

Sorption and Desorption of Atrazine on Natural Bentonite and Organically Modified Bentonite

Mohamed A Osman^{1*}, Fawzy M. Kishk², Abdalla A. Moussa¹, and Hesham M. Gaber²

ABSTRACT

In order to increase the effectiveness of bentonite clay in the retention of atrazine, natural bentonite clay was modified using humic acid and hexadecyltrimethylammonium bromide (HDTMA) as the intercalation agent and a cationic surfactant at 100 % of the cation exchange capacity. Such organic modification changes the nature of clay from hydrophilic to hydrophobic, which insures surfactant loading. The performance of the natural and modified bentonite was evaluated in terms of elemental analysis, BET surface area, X-ray diffraction (XRD), FTIR spectroscopy, and thermogravimetric analysis (TGA). The batch equilibrium technique was applied to conduct atrazine adsorption/desorption isotherms with the natural and the modified bentonite. The data fitted well to the simple linear and Freundlich adsorption isotherms while desorption data agreed with Freundlich adsorption only. Desorption kinetic was successfully fitted with the first order reaction model. Natural bentonite was a poor adsorbent of atrazine with distribution coefficient of $K_d = 3.07 \pm 0.04 \text{ L kg}^{-1}$. The complexation with humic acid did not improve atrazine adsorption on bentonite, $K_d = 2.15 \pm 0.14 \text{ L kg}^{-1}$, whereas, the HDTMA-bentonite exhibited high affinity to sorb atrazine with K_d value of $197.97 \pm 0.77 \text{ L kg}^{-1}$. Natural bentonite and humic-bentonite clearly exhibited nonsingularity of sorption/desorption isotherms. The desorption curve of HDTMA-bentonite revealed that the sorption of atrazine is reversible with no hysteresis. These results indicate the potentiality of HDTMA-bentonite for environmental applications.

Keywords: Bentonite, Organoclays, HDTMA-Br, Humic acid, Atrazine, Adsorption, Desorption, Freundlich Isotherm.

INTRODUCTION

Pesticides discharged from agricultural soils are a significant class of environmental pollutants because of their toxicity even at trace levels. The removal of these pesticides from drainage water is required for sustaining environmental natural resources (Cara and Jitoreanu 2015). Numerous techniques such as adsorption, degradation, photocatalytic, electrochemical degradation, oxidation, membrane filtration, nano-filtration are applied to decrease pesticides levels from discharges (Srivastava *et al.*, 2009). The adsorption

based-technique is a promising process for pesticides removal because of its simplicity and the availability of various adsorbents (Tan *et al.*, 2013).

Atrazine is widely utilized as a selective herbicide. It is applied to control annual broadleaf and grassy weeds for many crops all over the world. Atrazine belongs to the moderately persistent organic pollutants that is relatively mobile in soil (LeBaron *et al.*, 2011). The half-life of atrazine in soil ranges from 14 to 108 days (Tuovinen *et al.* 2015). Atrazine contamination has become a growing public concern because of its toxicity to the living organisms; atrazine may cause damages to the central nervous system, endocrine system, and immune system (Fan and Song 2014). The biological transformation and chemical retention are two major processes that affect the availability and the mobility of atrazine in the soil environment (Koskinen and Clay 1997).

Humic substances and clay minerals are considered the most essential soil constituents in the retention of soil-applied pesticides. Humic-clay complexes play considerable roles in controlling the retention and transport of hydrophobic organic pollutants in soils and sediments (Wang and Xing 2005). Natural clays are insignificant adsorbent of nonionic pesticides (Srivastava *et al.*, 2009). It is well established that the uptake of nonpolar organic compounds from aqueous solution strongly corresponds with soil organic carbon content. In order to increase adsorption capacity of clay minerals, modification with quaternary ammonium surfactant has a high affinity towards most of hydrophobic organic compounds (Li *et al.*, 2003; Ismadji *et al.*, 2015).

Modified clays are used in many applications such as polymer nanocomposites, adsorbents of organic pollutants, gel formation, catalyst in organic synthesis, paints, cosmetics, petroleum industry, thixotropic fluids, etc. (DePaiva *et al.*, 2008; Ahmed Gurses *et al.*, 2011; Park *et al.*, 2011). Furthermore, organoclays have been proposed for improving the controlled-release formulation efficacy and reducing the negative environmental impact of pesticides (Nir *et al.*, 2006; Trigo *et al.*, 2010).

¹ Water Resources and Desert Land Division, Desert Research Center, Cairo, Egypt.

² Soil and Water Sciences Dept., Faculty of Agric., Alexandria University, Egypt.

*Corresponding Author: m.ali.osman@alexu.edu.eg

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Literature suggested that the herbicide adsorption capacity of organoclays is influenced by the nature of organic moiety that is applied for the modification process (DePaiva *et al.*, 2008; Ismadji *et al.*, 2015; Zhu *et al.*, 2016). The objectives of this research were to examine the sorption/desorption characteristics of atrazine through equilibrium batch techniques on natural bentonite and organically modified bentonite clays and explore to contribute the methods of combating environmental pollution by atrazine.

MATERIALS AND METHODS

Chemicals

Analytical grade Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) with purity 98.8% and humic acid (HA) powder were purchased from Sigma-Aldrich Co. Hexadecyltrimethylammonium bromide (HDTMA) obtained from Fluka with a reported purity 98% (Table 1). All solvents used were high performance liquid chromatography (HPLC) grade from Sigma-Aldrich.

Preparation of organo-bentonite

The natural bentonite (bent.) was obtained from Egypt Company for Mining and Drilling Chemicals under the brand name (MB1100). The clay was used without performing any further purification. The CEC of the natural bentonite was 85.21 cmol kg⁻¹ as determined by neutral normal ammonium acetate (Rhoades 1982). Humic-bentonite complex (Humic-bent.) was prepared at a ratio of 1:100 following the procedure of Wang and Xing (2005) and Li *et al.*, (2003). The syntheses of surfactant modified bentonite (HDTMA-bent.) was performed by exchanging the sodium on the surface of Na-bentonite with cationic surfactant (HDTMA) at 100% of CEC according to He *et al.* (2010) and Oyanedel-Craver *et al.* (2007).

