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Phosphate removal from wastewaters by a naturally occurring, calcium-rich sepiolite

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ABSTRACT

Developing an easily handled and cost-effective phosphate absorbent is crucial for the control of water eutrophication. In this study, a naturally occurring, calcium-rich sepiolite (NOCS) was evaluated for its feasibility as a phosphate absorbent candidate. Batch studies showed that phosphate sorption on NOCS followed a stepwise isotherm for concentrations between 5 and 1000 mg P/l, and the phosphate sorption was fitted well by the Freundlich equation. The estimated maximum phosphorus sorption capacity was 32.0 mg P/g, which was quite high compared with other natural materials and was comparable to some efficient manmade P absorbents. The NOCS sorption kinetics followed a pseudo-first-order model with an R^2 value of 0.999. The adsorption of phosphate was highly pH dependent. Phosphate adsorption decreased moderately with increasing pH values from 3.0 to 6.0, and it decreased sharply in alkaline conditions. Ionic strength, sulfate, nitrate and chloride anions had no effects on the phosphate removal capacity of NOCS, but fluoride and bicarbonate anions exerted large effects. Phosphorus fractionation indicated that phosphate removed from the solution was primarily formed as a calcium-bound phosphorus precipitation, which was further confirmed by SEM–EDS analysis. Moreover, phosphate was barely (<1.5%) desorbed from the phosphorus-adsorbed sepiolite regardless of pH value.

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1. Introduction

Lake eutrophication has become a serious environmental problem worldwide. Approximately 50% of the lakes and reservoirs in all continents except Africa and Oceania are eutrophic [1]. Lake eutrophication is even more serious in China. Recent data have shown that 85.4% of the 138 investigated lakes with surface area greater than 10 km^2 were considered to be in a eutrophic status. Moreover, 40.1% of lakes are heavily eutrophic [2]. The most famous lakes in China, including Lake Taihu, Lake Dianchi and Lake Chaohu, have even become hypereutrophic. These degraded water bodies have caused many critical side effects, damaging the ecological balance, threatening drinking water safety, shrinking fish cultures and hampering tourism. Therefore, urgent measures must be taken to suppress eutrophication and to improve the degenerated water quality.

Lowering the phosphorus concentrations of the receiving water body is considered to be the most effective way to control water eutrophication. Phosphorus has been recognized as the main limited nutrient in freshwater ecosystems. Primarily, phosphorus can enter into freshwater ecosystems through agricultural runoff, domestic sewages and industrial effluents [3,4]. In recent years, physical, chemical, biological and combination methods have been developed to remove phosphorus from wastewaters. Among these methods, using absorbents with high phosphorus sorption capacity to remove phosphorus in wastewaters have become popular worldwide [3–5]. These absorbents include minerals (limestone, opoka, wollastonite, bauxite and zeolites), soils (laterite and marl), industrial byproducts (fly ash, red mud, burnt oil shale and slag materials) and manmade products (lightweight aggregates) [6]. Most studies have shown that excellent and efficient phosphorus absorbents are all characterized by their high aluminum, iron or calcium contents and that they can effectively remove phosphorus from wastewaters by the absorption and/or precipitation of chemically stable phosphorus phases [7–10]. Thus, substrates with high contents of aluminum, iron or calcium may have the potential to be phosphorus-removing absorbents. In addition, the absorbents must be environmentally friendly, economically feasible and geographically available [4,11].

Sepiolite is a hydrated magnesium silicate clay mineral with a fibrous chain structure, and it is nontoxic and relatively inexpensive. The main deposits of sepiolite are located in Anatolia in Turkey, Ceelbuur in Somalia, South Central China and Spain with 70% of the world reserves and annual output being approximately 1,300,000 tons [12]. Structurally, sepiolite consists of ribbons alternating with open channels along fiber axes, which provide sepiolite

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with good adsorption properties [13]. Furthermore, sepiolite does not exhibit swelling properties, as other clay minerals do, which can present difficulties (clogging hardware or jamming filters) in treatment systems [12]. In environmental studies, sepiolite has been widely used to absorb heavy metals [14], chloride [13], basic dyes [15] and cationic surfactants [16]. However, no study has been conducted to investigate the suitability of using sepiolite as a phosphorus absorbent in wastewaters.

Previously, researchers have attempted to chemically and physically modify the absorbents studied to enhance their phosphorus sorption capacity or to remove harmful elements embedded in them [17,18]. However, this process normally adds cost to the absorbents and makes the process complicated. Moreover, it is meaningless to activate an absorbent with high sorption capacity in its original form or in a form with little enhancement after activation. Therefore, an easily handled, natural and inexpensive absorbent with excellent adsorption capacity is appreciated. Therefore, this study aimed to develop a naturally occurring and cost-effective phosphorus absorbent.

Approximately 10 million tons of sepiolite deposits exist in China (approximately 1/5 of the world's reserve). The chemical composition of sepiolite varies geographically [19], and the sepiolite in China is characterized by high calcium content, which has been found to have a calcium oxide content as high as 30% [20]. Previous studies have shown that calcium-rich materials can effectively remove phosphorus from wastewater [8–10]. Therefore, the purpose of this study was to assess the performance of this calcium-rich sepiolite for its phosphorus-removal ability. The phosphorus sorption isotherm and kinetics of the sepiolite were evaluated in batch experiments. Moreover, the matrix effect on phosphorus removal and phosphorus binding mechanisms were also discussed. To the best of our knowledge, this is the first paper to evaluate the feasibility of using sepiolite as a phosphorus adsorbent in wastewater. This study is also a necessary preliminary work for the full-scale use of sepiolite in the treatment of phosphorus-contaminated water.

