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RESEARCH ARTICLE

Surfactant-modified bentonite clays: preparation, characterization, and atrazine removal

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Abstract Bentonite clay was modified using quaternary ammonium cations, viz. phenyltrimethylammonium (PTMA), hexadecyltrimethylammonium (HDTMA), trioctylmethylammonium (TOMA) [100 % of cation exchange capacity of clay], and stearylkonium (SK) [100 % (SK-I) and 250 % (SK-II) of cation exchange capacity of clay]. The organoclays were characterized using X-ray diffraction (XRD), infrared (IR) spectroscopy, and scanning electron microscopy (SEM). Atrazine adsorption on modified clays was studied using a batch method. Bentonite clay was a poor adsorbent of atrazine as 9.4 % adsorption was observed at 1 μg mL^{-1} atrazine concentration. Modification of clay by PTMA cation did not improve atrazine adsorption capacity. However, atrazine adsorption in HDTMA-, TOMA-, and SK-bentonites varied between 49 and 72.4 % and data fitted well to the Freundlich adsorption isotherm (R>0.96). Adsorption of atrazine in organoclays was nonlinear and slope (1/n) values were <1. The product of Freundlich adsorption constants, $K_f(1/n)$ in HDTMA-, TOMA-, and SK-I-bentonites was 239.2, 302.4, and 256.6, respectively, while increasing the SK cation loading in the clay (SK-II) decreased atrazine adsorption [$K_f(1/n)-196.4$]. Desorption of atrazine from organoclays showed hysteresis and TOMA- and SK-I-bentonites were the best organoclays to retain the adsorbed atrazine. Organoclays showed better atrazine removal from wastewater than an aqueous solution. The synthesized organoclays may find application in soil and water decontamination and as a carrier for atrazine-controlled released formulations.

Keywords Bentonite · Quaternary ammonium cations · Organoclays · Atrazine · Adsorption · Desorption

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Introduction

Intensification of agriculture has resulted in increased use of pesticides. Widespread use of these plant protection chemicals has raised the concern of environmental contamination, especially surface and groundwater resources. Improper disposal of empty pesticide containers, washing of spray instruments, and unregulated discharge from the manufacturing units are other causes of contamination. To protect and restore the contaminated soils and aquifers, researchers are frequently looking for suitable materials to be used as adsorbents, contaminant carriers, and pollutant stabilizers (Boyd et al. 1991). Different pesticide carriers have been proposed for developing controlled release formulations to minimize the impact and load of pesticide in the environment (El-Nahhal et al. 2000; Undabeytia et al. 2000; Trigo et al. 2010).

Atrazine, a triazine herbicide, has great environmental concerns due to its endocrine disruptor status (USDHHS 2003; USEPA 2006). United States Environmental Protection Agency (USEPA) has classified atrazine as a class C chemical (“possible human carcinogen”) and has fixed the maximum contaminant level in drinking water as 3.0 μg L^{-1} (USEPA 2009), whereas level is below 0.1 μg L^{-1} for the European Union. Due to its chemical properties, atrazine is susceptible to leaching and runoff losses, especially during heavy rain to contaminate surface and groundwater and possesses threat to the environment. Many surveys report the presence of atrazine/metabolites in surface and groundwater in the USA (Gaynor et al. 1995; Gilliom 2007). Poinke et al. (1998) reported that out of the 20 well water samples collected from Pennsylvania, 14 samples contained atrazine in concentrations ranging between 13 and 1,110 ng L^{-1}.

Natural clays are the poor adsorbent of nonionic pesticides. However, modification of clays using surfactants introduces an organic phase in/on the clay interlayers/surface that acts as a partitioning medium for the nonionic contaminants. The organic phase of organoclays has been shown to be 10–20 times more effective than the natural soil organic matter and the natural clays in adsorbing pesticides (Sánchez-Camazano and Sánchez-Martín 1994). During past few decades, there has been increasing interest in the use of organoclays to address the issue of environmental contamination. However, before an organoclay can be used in protection and restoration of soil and water resources, information is required on specific sorbent–pesticide interactions, including its adsorption–desorption behavior.

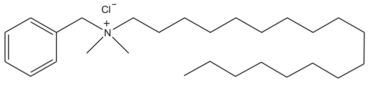
Few studies are available on atrazine adsorption on cationic surfactant-modified clays. Borisover et al. (2001) were able to remove 98 % atrazine from water at high clay–water ratio of 50 g L^{-1}. Abate and Masini (2005) reported that hexadecyltrimethylammonium-vermiculite removed 56–63 % of atrazine, 43–45 % of deethylatrazine, and 12–19 % hydroxyatrazine from water at 1:125 (*w*/*w*) ratio at initial concentrations of 0.05 and 1 μg mL^{-1}. Sánchez-Martín et al. (2006) reported that among the octadecyltrimethylammonium-modified montmorillonite, illite, muscovite, sepiolite, and palygorskite (expendable and non-expandable layered and nonlayered clays), organo-montmorillonite exhibited best atrazine adsorption which was nearly tenfold more than that of the unmodified montmorillonite. Undabeytia et al. (2008) observed 60 % atrazine adsorption on didodecyltrimethylammonium-montmorillonite (0.5 %, *w*/*w*) at 10 μg mL^{-1} concentration. Organoclays not only serve as adsorbents for the herbicide removal from water but also have been utilized as a carrier for developing controlled release (CR) formulations. They are highly effective in reducing the herbicide leaching losses and greater part of the herbicide was retained in the application zone. Trigo et al. (2010) reported that atrazine, when formulated as organoclay complex, was more sorbed in the soil and was bioavailable for degradation, therefore less likely to leach down.

