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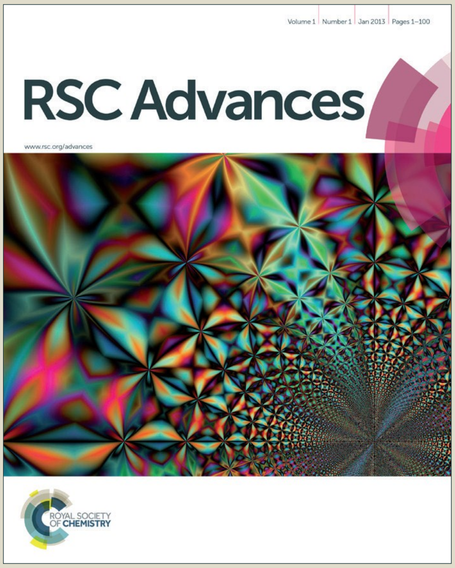

Influence of removal of organic matter and iron and manganese oxides on cadmium adsorption by red paddy soil aggregates

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Abstract: The ability of soil aggregates to adsorb heavy metals is controlled by their different component contents. However, the influence of specific components on the adsorption behavior is uncertain. In this study, organic matter and iron and manganese oxides in aggregates of different particle sizes from red paddy soil were selectively removed. The influence of these components on cadmium adsorption was also examined. Results showed that Langmuir equation could accurately describe the adsorption characteristics of Cd in bulk soil and aggregates. The < 0.002 mm fraction had the largest adsorption capacity for Cd because of its higher content of organic matter and Fe and Mn oxides. Removal of organic matter, amorphous Fe oxides or Mn oxides could cause obvious decrease in Cd adsorption, whereas an opposite result was observed for free Fe oxides removal. Removing unit mass of Fe or Mn oxides showed stronger effect on the adsorption capacity compared with that of organic matter. Desorption characteristics of Cd in various aggregates appeared to be unaffected by organic matter but more determined by free and amorphous Fe oxides.

Key words: Soil aggregates; Cd adsorption; red paddy soil; organic matter; Fe/Mn oxides

1. Introduction

Cadmium is a ubiquitous element with high toxicity to organisms. This element is more mobile and bioavailable than other metals. In the past few decades, an increasing number of anthropogenic Cd have entered soil environment. Soil contamination with Cd usually originates from various practices, such as mining, sewage sludge application and chemical fertilization[1, 2]. Recently, soil Cd pollution has become one of the most serious issues confronting rice production and soil management in some Asian countries[3, 4]. According to a previous study[5], the area of cultivated land contaminated by Cd reaches nearly 2.8×10^5 hm^2 in China. Excessive levels of Cd retained in paddy soil significantly increase the potential risk of uptake by rice, which, in turn, inevitably posts threat to human health.

Adsorption/desorption is the most important process that controls the transformation and migration of Cd in soil[6]. The major factors influencing adsorption/desorption process include soil physicochemical properties, temperature, and moisture condition[6-8]. Aggregates are the basic structure units of soil, and the ability of aggregates to adsorb/desorb heavy metals is different[9]. Soil component (e.g., organic matter or iron and manganese oxides) has an important function in deciding the adsorption capacity of soil aggregates for metal ions. Several previous studies[10-12] have indicated that the content of organic matter and Fe oxides could strongly influence the accumulation of metals among aggregates of different size fractions in contaminated soils. Huang et al.[13] also showed that the maximum adsorption capacities (obtained from the batch experiments) for Cu and Zn of aggregates of different particle sizes were positively correlated with their organic matter and free Fe_2O_3 contents; and soil organic matter (SOM) was inferred to have a larger sorption capacity toward metals compared with other soil fractions. In summary, all these aforementioned studies were based on analyzing correlations between the mineralogical properties of soil particles and their metal content or capacity to adsorb metals, whereas the effect of specific components on the affinity of metals in soil has been unexplored.

The influence of soil components on adsorption of metals can be examined in several ways, such as studying adsorption capacity of synthetic or semisynthetic pure substances[14, 15] and selectively removing a specific component from the soil and evaluating its effect by comparing the variation of metal adsorption capacity[16-18]. The former method may inaccurately reflect the sorption behavior of different soil components that are naturally formed. The latter method has already been used to evaluate the influence of organic matter and Fe and Mn oxides on Cd adsorption in several previous studies[19-22]. Elliott et al.[19] found that Fe oxides extraction reduced Cd adsorption on a wide range of soils, whereas some other researchers found that this treatment showed insignificant effect on certain acid soils[20]. Removing organic matter usually resulted in the reduction of Cd retention, and the decreasing degree also deepened on the physicochemical characteristics of the used soil[21-22]. All these reports indicated that organic matter and oxides are important in Cd adsorption, but their relative importance may be different. Selective removing technology is an effective method in evaluating the influence of various soil fractions on metal adsorption and can be helpful in further understanding the adsorption mechanism of heavy metals in soil[17, 18]. However, this method has not been applied with the subject of soil aggregates.

