



HAL
open science

Adsorption of Bisphenol A from Aqueous Solution by HDTMA-Tunisian Clay Synthesized Under Microwave Irradiation: A Parametric and Thermodynamic Study

Oumaya Issaoui, Hedi Ben Amor, Mohamed Ismail, Laurence Pirault-Roy,
Mohamed Razak Jeday

► To cite this version:

Oumaya Issaoui, Hedi Ben Amor, Mohamed Ismail, Laurence Pirault-Roy, Mohamed Razak Jeday. Adsorption of Bisphenol A from Aqueous Solution by HDTMA-Tunisian Clay Synthesized Under Microwave Irradiation: A Parametric and Thermodynamic Study. *Clays and Clay Minerals*, 2020, 68 (4), pp.361-372. <10.1007/s42860-020-00079-5>. <hal-03533605>

HAL Id: hal-03533605

<https://hal.science/hal-03533605v1>

Submitted on 20 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

This paper was published the 08 September 2020 in **Clays and Clay Minerals**

Cite this article as

Issaoui, O., Amor, H.B., Ismail, M. *et al.* Adsorption of Bisphenol A from Aqueous Solution by HDTMA-Tunisian Clay Synthesized Under Microwave Irradiation: A Parametric and Thermodynamic Study. *Clays Clay Miner.* **68**, 361–372 (2020).

<https://doi-org.ressources.univ-poitiers.fr/10.1007/s42860-020-00079-5>

Adsorption of Bisphenol A from Aqueous Solution by HDTMA-Tunisian Clay Synthesized Under Microwave Irradiation: A Parametric and Thermodynamic Study

Oumaya Issaoui^{1,2}, Hedi Ben Amor², Mohamed Ismail², Laurence Pirault-Roy³ and Mohamed Razak Jeday²

1. University of Gabes, Faculty of Sciences of Gabes, 6072, Gabes, Tunisia
2. University of Gabes, Engineering School (ENIG), RL Processes, Energetic, Environment, and Electric Systems, 6072, Gabes, Tunisia
3. Université de Poitiers, CNRS UMR 7285, Institut de Chimie des Milieux et des Matériaux de Poitiers (IC2MP), B27, 4 rue Michel Brunet, 86073, Poitiers, Cedex 9, France

Corresponding author Oumaya Issaoui. oumayaisaoui@gmail.com

Keywords

- Adsorption
- Bisphenol A
- Clay
- Hexadecyltrimethylammonium bromide
- Microwave

Abstract

Bisphenol A (BPA), an endocrine disrupting compound, is of concern because of its wide presence throughout the environment and its harmful effects. The present study aimed to prepare an eco-friendly, low-cost, and efficient adsorbent for removal of BPA from wastewater. A natural Tunisian clay was used as a raw material. First, the clay was purified and then modified with hexadecyltrimethylammonium bromide (HDTMA) using microwave heating. The optimal conditions for clay modification were as follows: activation ratio = 0.3:(g/g), solid/liquid ratio = 5%, and microwave heating condition (2:min, 100:W). The purified and modified clays, abbreviated as HP and HMH, respectively, were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and nitrogen adsorption/desorption analysis (BET). Adsorption tests were conducted in a batch reactor process under various conditions. The tests

showed that the BET specific surface area of HMH is considerably smaller than that of HP, whereas the basal spacing increased from 14.99 to 22.07 Å after modification, indicating the success of HP organophilization. The adsorption of BPA onto HMH was not affected by the pH of solution between 2 and 10 and only slightly by temperature variation from 23 to 50°C, but was affected significantly by the initial concentration of BPA, contact time, and organo-clay dose. At equilibrium, the data obtained were fitted to Langmuir and Freundlich models. The best fit was obtained by the Langmuir model with a maximum monolayer adsorption capacity of 217.39 mg/g at 23°C. The thermodynamic study suggested that the removal of BPA by HMH was spontaneous ($\Delta G < 0$), exothermic ($\Delta H < 0$), and favorable. The present study demonstrated that HMH synthesized from an abundant and cheap natural clay could be used successfully as a low-cost adsorbent for the removal of BPA from wastewater.

Introduction

Bisphenol A (BPA) is used widely, mainly as a monomer in the industrial production of polycarbonate plastics, epoxy resins, and as a non-polymer additive to other plastics (Bing-zhi et al. 2010). The annual production of BPA is ~6.8 million tonnes (Jandegian et al. 2015) and release into the environment has exceeded 450 tonnes per year (USEPA 2010). Concentrations of BPA were reported to be between 0.001 and 20 mg/m³ in groundwater, between <0.001 and 92 mg/m³ in surface water, and between <0.24 and 492 µg/kg on a dry-weight basis in sediments (Careghini et al. 2015). A maximum concentration of 17.2 mg/L was detected in waste landfill leachates (Laatikainen et al. 2014). Many studies reported that even at very low concentrations, BPA can provoke endocrine disruption and affect health, therefore, especially reproduction (Okugbe and Songhe 2019). In accordance with standardized toxicological testing procedures, government agencies in the United States (US Environmental Protection Agency, USEPA), Canada (Health Canada), and Europe (European Food Safety Authority, EFSA) have established tolerable daily intake levels, ranging from 25 to 50 µg of BPA/kg of body weight/day (Kinch et al. 2015). Among the various methods developed to remove BPA from wastewaters (Liang et al. 2015), adsorption has significant advantages such as its efficiency, low operating cost, high selectivity, easy handling, etc. (Crini 2006). In recent years, the application of clay materials as adsorbents has attracted much attention due to their natural abundance, large specific surface area, layered structure, and large ion exchange capacity (Bergaya et al. 2013). The adsorption efficiency of clays can be enhanced by intercalation with cationic surfactants, which increases the interlayer space and modifies the surface charge, thus making the clay an organophilic adsorbent for some hydrophobic compounds (Bergaya and Lagaly 2011). HDTMA is preferred to other surfactants (Neel and Bowman 1992) because of its low cost and efficiency as a modifying agent for commercial clays used in the adsorption of pollutants, especially BPA (Zhu et al. 2009; Liu et al. 2016).

The purpose of the current study was, therefore, to synthesize an organo-clay from a natural Tunisian clay under microwave irradiation and without sodium pre-exchange, then to test the potential

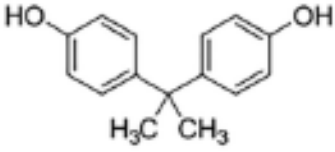
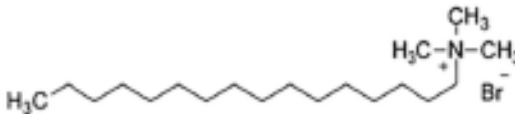
performance of the prepared organo-clay for the removal of harmful pollutants, such as BPA, from aqueous solutions. The hypothesis was that synthesized organo-clay will adsorb a significant amount of BPA at ambient temperature.

