Surface modification of goethite by phosphate for enhancement of Cu and Cd adsorption

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Abstract

In order to understand the role of phosphate in the reactions of heavy metals on mineral surfaces, phosphate was used to modify goethite and then adsorption of copper and cadmium on the pristine and phosphate-modified goethite was investigated. Compared with the pristine goethite, the phosphate-modified goethite had a higher adsorption capacity and a faster adsorption rate. Surface characteristics, such as specific surface area, pore size distribution, zeta potential and surface charges, were then systematically investigated in order to examine the relevant mechanism for the enhancement of copper and cadmium adsorption onto the phosphate-modified goethite. It was found that the decreased surface charge contributed most to the higher adsorption capacity and the enlarged average pore size was mainly responsible for the fast adsorption kinetics, while there was no direct link between specific surface area and the adsorption capacity.

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1. Introduction

Heavy metal pollution in soil may cause risks to environment [1,2] as well as threaten human health through the food chain. So it is rather significant to find out an effective environmental-benign way to treat and remediate heavy metal contaminated sites. Heavy metals cannot be degraded, therefore, immobilization technique through precipitation or sorption to solids is a main approach to treat the metal-contaminated waters or soils, by which the bioavailability of heavy metals can be reduced.

Since heavy metal ions have different affinities for different surface functional groups, modification can be performed by complexing of foreign inorganic or organic compounds with adsorbents to improve their adsorption capacity. For examples, modified activated carbons have been used as adsorbents to remove heavy metals for decades and were recognized as an attractive approach to enhance the heavy metals removal [3]. However, recently natural minerals earn more favor than activated carbons as new adsorbents due to the wide sources and

relatively low cost, and surface modification were tried in order to enhance their adsorption capacity. Jiang and Zeng [4] compared different modification methods for montmorillonite to acquire the optimum conditions, attempting to obtain the best adsorption performance. Wingenfelder et al. [5] modified the nature zeolite with amine in order to improve its removal ability of Pb and Cd. Adebawale [6] treated kaolin by sulfate and phosphate. The results showed phosphate-modified kaolin possessed a higher adsorption capacity for Cu, Pb, Cd, and Zn; the Cd adsorption, as an example, was increased by 70.5% compared to the unmodified kaolin.

Iron oxides, such as goethite, can effectively adsorb heavy metals in soil aqueous solutions [7], leading to the immobilization of heavy metals on mineral surface, thus reducing their mobility and bioavailability. Phosphorus, which has a high affinity to iron hydroxide surfaces, was reported to enhance Cd adsorption on iron hydroxide [8–11]. Phosphate has also been used as an in situ chemical immobilizer [12]. Therefore, in this study, goethite, the most abundant iron oxides in soil, was selected as the adsorbent and phosphate as the modifier.

The objective of this work was to test the adsorption performance of phosphate-modified goethite and to compare the adsorption capacity for Cu and Cd with the unmodified goethite.

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Besides, since the surface characteristics and mineral structure were recognized to have a great impact on the retention of heavy metals [13–15], physical and chemical properties of the modified goethite surface were systematically characterized in order to better understand the relationship between metal adsorption performance and the adsorbent surface characteristics.

2. Materials and methods

2.1. Preparation and characterization of phosphate-modified goethite

Pristine goethite was prepared using the method of Schwertmann and Cornell [16]. Briefly, ferrihydrite was precipitated by rapidly adding 400 ml of a 1 M $\text{Fe}(\text{NO}_3)_3$ solution to 3600 ml of KOH solution to yield a final OH^- concentration of 0.7 M. The suspension was then stored in polyethylene bottles at 10°C for 2 months. Afterwards the goethite was washed thoroughly with de-ionized water to remove NO_3^- and K^+ , and finally dried at 60°C and ground in an agate mortar. The prepared sample showed a typical X-ray diffraction pattern of goethite, and only 0.8% of the total iron remained soluble in oxalate solution, indicative of nearly complete crystallization from ferrihydrite. The surface topographic study showed that the obtained goethite was as same as the sample used by Fischer et al. [17].

