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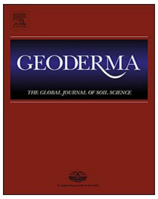

Kinetics, adsorption and desorption of Cd(II) and Cu(II) on natural allophane: Effect of iron oxide coating

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ABSTRACT

Volcanic soils are a potential source of abundant and low-cost adsorbent materials. Allophane and iron oxides are the main inorganic constituents of Andisols, soils derived from volcanic-ashes abundant in the central and southern continental Chilean territory. The present study aimed to elucidate the effect of free iron oxides on the adsorption of Cd(II) and Cu(II) from aqueous media on natural allophane (NA). Allophane samples consisted of natural allophane, obtained from a Chilean Andisol series, with (NA-FeOx) and without (NA) an iron oxide coating. Material characterisation showed that NA-FeOx was formed by nanometric (100–500 nm) sized spheres coated with an iron oxide layer that most likely consisted of a ferrihydrite-like mineral. On the other hand, NA consisted of aggregates (with particles as big as 1.0 μm) mostly constituted by allophane. The specific surface area of NA-FeOx and NA were ca. 150 and 17 $m^2\,g^{-1}$, respectively, and presented variable surface charge with an isoelectric point of 10.3. and 5.4. From the kinetic studies, equilibrium adsorption was achieved within 60 min and was almost independent of the presence of the iron oxides. Among the kinetic models evaluated, the pseudo-second order model presented a better correlation with the experimental data. The adsorption studies revealed that NA has a greater adsorption capacity of both Cd^{+2} and Cu^{+2} compared to NA-FeOx. Langmuir and Freundlich adsorption models fit the experimental data well, suggesting that the adsorption process is a combination of physical and chemical phenomena. The Freundlich constant (adsorption coefficient, K_F) values obtained confirmed the superior affinity of NA active surface sites compared to NA-FeOx. Desorption studies demonstrated that the majority of adsorbed cations were retained by the adsorbent, indicating irreversible chemical adsorption on specific active sites of the adsorbents.

1. Introduction

Pollution by metals is a growing problem due to industrial activities and anthropogenic activities. The main sources of heavy metals are mining and refining processes; the use of pigments, plastics, and Cd-Ni batteries; the foundry and electroplating industry, as well as the intensive use of phosphate fertilizers and pesticides (Hashim et al., 2011; Ihsanullah et al., 2016; Molina et al., 2009; Uddin, 2017). Once introduced into the environment, metals permeate air, soil, and water compartments. As metals are not biodegradable, they may accumulate in organisms and are toxic to the aquatic flora and fauna as well as to human beings (Hegazi, 2013; Uddin, 2017). Remediation technologies for the removal of these pollutants from aqueous environments include chemical precipitation, electrochemical treatments, oxidation, reduction, coagulation, ion exchange, membrane filtration, bioremediation, phytoremediation, bioadsorption, and adsorption (Hashim et al., 2011; Hegazi, 2013; Hua et al., 2012; Ihsanullah et al., 2016; Mahar et al., 2016; Mosa et al., 2016). Among these options, adsorption processes have garnered much attention due to their operation feasibility and simple design, among other attributes.

One of the challenges of adsorption is identifying low cost materials with a high adsorption capacity. As a result, adsorbents obtained from natural sources have gained much consideration (De Gisi et al., 2016). In this context, soils in general and particularly Andisols (soils of volcanic origin) constitute a potential economic source of absorbent materials due to their natural allophane content (De Gisi et al., 2016; Kaufhold et al., 2009; Yuan and Wada, 2012). Allophane is an aluminosilicate with predominant short-range organisation that presents large specific surface area and high buffering capacity, among other properties. Allophane is known to have variable surface charge, which

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may be positive or negative depending on the conditions of the medium (mainly pH), facilitating interactions with positive or negative ions through ion exchange or adsorption reactions (Bolan et al., 2013).

Although allophane is a main component of Andisols, other minerals are also present in these types of soil. Iron oxides are widespread minerals in materials derived from volcanic-ashes, distributed mainly as coatings of primary or secondary minerals or infiltrated in clay aggregates. Their presence alters the electric charge and modifies the surface properties of allophane. Several reports point out that iron oxide minerals may participate in the adsorption mechanisms of toxic trace elements as As, Sb, Cd, Cu, Pb, V, etc. (Michalkova et al., 2014; Uwamariya et al., 2016; Yan et al., 2016). Michalkova et al. (2014) demonstrated that amendment of soils with different types of iron oxides has little effect on the adsorption of Cd and Cu. Synthetic magnetite/bentonite compounds have been shown to enhance adsorptive capacities for immobilisation of Pb, Cd and Cu in water samples (Yan et al., 2016). Uwamariya et al. (2016) established that the use of iron oxide-coated sand has interesting Cd and Cu removal capacities. Finally, Suda and Makino (2016) established that iron oxides from soils have a significant capacity to absorb pollutants such as arsenate, vanadate, and antimonate, among others. However, there is no clear consensus if iron oxides, when found forming coatings over natural aluminosilicate minerals, play a detrimental role in the adsorption capacities of cationic pollutants over a classical-cation adsorbent, such as allophane. Another aluminosilicate, also present on volcanic-ashes derived soil, at much lower concentration than allophane, is imogolite, which has been studied for copper and cadmium adsorption kinetics by Arancibia-Miranda et al. (2015).