Experimental

Materials

The crude clay used in this study was from the El Hicha-Gabes region of Tunisia. The purified clay (HP) has been the subject of previous studies and it is known to be a smectite with a chemical composition of 52.61% SiO₂, 14.28% Al₂O₃, 11.70% CaO, 8.50% Fe₂O₃, 0.81% K₂O, 0.37% SO₃, and loss on ignition of 11.81%. The cation exchange capacity (CEC) of HP is 86.5 meq/100 g (Sassi et al. 2018). Hexadecyltrimethylammonium bromide (HDTMA) was purchased from Alfa Aesar (Karlsruhe, Germany). BPA was purchased from Sigma-Aldrich (St. Louis, Missouri, USA) and both were used without further purification; their principal relevant physicochemical properties are listed in Table 1. All other reagents used were of analytical grade. A domestic microwave oven (model ME711K, Samsung, Shenzhen, Guangdong, China) with continuous power and a frequency of 2.45 GHz was used to prepare the modified clay.

Table 1. Physicochemical characteristics of BPA and HDTMA

	Pollutant	Organic modifier
Name	2,2-bis(4-hydroxyphenyl) propane	Hexadecyltrimethylammonium bromide
Abbreviation	BPA	HDTMA
Molecular formula	C ₁₅ H ₁₆ O ₂	C ₁₉ H ₄₂ NBr
Molecular structure		
Molecular weight (g.mol ⁻¹)	228.29	364.45
Water solubility	120-300 mg/L (21.5°C)	13 g/L (20°C)

Preparation of Organo-Clay Samples

For the preparation of organo-clay, a given mass (g) of HP was added to the HDTMA solution. After magnetic stirring for 30 min, the suspension was irradiated in the microwave to induce the organophilization of the clay. After that, the organo-clay was separated by centrifugation and washed with distilled water repeatedly until a negative AgNO₃ test for bromide was attained. Finally, the solid was dried at 65°C for 10 h, ground manually into powder, and stored in tightly closed bottles.

Determination of the Optimal Conditions for the Organophilization Process by Microwave Irradiation

In order to optimize the conditions for the synthesis by microwave, various parameters were considered such as irradiation conditions (Power (P), time (t_i)), activation ratio (AR = HDTMA/clay (g/g)), and solid/liquid ratio (S/L = clay mass/volume of HDTMA solution (g/100 mL)). The influence of each parameter was studied by varying one parameter while keeping the others constant. To target the optimal preparation parameters, all samples of HMH were evaluated by a BPA adsorption test using the following conditions: 0.05 g of organo-clay into 100 mL of BPA at 100 mg/L and contact time for 2 h at ambient temperature under magnetic stirring.

Adsorption Experiments

The BPA adsorption experiments were performed in batch reactors by adding known amounts of HMH to 100 mL samples of BPA solution at the given initial concentration without pH adjustment (~6.5 except when the effect of pH was studied). The mixtures were agitated continuously by a magnetic stirrer. After various times and at equilibrium, the samples were filtered through 0.45 μ m PES membranes and then the filtrates were analyzed using a UV-visible spectrophotometer (T60 UV VIS Spectrophotometer, PG instruments Ltd, Alma Park, Wibtoft, Lutterworth, UK)) at $\lambda_{\max} = 276$ nm. The amount of BPA adsorbed onto HMH was determined using the following equation:

$$q_t = \frac{(C_0 - C_t) V}{W} \quad (1)$$

where q_t (or q_e) is the amount of BPA (mg/g) at adsorption time t (or at equilibrium); C_0 and C_t (mg/L) are the concentrations of BPA at the start and after a known time t , respectively; V (L) is the volume of BPA solution; and W (g) is the HMH dosage.

The sorption efficiency (%) of BPA (R) was calculated by applying the following equation:

$$R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

Clay saturated by adsorbed BPA was labelled as HMS.

Characterization of Clays

To assess the effect of HDTMA on the purified clay properties, HP, HMH, and HMS were characterized by SEM, FTIR, XRD, and surface area analysis (BET method). The SEM analyses were conducted using a TEM/STEM JEOL 2100 UHR 200kV JEOL (Lab₆) instrument (JEOL Ltd, Akishima, Tokyo, Japan) at a resolution of 0.14 nm, to examine the surface texture and morphology. The FTIR spectra in the mid-infrared region (MIR) were examined to identify the surface functional groups. The spectra were collected using a Magna-IR 760 Nicolet 760 spectrometer (Woodland, Texas, USA) equipped with a KBr beam splitter and a DTGS-KBr detector, with wavenumbers ranging from 400 to 4000 cm^{-1} , resolution of 4 cm^{-1} , and a co-addition of 100 scans. KBr pellets were prepared by mixing (sample (mg)/KBr (mg)) powder at a ratio of 1/150, pressing, and then heating in an oven overnight at 110°C before analysis. In order to determine the basal spacing (d_{001}) values, XRD was applied. The XRD patterns of HP and HMH were recorded using a PANalytical “Empyrean” diffractometer (Lelyweg, Almelo, Netherlands) equipped with a fast Xcelerator detector with $\text{CuK}\alpha$ radiation at 45 kV and 40 mA, over a 2θ range of 3–30° 2θ . The BET specific surface area and pore structure parameters were measured by N_2 adsorption using a Micromeritics Tristar 3000 instrument (Norcross, Georgia, USA) at 77 K. The pore sizes were determined using the BJH method. Before analysis, the clay samples were out-gassed overnight under N_2 at 90°C using a Micromeritics (Norcross, Georgia, USA) Asap 2010 degasser.

Results and Discussions

Optimization of the Clay Organophilization Process by Microwave Irradiation

A preliminary study showed that the HP did not take up a realistic amount of BPA (~2 mg/g after 24 h of contact time). To improve its capacity to adsorb, HP was modified with HDTMA under microwave irradiation. To optimize the organophilization conditions, various samples were prepared by varying P from 100 to 300 W, t_i from 2 to 6 min, AR from 0.1 to 0.4, and S/L from 1 to 10%. Each prepared sample was tested as an adsorbent of BPA and the values of sorption efficiency obtained indicated that the increase of P from 100 to 300 W, while keeping t_i at 2 min (Fig. 1a) or varying t_i from 2 to 6 min at fixed P of 100 W (Fig. 1b), did not improve the BPA removal efficiency. To save time and energy, the lowest irradiation conditions (100 W, 2 min) were selected for the further work.

