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Adsorption and desorption of Cu^{2+} on paddy soil aggregates pretreated with different levels of phosphate

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ABSTRACT

Interactions between anions and cations are important for understanding the behaviors of chemical pollutants and their potential risks in the environment. Here we prepared soil aggregates of a yellow paddy soil from the Taihu Lake region, and investigated the effects of phosphate (P) pretreatment on adsorption-desorption of Cu^{2+} of soil aggregates, free iron oxyhydrates-removed soil aggregates, goethite, and kaolinite with batch adsorption method. The results showed that Cu^{2+} adsorption was reduced on the aggregates pretreated with low concentrations of P, and promoted with high concentrations of P, showing a V-shaped change. Compared with the untreated aggregates, the adsorption capacity of Cu^{2+} was reduced when P application rates were lower than 260, 220, 130 and 110 mg/kg for coarse, clay, silt and fine sand fractions, respectively. On the contrary, the adsorption capacity of Cu^{2+} was higher on P-pretreated soil aggregates than on the control ones when P application rates were greater than those values. However, the desorption of Cu^{2+} was enhanced at low levels of P, but suppressed at high levels of P, displaying an inverted V-shaped change over P adsorption. The Cu^{2+} adsorption by the aggregate particles with and without P pretreatments was well described by the Freundlich equation. Similar results were obtained on P-pretreated goethite. However, such P effects on Cu^{2+} adsorption-desorption were not observed on kaolinite and free iron oxyhydrates-removed soil aggregates. The present results indicate that goethite is one of the main soil substances responsible for the P-induced promotion and inhibition of Cu^{2+} adsorption.

Introduction

Atmospheric pollutant precipitation, agricultural applications of industrial sludge and sewage, and long-term applications of mineral fertilizers and pesticides containing heavy metals, have caused the accumulation of heavy metals in farmland soils at an unprecedented rate (Luo et al., 2009), which thus poses serious risks to human health and environmental quality (Das, 2010). Studies have shown that the adsorption and desorption of heavy metals determine their retentions in the soil and the forms of heavy metals control their mobility and bioavailability in the soil (Mirlean et al., 2009). Currently, a lot of research has been done on the chemical behaviors of Cu^{2+} in soil and the prevention and the control of soil Cu^{2+} pollution. Adsorption of Cu^{2+} in soil is influenced by many environmental factors (soil surface charge, pH, ionic strength, coexisting ions, oxides, organic matter, *etc.*). The net results show the promotion or inhibition of Cu^{2+} adsorption–

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desorption by soil (Arias et al., 2005; Basta et al., 2005; Kumpiene et al., 2007).

Phosphorus (P) fertilization is one of major means to improve crop production in modern agriculture (Van Rotterdam et al., 2012). Since the 1980s, the applications of P fertilizers have increased greatly but the organic fertilizer uses have declined in most areas. In Jianghan plain of China, over 30% of farmland is P-rich, causing soil structure to change gradually (Li et al., 2007). In addition, P-containing compounds are often used for in-situ remediation of heavy metal polluted soils and it is one of the commonly used methods at home and abroad (Raicevic et al., 2005; Garrido et al., 2006; Ma et al., 2008). On one hand, P may directly interact with heavy metals to form precipitates. On the other hand, P adsorption by soil often changes surface charge properties, affecting the adsorption–desorption of metals in soil and the heavy metal bioavailability and the trace element supplies to plants (Pérez-Novo et al., 2009; Zhao and Selim, 2010). So far, there have been many investigations of phosphate adsorption impacting heavy metal adsorption by soils and soil minerals. These studies have showed that P increases soil surface negative charges and forms the coprecipitation with heavy metals on the soil surface, which could enhance the adsorbing capacity of heavy metals by soils (Pérez-Novo et al., 2011a; Tiberg et al., 2013). Pérez-Novo et al. (2009) found that the presence of large amount of P reduced the adsorption of Cu^{2+} on aluminum oxide and mineral surfaces. Li et al. (2007) noticed that the adsorption of phosphorus on goethite enhanced copper adsorption. Nelson (2012) has attributed the anion enhancement of Cu^{2+} adsorption on goethite to the formation of two ternary complexes on the surface. In these studies, the relatively high concentrations of P (greater than 100 mg/kg) have been used (Peltovuori and Soinne, 2005; Tiberg et al., 2013). They were much higher than the actual levels of P fertilizers for agricultural soils. For agricultural soils, the actual amount of P fertilizers (superphosphate) was usually less than 75 kg/km annually (Jiao et al., 2007), or about 5 mg/kg. while the usage amount of phosphates in the immobilization technology of heavy metal contaminated soil is larger, reach to 352 mg/kg (Huang et al., 2012). Thus, it is critical to study the adsorption of heavy metals by soil under low concentrations of P. In fact, a few studies have showed that P pretreatments at different concentrations had different impacts on the adsorption of heavy metals by soils. Li et al. (2006) observed that the pretreatment with the low concentrations of P suppressed the adsorption of Cu^{2+} and Cd^{2+} on hematite and had different influences for heavy metal adsorption. Currently, the most research for heavy metal on P pretreated soil was carried out using higher concentration P pretreatment, which led to increase the heavy metal adsorption capacity (Tiberg et al., 2013; Pérez-Novo et al., 2011a, 2011b) However, the effects of the heavy metal adsorption on lower concentration P preteated soil may be different from the higher concentration P preteated soil, and the mechanism should be investigated. Due to the large differences between the actual P content of soil environment, in the present study, the paddy soil aggregates from the Tai Lake region and soil minerals (goethite and kaolinite) were employed to investigate Cu^{2+} adsorption–desorption and their mechanisms by the soil aggregates and the clay minerals pretreated with different P concentrations. This work would shed light on the appropriate agricultural use of P fertilizers, the in-situ P immobilization remediation of heavy metal-polluted soils, and the environmental risk assessment of heavy metals.

