Sorption of Tannin from Aqueous Solutions on Organo-Modified Smectite-illite

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ABSTRACT: An organophilic clay-based adsorbent was prepared by incorporating a cationic surfactant, hexadecyltrimethylammonium (HDTMA) at different levels of CEC in Tunisian smectite-illite clay. The presence of the HDTMA surfactant enhanced the adsorption ability of the clays toward plyphenolic compounds from aqueous systems. Adsorption experiments were carried out using a batch equilibration technique to investigate the removal of tannin by the surfactant modified clay. Adsorbent characterizations were investigated using X-ray diffraction, infrared spectroscopy, surface area analysis, and potentiometric titration. The effects of pH, contact time and initial solute concentration on the adsorption of tannin onto modified clay were investigated. The adsorption process was much dependent on the pH and was found to follow pseudo-second-order kinetics. The optimum pH value was at pH ranging from 4.5 to 6. The maximum removal efficiency of tannin from aqueous solution was 91%. The adsorption isotherms were measured and correlated to Langmuir isotherms. From the results it can be concluded that the surfactant-modified clay could be a good adsorbent for treating tannin-contaminated waters.

Key words: Clay, HDTMA, Tannin, Adsorption, Langmuir isotherm

INTRODUCTION

Organic contaminants include many categories of compounds, of which phenolics are recognized as hazardous chemical pollutants. Tannins are water-soluble polyphenolic compounds having molecular weight between 500 and 3000, giving the usual phenolic reactions. The main sources of tannin are industrial water streams including paper and pulp board mills, and tanneries. In general, tannin is often found in the tannery industry zone. Tannins are simple esters of gallic acid and may contain up to 5 galloyl groups esterified directly to the polyol and additional galloyl groups (Bravo *et al.,*1993). Since they are esters, the tannins are hydrolyzed, yielding gallic acid or hexahydroxydiphenic acid and the parent polyol. Numerous studies have demonstrated the harmful effects of tannin on animals and humans (Liu and Luo 2010). Toxicity of tannin to aquatic organisms has been demonstrated for algae, phytoplankton, fish, and invertebrates. Many methods have so far been reported for removal of tannins from wastewater, such as chemical sedimentation, biodegradation, adsorption, electrochemistry, membrane, chemical oxidation, and photo-catalytic degradation (Murugananthan etal., 2005; Boye *et al.,* 2005; Munz 2009). Adsorption

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techniques are rapidly gaining prominence as a treatment process that provides high-quality effluents that are low in concentration of dissolved tannin (Walker and Weatherley 1998). A number of adsorbents, such as activated carbons, peat moss, brown coal, industrial waste, agricultural products, polymers, chitosan, fly ash, clay minerals and organoclays, have been used for tannin removal (Chang and Juang 2004; Liu and Luo 2010; Marsal *et al.,* 2009; Liao and Shi 2005). Cost effectiveness, availability, and adsorption properties are the main criteria for choosing an adsorbent to remove pollutants. Among the low cost adsorbents clay is the best (Nayak and Singh 2007). However due to its hydrophilic character of the surface, its adsorption capacity for apolar non-ionic organic compounds is low. Exchange reactions with large organic cations render the surface hydrophobic so that adsorption of apolar non-ionic organic compounds is considerably increased (Churchman etal., 2006). The characteristics of these so-called organoclays can be altered by variation of surfactant properties (Pernyeszi *et al.,* 2006) such as alkyl chain length, number and branches (Klumpp *et al.,* 2003; Bonczek *et al.,* 2002). Previous studies using batch systems have shown the role of the type and

amount of cationic surfactant in the adsorption behaviour of partially modified clays and in their applicability for bioremediation (Witthuhn *et al.,* 2005). The low amount of exchanged surfactant of organoclays has several advantages: higher compatibility with soils and bacteria as well as lower costs. Organo-smectites, such as hexadecyl trimethylammonium- smectite, behave as a dual sorbent for organic compounds, in which the mineral fraction functions as a solid adsorbent and the organic (HDTMA) phase as a partition medium (Marsal etal., 2009).

In the present study, an attempt has been made to evaluate the tannin removal potentials of hexadecyltrimethylammonium bromide (HDTMAB) modified Tunisian smectite-illite clay. This paper contains the adsorbent characteristics and the effects of the operating variables (pH of the solution, initial concentration of solute and contact time) on the performance of organo-modified smectite-illite clay in adsorbing tannin.

