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Adsorption of berberine on commercial minerals

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ABSTRACT

There is interest in studying interactions between organic modifiers and raw commercial clays aiming the production of low-cost "organoclays". In this study we report the interaction between berberine — a monovalent organic cation — and three commercial bentonites and a Turkish zeolite. The Turkish zeolite exhibited adsorption at values of 5–10% of the cation exchange capacity (CEC) with no neutralization of the particles. Adsorption of the organo-cation on Egyptian bentonite, Volclay KWK and Pure-Flo B80, was above the CEC of the bentonites, yielding neutral and even slightly positively charged particles. Electron microscopy and X-ray diffraction results showed expansion of the basal spacing of the smectite. Such low-cost organo-bentonites might be suitable for environmental applications as removal of pollutants, drug and pesticides delivery, or water treatment. Application in turbidity reduction of industrial effluents is demonstrated.

1. Introduction

Clays and clay minerals are characterized by excellent adsorption capability for cations but are generally ineffective adsorbents for anionic contaminants and hydrophobic or non-polar organic pollutants (Shen, 2004; Sheng et al., 2001). The adsorption properties of clay minerals can be modified by replacing the inorganic interlayer cations with selected alkylammonium cations (Harvey and Lagaly, 2006; Koh and Dixon, 2001; Lagaly et al., 2006; Mortland et al., 1986), or other monovalent organic molecules or dyes (Borisover et al., 2001; Lagaly et al., 2006; Rytwo et al., 2007). The resulting organophilic clay minerals, known as "organoclay minerals", efficiently adsorb organic compounds (Beall, 2003; Churchman et al., 2006; Lagaly et al., 2006; Shen, 2004, Yelmiz and Yapar, 2004; Zhang and Sparks, 1993), and were proposed for several environmental applications such as for effluent treatment (Zhu et al., 2000), removal of high molar mass hydrocarbons from liquid media (USACE, 2001 p.3.32), remediation of groundwater (Zhao and Vance, 1998), encapsulation of solid waste (Dultz et al., 2005), preparation of herbicides formulations (Nir et al., 2006) and several additional uses (Churchman et al., 2006).

Bentonites and organo-bentonites have been also widely used for the pretreatment of effluents (Beall, 2003). Combination of clay minerals and organic cations was used for the removal of colloidal matter in olive mill wastewater (Mousavi et al., 2006), winery effluents (Rytwo et al., 2011) and other industrial wastewaters. In all cases, considerable changes in the colloidal properties of the effluent, including reduction of turbidity, total suspended solids (TSS), chemical oxygen demand (COD) and other quality parameters were achieved.

Most of the studies mentioned above were performed with purified clays of specific sources. Although such purifications were essential for research purposes, they are generally not performed for commercial or industrial uses, due to high cost. Thus, there is interest in studying and understanding interactions between organic modifiers and raw commercial bentonites in order to explore their applicability for producing low-cost adsorbents, since in most cases the cost of the prepared organo-bentonite would be crucial in the decision whether to use this material.

In this study we report the interaction between berberine, an organic cation, and four different commercial minerals.

Berberine (5,6-dihydro-9,10-dimethoxybenzo[g]-1,3 benzodioxolo[5,6-a] quinolizinium), $(C_{20}H_{18}NO_4)^+$ is a plant alkaloid used in the traditional oriental medicine (Tsai and Tsai, 2004). Due to its strong yellow color it was used to dye wool, leather and wood (Leona and Lombardi, 2007). Combination of berberine with montmorillonite was also found suitable for the photostabilization of bioactive agents (Cohen et al., 2001), for the adsorption of vaccine related proteins (Rytwo et al., 2010), and for the preparation of herbicide formulations (Rytwo et al., 2008). The latter study presented details of the

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Abbreviations: BER, berberine; CEC, cation exchange capacity; EB, Egyptian bentonite; NTU, nephelometric turbidity units, PF, Pure-Flo B80; TZ, Turkish zeolite; UV–Vis, ultraviolet and visible; VO, Volclay KWK; XRD, X-ray diffraction; SEM, scanning electron microscope; SWy-2, Wyoming montmorillonite.

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interaction between berberine and SWy-2 montmorillonite, providing a reference for comparison with the commercial bentonites used for this study.

Volclay KWK (VO) is a fine granular sodium bentonite with an average particle size between 20 and 70 mesh, used in the "fining" step of suspended solids removal from wine, juices, cider, and vinegar. It is particularly useful in preventing cloudiness and removing heat-sensitive proteins (American Colloid Company, 2001; Pocock and Waters, 2006). Egyptian bentonite (EB) is commercially used to quickly build viscosity and to support bore-hole walls for preventing collapse and sloughing. Studies on its beneficiation and applications (Hassan and Abdel-Khalek, 1998) and the influence of polyacrylamide addition on its rheological properties (Mostafa et al., 2007) report its possible uses specially as drilling mud. Turkish commercial zeolite (TZ) contains >90% clinoptilolite/heulandite (Saltali et al., 2007). Interesting properties of zeolites are the relatively large cation exchange capacity (CEC) when compared with smectites, and the three dimensional network of interconnected pores and channels that leads to permanent porosity. Is used as soil conditioner, to improve physical and chemical properties and remove hazardous chemicals. In recent studies, its application for ammonium removal in aqueous effluents was emphasized (Karadag et al., 2006; Saltali et al., 2007). Pure-Flo B80 (PF) is defined by the distributor as an intergrowth of smectites and minerals from the palygorskite/sepiolite group (Oil-Dri Corp. 2005), and is suggested for the use in color and chlorophyll removal from liquids and removal of soaps and detergents from effluents. Several studies used it for oil-refining and pretreatment (Antoniassi et al., 1998), and even removal of iodine (Jain and Proctor, 2007).

