Cadmium desorption from goethite in the presence of desferrioxamine B and oxalic acid

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Abstract
Microorganisms such as bacteria and fungi, under aerobic environments, produce siderophores like desferrioxamine B (DFOB). DFOB enhances the availability of iron (III) in Fe deficient soils. Organic acids like oxalic acid (OA), are also frequently found in the rhizosphere. These compounds chelate heavy metals and thus affect their mobility and bioavailability. We carried out experiments to evaluate the effects of DFOB and OA on Cd desorption from goethite. In these experiments desorption behaviour of Cd adsorbed on goethite was studied at two initial Cd concentrations (i.e. 180 and 300 μM) in the presence of 300 μM DFOB and 200 μM OA and the combination of two. Following adjustment to pH 6.0, goethite samples were equilibrated overnight with DFOB/OA at 25 ± 2 °C using 0.01 M $Ca(NO_3)_2$ as the background electrolyte.

The presence of the DFOB and OA enhanced Cd desorption substantially. Approximately 70 and 77% of initially adsorbed Cd from 180 μM Cd was desorbed after 15 successive desorptions in the presence of DFOB and OA, respectively compared with 46% desorption in the control sample. The corresponding desorptions from 300 μM Cd had almost the similar trend to that of 180 μM Cd. Furthermore, Fe concentration in the equilibrium solution increased in the presence of DFOB as compared to control, which showed that dissolution of Cd adsorbed goethite possibly enhanced the desorption of Cd in the presence of DFOB. However, in presence of OA increased Cd desorption was mainly due to decreased equilibrium pH from 6.0 to 4.8. The study shows the significant role that siderophores and organic acids can play in geochemcial transformations and in enhancing the release of adsorbed heavy metals in environment.

Keywords
Cadmiun, desorption, goethite, desferrioxamine B, hysteresis, oxalic acid, siderophores

Introduction
Siderophores are low molecular weight complexing agents which are excreted by bacteria and fungi under conditions of Fe deficiency (Raymond *et al.* 1984). For example, fungi produce mainly trihydroxamate siderophores, a typical example being desferrioxamine B (DFOB) as reported by Crumbliss (1991) and Albrecht-Gary and Crumbliss (1998). Siderophores are common in soil environment and their soil solution concentrations increases significantly in the presence of organic matter and in proximity to living plant roots (Powell *et al.* 1982; Crowley *et al.* 1987).

Siderophores also form stable complexes with divalent metal cations but the stability of such complexes is lower than stability constants with Fe(III) (Neubauer *et al.* 2000). In recent years, DFOB has been used to study its effects on adsorption and transport of toxic metals in soil minerals (Neubauer and Furrer 1999; Neubauer *et al.* 2000; Cervini-Silva and Sposito 2002; Kraemer *et al.* 2002; Neubauer *et al.* 2002). For example, 300 μM DFOB enhanced Cd concentration as a result of goethite dissolution at pH 8.0 (Neubauer *et al.* 2002). Cervini-Silva and Sposito (2002) found much higher Al release as a result of goethite dissolution in the presence of DFOB and OA than the control. In goethite, three hydroxamate groups of DFOB promote its dissolution in much the same way as in aqueous solution through bidentate ligation (Watteau and Berthelin 1994; Kraemer *et al.* 1999).

Low molecular weight OA is commonly found in the soil system, whose rate of production depends on the time and nature of environment (Stevens 1977; Harter and Naidu 1995). Oxalic acid may also enhance the dissolution of goethite (Eick *et al.* 1999). The presence of OA weakens the metal-$RCOO^-$ ligand stability due to decrease in soil pH, which enhances metal availability (Reuter and Purdue 1977).

Contrary to this Naidu and Harter (1998) found decreased Cd extractability in the presence of increasing concentrations of OA from the goethite rich soils, adsorbed form 303 mg/kg Cd at pH 3.1 to 3.4.