Literature suggested that the herbicide adsorption capacity of organoclays is affected by the nature of organic moiety used to modify them. Therefore, organoclays were prepared by modifying the bentonite clay with different cationic surfactants; characterized and adsorption–desorption behavior of atrazine was studied by batch adsorption method. Further, atrazine removal efficiency of these organoclays was verified using wastewater collected from a pesticide manufacturing unit.

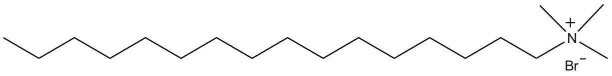
Materials and methods

Chemicals

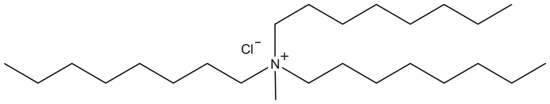
Analytical grade atrazine (94.3 % purity) was purchased from the Rallis India Limited, Bangalore, India. Atrazine has aqueous solubility of 0.03 g L^{-1} and octanol–water partition coefficient (Log K_{ow}) is 2.75. The chloride or bromide salts of quaternary ammonium cations (Fig. 1), viz. phenyltrimethylammonium (PTMA), trioctylmethylammonium (TOMA), hexadecyltrimethylammonium (HDTMA), and stearylkonium (SK); Na-bentonite clay, solvents, and other chemicals used were of analytical grade and were locally purchased (SDFCL, Mumbai, India). The cation exchange capacity (CEC) of the bentonite clay was determined by $CaCl_2$-$MgCl_2$ method (Jackson 1967) and surface area was calculated using BET method.



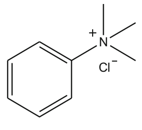
Stearylkonium (SK) chloride



Hexadecyltrimethylammonium (HDTMA) bromide



Trioctylmethylammonium (TOMA) chloride



Phenyltrimethylammonium (PTMA) chloride

Fig. 1 Structures of the cationic surfactants used in the study

Wastewater

Wastewater, collected from an atrazine manufacturing and formulating factory of North India, was filtered through 0.45 μm Millipore membrane filter to remove suspended particles and total suspended solid (TSS) percentage was determined. Wastewater was characterized for the physico-chemical properties, viz. pH, electrical conductivity (EC), ammonium, nitrite, and nitrate-nitrogen content (Keeney and Nelson 1989) and atrazine/metabolites using high-performance liquid chromatography (HPLC) (Table 1).

Preparation of organoclays

The organoclays were prepared by dropwise addition of aliquots of 0.1 M aqueous solution (~250 mL) of chloride or bromide salts of PTMA, TOMA, HDTMA (equivalent to CEC of clay), and SK (equivalent and 2.5 times of CEC) to a 10 g L^{-1} aqueous suspension of Na-montmorillonite clay under continuous stirring. The clay suspension was

Table 1 Physicochemical characteristics of wastewater

pH	Electrical conductivity (dS m^{-1})	Total suspended solid (mg L^{-1})	Nitrogen content (μg mL^{-1})			Contaminant (μg mL^{-1})	
			NH_4^+	NO_2^-	NO_3^-	Atrazine	Cyanuric acid
9.5	209	1.09	–	0.014	–	53.92	1,360

equilibrated for 24 h and then centrifuged at 6,000 rpm for 10 min. Finally, the organoclays were washed with distilled water till free of chloride or bromide ions and dried at 60 °C. The dried clay pellets were ground using ball mill to a fine powder and sieved to uniform size. Elemental analysis of bentonite and organoclays was performed using Vario EL CHNS Element Analyzer, Elementar Analysensysteme GmbH, Germany.

X-ray diffraction analysis of organoclays (Philips PW 1710 X-ray diffractometer) was performed using automated powder diffraction (APD) software with following setting of the instrument: radiation type Cu-Kα, generator voltage 40 kV, tube current 20 mA, start angle (°2θ) 3.00, and end angle (°2θ) 16.00. Infrared spectroscopy of the samples was carried out as KBr pellet using Bruker ALPHA, FTIR/ATR system (typically 24 scans, resolution 4 cm^{-1}), and samples were scanned in 4,000–500 cm^{-1} region. Scanning electron microscopy (SEM) photographs of organoclays were taken using the EVO/MA10 scanning electron microscope (Carl Zeiss Instrument, USA) equipped with backscattered electron imaging (BSE) and secondary electron imaging (SEI) detectors. The system was maintained at high vacuum of 1.7 e-0.005 mbar. The emission heat target varied from 15 to 20 KeV, with flame current, probe current, and working distance of 2.223 A, 106 pA, and 9.5–11 mm, respectively.

Adsorption–desorption studies

Adsorption isotherms for atrazine on clays/organoclays were obtained using a batch method. One hundred milligrams of oven dry (70 °C) clay/organoclay and 20 mL of an aqueous solution of atrazine in 30 mL oak-ridge tubes were equilibrated on an end-over-end shaker for 24 h at room temperature. Concentration of atrazine ranged between 1 and 5 μg mL^{-1} and each concentration was replicated thrice. After equilibration, clay suspension was centrifuged at 13,500 rpm for 10 min and herbicide residue was quantified in the supernatant. A blank, without clay, was maintained to observe any sorption of herbicide on tube surface or degradation during the equilibration. The amount of herbicide adsorbed by clay was calculated from the difference of initial and final concentration of herbicide in the supernatant. Mass balance calculations indicated that there was no sorption of herbicide on tube surface and herbicide was stable during the equilibration period.