In the present study, organic matter and Fe and Mn oxides in aggregates of different particle sizes from red paddy soil were selectively removed by using corresponding chemical reagents. Their influence on Cd adsorption was then evaluated by comparing with the adsorption results of the untreated aggregates through batch experiments. The information provided in this study will be helpful in explaining the different adsorption behavior of various soil aggregates.

2. Materials and methods

2.1. Soil samples and aggregates fractionation

Surface soil samples (0–20 cm) were collected from a paddy field. This area is 15 km away from the center of Changsha City in Hunan Province (28º09′35″N, 112 º52′37.5″E). The study site has mean monthly air temperatures ranging from 5.26 °C in January to 29.68 °C in August and has mean annual precipitation of 1361 mm. The soil is mainly derived from the Quaternary red clay and recent alluvial deposits. No heavy metal pollution source exists nearby, and the background concentration of Cd in the soil is very low (0.07 mg/kg) [23]. Five sampling sites were selected in the paddy field of this area, and approximately 5 kg soil in each site was collected. The sampled soil was transported back to the laboratory, air dried at room temperature, and mixed thoroughly.

The soil samples were sieved to pass through a 2 mm nylon sieve and were partitioned into four aggregate–size fractions (2–0.25 mm, 0.25–0.05 mm, 0.05–0.002 mm, and < 0.002 mm), as described in a previous study [11]. Briefly, 30 g of soil sample was immersed in 150 ml deionized water and dispersed with ultrasonic (100 J/ml)[24]. The 2–0.25 mm fraction was obtained by wet sieving; the 0.25–0.05 and 0.05–0.002 mm fractions were obtained by sedimentation and siphoning; the < 0.002 mm fraction was finally obtained after centrifugation. The soil particles were collected respectively and freeze-dried. A few basic properties of soil are presented in Table 1.

2.2. Removal of organic matter and Fe and Mn–oxides

The prepared soil particles (bulk soil and aggregates) were subjected by using corresponding chemical reagents to remove various soil components. Organic matter was removed by sodium hypochlorite (NaOCl) extraction method[25]. NaOCl has several advantages over hydrogen peroxide (H_2O_2) for SOM removal; NaOCl was found to destroy more organic matter than H_2O_2 with minimal loss of Fe and Mn and little alteration of sesquioxides[26, 27]. Free Fe–oxides were removed by using dithionite–citrate–bicarbonate (DCB) method[28]. Amorphous Fe–oxides were removed by $(NH_4)_2C_2O_4$–$H_2C_2O_4$ method[29]. Mn–oxides were removed by $NH_2OH{\cdot}HCl$

method[30]. A brief description of the above-mentioned methods is presented in Table 2. All the threated residuals were repeatedly washed and then freeze–dried and grounded to pass a 0.25 mm nylon screen.

2.3. Adsorption and desorption experiments

Original or treated soil particles were placed into a 50 ml polypropylene centrifuge tube, and 25 ml 0.01 M $NaNO_3$ solution containing a series concentration levels (1, 5, 10, 20, 50, 100, 200 mg/l) of Cd (as $Cd(NO_3)_2$) was added to each tube. The suspensions were shaken at 160 rpm for 4.0 h and kept still for 20.0 h at constant temperature of 25 ± 0.2 °C. Then, the suspensions were centrifuged and supernatant were filtrated to measure of Cd concentration. Cd adsorption was calculated as the difference between that added and that remaining in the supernatant. Langmuir and Freundlich equations[31] were applied to fit the data from the batch experiment, Eqs. (1) and (2):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{1}$$

$$q_e = K_F C_e^{1/n} \tag{2}$$

where q_e is the amount of adsorbed metal concentration at equilibrium (mg/kg); C_e is the concentration of the metal in solution at equilibrium (mg/L); q_m is the maximum adsorption amount of metal on soil (mg/kg); and K_L (L/kg), K_F (L/kg) and $1/n$ are constants.

Soil residual in centrifuge tubes containing initial $Cd(NO_3)_2$ of 200 mg/l was used for desorption experiment. After the supernatant was discarded, 25 ml 0.01 M $NaNO_3$ was added to the tubes to replace the adsorbed Cd^{2+}. The followed procedures (shaken, equilibration, centrifugation and separation) were the same as those in the adsorption experiments. The total desorption capacity of the adsorbed Cd was obtained by repeating this sequence of operation for three times.