Organoclay characterization

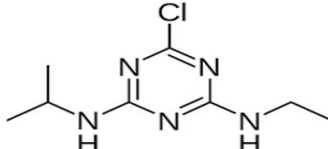
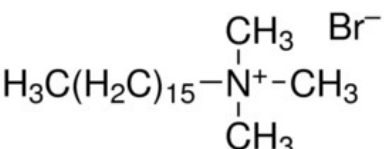
Prior to the analysis, the materials were sieved and passed through a 170 mesh sieve. The Brunauer, Emmett and Teller [BET] surface area of clays was

determined using N₂ adsorption isotherm after degassed at 100 °C for 4 h under vacuum (BELSORP-mini II). X-ray diffraction (XRD) was performed on dried powder samples. The XRD patterns of natural bentonite and modified bentonite were recorded on a Philips diffractometer (PW 3710) using Co K α radiation ($\lambda=1.78897 \text{ \AA}$) at 40 kV and 35 mA. The diffractogram was scanned from (2 θ) 5 to 45 at scan rate 0.5° min⁻¹ (Rebecca 2004). The analysis of the infrared absorption of the clay samples were carried out in KBr pellets, using Jasco FTIR-4100 from wave number of 400 to 4000 cm⁻¹ (Ma *et al.* 2010). Thermogravimetric analysis (TGA) was carried out for the clays using a Shimadzu TGA -50 instrument. The sample was heated in a platinum pan at temperature from 30 to 1000 °C, at a rate of 10 °C min⁻¹ in a following N₂ atmosphere (Rebecca 2004). The percentages of C, H, and N in adsorbents were determined by Vario EL III Element Analyzer.

Adsorption-desorption experiment

Atrazine adsorption isotherms were determined in duplicate by using the batch equilibration technique (OECD. 2000). Stock solution was prepared by dissolving an appropriate amount of atrazine in methanol (HPLC grade) and kept in the freezer at -20°C. Stock concentrations and volumes transferred were intended to safeguard a methanol concentration of 0.2% by volume in the working solutions. The atrazine solutions are prepared directly in a background solution consists of 0.01M CaCl₂, besides 0.01% NaN₃ (pH 7.20). For adsorption batch experiments, solid to solution ratios of 1:100 and 1:25 were applied for HDTMA-bent, and both of bentonite and Humic-bentonite complex batches, respectively. Six initial concentrations (C_i) ranged from 0.5 to 16 mg L⁻¹ were used in Oak-ridge polypropylene tubes. The tubes were shaken (end-over-end) in the dark for 24 h at room temperature (22 ± 1°C). The pH values of the dispersions were measured after 24 h in separated tubes.

Table 1. Selected physicochemical properties of Atrazine and HDTMA

Properties	Atrazine	HDTMA
Molecular structure		
Molecular formula	C ₈ H ₁₄ ClN ₅	C ₁₉ H ₄₂ NBr
Molecular Weight	215.68 g mole ⁻¹	364.46 g mole ⁻¹
Water Solubility	33 mg/L @ 25°C	13 g/L @20 °C
pKa*	1.68 @ 20°C	-

* (LeBaron *et al.* 2011)

The aqueous phase was separated by centrifugation at 5000 rpm for 15 min. Subsequently, 10-ml aliquot of supernatant was withdrawn directly from the centrifuge tube and filtered through a disposable 0.45- μm PTFE syringe filter. A control was conducted without sorbents, in the same way, to determine the amount of solute sorbed by the used tube. Blank was prepared with sorbents and background solution for background correction. The amount of atrazine adsorbed (S) was calculated based on the mass balance between the initial and the equilibrium atrazine concentrations in solution. $S = V(C_i - C_e)/M$ where M is the mass of adsorbent (g) and V is the solution volume (ml). Desorption procedure was performed immediately after adsorption step from the highest three equilibrium points of the adsorption isotherms. Desorption's cycles were executed by replacing 50% of the supernatant with a fresh (sorbate-free) background solution. The tubes were re-dispersed by vortex mixer and shaken under the same conditions of the applied adsorption experiments. Each desorption cycle was repeated six times consecutively.

HPLC analysis

Atrazine in the supernatant solution was determined using Thermo Scientific–Surveyor plus HPLC System equipped with UV/Vis plus detector at a wavelength of 220 nm. A Hypersil GOLD, 5 μm reverse phase column was used with a length of 150 mm and an inner diameter of 4.6 mm. The HPLC analyses were carried out using an isocratic elution mode with a mobile phase constituted by 55% (v/v) water contains 5% methanol and 45% (v/v) methanol. The analyses were performed at a flow rate of 1.0 ml min^{-1} . The injection volume was 20 μl . Under these analytical conditions, an atrazine retention time was 7.8 min.

Data analysis

Two mathematical models were used to describe experimental data of adsorption isotherms (Selim and Zhu 2005; McDonald *et al.*, 2013). A simple linear model: $S = K_d C_e$, where S is the adsorbed amount per unit mass (mg kg^{-1}), C_e is the equilibrium concentration of the solute in the bulk solution (mg L^{-1}), and K_d is a distribution coefficient (L kg^{-1}). Freundlich isotherm model: $S = K_f C_e^N$, where K_f is a Freundlich capacity coefficient ($\text{mg kg}^{-1}/(\text{mg L}^{-1})^N$) and N is the adsorption

intensity describes the isotherm curvature (dimensionless). The organic carbon-normalized distribution coefficients (K_{OC}) were calculated as: $K_{oc} = 100 \times K_d / OC$, where OC is the organic carbon content in percentage. The percentage of removal efficiency (R) was calculated as: $R\% = (C_i - C_e)/C_e \times 100$. The ratios of the Freundlich exponents for desorption and adsorption (N_{des}/N) refers to Hysteresis Index (HI). Lower index values show increased difficulty of the sorbed analyte to be desorbed from the adsorbent (Lima *et al.*, 2010; Hedia and Al-Aswad 2016). Observed desorption data has been fitted to first-order kinetic model as: $S_t/S_0 = e^{-k_1 t}$ where S_0 is the amount initially adsorbed (g kg^{-1}), S_t is the amount desorbed at different times (g kg^{-1}), and k_1 is the rate constant for the first order reaction (h^{-1}) (Daneshvar *et al.* 2017).