The objective of this research was to obtain natural allophane with (NA-FeOx) and without (NA) iron oxides from a Southern Chilean Andisol, and determine the influence of the natural free iron oxide coatings on the adsorption of cationic pollutants Cd(II) and Cu(II) in aqueous media.

2. Materials and methods

2.1. Adsorbent preparation

2.1.1. Soil samples

Andisol samples were taken from 20 to 40 cm depth of Santa Barbara (ashy, medial, mesic, Typic Dystrandept; (Mella and Kuhne, 1985)) uncultivated soil (36°47′ S 72° 8′ W). The series are dominated by allophane (> 50% of total minerals) and have a high content of Fe oxides. This profile was selected because allophane is known to be more concentrated in the B horizon of soil (Mella and Kuhne, 1985). Basic soil characterisation included organic carbon (Walkley-Black method, (Allison, 1965)), pH (1:2.5 soil: solution ratio), cation exchange capacity, and surface charge.

2.1.2. Removal of organic matter

The organic matter was removed by an oxidative process with 30% hydrogen peroxide (H_2O_2) as described by Kunze and Dixon (Kunze and Dixon, 1965). The soil samples were suspended with double distilled water and heated to 60 °C. Addition of 10 mL of 30% H_2O_2 was followed by digestion for 24 h. This process was repeated until the residual organic carbon content was minimal, monitored by the wet oxidation method described by Kunze and Dixon (Kunze and Dixon, 1965).

2.1.3. Extraction of the < 0.002 mm fraction

After removal of the organic matter, the required fraction was extracted from aqueous suspensions of the soil treated by a sedimentation procedure based on Stokes' law. This sample corresponds to natural allophane with iron oxides (NA-FeOx).

2.1.4. Removal of free iron oxides

Removal of free iron oxides was performed according to the procedure of Mehra and Jackson (Mehra and Jackson, 1960) but modified using the dithionite citrate bicarbonate (DCB) mixture. A 50 mL sample of the < 0.002 mm fraction was mixed with 100 mL of sodium citrate (0.3 M) and 12.5 mL of 1 N sodium bicarbonate in a thermostatic water bath set at < 80 °C. Following addition of 1 g of sodium dithionite, this mixture was allowed to react during 15 min with occasional stirring. The solid was purified using centrifuge and re-suspended in 50 mL of double distilled water. Purification steps were repeated four times. Finally, to remove the organic anions (citrate) adsorbed on the solids, the samples were washed with H_2O_2 (Escudey et al., 1986). The final sample was considered to be natural allophane (NA).

2.2. Adsorbent characterisation

2.2.1. Total elemental analysis

The elemental composition of samples (Al, Si, and Fe content) was determined by X-ray fluorescence by energy dispersion on a Shimadzu EDX-720 apparatus equipped with a rhodium (Rh) X-ray tube at a voltage of 5 to 50 kV and an X-ray Si detector.

2.2.2. X-ray diffraction

The allophane samples, freeze-dried and homogenised in an agate mortar, were analysed by means of non-oriented powder diagrams. Diffractograms were acquired scanning between 10 and 80° (2θ) using Cu Kα ($\lambda = 0.154$ nm) radiation, 40 mA, and 40 kV and a nickel filter on a Bruker model D8 Advance diffractometer, with a path of 0.02° and a time of 1 s per path.

2.2.3. Scanning electron microscopy (SEM)

The SEM micrographs of NA-FeOx and NA samples were obtained on a model EVO/MA10 (ZEISS) high vacuum scanning electron microscope.

2.2.4. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of the aluminosilicates were obtained on a Bruker Tensor 27 spectrometer (Bruker). A 3 mg dry sample was compacted in a spectral-grade KBr matrix. The spectra were scanned 32 times at a resolution of 2 cm^{-1}.

2.2.5. Mössbauer spectroscopy

The NA-FeOx samples were weighed to provide a concentration between 5 and 10 mg of total Fe cm^{-2}. The sample, ground in an agate mortar, was placed on an approximately 3.4 cm diameter sample holder (~5 cm^2), and the spectrum was recorded at ambient temperature (25 °C) at a speed rate of ± 10 mm s^{-1} using a transmission spectrometer with a constant acceleration and a 20 mCi source of ^{57}Co inserted in a Rh matrix. The calibration was made with respect to an iron foil sheet, α-Fe; the middle point of the hyperfine spectrum of the Fe was defined as zero on the velocity axis.

2.2.6. Total specific surface area (TSSE)

The specific surface area was determined gravimetrically by applying the ethylene glycol monoethyl ether (EGME) technique, proposed for determining the surface area of soils and their fine fraction, as well as of mineral silicates (Carter et al., 1965).

2.2.7. External specific surface area (ESSA), pore size distribution and pore volume

A sample of approximately 0.3 g was first degassed. Then, the adsorption-desorption isotherms of N_2 at − 195 °C (77 K) were acquired, changing the relative pressure (P/P_o) of the gas and recording the volume adsorbed on the solid's surface. Specific surface area was calculated from the amount of N_2 adsorbed employing the Brunauer-Emmett-Teller or BET equation (Brunauer et al., 1983). Pore size distribution