2.4. Analytical methods

Soil pH was measured at a soil/solution ratio of 1:2.5 using a HI 3221 pH meter (Hanna Instruments Inc., USA). SOM was determined by $K_2Cr_2O_7$ oxidation method[32]. Cation exchange capacity (CEC) was determined by $BaCl_2$ displaced method[33]. Free Fe–oxides (Fe_d) were determined by Na_2S_2O4-$Na_3C_6O_7$ extraction method[28]. Amorphous Fe–oxides (Fe_o) were determined by $(NH_4)_2C_2O_4$-$H_2C_2O_4$ method[29]. Fe, Mn, and Cd (after HNO_3–HF–$HClO_4$ digestion) content in soil were determined using atomic absorption spectrophotometer (AA700, PerkinElmer, USA). BET surface area was measured by a NOVA 2200e surface area and pore size analyzer (Quantachrome Inc., USA). All the glassware used in experiments were) thoroughly soaked overnight in HNO_3 solution (3%, v/v and were rinsed with deionized water. All the experimental data were the average of triplicate determinations. Statistical analyses were conducted using SPSS 10.0 software. Comparisons of the means were conducted by Duncan's multiple range test at the $p \leq 0.05$ level.

3. Results and discussion

3.1. Soil properties

Red paddy soil is a typical agricultural soil that is widely distributed in subtropical area with slight acidity (pH = 5.86). This type of soil is considered to have a strong retention capacity for metal ions because of its relatively high organic matter content (56.37 g/kg), which is far above the mean level[34] (22.90 g/kg) in northeastern China. The 0.25–0.05 mm (23.45%) and 0.05–0.002 mm (49.68%) aggregates were the dominant fractions of the sampled paddy soil. Among all the fractions, the clay size fraction (< 0.002 mm) showed the highest values in content of organic matter, Fe–oxides, free Fe–oxides, Mn–oxides, as well as CEC and BET surface are, but the lowest in amorphous Fe–oxides content. Fine soil particles were also found to have higher organic content in many other types of soil[35, 36]. Smaller aggregates process stronger ability to protect organic matter and thus retain more carbon matter[37]. The Fe_o/Fe_d ratio ("activity ratio"), which is used as a relative measure of the degree of aging or crystallinity of free Fe–oxides, indicates that the activity of free Fe oxides in the < 0.002 mm fraction was the lowest. Removal of components could reduce the surface area of soil particles to different degrees. For example, the surface areas of bulk soil after the treatment were 8.1 (organic matter removal), 6.65 (free Fe–oxides removal), 10.08 (amorphous Fe–oxides removal), and 11.01 m^2/g (Mn–oxides removal). By contrast, free Fe–oxides removal caused the most decrease in surface are.

3.2. Adsorption isotherm

The experimental data and adsorption isotherms for Cd adsorption onto original bulk soil and aggregates are shown in Fig. 1. The amount of Cd adsorbed in soil showed a gradual ascending trend in general. Cd was nearly adsorbed completely under the condition of low initial concentration (0–50 mg/l) addition. Moreover, the adsorption amount in soil showed no apparent increase when the initial concentration exceeded 50 mg/l, which meant the adsorption had gradually reached the balance value. The variation trend of the adsorption curves was similar to that obtained in many other batch experiments that were used to examine the adsorption characteristic of heavy metals in various soils[38-40]. The fitting accuracy of Langmuir ($0.9168 \le R^2 \le 0.9978$) model is better than that of Freundlich model ($0.8417 \le R^2 \le 0.9815$) (Table 3). As listed in Table 3, the maximum adsorption capacity (q_m) of different particle size fractions decreased in the following order: (< 0.002 mm) > bulk soil > 2–0.25 mm >0.05–0.002 mm > 0.25–0.05 mm. The maximum adsorption capacities (q_m) of the < 0.002 mm fraction was 1.21–1.44 times than that of other fractions. Compared with the date obtained in our previous study[13], this range was close to the values of Cu (1.14–1.49) but less than that of Zn (1.45–2.22) under the same experimental conditions. In addition, the adsorption capacity of red paddy soil for the three metals followed the order: Cu > Zn ≈ Cd. Cu is generally adsorbed and retained to a higher extent than Zn and Cd in soils[41, 42]. The different adsorption behavior of the three metals in soil mainly depends on their ionic potential, hydrolysis, and softness [43].

Spearman correlation analysis was performed to evaluate the relationship between q_m and the soil component content in bulk soil and aggregates (Table 4). The results showed that the maximum adsorption capacity (q_m) was significantly related to the organic matter content ($p < 0.01$), but had no correlation with the contents of free Fe–oxides, amorphous Fe–oxides, and total Fe– or total Mn–oxides. Organic matter appeared to be a more important factor in determining the adsorption capacity than the other soil components. Similar result was also obtained for Cu and Zn[13]. Organic matter has been verified to influence the retention and release ability of metals in soil[43], and is also considered to be the major contributor to the ability of soils for retaining heavy metals in an exchangeable form because of its high CEC[45]. However, whether the other components had no effect on the adsorption capacity could not be determined based on the result of correlation analysis alone. In fact, clay and hydrous oxides of Fe and Mn can also adsorb foreign metal ions through different binding mechanisms. Ion exchange and surface complexation and precipitation are the main process controlling the adsorption behavior of metals in SOM. As for clay and metal oxyhydroxides, specific adsorption and cation exchange are the main mechanisms[6].

