Simultaneous sorption of phosphate and phenanthrene to inorgano–organo-bentonite from water

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Abstract

The nonbiodegradable organic pollutants and excess phosphate can not be effectively removed from municipal wastewater by the widely used bioprocess, thus they are harmful to aquatic environment. In this investigation, the feasibility of utilizing inorgano–organo-bentonite (IOB), which was bentonite mineral modified with both Fe polycations and cetyltrimethylammonium bromide (CTMAB), was explored to simultaneously remove phosphate and phenanthrene from water. The results showed that the IOB had strong affinity for both phosphate and polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene in water. It was found that more than 95% phosphate and 99% phenanthrene were removed from water within 30 min. The sorption of phosphate on IOB proved to be an anion/OH$^-$ exchange reaction. Compared with organobentonite and bentonite mineral, the settlement separation of IOB from aquatic phase was greatly improved. The residual turbidity reached a minimum value of 10 nephelometric turbidity units (NTU) in 60 min. It was indicated that IOB is a favorable sorbent and can simultaneously remove nonbiodegradable organic pollutants such as phenanthrene and phosphate after the bioprocess in wastewater treatment.
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1. Introduction

The most widely applied biological wastewater treatments such as activated sludge process are not effective in the removal of phosphate [1]. Burdick et al. [2] reported that there was 93% removal of total nitrogen and only 65% removal of total phosphate with the anaerobic process. In addition, the industrial wastewater containing high concentration of nonbiodegradable organic pollutants (NOP) is usually merged into domestic wastewater to improve its bioavailability in many wastewater treatment plants like in China and Spain [3]. The biological oxygen demand (BOD) and chemical oxygen demand (COD) of wastewater are greatly reduced after the treatment. However, the NOP such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) still exist in the treated water at low concentrations, which will cause a large amount of NOP and phosphate to discharge from the wastewater treatment plant.

Phosphate is an essential nutrient in aquatic environment, but excessive phosphate input may lead to eutrophication. NOP represents a group of contaminants including PAHs, known for their prevalence and persistence in environment and their carcinogenic, mutagenic, or teratogenic effects on various organisms [4]. Even PAHs at low concentrations in aquatic environment may lead to bioaccumulation into animals and plant tissue.

Sorption is relatively useful and economical for the removal of phosphate [5,6] and PAHs [7,8]. Activated carbons are among the most effective adsorbents. Due to its relatively high cost, attempts have been made to utilize low-cost, naturally occurring sorbents to remove trace contaminants from wastewater. The application of low-cost and easily obtainable materials in wastewater treatment has been widely investigated [9,10]. In recent years, there has been increasing interest in utilizing natural clay minerals like bentonite [11], kaolinite, zeolite and illite for the removal of toxic metals and some organic pollutants from aqueous solutions [12–14].

Bentonite is primarily expandable montmorillonite clay. Montmorillonite is a 2:1 type of mineral, and its unit layer structure consists of one Al^{3+} octahedral sheet placed between

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two Si^{4+} tetrahedral sheets [15]. Basically, the modification reactions are accomplished by replacing the interlayer cations (e.g. Na^+, K^+, Ca^{2+}) with specific species (e.g. organocations or polymeric metal species) to alter the surface and/or structural characteristics of the clay. The bentonite modified with organocation had strong affinity for organic compounds [16–18]. But the experimental observations showed that the organobentonite was difficult to be separated from the treated water. On the other hand, the bentonite pillared with inorganic metal ion could settle easily, but without any affinity for organic contaminants. Partial modification of montmorillonite has lead to a significant sorption of organic herbicides [19]. Recently, bentonite, modified with both the organocations and polymeric metal species, named inorgano–organo-bentonites (IOB), has been studied to show its sorption of phenol, chlorinated phenol and textile dye [20,21]. But few researches on its more comprehensive application in wastewater have been reported.

The objective of this work is to study the feasibility of using IOB as a sorbent to simultaneously remove phosphate and phenanthrene (as a representative PAH) for the post-treatment of bioprocess.

