



Adsorption of phosphorus on sediments from the Three-Gorges Reservoir (China) and the relation with sediment compositions

Ying Wang^{a,b}, Zhenyao Shen^{a,*}, Junfeng Niu^a, Ruimin Liu^a

^a State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, PR China

^b Ministry of Education Key Laboratory of Environmental Remediation and Ecological Health, College of Natural Resources and Environmental Science, Zhejiang University, Hangzhou 310029, PR China

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ABSTRACT

The adsorption of phosphorus (P) on four sediment samples (CunTan, XiaoJiang, DaNing and XiangXi) from the Three-Gorges Reservoir on the Yangtze River in China was studied systematically in batch experiments. A sequential chemical extraction experiment was conducted to clarify the effect of sediment composition on P adsorption. The results showed that P adsorption on four sediment samples mainly occurred within 6 h. P adsorption kinetics can be satisfactorily fitted by both power function and simple Elovich model. A modified Langmuir model may describe well the P adsorption on all the samples in our study. Theoretically, the maximum adsorption amount (Q_{\max}) was 0.402 mg-P/g for XiaoJiang sediment, 0.358 mg-P/g for DaNing sediment, 0.165 mg-P/g for CunTan sediment, and 0.15 mg-P/g for XiangXi sediment. The sediment compositions such as organic matter, metal hydroxides, calcium and clay content showed influences on the P adsorption. Wherein, organic matter and metal hydroxides were the main factors affecting the P adsorption. The maximum P adsorption capacity (Q_{\max}) enhanced with the increase of the content of (Fe + Al + Ca). Compared the zero-equilibrium P concentration (EPC_0) values obtained by the modified Langmuir models with actual P concentrations in water, all the sediments studied in this paper except for XiaoJiang showed a trend of releasing P as a source role, which could enhance the risk of eutrophication occurrence in the Three-Gorges Reservoir.

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1. Introduction

The Three-Gorges Dam, in China, is the world's largest dam, measuring 2335-m long and 185-m high, and the reservoir created by it will have an area of 1080 km² in 2009 [1]. The construction of the Three-Gorges Reservoir will bring profound impacts on environment [2]. Wherein, eutrophication is a potential threat [3]. Phosphorus is a major nutrient for aquatic ecology, and its excess supply can lead to eutrophication. When external loading of P increased, the sediments as a pool can adsorb it. However, after external loading reduced, the sediments as a source would release adsorbed P into water. The characteristics of sediments, as well as overlying water quality, will affect the transfer direction of phosphate on the interface of the sediment–water [4–6]. Therefore, intensive study for P adsorption on sediments and the effect of sediment compositions would help to predict and further prevent the occurrence of eutrophication.

To clarify the mechanism of P adsorption, much of the emphasis has been focused on developing mathematics models to describe P adsorption characteristics on natural sediments. Lopez et al. [7] reported that adsorption kinetics of phosphate on the sediments followed a nonlinear model. Tu et al. [8] adopted Langmuir, Freundlich and Temkin equations to fit P adsorption isotherm, and found that the Langmuir model was the best. This result was also obtained by many other researchers [7,9,10]. However, when the existence of native adsorbed P (NAP) was concerned, adopting directly the Langmuir model is unreasonable because NAP in sediment also takes part in the adsorption equilibrium. To improve it, Zhou et al. [11] brought forward a modified Langmuir model which can described well for P adsorption on sediments with NAP.

So far, many studies have demonstrated that adsorption capacity for P on different sediments was related to sediment composition, such as contents of organic matter, Fe/Al hydroxides, clay and CaCO₃ [12–14]. Wang et al. [15] reported that there occurred a positive correlation of organic matter with P adsorption. The content of metals was thought to be the main factor that determined adsorption capacity, because of the high specific surface of the Fe/Al

* Corresponding author. Tel.: +86 10 5880 0398; fax: +86 10 5880 0398.
E-mail address: z.y.shen@163.com (Z.Y. Shen).

