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Surface properties and phosphate adsorption of binary systems containing goethite and kaolinite

ShiYong Wei [a,b], WenFeng Tan [b,c,*], Fan Liu [c], Wei Zhao [b], LiPing Weng [d]

[a] Key Laboratory of Biologic Resources Protection and Utilization of Hubei Province, Department of Chemistry and Environmental Engineering, Hubei University for Nationalities, Enshi, Hubei 445000, PR China
[b] State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Institute of Soil and Water Conservation, Chinese Academy of Sciences & Ministry of Water Resources, Yangling, Shanxi 712100, PR China
[c] College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, PR China
[d] Department of Soil Quality, Wageningen University, P.O. Box 8005, 6700 EC, Wageningen, The Netherlands

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ABSTRACT

In soils goethite and kaolinite are often cemented together as a binary association, which has a significant influence on the physical and chemical properties of soils. In this study, the surface properties and phosphate adsorption of goethite, kaolinite, goethite–kaolinite association (GKA) and goethite–kaolinite mixture (GKM) were investigated. Compared to the average simple sum values of goethite and kaolinite, the pore volume and specific surface area (SSA) of GKA increased, and those of GKM remained almost unchanged. Goethite, kaolinite, GKM and GKA have a pH of point of zero charge (PZC) at around 8.2, 4.1, 6.1, and 7.0, respectively; and their surface charge is 0.561, −0.092, 0.041, and 0.097 mmol/g at pH 5.0, respectively. The phosphate adsorption data of goethite and kaolinite could be fitted by one-site Langmuir model ($R^2 = 0.963$ and 0.956, respectively). Two-site Langmuir model described the phosphate adsorption by GKM and GKA well ($R^2 = 0.985$ and 0.982, respectively); and the Freundlich correlation coefficients of GKM and GKA were 0.967 and 0.924, respectively. This indicated that GKM and GKA possessed the surface with two types of reactive sites, and the surface heterogeneity of GKM was higher than that of GKA. Compared to the average value of goethite and kaolinite, the adsorption capacities of GKM ($q_{max} = 198.17$ and $q_t = 226.11$ mmol/g) increased slightly and those of GKA ($q_{max} = 230.24$ and $q_t = 235.96$ mmol/g) significantly increased, indicating that GKA was a highly effective adsorbent for phosphate.

1. Introduction

Iron oxides are ubiquitous in soils (Davey et al., 1975; Krishnamurti, 1997), most of them possess a high surface area and a large amount of reactive surface hydroxyl sites (≡Fe – OH) (Arai and Sparks, 2001; Herbert, 1996; Tombácz et al., 2004). Iron oxides have a significant effect on the migration and transformation of nutrients and pollutants in soils (Arai and Sparks, 2001; Murray and Hesterberg, 2006; Violante and Pigna, 2002). Phyllosilicates are the important components of reactive soil minerals. Kaolinite is a typical 1:1-type phyllosilicate with the chemical composition $Al_2Si_2O_5(OH)_4$. The surface sites of kaolinite are mainly aluminol groups (≡Al – OH) situated at the edges and the hydroxyl-terminated planes of the clay lamellae (Ioannou and Dimirkou, 1997; Landry et al., 2009). In addition, permanent negative charges on the basal surfaces of kaolinite may have a great effect on the surface electrochemical behavior and the sorption properties of clays (e.g. Landry et al., 2009; Tombácz et al., 2004).

Iron oxides and phyllosilicates are often simultaneously present in soils, where they tend to form associations by forming oxide coatings on clay mineral surfaces (e.g. Bigham et al., 2002; Davey et al., 1975; Qafoku et al., 2000). The formation of these associations is very important to the physical and chemical properties of soils (Bronick and Lal, 2005; Duiker et al., 2003; Fitzpatrick, 1988; Rhoton et al., 1998). It was shown that the specific surface area (SSA) and cation exchange capacity (CEC) of iron oxide–phyllosilicate systems were obviously different from those of discrete phyllosilicates (Dimirkoua et al., 2002; Ioannou and Dimirkou, 1997). Gallez et al. (1976) and Hou et al. (2007) found that in binary systems iron oxides accumulated on the negatively charged surfaces of phyllosilicates and decreased the surface charge of the clay colloidal particles. Hendershot and Lavkulich (1983) and Tombácz et al. (2004) found that the point of zero charge (PZC) and the isoelectric point (IEP) of iron oxide-coated phyllosilicates were significantly higher than those of discrete phyllosilicates, reflecting the surface properties of the iron oxide.