3.3. Effect of removal of different components on Cd adsorption

The results of Cd adsorption by the treated bulk soil and aggregates are shown in

Fig. 2. Removal of different components (organic matter (Fig. 2(a)), free Fe–oxides (Fig. 2(b)), amorphous Fe–oxides (Fig. 2(c)) and Mn–oxides (Fig. 2(d)) insignificantly influenced the general adsorption characteristics of Cd, and Langmuir model was also more suitable to fit the experimental data ($0.9168 \leq R^2 \leq 0.9978$, Table 5). All the treatments caused decrease in Cd adsorption except for the free Fe-oxides removal. Through the calculated q_m, the variation in adsorption ability before and after specific component removal treatment can be quantitatively compared. The decrease ($p < 0.05$) in q_m was 456.63–858.66, 200.17–477.75 and 178.69–438.66 mg/kg under the condition of organic matter, amorphous Fe-oxides and Mn-oxides removal, respectively. Organic matter removal could reduce the adsorption of Cd to the highest extent. Comparatively, the decrease amounts caused by the removal of amorphous Fe-oxides or Mn–oxides were far less and their values were very close (no significant difference was observed between them). Free Fe–oxides removal caused significant increase (1441.38–2229.39 mg/kg) in Cd adsorption ($p < 0.05$). Linear regression analysis reveals that the decrease/increase in q_m caused by removal treatment was positive with the corresponding component content in soil particles ($b > 0$) (Fig. 3). This result reveals that organic matter, and Fe– and Mn–oxides are all influential soil components involved in Cd adsorption in red paddy soil. The decease/increase amount of Cd concentrations in soil phase caused by unit removed component content (judged from the slops in regression equations in Fig. 3) followed the order: amorphous Fe–oxides > Mn–oxides > free Fe–oxides > organic matter.

Both lab and field studies have shown that organic matter is one of the most important soil properties affecting Cd adsorption in soil[21, 46-47]. Usually, the higher the organic content in soil, the more metal ions can be adsorbed. Zhao et al. [22] also found that organic matter removal produced a significant decrease in Cd adsorption of soil, although they used different types of soil and H_2O_2 as the organic matter removal reagent. He et al. [48] indicated that the addition of organic matter increased soil CEC and decreased soil pH, which may result in changes in the solid phase of Cd. The variation trend of Cd adsorption capacity depends on the content of organic matter in soil. Reid and McDuffie[20] found that treatment of illite with 30% H_2O_2 to remove organic matter produced no significant change in adsorption using 100 ppb Cd. Organic matter contents of the soil would be relatively low, and their adsorption capacity for Cd was low. Notably, red paddy soil is in relatively high organic matter content, which would obviously influence the adsorption capacity. For aggregates of different particle–sizes, organic matter removal produced the most variation in the < 0.002 mm fraction. This result further demonstrates the importance of organic matter because its content was the highest in this fraction.

Free Fe–oxides in soils mainly present specific adsorption for metal ions[18]. However, the obtained result appeared to contradict the widely held view that Fe–oxides have an important function in fixing metal ions in soil. Free Fe–oxides removal by DCB procedure may cause different effects on the adsorption capacity, which also depends on the physicochemical properties of the used soil. Silveira et al. [49] observed that Cu adsorption significantly decreased in some tropical soils with high Fe oxide content. Elliot and Liberati[50] found similar result for Cd when investigating acidic soils from the Altantic Coastal Plain. Meanwhile, in the considerable research conducted by Elliott et al.[17], Shuman[51], and Agbenin and Latifatu[52], Fe–oxides removal by DCB procedure increased the adsorption capacity of soils for Cd and other metals. As concluded in the above–mentioned works, the increase phenomenon could be attributed to two reasons. First, DCB treatment eliminated Fe oxide/hydroxide, which, in turn, exposed additional sites for heavy metal adsorption; second, the adsorption sites on the free Fe–oxides coating were not as numerous as those released when the coating were removed. On the one hand, Fe oxides in soils are usually positive charged; removal of this component could low the zero points of charges (ZPC) of soil and exposed negative surface charged that was previously combined by Fe–oxides[53]. On the other hand, the DCB extraction procedure could release additional exchange sites by removing organically complexed Fe/Al and by stripping interlayer Fe/Al hydroxypolymers from silicate clay minerals[54].

Amorphous Fe-oxides are more active fractions in free Fe–oxides, and are characterized as huge surface area and as specific adsorption for cation and anion[55]. Similar to organic matter, amorphous Fe–oxides removal decreased the adsorption ability, which was just only contrary to the result obtained for free Fe oxides removal. The possible reason was the affinity of amorphous Fe–oxides for Cd was much higher; extraction of this part may expose some new adsorption sites that were previously combined by amorphous Fe–oxides. However, the amount of the new adsorbed Cd was less than the adsorption capacity of the removed amorphous Fe–oxides.

