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Mild pre-heating of organic cation-exchanged clays enhances their interactions with nitrobenzene in aqueous environment

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Abstract Aqueous sorption kinetics and equilibrium isotherms of nitrobenzene were studied on two series of sorbents that were prepared by (i) replacing inorganic exchangeable cations in Wyoming bentonite with tetraethylammonium (TEA) and benzyltrimethylammonium (BTMA) and (ii) heating synthesized complexes in air at different temperatures (between 150 and 420°C). The aim of this work was to examine recently observed enhancement of aqueous sorption of a probe organic sorbate on organoclays after mild thermal pre-treatment of sorbents. Thermal pre-treatment of TEA- and BTMA-clays at 150°C results in the maximal enhancement of nitrobenzene–sorbent interactions as compared with treatment of original bentonite and its exchange complexes formed with long-chain quaternary ammonium (*n*-hexadecyltrimethylammonium, HDTMA). Based on C, N content data and FTIR spectra of TEA- and BTMA-clay complexes, no indications of decomposition of organic matter were found in organoclays heated at 250°C (and below this temperature). Suppressed hydration of pre-heated sorbents resulting in a lessening of water–organic sorbate competition for sorption sites is considered to be responsible for thermally induced enhancement of nitrobenzene–sorbent interactions. In the HDTMA-based organoclays, the long-chain aliphatic groups of the quaternary ammonium can additionally interact with clay surface thus competing with organic sorbate–sorbent surface interactions and, in this way, mitigating the enhancement of nitrobenzene sorption on thermally treated sorbents.

Keywords Organoclays · Thermal treatment · Sorption enhancement · Montmorillonite · Water-sorbate competition · Clay hydration

1 Introduction

Due to the structural varieties of clay minerals, organic cations and the different possibilities for their combination, the replacement of exchangeable inorganic cations in clays with organic cations opens broad opportunities in creating new organic–inorganic composites (further, organoclays). Important practically-oriented motivation in studying organoclay complexes and their interactions with organic compounds results from the ability of such materials to sorb multiple organic substances from water, and, specifically, to remove effectively oils and greases (e.g. Mortland et al. 1986; Boyd et al. 1991; Yariv and Cross 2002; Alther 2008). Elucidating of mechanisms of organic compound interactions with organoclays may assist in developing sorbents with controlled properties.

Examination of interactions of organic compounds with organoclays pre-treated thermally in controlled conditions can be helpful for better understanding of mechanisms of organic compound–organoclay interactions and, possibly, for improvement of sorptive properties of organoclay sorbents. For example, it was found (Borisover et al. 2010) that Wyoming bentonite in which exchangeable inorganic cations were replaced, in different extents, with *n*-hexadecyltrimethylammonium (HDTMA) demonstrated an enhancement of its capability to sorb a model organic sorbate, nitrobenzene, from water after being mildly heated

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in air. This enhancement of nitrobenzene sorption from water was observed on organoclay sorbents heated at 150°C; no remarkable degradation of clay-attached organic cations was expected. Reduced hydration of a thermally treated organoclay (as compared with non-heated sorbent) and, hence, diminished water–organic sorbate competition for organoclay sorption sites were suggested to explain the enhanced interactions of nitrobenzene with pre-heated organoclays (Borisover et al. 2010).

The understanding of the effect of thermal pre-treatment of organoclays on their capability to interact with organic substances could be also useful for thermal regeneration of organoclays exploited in removal of organic pollutants from water (Zhu et al. 2009). So, the thermal treatment of different organoclays in the inert nitrogen atmosphere was shown to result in a high extent of organoclay regeneration after use for sorption of organic pollutants from water (Lin and Cheng 2002). It was also demonstrated that the heating of organoclays at 200°C for two hours in the nitrogen atmosphere was optimal to significantly regenerate the sorbents.

Importantly, a thermal treatment-induced increase of sorptive capability was observed also for original Wyoming bentonite interacting with nitrobenzene in aqueous environment (Borisover et al. 2010). Earlier, the increased aqueous sorption of organic pesticide (metolachlor) was distinctly observed on sodium-rich Wyoming bentonite undergoing calcination at temperatures above 350°C (Bojemueller et al. 2001). The effect of clay calcination on aqueous metolachlor sorption was assigned to the enrichment of aluminum ions or hydroxo-aluminum species at the clay edges. Since such a calcination effect was observed at relatively high temperatures, it is hardly related to enhanced sorptive capability of Wyoming bentonite pre-heated at lower temperatures (i.e. in the range between 150 and 360°C; Borisover et al. 2010). On the other hand, Prost and Yaron (2001) mentioned an increased retention capacity of clays for organic molecules due to thermally induced dehydration.

Such a sorbent dehydration involving a partially irreversible loss of residual water (and, therefore, reduced hydration upon further immersion in aqueous environment) could contribute to enhanced organic sorbate interactions with both thermally pre-treated regular Wyoming bentonite and HDTMA-based organoclays. In addition, heating-induced changes in organization of long-chain organic groups in HDTMA-clays could result in their better contact with a clay surface. This can suppress both sorbent hydration and organic sorbate–clay interactions. The latter effect should mitigate any enhancement of organoclay sorptive capability due to a sorbent pre-heating. Therefore, organoclays formed with smaller-size organic cations could demonstrate even greater intensity of sorbate–sorbent interactions after thermal pre-treatment as compared with long-chain HDTMA-based organoclay complexes.