Abbreviations: GKA, goethite–kaolinite association; GKM, goethite–kaolinite mixture; PZC, point of zero charge; SSA, specific surface area.

[*] Corresponding author at: College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, PR China. Tel.: +86 27 8728 7508; fax: +86 27 8728 8618.

E-mail address: wenfeng.tan@hotmail.com (W. Tan).

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Phosphorus is an essential nutrient for the growth of organisms in ecosystems, but excess phosphorus can also cause eutrophication and deteriorate water quality. Phosphate adsorption onto minerals is an important process that significantly affects the mobility and bioavailability of phosphorus in natural environments (Devau et al., 2009; Khare et al., 2004). The phosphate adsorption behavior by iron oxide–phyllosilicate associations is different from that by discrete iron oxides and phyllosilicates (Borgnino et al., 2009, 2010; Fontes and Weed, 1996; Zhu et al., 2008; Zhuang and Yu, 2002). Compared to phyllosilicates, iron oxide coatings showed a higher phosphate surface complexation constant and adsorption capacity (Borgnino et al., 2009; Ioannou and Dimirkou, 1997; Yan et al., 2010).

Many studies on goethite-coated kaolinite have been conducted, since goethite and kaolinite are very common clay minerals. Binary systems of goethite and kaolinite have been prepared in the laboratory by either: (1) mechanically mixing crystallographically pure goethite in a suspension with kaolinite (Hou et al., 2007; Ioannou and Dimirkou, 1997); or (2) synthesizing goethite in a suspension in which kaolinite is present (Saleh and Jones, 1984; Schwertmann, 1988; Violante et al., 1998). The binary system obtained by the former method is considerably different from natural goethite–kaolinite association due to the weak extent of the goethite coating. The latter method is difficult to prepare goethite–kaolinite association in a high purity and sufficient quantity because the formation of goethite is inhibited in the presence of kaolinite (e.g. Bigham et al., 2002; Cornell and Schwertmann, 2003; Schwertmann, 1988).

Recently, we reported the formation and transformation of iron oxides–kaolinite associations in Wei et al. (2011), and the microstructure and interaction mechanisms of goethite–kaolinite association (GKA) in Wei et al. (2012). In the present study the surface properties and phosphate adsorption on GKA were be investigated and compared with those of goethite, kaolinite and a goethite–kaolinite mixture (GKM). With this information a better understanding of the surface properties and ion adsorption behaviors of natural goethite–kaolinite association may be obtained.

2. Materials and methods

2.1. Materials and sample preparation

Analytical grade reagents and double distilled water (DDW) were used in all experiments. The polyethylene flasks, syringes and distilled water needed for the preparation of goethite and the goethite–kaolinite association were all flushed with pure N_2 to remove the dissolved oxygen. The $FeCl_2$ solution was filtered through a 0.22-μm membrane filter in a cabinet which was flushed with N_2 to remove particulate contaminants. Raw kaolinite was purchased from the Maoming Kaolin Clay Company (Guangdong Province, China) and pretreated according to the procedure described by Kunze and Dixon (1986). 30% H_2O_2 was added to raw kaolinite in a glass flask under manual stirring to remove organic matter, and then the <2 μm fraction was collected by dispersion and sedimentation. The particles of <2 μm were flocculated with 2 mol/L NaCl solution, centrifuged and washed with DDW and 95% methanol to remove residual NaCl. The pretreated kaolinite was dried at 40 °C, ground to pass a 100-mesh sieve, and stored in a desiccator.

