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Research paper

The potential of thermally treated organobentonites to adsorb organic compounds from water

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ABSTRACT

The effects of thermal treatment of selected quaternary ammonium-exchanged bentonites formed with *n*-hexadecyltrimethylammonium, benzyltrimethylammonium and tetraethylammonium on their adsorption of a series of organic compounds from water were examined. The examined compounds were phenanthrene, atrazine, phenol, and *m*-nitrophenol, which differ substantially in their molecular structures and are capable of various types of interactions with adsorbents and solvent. The thermal pretreatment of organobentonites and of original bentonite involved 2 h of heating in air at 150, 250, 360 and 420 °C. Heating of organoclays at 150 °C did not cause obvious changes in the structures of the adsorbents but might have enhanced their interactions with organic adsorbates. The extent of the enhancement differed among the adsorbates and could reflect their differing abilities to compete with water molecules for adsorption sites on organoclays. The loss of organic carbon and significant changes in the organoclay chemical structures caused by preheating in air at higher temperatures did not result in significant loss of the organoclay potential to adsorb organic compounds present in the aqueous solution.

1. Introduction

Organoclays, i.e., clays in which exchangeable inorganic cations were replaced with organic cations (often quaternary ammonium or N-alkylpyridinium), were widely considered for multiple environmental applications because of their potential to interact strongly with organic compounds in aqueous environments. Thermal treatment was suggested as one possible means of regenerating organoclays after their use for removing organic pollutants from water (Lin and Cheng, 2000; Yapar, 2006; Zhu et al., 2009). Tests of adsorption of phenols on organobentonites formed with quaternary ammonium and N-alkylpyridinium demonstrated the possibility of thermal regeneration of organoclays (Lin and Cheng, 2000). For example, heating of quaternary ammonium-based organoclays at 200 °C for 2 h under a nitrogen atmosphere significantly regenerated the adsorbents after their use for adsorption of phenol and *m*-chlorophenol from water (Lin and Cheng, 2002). On the other hand, regeneration in air caused oxidation of quaternary ammonium in organoclays and considerable loss of the adsorption capacity of the regenerated adsorbents (Lin and Cheng, 2002).

However, it was not generally known how the adsorptive capacity of organoclays is affected by thermal treatment prior to their interactions with organic compounds in water. Such knowledge is important to enable comparison with the performance of organoclays thermally regenerated after use. Specifically, this knowledge could contribute to the better understanding of changes in the adsorbent that occur during thermal regeneration of organoclays and could be helpful in the search for organoclays and appropriate treatment regimes to enable their effective thermal regeneration. Therefore, it is of interest to determine the ability of thermally treated organoclays to adsorb organic compounds from water.

Borisover et al. (2010a,b) demonstrated that, in the case of nitrobenzene, preheating of organoclays could even enhance their potential to interact with an organic compound in aqueous solutions. The aqueous adsorption of nitrobenzene on several organobentonites formed via exchange with *n*-hexadecyltrimethylammonium (HDTMA), benzyltrimethylammonium (BTMA), and tetraethylammonium (TEA) was enhanced when organoclays were subjected to 2 h of heating in air, at temperatures ranging between 150 and 360 °C. This adsorption increase was hypothesized to reflect suppression of organoclay rehydration by the thermal pretreatment, with consequently reduced water-adsorbate competition for adsorption sites. Even the significant loss of carbon from thermally treated organoclays may not be linked to the loss of their adsorptive potential (Borisover et al., 2010a). Nevertheless, there is a need to examine the effects of thermal treatment of organoclays on adsorption of organic compounds of various structures. The examination of a variety of organic

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adsorbates could contribute to better understanding of the impact of thermal treatment of organoclays on adsorbate-adsorbent interactions, and of the implications for regeneration of organoclays.

Therefore, the aim of this study was to evaluate the effect of thermal pretreatment of selected quaternary ammonium-exchanged bentonites formed with HDTMA-, BTMA-, and TEA-cations on adsorption of a series of organic compounds from water. The compounds examined as probe adsorbates were phenanthrene, atrazine, phenol, and *m*-nitrophenol, which differ substantially in their molecular structure, and are the typical representatives of some groups of organic pollutants, i.e., polycyclic aromatic hydrocarbons, heterocyclic herbicides, and substituted phenols, respectively. These compounds are capable of various types of interactions with adsorbents and solvent.

2. Experimental part

2.1. Materials

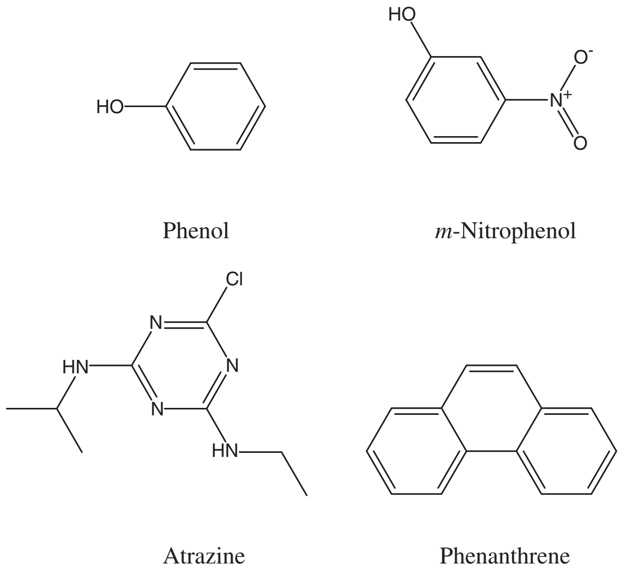
Wyoming bentonite (Na-montmorillonite-rich clay) with cation exchange capacity (CEC) of 90.7 meq/100 g was purchased from Fisher Scientific (USA). Phenol (>99.5%), *m*-nitrophenol (>99%), atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, >98%), and phenanthrene (>98%) were obtained from Aldrich Chemical Co. The chemical structures of the organic compounds are shown in Fig. 1.