2. Materials and methods

2.1. Absorbent

Naturally occurring, calcium-rich sepiolite (NOCS) used in this study was collected from Liuyang (Hunan Province), Nanyang (Henan Province) and Yixian (Hebei Province). These three sites are the main deposits of sepiolites in China that account for more than 80% of the total deposits in China. Sepiolites from the Hunan Province, Henan Province and Hebei Province were denoted as NOCS1, NOCS2 and NOCS3, respectively. These samples were manually ground and sieved with a 100-mesh sieve. The chemical compositions of the NOCSs, as identified by X-ray fluorescence spectroscopy (XRF), are shown in Table 1. X-ray diffraction (XRD) was used to study the mineralogical composition of the NOCSs. Power samples were measured using a D/MAX2200 X-ray diffractometer with Cu Kα radiation (40 kV and 40 mA) and a Ni filter from 3.0° to 51° with a scan speed of 4.0°/min. The quantitative analysis performed by XRD used internal standards by comparing the reflection from standard substances to the reflection from components. Scanning electron microscope (SEM) observations and semiquantitative energy dispersive spectrometry (EDS) electron microprobe analyses were performed on the powder samples using a Hitachi S-3400N II with a Horiba EX-250 Energy Dispersive Spectroscope. After absorption of phosphorus, the sepiolites were analyzed by XRD and SEM–EDS using the same methods as with the original samples. Exchangeable Ca and Mg in the sepiolites were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after extracting the samples with neutral ammonium acetate.

Table 1
Chemical composition of naturally occurring sepiolite from different regions and countries.

Chemical composition	NOCS1	NOCS2	NOCS3	Turkey[b]	Spain[c]
SiO_2 (%)	38.3	31.0	24.9	58.7	53.2
MgO (%)	12.9	21.4	16.4	25.0	18.8
CaO (%)	20.5	22.3	27.1	0.50	4.48
Al_2O_3 (%)	4.0	1.49	0.42	0.50	3.33
Fe_2O_3 (%)	1.2	0.18	0.12	0.05	1.22
K_2O (%)	0.4	0.14	0.07	–	1.10
LOI[a] (%)	22.3	23.5	31.0	14.8	17.5
Exchangeable Ca (mg/g)	123.9	142.1	129.6	–	–
Exchangeable Mg (mg/g)	0.94	4.21	3.76	–	–

[a] Loss on ignition at 950 °C.
[b] Kocaoba [14].
[c] González-Pradas et al. [13].

2.2. Batch studies

A prescreening experiment was performed to evaluate phosphorus sorption capacity of the three sepiolites. Briefly, 0.50 g of NOCS was added into 25 ml of low (5 mg/l), medium (30 and 100 mg/l) and high (800 mg/l) concentration phosphorus solutions. After equilibrium for 24 h in the temperature-controlled shaker (25 °C), solutions were centrifuged, filtered and measured. The optimal NOCS was selected and used for further study.

The phosphorus sorption isotherms and kinetics on the optimal NOCS were evaluated by batch experiments. For the sorption isotherms, 0.50 g of the absorbent was added into 50-ml polyethylene centrifuge tubes with 25 ml of various phosphorus solutions (5–1000 mg P/l). The tubes were then placed on a constant temperature shaker (25 °C) for 24 h at 160 rpm to ensure complete mixing. The solutions were then centrifuged, and the supernatants were filtered through a 0.45-μm membrane. The resulting solutions were kept at 4 °C until analysis. Analysis of the phosphorus sorption kinetics was carried out at 25 °C with an initial phosphorus concentration of 100 mg/l. Briefly, 10.0 g of the NOCS was added into 500 ml of a phosphorus solution in three 1-l Erlenmeyer flasks, which were subsequently placed on a rotary shaker at 160 rpm. Periodically, 1 ml of each of the well mixed aliquots in the flasks was sampled, centrifuged and filtered as above.

To examine the effect of pH, ionic strength and coexisting anions on the phosphorus sorption capacity of the NOCS, a series of batch studies were carried out. To obtain the optimal pH values, 1 M NaOH or 0.5 M HCl was used to adjust the tested phosphorus solution pH values. To provide a better understanding of the function of pH on phosphorus removal capacity, metal concentrations (Ca and Mg), Si leaching from NOCS and zeta potentials at various pH values were measured by ICP-AES and JS94H microelectrophoresis meters. To determine the ionic strength and coexisting anions, 100 mg/l phosphorus with various concentrations of NaCl and different anions were evaluated. All of the experiments were carried out in triplicate. Phosphorus concentration was measured by the molybdenum blue method with a spectrophotometer at 700 nm (UV-2550).

2.3. Fractionation of the P-saturated absorbent

To understand the NOCS phosphorus sorption retention mechanism, fractionation of the P-saturated absorbent was carried out. NOCS (10.0 g) was added into 500 ml of a 100 mg/l phosphorus solution, which was kept thoroughly mixed in a temperature-controlled shaker (25 °C) at 160 rpm. The concentration of the solution was analyzed daily. The experiment was ended when the

Table 2
P fractionation procedure, proposed by Chang and Jackson [21] and modified by Gu and Jiang [22], showing the extraction reagents and target P forms.

Extraction reagents	Target P forms
$NaHCO_3$	Dicalcium phosphate (Ca_2-P)
NH_4Ac	Octacalcium phosphate (Ca_8-P)
NH_4F	Aluminum phosphate (Al-P)
$NaOH–Na_2CO_3$	Iron phosphate (Fe-P)
$Na_3C_6H_5O_7·H_2O–Na_2S_2O_4–NaOH$	Occluded phosphate (O-P)
H_2SO_4	Ten-calcium phosphate (Ca_{10}-P)

phosphorus concentration was kept constant. The P-saturated sepiolite was freeze-dried and sieved through a 100-mesh sieve.