MATERIALS & METHOD

The clay sample (H) used in this study was provided from Gabes (south east of Tunisia). The main fractions are smectite-illite and kaolinite associated to quartz and calcite. In order to illuminate these impurities from clay fraction, the raw powder sample were saturated with Na^+ by 5 washing cycles (successive centrifugal treatments) with 1 mol/L NaCl solution. After each centrifugation of the suspension, the supernatant was discarded and replaced with a fresh solution of NaCl.

After that, the recuperated samples were dialysed through a specific membrane until free from Cl^- and dried at 80°C. Fig. 1 shows the diffractogram of Na-clay (normal untreated, heated at 550°C and glycolated), after treatment by ethylene glycol the *d* 002 of smectite appeared at 8.8 Å, is attributable to an interstratified smectite-illite (Reynolds 1985). In addition, basing on the chemical analysis the average structural formula of the Na exchanged purified clay is: $Na_{0.62} K_{0.39} [Si_{7.49} Al_{0.51}]^{IV} [Al_{2.85} Fe_{0.71} Mg_{0.42} Ti_{0.02}]^{IV} O_{20} (OH)_4$

This one shows that the two types of substitutions exist (octahedral and tetrahedral substitutions) and which give a character beidellitic-montmorillonitic to this smectite.

Na-clay powder with particle size below 100μm was used. The surfactant is Hexadecyltrimethylammonium (HDTMA) bromide was supplied by Sigma-Aldrich (St. Louis, MO). It is a cationic surfactant $(C_{19}H_{42}NBr)$ with a critical micelle concentration (CMC) of 0.9 mM and it has an average molecular weight of 364.45 g.mol^{-1}. The organoclay was prepared by adding a quantity of the HDTMA$^+$ cations equal to 0.5, 1 and twice the CEC of the Na-clay. This quantity was used in order to show the evolution of the structure of clay until to fully saturate the exchange sites.

Three organoclays were prepared, for each case ten grams of Na-clay was added to 0.5 L of HDTMA solution with concentration respectively (113.25, 226.5 and 453 mg/L). These solutions were stirred for 6 h at room temperature and were centrifuged in order to
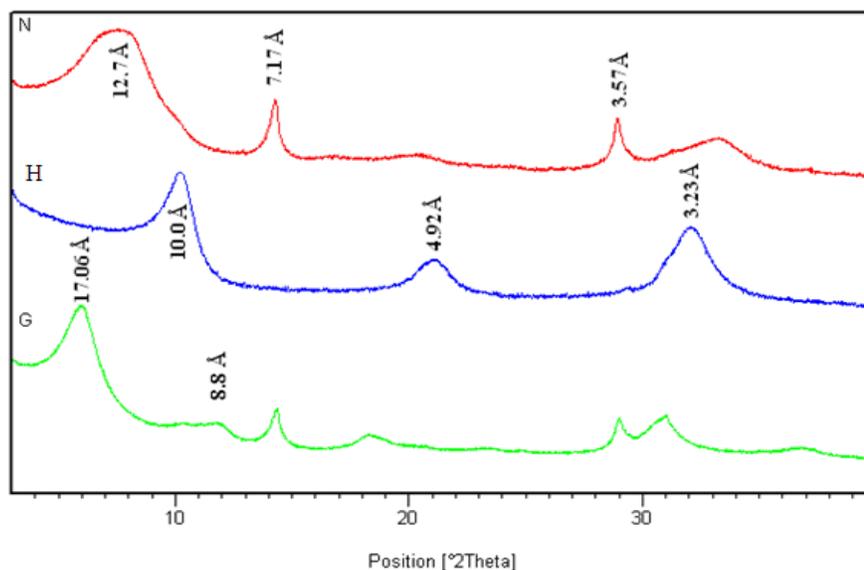
Fig. 1. X-Ray Diffraction patterns of the oriented Na-clay (fraction <2ìm)
(N: normal untreated, H: heated and G: glycolated)

separate the solid from liquid phase. The separated organoclay was washed repeatedly to remove the water-soluble particles and was filtered. The product was dried at 70 °C for 24 h and was sieved lower than 100μm. The prepared samples were noted $H_{0.5}$, H_1, H_2 for respectively to 0.5, 1 and 2CEC.

