



ORIGINAL ARTICLE

Adsorption of divalent metals on natural and functionalized nontronite hybrid surfaces: An evidence of the chelate effect



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Received 16 April 2012; accepted 30 March 2013

Available online 6 April 2013

KEYWORDS

Nontronite;
Adsorption;
Dynamic adsorption procedures;
Calorimetry

Abstract Nontronite is an important phyllosilicate with a high concentration of ferric iron in the octahedral layer. A new occurrence of Brazilian nontronite sample was used for the organofunctionalization process with 3-aminopropyltriethoxysilane. Due to the increment of basic centers attached to the pendant chains, the metal adsorption capability of the final chelating material, was found to be higher than its precursor. The ability of these materials to remove Pb^{2+} , Mn^{2+} , and Zn^{2+} from aqueous solutions was followed by a series of adsorption isotherms at room temperature and pH 6.0, in batch adsorption experiments in order to explain the adsorption mechanism. In order to evaluate the phyllosilicate samples as adsorbents in a dynamic system, a glass column was fulfilled with nontronite samples (1.5 g) and it was fed with 2.1 mmol dm^{-3} divalent cations at pH 6.0. The energetic effects caused by metal cations adsorption were determined through calorimetric titrations. The effects of three divalent metals adsorption in the zero point of charge of each material were investigated.

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1. Introduction

Smectite types belong of the group of clay minerals, which expand upon contact with strongly hydrated media such as ethanol and methanol. In ferruginous smectites, some or all

the aluminum atoms localized in the octahedral layer are replaced with Fe^{3+} (Frost and Klopogge, 2000); the ferruginous smectite type is called nontronite. Nontronite is an important phyllosilicate with layered morphology in industrial applications due to its unique physical and chemical properties, including gellants and adsorbents. The ideal structural formula for nontronite is $(M_x^+ nH_2O)(Fe_4^{3+})(Si_{4-x}Al_x)-O_{20}(OH)_4$, where M_x^+ is a monovalent cation that counterbalances the layer charges (Sun et al., 2012; Dekov et al., 2007; Jaisi et al., 2007; Ding and Frost, 2002; Keeling et al., 2000). A potentially important adsorbent of divalent metals and other toxic pollutants is layered silicate, such as smectite types. The strong propensity of heavy metals to form complexes with various natural organic molecules facilitates the fast

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Nomenclature			
N_f	the maximum adsorption capacity of the adsorbent (mmol g^{-1})	K_{RP}	Redlich–Peterson constant ($\text{dm}^3 \text{g}^{-1}$)
C_S	metal concentration at equilibrium (mmol dm^{-3})	n_S	dimensionless exponent of Sips equation
N_L	amount of adsorbate adsorbed at the equilibrium–Langmuir (mmol g^{-1})	N_t	amount of adsorbate adsorbed at time t (mmol g^{-1})
K_L	Langmuir affinity constant ($\text{dm}^{-3} \text{mmol}^{-1}$)	N_E	amount of adsorbate adsorbed at the equilibrium–kinetic (mmol g^{-1})
K_F	Freundlich constant related to adsorption capacity [$\text{mmol g}^{-1}(\text{mmol dm}^{-3})^{-1/n_F}$]	k_{AV}	Avrami kinetic constant (min^{-1})
n_F	dimensionless exponent of Freundlich equation	t	time of contact (min)
N_S	amount of adsorbate adsorbed at the equilibrium–Sips (mmol g^{-1})	k_f	pseudo-first-order rate constant (min^{-1})
K_S	Sips constant related to the affinity constant [$(\text{mmol dm}^{-3})^{-1/n_S}$]	k_s	pseudo-first-order rate constant ($\text{g mmol}^{-1} \text{min}^{-1}$)
A_{RP}	the Redlich–Peterson constant (mmol dm^{-3}) ^{-g}	α	the initial adsorption rate ($\text{mg g}^{-1} \text{h}^{-1}$) of Elovich equation
g	dimensionless exponent of Redlich–Peterson equation	β	Elovich constant related to the extent of surface coverage and also to the activation energy involved in chemisorption (g mg^{-1})

distribution of pollutants in an aquatic ecosystem. The industrial effluents may present an eco-toxic hazard and introduce the potential danger of bioaccumulation. The adsorption of heavy metals on clay surfaces has become an important subject of continuously growing interest (Manohar et al., 2006).