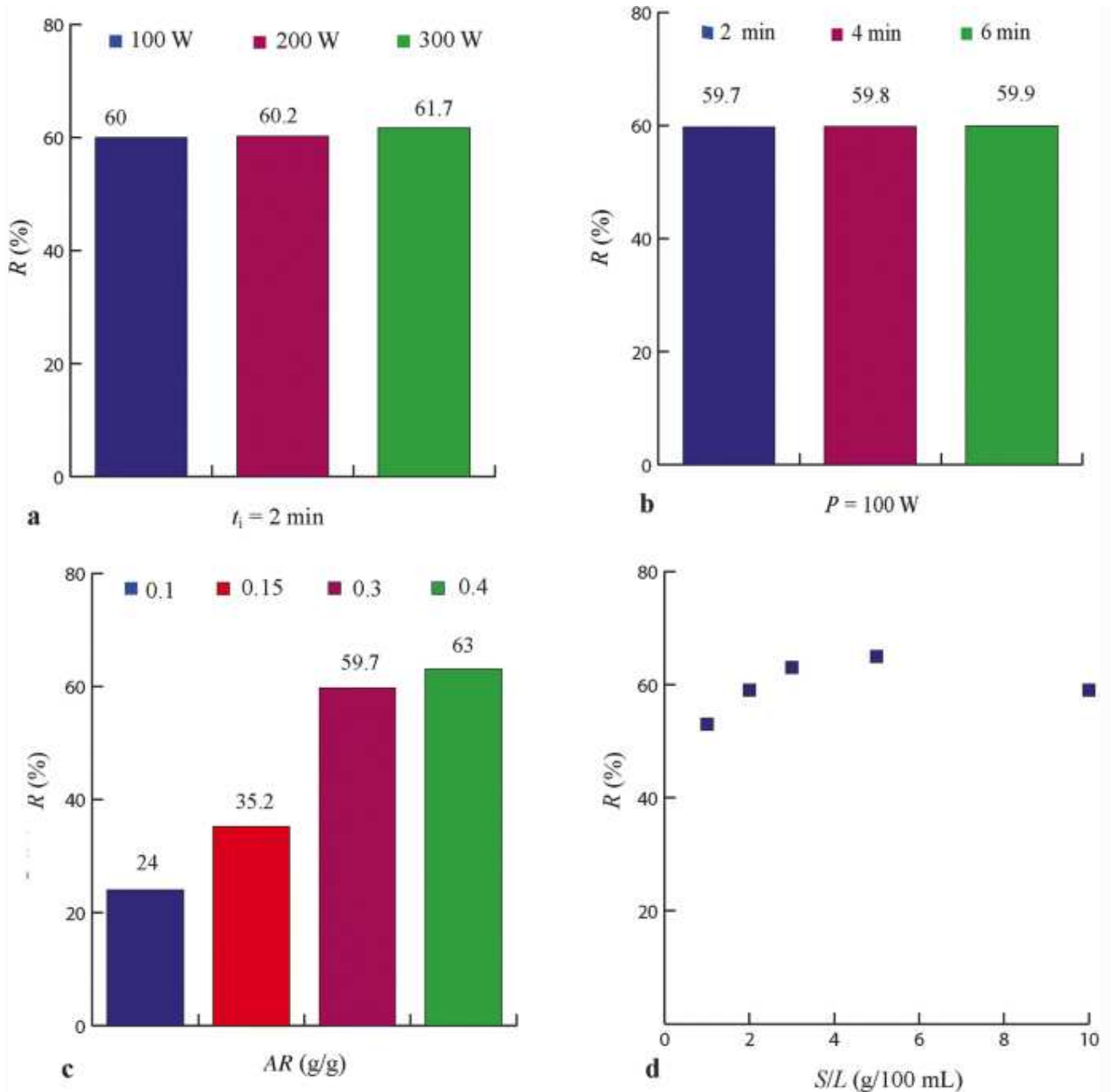


Fig. 1 : Effects of the synthesis parameters of organo-clay on the efficiency of removal of BPA (R): **a** power of irradiation, **b** duration of irradiation, **c** activation ratio (AR), and **d** solid/liquid ratio (S/L)

The BPA removal efficiency (Fig. 1c) increased sharply with increase in AR up to 0.3; above that, further increase was insignificant (59.7% for $AR = 0.3$ vs. 63% for $AR = 0.4$). The activation ratio of 0.3 (g/g) was taken as optimal. In addition, the results obtained (Fig. 1d) showed clearly that the adsorption efficiency increased by increasing the S/L ratio from 1 to 5% but decreased when the ratio was 10%; the latter may be due to the fact that there was insufficient heating (100 W, 2 min). The 5% ratio for S/L was selected, therefore, for further work. Note that this value is larger than that applied usually, 1–2%, in classic methods of clay modification, according to the literature; this finding was very significant because it allowed the use of less water. Finally, use of the microwave technique

enabled the modification of the clays with a surfactant under very mild conditions (Table 2), thus making this process very simple, effective, and economical.

Table 2. Optimal conditions for HMMH synthesis assisted by microwave heating

Conditions	Values
P (W)	100
t_i (min)	2
S/L (%)	5
AR (g/g)	0.3

Characterization of the Clays

SEM.

Scanning electron microscopy was used to examine the change in morphological features of modified compared with purified clay. The SEM image of HP (Fig. 2a) shows that the clay has a compact morphology with irregular flakes. After modification (Fig. 2b), the structure was transformed into small layered flakes with a soft appearance, suggesting the occupation of the intraparticle space by HDTMA molecules, as reported by Meera et al. (2012). After adsorption of BPA (Fig. 2c), the clay structure became agglomerated, indicating a high density of adsorbed BPA molecules on the surface of the modified clay as reported by Zhang et al. (2015).