The batch experiments were carried out in polyethylene bottles containing 30mL varying initial concentration of tannin solutions and 0.2 g of adsorbent (Na-clay or organoclays). The pH of the solution was carefully adjusted by adding NaOH (0.1 or 0.01 mol/L) or HCl (0.1 or 0.01 mol/L) solution. Then the samples were agitated in a thermostatic orbital shaker with a shaking of 200 r/min at ambient temperature. On reaching equilibrium the adsorbent was eliminated by centrifugation at 3000 r/min. The amount of tannin adsorbed at equilibrium (Q_{ad}, mg/g) was calculated by using the following (Eq.1):

$$Q_{ad} = \frac{(C_i - C_{eq}) \times V_s}{m} \tag{1}$$

Where, C_i (mg/L) and C_{eq} (mg/L) are the initial and equilibrium concentrations of tannin solution, respectively; V_s (L) is the volume of tannin solution and m (g) is the weight of sorbents (Na-clay or organoclay).

It has been found that adsorbent behaviour and ability are dependent on the physicochemical properties of the adsorbent such as the structure, surface area and pore volume. Smaller pore may be blocked by the transport of adsorbate in the pore structure, thus can be influenced the adsorption. The following methods were used to characterize the aforementioned physicochemical properties. BET surface area and pore volumes of adsorbent were measured using the physical adsorption of nitrogen by Quantachrome Autosorb-1 instrument. X-Ray diffraction (XRD) was also used to determine the interlayer d_{001}-spacing, of the surfactant-treated clay and, for comparison, the starting smectite-illite clay. XRD analysis was carried out using a PANalytical X'Pert HighScore Plus diffractometer, CuKa radiation. The cationic exchange capacity (CEC) of sample was determined using ammonium acetate method (Reeuwijk 1992). The FTIR spectrum of the clay was recorded on a KBr disk, which contains 1% sample by weight, using a Perkin-Elmer (model 783) spectrophotometer. To determine the point of zero charge (pHpzc), the potentiometric method was used (Kriaa etal., 2008). The tannin concentrations in aqueous solutions were determined using a UV–visible spectrophotometer (Hach DR/4000) at a wavelength of 270 nm.

RESULTS & DISCUSSION

The XRD patterns of the Na-smectite clay and organoclay are shown in Fig. 2. The X-ray diffraction analysis of pure clay Hp (Fig. 2) indicates the presence of smectite at 12.69 Å, after treatment by surfactant ($H_{0.5}$, H_1, H_2) this peak moved to 17.59, 19.25 and 21.62 Å respectively. Also the characteristic d spacing of 7.17 Å confirms that the sample contain a small amount of the kaolinite. The increase in the basal spacing of Na-clay with HDTMA$^+$ cations can be attributed to replacement of the inorganic interlayer cations and their hydration water with HDTMA$^+$ cations. On the basis of information given by earlier workers (Bergaya etal., 2006) regarding the orientation and the number of molecular layers in the interlamellar spacing of clay minerals, and considering the molecular size of HDTMA, the increases in the basal spacing point to a bi-layer and tri-layer arrangement for HDTMA.

The FTIR spectra of Na-clay and organoclay are shown in Fig. 3. The broad bands at around 3423 cm^{-1} (H–O–H stretching) and 1640 cm^{-1} (H–O–H bending) for Na-smectite and for organoclay indicate the presence of adsorbed water. The presence of an asymmetric stretching mode of Si–O–Si in Na-clay and organoclay was suggested by the absorption band at 1026 cm^{-1}. The asymmetric and symmetric bending modes of O–Si–O are observed at 523 and 465 cm^{-1} for both Na-clay and organoclay, as in other silica and silicate systems. The additional peaks at 1425 and 1467 cm^{-1} in organoclay, which are absent in Na-clay, indicate the presence of C–N vibrations in tertiary amines. This observation clearly indicates that the surface modification of Na-clay is achieved by surfactant.

The examination of the HTDMA-modified smectite comparing to the HTDMA spectra (Fig. 3a) shows the presence of C-H stretching bands of CH$_2$ and aliphatic C-H stretching bands at 2918 and 2848 cm^{-1} respectively, which are absent in Na-clay.

For all organoclays, it was noted that the frequency and the intensity of asymmetric and symmetric stretching bands of CH$_2$ changed with the amount of intercalated surfactant. These frequencies are extremely sensitive to the conformational ordering of the chain of cationic surfactant into clay (Li and Gallus 2005).