RERSULTS AND DISCUSSION

Physicochemical properties of adsorbents

The Egyptian natural bentonite was characterized by CEC of 85.21 cmol kg^{-1} and by particle size distribution consists of 24.32% sand, 3.45% silt, and 72.23% clay. Physicochemical properties of bentonite, surfactant modified bentonite, and humic bentonite complex are presented in Table 2. Natural bentonite was alkaline in nature, pH value of 10, while intercalation of organic substances resulted in a decrease of the pH values to slight alkaline. Based on elemental analysis, the carbon and nitrogen content of bentonite was negligible and was increased by organic modification. The carbon content reached 0.82 % in Humic–bent and 15.28 % in HDTMA–bent. The ratio of C/N for HDTMA-bent was 16.44. This value is close to the theoretical estimation of C/N ratio which was computed as 16.29. This ratio demonstrates that the modification of natural bentonite by HDTMA was effectively realized (Erdem *et al.*, 2010). The BET surface areas and total pore volume of natural bentonite were 44.77 $\text{m}^2 \text{g}^{-1}$ and 0.062 $\text{cm}^3 \text{g}^{-1}$, respectively, which is consistent with Mockovčiaková *et al.*, (2009) and Jiang *et al.*, (2002). A significant decrease of the surface area and pore volume was observed upon organic modification. In Humic bentonite complex, low surface area probably attributed to coating the outer surface of bentonite particles with humic acid.

Table 2. Characteristics of natural bentonite and modified organo-bentonite

Sorbent	pH	Surface area	Pore volume	Elemental composition (%)			d(001)
		$\text{m}^2 \text{g}^{-1}$	$\text{cm}^3 \text{g}^{-1}$	C	H	N	Å
Bentonite	10.0	44.77	0.062	0.32	1.27	Nil	14.05
Humic–bent.	8.16	5.51	0.016	0.82	1.89	Nil	15.99
HDTMA–bent.	7.90	5.68	0.022	15.28	3.23	0.91	21.70

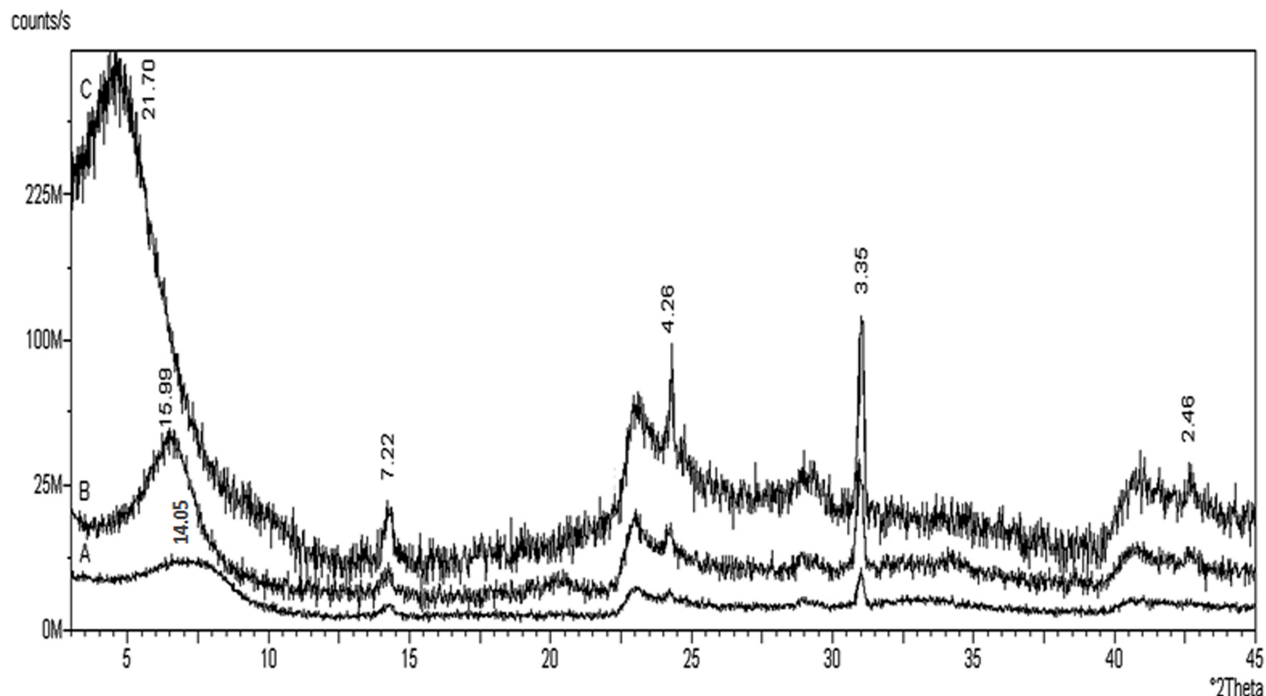


Figure 1. XRD chromatograms for natural and modified clays: (A) Natural bentonite, (B) Humic-bentonite, (C) HDTMA-bentonite

Ksiezopolska and Pazur (2011) reported that the specific surface area of bentonite and illite reduced after complexation with humic acids at all pH values as a result of lodged humic acid in the active sites on clays and making the surface of the complex hydrophobic. Whereas, in surfactant modified bentonite the interparticle pores are covered and clogging of the interlayer space by HDTMA molecules prevented the N_2 access to the inner surface of material (He *et al.*, 2010; Erdem *et al.*, 2010; Emam 2013).

X-Ray Diffraction analysis

XRD diffractograms of bentonite and its modifications are presented in Figure 1. XRD pattern of natural bentonite approved montmorillonite as the dominant mineral phase and quartz as the main impurity mineral with traces of kaolinite. The modification of bentonite with organic substances, through their incorporation into interlayer space, leads to expansion of bentonite. It was confirmed by a decrease in the 2θ values and increment basal spacing (d-value) for modified bentonite (Table 2). Intercalation of humic acid and HDTMA in the interlayers of bentonite displayed a different effect on d_{001} -spacing value. The d-value for natural bentonite corresponded to 14.05 Å expanded to 21.70 Å for HDTMA-bent which is in agreement with other studies (Erdem *et al.*, 2010 and Dutta and Singh 2015). The basal spacing expansion is

owing to the interpenetration of HDTMA ion into the layers of bentonite. It was demonstrated that the structural configuration of alkyl chains, in the interlamellar space, is pseudotrimolecular layer which is comprised of three alkyl chains in which the nonpolar chain ends are moved one above the other by the formation of kinks (Nuntiya *et al.*, 2008). Conversely, Humic-bent. exhibited a small expansion at d-value of 15.99 Å, which indicates that humic acid was associated mainly with the external surfaces of the bentonite due to the large size of humic acid molecule (Li *et al.*, 2003; Sun *et al.*, 2016).