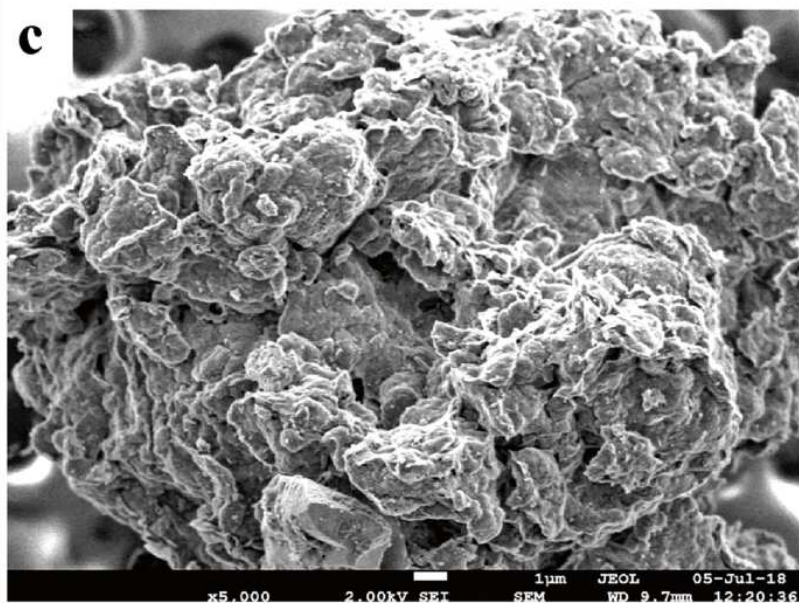
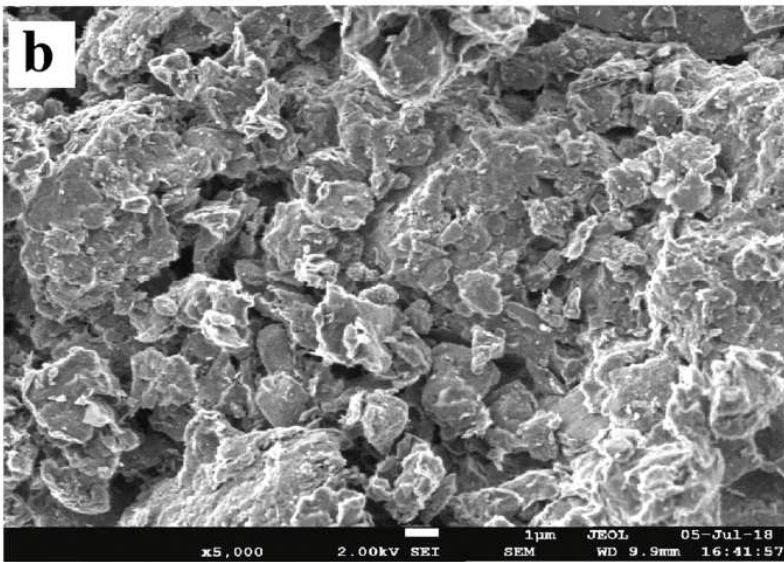
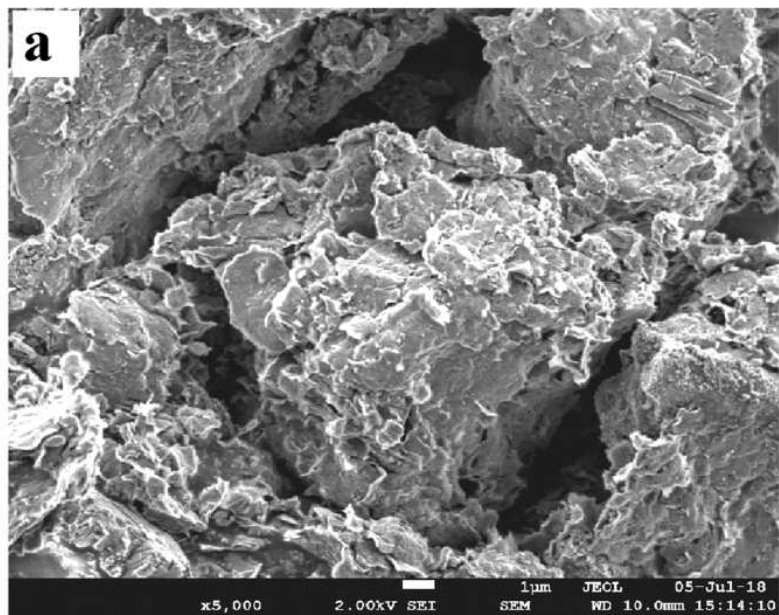


Fig. 2 : SEM images of: **a** HP, **b** HMH, and **c** HMS. Scale bars = 1 μm

FTIR Spectra and XRD Patterns.

Infrared spectroscopy was used to study changes in the clay structure after modification by HDTMA. The FTIR spectra of HP and HMH (Fig. 3a) showed peaks at 3621 and 3411 cm^{-1} which were assigned to the O–H stretching vibration of the silanol (Si–OH) groups and HO–H vibration of the water molecules fixed on the clay surface. For HMH, two new peaks appeared at 2924 and 2853 cm^{-1} , which were attributed to the asymmetric and symmetric stretching vibrations of $-\text{CH}_2$, also seen in the HDTMA spectrum, indicating that HDTMA molecules were introduced successfully into the clay network. The peak at 1621 cm^{-1} was attributed to the $-\text{OH}$ bending vibrations of adsorbed water present in the purified clay (Erdem et al. 2010). The intensity of this band for HMH was less than that for HP, suggesting that the surface property of purified clay had become more hydrophobic due to the presence of HDTMA. The peak at ~ 1431 cm^{-1} was associated with the $-\text{CH}_2$ deformation peak, whereas the absorption peaks at 1034, 520, and 469 cm^{-1} were assigned to the Si–O, Al–O–Si, and Si–O–Si stretching and bending vibrations of dioctahedral clay, respectively (Farmer and Russell 1964; Farmer 1974).

The results above were corroborated by comparing the XRD patterns of purified clay with those of the modified clay. The XRD patterns, restricted to the range 2 to $30^\circ 2\theta$ (Fig. 3b), revealed that HP has a basal spacing of 14.99 Å, which increased to 22.07 Å in HMH. This significant increase in the d_{001} value proved the successful intercalation of HDTMA between the clay layers. According to Zhang et al. (2015), a basal spacing of 22.07 Å indicates that the HDTMA molecules are deposited in lateral bilayers or pseudo-trimolecular layers between the clay layers. This arrangement of the surfactant molecules was key in terms of understanding the adsorption mechanism.

Textural Parameters.

The Brunauer-Emmett-Teller (BET) method was applied to HP and HMH clays to elucidate the effect of HDTMA on the textural parameters such as specific surface area (S_{BET}) and pore volume (V_{P}). The results of N_2 adsorption isotherms (Table 3) indicated clearly that the surface area, as well as the pore size of the HMH, had decreased significantly after modification. This decrease was due to the intercalation of HDTMA which led to increases in the average pore diameter of HMH and caused an interlayer expansion (as shown by XRD analysis), so that surfactant molecules inhibited the passage of N_2 molecules, causing a decrease in the S_{BET} to 5 m^2/g (He et al. 2006).

