



Research paper

Some effects of trivalent chromium exchange of thermo-exfoliated commercial vermiculite



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ARTICLE INFO

Article history:

Received 20 June 2012

Received in revised form 16 December 2013

Accepted 20 December 2013

Available online 24 January 2014

Keywords:

Commercial vermiculite

Trivalent chromium

Adsorption

Thermo-exfoliation

ABSTRACT

This manuscript presents the investigation on some effects of the Cr^{III} adsorption from aqueous solution by thermally expanded commercial vermiculite. Three effects were studied: 1) contact time between the adsorbent and chromium dissolved in the retention process; 2) adsorbent mass; and 3) concentration of chromium in adsorption. The original and treated vermiculite samples were characterized by X-ray diffraction and infrared spectroscopy. The findings of this study showed, on the one hand, that vermiculite with high mica-like content, after abrupt heating to high temperatures, is very suitable for the recovery of traces of Cr^{III} in waters of relatively high salt content due to its high degree of exfoliation and adsorption coefficient ($K_d = 0.74 \times 10^5 \mu\text{g kg}^{-1}$). On the other hand, that the mica-type structure originated by the sudden heating of vermiculite would have shifted again to that of the vermiculite, due to adsorption of Cr^{III} (probably by ion exchange) and probably its binding with the water trapped in the structure.

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1. Introduction

Vermiculite is an interesting mineral because of its high cation exchange capacity and reactive surface area (da Fonseca et al., 2005; Marcos and Rodríguez, 2010; Marcos et al., 2009; Seaborn and Jameson, 1976). The importance of vermiculite is based on its lamellar structure (Argüelles et al., 2010; de la Calle et al., 1988; Shirozu and Bailey, 1966). On the other hand, it is well known that when vermiculite is strongly heated at a high temperature (≈ 1000 °C) during a short period of time, the water situated between layers is quickly converted into steam, exerting a disruptive effect upon the structure (Baumeister and Hahn, 1976; Marcos and Rodríguez, 2010; Marcos et al., 2009; Obut and Girgin, 2002; Wada, 1973a,b; Walker, 1961). As a consequence, a highly porous thermally exfoliated material is formed. This material as raw or when exfoliated finds use in construction products, agriculture, horticulture, as acoustic and thermal insulators, adsorbent and other applications (Bergaya et al., 2006; Brigatti et al., 2005; da Silva et al., 2003; de Haro et al., 2005; Hindman, 1992; Jayabalakrishnan and Mahimaraja, 2007; Obut and Girgin, 2002; Sancho et al., 2008; Strand and Stewart, 1983; Sumathi et al., 2005; Verdeja et al., 2008; Wada, 1973b; Williams-Daryn and Thomas, 2002; Xu et al., 2005). The thermal exfoliation occurs in a direction approximately perpendicular to the layers. This property of exfoliation is explained as due to the explosive release of interlamellar water molecules by heating (thermal treatment), and causes the vermiculite to expand to twenty or thirty times of their original size normal to the basal cleavage and to change its

structure. The silicate structure vanishes after dehydration and the reappearing of a new structure depends on interlayer cations and their content, particle size and time of treatment. During the final stage, individual water molecules tend to be trapped in the interior of the crystal by the convergence of the silicate layers near the edges (MacEwan and Wilson, 1980). Under these conditions, the interlayer cations also were trapped in the cavities of the tetrahedral sheet (Fripiat et al., 1960; Walker, 1949).

Chromium does not exist in a very high concentration in the water by its low solubility; however there are examples of water pollution, in some cases very serious, when effluents containing chromium compounds have been evacuated in rivers. The valence of the chemical form in which chromium is found in natural seawaters is influenced by the acidity of water. Normal levels of total chromium in the water tend to be 0.01 mg l⁻¹ or less (Świetlik, 1998).