Phosphate-modified goethite was prepared by the following procedures: several copies of goethite (0.5 g) were shaken with 30 mL 1 mM of Na_2HPO_4 in a rotary shaker for 7 days at 40°C . The samples were washed three times with de-ionized water to remove excess HPO_4^{2-} ions, then dried and ground to pass through a 0.15-mm sieve.

2.2. Specific surface area and pore size distribution analyses

Scanning electron micrographs (SEM, Hitachi-S-2400, Japan) was employed to obtain a photomicrography of the exterior surfaces of the pristine and the phosphate-modified goethites. Specific surface area (SSA), micropore volume and pore size distributions were determined by a five-point N_2 Brunauer-Emmett-Teller (BET) gas adsorption isotherm method with an ASAP 2000 micropore analyzer (Micromeritics USA). The nitrogen adsorption was carried out at 77 K. The pore size distributions were calculated using the Dubinin-Radushkevich-Stoeckli (DRS) equation [18] for adsorbents with heterogeneous micropore size distributions. The ordinate shows the differential change in total volume (V) with pore size (D).

2.3. Zeta potential and surface charge measurements

The electrophoresis mobilities (EMs) of oxide suspensions containing 0.02% of solid in the 0.01 M NaNO_3 solution were determined at various pH values by microelectrophoresis using a Zeta-Meter 3.0 system. The isoelectrical point (IEP) was obtained by interpolating the data to zero EM.

Acid–base titration was conducted to determine the point of zero salt effect (PZSE) as well as the total adsorption sites. 1 g L^{-1} goethite was introduced into a glass beaker and the volume was kept at 100 mL. A known amount of 0.1 M HCl was added to the suspension to get a final pH of ~ 3.0 . Standardized NaOH solution with the concentration of 0.1 M was titrated at an increment of $50\text{ }\mu\text{L}$ to increase the pH value. Stable pH values were recorded when the drift of potential of the glass electrode cell was less than $10\text{ }\mu\text{V s}^{-1}$ [19]. Prior to and during titration, the solution was purged with high-purity nitrogen gas to eliminate the influence of CO_2 . The titration of blanks was also conducted under the same experimental conditions. Ionic strengths were adjusted with NaNO_3 at 0.005, 0.01, and 0.1 M, respectively. The PZSE was the pH at which the three-potentiometric titrations curves intersect.

2.4. Adsorption experiments

To determine the equilibrium time, adsorption kinetics was conducted by the batch technique at pH 5.5 with the contact time ranging from 10 min to 48 h.

Adsorption isotherm was measured by preparing a series of initial concentrations of Cu and Cd in centrifuge tubes with each tube having the solid concentration of 2.5 g L^{-1} . Adsorption suspensions were generated using 0.01 M NaNO_3 to maintain a constant ionic strength. A small portion of 0.1 M NaOH or 0.1 M HNO_3 was added to adjust the pH to 5.5 during the course of the experiment. The tubes were capped and shaken at 25°C for 24 h. After equilibration, solids were removed by centrifugation and filtrated through a $0.2\text{-}\mu\text{m}$ membrane filter. Filtered supernatants were served for metal analysis.

Adsorption curves (edges) were conducted as follows: a large number of samples (at least 20) with the same initial metal concentration ($10\text{ }\mu\text{M}$) were used at various pH values rather than employing duplicates or triplicates at a same pH, due to the extreme difficulty to achieve the same pH for replicates. Other conditions, such as ion strength and solid–solution ratio, remained the same as the above. In all the experiments, equal amount Cu and Cd were added simultaneously.

2.5. Analysis methods

Cu and Cd were analyzed by inductively coupled plasma – optical emission spectroscopy (ICP-OES, Optima 3300 DV, Perkin Elmer, Norwalk, CT, USA), equipped with a 40-MHz, free-running RF generator and an array detector allowing for the simultaneous determination of the elements using two different wavelengths. Multi-element standards (National Research Center for Certified Reference Materials, Beijing, China) and the analyzed samples were prepared in 2% nitric acid. Phosphate was determined by using the molybdate blue method with a Perkin Elmer Lambda 3 spectrophotometer at 670 nm. Solution pH was determined using a Fisher Scientific Accumet model 20 pH/conductivity meter. All reagents used were of analytical grade or better.

