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Characterization of phosphorus sorption on the sediments of Yangtze River Estuary and its adjacent areas

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ABSTRACT

This paper studied the kinetics, isotherm and thermodynamics of phosphorus sorption onto the sediments of the Yangtze River estuary and its adjacent waters, as well as the sediments' compositions and physicochemical properties. The process could be described well by a two-compartment first order equation. The sorbed phosphorus mainly consisted of Ex-P and Fe-P, with Ex-P being the dominant. The equilibrium isotherms could be fitted well with a modified Langmuir equation. The calculations of the thermodynamic parameters indicated that the process was spontaneous and exothermic. The CEC and the fractions of clay, calcite and organic matter were correlated with the sorption parameters, while the surface proton charge of the sediments was significantly negatively correlated with them. Considering the kinetics and phosphorus forms changes during the process, the sorption in our study could be considered that the physical process plays an important role.

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1. Introduction

Phosphorus is a primary and basic nutrient for marine biological system. Its biogeochemical cycling plays a significant role on controlling the primary production process in the marine ecosystems. Marine sediment is regarded as an important carrier of phosphorus cycling. When the external loading of P is higher, the sediments can sorb it as a pool, while as the water loading is reduced, the sediments would release the sorbed phosphorus to the aquatic surroundings as a source (Junior et al., 2014; Meng et al., 2014; Wang and Li, 2010).

Total phosphorus (TP) evaluation may give some information on the trophic status of sediments in marine biological system. However, not all of the phosphorus fractions can be released from sediment into the overlying water, and the released phosphorus fractions barely have the similar mobility and bioavailability. To the study of phosphorus behavior in sediments for assessing the trophic status, it is more efficiently to be evaluated based on the phosphorus fractions (Zhu et al., 2013; Zhang et al., 2012; Zhu et al., 2012; Kaiserli et al., 2002). During sorption process, considering phosphorus fractions is also helpful to study the bonding mode of phosphorus and sediment, which may contribute to understanding the mechanism of phosphorus sorption on sediments and evaluate the mobility and bioavailability of the sorbed phosphorus.

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http://dx.doi.org/10.1016/j.marpolbul.2016.09.026 0025-326X/© 2016 Elsevier Ltd. All rights reserved. The phosphorus fractions can be characterized as IP, Fe/Al–P, Ca–P, OP, and TP according to the SMT protocol (Jin et al., 2013; Zhang et al., 2012).

Phosphorus sorption/desorption at the sediment-water interface is an important process affecting the phosphorus cycling in marine ecosystems (Jalali and Peikam, 2013; Jin et al., 2013; Wang and Li, 2010). The transport of phosphorus in natural aquatic environment mostly depends on the reactions occurring at the water-sediment interface (Borgnino et al., 2010). Besides temperature, salinity and pH of the media, properties of sediment particles, such as particle size, specific surface area, surface charge density, can be also of significant importance for phosphorus sorption process (Borgnino et al., 2006). It is essential to know the surface characteristics of natural sediments in order to improve the ability to predict the fate of phosphorus in aquatic environment. Potentiometric acid-base titration is the method used most widely to characterize the surface charging equilibria of oxides. The surface charge develops in the process of protonation/deprotonation of surface hydroxyl groups which is designated as SOH (Szekeres and Tombácz, 2012). The protonation/deprotonation constants of the interfacial equilibrium processes in acidic/alkaline solutions can characterize the surface reaction ability and the surface charge property. As sediments are a heterogeneous mixture of minerals with different charging behavior, the reactions are usually considered to be identical for all the ligand sites on the surface, and the surface properties of sediments are the result of the combined contributions from various composite minerals in the sediments. Therefore, the adsorption properties

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of the multi-component surface can be considered as the sum of the discrete contributions of the single components (Gulmini et al., 1998; Wang et al., 1997).

Studying of phosphorus sorption behavior on sediment interface, combining with the physicochemical properties of the sediments, can enrich our comprehension of the phosphorus biogeochemical cycles. Surface complexation theory has been considerable developed, which was based on the surface acid-base properties of the adsorbent. The acid-base properties of individual minerals in sediments and the interaction between metal ions and particle surface have been extensively studied, which is of importance when discussing the sorption of trace metals on sediments (Gulmini et al., 1998; Sako et al., 2009). Borgnino et al. (2006) have researched the surface properties and phosphate release rates of sediments from two Argentinean reservoirs, successfully revealed that the rate-controlling step is the breaking of the bonds between phosphate and surface groups accompanied by the sediment surface deprotonation reaction. Researches related to reactivity for nutrients and surface-water interface properties of sediments, in general, are still scarce.

