



Competitive sorption of nickel, cadmium, zinc and copper on palygorskite and sepiolite silicate clay minerals

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ABSTRACT

The fate of heavy metals in the environment is largely controlled by sorption reactions. In the current study, sorption of Ni, Cd, Zn and Cu to distinctive silicate clay minerals that occur primarily in arid and semiarid regions, namely palygorskite and sepiolite, was assessed in multi-metal batch experiments. The results confirmed that competitive sorption pattern of Ni, Cd, Zn and Cu on the minerals varies with mineral type and the metal concentrations of the solution. Sorption of all four metals on palygorskite increased with increasing of metal concentrations in solution from 0 to 100 mg L⁻¹. The sequence of sorption maxima on palygorskite was Cu > Zn > Cd > Ni. In the case of sepiolite, sorption isotherms of Zn, Cd and Ni showed an initial increase, up to metal concentrations of about 10 mg L⁻¹, but declined significantly afterward in the presence of increasing Cu concentration. Overall, Cu and Ni were the most and the least preferentially retained metals, respectively, by both palygorskite and sepiolite minerals.

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1. Introduction

The presence and movement of potentially toxic metals such as Cu, Zn, Cd, and Ni in soils and aqueous systems have created concerns for environmental and human health. Heavy metals can be introduced into soils and aqueous environments either naturally or as a result of human activities such as agricultural, industrial and mining operations (Sparks, 2003). Sorption reactions at the clay surfaces can dramatically retard the release of metal ions from the geosphere (Dähn et al., 2003; Usman, 2008). Metal sorption on minerals, however, is usually a competitive process and greatly depends on the ion composition of the solution, especially at higher levels of saturation, because of the limited availability of sorption sites (Gutierrez and Fuentes, 1991). In addition, the preference of soil particles for different species of heavy metals varies among soil minerals and is another important factor governing bioavailability, mobility and toxicity of these metals to plants.

Most multi-ion sorption studies have focused on the competitive effects of calcium, magnesium and potassium on the retention of heavy metals in soils (Covelo et al., 2007; Gomes et al., 2001; Vega et al., 2006). Relative metal concentrations, metal characteristics, and environmental factors can determine the adsorption selectivity of metals in a soil (Covelo et al., 2004a, 2004b; Vega et al., 2006). Echeverria et al. (1998), assessing mono- and multi-metal sorption isotherms for Cd, Cu, Ni, Pb and Zn in three different soils, showed that Langmuir sorption maxima and Freundlich distribution coefficients were greater for mono-metal systems compared to multi-metal systems. Moreira and Alleoni (2010)

established the metal affinity sequence of metal adsorption in 14 surface samples of representative soils of the Brazilian humid-tropical region in competitive systems as Cu > Cd > Zn > Ni. Sorption preference for Pb and Cu over Zn, Cd and Ni in soils has also been reported by some other researchers (Gomes et al., 2001; Lu and Xu, 2009). Such sorption selectivity sequences can be explained by metal characteristics such as electronegativity, ionic radii, hydrolysis constant and hardness (Sdiri et al., 2012; Vidal et al., 2009).

Given the differences among soils regarding their adsorbing surfaces, more specific research is needed to characterize the adsorption preference of particular soil components, such as organic matter, Fe oxides and hydroxides and different clay minerals for metals in multi-solute sorption systems (Saha et al., 2002; Srivastava et al., 2005). There have been few studies on the simultaneous sorption of heavy metals on clay minerals especially on fibrous minerals such as sepiolite and palygorskite. Both of these soil minerals are most likely to occur in arid regions; however, the occurrence of palygorskite in soils is more frequent than that for sepiolite. Palygorskite and sepiolite comprised noncontiguous silicate sheets with dioctahedral characteristics. Inverse tetrahedra (SiO₄) form a framework of longitudinal paralleled canals. Presence of empty spaces together with particular surface functional groups give them unique sorption features (Guggenheim and Krekeler, 2011). Despite the low CEC of palygorskite and sepiolite, they have a large capacity for adsorbing heavy metals due to their specific structure (Fan et al., 2009; Shirvani et al., 2006).

Although several studies have been performed on sorption of metal ions on palygorskite and sepiolite, information about competitive sorption of metals on these minerals is very rare and needs to be taken into account. Regardless of the sources contributing metals to soil environments,

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mono-metal pollution is uncommon and several metals usually enter the soil simultaneously. Therefore, it can be expected that the fate and behavior of each individual metal is affected by the presence of other metals. In the current study, our objective was to assess the sorption behavior of Ni, Cu, Cd and Zn on palygorskite and sepiolite in competitive systems.

2. Materials and methods

2.1. Preparation of the minerals

Two minerals used in this study were palygorskite from Florida (the Source Clay Minerals Repository, Purdue University, IN) and sepiolite from Yazd (Iran). The PFL-1 has specified mineralogical composition of 80% palygorskite, 10% smectite, 7% quartz, 2% feldspar and 1% other (Chiperá and Bish, 2001). The Yazd sepiolite, however, is a newly discovered mineral whose exact mineralogical composition has not been determined yet. X-ray diffraction analysis was performed on the both minerals by a XD-610 Shimadzu X-ray Diffractometer (Cu-K α).