Coexistence of DFOB and OA in the soil environment is quite common and may significantly affect the Cd release from minerals (Cervini-Silva and Sposito 2002). Therefore, the objective of this study was to investigate the effects of DFOB and OA separately and the combination of both on the desorption behaviour of Cd from goethite at low initial Cd concentrations.

Materials and methods
Synthesis and characterization of goethite
Goethite was prepared following the method described by Schwertmann and Cornell (1991). Gel was prepared by mixing 1800 ml of 5 M KOH to 1000 ml of 1 M ferric nitrate in a plastic container. The gel was immediately diluted to 20 litre with ultra pure water and solution was aged for 22 days at room temperature (18±2°C). The pH of the suspension was maintained ≥ 13 through out the ageing period. At the end of equilibrium period, suspension was dialysed for 7 days in a cellulose membrane against ultra pure water to remove excess salt. When there was no change in the electrical conductivity (5 μS/cm) of the ultra pure water, the suspension was transferred into plastic container and mixed well.

A sub-sample of synthesized material was oven dried at 45±2°C until constant weight and characterized by various techniques. For powder X-ray diffraction (XRD) a finely ground sample was scanned from 10-70° 2 θ using a step size of 0.02°/min on Siemens D5000 diffractometer using a monochromatic CuKα radiation. Surface area of goethite was measured by nitrogen adsorption method and using the Brunauer-Emmett-Teller (BET) equation (Brunauer *et al.* 1938). Finely ground goethite sample was degassed for 24 h at 60 °C. After a constant weight had been achieved, sample was analysed for surface area measurements using Autosorb-1 Quantachrom. For transmission electron microscopy (TEM), a drop of dispersed goethite suspension was placed onto the carbon coated copper grid. The grid was allowed to dry for 60 min under the 100 V Tungstun bulb prior to TEM examination. Digital images were captured using a Phillips Biofilter microscope fitted with a LaB_6 filament and a lithium-drifted silicon detector, which was operated at 120kV. The point of zero salt effect (PZSE) of goethite was determined using the batch method as described by Zelazny *et al.* (1996).

Adsorption procedure
For Cd adsorption ~ 9.5 ml of goethite suspensions were weighed into 12 polypropylene tubes of 50 ml capacity. Ten ml of 0.01 M $Ca(NO_3)_2$ previously adjusted to pH 6.0 was added into each tube. Samples were equilibrated for 18 h on a wheel shaker at 30 rpm. Suspension pH was adjusted to 6.0 using 0.1 M HNO_3 periodically up to 6 days. The set of 12 tubes was divided into 3 subsets each of 4 tubes. One ml of 180 (Cd180) and 300 (Cd300) μM Cd solutions were added into 4 tubes each. The third subset was kept as control with background solution ($Ca(NO_3)_2$ only and no Cd was added (Cd0). Samples were equilibrated on a wheel shaker at 30 rpm for 18 h at 25 ±2 °C. After equilibration, solution pHs were measured using PHM 210 standard pH meter and samples were centrifuged at 9220 *g* for 25 min using Sorvall-5 super speed centrifuge. Supernatant solutions were filtered through 0.2 μm filter membrane and analysed for Cd and Fe using flame atomic absorption spectrophotometer (FAAS). Cadmium adsorption was calculated from the difference in Cd concentration of initial and final solutions.

Desorption procedure
Following Cd adsorption on goethite samples from 180 and 300 μM Cd initial concentrations and control samples, 10 ml of 0.01 M $Ca(NO_3)_2$ (pH 6.0) was added into each tube. One ml each of 300 μM DFOB and 200 μM OA were also added into the tubes either individually or together as designated in the Table 1. Samples were equilibrated on wheel shaker at 30 rpm for 18 h at 25 ±2 °C and centrifuged as described in the adsorption procedure. Volume of entrained solutions were determined by weighing tubes after each desorption step. The desorption step was repeated for 15 times. The equilibrium solution pH was measured after 1st, 5th, 10th and 15th desorption to avoid loss of goethite suspension. Solutions after successive desorption steps were analysed for Fe and Cd using FAAS and graphite furnace spectrophotometer (GFAAS), respectively.