Desorption of atrazine from the organoclays was studied in the same tube after adsorption. Desorption was studied at two concentrations. After adsorption, the supernatant was decanted and replaced with an equal volume of fresh distilled water and suspension was equilibrated for another 24 h. The suspension was centrifuged and atrazine concentration was estimated in the supernatant. Total of three desorption cycles were performed for each sample. Total amount of atrazine desorbed was estimated by summing the amount of atrazine desorbed during each desorption.

Removal of atrazine from wastewater using HDTMA-, TOMA-, and SK-I-bentonites was studied by batch method. Wastewater was diluted using distilled water to obtain initial atrazine concentration of approximately 5.4 μg mL^{-1}. Experiment was performed at 1:200 (*w/v*) clay/water ratio as per details mentioned above for atrazine adsorption from aqueous solution.

Extraction and analysis

Aqueous samples were either injected directly after filtration through 0.45 μm filter or extracted by shaking 1 mL sample with 2 mL ethyl acetate for 1 min. The ethyl acetate fraction was separated and was dried over anhydrous sodium sulfate. Ethyl acetate was allowed to evaporate and the residue was redissolved in 1 mL acetonitrile for analysis by HPLC.

Atrazine was analyzed using HPLC (Varian, Prostar) equipped with quaternary pump and UV detector and connected with Rheodyne injection system using LiChrospher C-18 stainless steel column [250 mm×4 mm (i.d.)] and acetonitrile:0.1 % aqueous *o*-phosphoric acid (70:30) as mobile phase at a flow rate of 0.5 mL min^{-1} at a wavelength of 222 nm. Under these conditions, the retention time of atrazine was 9.1 min. The recovery of atrazine from water samples was studied at fortification levels of 0.1, 1, and 10 μg mL^{-1} by fortifying 10 mL water with required amount of atrazine in 0.1 mL of acetone. The atrazine recoveries ranged from 92.8±1.1 to 93.4±1.0 %.

Results and discussion

Properties of clay/organoclays

Table 2 shows the physicochemical properties of bentonite and organoclays. Bentonite clay was alkaline in nature (pH

Table 2 Characteristics of bentonite and organo-bentonite clays

Clay	pH	Surface area ($m^2 g^{-1}$)	Cation exchange capacity (meq 100 g^{-1})	Elemental composition (%)			Organic cation (meq 100 g^{-1})	d(001) Å
				C	N	H		
Bentonite	10.2	21.0	111.3	0	0	0	0	14.47
PTMA	9.0	–	–	6.51	0.78	2.40	52.72	14.95
HDTMA	8.3	–	–	17.8	1.06	4.39	85.03	22.65
TOMA	7.8	–	–	24.0	1.01	5.11	86.54	24.52
SK-I	7.3	–	–	26.12	1.05	5.01	93.01	28.52[a]
SK-II	6.8	–	–	40.52	1.59	0.20	142.5	28.52[a]

[a] XRD pattern of SK-bentonites did not show peak maxima till lowest possible limit of angle measurement (2θ=3.1); therefore, the basal spacing was calculated at the minimum 2θ value

10.2), while intercalation of organic cation resulted in the decrease in pH, and organoclays were mild alkaline or neutral in nature. Based on elemental analysis, the intercalation percent of the organic cation was determined. Results suggested that none of the organic cations showed 100 % intercalation. PTMA cation showed around 53 % exchange, while maximum exchange was observed with SK cation, which showed around 93 % exchange when used at 100 % of CEC and nearly 140 % exchange when used at 250 % of CEC. The differences in exchange capacity can be attributed to the varied chain length and structure of the substituents attached with the quaternary ammonium ions (Zhang et al. 1993; Li et al. 2002).

XRD analysis

XRD patterns of bentonite and modified clays are presented in Fig. 2. The *d*(001) spacing was obtained by first rational order corresponding to 001 reflection. Intercalation of surfactant cation in the interlayer of clay lattice was confirmed by decrease in the 2θ values and increase in the *d*(001) spacing values in modified clays (Table 2). The *d* spacing for bentonite clay corresponded to 14.47 Å and was comparable to the *d* spacing of a typical montmorillonite clay. Intercalation of different cationic surfactant in the interlayers of clay showed different effect on *d* spacing and it varied with the nature of the