To check this hypothesis, aqueous sorption of a probe compound, nitrobenzene, was examined in this study on two different organoclay complexes formed from Na-montmorillonite-rich Wyoming bentonite with tetraethylammonium (TEA) and benzyltrimethylammonium (BTMA), and on their modifications obtained by thermal treatment. Both series of sorbents are considered to represent so-called "adsorptive" organoclays (Smith and Galan 1995; Jaynes and Vance 1999; Borisover et al. 2001) since they are lacking the long-chain aliphatic fragments. By using these smaller-size organic cations (as compared with HDTMA), we intended to get the better understanding of the role of organic cations in sorptive properties of thermally treated organoclays. Specifically, by comparing TEA- and BTMA-clays with earlier studied HDTMA-clays (Borisover et al. 2010), we planned to examine whether the presence of long aliphatic chains in organoclay structure and therefore, possibly, the changes in their conformation and orientation due to the organoclay pre-heating play a dominant role in thermally induced enhancement of organoclay sorptive properties.

2 Experimental

2.1 Materials

Wyoming bentonite (Na-montmorillonite rich clay, $[(Al_{3.07}Ti_{0.01}Fe_{0.40}Mg_{0.49})(Si_{7.79}Al_{0.21})O_{20}(OH)_4]\cdot Na_{0.75}$; Newman and Brown 1987) with cation exchange capacity (CEC) of 90.7 meq/100 g was obtained from Fisher Scientific (U.S.). This bentonite clay differently heated was characterized earlier using XRD (Burstein et al. 2008), DTA/TG/DTG (Langier-Kuźniarowa 2002) and with C/H analyses (Lapides et al. 2010). Nitrobenzene (99%), tetraethylammonium (TEA) chloride hydrate and benzyltrimethylammonium (BTMA) chloride (both 98%) were purchased from Sigma-Aldrich and used without further purification.

2.2 Preparation and characterization of organoclays

Organoclay complexes were prepared by exchanging inorganic cations in Wyoming bentonite with quaternary ammonium cations (i.e. TEA and BTMA) according to the procedure described by Burstein et al. (2008). In brief, 3 L of homogeneous 1.5% w/w aqueous bentonite suspension was prepared by continuous stirring during four hours. Then, 1 L of the aqueous solution containing 0.044 mol/L of TEA chloride or 0.064 mol/L of BTMA chloride was added, with the rate of 1–1.5 mL/min. Nominal ratio of organic cation added (per 100 g of clay) to the clay CEC was 1.08 and 1.58 for TEA and BTMA, respectively. After additional overnight stirring, suspension was centrifuged, washed repeatedly with distilled water until negative reaction with

$AgNO_3$ and freeze-dried. Remaining moisture content of both freeze-dried organoclay sorbents named TEA-clay and BTMA-clay was 3.0–3.1% w/w (determined by oven-drying at 105°C). Thermal treatment of synthesized organoclays involved heating during two hours at 150, 250, 360 or 420°C in an oven (in air). After heating, the sorbents were kept hermetically closed in a desiccator.

Prepared and thermally treated sorbents were characterized by their C and N contents using Thermo-Finnigan C/N analyzer. Based on C contents of freeze-dried synthesized organoclays, the extent of cation exchange (relative to CEC) was determined as 77% for TEA-clay and 81% for BTMA-clay. FTIR spectra of KBr disks of non-heated and thermally treated organoclays (at the clay : KBr mass ratio 1 : 100) were recorded on a Tensor-27 Bruker spectrometer, at a resolution of 4 cm^{-1}. X-ray diffractions of non-heated organoclays were recorded in air atmosphere at room temperature by Phillips Automatic Diffractometer (PW 1710) with a Cu tube anode between 3.7 and 40° (2Q).

2.3 Batch sorption experiments

Similarly to the previous study (Borisover et al. 2010), a sorptive potential of organoclays and their thermal modifications was probed using aqueous nitrobenzene sorption. Mechanisms of nitrobenzene interactions with organoclays in aqueous and water-free environments were examined earlier (Burstein et al. 2008; Borisover et al. 2008). It is recognized that the effect of a thermal treatment of organoclays on their sorptive properties may strongly depend on the nature of organic sorbates (e.g. the ability to participate in specific interactions of different types, the sorbate molar volume etc.). Obviously, a caution is needed when the understanding derived from nitrobenzene sorption on thermally treated organoclays is projected towards organic sorbates of a different structure.

Sorption experiments were performed at 22 ± 2°C using the batch technique (Borisover et al. 2010). In brief, 1.0 mL of aqueous nitrobenzene solution was added into a 2.0 mL glass vial equipped with a Teflon-lined screw cap which contained 20–50 mg of a sorbent. The vial content was mixed in the dark on a horizontal shaker. Initial nitrobenzene concentrations in aqueous solution ranged between 0.24 and 12.2 mmol/L. Aqueous solution of nitrobenzene contained also 200 mg/L of sodium azide (to minimize a biodegradation of nitrobenzene) and 0.01 mol/L of $CaCl_2$. Sorption experiments were carried out in triplicate with a corresponding duplicated blank (i.e. solute, no sorbent). pH of a supernatant varied between 7.0 and 7.5. Since nitrobenzene does not ionize in aqueous solution, then, small variations in pH are not expected to influence the nitrobenzene sorption.

For analysis, the suspensions had been centrifuged, and concentrations of nitrobenzene in aqueous supernatants were measured using a Shimadzu HPLC equipped with a UV diode array detector (Borisover et al. 2010). Nitrobenzene losses in the blank vials were less than 2%. The amount of sorbed solute was determined by the difference between the initial and final solute concentrations in the liquid phase and reported on a dry sorbent weight basis. Sorption kinetics was tested, and the same time (48 hours) was allowed for equilibration in all sorption systems.