Table 1. Volume (ml) of DFOB (300 μM) and OA (200 μM) added to the tubes containing goethite suspension following Cd adsorption from 0, 180 and 300 μM Cd solutions at an equilibrium pH 6.0 and in the presence of 10 ml of 0.01 M Ca(NO₃)₂ as the background electrolyte.

Initial Cd solution concentration (μM)		0.01 M Ca(NO₃)₂	DFOB+Ca(NO₃)₂	OA+ Ca(NO₃)₂	DFOB+OA+ Ca(NO₃)₂
0	(Cd0)	10	1+10	1+10	1+1+10
180	(Cd180)	10	1+10	1+10	1+1+10
300	(Cd300)	10	1+10	1+10	1+1+10

Results and discussion

Characterization of goethite

Synthesized material was characterized for its crystalline phase by XRD. X-ray diffraction pattern showed that goethite was the only crystalline phase present in the synthesized material (Figure 1a). Relatively flat background in the sample indicated no amorphous material was present in the sample. Transmission electron microscopy showed needle shape crystals of goethite (Figure 1b). The average size of multidomainc crystal was approximately 0.7 μm. Specific surface area of goethite as measured by the N_2-BET method, was 71 m^2/g. The point of zero salt effect (PZSE) was found at pH 8.25.
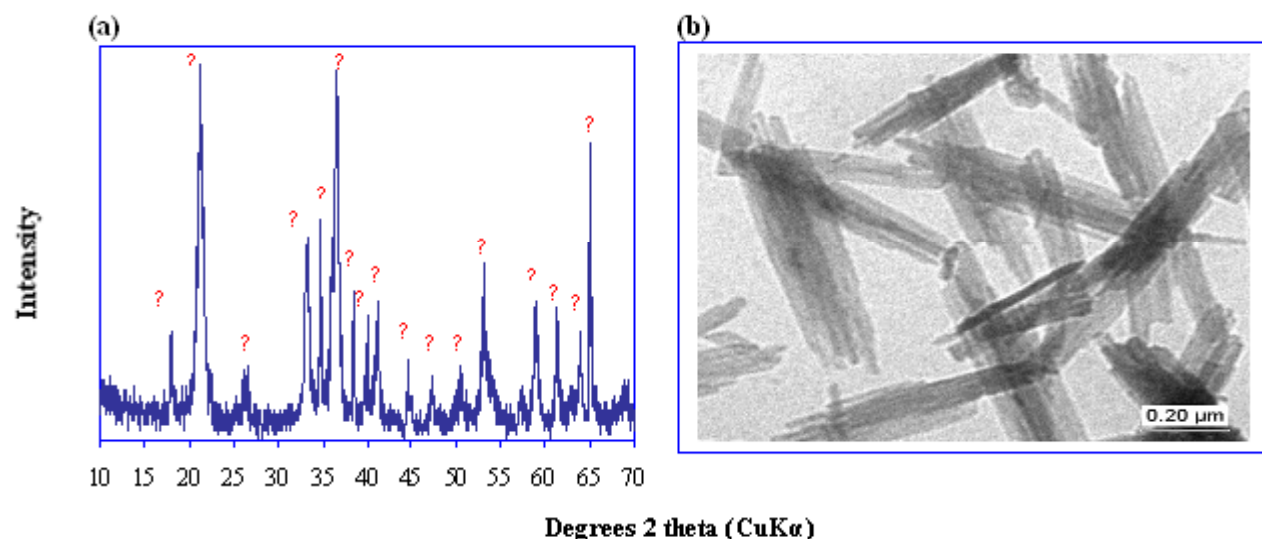
Figure 1. (a) X-ray diffraction pattern of synthetic goethite used for the Cd adsorption-desorption study. All the marked peaks (○) belong to goethite and there is no evidence for the presence of amorphous material; (b) TEM micrograph of synthetic goethite showing multidomainic crystals of acicular morphology.