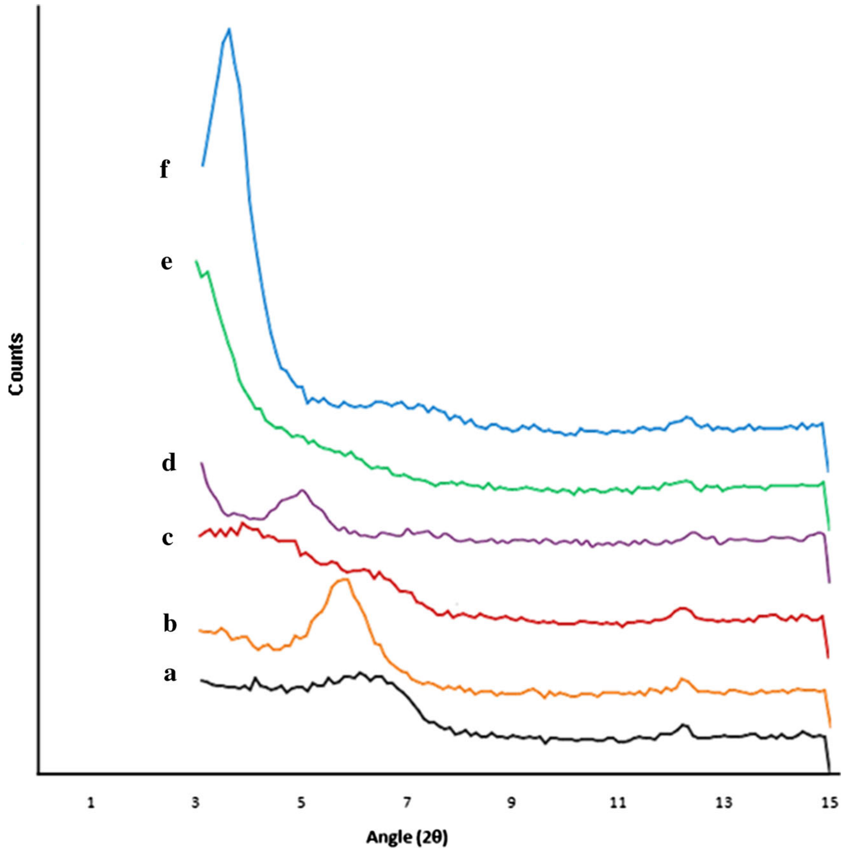


Fig. 2 XRD chromatogram of different types of clays. *a* Bentonite. *b* PTMA-bentonite. *c* HDTMA-bentonite. *d* SK-II-bentonite. *e SK-I-bentonite*. *f* TOMA-bentonite

surfactant. The 2θ values for PTMA-bentonite, HDTMA-bentonite, TOMA-bentonite, and SK-bentonite were 5.9, 3.9, 3.6, and 3.1, respectively, and these corresponded to respective *d* spacing of 14.95, 22.65, 24.52, and 28.52 Å [XRD pattern of SK-bentonites did not show peak maxima till lowest possible limit of angle measurement (2θ=3.1); therefore, the basal spacing was calculated at the minimum 2θ value]. The result suggested that change in basal spacing was minimum when PTMA cation was intercalated in the clay lattice. Probably, PTMA cation lied horizontally between the bentonite layers. Increase in *d* spacing in HDTMA-bentonite and TOMA-bentonite was 8.18 and 10.05 Å, respectively. Maximum increase in *d* spacing was observed in SK-bentonites and was of the order of 14.05 Å.

IR analysis

IR spectra of bentonite and modified bentonite clays were recorded over the range 4,000–500 cm^{-1} and are reported in Fig. 3. A broad band at 3,450–3,440 cm^{-1} region was assigned to the OH stretching vibration, whereas band at 1,639 cm^{-1} was assigned to the OH bending vibrations of water present in the bentonite. An Al-Al-OH stretching band at 3,620 cm^{-1} and an Al-Mg-OH stretching band at 3,693 cm^{-1} were typical of bentonite clays (Farmer 1974; Akçay and Yurdakoç 1999). The bands at 915 and 879 cm^{-1} can be assigned to the Al-Al-OH and Al-Fe-OH bending vibrations, respectively. Thus, the bentonite clay used in the present study was rich in aluminum and contained a portion of magnesium and iron too. The Si-O stretching band was observed at 1,045–1,040 cm^{-1} region, and a band at 527 cm^{-1} was assigned to the Si-O bending vibration. A doublet at 780 and 795 cm^{-1} indicated the presence of quartz in the bentonite.

All the bands belonging to typical bentonite were reserved following modification by cationic surfactants (Fig. 3b–e) and were indicative of the fact that clay had been modified by the surfactant moieties. There was slight shift in the position of these bands following modification with cationic surfactants. A pair of bands at 2,925 and 2,850 cm^{-1} in cationic surfactant-modified bentonites was assigned to the symmetric and asymmetric C–H stretching vibrations of methyl and methylene groups and suggested the presence of cationic surfactants in the bentonite. These bands were absent in the natural bentonite (Fig. 3a). The bands at 1,470 and 1,375 cm^{-1} were assigned to the asymmetric and symmetric C–H bending vibrations, respectively. All these bands were less intense in PTMA-modified bentonite, further suggesting that intercalation by PTMA cation was less as compared to the interaction by remaining organo-cations.

SEM characterization

The SEM photographs of natural and modified bentonites are shown in Fig. 4. The photograph of bentonite clay suggested smooth surface with flat crystal. However, following the intercalation of cationic surfactant, the clay lattice appeared swollen and fluffy. This might be due to an increase in the basal spacing of clay. These changes were clearly evident in HDTMA-bentonite (Fig. 4b), TOMA-bentonite (Fig. 4c), and SK-bentonite (Fig. 4d). PTMA-bentonite clay did not show much change, and this result was in agreement with the intercalation percent of the PTMA cation and XRD results which suggested a minimum increase in the *d* spacing in PTMA-bentonite.