Fourier transform infrared (FTIR)

The FTIR spectrum specifies the physisorption and chemisorption of the organic modifier onto the bentonite due to the existence, shift or disappearance of the peaks of functional groups. FTIR spectra of natural bentonite and modified bentonites were examined and compared to each other over the range 4000–400 cm^{-1} (Figure 2). The bands at 3696 cm^{-1} and 3624 cm^{-1} was assigned to Al-Mg-OH stretching and Al-Al-OH stretching respectively. Al-Al-OH bending vibrations band at 916 cm^{-1} and Al-Fe-OH bending vibrations at 795 cm^{-1} were typical of bentonite clays. Consequently, the bentonite utilized in the present study was rich in aluminum and contained a portion of magnesium and iron too (Sikdar *et al.*, 2008). The Si-O stretching band was seen at 1031

cm^{-1} , and the band at 525 cm^{-1} was allotted to the Si-O bending vibration. A doublet at 780 and 795 cm^{-1} demonstrated the presence of quartz in the bentonite. A broad band at $3450\text{--}3440 \text{ cm}^{-1}$ region was allocated to the -OH stretching vibration, whereas band at 1637 cm^{-1} was assigned to the -OH bending vibrations of water adsorbed in the bentonite (Dutta and Singh 2015; Shehata *et al.*, 2016).

The spectra of pure humic acid distinguished with peaks at 1740 , 1640 , and 1260 cm^{-1} were attributed to C=O stretching vibration of the carboxyl group, C=C stretching vibrations of aromatic structures and C-O stretching vibration, respectively (data not shown). Interactions of humic acid with bentonite have occurred leading to the absence of peak 1740 and 1260 cm^{-1} or diminished considerably, while the C=C of the aromatic structures peak in the region of 1640 cm^{-1} was overlaid to -OH bending model of adsorbed water (Sun *et al.*, 2016). Generally, Humic-bentonite complex did not show any distinct peak than bentonite (Figure 2). Specifically, there was a slight shift in the position of bands after modification with cationic surfactants. Furthermore, sorbed water content declined with the intercalation of HDTMA which resulted from the substitution of hydrated cations by HDTMA⁺ ions. A couple of peaks at 2924 and 2851 cm^{-1} can be relegated to the symmetric and asymmetric stretching -CH₂ vibrations of methylene groups and their bending

vibrations at 1473 and 1408 cm^{-1} were only observed on HDTMA-bentonite (Hongping *et al.*, 2004; Ma *et al.*, 2010).

Thermogravimetric analysis (TGA)

TGA analysis was used to determine the thermal stability of natural bentonite and modified bentonite. As shown in Figure 3, unmodified bentonite shows two stages of weight losses. The first stage at $39\text{--}136 \text{ }^\circ\text{C}$ leads to weight loss about 11.37% , which corresponds to surface-adsorbed water and water associated with the interlayer cations. The second stage at $458\text{--}591 \text{ }^\circ\text{C}$ included weight loss of 3.14% which is related to structural water arising from dehydroxylation of the clay layers (Xi *et al.*, 2004; Huskic *et al.*, 2009; Mallakpour and Dinari 2013).

Regularly, bentonite does not experience thermally incited changes in the temperature range of $170\text{--}450 \text{ }^\circ\text{C}$, subsequently the weight loss in this temperature range should be attributed to the decomposition of the surfactant. In this respect, the occurrence of organic cations increases the number of decomposition steps for organo-clay. Several studies have documented that the decomposition of an organo-clays takes place in four steps: water desorption, dehydration, desurfactant, and dehydroxylation of the organoclays (Xi *et al.*, 2005; Mallakpour and Dinari 2013).

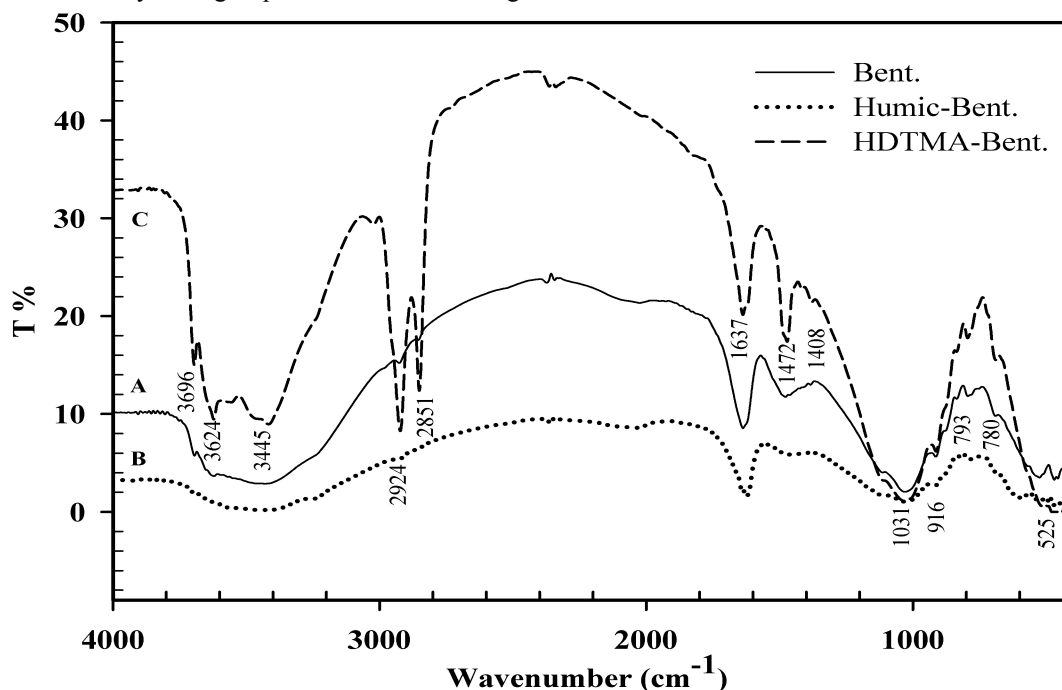


Figure 2. FTIR spectra of natural and modified clays: (A) Natural bentonite, (B) Humic-bentonite, (C) HDTMA-bentonite