Fig. 4 shows the adsorption-desorption isotherms of nitrogen at 77 K of Na-clay and organoclay. These isotherms correspond to type II in the IUPAC classification (Sing etal., 1985), typical of macroporous or nanoporous materials. The hysterisis was of H3 type, characteristic of layered materials with slit-shaped pores (Sing *et al.,* 1985). The decrease in adsorbed
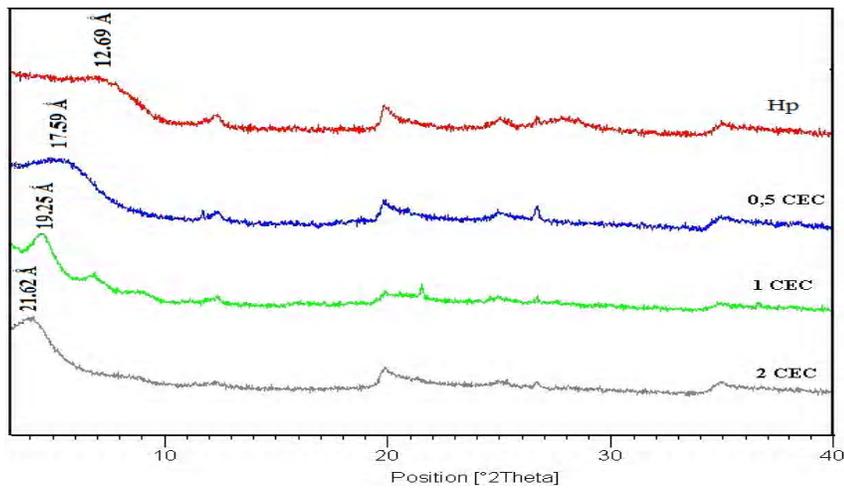
Fig. 2. XRD patterns of Na-clay and organoclays
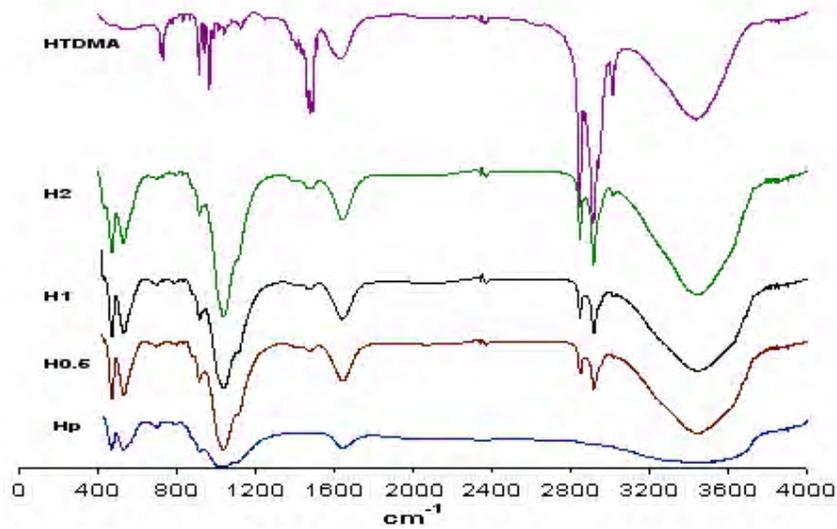
Fig. 3. FTIR spectra of Na-clay and organoclays
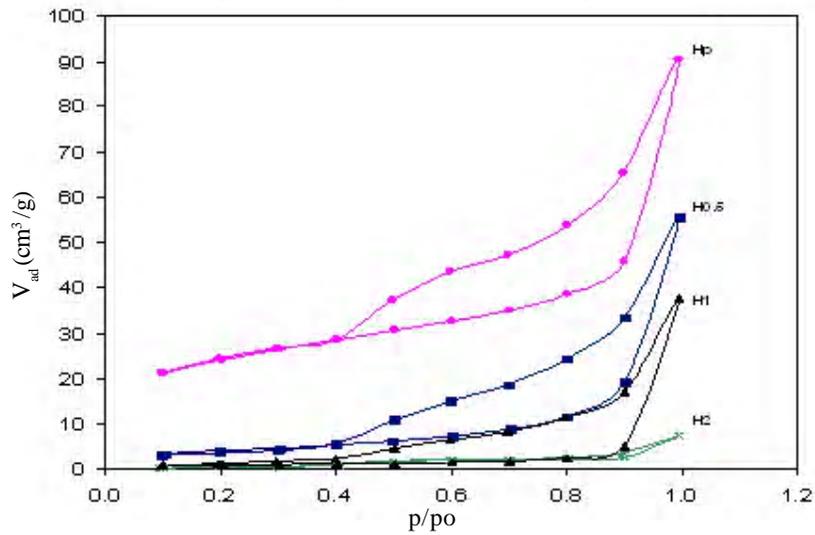
Fig. 4. Nitrogen adsorption isotherms of Na-clay and organoclays

