

Research papers

Factors influencing phosphorus adsorption onto sediment
in a dynamic environmentZhiwei Li ^{a,b}, Hongwu Tang ^{a,b,*}, Yang Xiao ^{a,b}, Hanqing Zhao ^b, Qingxia Li ^b, Fei Ji ^b^a State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai University, Nanjing 210098, China^b College of Water Conservancy and Hydropower Engineering, Hohai University, Nanjing 210098, China

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Abstract

The adsorption of phosphorus onto sediment in a batch reactor and a dynamic flume was studied experimentally. The effect of velocity, sediment transport patterns, sediment supply, and phosphorus added to water was investigated in the two systems. Results showed that the equilibrium isotherm adsorption was better described using the Langmuir model. The adsorption amount increased as the initial phosphorus concentration in water increased before reaching saturation state, which was described as maximum amount of adsorption; the rate of increase in adsorption however decreased because of the limit adsorption sites and the increasing desorption. The kinetics of soluble reactive phosphorus (SRP) in water over time in both the batch reactor and the dynamic flume were well described using a pseudo-second order equation that gave good predictions of both the adsorption rate at the initial stage and the amount of adsorption in a state of quasi-equilibrium. The amount of adsorption per unit mass of sediment in the quasi-equilibrium state increased as the initial phosphorus concentration in water increased or as the sediment concentration decreased. In the quasi-equilibrium state, the adsorption amount of the SRP fluctuated within a larger range in the dynamic flume than in the batch reactor, because of continuous exchange between the suspended sediment and the bed sediment in the flume. The adsorption rate of the suspended sediment was greater than that of the bed sediment. The amount of adsorption decreased as the velocity increased when the phosphorus concentration was low, while it increased when the phosphorus concentration was high, as a result of a different concentration gradient at the water–sediment interface. The distribution coefficient and the adsorption rate coefficient both decreased as the initial phosphorus concentration increased when the sediment concentration was fixed. The variation of the distribution coefficient (K_D) indicated that the adsorption amount at equilibrium in the dynamic flume was larger than that in a quiescent environment when the phosphorus concentration was low, while the difference between the two systems was small when the phosphorus concentrations were high. However, the K_D value in both the flume and in static conditions was smaller than the value for the continuous disturbed environment in the batch reactor, indicating that the adsorption capacity was over-estimated in the latter.

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1. Introduction

Nowadays, many kinds of pollutants from agricultural and industrial activities are discharged into rivers and have subsequent impacts on ecosystems (Jalali and Peikam, 2013; Sultan et al., 2011). Phosphorus (P) is a well-known pollutant, and is the primary factor that limits eutrophication of surface waters. Excessive P discharges from point and diffuse sources can lead to eutrophication in water bodies (Lake et al., 2007). Phospho-

rus has a strong affinity for sediment, such as suspended particles and bed sediments in river water, and can be adsorbed by sediment particles. The process of P adsorption and retention at the sediment–water interface is important for P transport, bioavailability and P concentrations in rivers and lakes. Sediment plays a key role in buffering soluble reactive phosphorus (SRP) concentration in rivers or lakes (House and Denison, 2002). Sediments are also a source or sink of P through exchange at the water–sediment interface, depending on the P concentration in water and the sediment properties (Jarvie et al., 2005; Kim et al., 2003; Wang et al., 2006). When the external loading of P increases and is larger than the equilibrium P concentration (EPC_0) for the sediment, P will be adsorbed by the sediment and transported with the moving sediment. If the

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P concentration is smaller than the EPC_0 or if the redox potential conditions change, P will be released from sediment, resulting in secondary pollution (Peng et al., 2007). Adsorption and desorption of P onto sediments are influenced by the P concentration and sediment characteristics, such as particle size, organic matter, ionic strength, Fe- and Al-oxides and the cation exchange capacity (CEC) (Wang et al., 2006). The adsorption amount at equilibrium and the adsorption rate in the initial stage increases as the P concentrations increase (Wang et al., 2009). The particle size distribution is also important for P adsorption onto sediment, because smaller particles have a larger specific surface area and high proportions of Fe- and Al-oxide minerals that can adsorb pollutants (Bowden et al., 1977). Metal hydroxides and organic matter are major factors that influence P adsorption onto sediment. The maximum adsorption amount (B_m) increases as the (Fe + Al + Ca) concentration increases (Wang et al., 2009).

So far, many studies have examined the behavior and mechanisms of P adsorption or desorption onto soil or sediment in quiescent environments in laboratory studies (Li and Huang, 2013; Li et al., 2012). In these experiments, the water was stirred using plungers, stirrers, or oscillating grids, which do not adequately consider hydrodynamic conditions and do not occur in natural systems. Consequently, the rates of P entrainment were probably overestimated and restricted (Huang et al., 2007). Few investigations have examined P adsorption or desorption onto river sediment under different flow conditions and sediment transport patterns.