2. Materials and methods

2.1. Preparation of IOB

The natural bentonite composed primarily of Ca^{2+}-montmorillonite, is obtained from Tianyu Co. Ltd. (Inner Mongolia, China). Its cation exchange capacity (CEC) is 108.4 mmol/100 g bentonite [22]. The bentonite sample was pulverized and passed through a 100-mesh sieve. Analytical grade cetyltrimethylammonium bromide (CTMAB) obtained from Bio Life Science & Technology Co. Ltd. (Shanghai, China) was used without any purification for the modification.

The Fe polycations solution was prepared by hydrolyzing 1 L of $FeCl_3$ solution (0.6 mol/L) by dropwise addition of sodium bicarbonate solution. The final hydrolysis ratio was OH:Fe = 1.0 at an Fe concentration of 0.3 mol/L. The complex solution was stirred and water bathed in 60 °C overnight.

The CTMAB solutions (50 mL) at various concentrations (0.04–0.28 mol/L) and 67 mL of Fe polycations solution (0.3 mol/L) were dropwise added into vigorously stirred bentonite suspension containing 10 g bentonite. The molar ratio of CTMAB to metal varied between 0.1–0.7:1 in the complex. After stirred for 8 h, the suspension was allowed to age overnight. The products were collected by centrifugation and washed with distilled water until chloride-free (as judged by the silver nitrate test) [23]. Finally, the product dried on a glass plate at 60 °C. The bentonite only modified with CTMAB was also prepared as above, omitting the presence of Fe in the modification solution.

The resulting IOB is identified by a suffix to surfactant (S) that states the quantity of surfactant added in the modification process. For example, S2–Fe–B identifies an IOB that 2 mmol CTMAB (9% CEC) was added.

2.2. General batch sorption procedure

The phenanthrene stock solution was prepared by dissolving an amount of solid phenanthrene (with a purity of 99%, purchased from Acros Organics, USA) in methanol solution. The presence of the carrier solvent was assumed to have little effect on solute equilibrium due to its low final concentration (<0.2%, v/v) [24]. The phosphate solution was prepared by dissolving analytical grade KH_2PO_4 (10,000 mg P/L) in distilled water.

For determination of phosphate and phenanthrene sorption, 20 mg of the IOB powder was loaded in a 50 mL Erlenmeyer flask; appropriate aliquots of aqueous stock solutions were diluted by distilled water to 20 mL. The ranges of phosphate and phenanthrene initial concentrations are 0–25 mg P/L and 0–350 mg/L, respectively. The flask was capped and placed on an orbital shaker at room temperature (25 ± 1 °C) and 180 rpm for 4 h to ensure apparent equilibrium. Preliminary kinetic investigations revealed that sorption equilibrium was reached in less than 2 h. When the equilibrium was attained, the sorbent was separated by centrifugation (3000 × g, 15 min) and then the supernatant was analyzed for residual concentrations of phenanthrene and phosphate. This procedure was used in all batch sorption experiments.

Sorption kinetic measurements were determined by shake a set of flasks each containing 20 mg S5–Fe–B, 8 mg P/L phosphate and 30 mg/L phenanthrene in total volume of 20 mL. The concentrations in one of the flasks were analyzed at a time interval. The effect of pH on the sorption was studied using the solution with different pH (from 3 to 10). The pH was adjusted by adding few drops of 1 mol/L HCl or 1 mol/L NaOH.

Phosphate was measured according to the ascorbic acid method stated in the Standard Methods [25]. Phenanthrene concentrations were determined using a Shimadzu UV-2450 Spectrophotometer at a wavelength of 250 nm.

Each experiment was duplicated under identical conditions. For each batch experiment triplicate blank samples (containing only phenanthrene and phosphate) were prepared and monitored. These blank samples indicated insignificant phenanthrene volatilization or sorptive losses on the glassware for the duration of the experiment.

2.3. Character of IOB

To determine the stability of IOB, a control procedure was employed. In brief, 20 mg of the IOB powder was loaded in a 50 mL Erlenmeyer flask with 20 mL water. The IOB suspension was shaken for 4 h, and then centrifuged (3000 × g, 15 min). The concentrations of extracted Fe and total organic carbon (TOC) content in the supernatant were determined by atomic absorption spectrometer (AAnalyst 700, Perkin-Elmer) and total organic-carbon analyzer (TOC-V CPH, Shimadzu), respectively [26].