Cadmium adsorption

The amounts of Cd adsorbed at the equilibrium pH 6.0 from initial concentrations of 180 and 300 μM Cd were 4.16 and 5.98 mmoles/kg, which constituted 60 and 51% of Cd in the initial solutions, respectively.

Cadmium desorption

Cadmium desorption isotherms and amount of remaining Cd (not desorbed) on goethite from Cd180 and Cd300 samples after 15 successive desorption steps at the equilibrium pH 6.0 are shown in Figure 2. For both initial Cd concentrations, the amount of Cd desorbed at each step of desorption was higher in the case of DFOB and OA than control (i.e. Ca(NO₃)₂ only). After 15 successive desorptions, the amount of Cd that did not desorb from Cd180 in the presence of 300 μM DFOB was 1.23 mmoles/kg compared with 2.26 mmoles/kg in control. In the presence of 200 μM OA, the amount of Cd desorbed was found to be even higher and Cd remaining on goethite was 0.96 mmoles/kg. In the case of the combined treatment of DFOB and OA, the amount of Cd desorbed was slightly higher than the individual DFOB and OA treatment and Cd remaining on goethite was 0.90 mmoles/kg (Figure 2a). The trend in Cd desorption for various treatments was similar for Cd300 sample (Figure 2b).
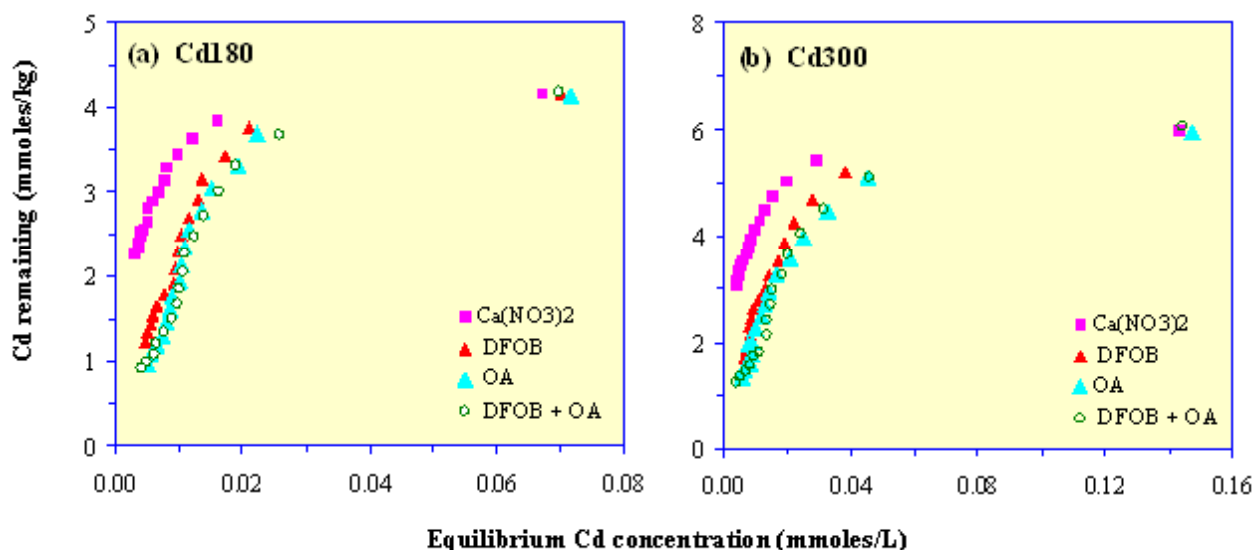
Figure 2. Amount of Cd remaining (i.e. not desorbed) on goethite with and without DFOB and OA, and the combination of both at an equilibrium solution pH 6.0 from (a) Cd180 and (b) Cd300 samples using 0.01 M Ca(NO₃)₂ as the background electrolyte.