A P fractionation scheme, which was initially proposed by Chang and Jackson [21] and subsequently modified by Gu and Jiang [22], was used in the present study. This method is normally used to fractionate P in calcareous soil, which includes six operationally defined phosphorus fractions (Table 2). P-saturated sepiolite (0.50 g in dry weight) was added into 50-ml polyethylene centrifuge tubes containing 25 ml of 0.25 M $NaHCO_3$ (pH 7.5). The mixture was shaken on an orbital shaker at 25 °C for 1 h, and the supernatant was separated by centrifugation at 5000 × *g* for 20 min. Next, the supernatant was filtered before analysis of dicalcium phosphate (Ca_2-P). The residue was washed twice with 95% ethanol (each wash was 12.5 ml). The supernatant was centrifuged and discarded before 25 ml of 0.5 M NH_4Ac (pH 4.2) was added. The mixture was left to stand for 4 h, which allowed the residue to thoroughly scatter during this time. The mixture was shaken for 1 h at 25 °C followed by centrifugation at 5000 × *g* for 20 min. The supernatant was then filtered before analysis of octacalcium phosphate (Ca_8-P). The residue was washed twice with saturated NaCl (each wash was 12.5 ml). The supernatant was centrifuged and discarded before 25 ml of 0.5 M NH_4F (pH 8.2) was added. The mixture was then shaken for 1 h at 25 °C followed by centrifugation, and the supernatant was filtered before the determination of aluminum phosphate (Al-P). The residue was washed twice with saturated NaCl (each wash was 12.5 ml). Next, the supernatant was centrifuged and discarded before 25 ml of a solution containing 0.1 M NaOH and 0.1 M Na_2CO_3 was added. The mixture was shaken for 2 h and was kept standing still for 16 h. The mixture was subsequently shaken again for 2 h before centrifugation and filtration of the supernatant and analysis of iron phosphate (Fe-P). The residue was washed twice with saturated NaCl (each wash was 12.5 ml). The supernatant was centrifuged and discarded before the addition of 20 ml of 0.3 M sodium citrate. The residue was scattered thoroughly before 0.5 g of $Na_2S_2O_4$ was added. Next, the mixture was put into a water bath for 30 min at 80 °C, and it was shaken intermittently before the addition of 5 ml of 0.5 M NaOH. The cooled supernatant was centrifuged and washed twice with saturated NaCl (each wash was 10 ml) before Milli-Q water was added to reach a final volume of 50 ml. A 5-ml aliquot of the solution was mixed with 5 ml of $H_2SO_4/HClO_4/HNO_3$ (1:2:7), and the mixture was heated on a plate until reflux of H_2SO_4 occurred. The cooled white residue was dissolved with Milli-Q water to reach a final volume of 50 ml before the measurement of occluded phosphate (O-P). The residue was subsequently extracted by 25 ml of 0.5 M H_2SO_4, and the mixture was shaken for 1 h at 25 °C followed by centrifugation and filtration of the supernatant before analysis of ten-calcium phosphate (Ca_{10}-P). Total P (TP) was analyzed by calcinations at 450 °C for 3 h, and subsequent extraction was carried out for 16 h with 3.5 M HCl. Phosphorus in the extracts was measured by the molybdenum blue method with a spectrophotometer.

2.4. *Stability of the P-saturated absorbent*

Safety of the P-saturated sepiolite was tested at various pH values. Freeze-dried, P-saturated absorbent (0.5 g) was added to 50-ml polyethylene centrifuge tubes with 25 ml deionized water, and the initial pH value of the solutions was adjusted by dilute NaOH or HCl to pH values of 3, 5, 7 and 11. Next, the tubes were placed in a shaker at 25 °C and 160 rpm for 48 h. An aliquot of the solution was sampled at 24 and 48 h followed by centrifugation and filtration. P in the solution was analyzed by the molybdenum blue method. The phosphorus desorption rate was calculated with the following equation:

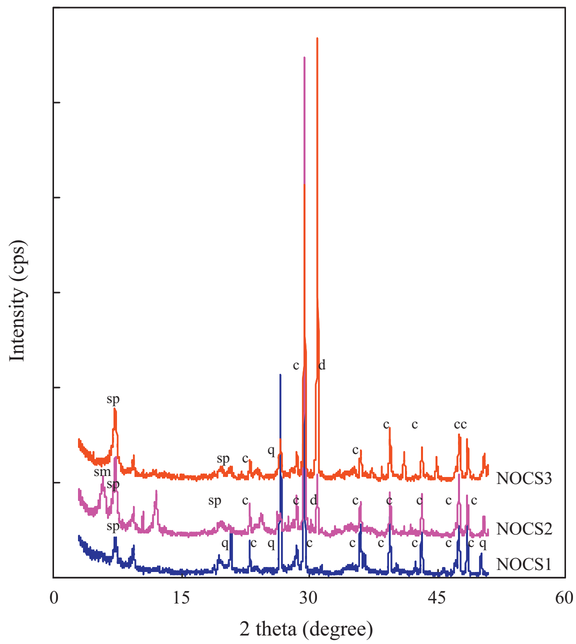

Fig. 1. XRD patterns of the naturally occurring sepiolites (NOCSs). The following abbreviations are used: sp, sepiolite; sm, smectite; c, calcite; d, dolomite; and q, quartz.

$$\text{Phosphorus desorption rate (PDR\%)} = \frac{C \times V}{TP} \times 100\%$$

where *C* is the phosphorus concentration in the solution (mg/l); *V* is the solution volume (ml); and *TP* is the phosphorus content in the P-saturated sepiolite.