2. Materials and methods

2.1. Materials

Food Grade Volclay KWK (American Colloid Company, Arlington Heights, IL), was supplied by Mr. Micha Vaadia (Galil Mountains Winery). Egyptian bentonite (EBDC Bentonite Co., Alexandria, Egypt) was obtained from Mr. Naheel Ibrahim (Ibrahim Construction Co.). Turkish zeolite (Rota A.S. Mining Company, Istanbul, Turkey) was kindly supplied by Mr. Ofer Avidan (Triple T Water Treatment Co.). Pure-Flo B80 (Oil-Dri Corp.) was gently supplied by Mr. Dov Shaked (Oil-Dri Corp.). Na-montmorillonite of Wyoming (SWy-2) was obtained from the Source Clays Repository of The Clay Minerals Society (Columbia, MO). Berberine chloride was purchased from Sigma-Aldrich (Rehovot, Israel). All materials were used without further treatment or purification.

Winery effluents were collected at the beginning of the vintage season from the effluent tanks of Galil Mountain Winery (Yiron, Israel). Brine effluents were collected from Bet Hashita Pickles Factory (Bet Hashita, Israel).

2.2. Adsorption/desorption of berberine onto/from clays

For the adsorption isotherms, a 0.5% bentonite or zeolite dispersion in distilled water was prepared. Two ml dispersion were mixed with suitable volumes of 2×10^{-3} M aqueous berberine solution in glass test tubes, and the final volume was brought to 10 ml. The tubes were sealed and kept at 25°C under continuous agitation using an orbital shaker. After 3 days the tubes were centrifuged at 2500 rpm for 30 min. The concentration of berberine in the supernatants was determined by UV–visible spectroscopy with an HP 8452A spectrophotometer at 344 nm, with ε of 22800 $M^{-1}\,cm^{-1}$. The limit of detection, assuming a minimal sensitivity of the instrument OD = 0.01, was 4.4×10^{-7} M. The amounts of berberine adsorbed were evaluated by mass balance. Experiments were performed in triplicate.

Desorption of berberine was tested by preparing berberine-loaded samples. After centrifugation of 10 ml of organo-bentonite dispersions, 7 ml of the supernatants were carefully removed and replaced by 7 ml of water. Light absorption of the supernatants at 344 nm was measured and released berberine was calculated. The tubes were re-shaken for additional 24 h, centrifuged before again 7 ml of the supernatants were removed and replaced by water. This process was repeated three times.

2.3. X-ray diffraction measurements

XRD analysis of the bentonites and the zeolite was performed with a Philips X-ray diffractometer (PW 1830/1710) operated with 40 kV and 30 mA, CuKα radiation, 1°, 0.1 mm, 1° slits, and sealed proportional detector. The APD software controlled the running, calculated and printed reflection locations and relative intensities, and controlled the diffractogram printout. Original powders were side loaded and scanned at 1 °2θ/1 min rate between 3 and 60 °2θ. The bulk mineralogical composition was qualitatively estimated from the X-ray patterns.

The clay fraction (<2 μm) was collected from thin dispersions in settling tubes according to Stokes Law after a low-intensity ultrasonic treatment for ~1 min. The dispersions were saturated with Sr^{2+} ions by adding $SrCl_2$. Oriented samples were prepared by pipetting the dispersions onto glass slides dried on warm (~35 °C) plates. The clay fraction was scanned at 1 °2θ/1 min rate after a) air-drying, b) equilibrating with ethylene glycol vapor (60 °C) for at least 8 h, and c) heating to 550 °C for 2 h. The berberine treated samples were run at 0.25 °2θ/1 min rate. The semi-quantitative composition was roughly estimated by comparison to calibration curves. The illite content of the illite–smectite was determined following Moore and Reynolds (1989).

2.4. Electrophoretic mobility and electron microscopy measurements

The same samples prepared for the adsorption isotherm were used for electrophoretic mobility measurements as a function of the amount of berberine added (Malvern ZETASIZER Nano ZS, Worcestershire, UK). The surface morphology of the VO, EB and TZ samples was observed under a FE-SEM instrument FEI-NOVA NANOSEM 230 equipped with an EDAX-Ametek detector that allows semi-quantitative analysis of elements. Sample preparation was performed by adhering particles on a carbon tap for direct observation without requirement of any conductive coating on the surface. Potential and deceleration voltages were varied with samples. The PF samples were coated with gold, and their morphology was by SEM (Jeol JSM-840) equipped with EDS (Link 10000 detector).

2.5. Pretreatment of industrial effluents

In order to demonstrate possible applications of the berberine-loaded samples dispersions of the berberine–bentonites and the berberine–zeolite were prepared at 10 g L^{-1} content. Berberine was added in amounts deduced from the adsorption isotherm and electrophoretic mobility experiments, which yielded complete adsorption of the dye, and almost neutral particles: 0.7 mol_c/kg for VO, 0.3 mol_c/kg for PF, 0.06 mol_c/kg for TZ, 0.6 mol_c/kg for EB and 0.72 mol_c/kg for SWy-2.

To 15 ml of winery or brine effluents, 3 ml of 1% of the dispersions was added, yielding a final solid concentration of 1.67 g L^{-1}. The turbidity was measured after 1 h, with a LaMotte 2020*i* turbidimeter (LaMotte, MD). Relative turbidities were evaluated by the ratio between the values of the dispersions and the turbidity of the raw effluent.

3. Results

3.1. Mineralogical composition

The bulk mineralogical composition of the original samples was dominated (>50%) by clay minerals (VO, EB, PF) or zeolite (TZ). The