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Research paper

The removal of molybdates and tungstates from aqueous solution by organo-smectites

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ABSTRACT

This paper presents the results obtained when studying the removal of molybdate and tungstate anions from aqueous using organically modified montmorillonite. In batch experiments, the influence of pH, reaction time, the initial concentration of Mo and W, and the influence of the amount and type of surfactant was investigated. The modification of smectite with leads to the formation of an organo-mineral complex characterized by a positively-charged surface and a high sorption capacity in the removal of Mo(VI) and W(VI). The pH effect determining the possibility of Mo and W removal from the aqueous solution. In the pH range of 1–5, the sorption of Mo and W efficiency is very high, while at $\text{pH} > 5$ sorption is limited or completely inhibited. DDTMA-smectite and DDDDMA-smectite were recognized as the best sorbents. With an increasing amount of surfactant used in modification process, the sorption efficiency increases. Molybdates are removed from solutions compared to tungstates to a much greater extent – maximum sorption capacities were 705 and 390 mmol/kg, respectively. Kinetic studies indicated that maximum sorption capacity is achieved faster in the case of Mo than of W, and that the main sorption mechanisms are chemisorption and ion exchange.

1. Introduction

Molybdenum (Mo) and tungsten (W) have been chosen for experiments due to their importance as environmental contaminants. In aqueous solutions, they are primarily present in oxyanions forms such as molybdates and tungstates. However, speciation of these elements in an aqueous solution is strongly dependent on the pH. These elements are common in the environment mostly on the VI oxidation state. The cationic species at lower oxidation states (II, IV) occur in minerals, but there is no recorded data concerning their toxicity. The environmental behavior of molybdenum and tungsten once they dissolve becomes very complex as Mo(VI) and W(VI) anions occur as a monomer only in alkaline or neutral solutions. Under even slightly acidic conditions they tend to polymerize to the form of isopoly molybdates and tungstates with possible biotic toxicity implications (Lessner and Schubert, 1999; Sen and Braida, 2014; Kapp, 2014). At a relatively high Eh (stability in terms of the high activity of electrons), Mo and W are presented in their hexavalent state. Taking into account equilibrium modeling, it can be anticipated that the fully dissociated MoO_4^{2-} and WO_4^{2-} are dominant over other forms at $\text{pH} > 4.4$ in the solutions (Cruywagen, 2000). At a lower pH, ions will protonate to acid forms such as $MoO_3(H_2O)$ and $WO_3(H_2O)_3$. At low pH and higher concentrations (>10 μM), Mo and W polymerize into a variety of polymolybdates and polytungstate forms (Cruywagen, 2000). Therefore, limiting the sorption experiments to the narrow pH range is inadequate and does not provide a complete set of data.

The concentration of molybdenum in the environment is significantly enhanced by anthropogenic inputs from coal-resource development, fly ash, sewage sludge and hard-rock mining activity (Kalembkiewicz and Sočo, 2009). Near industrial sources the molybdenum concentrations in surface water may reach concentrations of 200 to 400 μg/L and in groundwater 25 μg/L (Barceloux, 1999; Verbinnen et al., 2012). Tungsten is an important strategic metal that is used in a variety of industrial applications. It tends to be mined from scheelite and wolframite deposits. W(VI) is released into the environment through its use in winter tires or by its application in industry e.g. enriches alloys or electrotechnics (Gustafsson, 2003). High concentrations of Mo and W in drinking water pose health risks to people. Therefore, the need to find effective methods of disposal of both compounds becomes one of paramount importance.

So far, molybdates adsorption on goethite and gibbsite has been studied (Goldberg et al., 1996). An evaluation of the adsorption of mono- and polytungstates onto kaolinites, illite, montmorillonite has been described by Sen and Braida (2014). A new sorbent mineral – zeolite-supported magnetite – represents an innovative approach for the removal of Mo anions (Verbinnen et al., 2012). Other work on the sorption of molybdenum and tungsten on a variety of materials has been described in previous literature (Gustafsson, 2003; Namasivayam and Sangeetha, 2006; Atia, 2008; Swarnkar et al., 2014). Despite the

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excellent sorption properties of organo-clays in terms of oxyanions, there is lack of information evaluating sorption mechanisms of anionic forms of Mo and W onto clay minerals modified by various organic surfactants. The influence of the amount and type of surfactants used during modification on the sorption efficiency has not yet been considered. To conduct these studies, the selection of the best mineral is of particular importance.