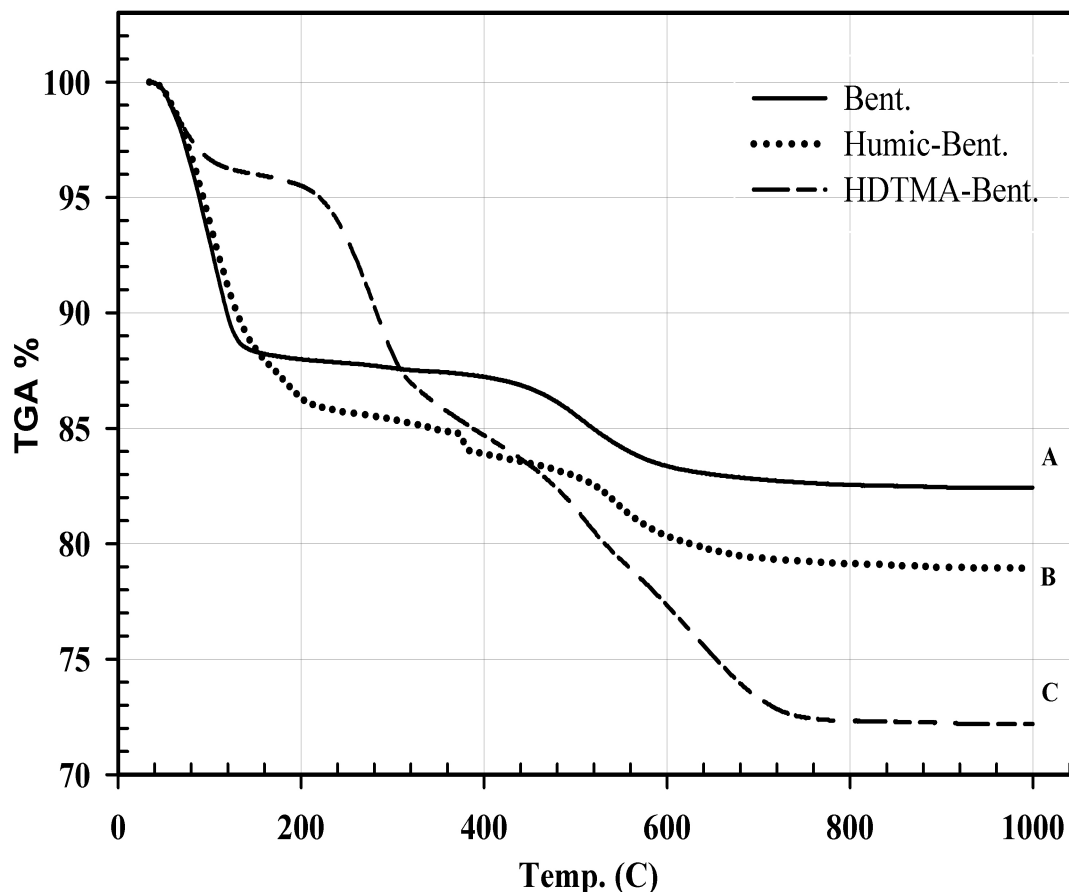


Figure 3. TGA curves of natural and modified clays: (A) Natural bentonite, (B) Humic-bentonite, (C) HDTMA-bentonite

In the case of HDTMA, the first two steps of decomposition involved the dehydration of the interparticle adsorbed and interlayer water which occurs between 49 and 127 °C with weight loss of approximately 3.46% (Figure 3). In comparing with the TGA of the raw bentonite, the HDTMA-bent. exhibited less weight loss during dehydration. The shift to the lower temperature indicates the existence of weakly bound physioadsorbed water and confirmed the replacement with surfactant between bentonite layers. A downward shift of similar magnitude was also reported by Yapar (2009). The third step attributed to desurfactant is split into two stages; the first stage is occurred around 198–306 °C with 8.16% weight loss is corresponding to the decomposition of some HDTMA cations on the surface of bentonite. The second stage at 306–449 °C with 4.86% weight loss is assigned to the decomposition of some HDTMA cations between the layers of bentonite (Tiwari et al., 2008; Erdem et al., 2010). The fourth step is referring to the loss of dehydroxylation of the structural OH units of the

bentonite at 449–745 °C (13% weight loss). These results emphasize that the surfactants has been located on the surface and entered into the interlayer spacing of bentonite. Many reviews mentioned that the intercalation of surfactant into the interlayer space increased the thermal stability of the surfactant (DePaiva et al., 2008; Ismadji et al., 2015).

Figure 3 displays the TGA for Humic-bent where the first weight loss of 13.81% was observed at 35 to 205°C and was related to the evaporation of bound water from humic acid beside humic-bent complexes. The second weight loss (1.99%) was observed between 205 and 377°C corresponds to humic acid decomposition. Decline of this ratio was a result of reduced carbon content in the elemental analysis. The third weight loss (3.24%) located a 428 and 599°C relates mainly to the dehydroxylation of the clay sheets (Sun et al., 2016).

Adsorption–desorption isotherms

The adsorption parameters of atrazine on natural bentonite and modified bentonite clays are shown in (Table 3). The sorption isotherm data is fitted well the

linear and Freundlich adsorption isotherms with correlation coefficients (R^2) which higher than 0.95. The natural bentonite exhibited low sorption affinity to atrazine with distribution coefficient of $3.07 \pm 0.04 \text{ L kg}^{-1}$ and removal efficiency of 10.98%. Herwig *et al.*, (2001) reported a K_d value of 3.27 L kg^{-1} for Namontmorillonite and the atrazine intercalate into the external surface by the relatively weak physical forces. The experimental results indicate the significant increase of bentonite affinity for atrazine due to the modification of natural bentonite with HDTMA. Specifically, the modified HDTMA-bentonite exhibited the maximum removal efficiency of 66.48% with distribution coefficient of $197.97 \pm 0.77 \text{ L kg}^{-1}$. On the other hand, the modified humic-bentonite exhibited low sorption affinity to atrazine with distribution coefficient of $2.15 \pm 0.14 \text{ L kg}^{-1}$ and removal efficiency of 7.38%. Our results on the contrast with those of Abate *et al.*, (2004) who found that humic substance enhanced adsorption of atrazine and some of its metabolites in soil. This difference can be attributed to pH, which slightly alkaline (8.16) (Table 2). Tan *et al.*, (2013) reported that the amounts of adsorbed atrazine decreased with increasing pH and the highest adsorption observed at pH equal to 2. Davies and Jabeen (2003) demonstrated that atrazine is adsorbed on humic acid by interacting with the C=O and -OH groups by hydrogen bonding and/or by protonation.