3. Results and discussion

3.1. *Absorbent characterization*

The chemical compositions of the three NOCSs identified by XRF are presented in Table 1. Compared with sepiolites in other countries, all of the sepiolites in China were characterized by high CaO contents (20.5–27.1%). Similar results have been reported by Hrenovic et al. [12], who found that sepiolite obtained from the Hebei Province of China has a CaO content of 19.34%, indicating that sepiolites in China are impure. The XRD results indicated that sepiolites used in this study contained 40–50% sepiolite and that other minerals, such as smectite (10–15%), calcite (15–20%), and dolomite (10–20%), were also important constituents (Fig. 1). The purity of sepiolite in these samples was considerably lower than the purity of sepiolite from Turkey or Serbia, which can contain more than 80% sepiolite [23,24]. The impurity of the samples from China caused by high calcareous minerals may result in an advantage over sepiolites from Turkey or Spain with regard to phosphorus-removal capacity in wastewater. Materials with high Ca content have a strong affinity for phosphorus [8–10]. Fig. 2a shows that the phosphorus sorption capacity was varied among the three NOCSs in different phosphorus concentrations. There was no significant difference among the

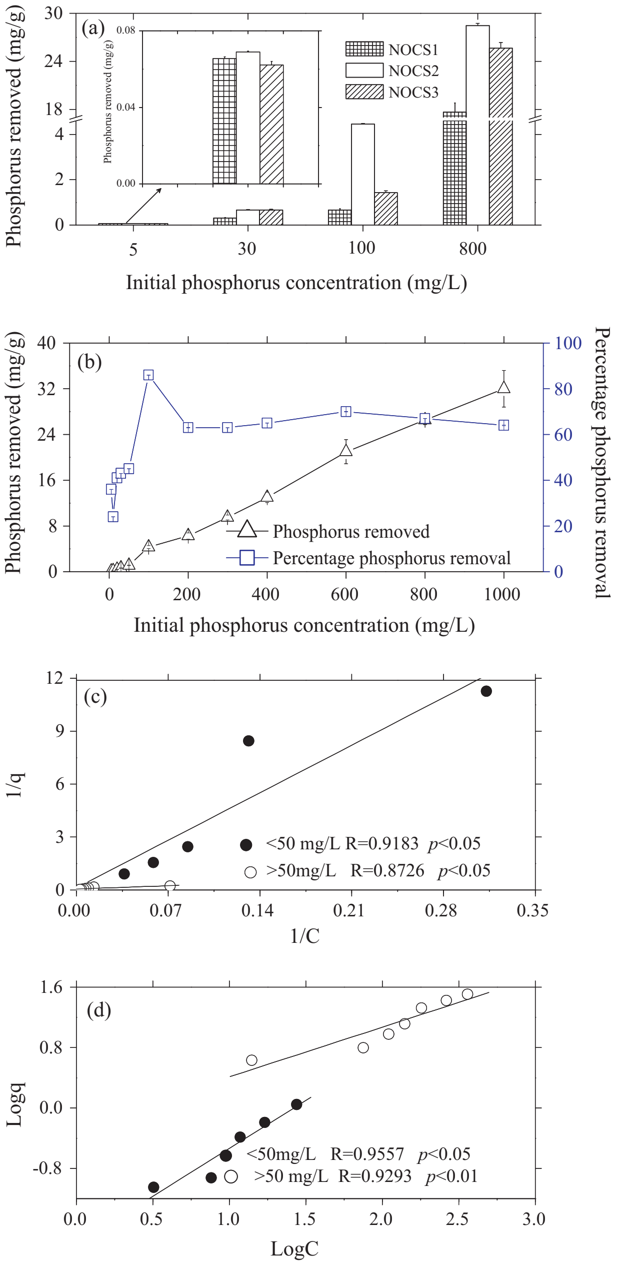

Fig. 2. Phosphorus sorption data of naturally occurring sepiolites (NOCSs). (a) Phosphorus-removal capacity of NOCS1, NOCS2 and NOCS3 at various P concentrations with an initial pH of 4.8. (b) Phosphorus removed and percentage of P removal by NOCS2 at various P concentrations with an initial pH of 4.8. (c) Phosphorus adsorption isotherm regression using the linear form of the Langmuir equation. (d) Phosphorus adsorption isotherm regression using the linear form of the Freudlich equation.

three NOCSs at low (5 and 30 mg/l) phosphorus concentrations. However, NOCS2 had a higher phosphorus sorption capacity than did the other two NOCSs at medium (100 mg/l) and high (800 mg/l) phosphorus concentrations. The high sorption capacity of NOCS2 was probably due to the high content of exchangeable Ca and Mg within this material (Table 1). Therefore, NOCS2 was used for further study.

3.2. Sorption isotherms and kinetics

3.2.1. Sorption isotherm

Fig. 2b shows that the amount of removed phosphorus increased with increasing initial phosphorus concentrations, which ranged from 0.09 mg P/g to 32.0 mg P/g. However, the percentage of phosphorus removal had a different tendency, which increased at low P concentrations, peaked at 100 mg/l P (86%) and subsequently leveled off at 60–70% with 200–1000 mg/l P. These results indicated that a different phosphorus removal mechanism was present upon P loading and P sorption isotherms. Thus, the mechanisms should be described separately in the two phases.