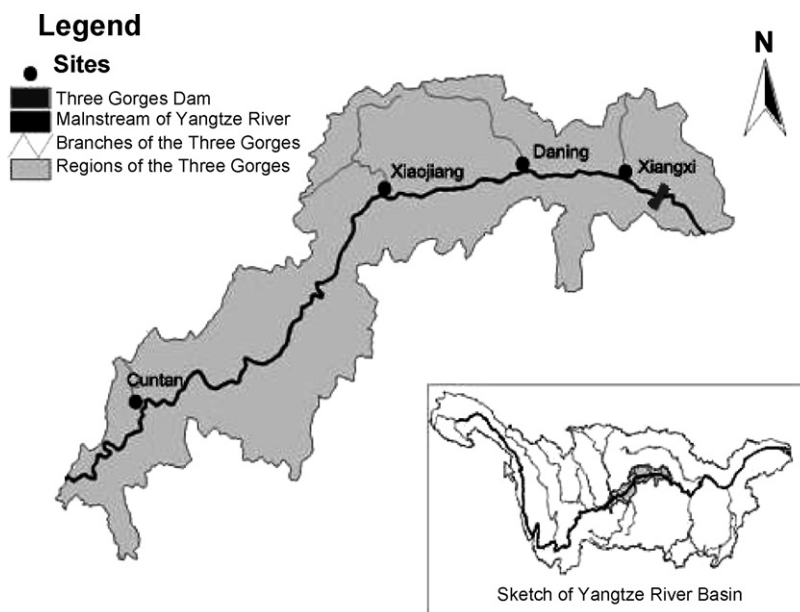


Fig. 1. Sketch of sample sites.

hydroxides. Sanyal and De Datta [16] found that the content of clay had a significant correlation with P adsorption. Additionally, the regulation of dissolved phosphate by adsorption or co-precipitation with calcite formed in situ has been widely reported in calcareous systems [17]. That is, solid-phase CaCO_3 usually governs P reaction in calcareous soil [17]. Therefore, the P adsorption process by sediments was co-controlled by many factors.

At present, there are many ways to study the effects of solid composition on adsorption, in which a sequential chemical extraction was regarded as a powerful method and consequently has been widely used for soil adsorption study for many years. Considering the similarities between sediments and soils, extraction procedures can be adapted from the method of soil chemical analysis. In 1979, this method was developed by Tessier et al. [18] who successfully used it in discussing the trace metal speciation on the sediments. Subsequently, Tang et al. [19] utilized improved the extraction method to study the adsorption capacity for metal on sediments.

The objective of this study was to evaluate the adsorption capacity for phosphorus on the sediments from the Three-Gorges Reservoir on the Yangtze River, China, and investigate the effect of sediment composition on P adsorption by a sequential chemical extraction method.

2. Experimental

2.1. Sampling

Sediment samples were collected at the influx of four main branches (CunTan, Xiaojiang, DaNing and XiangXi River) of the Three-Gorges Reservoir on the Yangtze River using a Van Veen stainless-steel grab sampler (Eijkelamp, Netherlands) in October 2006 (Fig. 1). The sampling site is subject to multiple pollution sources including shipping activities, urban runoff and combined sewer overflows from ambient cities. The samples were taken to the laboratory in air-sealed plastic bags and were kept at 4 °C. They were then air-dried at room temperature and ground to pass through a 100-mesh sieve for adsorption experiments.

2.2. Chemical extractions of the sediments

A sequential chemical extraction was done according to the procedure described by Tang et al. [19] as follows:

- (i) Removal of carbonates and exchangeable calcium
The sediment was extracted at room temperature for 6 h by 1 mol/L NaOAc adjusted to pH 5.0 with acetic acid (HOAc) with continuous agitation. After stewing overnight, the sediment was filtered, washed thoroughly with deionised water and subsequently dried at 60 °C. This residual sediment was mentioned as A1.
- (ii) Removal of organic matter and hydrated metal oxides
Hydrogen peroxide solution was added dropwise into a triangular flask containing the residue obtained from step (i) at 40 °C with intermittent agitation, and a large number of bubbles were generated. After 12 h reaction, the mixture was evaporated to dryness. To remove organic matter thoroughly, above steps was repeated for three times. Then the residue was extracted by mixed solution (0.8 mol/L $\text{H}_2\text{C}_2\text{O}_4$ and 1.2 mol/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$, pH 3.2) for three times in order to prevent adsorption of extracted phosphorus onto the oxidized sediment and remove metal hydroxides. This residual sediment was mentioned as A2.

2.3. Analyses

Particle size analysis was performed by X-ray sedimentography using a SALD-3001 Particle Analyzer (0.269–2000 μm , R.S.D. <3%) (Shimadzu, Japan). Total organic carbon (TOC) contents of sediments were determined using a Liqui TOC (Elementar, Germany) analyzer. Loss on ignition (LOI) measurement was based on weight losses after combustion at 550 °C. Total nitrogen (TN) and total phosphorus (TP) of sediments were analyzed by colorimetry after the digestion. Phosphate (PO_4^{3-}) was determined using the molybdenum-blue complex method [20]. The contents of Fe, Al and Ca were measured by ICP-AES (JY-ULTIMA). Transmission electron microscope (TEM) was carried out by using a Hitachi-600 model microscope.

