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CHARACTERIZATION AND STUDY OF SORPTIVE PROPERTIES OF DIFFERENTLY PREPARED ORGANOCLAYS FROM A BRAZILIAN NATURAL BENTONITE

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Organoclays are used in cleaning natural waters from dissolved hydrocarbons by secondary sorption. Aiming future applications in this field, a Brazilian polycationic bentonite was used to prepare HDTMA organoclays, by using different quaternary ammonium salt loadings and clay content slips, to evaluate how these conditions may affect their sorption properties. The organoclays were characterized by CHN analysis, X-ray diffraction, thermogravimetry, and differential thermal analysis. For secondary sorption tests, to compare with published studies, toluene was used as a reference sorbate. Characterization and sorption results indicate that the Brazilian bentonite organoclays prepared in this study have a potential industrial use in environmental applications.

Keywords: *organoclays, thermal analysis, toluene sorption, X-ray diffraction*

Introduction

Dissolved hydrocarbons, specially benzene, toluene, ethylbenze and xylenes (BTEX), are the regular contaminants measured in groundwater that has become contaminated by leakage from underground gasoline storage tanks. In the USA, there are about 150.000 underground storage tanks (USTs) sites remaining to be treated [1]. In the Metropolitan Region of São Paulo city in Brazil, where about 15 million people live, there are 43.000 of potentially contaminated sites [2]. In São Paulo State, which is the most industrially advanced Brazilian state, USTs are responsible for 58% of all contaminated sites [3]. Organobentonites have been investigated as potential sorbents by secondary adsorption for neutral organic contaminants (NOCs) in a wide variety of environmental applications. They are produced by replacing inorganic exchangeable cations of natural clays like Na^+ and Ca^{2+} by quaternary ammonium cations (QACs) of the form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$, where R and R' are hydrocarbon groups. This exchange results in materials that are highly effective sorbents of NOCs from an aqueous phase by a secondary adsorption [4, 5]. Because of their low permeability in the presence of nonpolar liquids and lesser compressibility than unmodified clays, organobentonites have been investigated as additives to clay barriers to immobilized dissolved NOCs and to prevent hydraulic failure of the barrier when exposed to concentrated or pure organic liquids [6, 7].

Organoclays are characterized as either adsorptive or organophilic depending on the type of quaternary ammonium ions used for the modification, and the nature of their interaction with NOCs [4]. Adsorptive clays are produced from relatively small quaternary ammonium ions such as tetramethylammonium (TMA) and trimethylphenylammonium (TMPA) ions. These relatively small size cations function as pillars to permanently open the interlayers of clay. The siloxane surfaces and the QACs in the interlayers are exposed to direct interaction with neutral hydrophobic compounds [8, 9].

Organophilic clays, which are produced from monovalent, long-chain alkyl quaternary ammonium cations such as hexadecyltrimethylammonium (HDTMA) and dioctadecyldimethylammonium (DODMA) ions, can form a hydrophobic partition medium within the clay interlayer and function analogously to a bulk organic phase [10, 11]. Secondary sorption of NOCs by organophilic clays is characterized by an essentially linear isotherm, dependence of sorption on organic content, and lack of solute competition. Thus, the organic cation alkyl groups effectively remove NOCs from water [4]. According to Chun *et al*. [5], these organophilic organoclays have

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the potential to be used as sorbents for high concentrations of NOCs in multi-contaminant water and they may not be effective for sorbing low concentrations of NOCs. Jaynes and Vance [11] and Sheng *et al.* [12] showed a synergistic NOC sorption by HDTMA-smectites in multisolute systems. The impressive sorption capabilities of organoclays make them potentially useful in a variety of environmental applications and technologies [13, 14].

Depending on the charge density of the clay and the degree of saturation by long chain alkylammonium cations relative to its cation exchange capacity (CEC), an organo-smectite can conceivably adopt interlamellar monolayer, bilayer, pseudotrimolecular, or paraffin arrangement and, respectively, basal spacings of 1.33, 1.77, 2.17 and >2.2 nm may be obtained, due to the adsorption of HDTMA by different smectites [15, 16].