volumes of the organoclay samples can be explained in terms of decreasing numbers of pores. This is due to the retention of HTDMA in the interlayer and at the surface of clay mineral. In addition, the hysterisis were closed after intercalation of surfactant showing the filling of the mesopores by the HTDMA.

The specific surface area, pore volume, and CEC of the Na-clay and organoclay samples are presented in Table 1. The specific surface area decreases significantly as a function of the increase of exchanged HTDMA in the specimen, from 106 m2/g (Na-clay) to 1.9 m^2/g for H2 sample. This is due to the exchange of HTDMA in the interlayer space and to adsorption on the surface of clay. The same results were obtained for the CEC, where the minimum (28 meq/100 g) was observed in sample H2. The pore volume (Vp), however, decreased considerably from 0.171 (Hp) to 0.0006 cm^3/g (H2). Table 2 show, that the surface area of micropores (Sµp) was annuled after the retension of the HTDMA surfactant.

The PZC of the organoclay was basic (Table 1) because the adsorption of the surfactant modified the surface character. The increase in pHpzc after surfactant treatment indicates that the organoclay becomes more positive and organophilic.

Fig. 5 presents the removal of tannin as a function of pH over the range 3.0–9.0 for Na-clay and organoclays. The pH of the aqueous solution is an important variable which controls the adsorption phenomena. It can be observe that the maximum removed quantity of the tannin from aqueous solution taking place at the pH range 4.0–6.0. Above and below this pH range, the extent of uptake was found to be considerably lower. The maximum adsorption at the pH range 4.5–6.0 is due to the external hydrogen bonds formed between phenolic–OH groups of tannin and the hydrogen-bonding sites on the clay (Boyd 1982). At this range of pH the undissociated tannin molecules are dominated and have the hydrophobic character more adsorbable than the ionized forms at basic pH because the hydrophobic bonding is the driving force for adsorption. The increase in pH improves the solubility of tannin; this means decreased uptake, as there is a nearly inverse relationship between sorbate solubility and adsorption potential. However, in this range of pH the organoclay samples show the higher uptake ability of tannin comparing to Na-clay, which may be due to its hydrophobic surface.

The results of tannin sorption kinetic experiments at room temperature, pH=5.5 and for a concentration of 30 µmol/L are shown in Fig. 6. The quantity removal of tannin increases with time for all samples. The initial rate was rapid and thereafter adsorption was gradual and equilibrium was reached after 6 h. The tannin removal versus time curves is single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of tannin on the surface of the adsorbent.

Table 1.Characterization results of the Na-clay and organoclays

Samples	S_{BET} (m^2/g)	Sµp(m^2/g)	Vp(cm^3/g)	CEC (méq\100g)	pH$_{PZC}$
Hp	106	8.310	0.171	83	6.2
H0.5	14.830	0.00	0.0861	56	7
H1	3.423	0.00	0.0157	33	7.9
H2	1.964	0.00	0.0006	28	8.4

Table 2. Comparison of the pseudo first and second-order adsorption rate constants, at constant concentration of tannin (30 µmg/L)