Table 1
The characteristics of the studied sediment samples (the results listed were average of parallel experiments)

| Samples | TOC (%) | LOI (%) | TN (mg/g) | TP (mg/g) | Fe (mg/g) | Al (mg/g) | Ca (mg/g) | Clay (%) | Silt (%) | Sand (%) | P/(Fe + Al) ($\mu\text{mol}/\text{mmol}$) |
|-----------|---------|---------|-----------|-----------|-----------|-----------|-----------|----------|----------|----------|---|
| CunTan | 0.39 | 2.92 | 0.14 | 0.83 | 31.44 | 47.29 | 47.60 | 23.25 | 43.76 | 32.99 | 11.58 |
| Xiaojiang | 1.17 | 6.82 | 0.56 | 0.95 | 43.32 | 54.78 | 38.65 | 53.82 | 46.17 | 0.01 | 10.94 |
| DaNing | 0.51 | 5.75 | 0.27 | 0.75 | 23.63 | 7.75 | 101.32 | 45.89 | 53.02 | 1.19 | 34.12 |
| XiangXi | 0.96 | 4.98 | 0.11 | 0.76 | 25.31 | 4.75 | 1.66 | 36.29 | 53.25 | 10.46 | 39.05 |

2.4. Adsorption capacity for phosphorus

All adsorptive tests in this work were carried out in a shaker at 20 °C. Two drops of 0.1% chloroform was added to inhibit bacterial activity.

Adsorption kinetics of phosphorus were obtained by mixing 1.5 g dried sediment and 200 mL solution with initial phosphate concentration of 1.39, 1.75 and 2.54 mg-P/L, respectively. Samples were taken at different time intervals, and then filtered through a 0.45- μm membrane immediately to analyze phosphate concentration.

To study adsorption equilibrium, adsorption isotherms were conducted as followed. Briefly, 0.5 g dried sediment samples were added in a series of 50 mL acid washed centrifuge tubes with 40 mL phosphate solution of 0, 0.5, 1, 2, 3, 4, 5 and 6 mg-P/L. After 48 h of equilibrium in a shaker, the solutions were centrifuged at 5000 rpm for 20 min and the supernatants were used for phosphate analysis. The phosphate adsorbed on sediment samples was calculated using the difference between the initial and equilibrium concentrations. Although the phosphate concentrations used were considerably higher than that in the natural, they allowed adsorption sites to reach saturation and the maximum adsorption capacity was then calculated.

3. Results and discussion

3.1. Sediments characteristics

Generally, the retention capacity of the sediments for phosphorus was obviously influenced by their characteristics such as contents of organic matter, metal hydroxides (Fe and Al), CaCO_3 and clay [12–14]. In this study, the main characteristics of sediments were summarized in Table 1.

Organic matter, expressed as TOC and LOI, showed the lowest value of 0.39% and 2.92%, respectively, in CunTan sediment, the highest of 1.17% and 6.82% in Xiaojiang sediment. TP contents in different sediments were in the decreasing order: Xiaojiang > CunTan > XiangXi > DaNing. That is, the Xiaojiang sediment with the highest content of organic matter exhibited a maximum capacity for phosphorus retention, while the sediment possessing the lowest content of organic matter (CunTan) did not showed the minimum capacity for phosphorus retention, but higher than XiangXi and DaNing sediments. This result indicated that, organic matter increased phosphorus retention on sediments, however, there must be other properties existed to influence the adsorption of phosphorus. The content of metal oxides (Fe and Al) has been considered to be a main factor that determines phosphorus retention because of the high specific surface of the hydroxides. In our study, the sum of Fe and Al followed the order of Xiaojiang > CunTan > DaNing > XiangXi, which may be the reason that CunTan showed higher retention capacity for phosphorus than DaNing and XiangXi. Another factor affecting the phosphorus retention is the grain size. It is noticeable that the sediments used in this study were primarily composed of clay- and silt-sized particles with little sand-sized particles. The Xiaojiang sediment showed the highest clay content and at the same time possessed maximum

values at contents of organic matter, TN and TP, indicating that the increase of clay fraction with the larger specific area accelerated the adsorption of the pollutant.