The organoclay must be chemically stable to prevent a secondary pollution from residual aqueous phase surfactants (e. g. HDTMA). According to Nye *et al.* [17] aqueous-phase HDTMA exerts considerable toxicity whereas the HDTMA adsorbed to clay is essentially nontoxic to pollutant-degrading bacteria in soils. Xu and Boyd [18] examined the stability of HDTMA organoclays through HDTMA adsorption-desorption to subsoil material; initially, HDTMA was adsorbed by cation exchange but, with increased loading, it was adsorbed by both cation exchange and hydrophobic bonding. Xu and Boyd [18] found that desorption was greater for HDTMA bound by hydrophobic interactions than by cation exchange. Sorptions of HDTMA modified the nature of smectite soils and like pure HDTMA-smectites they became useful in the secondary adsorption of organic contaminants [19].

The thermal stability of natural bentonites and organobentonites has been studied by thermal analysis [20–22]. The main differences on thermal behavior are that organoclay TG curves show a less free and/or sorbed water content than the original clay, as well as new mass loss steps due to their organic content being burnt, characterized by exothermic DTA peaks. After the dehydroxylation of the bentonite structure, which is characterized by an endothermic peak, other exothermic peaks occur, due to the burning of residual carbonaceous matter formed in the previous organics pyrolisis step [22, 23].

Yermiyahu *et al.* [24] studied the adsorption of the organic anionic dye Congo-red (CR) onto montmorillonite by thermo-XRD-analysis. Smectites possess a net electrical charge which is compensated by exchangeable cations in the interlayer space. It is expected that anionic species will not be adsorbed into this space, but this may happen, as the case of CR, which may be adsorbed into the interlayer space of montmorillonite in considerable amounts due to protonation and H-bonds formation [24]. Simultaneous DTA-TG study of the anionic dye Congo-red adsorbed by montmorillonite showed that π interactions between adsorbed aromatic compounds and oxygen atoms from the oxygen plane are essential to the formation of the high-temperature stable charcoal, which is burnt with characteristic exothermic peaks in the DTA curves of aromatic-montmorillonite complexes [25].

Brazil appears among the ten major bentonite world producers, but its production in this context is still quite negligible (1.7%) [26]. As known deposits of natural bentonites with a high swelling capacity do not exist, in Brazil usually these bentonites are treated with sodium carbonate in order to exchange the interlayer cations for sodium and to obtain swelling clays [14, 27].

In the present study, a Brazilian polycationic bentonite is used to prepare HDTMA organoclays, by applying different quaternary ammonium salt loadings and clay content slips, to evaluate how these conditions may affect its secondary adsorption properties. The organoclays were characterized by CHN analysis, X-ray diffraction, thermogravimetry, and differential thermal analysis. For secondary sorption tests, to compare with literature, toluene was used as a reference sorbate. This study aims to get a better knowledge of some properties of Brazilian bentonite, and to see its potential industrial use in environmental applications.

Materials and methods

Lages bentonite (montmorillonite) was collected from Boa Vista, PB, Brazil (SVCL Nat). It is a polycationic bentonite, with a cation exchange capacity (CEC) of 80 mmol per 100 g clay, determined by methylene blue [28]. The hexadecyltrimethylammonium chloride (HDTMA-Cl) was obtained from Clariant Brazil, Functional Chemicals Division, São Paulo, SP, Brazil. Analytical grade toluene is from Vetec Química Fina Ltda., Duque de Caxias, RJ, Brazil.

The bentonite was dispersed in distilled water in two different concentrations (1 and 4 mass%). The clay was Na-saturated by the adding sodium carbonate solution (200 g L^{-1}) in the amount equivalent to 100 mmol per 100 g clay, stirring for one hour at 90ºC and for additional three hours at room temperature. The HDTMA-Cl was dissolved in distilled water and added to the sodium saturated SVCL Nat clay slips, in amounts of 80 and 100 mmol of HDTMA-Cl per 100 g clay and stirred for 4 h at room temperature. The HDTMA-smectite complexes thus formed were washed with distilled water until free of Cl^{-} ions. After each washing step, the aqueous phase was removed by phase separation. The organoclay was dried at 60ºC, and then mechanically milled until 100% was passing in 200 mesh sieve.