Samples	Pseudo-second-order model			Pseudo-second-order model		
	k_1 (h^{-1})	Q_e (mg/g)	R^2	k_2 (g.mg^{-1}.h^{-1})	Q_e (mg/g)	R^2
Hp	0.185	2.830	0.836	0.252	5.552	0.998
H0.5	0.236	4.820	0.845	0.126	10.893	0.998
H1	0.375	3.995	0.841	0.399	13.927	0.999
H2	0.375	3.995	0.841	0.322	14.430	0.999
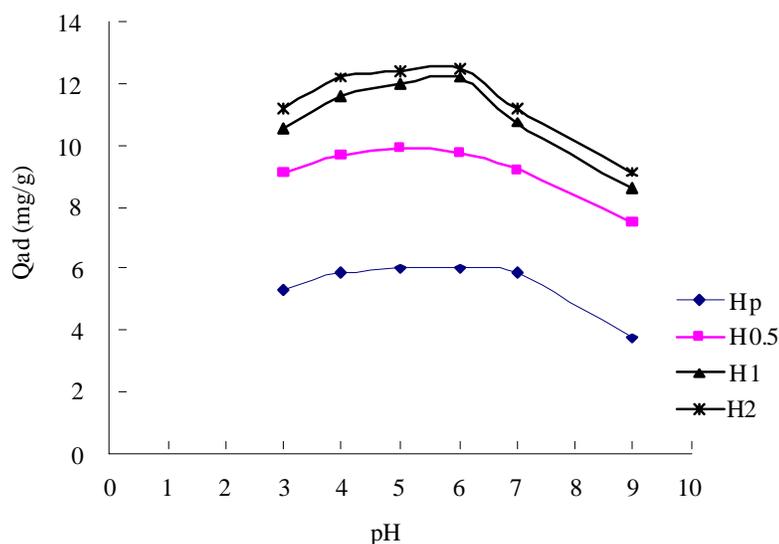
Fig. 5. Effect of pH on the adsorption of tannin (25 µmol/L) onto Na-clay and organoclays
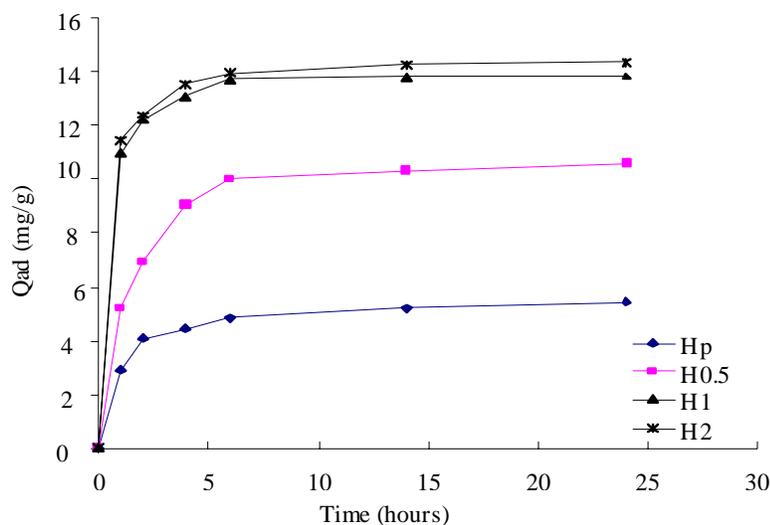
Fig. 6. Effect of contact time on the adsorption of tannin (30 µmol/L) onto Na-clay and organoclays

Various models such as pseudo-first-order and pseudo-second-order have been used to describe the kinetics of adsorption. The pseudo-second-order rate equation is the one most widely used for the adsorption of a solute from a liquid solution. The rate constants of tannin adsorption on Na-clay and organoclays were determined using the both models expression shown below,

The linear form of the pseudo first-order equation is given by Eq. (2):

$$Log\,(Q_e - Q_t) = Log\,Q_e - k_1 t \qquad (2)$$

The linear form of the pseudo second-order model (Ngah and Fatinathan 2010) is given by Eq. (3):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^{\,2}} + \frac{1}{Q_e} t \qquad (3)$$