Before sorption studies, possible carbonates, organic matter and iron/manganese oxides in the clay samples were removed by using acetate-buffer of pH 5, 30% H₂O₂ and citrate-bicarbonate-dithionate, respectively, according to Kunze and Dixon (1986). The minerals were then saturated with Ca ions using a 0.5 M CaCl₂ solution and washed with water:ethanol solution to remove excess salt until no Cl⁻ was detected by AgNO₃ test. The Ca-saturated minerals were powdered in a mortar and sieved through 230 mesh standard wire sieve. The cation exchange capacity (CEC) and specific surface area (SSA) of the clays were measured by the Na-acetate method (Rhoads, 1986), and N₂-BET adsorption analysis using a Surface Area Analyzer, respectively. Elemental composition of the pretreated clay samples was determined by XRF analysis.

2.2. Sorption procedure

In 100 mL polyethylene centrifuge tubes, mineral samples (0.3 g) were suspended in 30 mL 0.01 M CaCl₂ solutions containing a multi-metal mixture of either 0, 5, 10, 20, 40, 60, 80 or 100 mg L⁻¹ of each chloride salt of Ni, Cd, Cu and Zn. All the chemicals used were of analytical reagent grade. Samples were shaken for 24 h at 180 \pm 2 rpm in 25 \pm 1 $^{\circ}$ C by an orbital incubator shaker. Immediately after shaking, suspension samples were centrifuged at 3000 rpm for 10 min and then supernatants were separated and analyzed for heavy metal concentrations by an AAnalyst 200 Perkin-Elmer Atomic Absorption Spectrophotometer (AAS). The concentration of metals retained on the minerals was calculated according to Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

where C_i and C_e are the initial equilibrium concentrations (mg L⁻¹) of metals in solution, respectively. V and W represent volume of the solution (L) and mass of the sorbent (g), respectively.

Sorption isotherms were acquired by plotting the amount of metal sorbed on each mineral versus the final concentrations of metals in equilibrium solutions. As mathematical models, Langmuir and Freundlich equations were used to describe the distribution of metals between liquid and solid phases (Sparks, 2003). Eq. (2) indicates the general definition of Langmuir isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where, q_m (sorption capacity of the solid phase) and K_L (energy constant related to the strength of sorption) are constants of the equation. The general description of the Freundlich model is as follows:

$$q_e = K_F C_e^N \quad (3)$$

where, K_F represents distribution coefficient and N is a correction factor. When N increases to its maximum value of 1, K_F can be considered as the partitioning coefficient showing the ratio of metal sorbed to solid phase to that remains in batching solution at equilibrium (Sparks, 2003).

Non-linear regression analysis was used to fit the isotherms to the sorption data using Graphpad prism ver. 5.0 software. The goodness of fit of the data to the models was examined based on determination coefficients (r^2) and standard errors (SEE) calculated as follows:

$$SEE = \left(\frac{\sum (q_e - q'_e)^2}{n-2} \right)^{1/2} \quad (4)$$

where q_e and q'_e are measured and calculated amounts of metal sorbed at equilibrium, and n is the number of measurements.

3. Result and discussion

3.1. Minerals

X-ray diffractograms for palygorskite and sepiolite samples are presented in Fig. 1. The high intensity characteristic (110) reflection peak of palygorskite at 10.4 $^{\circ}$ confirms that palygorskite is the main mineral in the sample. A sharp and intense peak at 12.3 $^{\circ}$ in the X-ray diffractogram of Yazd sepiolite sample indicates that it is also a relatively pure sepiolite. The 4.40 and 2.58 $^{\circ}$ peaks are also related to sepiolite. Some quartz ($d = 4.27$ and 3.33 $^{\circ}$) and dolomite ($d = 2.86$ and 2.39 $^{\circ}$) impurities are also present in the sample. Table 1 shows some characteristics of the clay minerals studied. Palygorskite has greater CEC and specific surface area than sepiolite. The minerals' chemical composition, obtained from XRF analyses, is also presented in Table 2.

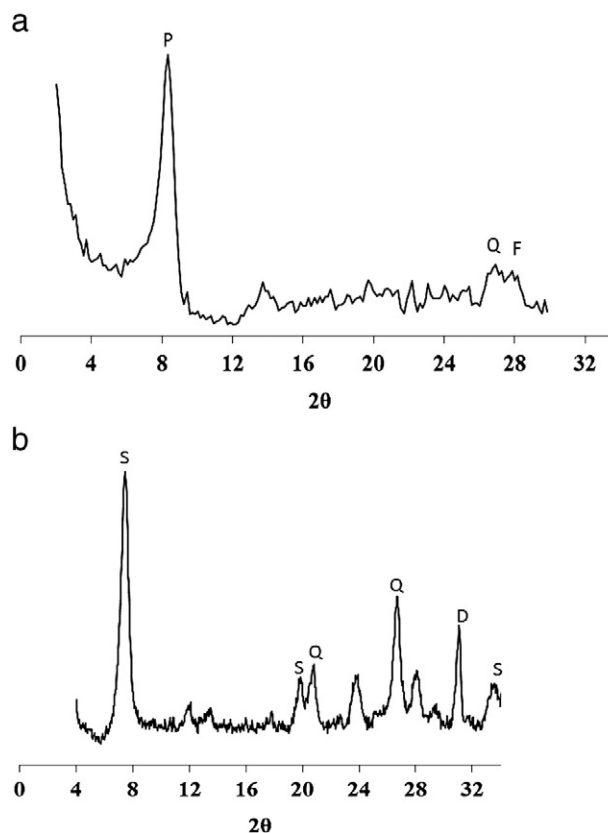


Fig. 1. X-ray diffraction pattern (XRD) of palygorskite (a) and sepiolite (b) clay samples. P: palygorskite; Q: quartz; F: feldspar; S: sepiolite; D: dolomite.

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