Basal spacings were determined by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were recorded using CuK$_\alpha$ radiation (λ=0.15416 nm) and a Philips XPERT-MPD X-ray diffractometer, in steps of 0.02º2θ at 1.0s step^{-1}.

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) were performed in platinum pans in a TA Instruments, model SDT2960, with 100 mL min^{-1} air flow, from 28^{o}C to 1000^{o}C with a 10^{o}C min^{-1} heating rate. Alpha-alumina was used as reference for DTA measurements. Derivative thermogravimetry curves (DTG) were obtained by using the data analysis software of the instrument.

Organic carbon, hydrogen and nitrogen contents were determined by LECO CHN1000 analyzer in replicates at the chemistry laboratory of the Geosciences Institute of the University of São Paulo.

Batch sorption tests of toluene with the organoclays were prepared by weighing 0.5 g organoclay samples into 30 mL glass centrifuge tubes and by adding 30 mL of deionized water. Hamilton micro-syringes (Hamilton Co. Reno, Nevada) were used to deliver toluene into the tubes, in replicates, at various amounts (2, 3 5, 9 and 15 μL) to yield a range of initial concentrations. To reduce vaporization losses, aluminum foil liners were placed on the tubes and screw caps were tightly sealed. To reduce vaporization losses during agitation, the tubes were put upside down in a reciprocating shaker to maintain the air bubble away from the tube cap. The duplicate blank solutions of toluene and those containing organoclays were shaken at 250 rpm for 22 h at 25ºC (Controlled Environment Incubator Shaker). Similar studies demonstrate that sorption equilibrium is reached in less than 20 h [2, 4, 6, 19]. After equilibration, the aqueous phase was separated by centrifugation at 4000 rpm for 30 min at room temperature using a BIO-ENG, type BE-4004. A 10 mL portion of the supernatant was then analyzed using gas chromatography. The amount of sorbed toluene was calculated from the difference between the amount added and that remaining in the final solutions. All measurements were done in duplicate, and the difference was generally <5%. The isotherms were obtained by plotting the average sorbed amount against the equilibrium concentration remaining in solution [5]. Sorption was analyzed using linear and Freundlich equilibrium isotherm models. In order to compare all the organoclays, sorption coefficients (K_d) were determined as the ratios of the amounts sorbed and equilibrium concentrations. To normalize toluene sorption on organic matter basis, organic matter corrected sorption coefficients (K_{om}) were calculated from the K_d values and organic carbon (OC) contents.

The concentrations of toluene were measured by gas chromatography. A 10 mL portion of the supernatant was transferred in 22 mL vials (SHIMADZU). The vials were sealed immediately with Teflon-lined septa (ref. 221-29084-91). It was used a Shimadzu Model GC - 17A, equipped with a flame ionization detector (FID) and electronic flow control. The GC separation column was a 30 m·0.25 mm i.d. DB-5 (equivalent to a 5% phenyl, 95% methylpolysiloxane) fused silica capillary column (J&W Scientific, Folsom, CA) with helium as gas carrier. The injector and detector port temperatures were 150 and 200ºC, respectively; the oven temperature 45ºC (held 4.5 min), heating rate 30ºC min^{-1} to 80ºC (held 5 min), and then a 60ºC min^{-1} v to 150ºC (held 7 min). A static headspace sampler was performed using a Shimadzu Headspace sampler model HSS-4A. This method was based on Flórez Menedez *et al.* [29]. Peak areas were recorded from a Class GC 10 series interface, communication module CBM-102, and compared with external standards to determine the concentrations of toluene.