The sorption isotherm linearity of the natural bentonite and HDTMA-bentonite is confirmed by the values of the dimensionless Freundlich constant (N) which is found to be close to the unity. These values of N indicate a constant relative affinity of the solute molecules by the adsorbent, C-type isotherm (Table 3). This implies that non-specific interactions occur amongst solute and adsorbent (Abate and Masini 2005). HDTMA-bentonite contain paraffin-like layer of organic phase in the interlayer of the clay lattice, which acts as the partition medium for the sorption of atrazine. Even at higher solute concentrations, there were enough sites available for the atrazine adsorption. The deviation of linearity observed in Humic-bentonite ($N = 0.79$) proposing L-type isotherms that is characterized by the decrease in the adsorption at higher aqueous concentrations of the solute. This demonstrates greater competition for adsorption sites which become limited as solute concentration in solution increased (Dutta and Singh 2015).

Atrazine Desorption and Hysteresis

Results of the desorption experiment (Table 4) suggest that a fraction of the sorbed atrazine was predisposed desorption, and the percentage of atrazine released from successive desorption steps was

dependent on the type of adsorbent. Atrazine desorption data fitted well to the Freundlich isotherm with R^2 greater than 0.95.

The desorption-Freundlich constant (N_{des}) values of the natural bentonite and the humic-bentonite were lower than the corresponding N constants suggesting that the rate of desorption was slower than the rate of adsorption and hysteresis was observed (see Table 3). The N_{des} values of bentonite and Humic-bent isotherms were less than unity, indicating an L-type isotherm. Humic acid was a source of increased hysteresis in humic-bentonite complexes (Li *et al.*, 2003). On the other hand, desorption process of atrazine onto HDTMA-bentonite is reversible, as shown in Figure 4,, which shows desorption curves overlapping the adsorption ones.

Hysteresis Index (HI) is manifested by an increase in the difference between the adsorption and desorption isotherm slopes demonstrating chemically non-ideal behavior (rate-limited desorption). HI is negative when it is more than one, while it is positive when it is less than one (Dutta and Singh 2015). In the case of HDTMA-bentonite, the HI value is about 1 indicating that the interaction is based on a partitioning mechanism. Such a behavior reveals that the surfactant modified bentonite has potential application in control-release formulation of atrazine (Trigo *et al.*, 2010). Moreover, another potential application is the improvement of stationary phases for chromatographic columns that could be eluted utilizing water as mobile phase (Abate and Masini 2005; Dutta and Singh 2015).

The hysteresis of atrazine adsorption-desorption isotherms on natural bentonite and modified bentonite clays are shown in Figure 4. Results revealed that the actual atrazine concentrations in solution after desorption were considerably less than the equilibrium concentrations in the case of natural bentonite and humic-bentonite isotherms. The nonsingularity is clearly observed for bentonite and humic-bentonite isotherms whereas HDTMA-bentonite exhibited no significant hysteresis (Figure 4). Such hysteresis is an indicative of the nonequilibrium adsorption of atrazine on the natural bentonite and the modified humic-bentonite. The percentage of atrazine released from successive desorption steps was dependent on the type of adsorbent. Celis *et al.*, (1997) stated that Atrazine was less hysteretic for bentonite than for humic acid, demonstrating that atrazine desorbs more difficultly from organic substances than from clay minerals owing to the contribution of hydrophobic interactions with humic acid.

Table 3. Adsorption parameters of atrazine on natural bentonite and modified bentonite

Sorbent	Removal efficiency %*	Linear model			Freundlich model		
		K_d (L kg ⁻¹)	R ²	K_{oc} (L kg ⁻¹)	K_f (mg kg ⁻¹)/(mg L ⁻¹) ^N	N	R ²
Natural bentonite.	10.98	3.07 ± 0.04**	0.998	959.38	2.81 ± 0.22	1.03 ± 0.03	0.999
Humic-bentonite	7.38	2.15 ± 0.14	0.957	626.20	3.77 ± 0.70	0.79 ± 0.07	0.982
HDTMA-bentonite	66.48	197.97 ± 0.77	0.999	1295.62	194.12 ± 1.97	1.01 ± 0.01	0.999

*Removal efficiency % related to the largest loading point in the initial concentrations

** Standard error

Table 4. Desorption parameters of atrazine from natural bentonite and modified bentonite

Sorbent	K_{des}^* (mg kg ⁻¹)/(mg L ⁻¹) ^N		N _{des}	R ²	HI
	K_{des}^*	K_{des}^*			
Bentonite	28.19 ± 1.87	0.24 ± 0.03		0.956	0.23
Humic-bentonite	26.45 ± 0.73	0.12 ± 0.01		0.956	0.15
HDTMA-bentonite	193.96 ± 1.22	1.02 ± 0.04		0.992	1.00