Adsorption–desorption studies

Results (Table 3) suggested that natural bentonite was a poor adsorbent of atrazine as only 9.4 % of atrazine was adsorbed at 1 μg mL^{-1} concentration, while no atrazine adsorption was observed at higher concentrations (2–5 μg mL^{-1}). Modification of bentonite by PTMA cation did not improve the atrazine adsorption capacity of bentonite. Non-sorption of atrazine in PTMA-bentonite can be explained by the non-expansion of clay. No change in clay *d* spacing was observed following intercalation of PTMA cation. Earlier, Trigo et al. (2010) reported that among the two PTMA-montmorillonites (Na-rich Wyoming-montmorillonite and Ca-rich Arizona-montmorillonite), only Wyoming-montmorillonite showed nearly 10 % atrazine adsorption while no atrazine adsorption was observed in the Arizona-montmorillonite. However, bentonite modification by HDTMA-, TOMA-, and SK-I-cations (equivalent to CEC of clay) significantly enhanced the sorption of atrazine in the modified clays and 55.2–58.8, 64.7–72.4, and 56.6–61.7 % of atrazine adsorption was observed in the respective clay. Thus, TOMA-bentonite showed maximum atrazine sorption followed by the SK-I-bentonite and HDTMA-bentonite. Further increase in SK cation in bentonite (SK-II-bentonite) slightly reduced the atrazine adsorption to 49–50.6 %. Earlier, Boyd et al. (1991) grouped organoclays into two types: adsorptive and organophilic with different sorptive mechanism in these types. Organophilic clays (clays modified using quaternary cations having large alkyl groups, e.g., HDTMA) contain paraffin-like layer of organic phase in the interlayer of the clay lattice, which acts as the partition medium for the sorption of the organic compounds. Adsorption mechanism involves simple partitioning of the organic compound in the synthetic organic phase. Adsorptive clays (clays synthesized using small quaternary cations, e.g., PTMA) act as the organic pillars and prop open the clay layers, thus exposing the abundant siloxane surfaces for the adsorption of organic compounds. Pesticides are adsorbed on the mineral surfaces between the organic pillars, not on the organic

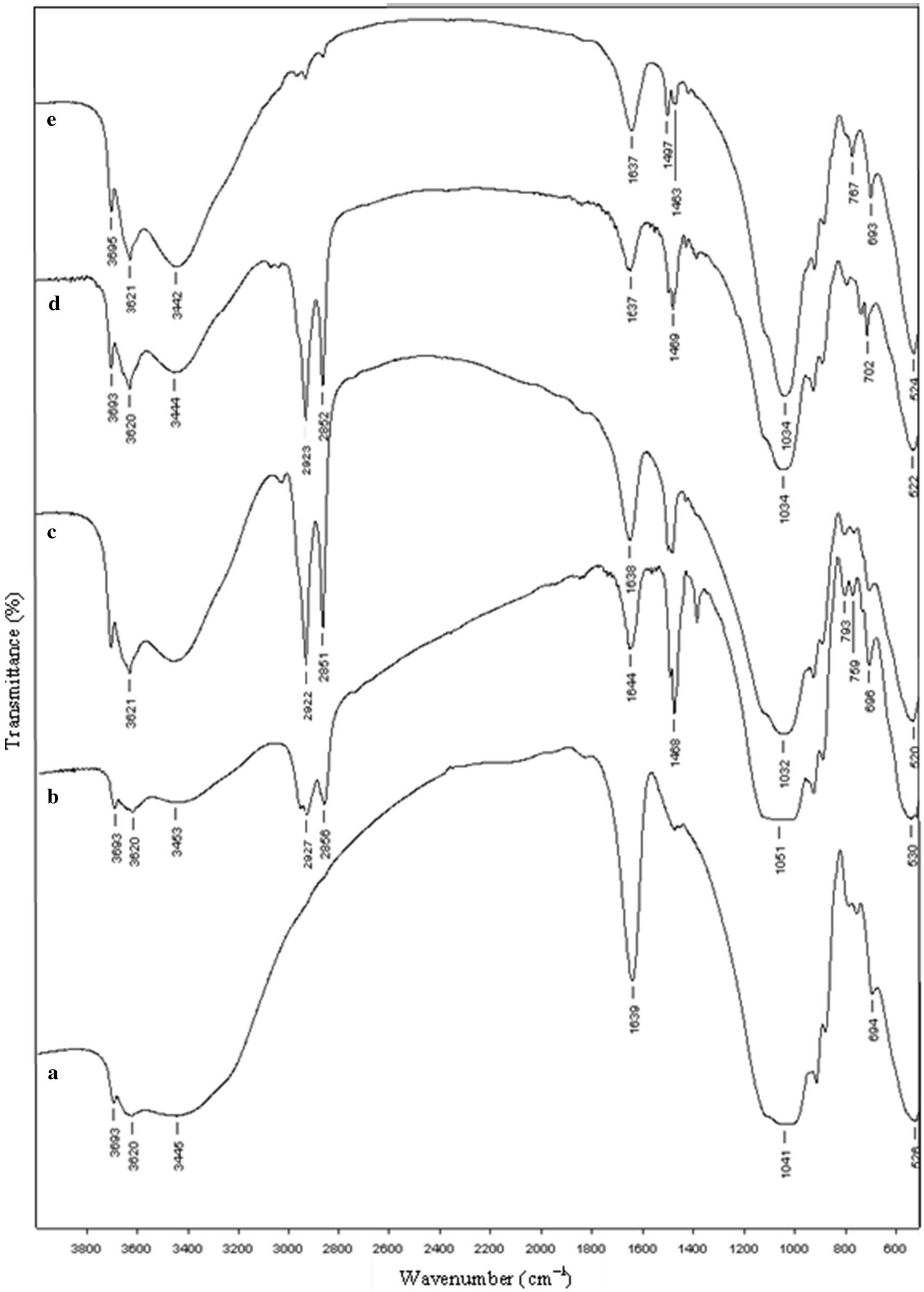


Fig. 3 IR spectrum of clays. *a* Bentonite. *b* TOMA-bentonite. *c* HDTMA-bentonite. *d* SK-I-bentonite. *e* PTMA-bentonite

phase. Sorption of atrazine in modified clays was the function of the organic phase introduced in clay interlayer following the adsorption of cationic surfactants in the lattice.