1. Materials and methods

1.1. Preparation of soil aggregates

Soil was sampled at 0–20 cm from a rice paddy field near Jinjiaba Township (31°5′N, 120°46′E), Wujiang Municipality, Jiangsu, China, using an Edelman auger. The soil sample was stored in refrigerator at 4°C. Soil fractions representing coarse sand of 2.00–0.20 mm, fine sand of 0.20–0.02 mm, silt of 0.02–0.002 mm, and clay of <0.002 mm, were obtained by using the method described by Stemmer et al. (1998). In brief, 50 g soil was placed in a glass beaker containing 250 mL distilled water (soil: distilled water ratio of 1:5) and allowed to stand overnight. Then, the soil in the beaker was subject to ultrasonic dispersion at low energy of 170 J/sec for 300 sec by a probe ultrasonic disaggregator (JYD-650, Zhisun Instrument Co., Ltd., Shanghai, China). Coarse sand fraction was obtained by wet sieving. Fine sand and silt fractions were isolated by sedimentation using Stock's law. Silk and clay fractions were fractionated by centrifugation. All fraction samples were dried in a freeze-drier (Thermo Savant 100 Colin Drive, Holbrook, USA). The soil samples of <0.2 mm were sieved through 0.25 mm mesh, homogenized, and stored for use (Wang et al., 2009).

1.2. Removal of free iron oxyhydrates (Fe_d) in soil aggregates

In order to investigate the effect of soil iron oxyhydrates on adsorption of Cu^{2+} on paddy soil aggregates pretreated with phosphate, the soil aggregates was treated with removal of free iron oxyhydrates (Fe_d). Subsamples from the above soil aggregate fractions were subject to removal of free iron oxyhydrates with dithionite-citrate-bicarbonate (DCB) according to the description by Wang et al. (2009). Briefly, 1.0 g aggregate sample was placed in a 50 mL plastic tube. Then, 15 mL of 0.3 mol/L citrate and 5 mL of 1 mol/L bicarbonate were added. The tube was heated to 80°C in a water bath, followed by addition of 0.5 g dithionite. After that, the tube was stirred for 10 min, and then centrifuged after cooling. Finally, the residue was washed with the distilled water for 2 to 3 times, and dried prior to use.

1.3. Clay minerals

1.3.1. Preparation of kaolinite

Kaolin was obtained from Maoming Municipality, Guangdong, China. It was treated with 30% H_2O_2 to remove organic matter (OM). Kaolinite (<2 μm) was separated by sedimentation, dried at room temperature, homogenized and stored for later use.

1.3.2. Synthesis and characterization of goethite

Goethite used in this study was synthesized using the method described by Schwertmann and Cornell (1991). To form iron hydroxide, $Fe(NO_3)_3$ solution was rapidly neutralized by adding NaOH solution to reach pH 12.0. The resultant suspension was