*Related to the largest loading point in the initial concentrations

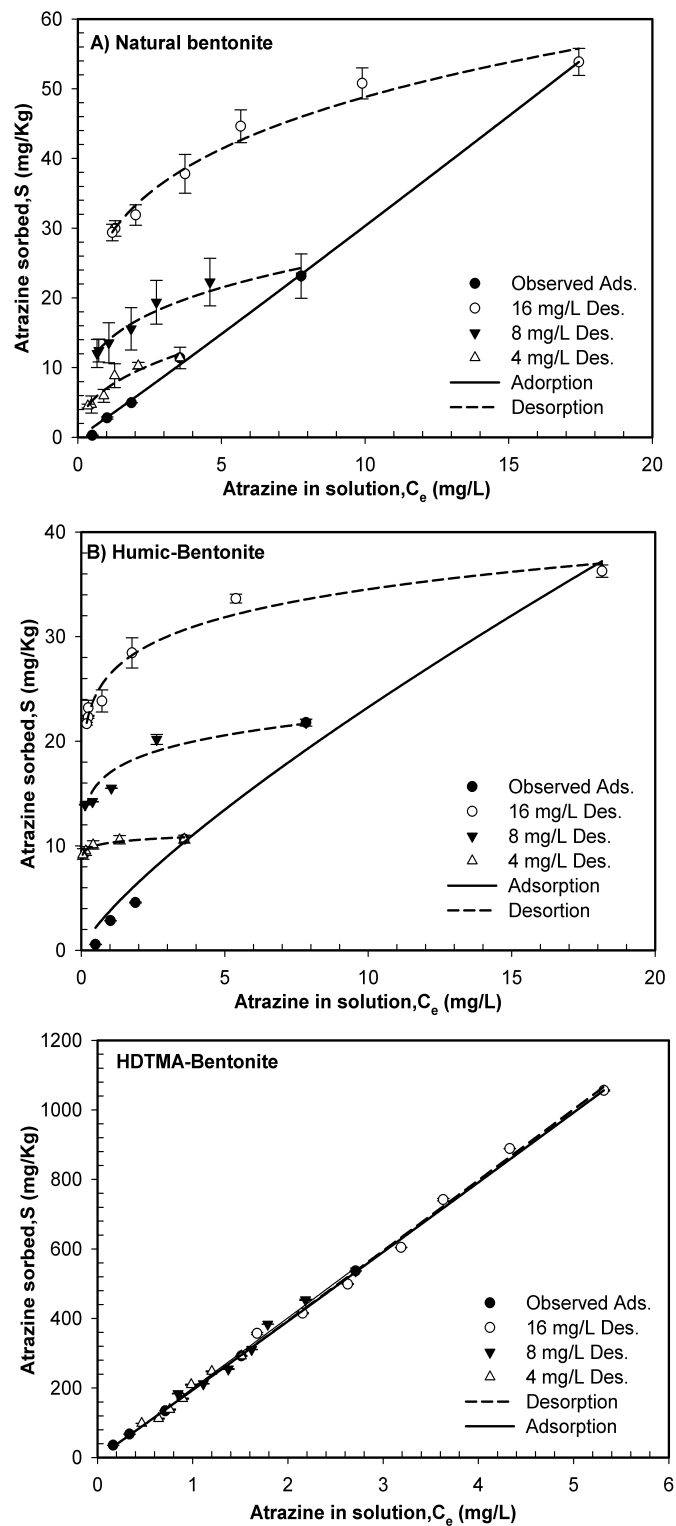


Figure 4. Adsorption and desorption of atrazine for natural and modified clays: (A) Natural bentonite, (B) Humic-Bentonite, (C) HDTMA-Bentonite. The solid and dashed curves are the fitted Freundlich isotherms model for adsorption and desorption, respectively while the symbols are the measured data

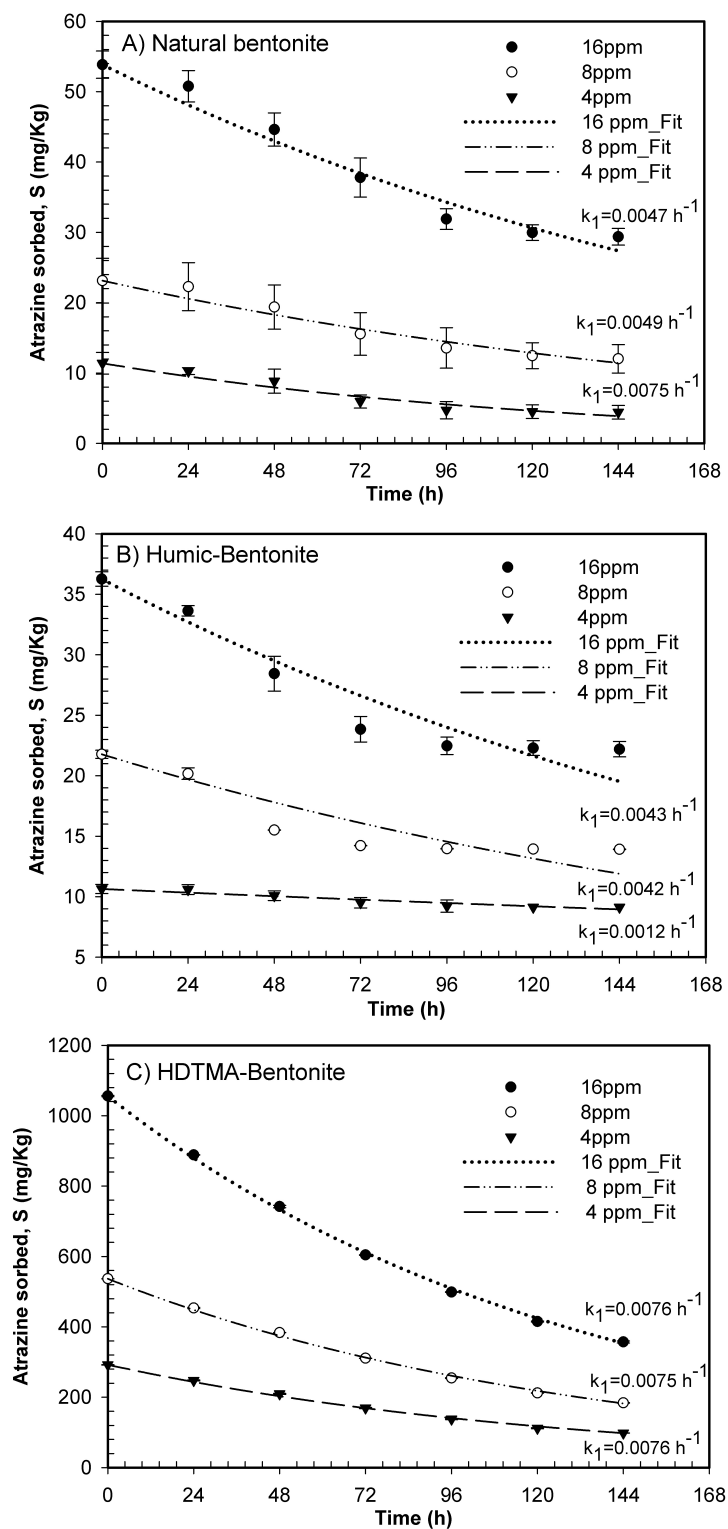


Figure 5. Kinetic of atrazine desorption for natural and modified clays: (A) Natural bentonite, (B) Humic-Bentonite, (C) HDTMA-Bentonite. The symbols are the measured data while the dashed curves are the predicted first order reaction

