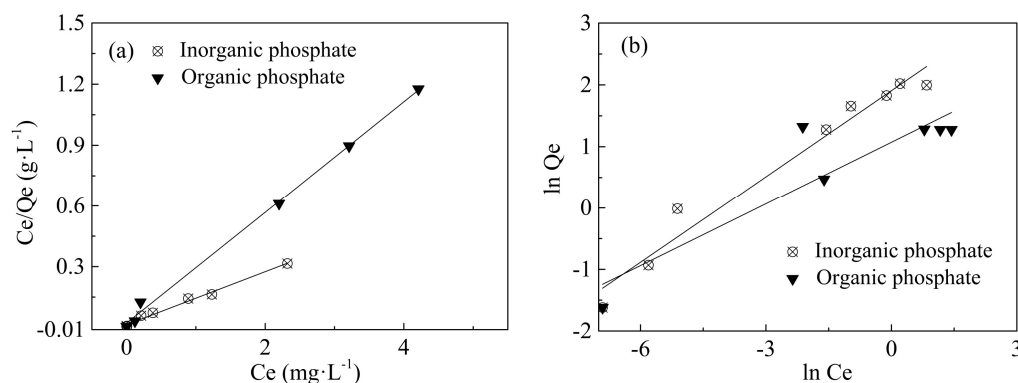
Figure 3. Kinetics of inorganic and organic phosphate adsorption by Fe–Mn plaque.

Table 1. Parameters of pseudo-first-order and pseudo-second-order kinetic models for phosphate adsorption by Fe–Mn plaque.

Different Phosphate	Pseudo-First-Order			Pseudo-Second-Order		
	R ²	Q _e (mg/g)	K ₁ (1/min)	R ²	Q _e (mg/g)	K ₂ (g/mg/min)
Inorganic Phosphate	0.927	5.11	0.0132	0.989	5.42	0.0004
Organic phosphate	0.906	3.33	0.0391	0.965	3.48	0.0017

3.3. Adsorption Isotherms

Isotherms for inorganic and organic phosphate adsorption by the Fe–Mn plaques at 298 K are shown in Figure 4. Isotherm parameters for the Langmuir and Freundlich models are shown in Table 2. It can be seen that the Langmuir model fitted better than did the Freundlich model. The R² values for inorganic and organic phosphate were 0.989 and 0.992, respectively. The Langmuir model generally describes monolayer adsorption, so the results suggest that the Fe–Mn plaques the active sites distributed homogeneously and that the adsorption energies for different sites were similar and no other interactions occurred [19]. The maximum inorganic and organic phosphate adsorption capacities were 7.69 and 3.66 mg/g, respectively. The phosphate adsorption parameters for the Fe–Mn plaques and for other adsorbents are shown in Table 3. The maximum inorganic phosphate adsorption capacity of the Fe–Mn plaques was lower than the maximum inorganic phosphate adsorption capacities for some synthetic iron oxide adsorbents (i.e., Fe–Mn oxide and iron oxide tailings) but ≥ 10 times higher than the maximum inorganic phosphate adsorption capacities for some natural adsorbents (i.e., marsh soil and expanded shale). The excellent adsorption capacity of the Fe–Mn plaques shows great potential for wetland systems to effectively remove phosphates from polluted water and phosphate removal can be promoted by regulating and controlling Fe–Mn plaques.

**Figure 4.** Linearized parameters of adsorption isotherm models for inorganic phosphate and organic phosphate on Fe–Mn plaque: (a) Langmuir isotherm model; (b) Freundlich isotherm model.**Table 2.** Parameters of Langmuir and Freundlich adsorption isotherm models for phosphate adsorption by Fe–Mn plaque.

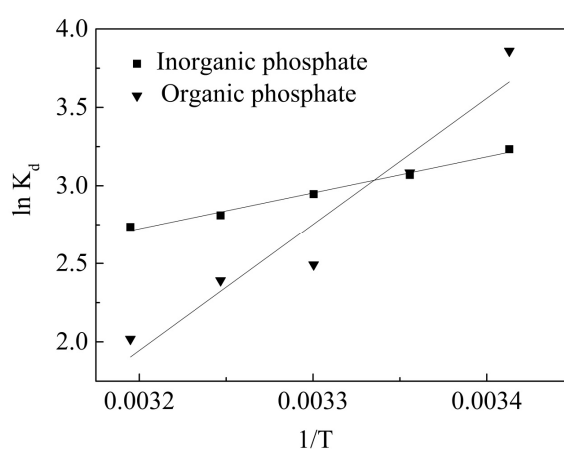
Different Phosphate	Langmuir			Freundlich		
	R ²	Q _m (mg/g)	K _L	R ²	K _F (mg/g)	n
Inorganic phosphate	0.991	7.69	9.29	0.962	6.75	2.17
Organic phosphate	0.992	3.66	12.41	0.782	2.91	2.94

Table 3. Maximum adsorption of phosphate of various adsorbents.