2.6. Data analysis

Elovich equation was employed to describe the adsorption kinetics:

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t, \quad (1)$$

where q_t is the amount of sorbent per unit mass of sorbent as time t and α and β are constants.

Langmuir equation was used to simulate the adsorption isotherm:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max}} KC_e, \quad (2)$$

where C_e is the equilibrium concentration (μM), q_e the amount absorbed at equilibrium ($\mu\text{mol g}^{-1}$), $q_{\max}$ the maximum adsorption capacity ($\mu\text{mol g}^{-1}$), and K Langmuir constant.

All the data obtained by three replicate analyses. Statistical analysis was performed by the Office XP-Excel and Origin 6.0. Significance of difference was analyzed by the student's t -test.

3. Results

3.1. Surface characteristics of the pristine goethite and phosphate-modified goethite

3.1.1. Specific surface area and pore volume analysis

As presented in Table 1, the BET specific surface area was $51.18 \text{ m}^2 \text{ g}^{-1}$ for the pristine goethite and $36.96 \text{ m}^2 \text{ g}^{-1}$ for the phosphate-modified goethite. Modification by phosphate reduced the surface area of goethite by 28%. This could arise from the blockage of surface pores by phosphate molecules. A previous study [17] reported that the pores on goethite surface were 20–30 nm in width and became narrower to 2 nm or less towards the interior of the crystals. Radius for phosphate was 0.22 nm; it was therefore possible for phosphate to diffuse into the pores or to block the pore entrances [20,21], which was confirmed by the decreased average pore volume after phosphate modification through the pore volume analysis in Table 1.

Pore size distributions (Fig. 1) indicated the diameters of pores in the pristine goethite were all less than 900 Å, including mesopores (diameter 20–500 Å) and micropores (diameter <20 Å). Part of the pores in the phosphate-modified goethite had the diameters bigger than 900 Å, with the widest close to 1500 Å.

Fig. 1. Pore volume and size distribution of the pristine goethite (●) and the phosphate-modified goethite (○).

It suggested that part of the pores in goethite were widened during the phosphate modification process, which could be also reflected to some extent by the SEM observation (Fig. 2).

3.1.2. SEM observation

Fig. 2 showed the SEM micrographs for the goethite samples before and after phosphate modification. Both of the samples were clearly porous and needle-like particles [16]. Comparison of the two micrographs revealed that modification did not significantly change the morphology of the mineral surface matrix; but it could be observed that some large pores disappeared after modification. It might suggest that parts of the micropores became clogged by phosphate molecules. This also explained the reduction in the surface area of the phosphate-modified goethite.

3.1.3. Zeta potential and surface charge measurement

Zeta potentials of the goethite surfaces can provide valuable information on the adsorbent surface chemistry. As expected, Fig. 3a showed the zeta potential decreased gradually with the increase in the solution pH for both the pristine and phosphate-modified goethites. And the surface charges tended to be negative at higher pH. The zeta potential for the pristine goethite was positive when the solution pH was higher than 7.9; while the IEP for the phosphate-modified goethite shifted from 7.9 to 6.3, which was consistent with the reported result [22]. The decreased IEP and the evident shift of EM indicated that phosphate ions were strongly bound to the goethite surface since outer-sphere complex (not directly adsorbed on the surface) with phosphate would not change the surface charge [23].