The Changjiang River estuary and its adjacent sea (ECS) is a highly dynamic region in China because of tidal mixing together with the interaction of different water types. This region is very productive with rich resources of aquatic ecosystem, while now the Changjiang Estuary is under the environmental stress of harmful algal blooms due to anthropogenic influences and phosphorus has been shown to be a limiting nutrient for the phytoplankton growth (Liu et al., 2003; Meng et al., 2014; Zhao et al., 2015). In recent years, many researches have been carried out focused on the distribution, biogeochemistry behavior and environmental significance of P in sediments of the ECS (Song and Liu, 2015). As dissolved inorganic P (DIP) in the water could remain high due to P release from the sediments despite the decrease in external loading (Rydin, 2014), it is essential to obtain a further understanding of P sorption and desorption behavior at the sediments interface.

In this paper, 6 sediment core samples were collected from the Yangtze River estuary and its adjacent waters and studied for the sorption behavior of phosphorus and the surface properties. The objectives of this study were (1) to investigate the characteristics of the phosphorus sorption kinetic and equilibrium isotherms; (2) to identify the characteristics of phosphorus fraction in sediments during the sorption process; (3) to explore the relationships between phosphorus sorption parameters and the physicochemical properties of the sediments. These studies try to further reveal the phosphorus exchange mechanism on the water/sediment interface and the results may improve our understanding of the geochemical behavior of phosphorus and its bioavailability in aquatic environment.

2. Materials and methods

2.1. Sediments

The sediment core samples were collected from the Changjiang River estuary and its adjacent water—the East China Sea (ECS) shelf in May 2013. The length of the core samplers was 40 cm, and the outer diameter was 10 cm. The collected cores were sliced at 1 cm intervals within the top 10 cm, then at 2 cm intervals from the length of 10 cm. The collected core samples were sealed in plastic bags and stored at -20 °C. Back to laboratory, the sediment samples were air-dried and ground, mixed thoroughly and sieved. The part that pass 40–80 mesh sieves (420–178 µm) was used for the sorption experiments. The mineralogical composition was measured using Cu K α radiation with an X-ray diffraction (XRD) instrument d8 advance (Bruker, Germany). The cationic exchange capacity (CEC) was analyzed by EDTA ammonium acetate method (NJISS, 1978). The sediment organic matter content was determined based on the weight loss after ignition at 550 °C for 6 h (Achat et al., 2011; Wang and Li, 2010).

The sampling locations are shown in Fig.1.

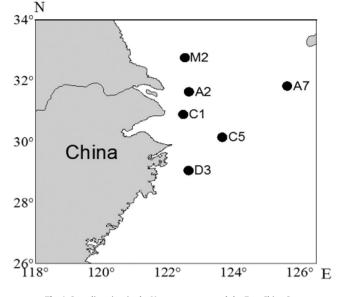


Fig. 1. Sampling sites in the Yangtze estuary and the East China Sea.

2.2. Sorption experiments

Natural seawater (NSW) from Qingdao inshore was used as the medium for phosphorus sorption experiments. The seawater was aged for about 3 months and filtered through $0.45 \,\mu\text{m}$ membrane. The total inorganic phosphorous content was lower than $0.001 \,\text{mg/L}$. The salinity and pH values were 30 PSU and 8.0, respectively. Phosphate solutions of different concentrations were prepared with KH₂PO₄ for kinetic and equilibrium sorption experiments.

2.2.1. Kinetic sorption experiments

The sorption experiments were performed using a batch technique. Briefly, 0.5000 \pm 0.0002 g sediment samples were added into a series of 40 mL phosphate solution at room temperature in a temperature-controlled shaker (THZ-82, Changzhou Guo hua Appliance Co., China). Because the initial concentration of the solution notably affected the kinetic process (Azizian, 2004; Cao et al., 2011), and most of the sorption isotherms were investigated in the range of 0–1.6 mg/L, the kinetic experiments were performed with the initial phosphorous concentration of 1 mg/L. The agitation speed was 150 rpm. Samples were withdrawn at appropriate time intervals. The aqueous phases were separated by centrifuge at 4000 rpm (Model LG10-2.4A, Beijing Physical Utilization Centrifuger Factory, China). The supernatant of each sample was analyzed by spectrophotometric with an UV spectrometry (UV-2550 spectrophotometer, Shimadzu Corporation, Japan) based on the law of Lambert-Beer. The phosphorus sorbed on sediment samples was calculated from the difference between the initial and equilibrium phosphate concentrations. Above experiments under the same conditions were carried out at four parallel, the relative error was <5%.

2.2.2. Equilibrium sorption experiments

Batch method was also used to obtain the sorption isotherms. The isotherm experiments were conducted in nature seawater with various initial concentrations of the phosphorus from 0 to 1.6 mg/L. An amount of 0.5000 ± 0.0002 g of sediment was added to a series of 100 mL glass-stopped flasks. Each flask contained 40 mL solution. The flasks were then agitated at a constant speed of 150 rpm in a temperature-controlled shaker. After equilibrium was established for 48 h, the supernatants were separated and the residual phosphorus concentrations were analyzed, and the amount of sorption onto the sediment was determined as in the kinetic experiments. Above experiments under the

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