



Phosphorus adsorption onto clay minerals and iron oxide with consideration of heterogeneous particle morphology



Hongwei Fang^a, Zhenghui Cui^a, Guojian He^{a,*}, Lei Huang^a, Minghong Chen^b

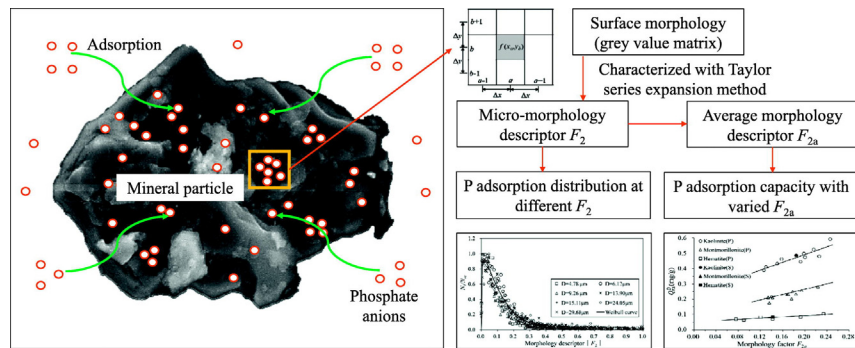
^a Department of Hydraulic Engineering, The State Key Laboratory of Hydrosience and Engineering, Tsinghua University, Beijing 100084, China

^b College of Water Resources and Civil Engineering, China Agricultural University, Beijing 100083, China

HIGHLIGHTS

- Impact of complex particle morphology on interface P adsorption is investigated from both micro and macro scale.
- A method based on Taylor series expansion is applied to quantitatively characterize the heterogeneous surface morphology.
- Analyze the statistical distribution of P adsorption probability and amount at different surface micro-morphology.
- Adsorption model incorporating the morphology role can better describe the P adsorption on heterogeneous solid surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Particle morphology plays an important role in solid-water interface adsorption, which affects the fate and behavior of phosphorus (P) in rivers and lakes and the resulting eutrophication. In this paper, three minerals including kaolinite, montmorillonite and hematite were considered to investigate the contributions of particle morphology to P adsorption using adsorption experiments and microscopic examinations. The Taylor expansion method is applied to quantitatively characterize the heterogeneity of surface morphology. The results reveal that local concave or convex micro-morphology characterized by the second order term of Taylor expansion F_2 , can affect the local adsorption capacity due to its effect on the distribution of surface charge and reactive sites. Moreover, the adsorbed P at different F_2 here fits to a Weibull distribution, which can further define the representative average adsorption onto individual particles. A weighted average morphology factor F_{2a} is derived to characterize the surface heterogeneity, and correlated with average P adsorption of particular mineral particles. In addition, the Sips model can successfully fit the experimental data of different minerals, and the heterogeneity parameters γ and adsorption capacity Q_m in the model are proved to be functions with the basic mineral properties, including particle size, surface site density and morphology characterization as well. It is concluded that the complex surface morphology plays a significant role in particle adsorption and the morphological role need to be considered in the adsorption model in order to better describe the adsorption in system with heterogeneous solid surface.

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1. Introduction

Phosphorus (P) plays a central role in biological system and often acts as the limiting nutrient for phytoplankton growth and production

* Corresponding author.
 E-mail address: heguojian@tsinghua.edu.cn (G. He).

(Schindler, 2006), but its excess supply can lead to eutrophication and massive harmful algal blooms in rivers and reservoirs (Xu et al., 2010; Elser et al., 2007). Sediment is a major carrier of P and controls the amount of highly available soluble P in water, due to its high specific surface area and potential adsorption sites. Sediment would act like both sink and sources of pollutant through exchange at water-sediment interface when physicochemical alterations occur in the environment (Jarvie et al., 2005; Oliveira et al., 2016). In addition, natural sediment has a complex mineral composition, which is also related to the particle size (Chien and Wan, 1999). For example, the high level of fine-grained sediments in lower reaches and estuaries, are mainly composed of clay minerals and oxides (Winterwerp and Van Kesteren, 2004), which have much larger capacity and significance than those non-clay minerals with regard to P adsorption (Edzwald et al., 2002; Shao et al., 2014; Gérard, 2016). Thus, understanding the P adsorption process onto sediment particle especially the minerals contained in the sediment is critical to knowing the fate and transport of P in aqueous systems.

Adsorption is the accumulation process of a chemical species (e.g. phosphate anions) at the solid-water interface whereby a surface structure is retained. A number of adsorption experiments have been conducted to investigate the affecting factors, including the external conditions such as temperature, pH value and ionic strength (Antelo et al., 2005; Huang et al., 2011; Liu et al., 2011), where pH value is an especially significant factor affecting both the amounts and processes of P adsorption (C. Wang et al., 2012). Moreover, intrinsic properties of sediment such as particle size and mineral compositions can also play important roles on adsorption (Cui and Weng, 2013; Palágyi et al., 2013; Tansel and Rafiuddin, 2016). For example, Wang et al. (2009) found that sediments with high proportions of Fe/Al oxide minerals tended to have a relatively high adsorption capacity. In these experiments, the adsorbent is typically treated as a homogeneous particle, while the effects of heterogeneous surface properties are not considered. Scanning electron microscope (SEM) has clearly shown the heterogeneous morphology and structure on clay minerals and iron oxide surface (Su et al., 2012; Zadinelo et al., 2015; Zhang et al., 2014). Atomic force microscopy (AFM) has also been used to present the non-uniform distribution of surface charge on mineral surfaces (Drelich and Yin, 2010; Kumar et al., 2016), which will influence the local electrostatic force and then affect the interfacial adsorption between the charged adsorbent and adsorbate (Koestner et al., 2011; Nagodavithane et al., 2014). However, few researches have related the negative phosphate adsorption with these heterogeneous surface properties.