The same batch of organobentonites prepared from Wyoming bentonite and their thermal modifications that had been previously used by Borisover et al. (2008, 2010a,b) was studied in the present work. The four different types of organobentonites used were: HDTMA41- and HDTMA90-clays, in which 41% and 90%, respectively, of inorganic cations were exchanged with *n*-hexadecyltrimethylammonium (HDTMA); BTMA-clay, in which 81% of inorganic cations were exchanged with benzyltrimethylammonium (BTMA); and TEA-clay, in which 77% of inorganic cations were exchanged with tetraethylammonium (TEA). In the organobentonites studied, the mol amounts of the exchanged organic cations were selected to reach the high extent of the cation exchange in order to significantly expand and dehydrate the interlayer space. On the other hand, the organic cation to bentonite ratios corresponding to the clay CEC (or exceeding it) were avoided in order to minimize the "hydrophobic bonding" interactions of organic cations with bentonite (Xu and Boyd, 1995). The preparation of HDTMA-exchanged organoclays was described by Burstein et al. (2008). The synthesis of BTMA- and TEA-clays was described by Borisover et al. (2010b). The residual moisture content of the freeze-dried adsorbents did not exceed 3% (w/w), as determined by oven-drying at 105 °C. The thermal treatments of the adsorbents involved heating for 2 h at 150, 250, 360, or 420 °C in an oven, in air (Borisover et al., 2010a,b). After heating, the adsorbents were kept hermetically closed in a desiccator. The carbon contents and basal spacings of the organoclay adsorbents studied and their thermal modifications are listed in Table 1.

2.2. Batch adsorption experiments

Adsorption from water was studied at 22 ± 2°C with a batch technique similar to that described by Borisover et al. (2010a,b). Some details of the adsorption experiments are presented in Table 2. In brief, a certain volume of the aqueous solution of a chemical compound was added to a glass vial containing a predetermined amount of an adsorbent and fitted with a Teflon-lined screw cap. The vial contents were mixed in the dark on a horizontal shaker. The aqueous solution also contained sodium azide at 200 mg L^{-1} to minimize solute biodegradation, and $CaCl_2$ at 0.01 M. The adsorption experiments were carried out in triplicate with corresponding duplicated blank vials, i.e., containing solute but no adsorbent.

Before analysis the suspensions were centrifuged at 2500 rpm for 20 min, the aqueous supernatants were passed through a 0.45 μm filter, and the concentrations of solutes in them were measured against external standards with a Shimadzu HPLC equipped with a UV diode array and fluorescence detectors, and fitted with a Merck LiChroCART® 250–4 LiChrospher® 100 RP-8 (5 μm) column. The mobile phase was a 70/30 acetonitrile/water mixture flowing at 1 mL min^{-1}. The UV absorption and fluorescence excitation/emission wavelengths used for detection of solutes are shown in Table 2. The



Phenol

m-Nitrophenol

Atrazine

Phenanthrene

Fig. 1. Chemical structures of organic compounds used as probe adsorbates.

Table 1
Basal spacing and carbon content of the adsorbents used.

Sorbent	Treatment temperature, °C	Basal spacing, nm	Carbon content[a], % w/w
Bentonite	RT[b]	1.25[c]	1.0
	150	1.19[c]	1.0
	250	0.99[d]	0.95
	360	0.97[c]	0.62
	420	0.95[d]	0.6
HDTMA41-clay	RT	1.45[c]	9.6
	150	1.43[c]	9.6
	250	1.38[d]	8.9
	360	1.28[c]	6.1
	420	1.25[d]	6.1
HDTMA90-clay	RT	1.81[c]	17.3
	150	1.77[c]	17.1
	250	1.38[d]	10.1
	360	1.28[c]	8.3
	420	1.25[d]	8.1
BTMA-clay	RT	1.45[e]	8.6
	150	na[f]	8.3
	250	na	8.3
	360	na	4.1
	420	na	3.2
TEA-clay	RT	1.36[e]	6.7
	150	na	6.8
	250	na	7.0
	360	na	3.1
	420	na	3.0

[a] the data for bentonite, HDTMA41-clay and HDTMA90-clay is from Lapides et al. (2011); the data for BTMA-clay and TEA-clay is from Borisover et al. (2010b).

[b] "RT" means "room temperature" indicating that the adsorbent was not heated.

[c] Burstein et al. (2008).

[d] Borisover et al. (2010a)

[e] Borisover et al. (2010b).

[f] "na" means "non-available.