The release of organic cations or products of their thermal transformation from organoclays was evaluated by measuring supernatant concentrations of dissolved organic carbon (DOC) in the control suspensions not including nitrobenzene. The DOC concentration varied between 8 and 70 mg/L (as determined by Scalar TOC/TN analyzer). Based on these DOC concentrations, the loss of carbon from sorbents due to its release into the aqueous solution was found to be between 0.5 and 4.1% (of a total C content of sorbents). If this DOC would produce a lipophilic microenvironment in aqueous solution, then, it would bind only 0.05–0.5% of nitrobenzene presented in water (based on relatively low hydrophobicity/lipophilicity of nitrobenzene as expressed by its *n*-octanol-water distribution coefficient 70.8; Hansch et al. 1995). Hence, the impact of released organic carbon both on the C content of sorbents and on the state of nitrobenzene in aqueous solutions was considered negligible.

3 Results and discussion

3.1 Organoclay changes due to thermal treatment

The d-spacing values of TEA- and BTMA-clays were found to be 1.36 and 1.45 nm, respectively, which exceeds d-spacing of original Wyoming bentonite in both freeze-dried and air-dried forms (1.12 and 1.25 nm, respectively; Burstein et al. 2008). d-Spacing of TEA- and BTMA-clays is close to that for Wyoming bentonite in which 41% of CEC was replaced with HDTMA cation (1.41 and 1.45 nm for freeze-dried and air-dried forms, respectively; Burstein et al. 2008). Thus, the expansion of the clay interlayer space indicates the intercalation of both TEA and BTMA cations. Table 1 provides the data on C and N contents of both synthesized organoclays prior thermal treatment and after heating at different temperatures. From data in Table 1, it is obvious that both TEA-clay and BTMA-clay begin to loose C and N only after heating at temperatures exceeding 250°C.

Thermal stability of exchanged organic cations in TEA- and BTMA-clays at 250°C (and below this temperature) is clearly supported by FTIR-spectra in the regions 3100–2750 and 1600–1150 cm^{-1} (Figs. 1 and 2). In these spectroscopic regions the stretching and the deformation of C-H in organic compounds are detected whereas the OH, Si-O, Al-O and Mg-O vibrations of the clay framework, as well as those of

Table 1 C, N contents[a] of organoclay sorbents subjected to different thermal treatments

Organoclay	*t*, °C	N, % w/w	C, % w/w
TEA-clay	Non-heated[b]	0.89	6.7
	150	0.88	6.8
	250	0.97	7.0
	360	0.68	3.1
	420	0.75	3.0
BTMA-clay	Non-heated[b]	0.96	8.6
	150	0.93	8.3
	250	0.95	8.3
	360	0.73	4.1
	420	0.64	3.2

[a] Averages of duplicated data, with standard deviations ranging between 0.1 and 4%.

[b] Indicates an organoclay sorbent prior any thermal treatment.

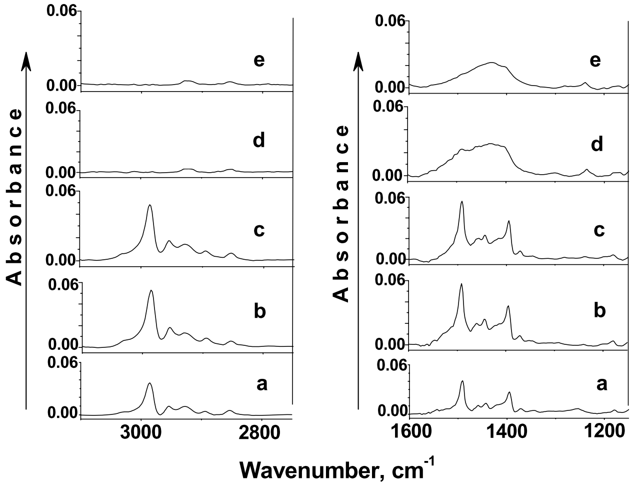

Fig. 1 FTIR spectra of KBr disks of TEA-clay non-heated (*curves* a) and after heating the organoclay at 150, 250, 360 and 420°C (*curves* b, c, d and e, respectively) in the spectroscopic regions 3100–2750 cm^{-1} (*left*) and 1600–1150 cm^{-1} (*right*), after correcting the baseline

the adsorbed water, do not appear and, therefore, do not interfere with the C-H bands of the exchanged organic cations. The absorption maxima of C-H vibrations in the FTIR spectra of TEA- and BTMA-clays, non-heated and after heating at 250°C, are collected also in Table 2 together with their assignments (Rao 1963; Parker and Frost 1996; Yapar 2009; Vidal and Volzone 2009) and relative intensities.

It is seen in Figs. 1 and 2 that curves b and c are very similar to curve a, proving that both organic ammonium cations persist in the clay complexes heated at 150 and 250°C. Minor changes are observed at 250°C in the relative intensities of the aromatic C-H stretching vibrations in the spectrum of BTMA-clay (Table 2; Fig. 2), and two of the aliphatic C-H deformation bands split each into two bands. This may indicate that the air-oxidation of BTMA cation might begin at 250°C.