Settlement experiment was conducted in a laboratory scale plexiglas tank contained the suspensions of IOB (1 mg/mL). The suspensions were provided with 20 min rapid-mixing and followed by 80 min settling. The turbidity of the supernatant was measured using a turbidimeter (2100 AN, HACH). Experiments
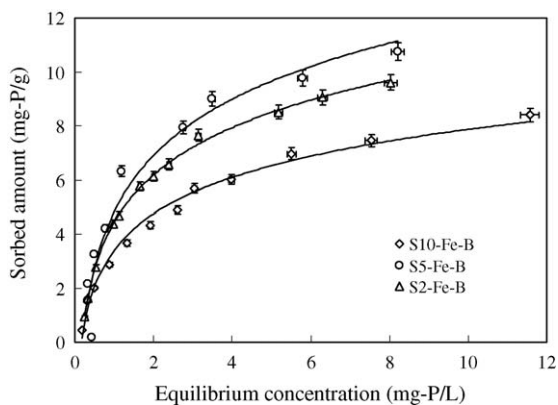
Fig. 1. Isotherm of phosphate sorption onto IOB. IOB: 0.02 g; contact time: 4 h; temperature: 25 °C; water: 20 mL.

were conducted at room temperature, while their pH values were maintained original at about 6.5.

XRD patterns of the prepared samples were acquired with an X-ray diffractometer (Max-2550PC, Rigaku D) using Cu Kα radiation (40 kV, 300 mA) of wavelength 0.154 nm to confirm the structure of the materials. All XRD patterns were obtained from 0.5° to 70° with a scan speed of 4°/min. The organic carbon content of IOB was analyzed by LECO CS-344 carbon–sulfate analyzer. The Fe content is determined by transmission electron microscopy (JEOL JEM-2010) equipped with Oxford INCA energy dispersive spectrometer.

3. Results and discussion

3.1. Isotherms

Figs. 1 and 2 are sorption isotherms of phosphate and phenanthrene onto different IOB, respectively. The sorption isotherms data were fitted by Langmuir and linear equations and the sorption parameters were determined (shown in Table 1). The high correlation coefficients, almost greater than 0.98, indicated that the data were accurately described by the Langmuir and linear model, respectively. As shown in the phosphate isotherms and the quantitative results in Table 1, S5–Fe–B had the high-
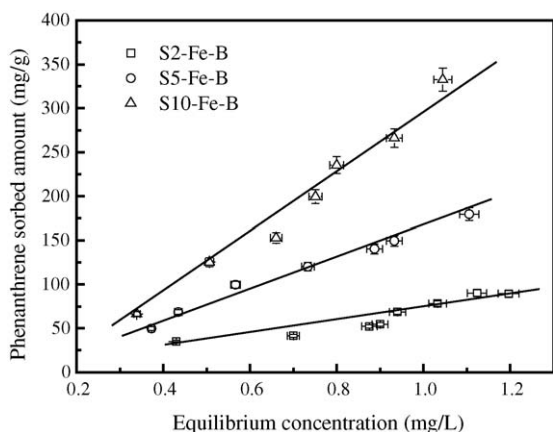
est sorption capacity for phosphate in the samples. The Q_{max} of S2–Fe–B, S5–Fe–B, S10–Fe–B was 11.60, 13.32, 9.82 mg P/g, respectively. Iron is the main sorption site of the phosphate [27,28]. The Fe content of S2–Fe–B, S5–Fe–B, S10–Fe–B was 12.35%, 11.38%, 5.44%, respectively. Interestingly, S5–Fe–B sorbed more phosphate than S2–Fe–B even though the latter had a larger Fe ratio at initial modification than the former. The amount of sorbed phosphate onto S5–Fe–B was similar to that sorbed on the goethite (17.05 mg P/g), which is regarded as effective absorbent to remove phosphate from water [29].

The isotherms in Fig. 2 show that sorption capacity of phenanthrene increased with increase of the ratio of surfactant to bentonite. The magnitude of partition action was generally measured by the partition coefficient (K_d) [17]. The K_d of phenanthrene sorption are summarized in Table 1. The organic carbon content of S2–Fe–B, S5–Fe–B, and S10–Fe–B was 4.05%, 7.11%, 16.13%, respectively. The K_d and the amount of sorbed phenanthrene were strongly affected by organic carbon content of IOB. With the increase of organic carbon content, the sorption capacity increased [13,30]. The organic carbon content also showed the surfactant intercalation would not be affected by the amount of Fe, although excess of the polymeric Fe species were in the preparation solution. That confirmed the result of Jiang and Zeng [31], and that could be an effective way to control the ratio of surfactants to metal polycations during the IOB synthesis.