3.2. Adsorption capacity for phosphate

The adsorption kinetics is important as they can provide valuable insights into the mechanism of sorption reactions. Fig. 2(a) showed the adsorption kinetics of phosphate on the DaNing sediment at different initial P concentrations of 1.39, 1.75 and 2.54 mg-P/L. It can be seen that phosphate adsorption on the sediment included quick and slow adsorption steps, which has been demonstrated by many reports. The quick adsorption step mainly occurred within 6 h, and then followed by a slower second step. There was no apparent difference in adsorption amount of phosphate on the DaNing sediment after 48 h, indicating that a pseudo-equilibrium occurred. The adsorption amount and the rate of the initial stage for phosphate adsorption advanced with an increase in the initial phosphate concentration. The similar

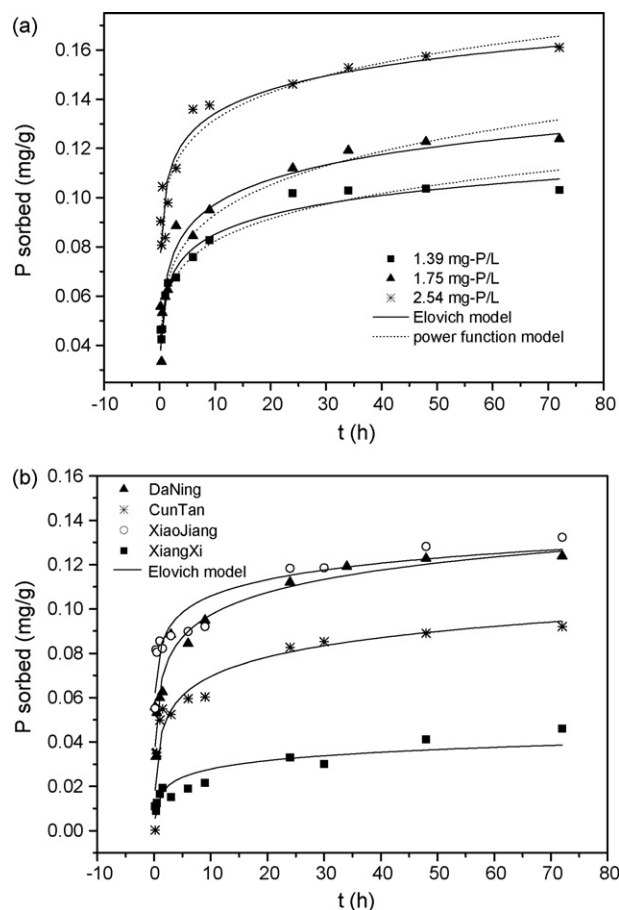


Fig. 2. Adsorption kinetics of phosphate: (a) on the DaNing sediment at different initial P concentration; (b) on the different sediments at the initial P concentration of 1.75 mg-P/L.

Table 2
Kinetic model parameters of phosphate adsorption on the different sediments