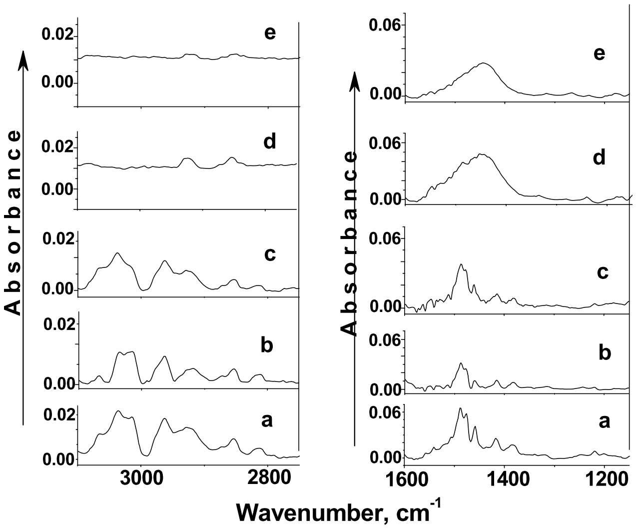

Fig. 2 FTIR spectra of KBr disks of BTMA-clay non-heated (*curves* a) and after heating the organoclay at 150, 250, 360 and 420°C (*curves* b, c, d and e, respectively) in the spectroscopic regions 3100–2750 cm^{-1} (*left*) and 1600–1150 cm^{-1} (*right*), after correcting the baseline

Maximal absorbance due to alkyl CH stretching vibrations in TEA-clay (at 2986 cm^{-1}) was also normalized by maximal absorbance associated with structural OH-stretching vibrations at 3633 cm^{-1}. This ratio was found to be 0.33, 0.32 and 0.30 for the non-heated TEA-clay and after heating at 150 and 250°C, respectively. Since it is hardly expectable that structural OH groups used as an internal reference and alkyl C-Hs have the same thermal stability in the 25–250°C temperature range, then, it appears that there is no significant deterioration of aliphatic groups. Hence, TEA- and BTMA-clays are even more stable against thermal degradation in air as compared with some HDTMA-clay complexes that showed a certain decomposition after heating at the same conditions (i.e. 2 hours in air) at temperatures above 150°C (Borisover et al. 2010).

Similarly, based on DTA-TGA data, Vidal and Volzone (2009) reported that below 200°C tetramethylammonium-montmorillonite undergoes only dehydration; the dehydration peak is shifted in the organoclay as compared with original Ca-montmorillonite to lower temperatures. By applying DTA-TGA to organoclays formed with long-chain quaternary ammonium cations, Xie et al. (2001) observed below 200°C only water loss. Combined DTA-EGA (evolved gas analysis) carried out in the oxidative atmosphere (Müller-Vonmoos et al. 1977; Cebulak and Langier-Kuźniarowa 1997; Langier-Kuźniarowa 2002; Yariv 2003; Ovadyahu et al. 2007) demonstrated that below 250°C many organoclay complexes undergo endothermic dehydration.

Table 2 FTIR absorption band maxima (in cm^{-1}) and their relative intensities[a] in spectra of TEA- and BTMA-clays, non-heated and after heating at 250°C

Assignment	Organoclay			
	TEA-clay		BTMA-clay	
	Non-heated	After heating at 250°C	Non-heated	After heating at 250°C
Aromatic C-H stretching			3064 m	3063 sh
Aromatic C-H stretching			3036 vi	3036 vi
Aromatic C-H stretching			3015 i	3017 t
Aliphatic C-H stretching as	2986 vi	2986 vi		
Aliphatic C-H stretching as	2955 m	2955 m	2962 i	2962 i
Aliphatic C-H stretching as	2927 m	2927 m	2929 m	2929 m
Aliphatic C-H stretching sym	2894 w	2895 w	2873 vw	2872 vw
Aliphatic C-H stretching sym	2853 w	2854 w	2855 w	2854 w
Aliphatic C-H stretching sym			2814 vw	2815 vw
Aliphatic C-H deformation	1492 vi	1491 vi	1488 vi	1487 vi
Aromatic ring vibration			1475 i	1478 i
Aliphatic C-H deformation	1459 vw	1459 vw	1459 m	1460 m
Methylene group	1443 w	1445 w		
Aliphatic C-H deformation				1420 vvw
Aliphatic C-H deformation	1420 vvw	1420 vvw	1418 w	1415 w
Aliphatic C-H deformation				1388 vvw
Aliphatic C-H deformation	1394 i	1394 i	1385 w	1382 w
Methylene group	1371 w	1371 w		
Methylene group	1347 vw	1347 vw		

[a] i, intense; m, medium; w, weak; sh, shoulder; t, tail; v, very; as, asymmetric; sym, symmetric; the intensities are related to the most strong CH band and not to any of the clay framework bands.

The organoclays heated at 360 and 420°C (curves d and e, respectively; Figs. 1 and 2) show different spectra which are supposed to be diagnostic for charcoal, thermally formed during the air-oxidation of the intercalated organic matter (Yariv 2003; Ovadyahu et al. 2007). In the region 3100–2750 cm^{-1}, where CH vibrations are expected to appear, there are only two bands at 2925 and 2854 cm^{-1}, and they are weak and very weak in spectra of samples heated at 360 and 420°C, respectively. Their presence suggests that few CH groups are still present in the charcoal at 360°C but their amount decreases at the higher temperature. In the region 1600–1150 cm^{-1} a very broad band is detected with maxima at 1431 or 1444 cm^{-1} in the spectra of heated TEA- or BTMA-clay, respectively (curves d and e, Figs. 1 and 2). These absorptions are characteristic for CC groups resonating between two canonic structures with a single and a double bond nature.