Results and discussion

The XRD and CHN analysis

Table 1 shows the XRD and CHN analysis results of the original Brazilian bentonite (SVCL Nat) and organoclays after being dried at 60^{o}C. Each organoclay was named by the abbreviation SVCL– followed by: 1 – the name of the organic cation HDTMA (hexadecyltrimethylammonium); 2 – the SVCL Nat concentration in distilled water (1 or

Table 1 XRD and CHN analysis results of the original bentonite and organoclays

Samples	D_{001} /nm	Organic C OC/mass%	Organic N mass%	Total H_2O mass%
SVCL Nat	1.36	0.05	<0.17	18.77
SVCL-HDTMA (1%, 80)	2.06	15.92	0.98	33.65
SVCL-HDTMA (1%, 100)	2.14	15.61	0.94	32.47
SVCL-HDTMA (4%, 80)	2.06	15.64	0.86	33.40
SVCL-HDTMA (4%, 100)	2.16	16.19	0.91	34.83

4 mass%); 3 – the number of HDTMA mmol used per 100 g of SVCL Nat. For instance, SVCL- HDTMA (1%, 80) identifies the organoclay which was obtained from a dispersion containing 1 mass% of the original bentonite, to which, after sodium saturation 80 mmol HDTMA cations were added per 100 g of the original SVCL Nat.

As presented in Table 1, the XRD analyses of the organoclays indicate that, for the same initial clay dispersion weight concentration, the higher is the added HDTMA mmol per 100 g of SVCL Nat, the higher is the resulting interlayer space. This fact could be explained by a higher tendency of hydrophobic organic tails to be drawn away from the aqueous system as their content increases [30] in a same sodium bentonite content suspension. The results also show that apparently the interlayer space depends only on the added amount of organic cations to obtain the organoclay. Based on the d_{001} spacings shown in Table 1 and according to Lagaly [16] and Jaynes and Boyd [15], the SVCL-HDTMA organoclay complexes have a pseudotrimolecular layer inside their interlayer space.

Thermal analysis

Figure 1 shows the TG, DTG and DTA curves of a sample of HDTMA chloride obtained from its alcoholic solution, dried at 60ºC. As it can be observed from the TG curve, there is still residual alcohol, which is removed before 78ºC. At 79ºC, melting begins and is completed at 134ºC. The HDTMA chloride begins to volatilize at 170°C, showing a high mass loss rate after 200ºC. This is characterized by a sharp DTG peak, which ends at 200ºC, with a corresponding endothermic DTA peak. It is interesting to note that combustion occurs right after volatilization begins, which is indicated by an exothermic DTA peak. As the volatilization proceeds, the mass releasing rate increases significantly and, as there is not enough oxygen from the flowing air within the furnace to have total combustion, a subsequent resulting endothermic effect occurs, as seen in Fig. 1.The residual carbonaceous matter is decomposed and is burnt up to 550ºC.

Figure 2 shows the TG, DTG and DTA curves of the Brazilian bentonite (SVCL Nat). It presents a 14.18% of free and adsorbed water, the evolution of which ends at 250°C. Dehydroxylation of the SVCL Nat clay mainly occurs from 350 to 550°C.

Figure 3 shows the TG, DTG and DTA curves on calcined basis of SVCL-HDTMA (4%, 80) and SVCL-HDTMA (1%, 80) organoclays. They present 4.2 and 4.6% of free and/or sorbed water, on initial mass basis, characterized by respective endothermic DTA peaks, which end at 130ºC. From this temperature to 230ºC, the organic matter begins to be released as seen by DTG peaks. The SVCL-HDTMA (4%, 80) organoclay, due to its higher interlayer spacing, is more thermally unstable than SVCL-HDTMA (1%, 80) one. From 230 to 420 ºC, the resulting DTA effect is exothermic, due to the burning of the organic matter.