| Samples | The initial concentration (mg-P/L) | Power function model ($Q = a \times t^b$) | | | Simple Elovich model ($Q = a + b \ln t$) | | | Model provided by Lopez et al. ($\ln Q = a \times t/(b + t)$) | | |
|-----------|------------------------------------|---|----------|-----------------------|--|----------|-----------------------|---|----------|-----------------------|
| | | <i>a</i> | <i>b</i> | <i>R</i> ² | <i>a</i> | <i>b</i> | <i>R</i> ² | <i>a</i> | <i>b</i> | <i>R</i> ² |
| CunTan | 1.39 | 0.034 | 0.242 | 0.93 | 0.035 | 0.013 | 0.95 | 3.369 | 0.079 | 0.87 |
| | 1.75 | 0.04 | 0.209 | 0.87 | 0.041 | 0.013 | 0.92 | 3.494 | 0.152 | 0.72 |
| XiaoJiang | 1.39 | 0.066 | 0.131 | 0.94 | 0.068 | 0.01 | 0.91 | 3.469 | 0.017 | 0.61 |
| | 1.75 | 0.08 | 0.115 | 0.91 | 0.081 | 0.011 | 0.89 | 3.536 | 0.015 | 0.68 |
| XiangXi | 1.39 | 0.01 | 0.276 | 0.95 | 0.011 | 0.004 | 0.88 | 2.818 | 0.051 | 0.684 |
| | 1.75 | 0.014 | 0.274 | 0.94 | 0.015 | 0.005 | 0.85 | 2.818 | 0.051 | 0.684 |
| DaNing | 1.39 | 0.058 | 0.153 | 0.96 | 0.059 | 0.011 | 0.97 | 3.439 | 0.022 | 0.64 |
| | 1.75 | 0.062 | 0.175 | 0.93 | 0.064 | 0.015 | 0.93 | 3.49 | 0.025 | 0.52 |
| | 2.54 | 0.101 | 0.116 | 0.92 | 0.102 | 0.014 | 0.91 | 3.631 | 0.013 | 0.48 |
| DaNingA1 | 1.39 | 0.057 | 0.094 | 0.97 | 0.057 | 0.006 | 0.98 | 3.368 | 0.014 | 0.74 |
| | 1.75 | 0.06 | 0.107 | 0.98 | 0.061 | 0.008 | 0.96 | 3.404 | 0.014 | 0.63 |
| | 2.54 | 0.078 | 0.116 | 0.9 | 0.079 | 0.011 | 0.91 | 3.52 | 0.014 | 0.5 |
| DaNingA2 | 1.39 | 0.027 | 0.104 | 0.77 | 0.027 | 0.003 | 0.79 | 3.069 | 0.023 | 0.81 |
| | 1.75 | 0.031 | 0.106 | 0.93 | 0.031 | 0.004 | 0.92 | 3.101 | 0.013 | 0.44 |
| | 2.54 | 0.038 | 0.117 | 0.92 | 0.039 | 0.005 | 0.89 | 3.208 | 0.013 | 0.38 |

phenomenon was also observed in other sediments (Fig. 2(b)). It was obvious that, at the same initial P concentration, the adsorption capacities for various sediments followed the order: XiaoJiang > DaNing > CunTan > XiangXi.

The adsorption kinetics analysis was tested using several kinetic models, namely power function, simple Elovich model and the model provided by Lopez et al. [7]. The estimated parameters of kinetic models for all the sediments studied here were summarized in Table 2. Based on *R*² values, power function and simple Elovich model can best describe adsorption kinetics of phosphate and there was no clear difference between them. But the model provided by Lopez et al. [7] cannot satisfactorily fit the kinetics data of all the sediments used in this study.

Adsorption capacity at different phosphate concentrations can be illustrated by the adsorption isotherm. As shown in Fig. 3, higher phosphate concentrations in water increased the adsorption amount of P on the sediments. At low initial P concentrations, phosphate adsorbed on the sediments was released, while at high initial P concentrations phosphate was adsorbed. That is, P will be exchanged on the sediment–water interface until a dynamic equilibrium reaches. This process can be analyzed by adsorption isotherm model.

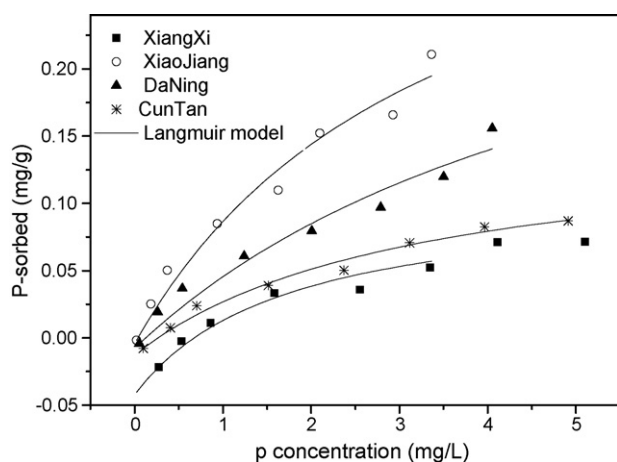


Fig. 3. Adsorption isotherms of phosphate on different sediments at 20 °C.

Taking native adsorbed exchangeable phosphorous (NAP) into account, a modified Langmuir model was put forward [11], which can be described as

$$\frac{(C_{\text{add}} - P_{\text{eq}})V}{w} = \frac{Q_{\text{max}}P_{\text{eq}}}{k + P_{\text{eq}}} - \left(\frac{Q_{\text{max}}P_{\text{eq}}^0}{k + P_{\text{eq}}^0} + \frac{P_{\text{eq}}^0 V}{w} \right)$$

where *C*_{add} is the initial concentration of newly added P in solution of adsorption test (mg/L), *P*_{eq} and *P*_{eq}⁰ are the equilibrium concentration of P in solution at the initial concentration of *C*_{add} and *C*_{add} = 0, respectively (mg/L), *V* is the solution volume (L), *w* is the dry weight of sediment (g), *Q*_{max} is the maximum P adsorption capacity at saturation conditions per mass unit of sediment (mg/g), *k* is the empirical constant with unit of concentration (mg/L) and corresponds to the concentration at which half the maximum sorption capacity is reached.