Consequently, a significant decrease was observed after amorphous Fe–oxides were removed. For Mn–oxides, the adsorption ability of different soil particles for Cd also decreased, which may be due to the reduction of available adsorption sites owing to the removal treatment. Mn–oxide minerals exist widely in soils and sediment in various forms of scattered weak crystalized aggregates, nodules, and coatings etc[56]. These minerals are commonly believed to have lower ZPC, high negative charge amount, and large surface area; these properties allow these minerals to have high adsorption capacity towards metal ions[57].

Although organic matter removal could reduce the adsorption capacity to the highest extent, the removal of Fe– and Mn–oxides exhibited the best ability in influencing the adsorption of Cd in soil. By contrast, the < 0.002 mm soil aggregate contained more organic matter, free Fe– and Mn– oxides. Accordingly, this fraction of aggregate can retain more Cd in soil. More attention should be paid to this fraction of aggregate because it can easily migrate in the environment. Furthermore, the combined metals in some specific components can be released as a result of the ambient condition variation. For example, Fu et al.[58] found that the adsorption capacities of Mn–oxides for Cd decreased by nearly 80% when pH changed from 8.0 to 5.5.

3.4. Effect on desorption after removal of different components

The calculated maximum adsorption capacity (q_m) was approximately equal to the adsorption amount under the initial concentration of 200 mg/l. Thus, the desorption experiment of different treated soil particles was conducted only with this level of Cd concentration, and the corresponding result was compared with the values in adsorption experiment. Desorption rate can reflect the nonspecific adsorption degree of metals in soil. As shown in Fig. 4, the desorption rates of the 0.25–0.05 mm fraction was the lowest and that of the 0.05–0.002 mm fraction was the highest. Removal of different components could increase or decrease the desorption rates, which depended on the particle size of the aggregates. For example, free Fe–oxides removal increased the desorption rate in the 2–0.25 mm fraction but decreased the rate in the 0.05–0.002 mm fraction. Specific adsorption is usually controlled by Fe– and Mn– oxides. Organic matter appeared to insignificantly affect the desorption rate (the desorption rates of untreated soil and organic matter removal were very close among all particle sizes). Fe-oxides (free and amorphous Fe–oxides) exhibited more influence on the desorption rate in the 0.05–0.002 mm fraction. After the Fe–oxides removal, nonspecific adsorption sites in these fractions decreased, which, in turn, led to a higher desorption rate. Apart from the < 0.002 mm fraction that had the extremely high adsorption capacity, the 0.05–0.002 mm fraction had the highest contents of free Fe–oxides and amorphous Fe–oxides content. This phenomenon was the reason why the desorption rate in this fraction was the most influenced.

4. Conclusion

Selective removal technology was applied and batch experiments were conducted to study the influence of different components (organic matter and Fe and Mn oxides) on Cd adsorption by soil aggregates. The adsorption characteristics of Cd in bulk soil and aggregates of different particle sizes could be accurately described by Langmuir equation regardless whether a specific component was selectively removed. All the removal treatments caused a decrease in Cd adsorption except for the free Fe–oxides removal. This result revealed that these components played different important roles in controlling adsorption behavior. Organic matter contributed most to the adsorption capacity but appear to insignificantly affect the desorption rate. By contrast, Fe– and Mn–oxides showed stronger influencing ability in determining the adsorption capacity of Cd in red paddy soil. The < 0.002 mm soil aggregate contained more organic matter, free Fe– and Mn–oxides. Thus this fraction of aggregates can retain more Cd in soil. More attention should be paid to the fine soil aggregates (the 0.05–0.002 mm and < 0.002 mm fractions) that contain higher Fe and Mn–oxides and that are easier to migrate in environment.

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Figure captions:

Fig. 1. Adsorption isotherms for Cd onto bulk soil and aggregates; the experimental data are reported as points and Langmuir model curves.

Fig. 2. Adsorption isotherms of Cd onto treated bulk soil and aggregates (organic matter removal (a), free Fe–oxides removal (b), amorphous Fe–oxides removal (c), and Mn–oxides removal (d)); the experimental data are reported as points and Langmuir model curves.

Fig. 3. Correlation between the decrease/increase amount of q_m and different soil component contents.

Fig. 4. Desorption rates of Cd in aggregate particles after different component removal treatments.