As the composition of the calcined organoclays is the same at 1000ºC, calcined mass basis TG curves allow one to directly know in which case there is a higher content of organic matter. On calcined basis,

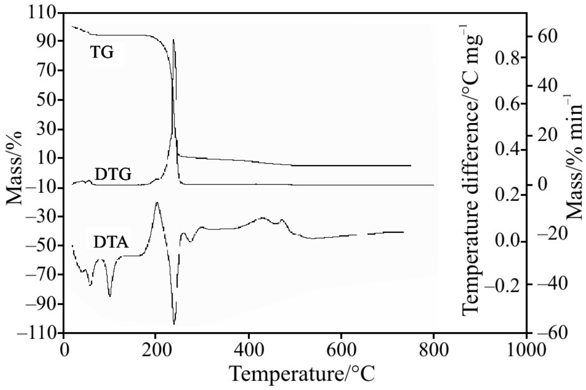

Fig. 1 TG, DTG and DTA curves of a sample of HDTMA chloride

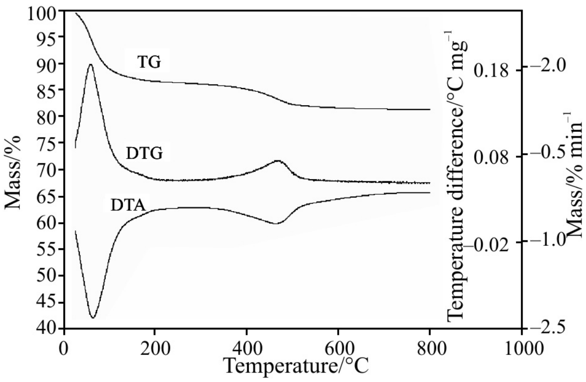

Fig. 2 TG, DTG and DTA curves of the natural Brazilian bentonite (SVCL Nat)

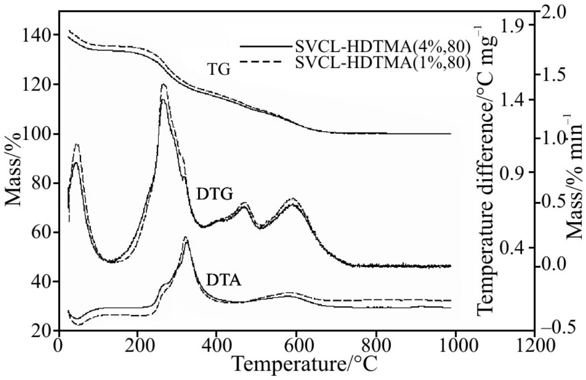

Fig. 3 TG, DTG and DTA curves of SVCL-HDTMA (4%, 80) and SVCL-HDTMA (1%, 80) samples

the water mass loss from the dehydroxylation of the bentonite, occurring simultaneously with the burning of the organic matter, is the same for any of the organoclays. Thus, as shown in Fig. 3, the higher dried mass (on calcined mass basis) at 130ºC, of SVCL-HDTMA (1%, 80) sample, indicates that this organoclay has more organics in its structure than the SVCL-HDTMA (4%, 80) one, as seen from the CHN analysis results (Table 1). This may be explained by the fact that the initial 1 mass% dispersion promotes a higher dilution of the HDTMA chloride in the aqueous media, which enhances ion dissociation, and consequently, better conditions for cation exchange, which is the main mechanism occurring at this loading level.

It must be noted from Fig. 3 that between 400 and 550ºC dehydroxylation occurs, as seen by respective DTG peaks within this temperature range. An endothermic peak is not observed in the DTA curve, because the dehydroxylation overlaps exothermic oxidation of the organic matter, but the curvature of the DTA curves changes downwards. Right after, there is a broad low height exothermic DTA peak, due to the combustion of the residual carbonaceous matter.

Figure 4 shows the TG, DTG and DTA curves on calcined basis of the organoclays prepared by using an excess of the HDTMA-Cl salt, with respect to the CEC of the SVCL Nat, which is 80 mmol$_c$ per 100 g of SVCL Nat. Respective mass loss steps, identified by DTG peaks, are similar to those of Fig. 3. DTA curves also present similar behavior. In these preparation conditions, the content of organic matter of the dried organoclay at 130 ºC, is higher in the case of the more concentrated initial bentonite suspension, very probably because of the occurrence of a secondary adsorption, which causes a higher basal spacing, as measured by XRD (Table 1).