Numerous studies have reported that biological systems in some rivers of the important regions of the planet are contaminated with divalent metals from illegal and inopportune mining and industrial operations. Pb^{2+} , Mn^{2+} , and Zn^{2+} are classified as toxic elements for the living organisms and dangerous side effects are manifested when these metals are present in higher than permissible limits (Elinder, 1986). The adsorption processes of divalent metals and other pollutants by silicates such as: smectites, kaolinites, and nontronite are in the field of purification of industrial effluents and the removal of environmentally harmful components from waste streams. In the adsorption process, an adsorbate is anchored on the layer surface of a reactive adsorbent by van der Waals forces, electrostatic forces, and the formation of chemical bonds. The characteristics of the adsorption phenomenon are influenced by surface porosity of the adsorbent, density and size of pores, fissures and defect of adsorbent crystals such as Frenkel defect, liner and/or planar defects, clusters and interactions between adsorbent-adsorbate couples and outer influencing agents (Leppäjärvi et al., 2012; Manohar et al., 2006; Bowen et al., 2004; Noble and Terry, 2004; Guerra et al., 2013).

The purpose of this publication is to report the results on a new occurrence of nontronite clay before and after carbon–nitrogen silane was anchored, mainly on the adsorption process. Divalent metal-reactive basic center carbon and nitrogen interactions were calorimetrically investigated, in order to understand the influence of the counter-anion in the chelating effect on adsorption processes better. The adsorption isotherms of Pb^{2+} , Mn^{2+} , and Zn^{2+} from aqueous medium at room temperature were explored, bearing in mind the influence of different parameters such as solution pH, contact time, and competitive adsorption with binary mixtures. Natural phyllosilicate sample has been chemically modified with 3-aminopropyltriethoxysilane (APS) using the homogeneous route. The performance in adsorbing divalent cations from original water under dynamic

flow (column) conditions was also studied and the results confirmed the batch experiments. The spontaneity of these systems, reflected in the negative Gibbs free energies and the favorable positive entropic values, agrees with the displacement of coordinated solvent molecules as the functionalization takes place. The zero charge points of materials were investigated before and after APS and divalent metal interactions.

2. Materials and methods

2.1. Raw material and reagents

The phyllosilicate sample used in this investigation was obtained from Governador Valadares and Araçuaí region in northeastern Minas Gerais State, Brazil. The natural nontronite sample was named NON. With less than $2 \mu\text{m}$ particles, it was separated by sedimentation and color varying from dark yellow to light orange, this variation of coloration in the sample can be attributed to the high content of iron in the nontronite structure. The nontronite types are divergent in terms of trivalent iron site occupancy and the natural reduction in the depositional medium [4]. The nontronite formulas are published by Keeling et al., 2000 with Fe_x , $x \rightarrow 3.68\text{--}3.83$. The original clay sample was activated in a stream of dry nitrogen by heating at $423 \pm 1 \text{ K}$ for 10 h, this procedure aims to expose the reactive sites in inaccessible regions in the structure of the original nontronite and used immediately.

The compound {3-aminopropyltriethoxysilane [$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$] (APS) (95.00%, $d = 1.00 \text{ g cm}^{-3}$ at $298 \pm 1 \text{ K}$, Sigma–Aldrich} was used without purification. Other chemicals such as methanol and ethanol were of reagent grade. Stock standard solutions $5000.0 \text{ mg dm}^{-3}$ of Pb^{2+} , Mn^{2+} , and Zn^{2+} , were obtained from primary-standard metal chlorides (99.998%, Merck). Double distilled deionized water (DDW) was used for the preparation of solutions, wherever required.

2.2. Organofunctionalization of nontronite

A sample of 5.0 g of NON was heated for 5 h at $383 \pm 1 \text{ K}$ under vacuum, and then immersed in approximately 60 cm^3 of

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