The modified Langmuir model parameters were listed in Table 3. It was evident that, modified Langmuir model had a good fit with the experimental data for the four sediments (*R*² > 0.96). Over the entire concentration range studied, the adsorption of phosphate by different sediments is in the order of XiaoJiang > DaNing > CunTan > XiangXi. This sequence was the same as the result of kinetics study. Theoretically, the maximum adsorption amount (*Q*_{max}) was 0.402 mg-P/g for XiaoJiang sediment, 0.358 mg-P/g for DaNing sediment, 0.165 mg-P/g for CunTan sediment, and 0.15 mg-P/g for XiangXi sediment.

Adsorption capacity has been related with sediment characteristics, such as contents of iron, aluminium, calcium, organic matter and the ratios of P/(Fe + Al) which provides an estimation of the free adsorption sites in metal particles. According to other reports [21], the content of metals seems to be the main factor that determines adsorption capacity, because of the high specific surface of the iron/aluminium hydroxides. In some cases, the adsorption sites can be occupied by phosphate, so the ratio of P/(Fe + Al) has been used to provide a better measure of the free sorption sites for phosphate in sediments. Moreover, for the calcareous sediments, a large fraction of the sedimentary phosphate associated with calcium minerals should be taken into account.

As shown in Tables 1 and 2, XiaoJiang sediment presented the highest concentrations of organic matter and (Fe + Al), the lowest ratio of P/(Fe + Al). According to the above argument, phosphate adsorption capacity should be the highest in XiaoJiang sediment, which was in accordance with the result of adsorption kinetics and

Table 3
Some adsorption parameters obtained from the modified Langmuir model for different sediments

| Samples | Q_{\max} (mg/g) | k (mg/L) | R^2 | P_{eq}^0 (mg/L) | $P_{(w)}$ (mg/L) | NAP (mg/g) | EPC_0 (mg/L) | K_p |
|-----------|-------------------|------------|-------|--------------------------|------------------|------------|----------------|-------|
| CunTan | 0.165 | 3.186 | 0.986 | 0.098 | 0.036 | 0.013 | 0.266 | 0.048 |
| XiaoJiang | 0.402 | 3.421 | 0.972 | 0.022 | 0.050 | 0.004 | 0.037 | 0.116 |
| XiangXi | 0.150 | 1.713 | 0.967 | 0.272 | 0.082 | 0.042 | 0.674 | 0.063 |
| DaNing | 0.358 | 5.743 | 0.959 | 0.054 | 0.033 | 0.008 | 0.126 | 0.061 |
| DaNingA1 | 0.205 | 3.921 | 0.991 | 0.040 | – | 0.005 | 0.103 | 0.051 |
| DaNingA2 | 0.083 | 3.433 | 0.970 | 0.022 | – | 0.002 | 0.098 | 0.023 |

isotherm. For DaNing and CunTan sediments, results were more difficult to interpret. Although the contents of (Fe + Al) and the free sorption sites for phosphate analyzed from the ratio $P/(Fe + Al)$ were both higher in CunTan than in DaNing sediment, higher adsorption capacity for phosphate was observed in DaNing sediment. As reported, the calcareous matter also exhibited the adsorption or co-precipitation for phosphate [17]. So higher adsorption capacity of DaNing sediment may be related with higher concentrations of calcium and organic matter. For the XiangXi sediment, the lowest capacity for phosphate adsorption was in associated with the lowest concentrations of (Fe + Al + Ca) and free adsorption sites (the highest ratio of $P/(Fe + Al)$).

NAP value, the intersection of y-axes and the regression curves, may be calculated by the equations with corresponding modified Langmuir model parameters [11]. As shown in Table 3, NAP values range from 0.004 mg/g in XiaoJiang to 0.042 mg/g in XiangXi sediment. Zero-equilibrium P concentration (EPC_0), the x-intercept of the model, was defined as the phosphate equilibrium concentration in water, at which there was no net adsorption or release of phosphate on sediments. This parameter has been highlighted because it can be used to understand the transfer direction of phosphate on the interface of the sediment–water. When EPC_0 was higher than actual phosphate concentration in water ($P_{(w)}$), the sediment would release P. Inversely, when EPC_0 was less, the sediment would adsorb P from water. That is, higher EPC_0 increased the risk of P releasing from the sediment to water.

