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Simultaneous sorption of benzene and heavy metals onto two organoclays

Vinka A. Oyanedel-Craver *, Megan Fuller, James A. Smith

Department of Civil Engineering, University of Virginia, P.O. Box 400742, Charlottesville, VA 22904-4742, USA

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Abstract

An experimental study was performed to determine the feasibility of using hexadecyltrimethylammonium bentonite clay (HDTMA-clay) and benzyltriethylammonium bentonite clay (BTEA-clay) for simultaneous sorption of benzene and one of four heavy metals (Pb, Cd, Zn and Hg). Specifically, the role of competition between benzene and each heavy metal was studied. The sorption of Pb, Cd, and Zn on both BTEA- and HDTMA-clay decreases in the presence of benzene relative to the sorption obtained without benzene present. This indicates that there is competition between Pb, Cd, and Zn and organic compounds during sorption onto both organoclays. On BTEA-clay, Cd, Pb and Zn sorption was reduced by 24, 37, and 51%, respectively. On HDTMA-clay, Cd, Pb, and Zn sorption was reduced by 25, 30, and 57%, respectively. Hg sorption was not affected either by the presence of benzene or by the organoclays used. The sorption of benzene onto BTEA-clay in the presence of Hg, Zn, Pb, and Cd was less than the sorption observed when no heavy metal was present. The presence of Hg resulted in the most significant decrease in sorption, causing a 59% reduction in benzene sorption. The presence of Zn, Pb, and Cd caused a 41, 35, and 31% reduction in benzene sorption, respectively. In general, sorption of benzene onto HDTMA-clay was not affected by the presence of the heavy metals, indicating there are no competitive effects observed with Zn, Cd, and Hg when HDTMA-clay was the sorbent. However, the presence of Pb did cause a 20% reduction in benzene sorption to HDTMA-clay. Both organoclays tested had dual sorptive properties for both heavy metals and an organic contaminant. While the competitive effects were greater for the BTEA clay, both organoclays are capable of simultaneously removing benzene and either Zn, Cd, Hg, or Pb from aqueous solution.

Keywords: Organoclay; Heavy metals; Benzene; Sorption; Competition

1. Introduction

Bentonite clay, comprised predominantly of montmorillonite, is often used in liners for municipal- and hazardous-waste landfills, wastewater impoundment, slurry cut-off walls and tank farms [1]. The primary function of the clay is to impede the movement of contaminated water and leachate to nearby ground water. Although conventional bentonite works well to reduced the hydraulic conductivity of a porous medium, its hydrophilic mineral surfaces make it a poor sorbent for relatively nonpolar organic solutes. Several researchers have shown that by decreasing the clay surface's hydrophilicity through the addition of quaternary ammonium cations (QACs), the resulting organoclays can sorb nonionic organic compounds from aqueous solutions [2,3]. This makes organoclays useful in applications where the removal of organic contaminants is of concern. Organoclays have been used in wastewater treatment facilities and military installations to remove chlorinated solvents and oil and grease generated from paint-stripping activities and degreasing operations [4,5]. Recently organoclays were used in a full-scale sediment cap at the McCormick and Baxter Company Superfund site [6].

The sorption mechanism of the organic contaminant by the organoclay is dependent on the structure of the QAC amendment. If the QAC contains short-chain alkyl groups and/or a benzyl group, such as benzyltriethylammonium clay (BTEA), the sorption of organic contaminants is generally characterized by isotherm non-linearity and competitive sorption, indicating that the organic contaminant is adsorbing to surface sites available on the clay's internal or external mineral surfaces [7,8]. On the other hand, if the QAC contains a long-chain alkyl group, such as hexadecyltrimethylammonium clay (HDTMA),

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* Corresponding author. Fax: +1 434 924 1041.
E-mail address: vac4n@virginia.edu (V.A. Oyanedel-Craver).

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the sorption mechanism is characterized by isotherm linearity, relatively low heats of sorption, and non-competitive sorption [8]. This indicates that the uptake is caused by solute partitioning between water and the amorphous organic phase created by the exchanged organic cations.

Although bentonite must be modified to sorb nonpolar organic compounds, it is naturally able to sorb heavy metals from aqueous solution through ion-exchange of its interlamellae cations [9,10]. There are also other sites in the bentonite structure that, depending on pH, are capable of sorbing heavy metals [11,12]. These Si–O^- and Al–O^- sites form inner-sphere metal cation complexes at the clay particle edges [10]. Metal sorption to bentonite can be described by a Langmuir-type model, indicating the adsorption of metals occurs at surface sites available on the mineral structure [9–13]. The ability of bentonite to adsorb heavy metals from aqueous solutions could be an additional benefit for organoclay use in landfill liners, geosynthetic clay liners, sediment caps, and slurry walls.