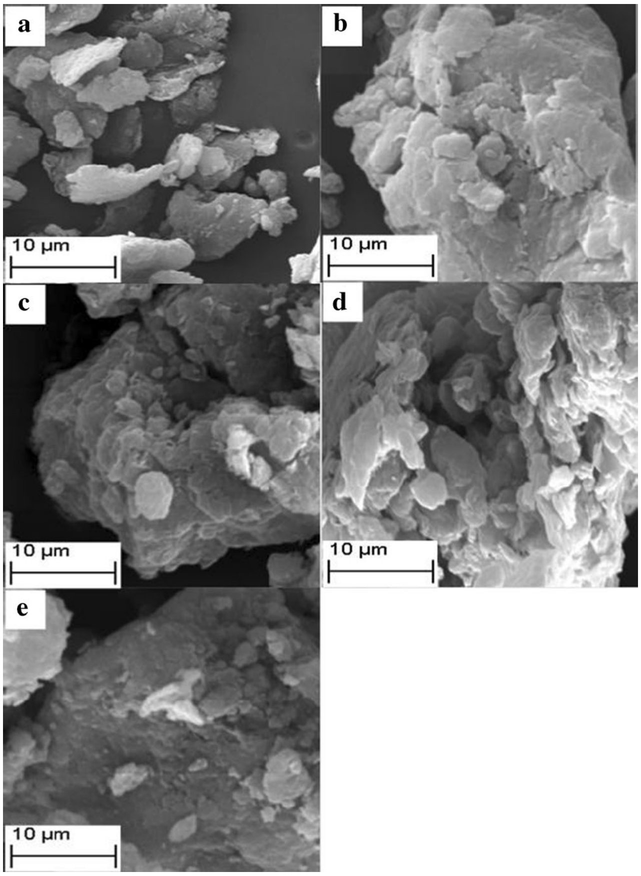


Fig. 4 SEM pictures of **a** bentonite, **b** HDTMA-bentonite, **c** TOMA-bentonite, **d** SK-I-bentonite, and **e** PTMA-bentonite clays

Data for atrazine sorption in HDTMA-, TOMA-, and SK-organoclays was fitted to the Freundlich adsorption equation,

$$\log x/m = \log K_\mathrm{f} + 1/n \log C$$

where x is the concentration of atrazine sorbed (μg), m is the mass of the clay (g), C is the equilibrium solution concentration of atrazine (μg mL^{-1}), and K_f and $1/n$ are the Freundlich constants. The Freundlich adsorption coefficient (K_f) represents the sorption of atrazine at an equilibrium concentration of 1 μg mL^{-1}, and $1/n$ (slope) reflects the degree to which sorption is a function of herbicide concentration. Atrazine adsorption data fitted well to the Freundlich adsorption isotherm as values of correlation coefficients (R) were >0.9 (Table 3 and Fig. 5).

The Freundlich $1/n_\mathrm{ads}$ values take into account the nonlinearity in the adsorption isotherms and are the index of the intensity of adsorption. The slope ($1/n_\mathrm{ads}$) values of atrazine adsorption isotherm in modified bentonite clays were less than unity suggesting L-type isotherms (Giles et al. 1960). L-type isotherms are characterized by the decrease in the adsorption at higher aqueous concentrations of the compound. This indicates greater competition for adsorption sites which become limited as solute concentration in solution increased. However, slope value for atrazine sorption in SK-II-bentonite was near unity (C-type isotherm). SK-II-bentonite had higher amount of organic phase; therefore, even at higher solute concentrations, there were enough sites available for the atrazine adsorption. It is well documented that the mechanism for contaminant sorption in the surfactant-modified clays is the simple partitioning of solute in the organic phase.

Table 3 represents the Freundlich adsorption parameters for atrazine in the modified clays. To get a meaningful comparison of the K_f values of atrazine sorption in different organoclays, the $1/n$ (slope) values in all organoclays should be statistically equivalent. Therefore, as suggested by earlier workers (Wang et al. 1999), $K_\mathrm{f}(1/n)$ was selected as a parameter of adsorption. The $K_\mathrm{f}(1/n)$ values for atrazine were highest in the TOMA-bentonite (302.4) followed by SK-I-bentonite (256.6), HDTMA-bentonite (239.2), and SK-II-bentonite (196.4). Thus, among the HDTMA-, TOMA-, and SK-bentonites, the TOMA-bentonite, which has maximum number of carbon in the alkyl chains (TOMA having total of 24 carbon), showed maximum atrazine sorption, followed by the SK-I-bentonite, having octadecyl (C_{18}) alkyl chain, and HDTMA-bentonite, having C_{16} alkyl substituent. However, sorption of atrazine decreased in SK-II-bentonite which was prepared by adding cation exceeding the clay CEC. Compared to SK-bentonite, low adsorption of atrazine in SK-II-bentonite can be explained by poor penetration by atrazine molecule into the organic phase of the clay. Earlier, Borisover et al. (2001) reported that compared to atrazine adsorption constant (K_d) of 440 L kg^{-1} in clay 1 (70 % of clay CEC), the K_d in clay 2 (>100 % of clay CEC) was 310 L kg^{-1}. They suggested that atrazine penetration into the organic carbon-rich clay 2 was