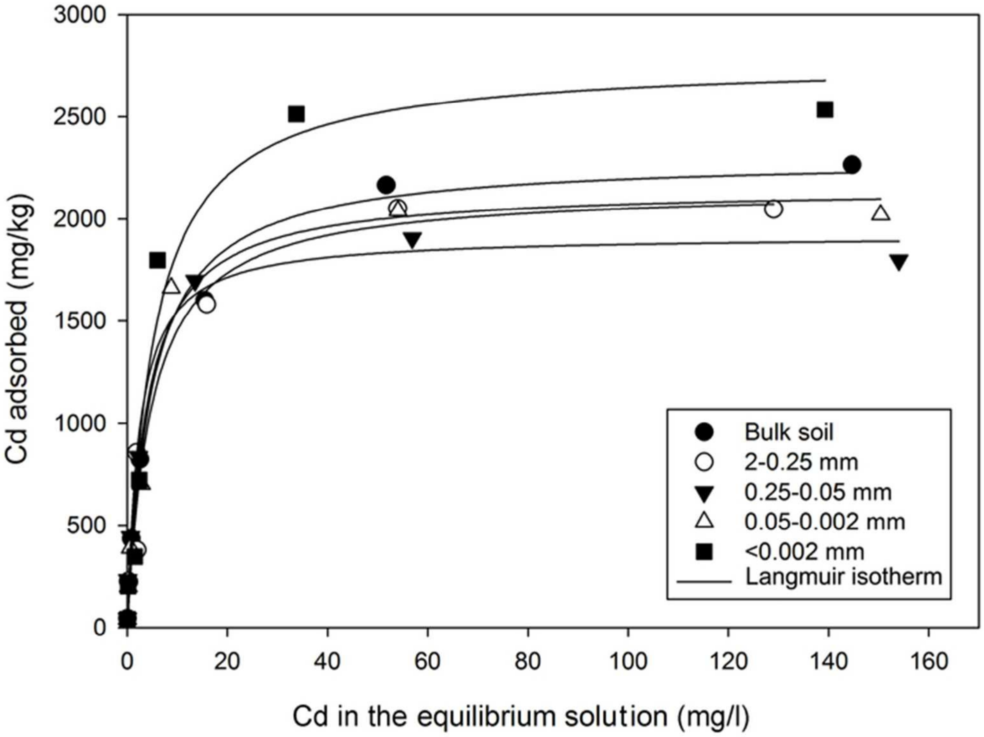

Fig. 1 Adsorption isotherms for Cd onto bulk soil and aggregates, the experimental data are reported as points and Langmuir model by curves.
61x45mm (300 x 300 DPI)

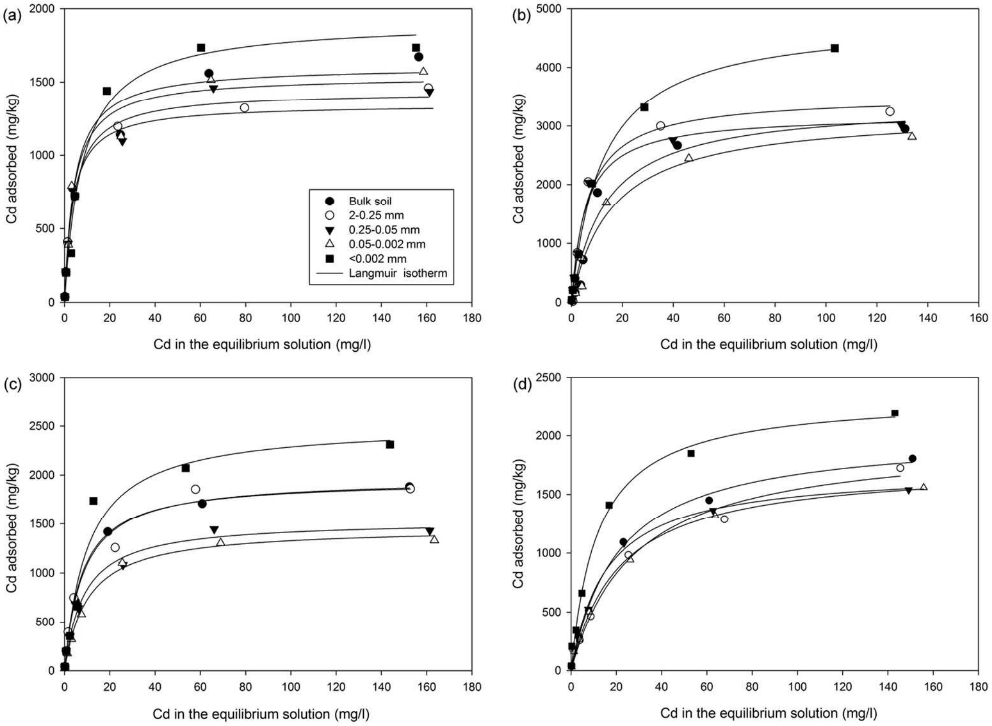

Fig. 2 Adsorption isotherms of Cd onto treated bulk soil and aggregates (organic matter removal (a), free Fe-oxides removal (b), amorphous Fe-oxides removal (c), Mn-oxides removal (d)), the experimental data are reported as points and Langmuir model curves.
125x91mm (300 x 300 DPI)