Adsorbent	Type	Phosphate Species	Adsorption Capacity (mg/g)	Ref.
Fe–Mn plaque	Natural	Inorganic	7.69	This study
		Organic	3.66	
Fe–Mn oxide	Synthetic	Inorganic	18.4	[28]
Iron oxide tailing	Synthetic	Inorganic	8.2	[29]
Marsh soil	Natural	Inorganic	0.26	[30]
Expanded shale	Natural	Total	0.52	[31]

3.4. Adsorption Thermodynamics

The ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of plots of $\ln K_d$ against $1/T$, as shown in Figure 5. The thermodynamic parameters for inorganic and organic phosphate adsorption by the Fe–Mn plaques are shown in Table 4.

**Figure 5.** Thermodynamic equilibrium constant $\ln K_d$ versus $1/T$ plot on inorganic and organic phosphate adsorption.**Table 4.** Thermodynamic parameters for adsorption of inorganic and organic phosphate by Fe–Mn plaque.

Temperature (K)	Inorganic Phosphate Adsorption				Organic Phosphate Adsorption			
	K_d	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)	K_d	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)
293	25.36	−7.88			47.76	−9.40		
298	21.53	−7.60			21.84	−7.64		
303	19.04	−7.42	−19.15	−38.58	12.08	−6.28	−67.05	−198.37
308	16.62	−7.20			10.92	−6.12		
313	15.42	−7.12			7.52	−5.25		

As shown in Table 4, the ΔG^0 values for inorganic and organic phosphate adsorption were negative, indicating that the inorganic and organic phosphates were spontaneously adsorbed by the Fe–Mn plaques. The absolute ΔG^0 values decreased as the temperature increased, implying that inorganic and organic phosphates were adsorbed more easily at lower temperatures than higher temperatures. This was supported by the phosphorus adsorption capacity being higher at low temperatures than at high temperatures. The ΔH^0 and ΔS^0 values were negative, indicating that the adsorption processes were exothermic and decreased disorder, respectively [32]. The adsorption characteristics described above indicate that Fe–Mn plaques on plant roots in wetlands play important roles on phosphorus removal at low temperatures. This will offset the limited degrees to which microbial assimilation and adsorption by plants remove phosphorus.

3.5. Adsorption Mechanism

Functional groups on the surfaces of iron and manganese particles commonly participate in the adsorption process and provide abundant adsorption sites for phosphorus. The mechanisms through which inorganic and organic phosphates were adsorbed by the Fe–Mn plaques were investigated by FTIR spectroscopy. The FTIR spectra of KBr pressed-disk containing Fe–Mn plaques before and after inorganic and organic phosphates had been adsorbed were obtained and are shown in Figure 6.

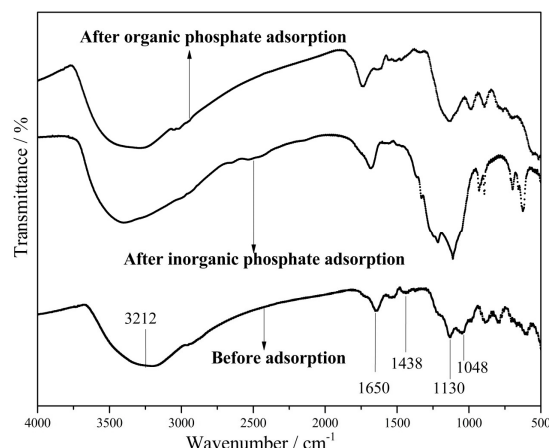
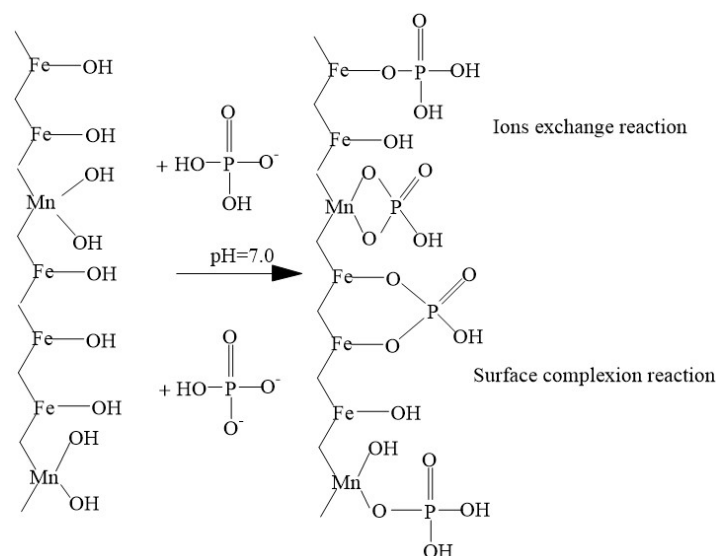


Figure 6. The FTIR spectra of Fe–Mn plaque before and after adsorption.