The Langmuir and Freundlich isotherm equations are widely used to describe the sorption processes in sorption experiments. The linear form of the isotherm equations can be written as follows (Langmuir isotherm equation, Eq. (1); and Freunlich isotherm equation, Eq. (2)):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{1}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

where q_e is the phosphate concentration on the sorbent (mg/g); C_e is the equilibrium phosphate concentration in the solution (mg/l); K_L, K_F and n are constant parameters of the models; and q_m is the maximum sorption capacity of the sorbent at given concentrations (mg/g). The phosphorus sorption of NOCS2 at low and high P concentrations was fitted by the Langmuir and Freundlich isotherm equations, respectively. As compared to R values fitted by the Langmuir model, the sorption curve was best fitted to the Freundlich equation regardless of phosphorus concentration. Two-phase sorption isotherms have also been reported by others in basic oxygen steel slag, calcareous material and calcite sorption experiments [25–27]. These authors have concluded that stepwise sorption isotherms result from sorption reactions at low P concentrations and that precipitation of Ca-P minerals occurs at higher initial P concentrations with the adsorbed P acting as nuclei for crystal growth [25–27]. The finding of the present study may be in agreement with these previous results. The maximum sorption capacity was not suitable, as estimated by the Langmuir plot, because the sorption process was not described well by the Langmuir isotherm. Del Bubba et al. [28] also reported that the Langmuir equation is not suitable for P removal data at high P concentrations when precipitation occurs. Therefore, the maximum sorption capacity can be estimated from the highest phosphorus loading of 1000 mg P/l in the present study, which was 32.0 mg P/g. The phosphorous sorption capacity found in the present study was high compared with other natural clay materials but was comparable with some industrial byproducts and functionalized materials [6,10,29] High P sorption capacity indicated that this naturally occurring, calcium-rich sepiolite may be a promising absorbent in wastewater treatment. However, the low removal efficiency (<50%) at low P concentrations (0–50 mg/l) limits the scope of sepiolite. Kõiv et al. [30] also found an incomplete removal of phosphorus at low P loadings during a pilot-scale leaching experiment when using a calcium-rich hydrated oil shale ash as filter material.

3.2.2. Sorption kinetics

The amount of P adsorbed on NOCS2 over time is shown in Fig. 2c and d. The phosphorus sorption on NOCS2 was completed in 18 h when it reached equilibrium (Fig. 3). The time needed to reach equilibrium has an important role in the efficiency and field deployment costs of a sorbent [29]. The equilibrium time of NOCS2 was longer than some iron-rich sorbents, which only need a few minutes (5 min or less) to reach equilibrium [11,29]. Rentz et al. [4] found that the equilibrium time is greater than 20 h for phosphorus sorption when using biogenic iron oxides as sorbents. The equilibrium time of the present study was shorter than the equilibrium time for other calcium-rich sorbents, which require days to reach equilibrium for phosphorus sorption [8,26]. The various equilibrium times among the sorbents may be due to the distinct

Table 3
Kinetic parameters for phosphorus sorption to NOCS2.

	First-order equation			Second-order equation			Elovich equation			Intraparticle diffusion equation	
	q (mg/g)	k_1 (1/h)	R^2	Q (mg/g)	k_2 g/(mg h)	R^2	a	b	R^2	k_i mg/(g h$^{1/2}$)	R^2
NOCS2	3.59	0.155	0.999	4.67	0.079	0.993	1.59	0.792	0.950	0.727	0.911

characteristics of the sorbents, thereby resulting in different sorption processes and mechanisms. The experimental kinetic data were fitted to the following four typical kinetic equations (Eqs. (3)–(6)) to provide a better understanding of the P sorption process in the calcium-rich sepiolite:

$$\text{Pseudo-first-order equation}: \quad \ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\text{Pseudo-second-order equation}: \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$\text{Simple Elovich equation}: \quad q = a + b \ln t \tag{5}$$

$$\text{Intraparticle diffusion equation}: \quad q_t = k_i t^{1/2} \tag{6}$$

where q_t and q_e are the amounts adsorbed at time t and equilibrium (mg/g), respectively; and t is the sorption time. The other parameters are different kinetic constants, which can be determined by the regression of the experimental data. The estimated parameters of the four common kinetic models with R^2 values are shown in Table 3. As compared with R^2 values, the pseudo-first-order model and pseudo-second-order model fit the experimental data best, yielding R^2 values of 0.999 and 0.993, respectively. The simple Elovich equation and intraparticle diffusion equation yielded lower R^2 values when compared with the R^2 values of the first two equations. Previous researcher suggested that sorption system were chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbent when experimental data fit well with the pseudo-first-order model and pseudo-second-model [17]. To verify this, changes in the free energy (ΔG°) were calculated according to Eqs. (7) and (8):

$$\Delta G^\circ = -RT \ln K_d \tag{7}$$

$$K_d = \frac{C_0 - C_e}{C_0} \cdot \frac{V}{m} \tag{8}$$

where ΔG° is the free energy of sorption (kJ/mol), T is the temperature in K, and R is the universal gas constant (8.314 J/(mol K)); K_d is the sorption distribution coefficient, C_0 is the initial phosphate concentration in the solution (mg/l), m is the mass of sepiolite (g) and V is volume of the solution (ml) during sorption experiment. The calculated ΔG° was −11.30 kJ/mol and was lower than 40 kJ/mol, which indicated that phosphorus sorption on NOCS2 was probably dominated by physical process. This result was contrary to the conclusion from the pseudo-first-order model. It was probably due to that the former was an experiential model and sometimes would deviate from the experimental data. Besides, it was believed that ligand exchange and precipitation would have great effect on phosphorus removal in the present study.