The present investigation is focused on some effects of trivalent chromium exchange of a thermally expanded commercial vermiculite from China in distilled water and natural and synthetic seawaters. Solutions with low concentrations of Cr^{III} (1 ppm) were used because of the low levels of Cr^{III} in water; furthermore, the World Health Organization since 1958 recommends a maximum concentration of 0.05 mg l⁻¹ of chromium in water. Exfoliated vermiculite has some useful properties. Apart from its ion exchange properties it is very easy to handle in comparison with other substances such as montmorillonite or bentonite which are difficult to separate from dispersion in water. Exfoliated vermiculite absorbs a considerable amount of water, but does not wet easily. The vermiculite could be regenerated, recycled and recovered after being saturated by heavy metals, so it could have new applications (Seaborn and Jameson, 1976). Moreover, the results of such

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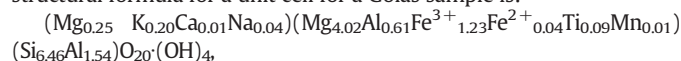
investigation can also be used to gain insight into the behavior of vermiculite in natural systems.

Other studies related to the present one include those of Seaborn and Jameson (1976), who investigated some ion exchange properties of exfoliated vermiculite from Palabora; Sumathi et al. (2005) tested biological wastes (sawdust, rice husk, coirpith and charcoal) and vermiculite in removing Cr from tannery effluent through batch and column experiments; da Silva et al. (2003) reported the adsorption of crude oil on vermiculite samples, expanded and hydrophobized with carnauba (*Copernicia Cerifera*) wax; da Fonseca et al. (2005) investigated vermiculite as an exchanger matrix in doubly distilled water solution to exchange magnesium inside the lamella with the heavy cations copper, nickel, cobalt, and lead at the solid/liquid interface; da Fonseca et al. (2006) used vermiculite as adsorbent for the removal of cadmium, zinc, manganese, and chromium from aqueous solutions and investigated parameters such as time of reaction, effect of pH and cation concentration; Jayabalakrishnan and Mahimaraja (2007) evaluated the adsorption of Cr on raw vermiculite grades 1 to 5 as a function of solution concentration onto raw vermiculites; Badawy et al. (2010) studied the adsorption of Cu^{II} and Cr^{III} ions by pure vermiculite in an aqueous solution; and Sis and Uysal (2012) investigated the optimum adsorbent (vermiculite) dosage, initial ion concentration, conditioning time and pH separately. Other studies that may be mentioned are those of Alvarez-Ayuso and Garcia-Sanchez (2003), Bourliva et al. (2004), and Wahba and Zaghoul (2007).

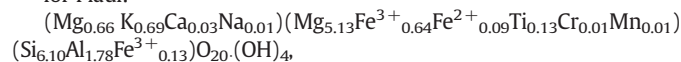
2. Materials and method

2.1. Investigated vermiculites

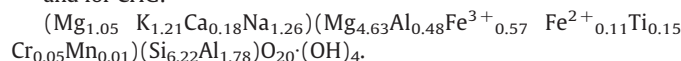
The vermiculites of this work originated from the Goiás and Piauí states of Brasil and from China (CHG). They were present in the form of small packets of green color with different tints, with maximum dimensions of ca. 1–2 mm in diameter and 0.5–1 mm in thickness. The structural formula for a unit cell for a Goiás sample is:



for Piauí:



and for CHG:



According to the division of commercial vermiculites proposed by Marcos et al. (2009), the two first samples would belong to *type-1* and the second one to *type-2*.

2.2. Sample preparation

Firstly, the samples were heated to 900 °C into porcelain crucible for 1–3 min in an oven once stabilized (~2 h) to expand them. Possible impurities present in the thermally expanded samples were eliminated by the flotation separation method, which consisted in suspending the samples in a beaker of 400 ml with distilled water. After reaching the equilibrium between the sample and the aqueous phase (15–30 min) the floating ore was filtered through a paper of filter and allowed to dry at 60 °C in an oven for 24 h.

2.3. Adsorption experiments

Several experiments were made in order to investigate three effects: 1) chromium adsorption in natural and seawaters; 2) contact time between the adsorbent and chromium dissolved in the retention process; 3) adsorbent mass; and 4) concentration of chromium in adsorption. All of them were carried out in polypropylene containers at room

temperature. The used chromium solution, (Cr in HNO₃ 2–5%) for ICP, was Panreac. Chromium standard solution is Cr = 1.000 ± 0.002 g l⁻¹.