3.2. Kinetic experiments

The results of the kinetics experiments of sorption at 25 °C are shown in Fig. 3. The sorption of phenanthrene increased linearly with the time increase and reached equilibrium within 2 h. More than 95% phosphate and 99% phenanthrene were removed in 30 min. The rates of phosphate sorption were determined by testing pseudo-first order and pseudo-second order kinetic models. Better agreement was achieved for the pseudo-second order model:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{1}$$

where q_t is the sorbed amount at time t (mg/g), k the equilibrium rate constant of the second-order sorption (mg/(g min)) and q_e is the sorbed amount at equilibrium (mg/g). Integrating Eq. (1) for the boundary conditions $t = 0$ to $t = t$ and $q_0 = 0$ to $q_t = q_t$, gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \tag{2}$$

Fig. 2. Isotherm of phenanthrene sorption onto IOB. IOB: 0.02 g; contact time: 4 h; temperature: 25 °C; water: 20 mL.

Table 1
Langmuir and linear parameters for each sample

Samples	Phosphate			Phenanthrene	
	b (L/g)	Q_{max} (mg/g)	R^2	K_d (L/g)	R^2
S2–Fe–B	0.188	11.60	0.994	84.5	0.930
S5–Fe–B	0.175	13.32	0.940	166.9	0.993
S10–Fe–B	0.144	9.82	0.992	355.3	0.983

Langmuir model: $Q/Q_{max} = bC_e/(1 + bC_e)$, b is the Langmuir constant, Q_{max} the maximum adsorbate adsorption amount, C_e the equilibrium concentration and K_d is partition coefficient ($K_d = Q/C_e$).
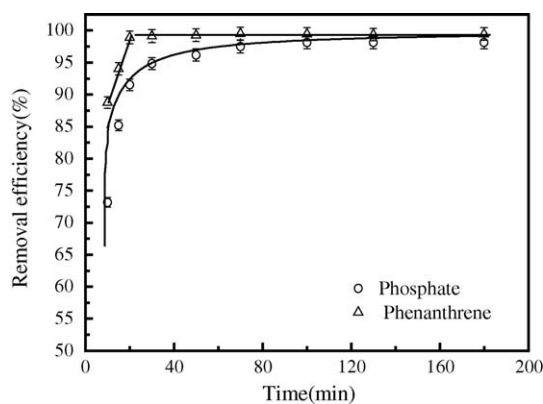
Fig. 3. Kinetics of phosphate sorption on IOB. S5–Fe–B: 0.02 g; water: 20 mL; concentration: 8 mg P/L phosphate, 30 mg/L phenanthrene; temperature: 25 °C.

Eq. (2) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (3)$$

Rate parameters, k and q_e, can be directly obtained from the intercept and slope of the plot of (t/q_t) against t. The equilibrium concentration can be further calculated as the value of q_e has been obtained from the fitting of Eq. (3). The kinetic parameters acquired from fitting results were summarized in Table 2. The rate of phosphate sorption by the IOB is faster than that adsorbed by nut shell activated carbon [32].

The sorption rates of phenanthrene fitted the linear equation and came to equilibrium in very short time (within 30 min). The fast sorption rate indicated the potential application for continuous water treatment systems.

3.3. Simultaneous sorption of phosphate and phenanthrene

The removal efficiencies of phenanthrene and phosphate sorbed onto various IOBs were summarized in Table 3. The removal efficiencies for phenanthrene were more than 99% of all samples except original bentonite. However, the phosphate removal efficiency increased slightly then decreased with the increase of surfactant/bentonite ratio. The trend could attribute to the change of basal space and the sorption site. The X-ray diffraction results (Fig. 4) showed that the interlamellar spacing of IOB was increased with the quantity of CTMAB increasing. The interlamellar spacing of S5–Fe–B is 14.62 Å which is bigger than that of S2–Fe–B. The increase of the interlamellar spacing indicated that the inner surfaces and regions of the sorbent may become more accessible for phosphate. However, the excess CTMAB occupied the affinity sites for phosphate, although the interlamellar spacing of S10–Fe–B is increased to 19.11 Å. As a result, the sorption amount and removal efficiency decreased.