Previous research has suggested that smectite and organo-smectites may be appropriate representatives for studies on the removal of anionic form of metals from aqueous solutions (Kłapyta et al., 2001; Say et al., 2006; Say et al., 2008; Bajda and Kłapyta, 2013; Bajda et al., 2015). Smectite clays, commonly known as bentonites, are widespread and often used in various industrial applications, which makes them the most utilized and an attractive group of clay minerals (Pereira et al., 2005). In thus study bentonite from the Jelšovy Stream in Slovakia, rich in montmorillonite phase was used. Smectites have a variable net negative charge, which is balanced by Na, Ca, Mg and, or, H adsorbed externally on interlamellar surfaces (Odom, 1984). The layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet is the basic structural unit in smectites. The bonds between layers are weak and have excellent cleavage, allowing water and other molecules to enter between the layers - causing a phenomenon known as swelling (Grim, 1962). In aqueous suspensions, smectite crystals are dynamic (Laird, 2006), as several small crystals may combine to make a single larger crystal and, conversely, a large crystal may break up to form many small quasicrystals (Pereira et al., 2008).

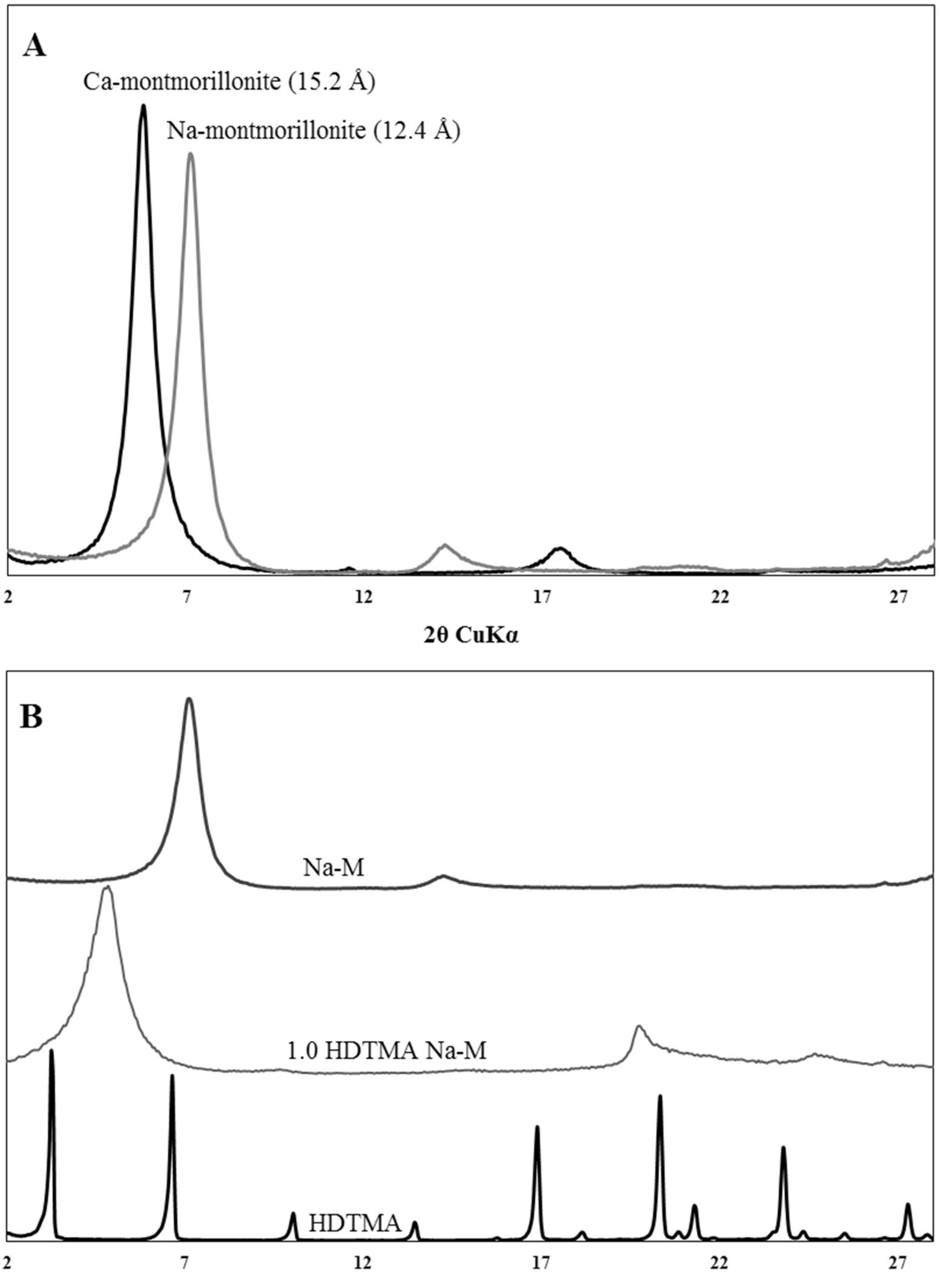

Fig. 1. XRD pattern of smectite used in the study. A – Ca-montmorillonite (before sedimentation procedure); Na-montmorillonite (after initial modification from calcium for sodium form). B – Na-M (Na-montmorillonite); 1.0 HDTMA Na-M – modification of Na-montmorillonite with HDTMA in amount of 1.0 of CEC; HDTMA – XRD patterns of HDTMA.