Empirical adsorption isotherms (e.g. Langmuir, Freundlich) have been widely used to quantitatively describe adsorption at an equilibrium state, and they can fit many experimental data with success (Zhou et al., 2005; Mortula et al., 2007; Zhao et al., 2015). These isotherms, however, provide little insight into the adsorption process and do not show how particle characteristics especially the irregular surface morphology affects the adsorption. Avnir et al. (1983) and Pfeifer and Avnir (1983) first applied fractal geometry to describe irregular particle surface. Then a series of experiments were conducted to provide fractal analysis of the physical adsorption on particle surface (Kanô et al., 2000; Mahnke and Mögel, 2003; Watt-Smith et al., 2005). Skopp (2009) derived a fractal Langmuir isotherm with a kinetic adsorption approach, providing a physical interpretation of the model parameters in terms of the characteristics of adsorbent surface. However, the fractal dimension is usually determined by gas adsorption and would vary significantly with the used adsorbate molecules and determination methods, resulting in a lack of consensus on the usefulness of the fractal idea (Qi et al., 2002). Meanwhile, the actual particle surface is never perfectly regular and never totally fractal, just as concluded by Rudzinski et al. (2001). The fractal-like Sips model was later proposed and demonstrated to be more applicable for adsorption in real systems with heterogeneous solid surfaces (Tosun, 2012; Haerifar and Azizian, 2014). However, the model parameters are generally simply fitted to the

experimental data in practice without directly relating to the surface properties.

In our previous work, Fang et al. (2013, 2014) characterized the particle micro-morphology with Gaussian curvature and mean curvature. The distribution of adsorbed P with non-spherical curvature was then measured on both natural and mathematical sediment surface. Huang et al. (2016) further derived the macro P adsorption of natural sediments by incorporating surface morphology characterized by Fourier Analysis. Sediment is a complex assemblage of various minerals, such as quartz, feldspar, Fe/Al oxides and clay minerals. However, the mineral composition was not incorporated into these morphological models.

In this paper, the role of particle morphology in P adsorption is studied for kaolinite, montmorillonite and hematite minerals, which are the major compositions of fine-grained sediment (Chien and Wan, 1999) and have strong P adsorption capacity. Scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) was used to obtain the distribution of adsorbed P on corresponding micro-morphology, which is described quantitatively by Taylor expansion. Especially the local concave or convex micro-morphology as depicted by the second order term F_2 , is related with the statistical probability and amount of P adsorption. Then an overall morphological descriptor F_{2a} is defined to characterize the degree of surface heterogeneity and related to the P adsorption on individual mineral particles. The Sips model incorporated with a heterogeneity coefficient is introduced to fit the experiment data, and the parameters are correlated to the morphology factor and other basic properties, providing a better understanding of P adsorption behavior on these mineral particles with heterogeneous surface.

2. Materials and methods

2.1. Sample preparation

The pure minerals (kaolinite, montmorillonite and hematite minerals) were purchased from National Center for Reference Material (NCRM), then dried and stored for further analysis and experiments. Particle size (D) distribution was determined by Laser Particle Size Analyzer (HORIBA LA-920). Specific surface area (SSA) was determined by N_2 adsorption/desorption isotherms (BET method) using an ASAP 2020M specific surface area and micro-porosity was evaluated by the t -plot method using the N_2 adsorption data. Surface reactive site density N_s is a significant factor for particle adsorption, hydroxyl group is usually the key component and can be ionized in water. For these three mineral samples, the range of N_s is preliminary determined with crystallographic characterization from other literatures (Sposito, 1984; White and Zelazny, 1988; Wieland and Stumm, 1992; Venema et al., 1998), then optimized to fit the adsorption data with MINTEQA2 software (the results are shown in Supplementary material), following the methods provided by Hayes et al. (1991).

2.2. Equilibrium adsorption experiments

Adsorption was measured in 10 g/L slurries in 0.1 M $NaNO_3$ for each of the pure minerals with a range of phosphorus (added as KH_2PO_4) concentrations (0.0, 0.8, 1.0, 2.0, 3.0, 5.0, 8.0, 10.0, 15.0 mg/L). Batch experiments were performed in an incubator shaker continuously shaking at 20 ± 2 °C with an oscillation rate of 190 rpm for 24 h. The suspension were adjusted to $pH = 6.5 \pm 0.5$ after P addition. After adsorption, the suspensions were centrifuged and supernatant solutions were extracted and filtered with 0.45 μm filter paper. The concentrations of phosphorus in the filtrate were determined with ammonium molybdate spectrophotometric method, using ultraviolet-visible spectrophotometer at a wavelength of 700 nm. The adsorbed amount was calculated by the change in solution concentration through mass balance. All adsorption experiments were performed in duplicate. The dried solid samples

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