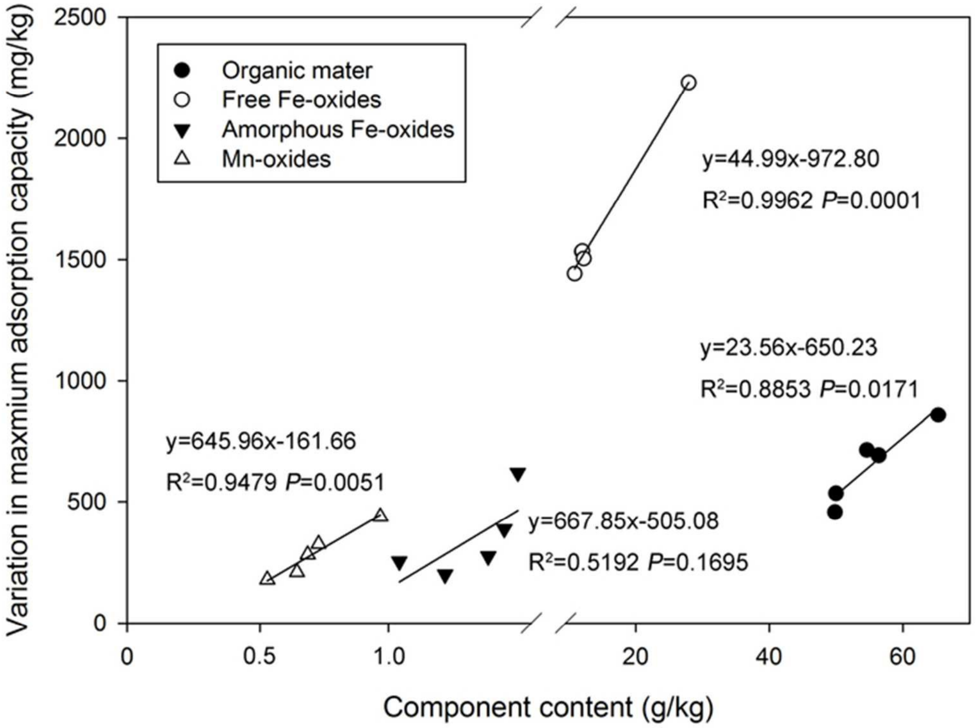

Fig. 3 Correlation between the decrease/increase amount of qm and different soil component content.
61x45mm (300 x 300 DPI)

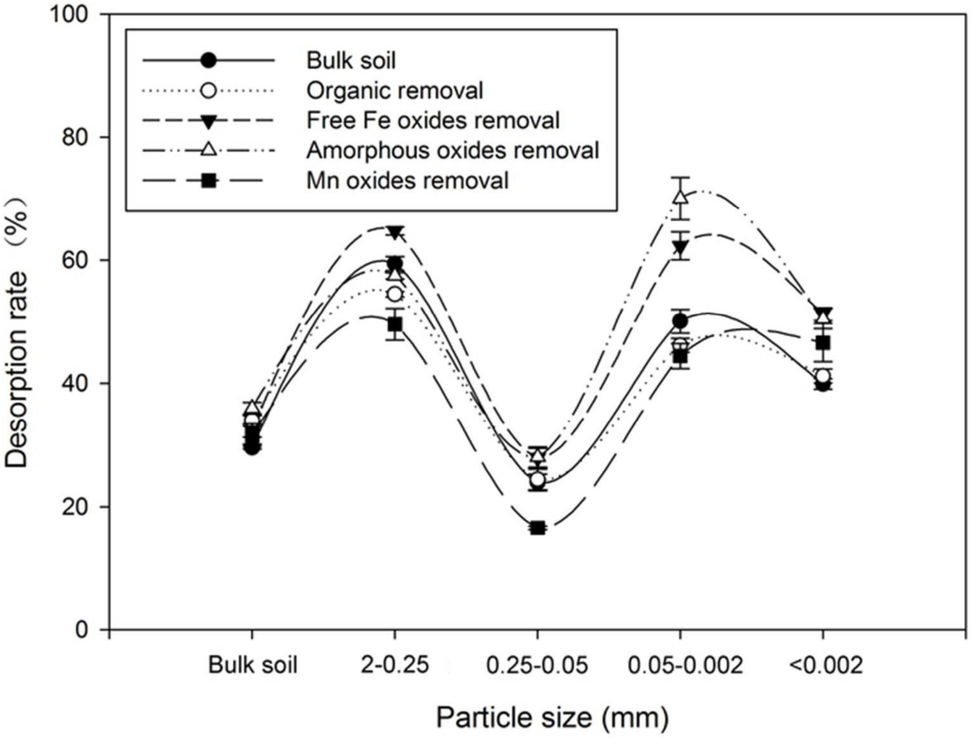

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Table 1

Physicochemical properties of bulk soil and various size fractions of aggregates.

Particle size (mm)	SOM (g/kg)	CEC (cmol(+)/kg)	Fe_d (g/kg)	Fe_o (g/kg)	Fe-oxide (g/kg)	Mn-oxides (g/kg)	BET surface area (m^2/g)	Cd (mg/kg)	%
Bulk soil	56.37	41.23	11.97	1.34	50.71	0.67	16.24	0.20	-
2—0.25	54.62	43.16	12.03	1.18	54.08	0.52	13.96	0.22	10.07
0.25—0.05	49.84	39.93	10.86	1.40	47.50	0.63	15.77	0.26	23.45
0.05—0.002	50.00	40.35	12.22	1.45	37.01	0.71	15.09	0.19	49.68
< 0.002	65.30	51.05	27.95	1.01	75.29	0.94	30.10	0.27	16.80

SOC: soil organic matter; CEC: cation exchange capacity. %: mass percentage; Fe_d: free Fe–oxide; Fe_o: Amorphous Fe–oxides.