Table 2
Kinetic parameters for phosphate and phenanthrene sorption

	k (mg/g min)	q_e (mg P/g)	R^2
Phosphate	0.06	7.68	0.953
Phenathrene	1.01	30	0.999

Table 3
Removal efficiency of phosphate and phenanthrene from water

Sample	Removal efficiency (%)	
	Phosphate	Phenanthrene
S2–Fe–B	96.84 ± 0.12	98.78 ± 0.20
S4–Fe–B	98.15 ± 0.15	99.02 ± 0.18
S5–Fe–B	98.81 ± 0.15	98.92 ± 0.19
S7.5–Fe–B	98.81 ± 0.12	99.13 ± 0.18
S8–Fe–B	96.84 ± 0.14	99.27 ± 0.15
S9–Fe–B	95.52 ± 0.14	99.51 ± 0.13
S10–Fe–B	94.33 ± 0.17	99.44 ± 0.16
S12–Fe–B	93.28 ± 0.13	99.36 ± 0.15
S14–Fe–B	91.57 ± 0.13	99.47 ± 0.13
Original-B	5.10 ± 0.10	0.60 ± 0.08
Organo-B	1.30 ± 0.07	99.63 ± 0.12

IOB: 0.02 g; 7 mg-P/L phosphate solutions and 30 mg/L phenanthrene; contact time: 4 h; temperature: 25 °C; wastewater: 20 mL.

The apparent inability of original bentonite to sorb both contaminants was observed. However, the organobentonite sorbed little phosphate though it had strong affinity for phenanthrene. The low sorption onto original bentonite was due to hydrated mineral surfaces and the hydrophobic nature of phenanthrene molecules. The modification magnitude increased the sorption ability of bentonite and the IOB become powerful sorbents for organic pollutants relative to original bentonite [13,30]. On the other hand, the presence of the Fe polycations in the interlayer of bentonite increased the affinity of the microporous interlayer sites towards the phosphate [27,28]. The presence of Fe polycations in IOB had little effect on the sorption of phenanthrene. However, the surfactant had some effects on the sorption of phosphate.

3.4. The effects of pH and temperature on sorption

To determine the sorption mechanism of phosphate and phenanthrene, the effects of pH and temperature on the sorption were investigated. Fig. 5 shows the removal efficiency of phosphate and phenanthrene at various pH values. The results showed that changing of pH had no effect on phenanthrene sorption, which is different from the sorption of ionizable organic
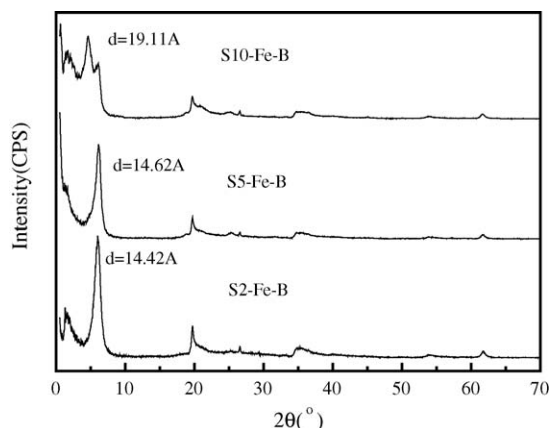

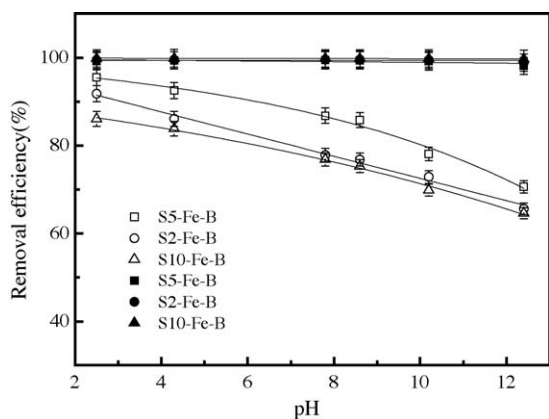Fig. 4. The X-ray diffraction pattern of IOB.