In our study, EPC_0 values calculated by adsorption isotherm ranged from 0.037 mg/L for the XiaoJiang sediment to 0.674 mg/L for the XiangXi sediment. So the XiangXi sediment showed the highest risk of P releasing from the sediment to water. Moreover, compared EPC_0 with $P_{(w)}$ values shown in Table 3, the values of $P_{(w)}$ in all the sediments except for XiaoJiang were lower than that of EPC_0 . This indicated that the sediments in CunTan, DaNing and XiangXi hold a trend of releasing P as a source role, while the XiaoJiang sediment may adsorb P from water as a pool role.

K_p refers to the ratio of NAP and EPC_0 , which denoted the attraction forces towards P. The higher value of K_p the sediment possessed, the stronger attraction forces towards P showed. In our study, the maximum value of K_p occurred in XiaoJiang sediment, indicating that XiaoJiang sediment hold the highest attraction forces towards P. That is, compared with other sediments in our study, P in water was easier to be adsorbed by XiaoJiang sediment, which was in accordance with the analysis of EPC_0 above-mentioned.

3.3. Effect of sediment compositions

Obviously, based on the above discussion, sediments compositions were considered to be the major factors controlling phosphate adsorption by sediments. Therefore, a sequential chemical extraction experiment was designed to further clarify the effect of different composition. In this study, DaNing sediment was taken as example and divided into three fractions by the sequential chemical extraction. DaNingA1 denoted the residue which was obtained by depriving carbonates and exchangeable calcium partially from DaNing sediment. After getting rid of organic matter and metal hydroxides from DaNingA1, the residue which was mainly composed of clay mineral was mentioned as DaNingA2.

The difference of sediment characteristics before and after treatment was shown in Table 4. It can be seen that no organic matter was removed for DaNingA1 sediment, while 31.3% of Ca was reduced. Simultaneously, a small quantity of Fe and Al dissolved. For DaNingA2 sediment, more than half of organic matter was lost. About 50% of Fe, Al and 47.3% of Ca dissolved. Those results were consistent with the expectant. Additionally, the proportion of clay in the DaNingA1 sediment decreased from 45.89% of the DaNing sediment to 33.14%, while the clay content in the DaNingA2 sediment rose to 60.36%.

The morphological differences in each grade sediment were shown in Fig. 4 by TEM analysis. Obviously, a large number of floccule was observed in DaNing sediment. After removing carbonates and exchangeable calcium, sediment particles aggregated into large form, which may be due to the effect of flocculation caused by metal hydroxides and humic acid. The larger size of sediment particles was in accordance with the result of clay content decreasing. Additionally, there was no apparent difference in floccule. For the DaNingA2 sediment, better dispersion occurred and the size of sediment particles obviously decreased, which was also demonstrated by the increasing of clay content. Moreover, most floccule disappeared, which made the profile of sediment particles clear. This result indicated that the floccule mainly consisted of organic matter and metal hydroxides. When most organic matter and metal hydroxides were removed, the effect of flocculation reduced and consequently, the degree of dispersion increased.

As shown in Table 2, the experimental data of the treated sediment (DaNingA1 and DaNingA2) was also in good agreement with the power function and simple Elovich model at the initial P concentration of 1.75 and 2.54 mg/L. But the model provided by Lopez et al. [7] was not the best fitting model. This suggested that the effects of carbonates and calcium, organic matter and metal hydroxides

Table 4
The characteristics of each grade sediment extracted from the DaNing sample

| Samples | TOC/RE ^a (%) | Fe/RE ^a ((mg/g)/%) | Al/RE ^a ((mg/g)/%) | Ca/RE ^a ((mg/g)/%) | Clay (%) | Silt (%) | Sand (%) |
|----------|-------------------------|-------------------------------|-------------------------------|-------------------------------|----------|----------|----------|
| DaNing | 0.51/– | 23.63/– | 7.75/– | 101.32/– | 45.89 | 53.02 | 1.10 |
| DaNingA1 | 0.51/0 | 21.01/11.1 | 6.33/18.3 | 69.62/31.3 | 33.14 | 62.54 | 4.32 |
| DaNingA2 | 0.24/52.9 | 12.19/48.4 | 3.83/50.6 | 53.41/47.3 | 60.36 | 39.63 | 0.006 |

^a RE (removal efficiency) denoted removal efficiency from DaNing sediment.