Cumulative Cd desorption after 15 successive desorptions from Cd180 and Cd300 samples is shown in Figure 3. The graph shows increased Cd desorption from goethite with individual and combined treatments of DFOB and OA than the control. It is clear from the figure that the trend in cumulative desorption was not affected by the amounts of initially adsorbed Cd on goethite. The total Cd desorption from goethite for Cd180 (4.16 mmoles/kg) in presence of 300 μM DFOB was 70%, which was significantly higher than that in control (46%). Enhanced Cd desorption could be due to the breakdown of Cd-Fe complex as a result of goethite dissolution. Kraemer *et al.* (1999) speculated that three hydroxamate groups in DFOB coordinate to surface Fe(III) centres independently while promoting goethite dissolution. The effect of DFOB on Fe oxide mineral dissolution may be due to the formation of hexadentate mononuclear surface complexes that enhance and play a significant role in mineral dissolution (Zinder *et al.* 1986). Neubauer *et al.* (2002) reported goethite mobilization due to DFOB was more dominant near neutral pH. They found weaker stability constants for DFOB-Cd complexes than DFOB-Fe complexes in the goethite suspension, which are responsible to release Cd upon their breakdown. This was supported by Fe analysis results in the equilibrium solution of goethite after each desorption step for two Cd concentrations (Figure 4). The results show higher Fe concentrations in the presence of 300 μM DFOB than OA and control (i.e. (Ca(NO₃)₂) samples . For example, Fe concentrations at Cd180 in the presence of 300 μM DFOB and control (Ca(NO₃)₂ ranged between 145-299 and 42-86 μM, respectively (Figure 4a, b). Slightly higher Fe concentrations were found from Cd300 in the presence of 300 μM DFOB (142-506 μM) with respect to control (61-129 μM) (Figure 4c). Iron concentrations in equilibrium solution from Cd0 were less than the Cd180 and Cd300, in all the treatments, showing the effect of increased Cd concentration on goethite dissolution (Figure 4a). This shows that increased Cd concentration promotes goethite dissolution under the same set of environmental conditions.

There was very small difference between the total amounts of Cd desorbed after 15 successive desorption steps from Cd180 in the presence of 200 μM OA (77%) and the combination of DFOB and OA (78%). In the case of OA, Fe concentrations in equilibrium solutions from Cd180 and Cd300 varied from 19-111 and 22-107 μM, respectively, which were higher as compared to respective control and ranged between 58-109 and 61-129, respectively.
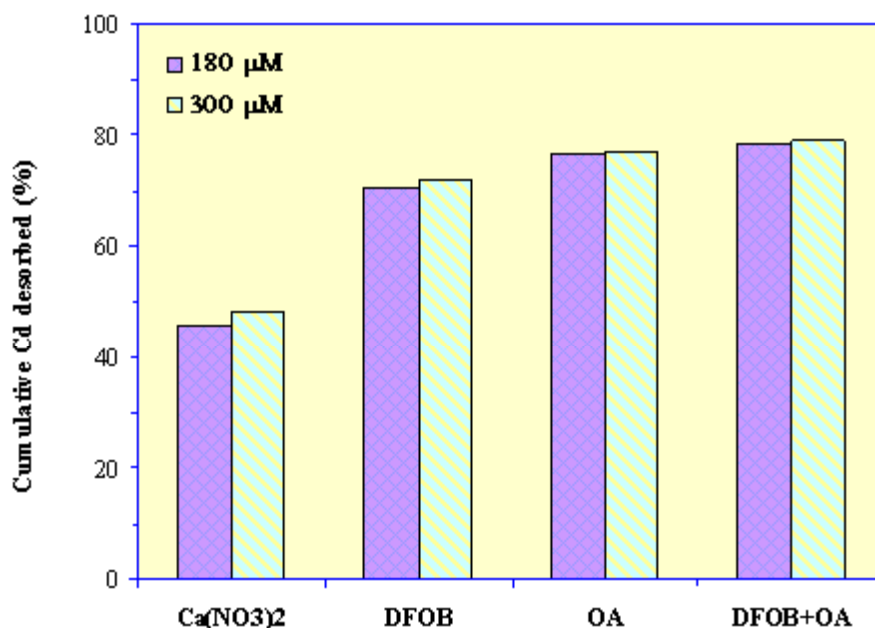
Figure 3. Cumulative Cd desorption at an equilibrium pH 6.0 from goethite with 0.01 M Ca(NO$_3$)$_2$ (control) and 0.01 M Ca(NO$_3$)$_2$ in the presence of DFOB, OA, and combination of both from Cd180 and Cd300 samples.