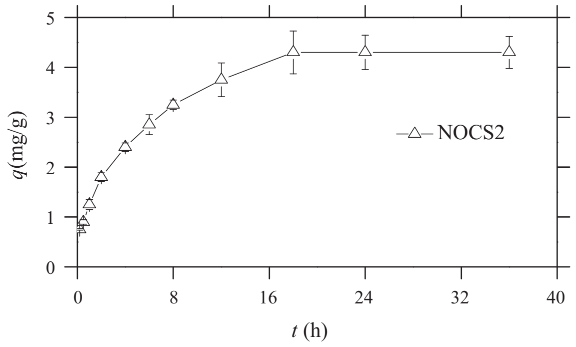

Fig. 3. Phosphorus sorption kinetics of NOCS2.

3.3. Matrix effects on P removal capacity

3.3.1. Effect of pH

The pH value of the solution during adsorption has a significant effect on the surface characteristics of the adsorbent particles and, consequently, the sorption capacity of the sorbents [3]. The phosphorus removal capacity of NOCS2 at various pH values was evaluated at 25 °C with 100 mg P/l. Fig. 4a shows that the pH value of the solution greatly influenced the phosphorus capacity of NOCS2. The amount of phosphorus adsorbed decreased with increasing pH values with the maximum phosphorus sorption capacity observed

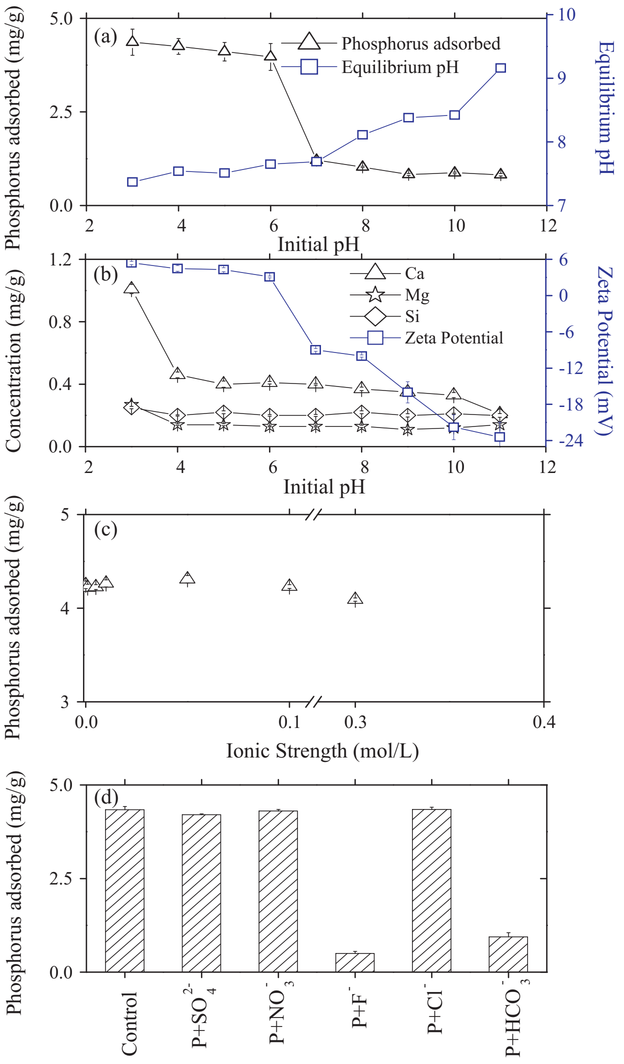

Fig. 4. (a) Effect of pH on phosphorus removal capacity. (b) Amount of Si and metals (Mg and Ca) leaching from NOCS2 and the zeta potential of NOCS2 at various pH values. (c) Effect of ionic strength on phosphorus-removal capacity. (d) Effect of coexisting anions on phosphorus removal capacity.

at a pH value of 3.0. The phosphorus sorption capacity dropped sharply when the pH value of the solution changed from acidic to alkaline with an approximate 20% phosphorus sorption capacity in the alkaline solution, which indicated that NOCS2 may work well in acidic solutions but not in alkaline solutions. This finding was in agreement with previous results reported by others using slag and palygorskite ash as adsorbents [17,27,31]. The pH dependency of phosphate removal is related to the dissolution of cations from the adsorbent, overall charge of the adsorbent and polyprotic nature of phosphate [17,29]. Fig. 4b shows that the amount of Ca leaching from NOCS2 decreased with increasing pH values. However, the amount of Mg and Si leaching from NOCS2 did not significantly fluctuate when the pH values were varied. The pH of solution has an impact on the speciation of phosphate ions in solution. Between pH of 3 and 7, the predominant species is $H_2PO_4^-$ and normally carries negative charge [29]. The dissolve Ca^{2+} and Mg^{2+} could react with $H_2PO_4^-$ to form the possible precipitate according to the following equations (Eqs. (9)–(13)) [32,33]:

$$Ca^{2+} + 2H_2PO_4^- + H_2O \rightarrow Ca(H_2PO_4)_2 \cdot H_2O \tag{9}$$

$$Ca(H_2PO_4)_2 + Ca^{2+} \rightarrow 2CaHPO_4 + 2H^+ \tag{10}$$

$$6CaHPO_4 + 2Ca^{2+} \rightarrow Ca_8(H_2PO_4)_6 + 4H^+ \tag{11}$$

$$Ca_8(H_2PO_4)_6 + 2Ca^+ + H_2O \rightarrow Ca_{10}(PO_4)_6(OH_2) + 4H^+ \tag{12}$$

$$Mg^{2+} + 2H_2PO_4^- \rightarrow Mg(H_2PO_4)_2 \tag{13}$$

Considering the structure of sepiolite, the $H_2PO_4^-$ and HPO_4^- also can react with silanols via hydrogen formation according to Eqs. (14) and (15) [34]:

$$\equiv Si{-}OH + H_2PO_4^- \Leftrightarrow Si{-}OH \cdots H_2PO_4^- \tag{14}$$

$$\equiv Si{-}OH + HPO_4^- \Leftrightarrow Si{-}OH \cdots HPO_4^- \tag{15}$$

Moreover, in the acid solution, the positively charged surface sites of NOCS2 also favored the sorption of phosphate, due to the electrostatic attraction, which was clearly illustrated in Fig. 4b where the zeta potential was positive when the pH value of the solution was below 7. When the pH increased, the amount of phosphorus adsorbed sharply decreased, which was mainly attributed to the high pH values. High pH values could cause the surface to carry more negative charges, thereby resulting in increased repulsion of the negatively charged phosphate in the solution.