Barlow et al. (2004) demonstrated that the velocity and the water depth have no significant effect on the adsorption of P onto heavy clay bed sediments in either the recirculating flume or sediment cores. House et al. (1995b) illustrated that the P influx to bed sediment increased as the water velocity increased. The constant rate of the pseudo-second order model k_p depends on the water velocity, $k_p = 0.357(0.046) \times 10^{-7} v + 0.500(0.285) \times 10^{-7} \text{ m}^4 \text{ h}^{-1} \mu\text{mol}^{-1}$ (v is the velocity in cm s^{-1}). House et al. (1995a) illustrated that the suspended sediment played an important role in transporting SRP when the suspended particle concentration was high, as suspended sediment makes an important contribution to the fast uptake of SRP. Phosphorus uptake by suspended sediment is several orders of magnitude larger than that of bed sediment, due to increased interactions between P and sediment particles (Li and Huang, 2013). Wan et al. (2010) clarified that different hydrodynamic conditions resulted in transformations between different P forms.

In this study, the Huaihe River was chosen as the research site to investigate the factors that influence P adsorption onto sediment. In the Huaihe River Basin, most of the lakes have become eutrophic since the 1980s, because of the rapid growth in industrial and agricultural. P in lake sediments has increased over the past decades and had increased dramatically to about 0.4 mg g^{-1} by 2004 (Zhang and Shan, 2008). The purpose of this study is to compare the kinetics of P interactions with river sediments in quiescent and dynamic systems. A better understanding of P adsorption onto sediments in dynamic systems will help to predict and further prevent the occurrence of eutrophication.

2. Materials and methods

2.1. Sediment collection

Sediment samples were collected from a depth of $>5 \text{ cm}$ from the bank of Huaihe River at the Wujiadu gauging station in October 2013. The TP concentration was 0.3196 mg g^{-1} in bed-sediment and 0.536 mg L^{-1} in pore water, which was three times the concentration in the overlying water. Sediments were immersed in deionized water for a month and then were air-dried in a ventilated environment. Some P may have been released from the sediment in this treatment process, but the surface character was maintained and the microorganisms were retained on the sediment surface. Stones and other solid materials were removed from the sediment. The dispersed sediment was screened through 200 mesh sieves, and particles finer than $90 \mu\text{m}$ were analyzed in this experiment. The grain size fractions were measured using a laser particle size analyzer (Malvern Mastersizer 2000, Malvern Instruments Ltd., Malvern, UK), as shown in Fig. 1. The median diameter of the samples was $22.719 \mu\text{m}$, and the D_{10} and D_{90} were $3.3 \mu\text{m}$ and $60 \mu\text{m}$, respectively. Fine sediment was stored in the dark at $8 \pm 2^\circ\text{C}$ for the 4 weeks of the experiment.

2.2. Batch reactor experiments

Test to determine P adsorption onto sediment in quiescent conditions were conducted in beaker flasks and the results were compared with those in the dynamic flume. Several beaker flasks with known initial P concentrations were used as reactors. Three sets of experiments were conducted to study the parameters in the adsorption isotherms with sediment concentrations (S_0) of 1.0 g L^{-1} , 3.0 g L^{-1} , and 5.0 g L^{-1} , and initial P concentrations (C_0) ranging from 0 to 10.0 mg L^{-1} , as shown in Table 1. A known amount of sediment and KH_2PO_4 solution were added into the reactor and stirred for 1 min every hour for the first 12 h of the experiment, and every 3 h for the next 12 h. Samples were filtered through a $0.45 \mu\text{m}$ filter membrane and SRP was determined using a molybdenum blue method on ultraviolet-visible spectrophotometer (TU-1810PC, Persee Co., Beijing, China). Each time, three replicate samples were collected and analyzed synchronously. The average of the three

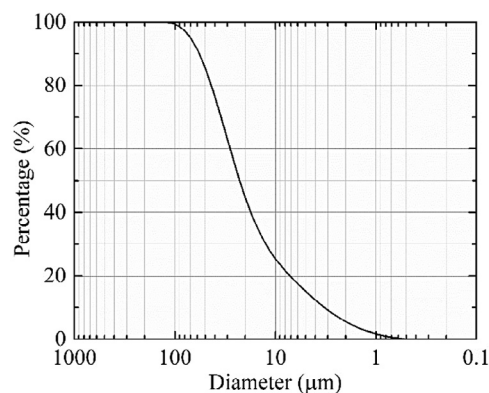


Fig. 1. Measured particle size distribution of Huai River sediment used in the experiments.

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