Equilibrium solution pH measured after 1st, 5th, 10th and 15th desorption steps progressively decreased from pH 6.0 to 4.8 (at both the initial Cd concentrations) in the presence of OA and the combination of DFOB and OA (Figure 5). In case of control and DFOB, the equilibrium pH changed only slightly i.e. it increased from 6.0 to 6.2 in control and decreased from 6.0 to 5.7 in case of DFOB. The decrease in equilibrium solution pH in case of OA appears to be the main reason of increased Cd desorption. Zinder *et al.* (1986) reported enhanced goethite dissolution in the presence of oxalate due to the bidentate surface binding between Fe(III) and oxalate ions. This surface reaction mechanism involve the detachment of Fe(III) from the goethite as a result of surface protonation and surface complex formation due to the transference of electron from oxalate to the surface of Fe(III), which converts Fe(III) to more soluble Fe(II) form. According to Reuter and Purdue (1977) enhanced metal availability in the presence of OA due to decrease in equilibrium pH may be the result of weakening of metal- RCOO⁻ binding. Equilibrium solution pH in case of control from Cd0 was slightly higher and increased to 6.2.

The desorption of Cd with combined addition of DFOB and OA from Cd180 and Cd300 were slightly higher (78 and 79%, respectively), than with the individual DFOB (70 and 72%), and OA (77% from Cd180 and Cd300) treatments. Iron concentrations with the combined treatment of DFOB and OA were also greater than DFOB which suggest that DFOB induced dissolution of goethite occurs in this treatment and may be enhanced by decreased solution pH to 4.8 in