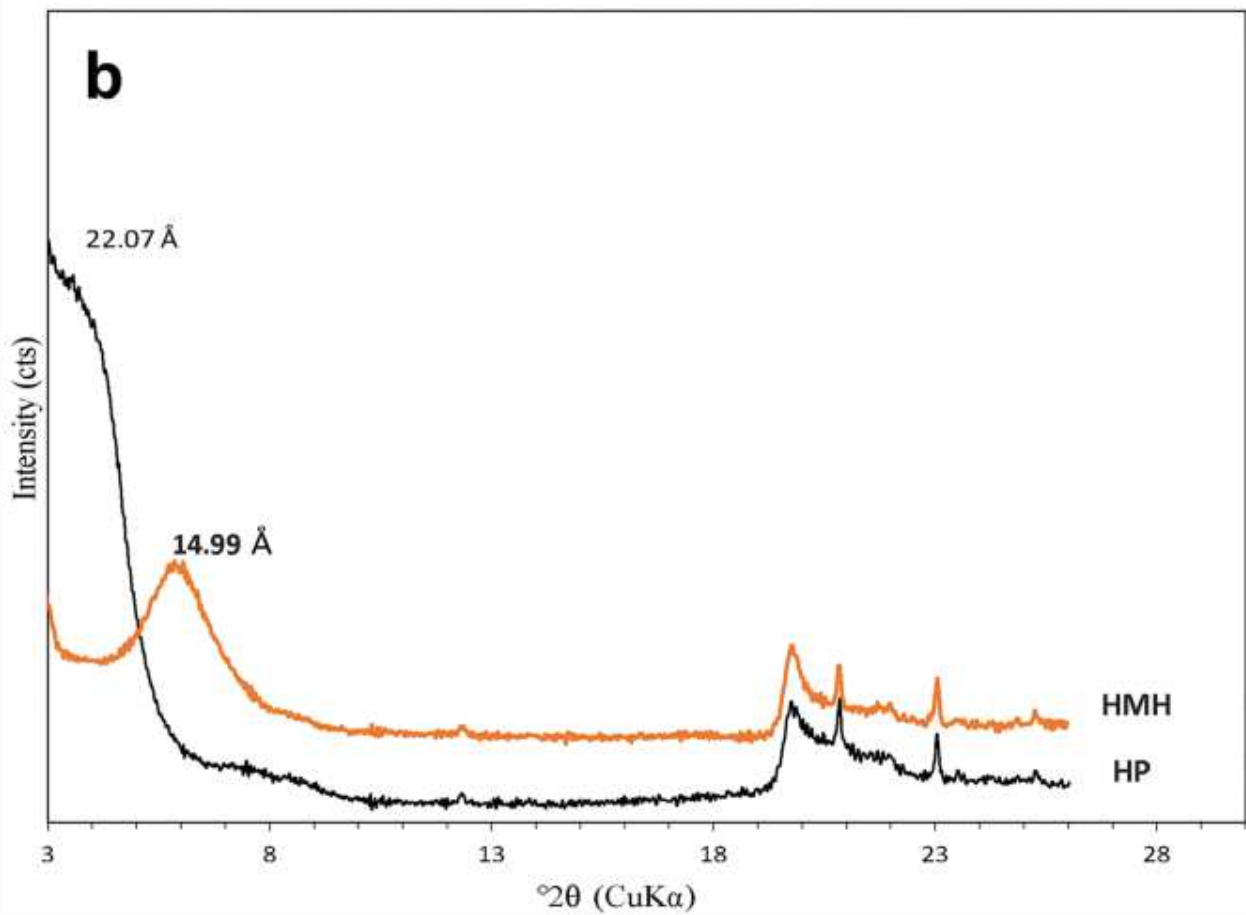
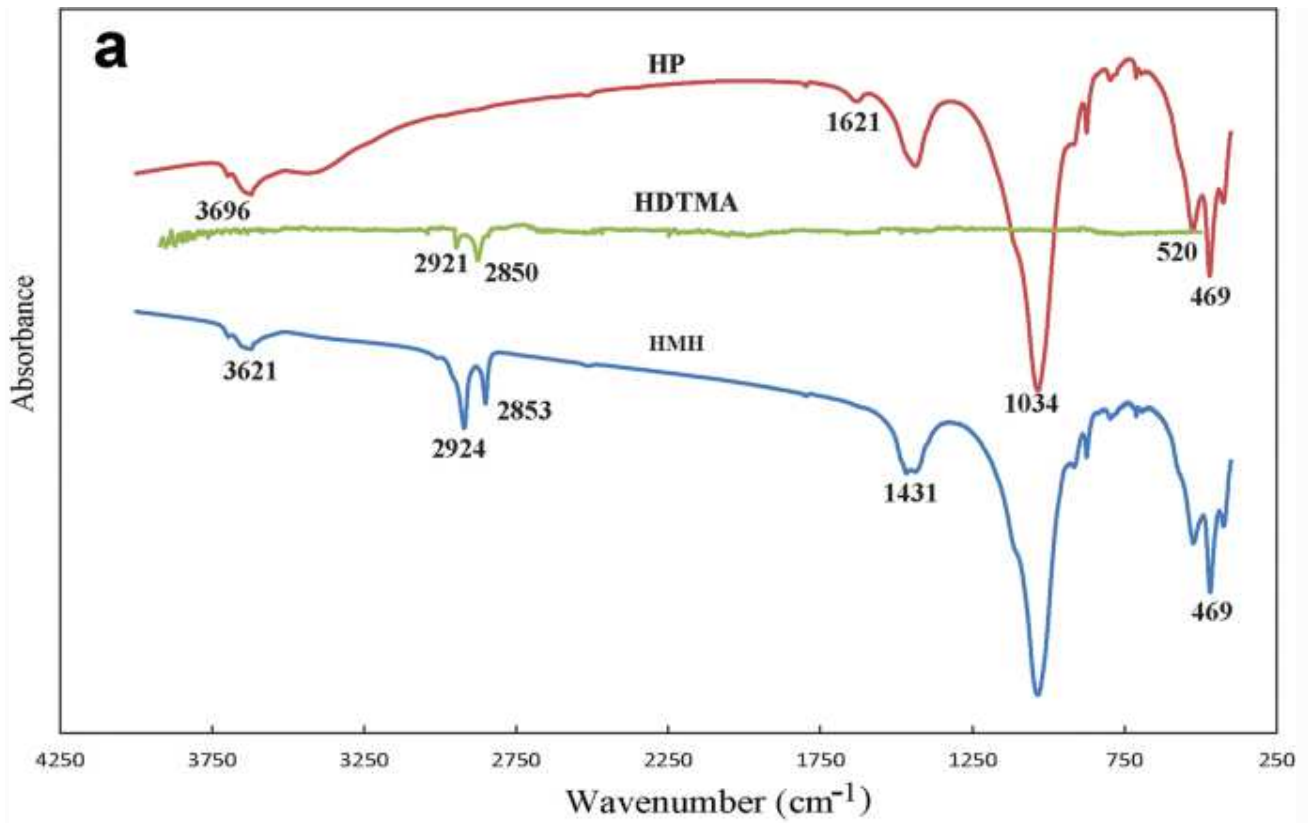