3.3.2. Effect of ionic strength

The influence of ionic strength on phosphorus removal was evaluated in solutions containing 100 mg/l phosphate with various concentrations of NaCl ranging from 0.001 to 0.3 mol/l NaCl. NaCl concentration did no have significant influence on phosphorus removal regardless of the NaCl concentrations used (Fig. 4c). Similar results have also been reported by Bowden et al. [27] and Chouyyok et al. [29], who performed phosphorus sorption studies using slag and Fe-rich material, respectively, as sorbents.

3.3.3. Effect of coexisting anions

Natural waters and wastewater normally contain coexisting anions, such as SO_4^{2-}, NO_3^-, F^-, Cl^-, and HCO_3^-, which can compete with phosphate to occupy reactive sites on the adsorbents, thereby resulting in a lower phosphorus removal percentage during water treatment. The effects of coexisting anions on phosphorus removal capacity of NOCS2 are summarized in Fig. 4d. The presence of SO_4^{2-}, NO_3^- and Cl^- had no effect on the phosphorus removal capacity of NOCS2 (Fig. 4d). However, the presence of F^- and HCO_3^- dramatically affected the phosphorus removal capacity with F^- having a larger influence (Fig. 4d). These results were similar to findings reported by Chouyyok et al. [29], who demonstrated that the phosphorus removal capacity of an iron-rich functionalized sorbent can be strongly inhibited by F^- and HCO_3^- but that the phosphorous removal capacity was high in the presence of SO_4^{2-}, NO_3^- and Cl^-. Thus, the phosphorous removal capacity is regarded as a superior characteristic of NO_3^- and Cl^-, which are commonly present in waste streams [29].

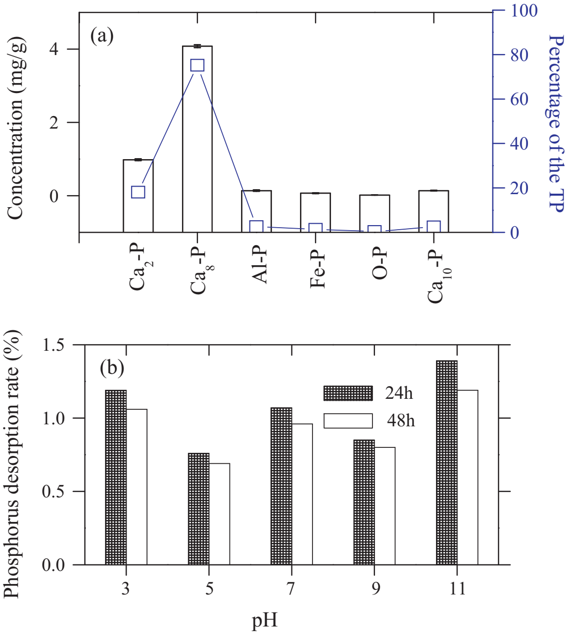

Fig. 5. (a) Phosphate fractionation in discrete chemical forms. (b) Percentage of phosphorus leaching from P-saturated sepiolite during different times.

3.4. Chemistry and mineralogy of the P-saturated sepiolite

To understand the phosphate binding mechanism, a phosphorus fractionation scheme used in calcareous soil was performed on the P-saturated sepiolite. The results suggested that calcium-bound phosphorus forms including Ca_2-P, Ca_8-P and Ca_{10}-P accounted for most of the total phosphorus (Fig. 5a) and that Al-P, Fe-P and O-P only accounted for a small part of the total phosphorus (Fig. 5a). The order of each fraction of P was distributed as follows: Ca_8-P (75.2%) > Ca_2-P (18.1%) > Al-P (2.53%) > Ca_{10}-P (2.50%) > Fe-P (1.37%) > O-P (0.35%). The relatively high percentage of Ca-P (Ca_2-P, Ca_8-P and Ca_{10}-P = 95.7%) indicated that the high concentrations of phosphorus removed by NOCS2 was effected mainly by precipitation. Previously, researchers have also suggested that P removed by soil colloids may occur through precipitation at high phosphorus concentrations [35]. The XRD results suggested that there were large quantities of calcite and dolomite in the sepiolite, which may supply a large amount of dissolved Ca^{2+} to the solution during sorption with time (Fig. 1). The phosphate and Ca^{2+} in the solution can form octacalcium phosphate (OCP), dicalcium phosphate dihydrate (DCPD) and hydroxylapatite (HAP). Furthermore, the poorly crystallized or amorphous DCPD and OCP form as precursor phases in solution containing Ca and P, and they are recrystallized into thermodynamically stable HAP over time [8,30]. SEM analysis showed that the natural sepiolite was a fibrous-like cluster (Fig. 6a and b). After phosphorus adsorption, several small spots formed on the fibrous-like clusters, which were suspected to be Ca-P precipitation (Fig. 6c and d). These results were similar to findings reported by Kõiv et al. [30] and Kaasik et al. [8], who found that Ca-P precipitation can form on calcium-rich materials after phosphate sorption, as confirmed by SEM and EDS. Immobilization of phosphorus into a Ca-phosphate form is considered to be a promising technology that