the presence of OA (Figure 5). This is supported by increased Fe concentrations in the equilibrium solution, higher (170-387 μM) than the OA alone from Cd180 samples (Figure 4b). Iron analysis of solutions from Cd300 samples during 15 extractions showed the same trend but interestingly higher concentrations were found in control, DFOB, OA and the combination of both treatments and Fe concentrations ranged between 61-129, 142-506, 22-107 and 223-566 μM, respectively (Figure 4c). Desferrioxamine B and OA, in combination, significantly influenced Cd desorption from goethite as a result of adsorption and release mechanism of both ligands from the surfaces of goethite (Cervini-Silva and Sposito 2002). In our study, as reported by Cervini-Silva and Sposito (2002), high concentration of DFOB (300 μM) made complexes with dissolved Fe(III), released as a result of oxalate promoted dissolution of goethite in the presence of 200 μM. Desferrioxamine B may also assist in removing oxalate from Fe-oxalate complexes and enhanced binding of uncomplexed oxalate ligands again with goethite to accelerate goethite dissolution.
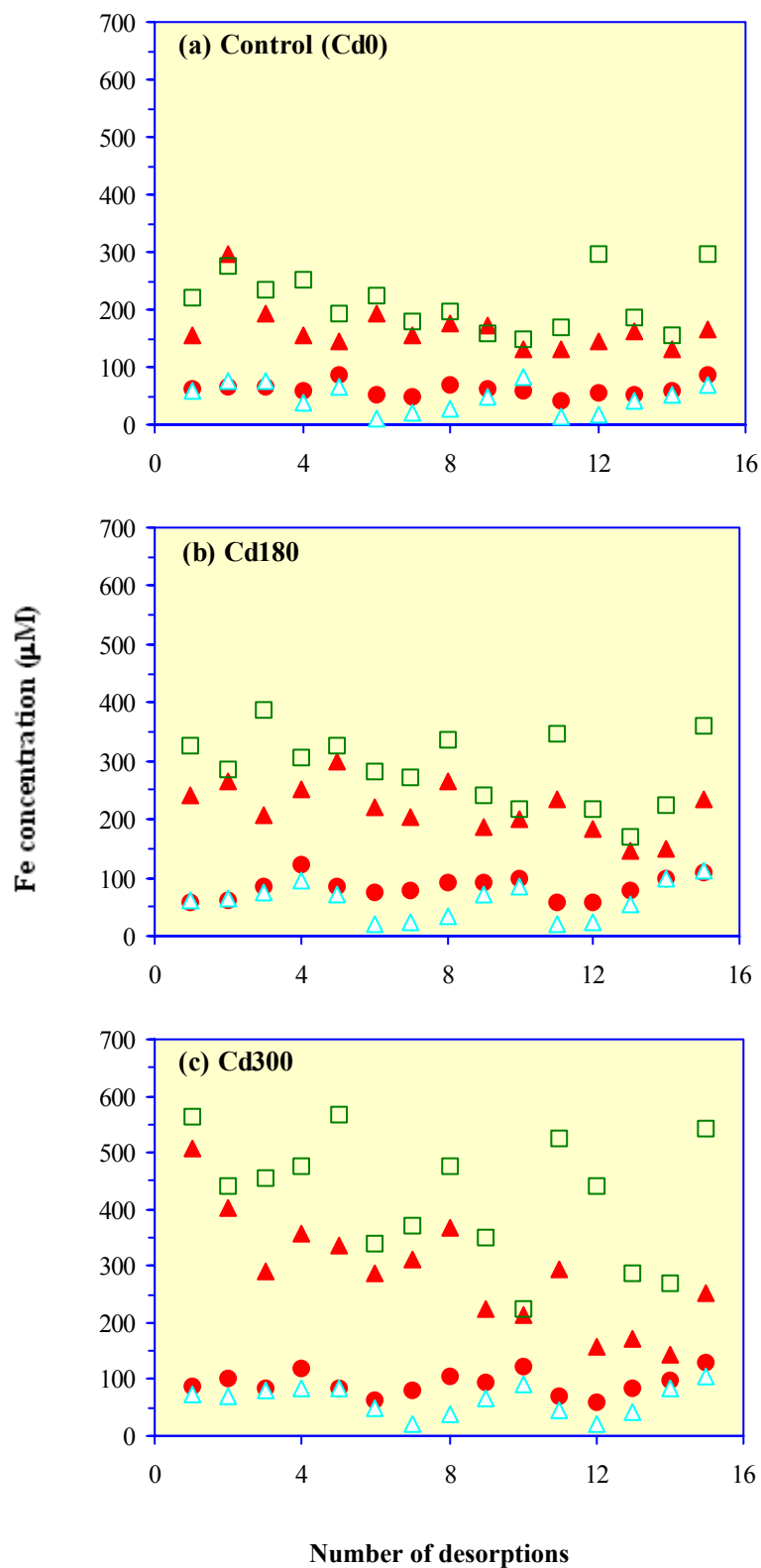
Figure 4. Iron concentrations in equilibrium solutions of (a) Cd0, (b) Cd180 and (c) Cd300 during 15 successive desorptions with 0.01 M Ca(NO₃)₂ (●) and 0.01 M Ca(NO₃)₂ in the presence of 300 μM DFOB (▲), 200 μM OA (△), DFOB+OA (□).
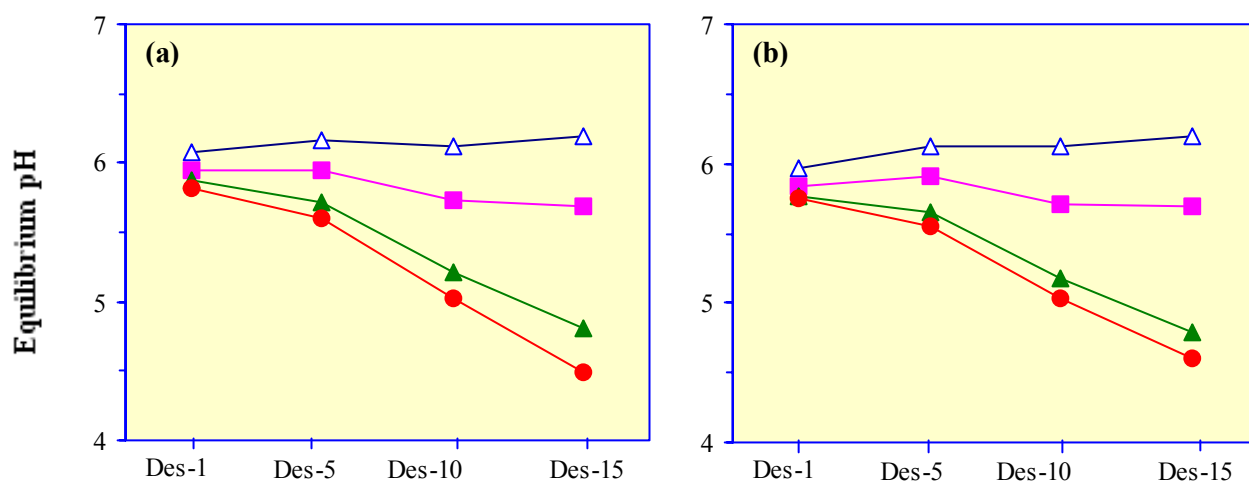
Figure 5. Equilibrium solution pH of control (0.01 M Ca(NO₃)₂) (Δ), DFOB (■), OA (▲) and DFOB + OA (●) samples measured after desorption 1, 5, 10 and 15 during Cd desorption procedure from (a) Cd180 and (b) Cd300 samples.