Table 3 Adsorption parameters for atrazine in organo-bentonite clays

Clay	K_f	$1/n$	R^2	K_d	R^2	K_oc	Amount sorbed (%)
HDTMA	262.9±5.6[a]	0.91±0.06	0.998	233.0±5.7	0.996	1,309.0	55.2–58.8
TOMA	373.3±6.9	0.80±0.07	0.991	336.3±9.3	0.998	1,401.3	64.7–72.4
SK-I	298.4±3.7	0.86±0.04	0.977	242.5±4.3	0.974	928.4	56.6–61.7
SK-II	190.7±3.8	1.03±0.02	0.997	204.9±4.8	0.993	–	49.0–50.6

[a] ±Standard error

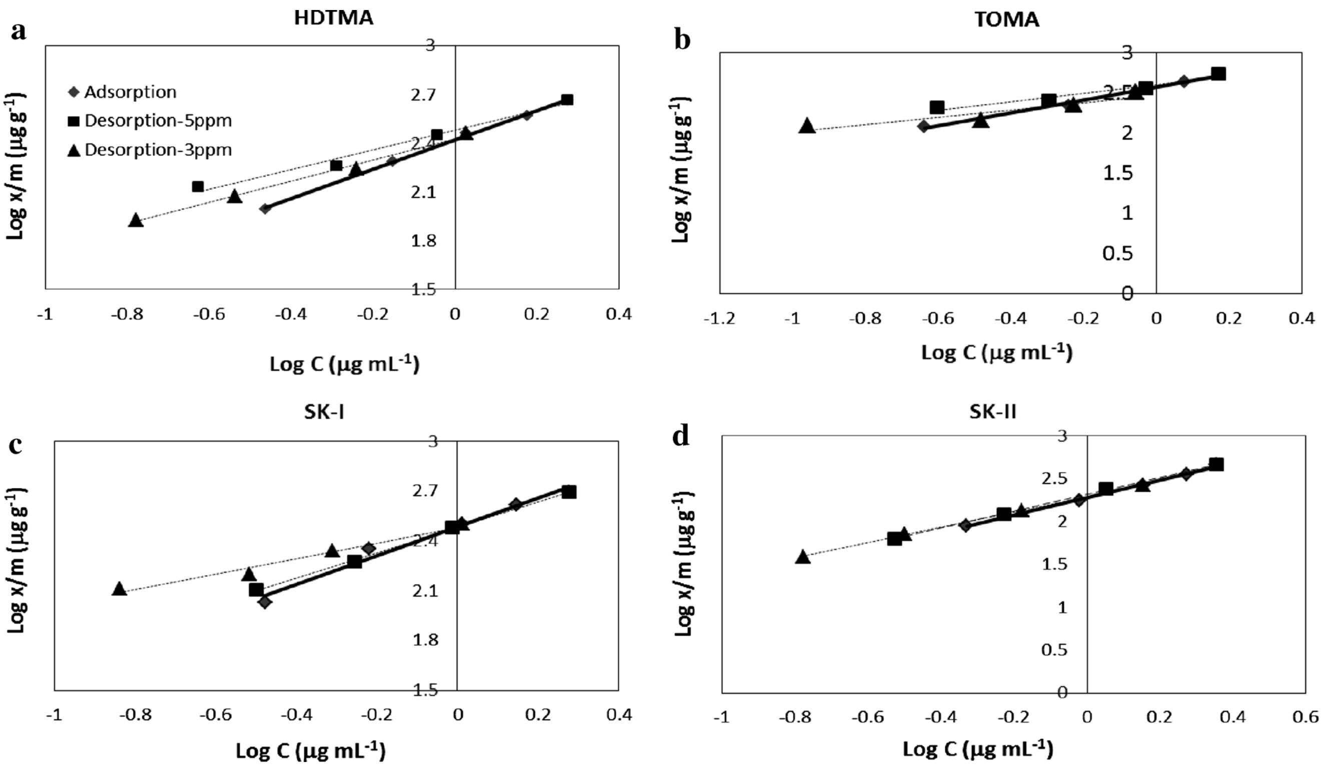


Fig. 5 Adsorption–desorption isotherms for atrazine in organo-bentonite clays (*HDTMA* hexadecyltrimethylammonium; *TOMA* trioctylmethylammonium; *SK* stearylkonium)

slower than the atrazine penetration in the organic carbon-poor clay 1.

Earlier, no study is available where organoclays modified using cationic surfactant of varying carbon chain length were evaluated for their atrazine adsorption potential. Abate and Masini (2005) compared atrazine adsorption in clay modified with different proportions of HDTMA cation. Compared to K_f of 10.5 in natural vermiculite, HDTMA-modified vermiculite had K_f of 102 in HDTMA-VT$_{0.5}$ (organo-cation loading equivalent to 50 % of clay CEC) and 135 in HDTMA-VT$_{1.0}$ (100 % of clay CEC), thus registering 9.5 to 13 times increase in the atrazine adsorption. Similarly, Sánchez-Martín et al. (2006) suggested that octadecyltrimethylammonium (ODTMA)-modified montmorillonite resulted in 14.5 times increase in the atrazine adsorption. Thus, K_f of atrazine in HDTMA-bentonite prepared in the present study was nearly double the atrazine K_f obtained by Abate and Masini (2005). Further, compared to HDTMA-bentonite, TOMA- and SK-I-