Fig. 5. The effect of pH on phosphate (open symbols) and phenanthrene (closed symbols) sorption onto IOB. IOB: 0.02 g; concentration: 10 mg P/L phosphate solutions, 30 mg/L phenanthrene; contact time: 4 h; temperature: 25 °C; water: 20 mL.

compounds [33]. However, the sorption of phosphate decreased with pH increasing. The amounts of sorbed phosphate at pH 10 were about 10% more than that at pH 4.5. Similar results had been reported on the pH dependence of phosphate sorption to ferrihydrite [27] and goethite [34]. A slight decrease of phosphate sorbed amount as the increasing of pH could be explained as that the surface charge of IOB changed to more negative at higher pH, which strengthened the electrostatic repulsion between the exchange site and the guest phosphate ion. The effect, however, appears to be minimal if IOB is used for water with pH < 8.5, so the material should be suitable for the post-treatment of bioprocess.

The effect of temperature (15–40 °C) on sorption of phosphate was examined (Table 4). The sorption of phosphate increased slightly with an increase of temperature. The amount of sorbed phosphate by S5–Fe–B was 7.2, 7.9 and 8.4 mg P/g at temperatures of 15, 30, and 40 °C, respectively. The variety trend of the sorbed amount was different from the usual surface adsorption which has the exothermic nature. The present result suggested that a chemical interaction involved the sorption of phosphate onto IOB in addition to the conventional electrostatic interaction.

3.5. Sorption mechanism

It is commonly accepted that sorption of organic compounds into organoclay are partitioning (dissolution) [35], and the characteristic of sorption isotherm is linear [36]. Moreover, parti-

Table 4
Effect of temperature on sorption of phosphate on IOB

Temperature (°C)	Sorbed amount (mg P/g)		
	S2–Fe–B	S5–Fe–B	S10–Fe–B
15	6.5 ± 0.3	7.2 ± 0.2	5.8 ± 0.4
30	7.1 ± 0.2	7.9 ± 0.2	6.4 ± 0.2
40	7.7 ± 0.3	8.4 ± 0.1	7.1 ± 0.1

IOB: 0.02 g; 10 mg P/L phosphate solutions and 30 mg/L phenanthrene; wastewater: 20 mL; contact time: 4 h.
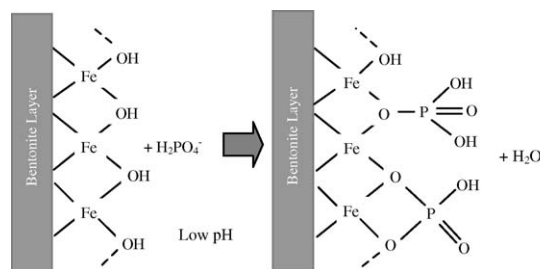

Fig. 6. The possible mechanism of the phosphate sorption on IOB.

tioning shows no competition between solutes. The presence of phosphate had little effect on the sorption of phenanthrene.

The curve in Fig. 5 showed that phosphate sorption onto IOB was an anion/OH⁻ exchange reaction [28,34]. The amount of sorbed phosphate decreased monotonically with increase of pH, not only due to the increase of OH⁻ concentration and the change of surface charge to negative, but also the increase of the binding strength of –OH on metal. The possible mechanism of phosphate sorption was shown in Fig. 6. The reactions are favored at low pH. At low pH, surface –OH groups are protonated to $-OH_2^+$, which facilitate the ligand exchange since $-OH_2^+$ is easier to displace from metal binding sites than –OH [37].

The sorption results of phosphate reasonably agreed with the pseudo-second order sorption kinetics shown previously. The attachment of phosphate must occur at the active sites in the interlayer of IOB. Therefore, the sorption of phosphate species can be reasonably speculated to occur in two steps: (i) transfer of sorbate (i.e. phosphate) from the aqueous solution to the sites on the sorbent (i.e. IOB); (ii) chemical complexation/ionexchange at these sites [27,34]. The ion-exchange process between phosphate and the hydroxide groups of Fe polycations proceeded in the inter layer.