Table 2

Methods for removal different soil components.

Soil component	Chemical reagents	Soil/solution	Reaction conditions
Organic matter	6% NaOCl (pH=8)	1:20	Room temperature, 8h shaking, repeated 4 times
Free Fe-oxides	0.3M $Na_3C_6HO_7 \cdot 2H_2O$+1 M $NaHCO_3$+$Na_2S_2O_4$	1:20	80 °C boiling in H_2O bath, 15 min, repeated thrice
Amorphous Fe-oxides	0.2 M $(NH_4)_2C_2O_4$+0.2 M $H_2C_2O_4$ (pH =3)	1:50	Room temperature, 4h shaking in dark, repeated thrice
Mn-oxides	0.1 M $NH_2 \cdot OH \cdot HCl$ (pH =2)	1:20	Room temperature, 30 min shaking, repeated thrice

Table 3

Langmuir and Freundlich model parameters and R-squared values calculated from isotherm experimental data of Cd.

Particle size (mm)	Langmuir			Freundlich		
	K_L(l/mg)	q_m(mg/kg)	R^2	K_F (l/kg)	n^{-1}	R^2
Untreated soil particles						
Bulk soil	0.2095	2299.66	0.9905	611.24	0.2865	0.9364
2–0.25 mm	0.2090	2149.57	0.9662	592.10	0.2738	0.8945
0.25–0.05 mm	0.4141	1920.18	0.9857	688.34	0.2233	0.8704
0.05–0.002 mm	0.2105	2080.14	0.9875	599.05	0.2664	0.9115
<0.002 mm	0.1970	2774.35	0.9681	746.22	0.2744	0.8417

Table 4

Spearman correlation analysis among q_m and different soil component content.

	q_m	SOM	Fe_d	Fe_o	Fe–oxides	Mn–oxides
q_m	1.000					
SOM	1.000^{**}	1.000				
Fe_d	0.600	0.600	1.000			
Fe_o	-0.800	-0.800	-0.400	1.000		
Fe–oxides	0.800	0.800	0.400	-1.000^{**}	1.000	
Mn–oxides	0.500	0.500	0.700	-0.100	0.100	1.000

**. Correlation is significant at the 0.01 level (2-tailed).

Table 5

Langmuir and Freundlich adsorption parameters of Cd in different aggregates after soil components were selectively removed.

Particle size (mm)	Langmuir			Freundlich		
	K_L(l/mg)	q_m(mg/kg)	R^2	K_F (l/kg)	n^{-1}	R^2
Organic matter removal						
Bulk soil	0.2294	1608.51	0.9718	419.84	0.2907	0.9420
2–0.25 mm	0.2390	1435.69	0.9943	398.66	0.2722	0.9144
0.25–0.05 mm	0.2114	1463.56	0.9835	399.75	0.2762	0.9229
0.05–0.002 mm	0.2395	1541.82	0.9718	417.98	0.2813	0.9213
<0.002 mm	0.1239	1915.69	0.9843	421.87	0.3086	0.8672
Free Fe–oxides removal						
Bulk soil	0.0407	3831.81	0.9168	484.26	0.3933	0.8495
2–0.25 mm	0.1518	3684.03	0.9704	701.85	0.3416	0.8448
0.25–0.05 mm	0.1715	3361.56	0.9806	704.54	0.3224	0.8628
0.05–0.002 mm	0.0435	3583.15	0.9419	416.56	0.4099	0.8872
<0.002 mm	0.0815	5003.74	0.9878	694.07	0.4093	0.9473
Amorphous Fe–oxides removal						
Bulk soil	0.1335	2024.00	0.9978	424.50	0.3163	0.9221
2–0.25 mm	0.1330	1949.40	0.9811	425.57	0.3174	0.9257
0.25–0.05 mm	0.1188	1533.34	0.9903	337.10	0.3168	0.9462

0.05–0.002 mm	0.1061	1602.39	0.9915	300.25	0.3177	0.9013
<0.002 mm	0.0973	2520.46	0.9639	471.24	0.3407	0.8712
Mn–oxides removal						
Bulk soil	0.0481	2018.29	0.9952	253.64	0.4033	0.9658
2–0.25 mm	0.0363	1970.88	0.9871	196.88	0.4416	0.9815
0.25–0.05 mm	0.0649	1710.36	0.9929	270.43	0.3654	0.9399
0.05–0.002 mm	0.0476	1755.49	0.9977	219.04	0.4033	0.9628
<0.002 mm	0.0851	2335.69	0.9940	421.10	0.3477	0.9512