where, Q_e (mg/g) and Q_t (mg/g) refer to the amount of tannin ions adsorbed at equilibrium and at any time, t (h), respectively, and k_1 (hr⁻¹) is the equilibrium rate constant of pseudo first-order kinetics and k_2 (g/(mg·hr)) is the equilibrium rate constant of pseudo second-order kinetics. Among the above kinetic models tested, tannin sorption kinetics could be well described using the pseudo-second-order (Eq. (3)) model with the correlation coefficients, R^2, above 0.99, the
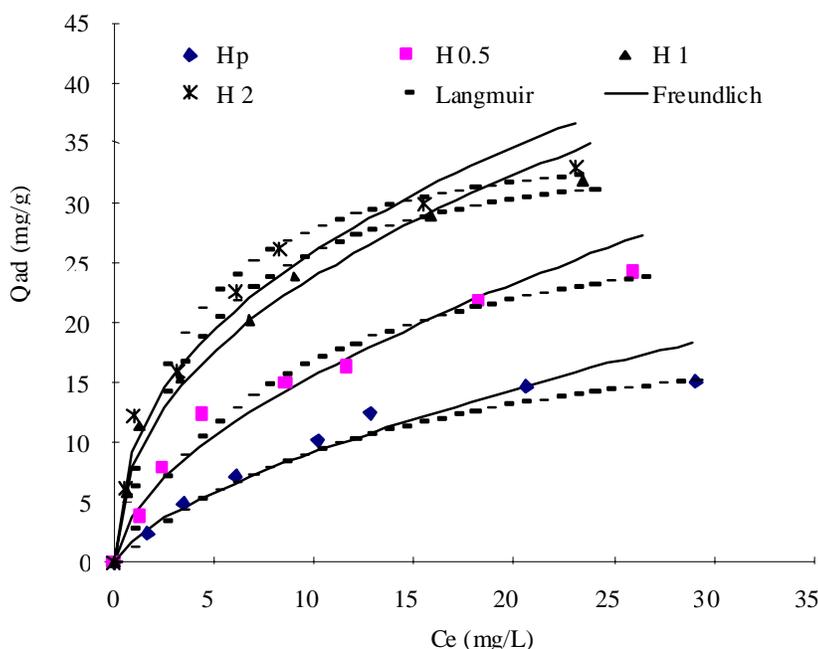
Fig. 7. Comparison of the experimental and model fits of the Langmuir and Freundlich isotherms for the adsorption of tannin onto Na-clay and organoclay

Table 3. Langmuir and Freundlich isotherm parameters for tannin sorption on Na-clay and organoclays

		Hp	H0.5	H1	H2
	Q_m (mg/g)	22.67	31.645	36.36	36.63
Langmuir model	b	0.007	0.011	0.025	0.032
	R^2	0.977	0.974	0.987	0.992
	K_F	0.446	1.109	3.133	3.768
Freundlich model	1/n	0.656	0.574	0.440	0.418
	R^2	0.961	0.940	0.974	0.944

calculated kinetic parameters are given in Table 2. While the calculated equilibrium sorption capacity for the first order model for the initial concentration, $Q_{e,calc}$, values are not close to the experimental values ($Q_{e,exp}$), for the second- order model, $Q_{e,calc}$, values are close to $Q_{e,exp}$ for the initial concentration.

To further study the adsorption, an equilibrium studies were carried out to determine the optimum conditions for maximum tannin removal by Na-clay and organoclays (H0.5, H1 and H2). The experimental sorption isotherm is used to plot the amount of tannin sorbed, expressed in mg/g of sample against the equilibrium tannin concentration (mg/L). Sorption isotherms are regular positive and concave to the concentration axis (Fig. 7). These isotherms were classified as L-type of Giles etal.,'s classification (Giles 1960). This indicates that tannin is strongly adsorbed

on the substrate particles and there is no competition from the solvent for sorption sites. The data obtained from tannin adsorption were fitted to the Langmuir isotherm and Freundlich isotherms (Deng etal., 2013) given respectively by (Eq. (4)) and (Eq. (5)).