Based on mass law concept, the sorption kinetics of phosphate on the IOB may be treated as a chemical reaction; that is, this equation may be represented by a second-order model of the form:

$$\equiv S-OH + P \rightarrow [SP] + OH^- \tag{4}$$

where P represents the dissolved phosphate, $\equiv S$ the available sorption sites, and [SP] is the sorbed state. It can be further derived from the irreversible bimolecular-type second-order reaction of the form [38,39]:

$$\frac{dq_t}{dt} = k'(q_e - q_t)(X - Y) \tag{5}$$

where q_t, q_e and t are described as Eq. (1). X, Y and k' are the maximum amount of sorption sites, amount of sorbed sites at time t, and proportionality constant, respectively. Obviously, X and Y are simultaneously proportional to q_e and q_t, respectively. Thus, this simplified Eq. (5) to be identical with Eq. (1).

3.6. Stability of IOB

The concentration of released Fe and TOC are shown in Table 5. The concentrations indicated that Fe and CTMAB were strongly combined with the interlayer of the bentonite. It was

Table 5
Concentration of released Fe and TOC

	S2–Fe–B	S5–Fe–B	S10–Fe–B
Fe (mg/L)	0.0315	0.0308	0.1280
TOC (mg/L)	2.749	1.615	1.850

IOB: 0.02 g; distilled water: 20 mL; contact time: 4 h.

found that the concentrations of released Fe were decreased with increasing of ratio of Fe and the amount of dissolved TOC had the similar trend. The results may be due to the Fe polycations and the CTMAB were competitive exchanging with the interlayer cations. However, overall, the result of dissolution seemed to have little effect on the quality of the water discharged. According to the European Directive 98/83/CE, Fe concentration in industrial wastewater to be discharged in natural water must not exceed 5 mg Fe/L. This observation implies that the sorbent is feasible for wastewater treatment.

3.7. Settlement experiment

The residual turbidities at an interval of 20 min were measured and the results are presented in Fig. 7, in which the residual turbidity reached a minimum value of 10 nephelometric turbidity units (NTU) in 60 min. The ratio of Fe to CTMAB had great influence on the result. The original bentonite could be separated easily from water. But when it was only modified with surfactant CTMAB, the sedimentation velocity decreased because its surface character was transferred form hydrophilic to hydrophobic. Micropores in the block were permeated with air that made some of the blocks floated on the surface of water or suspended in the water. However, when the modification combined with Fe polycation, the character of superficial changed. With the increase of the ratio of Fe in the modified bentonite, the settling ability increased. The settling velocity of S2–Fe–B was greater than the original bentonite. After settled, the sludge volume of S2–Fe–B was smaller than that of original bentonite and organobentonite. That implies the sorbents is suitable to be applied in wastewater treatment.
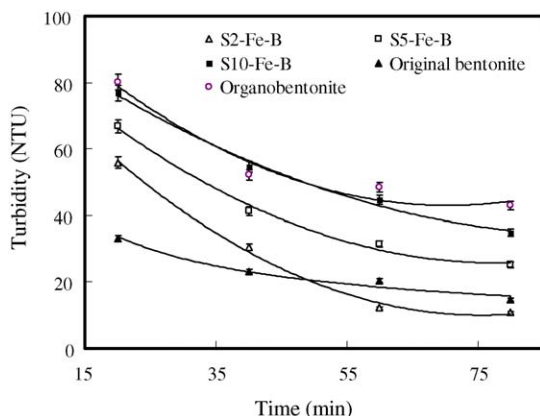

Fig. 7. Turbidities of the supernatants of various samples suspended water as a function of settling time. Dose: 1 g/L.

4. Conclusion

Bentonite modified with both Fe polycations and CTMAB is an effective sorbent for simultaneous removal of phenanthrene and phosphate from water. The sorption of phosphate and phenanthrene were accurately described by the Langmuir and linear model, respectively. More than 95% phosphate and 99% phenanthrene were removed from water within 30 min. The removal rates were well described by the pseudo-second order model. The amount of sorbed phosphate increased as pH decreased and the sorption amount increased slightly with increase of temperature, which implied that the phosphate sorption on IOB was an anion/OH^- exchange reaction. The stability results indicated that the Fe polycations and CTMAB were strongly combined within the interlayer of the mineral. The sedimentation velocity of IOB was greater than that of organobentonite, thus bentonite modified with the Fe and CTMAB shows good solid-liquid separation property. This investigation indicated that IOB is a favorable sorbent and can simultaneously remove nonbiodegradable organic pollutants such as phenanthrene and phosphate from water.

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