

Supplementary Information

Chemical speciation and distribution of adsorbed Cd(II) on goethite: influence of pH and sulfate

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Text S1. Detailed Extraction procedure

The amounts and bonding forms of Cd(II) retained by goethite were evaluated, and three fractions were operationally quantified in this study: the Mg(NO₃)₂-extracted fraction (MF), the EDTA-extracted fraction (EF), and the tightly integrated fraction (TF). Each fraction obtained during the adsorption process was extracted/calculated as follows:

(1) At each time interval, the reaction tubes were withdrawn for centrifuging, and 1 mL of the supernatant was passed through 0.22- μ m filter and stored for quantification of total adsorbed Cd(II) concentration. The total adsorption capacity of Cd(II) by goethite at time t was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m \times M} \times 1000 \quad (1)$$

where q_t is the amount of total adsorbed Cd(II) on the goethite (μ mol/g) at time t ; C_0 is the initial Cd(II) concentration in the centrifuge tubes (mg/L); C_t is the Cd(II) concentration at time t (mg/L); V is the reaction volume of the solution (L); m is the mass of the goethite (g); and M is the molar mass of cadmium.

(2) After removing the supernatant and rinsing with deionized water, 10 mL of Mg(NO₃)₂ solution (1 M, pH=7.0) was added to the tubes shaking for 2 h. The tubes were then centrifuged, and the supernatant was collected to acquire the MF Cd(II). The literature has reported that the most frequently used chloride salt extractant (MgCl₂/CaCl₂) may induce an over-estimated result for the Cd(II) extraction because of the unignorable stability constant of the complexes of cadmium with chloride (Krishnamurti et al., 1995; Gommy et al., 1998). Therefore, the more inert magnesium nitrate solution was used in the present proposed procedure.

(3) After removing the supernatant and rinsing with deionized water, 10 mL of EDTA solution (0.05 M, pH=10.0) was added to the centrifuge tubes shaking for another 18 h. Subsequently, the tubes were centrifuged again, and the supernatant was collected to quantify the EF Cd(II). Hydrogen ions in the extractant solution will react with EDTA to form conjugated acids. This side reaction reduces the ability of EDTA

to complex with metal ions (Norkus et al., 1996; Noorhasan and Sharma, 2008). In addition, it is worth mentioning that the adsorption of EDTA in the extraction process as well as the re-adsorption of metal(II)-EDTA complex on goethite was negligible in alkaline conditions, especially in pH>9 systems (Nowack and Sigg, 1996; Yang and Davis, 1999). Besides, lots of studies have suggested that pH higher than 8, the dissolution effect of goethite by EDTA is negligible (Nowack and Sigg, 1997; Campbell and Eick, 2002; Norén et al., 2009). Therefore, we used an alkaline EDTA solution with pH 10 as the extractant to inhibit its acid effect, dissolution effect, re-adsorption effect and to obtain sufficient Cd(II) complexing ability.

(4) The amount of Cd(II) in the residuals after two extraction steps was identified as the TF Cd(II) and calculated as follows:

$$q_{TF} = q_t - q_{MF} - q_{EF} \quad (2)$$

After the extraction procedures were complete, the residue was stored in a refrigerator at $-20\text{ }^{\circ}\text{C}$ for subsequent characterization. Preliminary extraction experiments suggested that the recovery efficiency of the adsorbed cadmium is around 95%–103%.

References:

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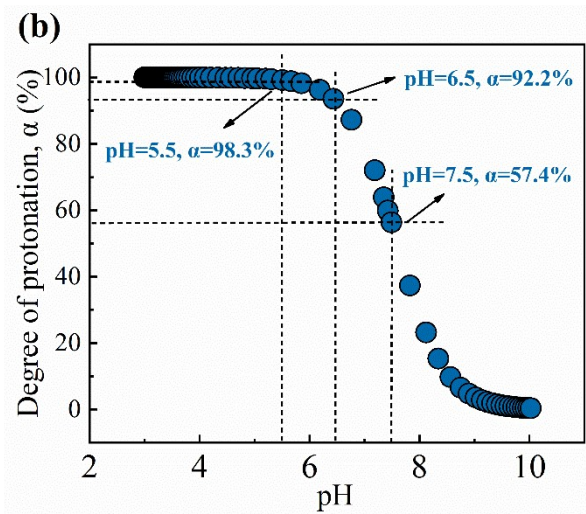
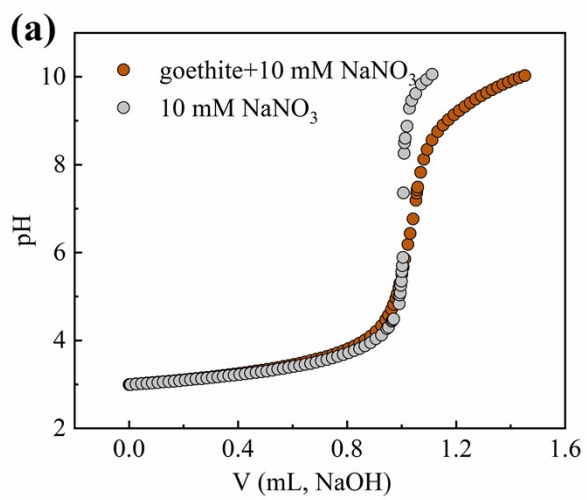


Fig. S1. The automatic potentiometric titration curves of goethite in NaNO₃ background solutions (a); and the degree of protonation (α) curve for the titration of goethite in 10 mM NaNO₃(b).