Fig. 3. : a FTIR spectra and b XRD patterns of HP and HMH

Table 3. Specific surface area (S_{BET}), pore volume (V_p), and pore diameter (D) of HP and HMH

Samples	S_{BET} (m ² /g)	V_p^a (cm ³ /g)	Mean D (Å)	
			BET ^b	BJH ^c
HP	71	0.09	56	81
HMH	5	0.03	235	131

^aBarrett-Joyner-Halenda (BJH) desorption cumulative pore volume of pores between 1.7 and 300 nm in diameter.

^bAdsorption average pore diameter (4V/A by BET).

^cBJH desorption average pore diameter.

Adsorption Experiments

Experiments were carried out to study the effect of some of the operating parameters (pH, contact time, adsorbent dose, solution temperature, and initial BPA concentration) on BPA adsorption by HMH.

Effect of Initial Solution pH.

pH is an important parameter in adsorption processes because it can affect both the adsorbent and adsorbate structure and thus the adsorption mechanism. The effect of pH on BPA adsorption was studied at room temperature, with an initial BPA solution concentration of 100 mg/L, an HMH dose of 0.5 g/L, and over a wide range of initial pH from 2 to 10 (adjusted by adding dilute HNO₃ or NaOH). The results obtained after 2 h of reaction (Fig. 4a) indicated that the amount of BPA adsorbed onto HMH was not influenced significantly by the initial pH value and remained practically constant whatever the pH value (2–10). These results were in good agreement with those reported by Park et al. (2014) and could be explained by the speciation of BPA and the nature of the surface charge of the organo-clay. The pK_a values of BPA, ranging from 9.6 to 10.2, involving the ionization of BPA, occurred at ~pH 9–10 to form the bisphenolate anion (Bautista-Toledo et al. 2005). The introduction of an organic cation (HDTMA) into the clay network caused enhancement of the hydrophobicity or organophilic nature of the surface (Li et al. 2000). The hydrophobic nature and positively charged surface created by loaded HDTMA molecules were responsible for adsorption of BPA. In addition, organo-clays which were intercalated with more surfactants or with longer surfactant molecules such as HDTMA were reported (Li et al. 2000) to be less influenced by the solution pH because of the increase in positive charge. The possible interaction of BPA with the HMH was thus attributed to the hydrophobic nature of the modified clay. In light of these results, all the adsorption tests were carried out, without adjustment, at pH ~6.5 (natural pH of the BPA solution).

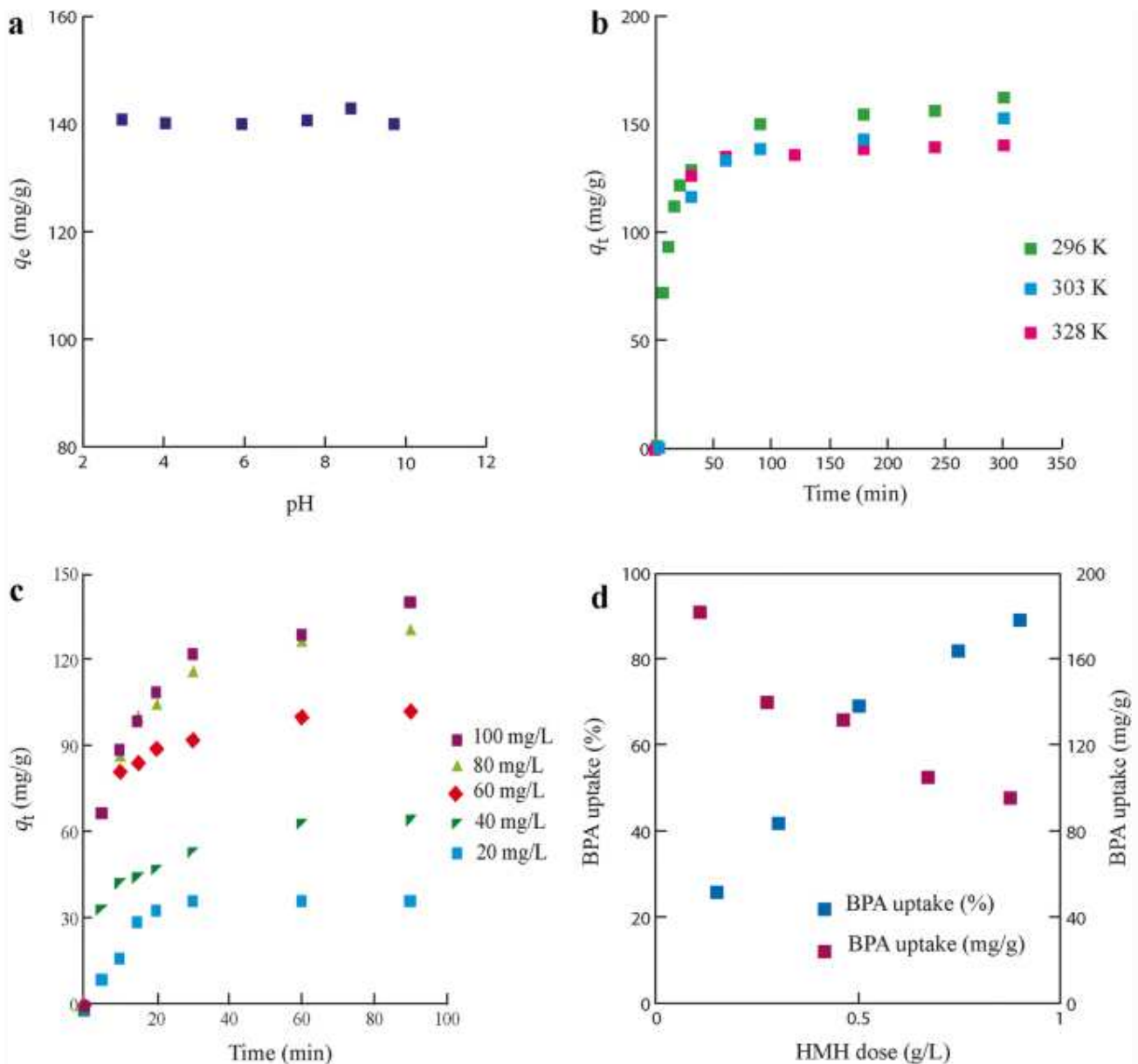


Fig. 4. : Effects of various parameters on the adsorption of BPA by HMH: **a** initial pH (pH_i); **b** contact time and temperature; **c** BPA initial concentration; and **d** HMH dose

Effect of Contact Time and solution temperature.