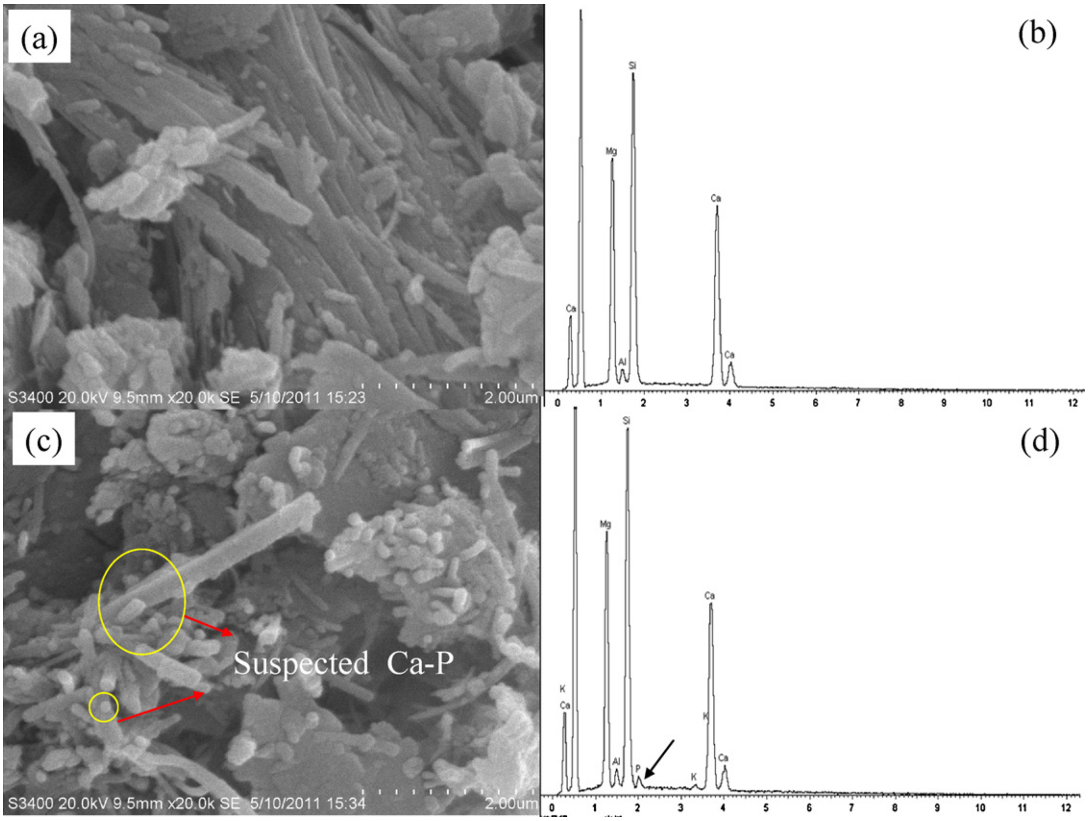

Fig. 6. SEM images and EDS analysis of sepiolite. (a) Microstructure of naturally occurring sepiolite (NOCS) before phosphorus adsorption (note the fibrous-like cluster). (b) SEM–EDS analysis spectrum of NOCS before phosphorus adsorption. (c) Suspected Ca-P precipitation on the fibrous-like cluster after phosphorus adsorption. (d) SEM–EDS analysis spectrum of NOCS after phosphorus adsorption.

may effectively control excess phosphorus in wastewater [8]. The results of this study suggested that NOCS2 is an efficient adsorbent when treating wastewater with high phosphorus concentrations.

3.5. Environmental safety assessment

It is important to avoid second pollution during wastewater treatment. Therefore, to assess the phosphorous desorption rate (PDR) of sepiolite, the P-saturated sepiolite was agitated in solutions with a wide range of pH values. The PDR ranged from 1.0 to 1.45% during a 48 h desorption experiment (Fig. 5b). The lower PDR in 48 h compared with 24 h may have been due to the readsorption to the sorbent used. The desorption rate of sepiolite was lower than the desorption rate of palygorskite, which has a PDR higher than 10% when used as phosphorus adsorbents [36]. The phosphorus fractionation experiment showed that calcium-bound phosphate dominated the phosphorus speciation (Fig. 5a). Previous studies have suggested that these Ca-P fractions are stable and are barely desorbed once formed [30,37,38]. Thus, these results indicated that NOCS2 can be safely used for wastewater treatment.

4. Conclusions

In this study, a naturally occurring calcium sepiolite (NOCS) was selected and evaluated for its feasibility as a phosphorus adsorbent. Batch studies showed that phosphate sorption on this NOCS followed a stepwise isotherm and could be fitted well by the Freundlich equation. As estimated by the Freundlich equation, the maximum phosphorus sorption capacity of NOCS can reach to 32.0 mg P/g, and is higher than those of other natural materials and even comparable with some efficient manmade phosphorus sorbents. The sorption kinetics were well described by the pseudo-first-order and pseudo-second-order models, yielding R^2 values of 0.999 and 0.993, respectively. The phosphate removed from the solution was mainly a calcium-bound phosphorus (Ca-P) precipitation. Considering various pH values, the formed precipitation was barely desorbed from the phosphorus-adsorbed sepiolite. Together, these data indicated that this naturally occurring, calcium-rich sepiolite can be regarded as an efficient phosphorus adsorbent. Future pilot-scale experiments mimicking the real condition should be carried out to study the phosphorus-adsorption capacity of the sepiolite.

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