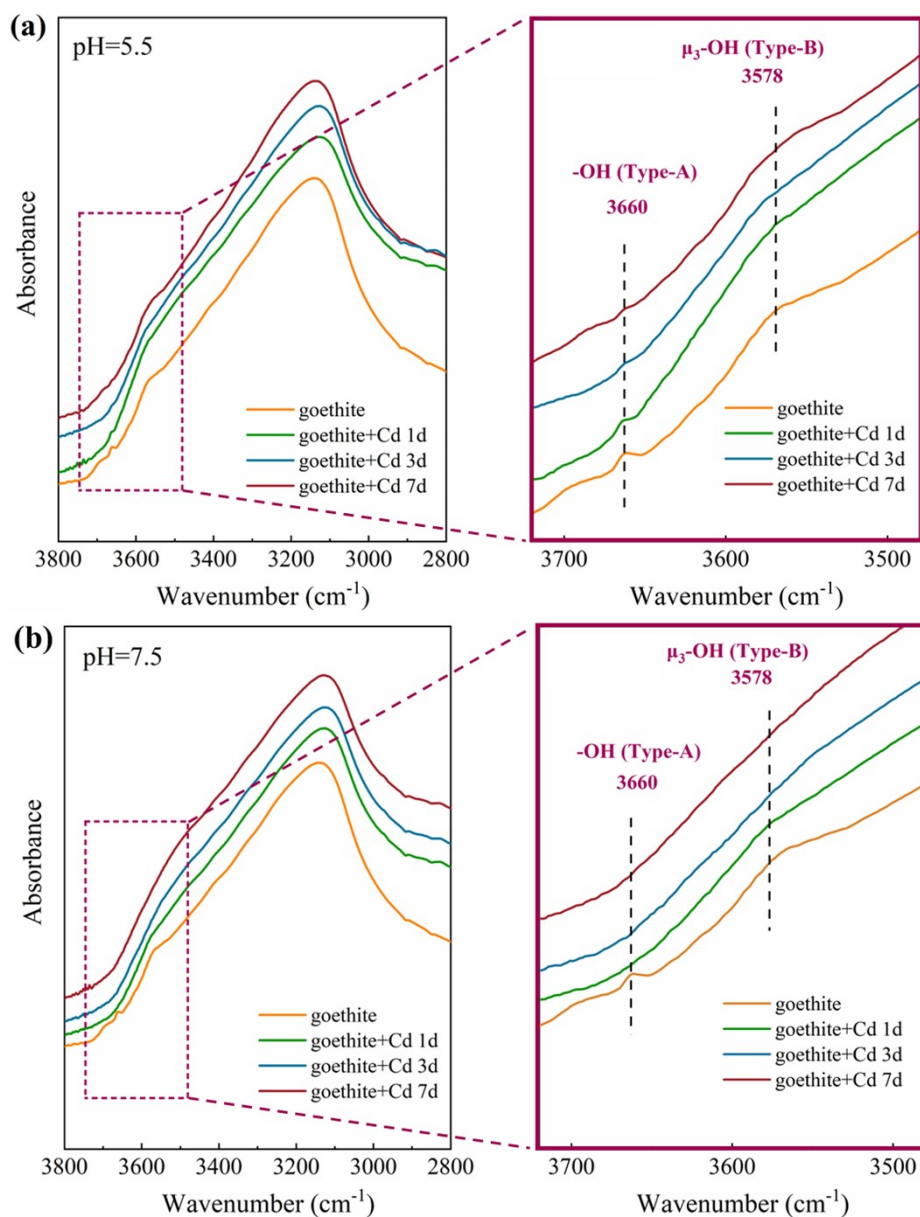


Fig. S2. DRIFTS spectra of goethite samples after different cadmium adsorption reaction times under acidic and alkaline systems: (a) pH 5.5; (b) pH 7.5. Reaction conditions: Cd(II) initial concentration=0.1 mM; goethite dosage=3.33g/L; ionic strength=10 mM NaNO₃; T=25.0°C; The type-A hydroxyl on the surface of goethite refers to the singly coordinated hydroxyl groups ($\equiv\text{FeOH}$) in which oxygen was connected with one Fe atom; the type-B hydroxyl refers to the triply coordinated hydroxyl groups ($\equiv\text{Fe}_3\text{O}$) in which oxygen was connected with three Fe atoms.

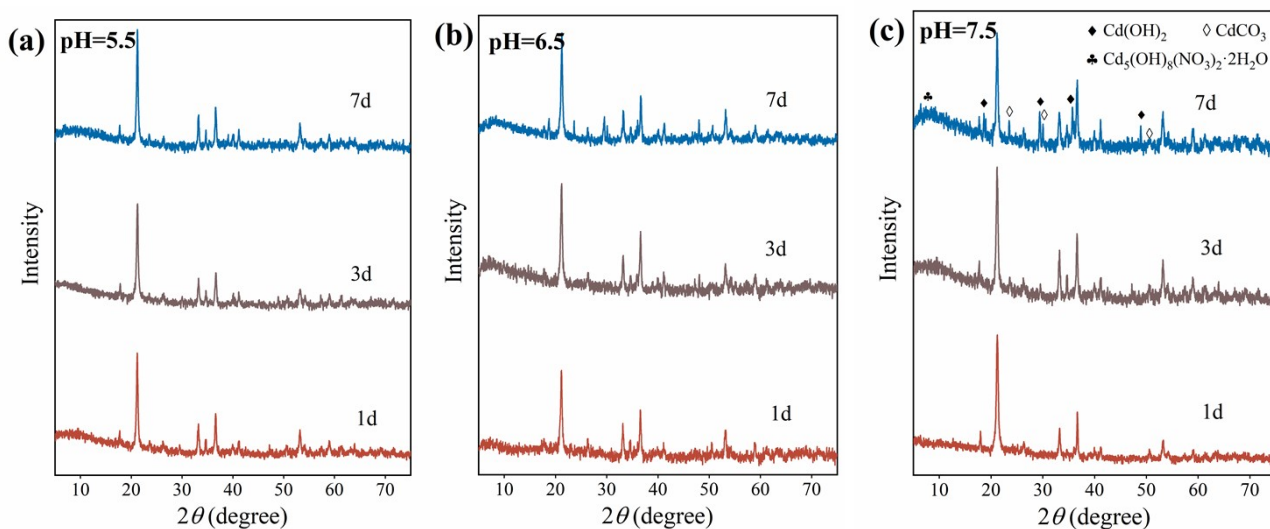


Fig. S3. XRD patterns of goethite after different cadmium adsorption reaction times under three pH conditions. The indicator symbols for the new cadmium phases are only shown in plot (c) for clarity. Reaction conditions: Cd(II) initial concentration=0.1 mM; goethite dosage=3.33 g/L; ionic strength=10 mM NaNO₃; *T*=25.0°C;