Actually, two adsorption mechanisms for cationic surfactants, ion exchange and hydrophobic bonding, are involved in the formation of organoclay/soil complexes [18]. The higher organic matter content in the case of a higher concentration suspension (4 mass%) and higher HDTMA-Cl salt loading, may be very probably due to a higher hydrophobic bonding, which may occur because loading level is higher than the CEC of the SVCL Nat. The 4 mass% former bentonite suspension promotes a higher HDTMA chloride concentration aqueous phase, which in turn promotes better conditions for a higher secondary adsorption at this loading level than in the 1 mass% case.

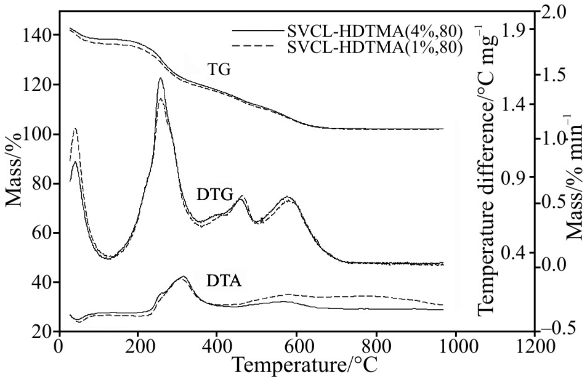

Fig. 4 TG, DTG and DTA curves on calcined basis of SVCL-HDTMA (4%, 100) and SVCL-HDTMA (1%, 100) samples

Previous studies [19] showed that the high chemical stability of HDTMA-modified soils occurs at loading levels between 0.1 to 0.8 CEC. The sorption characteristics of HDTMA modified smectite soils for organic contaminants are similar to those of pure HDTMA-smectites [19]. As can be seen by the respective DTG curves, the organoclays prepared by using loading levels higher than the CEC of the SVCL Nat produced a lower thermal stability, which is correlated to the respective chemical stability.

Secondary sorption tests

Two equilibrium isotherms models, linear and Freundlich, were used to analyze toluene sorption from aqueous solutions by the SVCL organoclays. Linear isotherms [15] were obtained, by plotting the average sorbed amount *vs.* the equilibrium concentration remaining in solution, according to equation: $X/M=K_d\,C_e$, where: X=mass of sorbate removed from solution (mg), M=mass of sorbent (g), C_e=solution equilibrium concentration (mg L^{-1}), K_d=distribution coefficient [(mg g^{-1})/ (mg L^{-1})].

The Freundlich equation can be expressed by: $X/M=K_fC_e^{1/n}$, where K_f (L kg^{-1}) and n (dimensionless) are, respectively, the constants to sorbate binding capacity and to conditional index, which describes the shape of the isotherm [31].

The results of model fitting to toluene sorption on organoclays are listed in Table 2, and the respective isotherms are shown in Fig. 5. The n values are greater than 1 for the organoclays, SVCL-HDTMA (1%, 100) and SVCL-HDTMA (4%, 100), which show convex up curvatures. The n values are less than 1 for both SVCL-HDTMA (1%, 80) and SVCL-HDTMA (4%, 80), which show concave curvatures (Fig. 5). Low correlations for Freundlich fitting with $n>1$ indicate that mainly a partitioning process occurs rather than surfacial interactions. Studies using the Freundlich model to describe BTEX sorption on Wyoming bentonite-HDTMA (SWy-HDTMA) have indicated a partitioning process [31]. A comparison among the correlation coefficient values (R^2), indi-

Table 2 Model parameters for toluene sorption organoclays

Samples	Linear		Freundlich		
	K_d/L kg^{-1}	R^2	K_f/L kg^{-1}	n_f	R^2
SVCL-HDTMA (1%, 80)	120.0	0.9891	87.7	0.9387	0.9985
SVCL-HDTMA (1%, 100)	140.3	0.9773	217.4	1.1367	0.9538
SVCL-HDTMA (4%, 80)	112.4	0.9445	36.5	0.7994	0.9888
SVCL-HDTMA (4%, 100)	131.0	0.9714	301.2	1.2737	0.8672
SWy-HDTMA [8]	114.0				
SAz-HDTMA [8]	317.0				
VSC-HDTMA [8]	251.0				
SWy-HDTMA [31]	79.43		135.0	0.7900	0.9530

cates that in a general the data fit better with the linear equation than with Freundlich model.