Surface charge was determined by surface titration. As shown in Fig. 3b, the surface charge for goethite was 0.622 C m^{-2} at pH 5.5 in 0.01 M NaNO_3 , whereas it decreased to 0.026 C m^{-2} for the phosphate-modified goethite in the same condition. The PZSE by choosing an origin that located by the common point of intersection of titration curves was 7.9 for the pristine goethite and 5.6 for the phosphate-modified goethite. The inconsistency between IEP obtained from EM and PZSE from potentiometric

Table 1
Physical characterization for pristine and phosphate-modified goethites

Characteristics	Pristine goethite	Phosphate-modified goethite
BET surface area ($\text{m}^2 \text{ g}^{-1}$)	51.18	36.96
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)		
Total volume	0.1763	0.1251
Micropores (<20 Å)	0.004198	0.002493
Mesopores (20–500 Å)	0.07393	0.05456
Average pore diameter (Å)	166.8	154.7
Average pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.1509	0.1034

Fig. 2. Scanning electron micrographs: (a) pristine goethite, (b) phosphate-modified goethite.

titration data was in agreement with the results by Parfitt et al. [24].

3.2. Adsorption of Cu and Cd in relation to surface properties

3.2.1. Adsorption kinetics

The adsorption of Cu and Cd on the pristine goethite and phosphate-modified goethite as a function of time was investigated (Fig. 4). Adsorption of both Cu and Cd achieved equilibrium after 24 h, characterized by an initial fast and followed by a slow continued uptake. This two-step sorption process was the characteristic of heavy metal sorption on clay and oxide surfaces [25]. The mechanism proposed for such process was first surface adsorption and then followed by diffusion into micropores of the minerals [26,27].

Fig. 3. (a) Zeta potential vs. pH of the pristine goethite (●) and the phosphate-modified goethite (○). (b) PZNC by acid–base titration of the pristine goethite in 0.1 M (▲), 0.01 M (●), 0.005 M (■) NaNO_3 and the phosphate-modified goethite in 0.1 M (△), 0.01 M (○), 0.005 M (□) NaNO_3 .

Adsorption of Cu and Cd on the phosphate-modified goethite achieved equilibrium earlier than on the pristine goethite, and it was more obvious for Cd. Elovich equation, $q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t$, was introduced to quantify the adsorption kinetics. Elovich equation was originally developed to describe the diffusion process of gases on solid surface. Chien and Clayton [28] later introduced it into soil chemistry, and the parameters of α and β were used to estimate the reaction rate. Though questioned by Sparks [29], the concept that the increase in α corresponds to the increase in reaction rate has still been adopted by some latest literatures [30,31]. In this study the good fit ($r^2 > 0.939$) of Elovich equation for both samples (Table 2) implied that a diffusion process was involved in the Cu and Cd adsorption. The relatively bigger rate constant α of the phosphate-modified goethite indicated that modification accelerated the metal ions uptake. Statistical analysis revealed a significant difference in Cu and Cd adsorption rates ($p < 0.01$) between the pristine and phosphate-modified goethite. It suggested that phosphate might block pores of goethite during pretreatment, which hindered metal ion diffusion into the inner surface binding sites [11]. As a result, more metal ions accu-

Fig. 4. Adsorption kinetics of copper and cadmium on the pristine goethite (●) and the phosphate-modified goethite (○).

multilayered on the particle surface or near surface and diffusion into inner surface and micropores would be shortened, causing a relative shorter equilibrium time and faster adsorption rate.

3.2.2. Adsorption isotherms

Adsorption isotherms of Cd and Cu were shown in Fig. 5. Langmuir isotherm equation was employed to simulate the adsorption and compare the adsorption capacities of the pristine and the phosphate-modified goethite (Table 3). A good fit was achieved within the concentration ranges studied ($r^2 > 0.983$). According to the results of adsorption equilibrium constant K and the maximum capacity $q_{\max}$, evidently the phosphate-

Fig. 5. Adsorption isotherms of copper and cadmium on the pristine goethite (●) and the phosphate-modified goethite (○).

modified goethite had a much higher sorption capacity for Cu and Cd than the pristine goethite.