Table 4 Atrazine desorption parameters in organo-bentonite clays

Clay	K_f	1/*n*	R^2	K_d	R^2	Amount desorbed (%)				*H* (1/n_d/1/n_s)
						I	II	III	Total	
Desorption—3 µg mL^{-1}										
HDTMA	266.5±2.8[a]	0.65±0.03	0.994	224.8±11.2	0.999	39.4	19.9	11.4	70.7	0.71
TOMA	298.0±6.9	0.45±0.04	0.853	273.7±8.4	0.960	36.0	19.9	6.6	62.5	0.56
SK-I	303.0±3.7	0.47±0.03	0.973	212.9±6.4	0.988	30.7	19.1	9.1	58.9	0.55
SK-II	195.4±8.4	0.89±0.04	0.999	179.2±6.9	0.999	49.4	25.3	12.7	85.3	0.86
Desorption—5 µg mL^{-1}										
HDTMA	301.9±6.9	0.61±0.02	0.980	201.9±9.4	0.996	38.8	22.0	10.1	70.9	0.67
TOMA	401.3±11.0	0.53±0.03	0.947	273.0±8.1	0.982	34.1	18.5	9.1	61.7	0.66
SK-I	303.7±8.7	0.76±0.05	0.999	231.4±6.1	0.996	39.0	22.4	12.7	74.1	0.88
SK-II	209.0±6.2	0.98±0.07	0.999	203.6±10.8	0.999	48.3	25.3	12.7	87.3	0.95

[a] ±Standard error

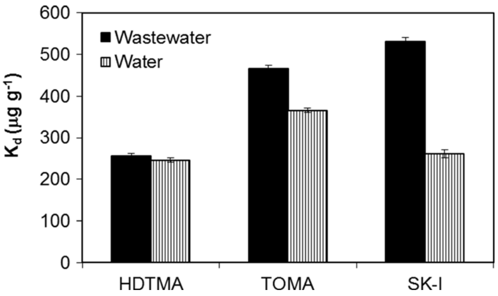


Fig. 6 Comparison of partition coefficient (K_d) for atrazine adsorption from wastewater and distilled water solution

bentonites were slightly better adsorbents for the atrazine removal from water.

Results of the desorption study (Table 4) suggested that a portion of the sorbed atrazine was prone to desorption, and amount desorbed was affected by the nature of cationic surfactant. Except SK-I-bentonite, where desorption was concentration dependent, other organoclays showed equal atrazine desorption at both levels of atrazine. Atrazine desorption data fitted well to the Freundlich isotherm as correlation coefficient (R) values were higher than 0.97. The slope values of isotherms were less than unity, suggesting L-type isotherm. The $1/n_{des}$ values were lower than the corresponding $1/n_{ads}$ values suggesting that the rate of desorption was slower than the rate of adsorption and hysteresis was observed. The hysteresis (H) was quantified using $(1/n_{des})/(1/n_{ads})$ ratio. Hysteresis is negative when H is more than 1, while it is positive when the value of H is less than 1. Except SK-II-bentonite, where the H value was nearly 1, atrazine desorption in the rest of the clays showed positive hysteresis.

Further, these organoclays were used to remove atrazine from the wastewater effluent. Results suggested that at 1:200 clay/water ratio, organoclays adsorbed 56–73 % of atrazine from wastewater containing 5.43 μg mL^{-1} of atrazine. HDTMA-bentonite showed least adsorption (56.4 %) followed by TOMA-bentonite (70.17 %) and SK-I-bentonite (72.84 %). Thus, compared to TOMA-bentonite, which showed maximum atrazine adsorption from aqueous solution, SK-I-bentonite was the better adsorbent for atrazine removal from wastewater. Partition coefficients (K_d=amount of atrazine (μg) adsorbed per gram of clay/equilibrium concentration in μg mL^{-1}) of atrazine in wastewater were 255.7, 465.4, and 530.8 μg g^{-1} in HDTMA-, TOMA-, and SK-I-bentonites, respectively. Comparison of K_d values of atrazine adsorption from water and wastewater (Fig. 6) suggested that the K_d values were higher in the wastewater than in aqueous solution. Maximum difference was observed in the SK-I-bentonite where K_d in wastewater was nearly twice than that in aqueous solution. Physicochemical properties of two atrazine solutions were different as atrazine was the sole solute in the aqueous solution, while wastewater contained some other organic (cyanuric acid, biurate, and two unidentified compounds) and inorganic contaminants (nitrite). Validation of atrazine removal from real wastewater further confirmed the potential of organoclays for atrazine removal in natural environment. However, Groisman et al. (2004) reported that compared to atrazine, ametryn, prometryn, or terbutryn sorption on octadectyltrimethylammonium bentonite from pure water as single solute, sorption of triazine herbicides on clay decreased when present as mixtures in tap water or wastewater.

These organoclays, which exhibited fairly good atrazine adsorption potential, can be utilized not only for atrazine removal from contaminated water but also can be successfully utilized as carriers for developing the CR formulation of atrazine. Herbicide incorporated in a matrix/carrier in CR formulations is gradually released, thus reducing the risk of offsite transport of herbicide, both runoff and leaching losses. Several workers have successfully demonstrated the potential of organoclay-based formulations of alachlor (El-Nahhal et al. 1998, 2000), metolachlor (El-Nahhal et al. 1999; Hermosín et al. 2001), fenuron (Hermosín et al. 2001), norflurazon (Undabeytia et al. 2000), sulfometuron (Mishael et al. 2002), hexazinone (Celis et al. 2002), and atrazine (Trigo et al. 2010).

The results of the present study suggest that organoclays prepared by modifying bentonite clay using different quaternary ammonium cationic surfactants varied in their atrazine adsorption capacity. Among the various clays, TOMA- and SK-bentonites were the best organoclays to retain atrazine and may find application in soil and water decontamination and as carrier for controlled released formulation of atrazine.

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