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Research paper

Montmorillonite and vermiculite as solid phases for the preconcentration of trace elements in natural waters: Adsorption and desorption studies of As, Ba, Cu, Cd, Co, Cr, Mn, Ni, Pb, Sr, V, and Zn

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ABSTRACT

An evaluation of the feasibility of vermiculite and K10 montmorillonite for use as adsorbent in the separation and/or preconcentration of elements prior to their determination was performed for As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V and Zn. The adsorption of elements onto both clay minerals was studied using a multi-element solution in trace concentrations by batch technique, and no stirring under ambient conditions. Effects of adsorbent concentration, pH and ionic strength were also investigated. The desorption process of the previously adsorbed elements onto clay minerals was studied using HCl and HNO_3 as extractors. In general, the adsorbents exhibited excellent sorption properties for most of the elements. The content of adsorption obtained was higher than 70% for almost all cases. On average, at low salt concentration (<0.05 mol L^{-1}) the sorption efficiency was only slightly higher in montmorillonite when compared to vermiculite, however the reverse is true at high salt concentration. The adsorption of metal ions onto vermiculite and montmorillonite reduces with decreasing pH and increasing ionic strength. An opposite behavior was observed in the adsorption of oxi-anionic species of arsenic and vanadium. The results of desorption experiments indicated that a single extraction with 1.0 mol L^{-1} HNO_3 or HCl was sufficient for the recovery of most elements with an average desorption of 82% and 90% for K10 montmorillonite and vermiculite, respectively.

1. Introduction

Clay minerals are hydrous aluminum, iron and magnesium silicates with layered structures (phyllosilicate), hydrophilic, which impart plasticity to the particles (Bergaya et al, 2006). Clay minerals occur in different environmental compartments such as rocks, soil, sediment and water, acting as scavengers of organic and inorganic pollutants (Bhattacharyya and Gupta, 2006, 2008). Adsorption and desorption of metals and metalloids onto clay minerals are important processes that can determine the bioavailability and ecotoxicological effects of the elements in the environment (Abollino et al., 2008; Shirvani et al., 2006).

Both montmorillonite and vermiculite are clay minerals with 2:1 crystalline structures, which contain two silica tetrahedral sheets with a central alumina octahedral layer. They have high ion exchange capacity, which is a consequence of replacing Si^{4+} and Al^{3+} for ions having lower valence, such as Al^{3+} instead of Si^{4+} in tetrahedral positions and Mg^{2+} instead of Al^{3+} in the octahedral positions. This process, known as isomorphic substitution, induces a negative charge that leads to the adsorption of alkaline earth metal ions in the interlayer space as counter ions (Abate and Masini, 2005a; Abollino et al., 2007, 2008; Bhattacharyya and Gupta, 2008). Features such as high ion exchange capacity, large surface area, chemical and mechanical stability, low cost, easy manipulation, as well as high abundance and harmlessness to the environment, make clay minerals widely used for various scientific and technological applications. We can mention their use in catalysis, industrial processes, wastewater treatment, for fire protection, as acoustic and thermal insulator, additives in concrete, and preparation of high value-added products such as cosmetics and medicines (Abollino et al., 2008; de Aguiar and Novaes, 2002; Joshi et al., 2009; Teixeira-Neto and Teixeira-Neto, 2009).

However, it is important to mention that K10 montmorillonite is a commercial material, being obtained from the natural montmorillonite by treatment with mineral acids at high temperature. As a consequence of the acid activation its natural structure is destroyed, with an increase in surface area and porosity compared to the natural clay (Varadway et al., 2013; Villegas et al., 2005; Younssi et al., 2012).

Clay minerals are appropriate adsorbents for metal ions and this interaction has received considerable attention because the process may have a strong influence in the behavior of elements in the environment,

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as well as in analytical separations and concentration systems (Chegrouche and Bensmaili, 2002).

Interactions between the elements and montmorillonite or vermiculite can occur by different processes. The ion exchange in the interlayer space is one possible mechanism, resulting from the interactions between metal ions and negative permanent charges which lead to outer-sphere complexes. The other mechanism is the formation of inner-sphere complexes through $Si-O^-$ and $Al-O^-$ groups at the clay particle edges (Abollino et al., 2003; Elzinga and Sparks, 1999; Malandrino et al., 2006). The magnitude of these processes depends on environmental factors such as pH, temperature, time, ionic strength, type and concentration of the species to be adsorbed and presence of ligands (Bhattacharyya and Gupta, 2008; Melo et al., 2000).

Abollino et al. (2008) studied the adsorption of Cd^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+} on vermiculite and montmorillonite. They reported that the total capacity of vermiculite with respect to the adsorption of the cations was higher than montmorillonite, and metal ion retention on vermiculite was more affected by the competition with Na^+ at high ionic strengths with respect to montmorillonite. Adsorption of Ni^{2+} on Na-montmorillonite was studied under ambient conditions by Xu et al. (2008). The results indicated that this clay mineral was a suitable candidate for the preconcentration and solidification of Ni^{2+} from large solution volumes. da Fonseca et al. (2006) used vermiculite for the removal of Cd^{2+}, Zn^{2+}, Mn^{2+} and Cr^{3+} from an aqueous solution under different times of reaction, pH values and element concentration. This clay mineral showed good adsorption potential for all the elements studied.