Pure goethite was prepared according to the procedure described by Schwertmann and Cornell (2000) and Wei et al. (2011). A solution of 6 mol/L NaOH was added drop by drop to 100 mL of 1 mol/L $FeCl_3$ solution in a 1 L polyethylene flask under vigorous magnetic stirring until pH 6.0 was reached. Subsequently pure N_2 was aerated through the suspension at a rate of 100 ml/min. After 30 min, 2 mL of 1 mol/L $FeCl_2$ solution was injected into the suspension with a syringe. The pH of the suspension was adjusted back to 6.0 with a dilute NaOH solution, and then the total volume was adjusted to 1 L with oxygen-free DDW. After another 30 min, both the stirring and N_2 supply were stopped. The polyethylene flask was tightly sealed and the suspension was aged in a glycerin bath of 55 °C for 5 days. The final product was centrifuged and washed with oxygen-free DDW till the conductivity of the supernatant was less than 6 μS/cm. The precipitated goethite was dried at 40 °C, ground to pass a 100-mesh sieve, and stored in a desiccator.

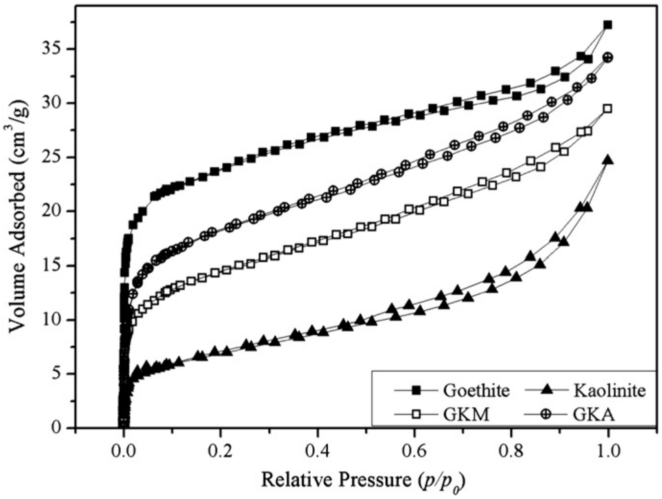

Fig. 1. Nitrogen adsorption/adsorption isotherms of goethite, kaolinite, goethite–kaolinite mixture (GKM) and goethite–kaolinite association (GKA).

For the preparation of the *goethite–kaolinite association* (GKA), 100 mL oxygen-free DDW was added to 7.99 g kaolinite in a 1 L polyethylene flask, followed by vigorous stirring for 5 min and ultrasonic dispersion for 30 min. Then 100 mL of 1 mol/L $FeCl_3$ solution was poured into the kaolinite suspension under vigorous magnetic stirring. These amounts of kaolinite and $FeCl_3$ were selected in order to reach a theoretical mass ratio (1:1) of goethite to kaolinite. The pH of the suspension was adjusted to 6.0 with a 6 mol/L NaOH solution; thereafter pure N_2 was aerated through the suspension at a rate of 100 ml/min. After 30 min, 6 mL of 1 mol/L $FeCl_2$ solution was injected into the suspension with a syringe. The pH of the suspension was adjusted back to 6.0 with a dilute NaOH solution, and then the total volume was adjusted to 1 L with oxygen-free DDW. After a reaction time of 30 min both the stirring and N_2 supply were stopped. The polyethylene flask was tightly sealed and the suspension was aged in a glycerin bath of 55 °C for 5 days, followed by a rest period of 30 days at room temperature. The product was centrifuged, washed, dried, ground, and stored in the same way as the goethite.

For the preparation of the *goethite–kaolinite mixture* (GKM), 50 mL DDW was added to 0.50 g goethite mixed with 0.50 g kaolinite in a 1 L polyethylene flask, magnetic stirring for 5 min and ultrasonic dispersion for 30 min. The pH of the suspension was adjusted to 6.0 with a dilute NaOH solution, and then the total volume was adjusted to 100 mL. The polyethylene flask was sealed, stirred with a magnetic stirrer for 2 days, and then aged at rest for 30 days at room temperature. The mixture was centrifuged, washed, dried, ground and stored in the same way as the goethite. The four samples were identified by X-ray diffraction (XRD) analysis and the results have been presented in Wei et al. (2012).

Table 1
Total pore volume and several surface areas of goethite, kaolinite, goethite–kaolinite mixture (GKM) and goethite–kaolinite association (GKA).

Samples	Total pore volume (cm^3/kg)	SSA (m^2/g)	Micropore area (m^2/g)	External surface area (m^2/g)
Goethite	49.07	51.24	11.41	39.83
Kaolinite	20.55	16.62	3.07	13.58
GKM	35.42	34.15	7.49	26.66
GKA	41.38	39.57	10.34	29.23