3.2 Sorption kinetics and equilibrium isotherms

Kinetics of nitrobenzene sorption on organoclays and their thermal modifications was evaluated at the same initial concentration of nitrobenzene in aqueous solution and shown in Fig. 3. In all systems, sorption equilibrium was attained after 24 hours, and in some cases even the 14 hrs mixing was sufficient to attain the equilibrium. Hence, the 48 hrs time period that was selected to measure isotherms corresponded well to the equilibrium state.

The aqueous sorption isotherms of nitrobenzene on TEA- and BTMA-clays and their thermally treated modifications are presented in Figs. 4 and 5, respectively. For further analysis, a simple model satisfying experimental sorption isotherms and allowing the comparison between different sorbents was chosen. Hence, the sorption isotherms were fitted using the Freundlich isotherm model: (Sorbed concentration) $= K_F \cdot$ (solution concentration)^n, where K_F (the Freundlich model constant) and n (the Freundlich model exponent) are the parameters assumed to be independent on a sorbate concentration. The K_F and n parameters are considered responsible for a sorption capacity of a sorbent and the site-energy distribution, respectively. The Freundlich model provided a good description of the data shown in Figs. 4 and 5. The Freundlich model parameters K_F and n describing sorption data in Figs. 4 and 5 are listed in Table 3, together with the proportion of variance accounted for (the r^2 values) and the square root of the mean squared error (RMSE). For further comparisons, isotherms of nitrobenzene sorption determined earlier on Wyoming bentonite, organoclays obtained by cation exchange with HDTMA and their thermal modifications (Borisover et al. 2010) were also fitted with the Freundlich model, and the

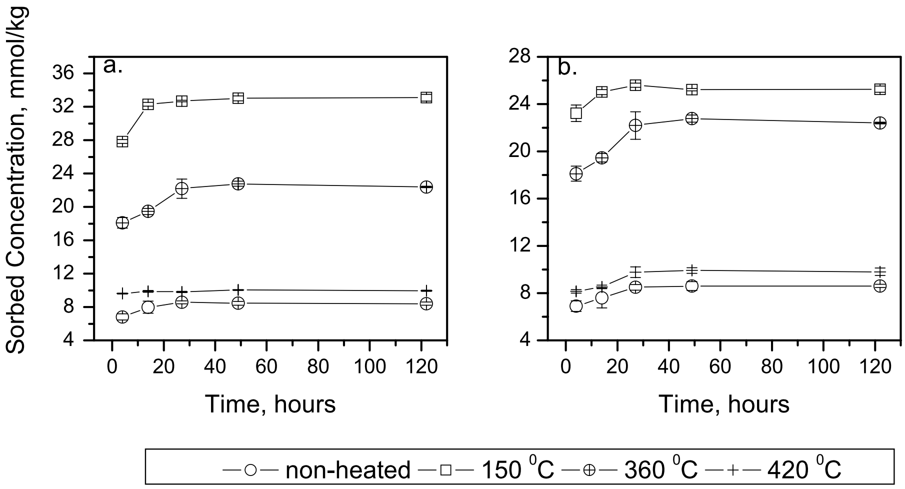

Fig. 3 Sorbed concentrations of nitrobenzene on differently heated TEA-clay (**a**) and BTMA-clay (**b**) plotted against the time of equilibration. Averaged data replicates are shown with standard deviations used as *error bars*. Initial concentration of nitrobenzene in solution was 0.82 mmol/L. Temperatures applied for sorbent treatment are indicated in the *legend*

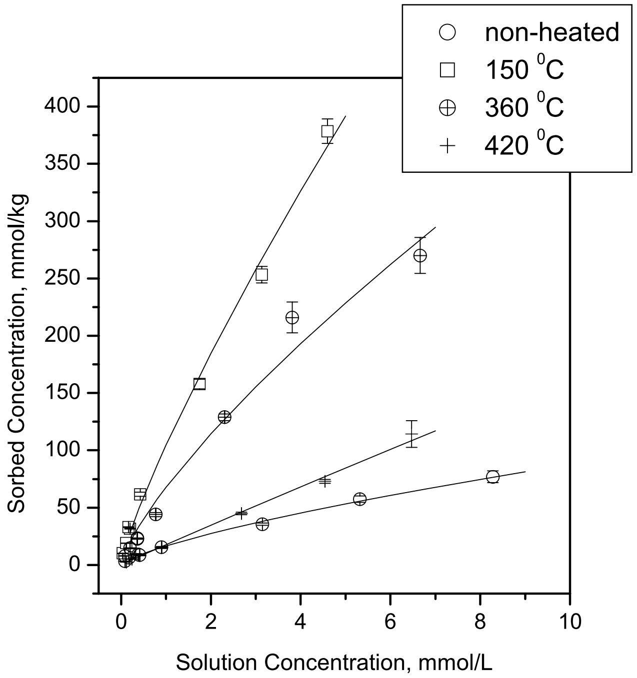

Fig. 4 Isotherms of aqueous sorption of nitrobenzene on differently heated TEA-clay. *Curves* depict the Freundlich model-fitted trends. Averaged data replicates are shown with standard deviations used as *error bars*. Temperatures applied for sorbent treatment are indicated in the *legend*