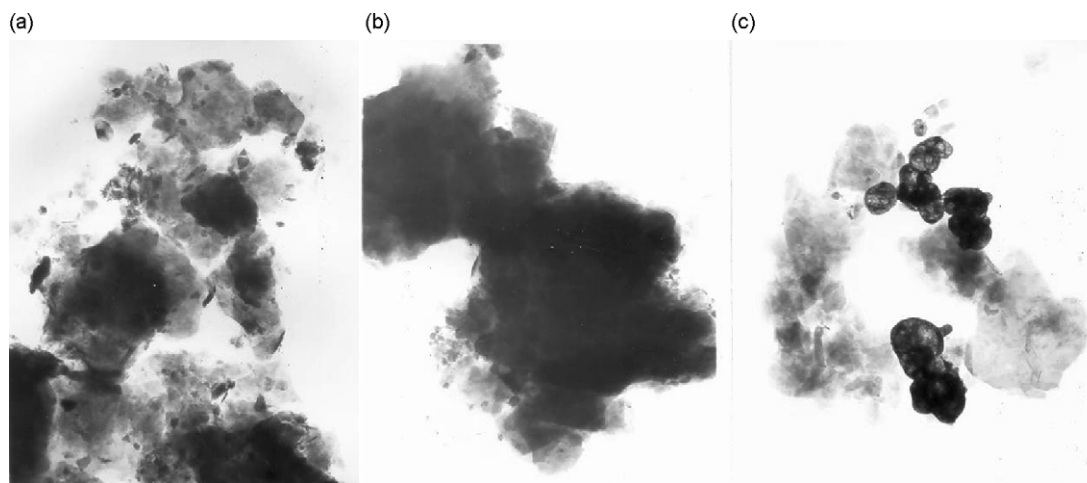


Fig. 4. TEM of each grade sediment extracted from DaNing sample (2×10^4 times): (a) DaNing sediment sample; (b) DaNingA1; (c) DaNingA2.

removed from sediments on phosphate adsorption were similar to the original sediment (DaNing sediment). Adsorption isotherms of the treated sediments for phosphate were fitted by the modified Langmuir model and the parameters were shown in Table 3. Based on R^2 (>0.97), good fits for DaNingA1 and DaNingA1 were observed. And the maximum adsorption amount (Q_{\max}) was 0.205 mg-P/g for DaNingA1 and 0.083 mg-P/g for DaNingA2, which was obviously lower than that for the DaNing sediment. Moreover, there was a decline trend in NAP and EPC_0 . Lower EPC_0 value increased the risk of P release from sediment to water. After the sediment was chemically extracted by NaOAC + HOAC, the decreasing of carbonates and exchangeable calcium content resulted in the reducing of Ca-bound P. Simultaneously, larger particles formed restrained P adsorption on the sediment. For the DaNingA2, obvious decrease in adsorption capacity for P was attributed to about half of organic matter and metal hydroxides removed in spite of the increasing of clay content. This result further verified organic matter and metal hydroxides were the main factor controlling P adsorption on sediments.

4. Conclusions

The sediments collected at the influx of four main tributaries (CunTan, Xiaojiang, DaNing and XiangXi River) of the Three-Gorges Reservoir on the Yangtze River for P adsorption were investigated thoroughly in our study. The adsorption of P by all the sediments included quick and slow adsorption and the quick adsorption mainly occurred within 6 h. The adsorption kinetics were best fitted by both power function and simple Elovich model. Considering NAP, the modified Langmuir model interprets well the experimental data of all the sediments for P adsorption. By the calculation of parameters EPC_0 and K_p , all the sediments except for Xiaojiang showed a trend of releasing P as a source role, which will enhance the risk of eutrophication occurrence. The adsorption capacity for phosphate was influenced by the sediment composition including contents of organic matter, metal hydroxides, calcium, clay and so on. As the concentrations of (Fe + Al + Ca) increasing, Q_{\max} for P adsorption rose. A sequential chemical extraction experiment was done to clarify the effect of different composition. The P adsorption kinetics and the adsorption isotherm of each grade sediment were also in good agreement with power function, simple Elovich model and the modified Langmuir model, respectively. After removing carbonates and exchangeable calcium, organic matter and metal hydroxides partially, Q_{\max} obviously decreased. Wherein, organic matter and metal hydroxides presented flocculent state observed

by TEM analysis was the main factor influencing the P adsorption on the sediments.

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