The effects of adsorption time and temperature on the removal of BPA were studied to determine the impact of equilibrium time and temperature on the amount adsorbed. BPA solutions (100 mg/L) were mixed with 0.5 g/L of organo-clay at three different temperatures: 296, 303, and 328 K. Analysis of samples taken at different times indicated that the BPA adsorption capacity (q_t) increased quickly over the first 30 min, then continued to increase slowly (Fig. 4b). Equilibrium was reached after 180 min of contact, which demonstrated the good affinity of HMH for BPA. In addition, the results revealed that when the temperature increased from 296 to 328 K, the amount of BPA adsorbed decreased from 162 to 140 mg/g. The best results were, thus, obtained at room temperature. Similar results were reported

by Liu et al. (2009) for BPA adsorption onto activated carbon. Those authors attributed this behavior to the exothermic physisorption mechanism for which the low temperature favors adsorption. In addition, overheating may disrupt the progress of the adsorption process and lead to an increase in the desorption kinetics.

Effect of Initial BPA Concentration.

The effect of initial concentration of BPA on adsorption was investigated at 296 K and pH 6.7. The initial concentration of BPA was varied from 20 to 100 mg/L while keeping the HMH dose equal to 0.5 g/L. The analysis of the remaining BPA in solution after 3 h of reaction (Fig. 4c) revealed that whatever the initial BPA concentration, the amount adsorbed increased rapidly over time to reach near-equilibrium after 20–30 min and continued to increase very slowly until equilibrium was reached. When the initial concentration increased, the amount adsorbed increased also. As the initial concentration increased, the driving force of mass transfer increased, thus resulting in greater adsorption of the BPA.

Effect of Adsorbent Dose.

The influence of the HMH dose on the removal of BPA from solutions was studied by applying different concentrations of HMH ranging from 0.15 to 0.90 g/L to BPA solutions at an initial concentration of 100 mg/L. The results obtained (Fig. 4d) demonstrated that at constant initial BPA concentration, the increase in the adsorbent dose enhanced the BPA percentage uptake. The boost in removal efficiency was associated with the largest surface area of HMH and the increased number of available adsorption sites when the largest adsorbent dose was applied. At greater HMH doses, some of the adsorption sites remained unoccupied, resulting in a decrease in the BPA adsorption capacity expressed as mg/g of organo-clay (Gupta and Rastogi 2008).

Kinetic Study

In order to understand the adsorption kinetics of BPA onto HMH, three kinetics models were applied: pseudo-first order, pseudo-second order, and intraparticle diffusion. The equations of the linear form of these models are:

Pseudo-first order kinetics model (Lagergren 1898):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Pseudo-second order kinetics model (Ho and McKay 1999):

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (4)$$

Intraparticle diffusion model (Weber and Morris 1962):

$$q_t = k_i t^{1/2} + C \quad (5)$$

where q_e and q_t are the amounts of BPA adsorbed (mg g^{-1}) at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the first-order rate constant and k_2 (g/mg.min) is the second-order rate constant, k_i ($\text{mg/g.min}^{1/2}$) is the intraparticle rate constant, and C (mg.g^{-1}) is a constant related to the external diffusion resistance. The values of these parameters (Table 4) were determined from the intercepts and slopes of the linear plots (Fig. 5).

Table 4. Kinetic parameters for BPA adsorption onto HMH

Pseudo-first order model				Pseudo-second order model			Intra-particle diffusion model		
$q_{e \text{ exp}}$ (mg/g)	k_1 (min^{-1})	$q_{e \text{ cal}}$ (mg/g)	R^2	k_2 (g/mg.min)	$q_{e \text{ cal}}$ (mg/g)	R^2	k_i ($\text{mg/g.min}^{1/2}$)	C	R^2
140.35	-0.063	96.59	0.992	0.0011	149.25	0.998	7.484	72.096	0.964