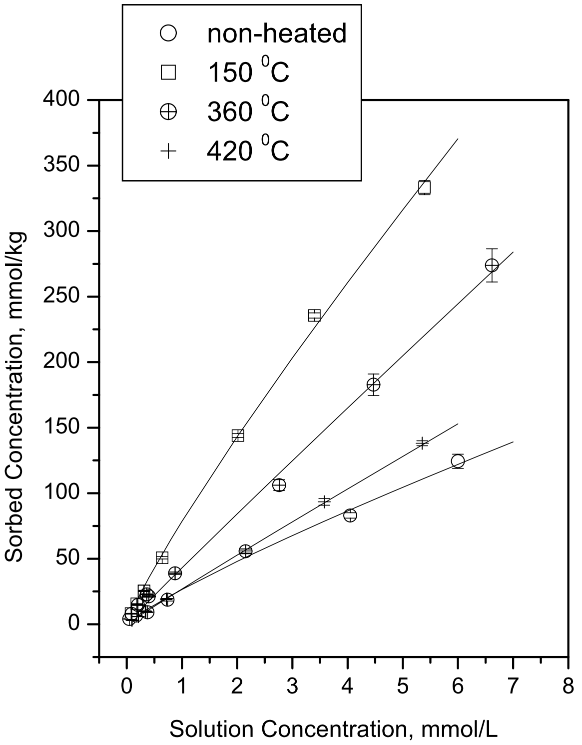

Fig. 5 Isotherms of aqueous sorption of nitrobenzene on differently heated BTMA-clay. *Curves* depict the Freundlich model-fitted trends. Averaged data replicates are shown with standard deviations used as *error bars*. Temperatures applied for sorbent treatment are indicated in the *legend*

model parameters for these systems are included in Table 3, too.

From Fig. 4 it is clear that the thermal treatment of TEA-clay at 150°C strongly enhanced its capability to sorb nitrobenzene from water as compared with the initial TEA-clay. This sorption enhancement may exceed 700% (e.g. at 5 mmol/L of nitrobenzene in solution). Heating of TEA-clay at 360°C reduced the nitrobenzene sorption as compared with that on the organoclay treated at 150°C. However, the sorptive efficacy of the TEA-clay treated at 360°C was yet greater than the sorptive efficacy of the initial, non-heated sorbent. Heating of TEA-clay at 420°C involved the further decrease of a sorptive capability as compared with the TEA-clay treated at 150°C: the TEA-clay sorbent treated at 420°C exceeded only slightly the non-heated TEA-clay in ability to remove nitrobenzene from water.

Effect of thermal treatment applied to BTMA-clay on aqueous sorption of nitrobenzene follows the same pattern

Table 3 Parameters of the Freundlich isotherm model used to approximate aqueous sorption of nitrobenzene on Wyoming bentonite, series of organoclays and their thermal modifications obtained by heating in air at different temperatures

Sorbent	Temperature of thermal treatment, °C	K_F[a]	n	r^2	RMSE[b]/number of fitted experimental points
TEA-clay	no[c]	16.7 ± 0.8[d]	0.72 ± 0.03	0.99	2.7/24
	150	104.7 ± 4.4	0.82 ± 0.03	0.99	12.7/24
	360	67.8 ± 5.0	0.76 ± 0.05	0.97	17.3/24
	420	17.7 ± 2.0	0.97 ± 0.07	0.97	6.9/24
BTMA-clay	no	26.6 ± 1.6	0.85 ± 0.04	0.99	4.8/21
	150	78.5 ± 1.8	0.87 ± 0.02	0.99	5.8/24
	360	43.0 ± 2.9	0.97 ± 0.04	0.99	9.8/24
	420	26.9 ± 0.8	0.97 ± 0.02	0.99	2.4/24
Wyoming bentonite	no	9.2 ± 0.9	0.75 ± 0.05	0.96	3.0/18
	150	15.9 ± 1.2	0.80 ± 0.04	0.99	2.8/18
	360	37.0 ± 1.6	0.76 ± 0.03	0.99	5.6/27
	420	23.7 ± 0.9	0.70 ± 0.02	0.99	3.3/27
OC-41[e]	no	13.6 ± 1.5	0.91 ± 0.06	0.98	4.6/17
	150	25.7 ± 2.0	1.3 ± 0.06	0.99	6.7/26
	360	35.7 ± 1.9	0.87 ± 0.04	0.98	6.8/27
	420	8.6 ± 1.3	1.31 ± 0.08	0.97	6.1/33
OC-90[e]	no	20.3 ± 3.2	2.27 ± 0.11	0.99	21.4/21
	150	62.8 ± 5.1	1.70 ± 0.08	0.99	16.8/27
	360	82.1 ± 3.3	0.87 ± 0.03	0.99	11.9/27
	420	10.5 ± 1.4	1.19 ± 0.07	0.97	8.3/33

[a] $\mathrm{mmol}^{(1-n)}\,\mathrm{L}^n/\mathrm{kg}$. [b] The square root of the mean squared error. [c] No thermal treatment applied; data corresponds to the initial, non-heated sorbent. [d] "±" corresponds to the standard error. [e] OC-41 and OC-90 depict the organoclays formed by replacing 41% and 90% of CEC in Wyoming bentonite with the HDTMA cation, respectively; the abbreviation follows the earlier used (Burstein et al. 2008; Borisover et al. 2010).

as found for TEA-clay. Heating of BTMA-clay at 150°C resulted in a significant increase of its sorptive ability as compared with that of the initial, non-heated sorbent (Fig. 5). Treatment at 360°C produced a sorbent more effective than the initial one but demonstrating worse removal of nitrobenzene from water as compared with the BTMA-clay treated at 150°C. Sorption of nitrobenzene on the BTMA-clay pre-heated at 420°C is similar to that on the initial, non-treated sorbent.