Bands around 3212 and 1650 cm^{-1} were assigned to the hydroxyl groups (O–H) stretching vibration and water molecular bending vibration, respectively [33]. A band at 1130 cm^{-1} was assigned to Fe–OH bending vibration [34,35], and a band at 1438 cm^{-1} was assigned to hydroxyl groups attached to MnO_2 [18]. The Fe–OH bending band (at 1130 cm^{-1}) was weakened, and a peak at 1048 cm^{-1} assigned to P–O vibrations was strengthened when inorganic and organic phosphate become adsorbed, suggesting that surface complexation reactions occurred and that hydroxyl groups attached to the Fe–Mn plaques may have been replaced with H_2PO_4^- or HPO_4^{2-} , (i.e., phosphate became bound to the Fe–Mn plaques through ligand exchange at pH 7.0) [27,36]. Possible adsorption mechanisms were determined taking the molecular structures of the phosphate species, the changes in the functional groups on the Fe–Mn plaques with and without adsorbed, and the characteristics of the chemisorption process into account, and the mechanisms are shown in Scheme 1.



Scheme 1. Schematic diagram of possible phosphate adsorption reaction.

3.6. Competitive Adsorption

Competitive adsorption by the Fe–Mn plaques was investigated by performing tests using different inorganic to organic phosphate molar ratios, and the results are shown in Figure 7. The presence of organic phosphate did not negatively affect inorganic phosphate adsorption by the Fe–Mn plaques, and the inorganic phosphate adsorption capacities at different molar ratios were 6.09–6.33 mg/g. The selective adsorption of inorganic phosphate indicated that inorganic phosphate was adsorbed by Fe–Mn plaques through inner-sphere complexes, which will not be sensitive to presence of organic ions [28]. The organic phosphate adsorption capacity was limited by the presence of inorganic phosphate coexisting and decreased as the inorganic phosphate concentration increased. However, organic phosphate can be hydrolyzed and transformed into inorganic forms by phosphatases released by plant roots in wetlands [23,37,38], then the inorganic phosphates can be removed by Fe–Mn plaques.

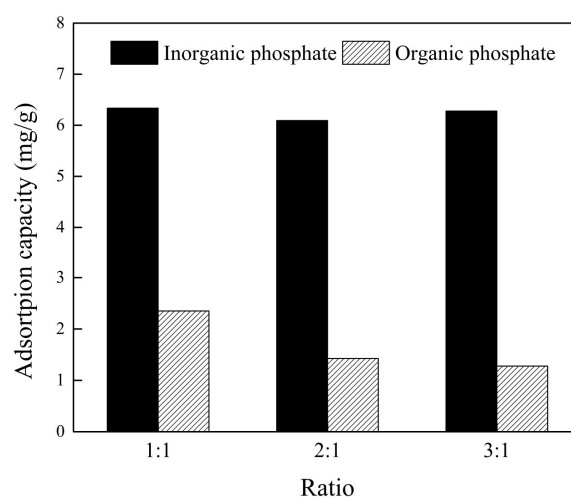


Figure 7. Inorganic and organic phosphate adsorption capacity at different ratios by Fe–Mn plaque.

4. Conclusions

Fe–Mn plaques were extracted from reed roots. The plaques were characterized and then batch tests were performed to investigate inorganic and organic phosphate adsorption from aqueous solutions by the plaques. The SEM images indicated that the roots with Fe–Mn plaques attached were rough and had heterogeneous porous structures and fine particles attached. X-ray photoelectron spectroscopy indicated that the iron and manganese in the Fe–Mn plaques were predominantly in the forms Fe(III) and Mn(IV), respectively. Fourier-transform infrared spectroscopy revealed that the adsorption process of phosphate was caused by hydroxyl substitution and inner-sphere surface complexation of orthophosphate or organophosphate ion groups. Pseudo-second-order model described both inorganic and organic phosphate adsorption kinetic well, indicating that both inorganic and organic phosphate adsorption processes were chemisorption. The Langmuir isotherm model fitted the adsorption data well, indicating that monolayer adsorption occurred. And the maximum inorganic and organic phosphate adsorption capacities at 298 K were 7.69 and 3.66 mg/g, respectively. Thermodynamic data indicated that both inorganic and organic phosphate adsorption processes were spontaneous and exothermic. The innovative use of low-cost, natural, and efficient adsorbents offers great potential for the sustainable removal of phosphorus from wastewater. Phosphorus removal by Fe–Mn plaques on plant roots should be enhanced by managing wetland habitats to promote Fe–Mn plaques production.

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