The conventional approach has been to study metal uptake by bentonite clays and organic contaminant uptake by organobentonite clays independently. However, most current and potential uses of organoclays, i.e. landfill additives and reactive barriers, are at sites in which a mixture of organic and metal contaminants is present. Heavy metals have a high priority for removal due to their harmful effects on humans and the environment [14]. The treatment of soil and water contaminated with mixed wastes poses a significant challenge because metals and organic contaminants have different fate and transport mechanisms [15]. Oyanedel-Craver and Smith [16] and Yuan [17] have both demonstrated that QAC modified organoclays can successfully sorb heavy metals, although not as effectively as unmodified bentonites. Few studies have investigated competitive sorption between the metal and organic contaminants to modified bentonites. Past work has focused on only two metals (Pb and Cd) and partitioning-type organoclays [18,19] with only one study of metal/organic competition on an adsorptive clay [20]. More work is needed to characterize the sorption of different metals on both adsorptive and partitioning-type organoclays in the presence of organic solutes in order to more fully understand the potential for, and effect of, competition.

This work investigates the role of competition between several heavy metals (Pb, Zn, Cd, and Hg) and benzene on both adsorptive clay (BTEA) and partitioning (HDTMA) clays. It is important to investigate individual metals because the magnitude of sorption is dictated by the intrinsic physical properties of the individual metals and the adsorptive capacity of the clay. It has been observed that the magnitude of metal sorption to organoclays is principally controlled by the degree of the organic cation loading rather than the type of QAC used [16]. The mechanism of organic solute sorption is a function of the type of QAC present on the surface of the bentonite. By studying both adsorptive and partitioning clays, it will be possible to elucidate the effect of the organic sorption mechanism on the sorption of heavy metals. Similarly the effect of the heavy-metal sorption mechanism on the benzene sorption will also be evaluated.

2. Materials and methods

2.1. Materials

The two organobentonites used in this study were synthesized from Wyoming bentonite (American Colloid Company). The base bentonite was composed of 3.6% sand, 7.3% silt and 89.1% clay. The cation-exchange capacity (CEC) of the clay was 0.814 mmol/g.

Two quaternary ammonium compounds were used to synthesize the clays: HDTMA bromide [$(CH_3)_3NC_{16}H_{33}Br$] and BTEA chloride [$(C_2H_5)_3NCH_2C_6H_5Cl$]. Both compounds were obtained from Aldrich Chemical Company, have a chemical purity of 99%, and were used as received.

The aqueous-metal solutions were prepared using the following salts: $CdCl_2$, $ZnCl_2$, $PbNO_3$ and $HgCl_2$ (Acros Organics). The salts were >97% pure and were used as received.

Benzene was obtained from Aldrich Chemical Company (99% purity) and was used as received. Benzene was mixed with its corresponding [^{14}C] isotope (Aldrich Chemical Company, 99% chemical and radiochemical purity) to create a radiolabeled stock solution.

2.2. Preparation of organobentonites

Homoionic clays were prepared in order to avoid different magnitude of exchange and/or competition between the sorbing metal and the ions originally present, and thus the final metal-adsorbing capacities. The exchangeable inorganic cations on the base bentonite were primarily sodium with a small percentage of Mg and Ca. The detailed procedure for homoionic clay preparation is given by Boyd et al. [21]. Briefly the Wyoming bentonite was treated with aqueous $CaCl_2$ in a fivefold excess of the CEC of the clay (0.814 mmol/g). The Ca-saturated clay was washed several times with distilled water and then dried.

The organoclay was prepared by exchanging the calcium on the surface of the homoionic clay with either of the two quaternary ammonium cations. The quantity of organic cation added to the bentonite was determined by

$$f=\frac{M_{\mathrm{cation}}}{\mathrm{CEC}\times M_{\mathrm{clay}}\times \mathrm{GMW}_{\mathrm{cation}}\times Z}, \tag{1}$$

where f = fraction of CEC satisfied by the organic cation, M_{cation} = mass of organic cation required to achieve the desired fraction of CEC, CEC = cation-exchange capacity of the base clay, M_{clay} = mass of the homoionic clay, $\mathrm{GMW}_{\mathrm{cation}}$ = gram molecular weight of the organic cation, and Z = moles of charge per equivalent. The detailed procedure of the organoclay preparation is given by Bartelt-Hunt et al. [22]. Briefly, the organobentonite was synthesized by the aqueous system exchange of the dissolved quaternary ammonium compound onto the internal and external mineral surfaces of the Ca-bentonite.

2.3. Sorption of heavy metals and benzene

Cadmium, zinc, lead, and mercury sorption to two organobentonites was evaluated by a batch equilibration procedure.