Both Cu and Cd adsorption by goethite were highly pH-dependent and increased by nearly 100% in a narrow pH range (Fig. 6). Compared with the pristine goethite, the adsorption edges on the modified with phosphate were markedly shifted to a lower pH. It meant the phosphate-modified goethite adsorbed

Table 2
Parameters for adsorption Elovich kinetics equation

Metal	Sample	Elovich kinetics equation parameters		
		α	β	r^2
Cu	Pristine goethite	11.33	0.2311	0.9625
	Phosphate-modified goethite	14.67	0.2629	0.9388
Cd	Pristine goethite	5.232	0.5025	0.9761
	Phosphate-modified goethite	6.532	0.5722	0.9781

Table 3
Parameters for Langmuir adsorption isotherm equation

Metal	Sample	Langmuir isotherm parameters		
		$q_{\max}$ ($\mu\text{mol g}^{-1}$)	K	r^2
Cu	Pristine goethite	26.46	3.62	0.9827
	Phosphate-modified goethite	31.81	4.66	0.9912
Cd	Pristine goethite	11.93	1.22	0.9863
	Phosphate-modified goethite	15.81	1.41	0.9881

Fig. 6. Adsorption pH edges of copper and cadmium on the pristine goethite (●) and the phosphate-modified goethite (○).

more Cu and Cd than the pristine goethite within the pH range from 3 to 8.

4. Discussion

Both the pH-constant (isotherms) and the pH-dependent adsorptions showed that phosphate treatment enhanced Cu and Cd adsorption on goethite, and such effect existed across a wide pH and cation concentration ranges (Figs. 5 and 6). Physical and chemical properties of the adsorbent surface were investigated to better understand the fast kinetics and high adsorption capacity on the phosphate-modified goethite.

In this work, specific surface areas did not show a positive correlation with adsorption capacities. The specific surface area of goethite reduced after modification, but both the pH-constant and pH-dependent adsorption data revealed that the adsorption capacity for both Cu and Cd significantly increased. Similar phenomenon had also been reported by Lakov et al. [32]; they even observed the copper adsorption capacity was enhanced by 50% though the specific surface area of the carbon decreased by 80% when they modified the activated carbons with 3-methyl-1-

phenyl-pyrazolone-5 (HMPP). It implies surface area does not have the direct relationship with adsorption capacity, especially in the chemical adsorption process. In fact, information offered by the BET specific surface area involves both the inner and outer surfaces of an adsorbent, while the outer surface is the main chemical reaction interface for the adsorption process.

Surface charge of goethite decreased after phosphate modification. At pH 5.5, upon the surface charge was decreased from 0.622 C m^{-2} to near zero (Fig. 3b), the exclusion between metal ions and the positive charged mineral surface also reduced, which would benefit the metal ions to move closer to the mineral surface and then being adsorbed. Among the changes of surface properties, the decrease of surface charge was the most significant. Therefore, it would be responsible most for the higher adsorption capacity of the phosphate-modified goethite, which was also in agreement with the previous studies [8–11]. Furthermore, enhanced adsorption of Cu and Cd could be also well explained by the rising amount of total adsorption sites possibly caused by phosphate surface precipitation on goethite, which leading to the generation of new adsorption sites.

The blockage of the mesopores and micropores by phosphate molecular may interpret the faster adsorption kinetics of the phosphate-modified goethite. Since the inner micropores were clogged, diffusion process was shortened and thus equilibrium time reduced. After modification, the fast adsorption step was shortened and the slow adsorption step extended. The diameter of Cd^{2+} is bigger than Cu^{2+} , therefore the effect in Cd adsorption was more evident.

5. Conclusion

This study presented the changes of goethite surface characteristics after modification by phosphate and the adsorption performance. During the modification process, the phosphate diffused into the meso- and micro-pores of goethite and reduced its specific surface area and impacted the heavy metal adsorption kinetics. The decrease of the surface charge led to the enhancement of metal ion uptake, as indicated by the decrease in the maximum adsorption capacity and the substantial shifts of adsorption edges to a lower pH. The influences of phosphate modification on the surface characteristics of goethite and the adsorption of Cu and Cd help us better understand the role of phosphate in the reactions of heavy metals on mineral surfaces.

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