3.3 Effect of a thermal treatment of a sorbent on sorbate interactions: comparison between different sorbents

To compare the effect of a thermal treatment of a sorbent on sorbate interactions in different sorbent systems, the Freundlich model constants K_F describing nitrobenzene interactions with differently heated TEA- and BTMA-clays are plotted in Fig. 6 against the treatment temperature. In addition, the K_F values related to nitrobenzene sorption on original Wyoming bentonite, organoclays obtained by cation exchange with HDTMA and their thermal modifications (Table 3) are also included into the comparison in Fig. 6.

It can be seen from Fig. 6 that the increase of the Freundlich model constant (and the enhancement of nitrobenzene–sorbent interactions) due to a sorbent pre-heating at 150°C takes place on original Wyoming bentonite and becomes slightly stronger on OC-41. On the OC-90 sorbent, the influence of the sorbent pre-heating at 150°C on the Freundlich model constant is even boosted as compared with Wyoming bentonite and OC-41. The K_F rise on the BTMA-clay pre-heated at 150°C is comparable to that on OC-90 (at the lesser extent of cation exchange in BTMA-clay as compared with OC-90, i.e. 81% vs. 90% relative to CEC, respectively). Introducing of TEA-cations (by 77% of CEC) into the clay involves the maximal thermal treatment-induced enhancement of nitrobenzene–sorbent interactions. Similarly to nitrobenzene sorption enhancement on thermally treated HDTMA-exchanged clays (Borisover et al. 2010), the strong rise in intensity of nitrobenzene interactions with the TEA- and BTMA-clays treated at 150°C occurs without a significant degradation of organic coverage of organoclays: no meaningful C, N losses (Table 1) and changes in FTIR spectra (Figs. 1 and 2) were observed on the TEA- and BTMA-clays treated at 150°C.

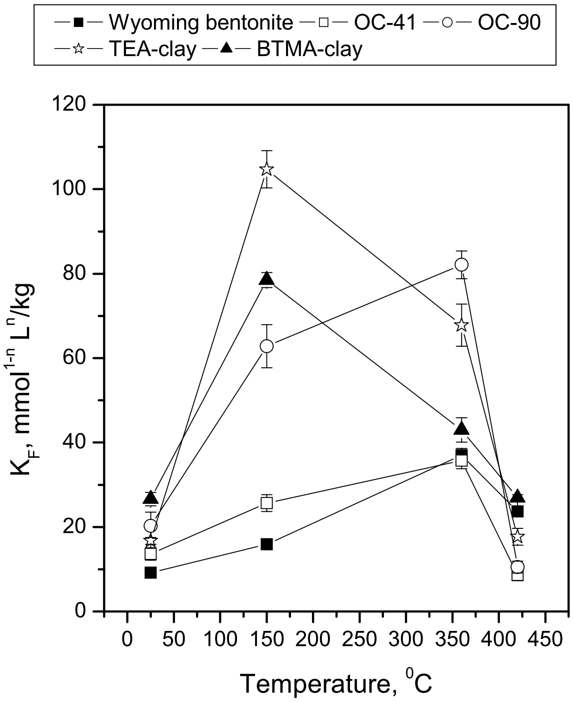

Fig. 6 Effect of temperature applied for thermal treatment of sorbents on the Freundlich model constant K_F related to nitrobenzene sorption from aqueous solutions. The K_F values at 25°C correspond to nitrobenzene sorption by non-heated sorbents. Standard errors were used as *error bars* for the K_F values

The enhancing effect of the mild sorbent heating (at 150°C) on nitrobenzene–sorbent interactions observed in the TEA- and BTMA-clay systems (Fig. 6) may be linked to the earlier suggested explanation (Borisover et al. 2010): thermal treatment involves a loss of remaining water from a sorbent and its reduced hydration upon immersing in water. Then, a lessening of a sorbate–water competition for sorption sites on a pre-heated sorbent may enhance nitrobenzene–sorbent interactions. The alumino-siloxane groups of clay sorbents may act as sorption sites for organic sorbates containing nitro-group and capable of electron donor-acceptor interactions (Haderlein et al. 1996; Weissmahr et al. 1997; Yariv and Cross 2002).

Replacement of inorganic cations in Wyoming bentonite with a less hydrated organic cation results, by itself, in a partial dehydration of a clay interlayer space (e.g. Sheng et al. 1996; Jaynes and Vance 1999) and may make a further loss of residual water at 150°C easier; greater fraction of organic cation (i.e. in OC-90 as compared with OC-41) results even in a greater dehydration of a sorbent. On the other hand, after thermal treatment, oriented aliphatic n-$C_{16}H_{33}$ chains of the attached HDTMA cations in OC-41 and OC-90 may also better interact with a clay surface. This surface interaction can (i) hinder a further sorbent hydration and weaken a water-competitive effect in a pre-heated sorbent, and (ii) compete with sorbate (nitrobenzene)–sorbent interactions. When the smaller size organic cations are introduced instead of HDTMA (even at a lesser extent of cation exchange), the interlayer space becomes also dehydrated, but, in addition, the clay surface is less solvated by organic fragments of a cation. As such, the heating of BTMA- and TEA-clays at 150°C involves a most significant sorbent activation (Fig. 6). Obtained results support our initial hypothesis that interactions of quaternary ammonium-associated long-chain aliphatic groups with a clay surface may mitigate the enhancing effect of pre-heating on a sorptive capability of an organoclay.