Desorption kinetic

The kinetic of atrazine desorption from natural bentonite and modified bentonite clays are plotted in Figure 5. The percentages of desorbed atrazine after 144 h from the natural bentonite were 58.6 %, 41.4%, and 40.8% for initial atrazine concentrations, C_0 , of 4.0 mg L⁻¹, 8.0 mg L⁻¹, and 16.0 mg L⁻¹, respectively, whereas humic-bentonite exhibited the lowest released atrazine and the respective percentages were 13.3 %, 35.9 %, and 36.1 %. However, desorption experimental time was extended to 144 h, there was no significant atrazine release from natural bentonite and humic- bentonite clays after 96 h. This limited kinetic of atrazine desorption can be attributed to the low sorption capacity of the natural bentonite and the modified humic-bentonite. On the other hand, the modified HDTMA-bentonite exhibited a time-dependent behavior for atrazine release. Specifically, a continuous decrease of the sorbed atrazine was observed during desorption experimental time (144 h). The HDTMA-bentonite showed the highest desorption of atrazine where the percentages of desorbed atrazine after 144 hours were 66.3 %, 65.7 %, and 66.2 % with total average of 66.1 %. Desorption kinetic data was seem fitted with first order kinetic reaction model with R^2 equal to 0.96, 0.87, 0.99 for bentonite, humic- bentonite, and HDTMA-bentonite respectively. Specifically in bentonite average estimated k_1 was 0.0057 ± 0.0007 h⁻¹ decreased to 0.0032 ± 0.0008 h⁻¹ in humic-bentonite, whereas increased to 0.0076 ± 0.00003 h⁻¹ in HDTMA- bentonite (Figure 5).

CONCLUSIONS

Equilibrium batch experiments were performed to assess the sorption/desorption of atrazine on natural bentonite, humic-bentonite complex, and HDTMA-modified bentonite. Characterization of natural and modified clays indicated the decrease in the pH and the surface area values of the modified bentonite. FTIR spectrum specified the similarity of natural bentonite and humic-bentonite peaks. Whereas HDTMA-modified bentonite exhibited a slight shift in the position of bands. Results revealed the low affinity of atrazine on natural bentonite and humic-bentonite complex with removal efficiencies of 10.98 and 7.38%, respectively. The HDTMA-modified bentonite exhibited the highest sorption affinity with removal efficiency of 66.48 % and distribution coefficient of 197.97 ± 0.77 L kg⁻¹. Natural bentonite and humic-bentonite clearly exhibited nonsingularity of sorption/desorption isotherms. The modified HDTMA-bentonite exhibited a limited hysteresis with a time-dependent release of atrazine. Atrazine desorption data was successfully fitted with the

first order kinetic reaction model confirmed with the statistical criteria of the goodness-of-fit. These results show the potential use of HDTMA-bentonite as a carrier for atrazine controlled release formulations as well as its application for environmental remediation.

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الملخص العربي

إدمصاص وانطلاق مبيد الأترازين على معدن البنتونيت الطبيعي والبنتونيت المعدل عضوياً

محمد على عثمان، فوزى محمد كشك، عبد الله عبد الغفار موسى، هشام محمد جابر

Simple linear و Freundlich بمعامل ارتباط ($R^2 > 0.95$). بينما نتائج عكس الإدمصاص كانت منطبقة على نموذج Freundlich فقط. وقد تم وصف نتائج حركية عكس الإدمصاص بنجاح باستخدام نموذج تفاعلات الدرجة الأولى. وأشارت النتائج أن معدن البنتونيت له سعة إمتصاصية منخفضة إنعكست في معامل التوزيع حيث بلغ ($K_d = 3.07 \text{ L Kg}^{-1}$)، أما معدن البنتونيت مع الهيومك لم يعمل على زيادة معامل التوزيع حيث كان ($K_d = 2.15 \text{ L Kg}^{-1}$)، على العكس من ذلك أظهر التعديل بالـ HDTMA سعة إمتصاصية عالية حيث بلغ معامل التوزيع ($K_d = 197.27 \text{ L Kg}^{-1}$). كما أشارت نتائج عكس الإدمصاص للأترازين أن جزء كبير منه لا يزال مرتبط بالبنتونيت المعدل بالهيومك حيث كان دليل عدم الإرتداد ($HI = 0.15$). أما في حالة البنتونيت المعدل بالـ HDTMA كانت ظاهرة عدم الإرتداد منعدمة ($HI = 1$) مما تجعل له إستخدامات فعالة في مجال المعالجة البيئية.

لزيادة فاعلية معدن البنتونيت الطبيعي في الإحتفاظ بمبيد الأترازين تم إجراء التعديل للمعدن باستخدام بعض المواد العضوية مثل حامض الهيومك وأحد أملاح الأمونيوم الرباعية (HDTMA) كمادة ذات نشاط سطحي Surfactant. وقد نتج عن هذا التعديل جعل المعدن محب للمواد العضوية Organophilic بدلاً من أنه محب للماء Hydrophilic. ولتوصيف البنتونيت الطبيعي و المعدل تم الإستعانة بعدد من الطرق مثل تحليل العناصر [CHN] وتقدير مساحة السطح النوعي وحيود الأشعة السينية والتحليل الطيفي بالأشعة تحت حمراء فضلاً عن التحليل الحراري. وأظهرت النتائج أن التعديل بالمواد العضوية المستخدمة أدى إلى تغير خواص البنتونيت ليصبح محب للمواد العضوية. كما تم إجراء تجارب الإدمصاص وعكس الإدمصاص بالإضافة إلى حركية عكس الإدمصاص لدراسة سلوك الأترازين على معدن البنتونيت والبنتونيت المعدل، فكانت نتائج الإدمصاص منطبقة على نموذجي