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \tag{4}$$

$$Q_e = K_F C_e^{1/n} \tag{5}$$

where, Q_e (mg/g) is the amount of ions adsorbed per unit weight of adsorbents, C_e (mg/L) is the equilibrium concentration, Q_m and *b* are the Langmuir constants related to capacity and energy of adsorption, respectively. K_F and 1/*n* are the Freundlich constants.
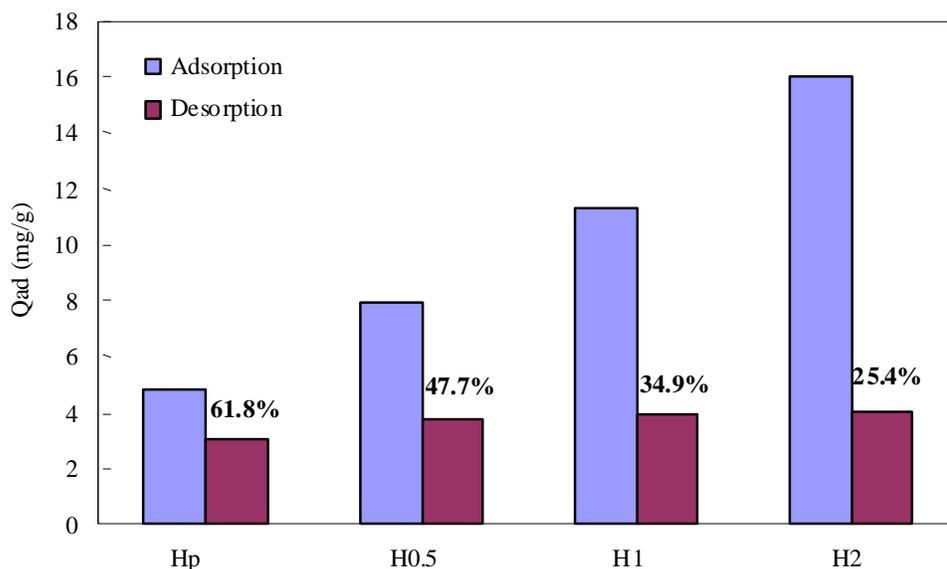
Fig. 8. Percentage of desorption of tannin for Na-clay and organoclays

The isotherm data for tannin sorption on the Na-clay and organoclays were fitted to the Langmuir and Freundlich equations (Fig. 7), and the calculated parameters are given in Table 3. As evidenced by the correction coefficient R^2, tannin equilibrium sorption on all samples could be much better described using the Langmuir model than using the Freundlich one. Based on the values of Qm and b (Table 3), the order of maximum sorption capacities and affinities of these samples for tannin is: Hp < H0.5 < H1< H2.
The increase in Q_m and b values with increasing HTDMA contents in the clay further confirmed the important role of surfactant played in the enhancement of tannin sorption.

The validity of Langmuir model suggested that the adsorption process was monolayer, and adsorption of each molecule has equal activation energy. b value was further used to calculate the dimensionless separation factor (R_L) as follows (Theivarasu and Mylsamy 2010):

$$R_L = \frac{1}{(1+bC_0)} \qquad (6)$$

$R_L = 0$: irreversible; $0 < R_L < 1$: favorable; $R_L > 1$: not favorable; $R_L = 1$: linear

Where, C_0 is the highest initial tannin concentration (mol/L). The dimensionless separation factor, R_L, is used to test whether the adsorption is favorable or not. For all sample the R_L value is between 0 and 1 indicates the spontaneous adsorption of tannin from aqueous solution by Na-clay and organoclays (H0.5, H1 and H2).

Samples prepared for the adsorption experiments were used in the desorption studies. Desorption experiments were conducted at same pH of adsorption study using the batch method. The results of desorption are presented in the fig. 8 after five successive solvent cycles. Irreversible sorbed amounts expressed as percentage of initially adsorbed tannin (figure) were determined in order to evaluate the reversibility of adsorption. All four materials (Na-clay, H0.5, H1 and H2) exhibited different desorption potential. Comparing to the Na-clay the desorption of tannin become very lower with the sample which contained the high proportion of HTDMA. It can be seen that the desorption of tannin in the case of H2 is about 25% of sorbed fraction. However, in order to desored the tannin from organoclay samples the NaOH solution has been tested. The result shows that 0.1 M NaOH can effectively regenerate the organoclay. The percentage of desorption reached the 95% and the organoclay can be reused for several adsorption-desorption cycles.

CONCLUSIONS

Organoclay developed from Tunisian smectite-illte clay has been demonstrated to be able to sorb tannin from aqueous solutions. Three organoclay have been prepared (H0.5, H1 and H2) using the surfactant HTDMA according to three levels of CEC (0.5, 1 and 2) respectively. The characterization of the prepared organoclays gives that the d-spacing increase with levels of HTDMA in the Na-clay. Besides, the surface area, the porosity and the CEC of H0.5, H1 and H2 were

decreased respectively. The PZC of the organoclays were displaced into the basic pH. The adsorbed amounts of tannin on the organoclays are considerably higher than that on the original Na-clay, and the adsorption on H2 is the highest. Maximum adsorption capacity of the tannin is occurred in the pH range 4.5–6.0. The kinetics of tannin adsorption show that an agitation time of 6 h is needed to reach equilibrium values within the experimental system used. The adsorption follows pseudo-second-order kinetics. The data obtained from adsorption isotherms for all samples were fitted to Langmuir model.

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