Smaller effect of the thermal treatment at 150°C observed on BTMA-clay as compared with TEA-clay (Fig. 6) could be explained by π interactions occurring between aromatic benzyl-group in BTMA-clay and siloxanes that compete with nitrobenzene-clay interactions (Yariv 2002). This supposed competing effect of benzyl group–siloxanes interactions is also in the agreement with the earlier experimental observation (Nir et al. 2000) that sorption of some herbicides (i.e. norflurazon, alachlor, metolachlor) by Wyoming Na-montmorillonite differently exchanged with the BTMA cation was maximal at a certain intermediate extent of the Na^+/BTMA replacement. Our understanding is that the initial increase of the BTMA content in the Wyoming Na-montmorillonite involved the removal of complexed water and the exposure of the clay surface for herbicide molecules. But, the further increase of the BTMA content resulted also in a competitive blocking of the clay surface due to the benzyl group–siloxanes interactions.

The above understanding of differences in thermal activation between HDTMA-, TEA- and BTMA-clays is interrelated also with the earlier idea (Jaynes and Vance 1999) that organic cations with larger size may block the access of an organic sorbate to the interlayer siloxane surfaces. Compact size and low hydration are organic cation properties that typically yield effective adsorptive-type organoclays (Jaynes and Vance 1999). In this case, the replacement of hydrophilic inorganic cations with organic cations involves a reduction of the amount of complexed water at the clay surface and the weakening of the clay-associated water network which contributes to the better accessibility of a clay surface for sorbates (Sheng and Boyd 1998; Lawrence et al. 1998; Jaynes and Vance 1999; Johnston and Tombacz 2002).

A mechanism of thermally induced enhancement of organic sorbate–sorbent interactions can be similar for clays with exchangeable inorganic cations and organoclays formed with short-chain organic cations. Mild sorbent heating (at 150°C) associated with a loss of residual water may result in a stronger interaction and tighter sticking of cations to the clay surface; a further hydration at room temperature and a loosening of formed "tight ionic pairs" may require overcoming a significant activation barrier. This explanation resembles the classic point that clay heating may involve a fixation of exchangeable inorganic cations. This fixation occurring generally at higher temperatures is significant for montmorillonite saturated with Li^+ and Ca^{2+}, but it is small when saturated with Na^+ (Grim 1953; Green-Kelly 1953; Ho and Handy 1964; Eckstein et al. 1970). The fixation of Li^+ is thought to be associated with filling vacancies in the octahedral layer. More work is needed to probe this hypothesized parallel between a cation fixation and a mechanism suppressing hydration of a sorbent after its mild thermal pretreatment and, hence, enhancing organic sorbate–sorbent interactions.

The application of higher temperature (360°C; Fig. 6) involves a further dehydration of the original bentonite thus distinctly increasing nitrobenzene-clay interactions (by a factor of 2.3, in terms of the K_F values, as compared with the clay treated at 150°C). The relevant increase of the K_F values in both less hydrated HDTMA-clays is much less, only by a factor of 1.3. Nitrobenzene interactions with organoclays treated at 360°C are affected also by destruction of clay-attached organic cations. Specifically, oxidation of organic matter in organoclays, formation of a hard, nonswelling carbonized material and the collapse of montmorillonite are expected to contribute to the further weakening of nitrobenzene interactions with the sorbents heated at 420°C (Borisover et al. 2010).

Significant variability was observed also for the Freundlich model-based parameter n (Table 3). When it was plotted against the temperature applied for sorbent treatment (not shown), virtually in all cases, the largest n parameters were found for nitrobenzene sorption on OC-41 and OC-90 (except the BTMA-clay heated at 360°C). This is in well agreement with the concept that with flexible long-chain quaternary ammonium cations (like HDTMA in OC-41 and OC-90) significant solute partitioning into the organic pseudo-phase of the organoclays is expected (Sheng et al. 1996). This dissolution-like behavior is associated with the n values close to 1 (or even exceeding 1 if the sorbent swelling or sorbate–sorbate interactions in the organoclay phase take place). Therefore, this dissolution component should contribute to increased apparent n values for nitrobenzene sorption on HDTMA-clays as compared with adsorptive sorbents such as Wyoming bentonite, TEA- and BTMA-clays.

4 Conclusions

Mild thermal pre-treatment of freeze-dried organoclays carried out at 150°C in air enhances their potential to interact with nitrobenzene (used as a probe organic compound) in aqueous environment. When comparing original Wyoming bentonite, its exchange complexes formed with long-chain aliphatic quaternary ammonium (HDTMA) and smaller-size quaternary ammonium (TEA and BTMA) cations, this thermally-induced enhancement of nitrobenzene–sorbent interactions expressed by the Freundlich model constants is as follows: Wyoming bentonite $<$ HDTMA-clay exchanged by 41% (of CEC) $<$ HDTMA-clay exchanged by 90% $\approx$ BTMA-clay exchanged by 81% $<$ TEA-clay exchanged by 77%.

Based on C, N content data and FTIR spectra of TEA- and BTMA-clay complexes, no indications of degradation of organic matter were found in organoclays heated at 250°C (and below this temperature). Reduced (incomplete) hydration of pre-heated sorbents involving decreased water–organic sorbate competition for sorption sites is considered responsible for thermally induced enhancement of organic sorbate–sorbent interactions. Decrease of a water–organic sorbate competition appears to be significant in organoclays formed with smaller size organic cations such as TEA and BTMA. This weakening of a water-competitive effect may be counteracted in the HDTMA-clays by interactions of long-chain aliphatic groups with a clay surface which is supposed to lessen also organic sorbate–sorbent surface interactions.

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