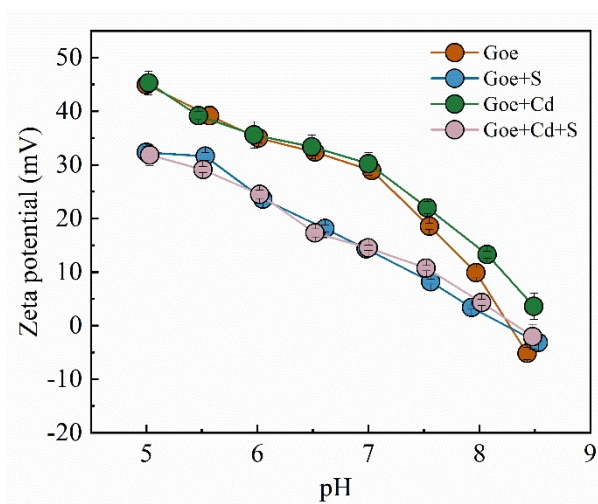


Fig. S4. Zeta potential of goethite versus pH under different sulfate and cadmium conditions. Reaction conditions: cadmium initial concentration=0.1 mM, sulfate initial concentration=1 mM, goethite dosage=3.33 g/L; ionic strength=10 mM NaNO₃; *T*=25.0°C.

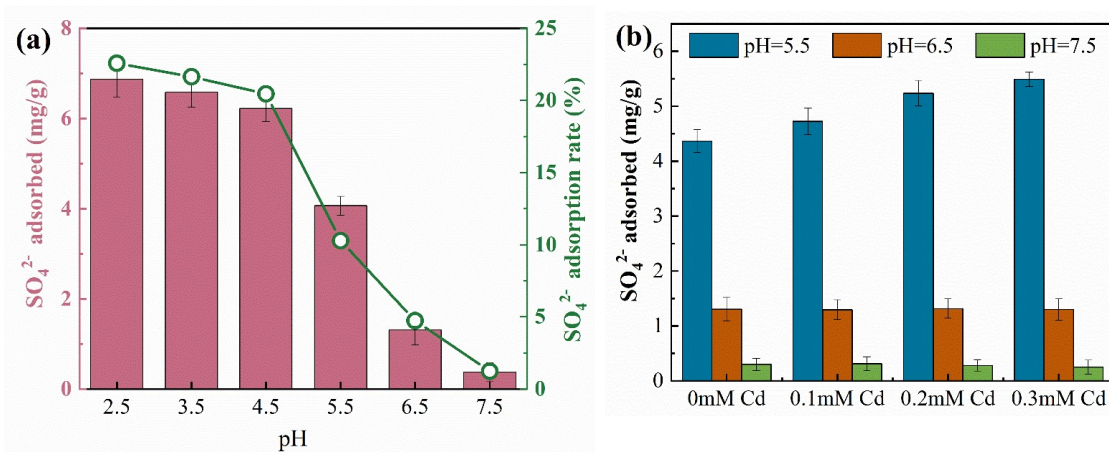


Fig. S5. Sulfate adsorption on goethite at various pH conditions (a), reaction conditions: sulfate initial concentration=1 mM, goethite dosage=3.33 g/L; ionic strength=10 mM NaNO_3 ; $T=25.0^\circ\text{C}$; Sulfate adsorption on goethite at various Cd(II) concentration conditions (b), reaction conditions: sulfate initial concentration=1 mM, goethite dosage=3.33 g/L; ionic strength=10 mM NaNO_3 ; $T=25.0^\circ\text{C}$.