Firstly, the chromium adsorption by different thermally expanded vermiculites was studied in distilled water, natural seawater (pH = 6.5) and synthetic seawater (pH = 7). The average composition (g) of 1 l natural seawater was: 24.0 NaCl, 5.0 MgCl₂, 4.0 Na₂SO₄, 1.1 CaCl₂, 0.7 KCl, 0.2 NaHCO₃, 0.096 NaBr, 0.026 H₃BO₃, 0.024 SrCl₂, 0.003 NaF, and distilled water 1.000 ml; with 35.15 g l⁻¹ of average salinity. The average composition (g) of 1 l synthetic seawater was: NaCl 27.9; MgSO₄ 3.31; MgCl₂ 2.66; CaCl₂ 1.12; KCl 0.6; NaHCO₃ 0.209; KBr 0.097; H₃BO₃ 0.027; SrCl₂ 0.03; and KI 0.0007; with 35.27 g l⁻¹ of average salinity.

Three sets of five containers were prepared. Each one containing, respectively, the three mentioned water types. The samples of about 0.3 g of the expanded vermiculites were dispersed in each container containing the solution and Cr^{III} cation at a concentration of 1 ppm. The solutions were mechanically stirred for 24 h at room conditions. After the time established the solid was separated by filtration. The content of the amount of cation not retained was determined by ICP-MS.

Despite the fact that the retention efficiency of chromium was similar in the 3 samples used at the beginning of the investigation (see in Section 3), the authors decided to continue the experiments only with the CHG vermiculite. There were two reasons: 1) CHG sample showed the greater expansibility because it contained more potassium in the interlayer than the Piauí and Goiás samples. K⁺ ions would be responsible of a larger exfoliation after heating at elevated temperatures (Marcos et al., 2009). 2) It is more commercialized than the other two samples and in our region there is an exfoliation plant that uses CHG.

The following experiments were carried out with the CHG vermiculite expanded thermally for 1 min (hereafter CHGE) and natural seawater.

- To study the influence of contact time between the adsorbent and chromium dissolved in the retention process, seven solutions were prepared with synthetic seawater, and seven with natural seawater enriched with 1 ppm chromium III, in which 0.3 g of vermiculite was introduced. The contact times were 1, 3, 5, 16, 24 and 48 h.
- To study the effect of the adsorbent mass six seawater solutions enriched with 1 ppm chromium were prepared, in which 0.1, 0.2, 0.3, 0.5, 0.7 and 0.1 g of CHGE vermiculite were introduced. The solutions were mechanically stirred for 16 h at room conditions. After this time the solid was separated by filtration and the content of the amount of cation which was not retained was determined by ICP-MS.
- To study the effect of the concentration of chromium in adsorption, six seawater solutions enriched with chromium 0.125, 0.250, 0.500, 0.750, 1.000 and 2.000 ppm, respectively, were prepared. In these solutions 0.6 g of vermiculite (hereafter CHGE_12, CHGE_25, CHGE_50, CHGE_75, CHGE_100 and CHGE_200) was introduced. The solutions were mechanically stirred for 16 h at room conditions. After the time established the solid was separated by filtration and the content of the amount of cation in the supernatant was determined by ICP-MS.

The adsorption coefficient (K_d), which provides an indication of the sorption capacity of the Cr^{III} by the CHGE vermiculite, was calculated by using the formula:

$$K_d = \left\{ \left[\text{Cr}_o^{\text{III}} \right] - \left[\text{Cr}_f^{\text{III}} \right] \right\} \times \frac{V_{\text{dissolution}} (\text{ml})}{\text{adsorbent mass} (\text{kg})}, \quad (1)$$

where: Cr_o^{III} is the initial concentration of Cr^{III}, Cr_f^{III} is the final concentration of Cr^{III}, V_{dissolution} is the dissolution volume in ml, and adsorbent mass is the mass of CHGE vermiculite in KG.

2.4. Characterization

A Bruker AXS D8 Advance diffractometer with an Anton Paar HTK1200 Oven was used at different temperatures: a) room temperature for the untreated starting samples and the treated

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