From K_d values and the organic carbon content (%OC=f_{oc}) of the organoclays, organic matter corrected sorption coefficients (K_{om}) can be calculated to normalize the hydrocarbon sorption on an organic matter basis [11], using the equation: $K_{om}=K_d$ / [f_{oc}.f], where f is the ratio between the organic cation mass present in the organoclay and the mass of C in the organic cation. Many of the measured log K_{om} values are comparable to the reference log K_{om} values listed in Table 3. The value of K_{ow} for a compound is equal to the ratio of the solubility of the compound in octanol to its solubility in water. Similarly, the K_{om} value for an organic compound, is a distribution ratio of the compound between an organic cation derived organoclay material and water. Thus, the adsorption efficiency of the organic matter in organoclays as a partition medium, can be compared with that of octanol by dividing the K_{om} values by the K_{ow} value (=2.69) as shown in Table 3 (i. e. [log ($K_{om}\cdot K_{ow}^{-1}$)]), [31].

As discussed previously, different preparations may differently enhance the final properties. Table 3 shows that lower dispersion concentrations of the original bentonite used to prepare the organoclays promote higher secondary adsorption properties. It can be seen that for a same HDTMA-Cl loading level, 1 mass% suspensions lead to higher distribution coefficients than the 4 mass% suspension.

The possible secondary adsorption promoted by using HDTMA-Cl loading levels higher than the CEC of the SVCL Nat, also enhances the secondary adsorption properties as shown in Table 3. In a same kind of initial bentonite dispersion, the higher loading levels, lead to higher distribution coefficients.

Positive log (K_{om} K_{ow}^{-1}) values indicate that SVCL-HDTMA organoclays resulted in greater retention of toluene as compared to an octanol medium. The results of SVCL-HDTMA (1%, 80) and SVCL-HDTMA (4%, 80) are similar and higher than SWy-HDTMA [8], but lower than SAz-HDTMA and VSC-HDTMA found by Jaynes and Vance [8].