In all treatments, after 15 successive desorptions, more than 20% Cd could not be desorbed. While it is possible that some more Cd could have desorbed if desorption cycles were continued. The Cd desorption isotherms in Figure 2, especially in case of OA and OA+DFOB treatments from Cd180 and Cd300, do not appear to be heading towards the origin. This indicates that a fraction of the adsorbed Cd would not be desorbed. There is possibility that the fraction of remaining Cd on the goethite may be the result of Cd entrapment in the cracks or defects in goethite structure (Bruemmer *et al.* 1988; Mustafa *et al.* 2004).

Conclusions
Cadmium desorption was higher in the presence of DFOB than control (0.01 M Ca(NO₃)₂ alone) in both Cd180 and Cd300 samples. Iron concentrations in equilibrium solutions were higher in the presence of DFOB than control, indicating that increased Cd desorption may be due to goethite dissolution. The increased Cd desorption in the presence of OA was possibly due to the decreased equilibrium pH from 6.0 to 4.8 in the samples (Cd180 and Cd300). The effect of DFOB on Cd desorption and goethite dissolution was dominant when DFOB and OA were present together. There was little difference in the fraction of total Cd desorbed, after 15 successive desorptions, due to the amount of initially adsorbed Cd on goethite. Iron concentrations in equilibrium solutions were comparatively higher in Cd300 than Cd180 and Cd0. The study showed that organic compounds such as DFOB and OA can significantly enhance the release of adsorbed Cd from goethite. The similar mechanisms may also operate for other heavy metals.

Acknowledgement

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