Numerous studies demonstrated the efficiency of 2:1 clay minerals in the adsorption of metal species. Nevertheless, investigations on their desorption behavior from these clay minerals are quite limited (Shirvani et al., 2006). It is recognized that there is a lack of knowledge on metal ion desorption behavior from clay minerals. In general, desorption studies have been conducted using electrolyte solutions such as $NaNO_3$, $CaCl_2$, KCl and organic ligands (citrate, EDTA) as extractors (Özdemir and Yapar, 2009; Shirvani et al., 2006; Xu et al., 2008).

Besides these aspects, most adsorption studies of metals onto clay minerals describe the results of batch type experiments that are commonly used to measure the adsorption of single or few metals at a time, generally at a concentration level of mg L^{-1}. However, in complex systems such as freshwater and effluents many metal ions are simultaneously present in different concentrations (Bradbury and Baeyens, 2005).

Taking these aspects into account, this work investigated the adsorption and desorption of a wide range of trace elements; As(V), Ba^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, V(V) and Zn^{2+} onto a sodium homoionic K10 montmorillonite in comparison with vermiculite aiming their use to concentrate, separate and determine trace amounts of elements in environmental samples.

Thus, these studies were carried out under experimental conditions similar to those found in natural waters and with multi-element solutions in concentrations of μg L^{-1} to allow the evaluation of the competition between elements during the adsorption process. Furthermore, it was necessary to evaluate the desorption process because it plays an important role in the recovery of the analytes from the solid phase for analytical purposes.

2. Materials and methods

2.1. Reagents and apparatus

All reagents used in this work were of analytical grade or better from Merck. Water was purified in a Milli-Q Academic System (Millipore). A certified reference material SRM 1643e from NIST was used in Quality Assurance and Quality Control (QA/QC) experiments.

Individual 1000 mg L^{-1} standard solutions of As(V), Ba^{2+}, Cu^{2+}, and Zn^{2+} were purchased from Merck Tritisol, and of Cd^{2+}, Co^{2+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+} and V(V) were acquired from AccuStandard.

The determination of all species was carried out by inductively coupled plasma optical emission (ICP OES) with a Thermo Scientific iCAP 6500 instrument. The instrumental conditions were: RF power of 1150 W; Ar nebulization flow rate of 0.2 L min^{-1}; Ar main flow rate of 12 L min^{-1}; Ar auxiliary flow rate of 0.5 L min^{-1}; and an axial mode for torch configuration. Analytical curves were prepared in the range of 0.001 to 1.00 mg L^{-1}. Yttrium (0.10 mg L^{-1}) was used as an internal standard. A Micronal B474 potentiometer coupled to an Ag/AgCl combination glass electrode was used for all pH measurements.

2.2. Clay minerals

K10 montmorillonite (Mt) was supplied by Aldrich, and vermiculite (Vm) was acquired from Eucatex Química e Mineral Ltda. (São Paulo, Brazil), from the Massapê mine located in Paulistana, state of Piauí, Brazil.

Approximately 10 g of Mt and Vm was individually treated with 50 mL of 1.0 mol L^{-1} HNO_3 under stirring for 2 h. Solids were centrifuged, washed with 100 mL of Milli-Q water and treated a second time with 1.0 mol L^{-1} HNO_3. After the acid treatment the solids were centrifuged and washed with 100 mL of water and then treated twice with 100 mL of 1.0 mol L^{-1} $NaNO_3$ under stirring for 1 h in order to obtain the Na^+ homoionic Vm and Mt. The solid phases were washed with Milli-Q water and the material obtained was dried at 80 °C (Abate and Masini, 2005a). The dry solids were sieved using Teflon sieves, and the particle size between 38 and 50 μm was obtained. The modified clay minerals (Mt-Na and Vm-Na) were used for all adsorption and desorption experiments.

To evaluate the acid treatment in removing impurities from the materials, samples of untreated (Mt and Vm) and modified (Mt-Na and Vm-Na) clay minerals were kept in 1.0 mol L^{-1} HNO_3 for 24 h. The concentration of extracted ions was determined by ICP OES.

The characterization of the two clay minerals was carried out with untreated and treated samples. X-ray diffraction (XRD) measurements were performed in a Shimadzu diffractometer model XRD 600, using Cu Kα radiation. Specific surface area was obtained by BET measurements of N_2 adsorption isotherms using an equipment from Micromeritics, ASAP 2010.

2.3. Adsorption of metal ions and As onto Vm and Mt

All adsorption studies were performed using batch experiments under ambient conditions in which known amounts of the treated clay minerals were equilibrated (without agitation) with standard solutions of elements at 20 ± 0.5 °C in Falcon polystyrene round-bottom centrifuge tubes. After the contact time (24 h), the dispersions were centrifuged (2000 rpm, 10 min) and the remaining concentrations of elements in the solution were determined by ICP OES. In any adsorption study, measurements were performed after 24 h of equilibrium time. Usually, the adsorption studies are performed under agitation or shaking conditions in order to achieve the maximum interaction between metals and adsorbents. Nevertheless, the samples are typically percolated through a solid phase (adsorbent) in the preconcentration or extraction systems for element trace. Thus, adsorption procedures were chosen taking into account the application of clay mineral in the preconcentration systems, which required the adsorption of different analytes without agitation.

The concentration of each analyte adsorbed on the clay mineral was calculated by the difference between the initial content in the sample and the remaining concentration in the solution after the experiment. Blanks were performed in order to check some possible contamination.

Preliminary studies were performed with 0.005; 0.020; 0.030 and 2.0 mg L^{-1} of Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}, respectively; and 1.0; 2.0 and 2.5 g L^{-1} Mt-Na and Vm-Na dispersions. The pH and ionic strength