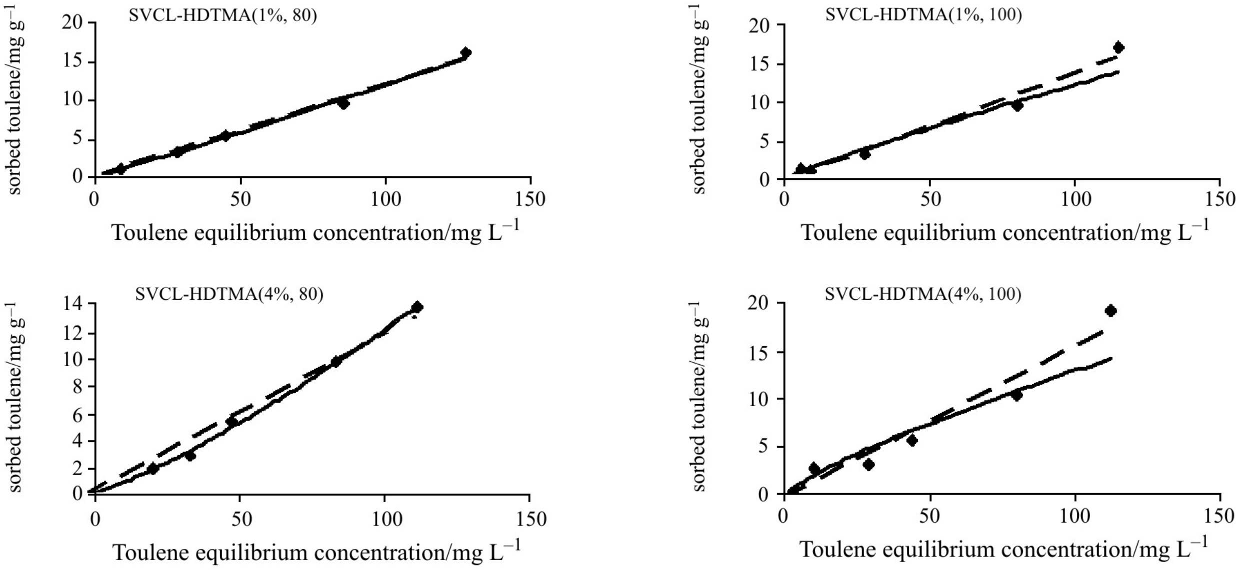

Fig. 5 Toluene sorption isotherms obtained by using SVCL-HDTMA organoclays

Table 3 Partitioning parameters for toluene retention by organoclays

Samples	K_d/L kg^{-1}	f_{oc}	K_{oc}/L kg^{-1}	log K_{oc}	K_{om}/L kg^{-1}	log K_{om}	log (K_{om} K_{ow}^{-1})
SVCL-HDTMA (1%, 80)	120	0.1592	753.77	2.88	605.15	2.78	0.09
SVCL-HDTMA (1%, 100)	140.3	0.1561	898.78	2.95	721.57	2.86	0.17
SVCL-HDTMA (4%, 80)	112.4	0.1564	718.67	2.86	576.97	2.76	0.07
SVCL-HDTMA (4%, 100)	131	0.1619	809.14	2.91	649.60	2.81	0.12
SWy-HDTMA [8]	114	0.1670	682.63	2.83	548.04	2.74	0.05
SAz-HDTMA [8]	317	0.2390	1326.36	3.12	1064.84	3.03	0.34
VSC-HDTMA [8]	251	0.1500	1673.3	3.22	1343.40	3.13	0.44
SWy-HDTMA [31]	79.43	0.1684	471.67	2.67	378.67	2.58	-0.11

$K_{oc}=K_d\ f_{oc}^{-1}$. Octanol-water partitioning constant (log K_{ow}) value is 2.69 [32]

Sharmasarkar *et al.* [31] obtained a negative value for log (K_{om} K_{ow}^{-1}) when using SWy-HDTMA, suggesting a lower toluene retention than octanol. Based on Table 3 results, the order of log (K_{om} K_{ow}^{-1}) for toluene is SVCL-HDTMA (4%, 80) ~ SVCL-HDTMA (1%, 80) < SVCL-HDTMA (4%, 100) < SVCL-HDTMA (1%, 100). Positive log (K_{om} K_{ow}^{-1}) values are not surprising because octanol is relatively hydrophilic compared with the C_{12} and C_{18} alkyl groups present in the organic cations [8]. The sorption efficiency of organic matter derived from organic cation exchange has practical consequences, because in the preparation of organoclays, the organic cation salt is far more expensive than the clay. To manufacture organoclays like SVCL-HDTMA (4%, 80) would be less expensive than organoclays like SVCL-HDTMA (1%, 100).

Conclusions

As confirmed by CHN analysis, TG curves of organoclays prepared in different conditions, by using the same quaternary ammonium salt and the same bentonite, when plotted on calcined basis, allows one to determine which preparation leads to the highest sorption.

When using HDTMA chloride loading level equivalent to the CEC of the original clay, the organic content of organoclays prepared from 1 mass% clay suspensions is higher than that in samples prepared from 4 mass% suspensions, due to the higher salt dilution condition in the former case, which enhances ion dissociation, and consequently, cation exchange mechanism.

When using HDTMA chloride loading level higher than the CEC, the opposite occurs, because, besides cation exchange, also hydrophobic adsorption occurs, which in turn promotes a lower thermal stability, as seen from the thermal analysis curves. In the 4 mass% case, there is a higher initial HDTMA chloride concentration in the aqueous phase, which enhances the adsorption, leading to a higher organic content.

As a consequence, the organoclay prepared from the more concentrated clay suspension (4 mass%) and using a HDTMA cation loading higher than the CEC of the original bentonite, present higher adsorptive properties as tested by using toluene as the reference adsorbate, because it has the highest organics content.

Secondary sorption properties of the organoclays prepared from the Brazilian bentonite studied in the present paper indicate that they have potential use in a variety of environmental applications and technologies, as, for instance, to treat groundwater contaminated with gasoline components.

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