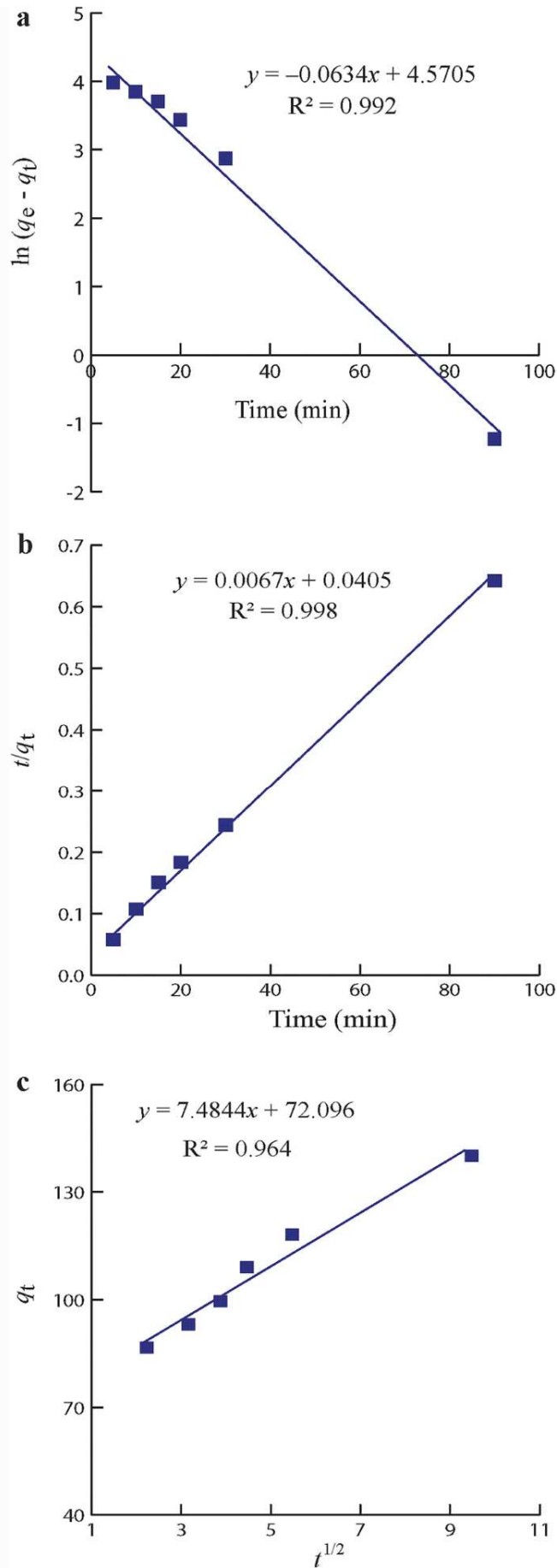


Fig. 5 : Kinetic models for the adsorption of BPA onto HMH at 296 K: **a** pseudo-first order; **b** pseudo-second order; and **c** inter-particle diffusion

Comparison of the correlation coefficient results (Table 4) indicated that the model with the best fit was the pseudo-second order model ($R^2 = 0.998$) compared to the pseudo-first order model ($R^2 = 0.992$). In addition, the q_e values ($q_{e \text{ cal}}$) calculated using the pseudo-second order model were very close to the experimental values ($q_{e \text{ exp}}$) with an error percentage of 6.3%. In the investigation of the diffusion mechanism, the R^2 values obtained from the intraparticle diffusion model exhibited good correlation ($R^2 = 0.964$) suggesting the presence of an intraparticle diffusion mechanism during BPA adsorption onto HMH. The linear plot of q_t vs. $t^{1/2}$ (Fig. 5c) does not pass through the origin, suggesting that the intraparticle diffusion was not the sole rate-limiting step and a film or external diffusion may be involved in the adsorption process (Karger and Ruthven 1992).

Adsorption Isotherms

Adsorption isotherms are useful for understanding the adsorption mechanism. In the current study, adsorption isotherms of BPA onto HMH were interpreted by applying the classic Langmuir and Freundlich models. The Langmuir model is based on a fixed number of available sites on the adsorbent surface, all having the same energy. Adsorption occurs as a monolayer because one site can fix only one molecule and the adsorption energy is constant. The Langmuir model in linear form has the following expression (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (6)$$

where q_e (mg/g) is the BPA adsorption capacity at equilibrium, C_e (mg/L) is the equilibrium concentration of BPA in solution, q_{max} (mg/g) is the maximum monolayer adsorption capacity, and K_L (L/mg) is the Langmuir constant related to the energy of adsorption.

In addition, the Langmuir model can be evaluated by a dimensionless constant separation factor (R_L) that is defined by:

$$R_L = 1 / (1 + K_L C_0) \quad (7)$$

where K_L is the Langmuir constant and C_0 (mg/L) is the initial BPA concentration. The R_L value reflects the nature of the adsorption process to be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$).

The Freundlich model is applicable when the adsorption is multilayer and the adsorbate surface is heterogeneous with exponential distribution of active sites. The Freundlich isotherm equation can be presented as follows (Freundlich 1906):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

where K_F and n (Freundlich constants) are associated with the capacity and intensity of adsorption, respectively.

Analysis of experimental data at equilibrium at 296 K by the models above gave straight lines (Fig. 6) which permitted determination of the equations and the parameters of the corresponding isotherms, their correlation coefficients (R^2), and the value of the dimensionless separation factor (R_L) (Table 5). According to the R^2 values, the Langmuir model (Fig. 6a) is more suitable than the Freundlich model (Fig. 6b) with a maximum adsorption capacity equal to 217.39 mg/g. This finding suggested the homogeneous distribution of the active sites on the HMH surface in accordance with the Langmuir hypotheses. The R_L value of 0.38 also indicates a strong interaction between HMH and BPA.

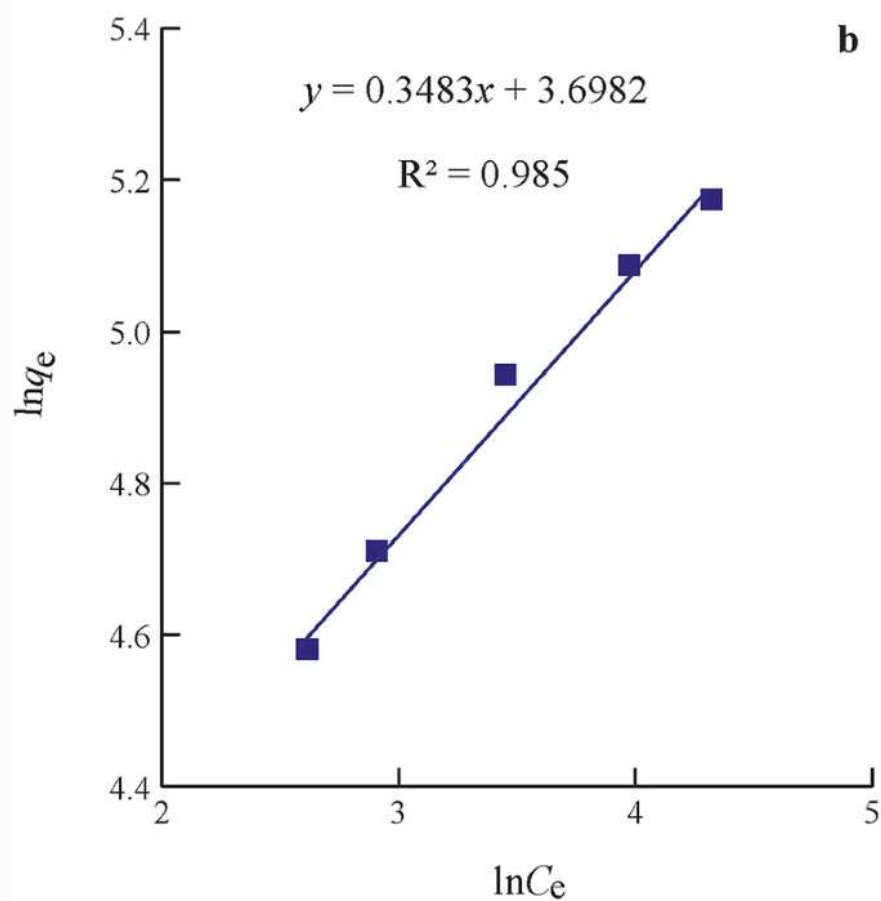
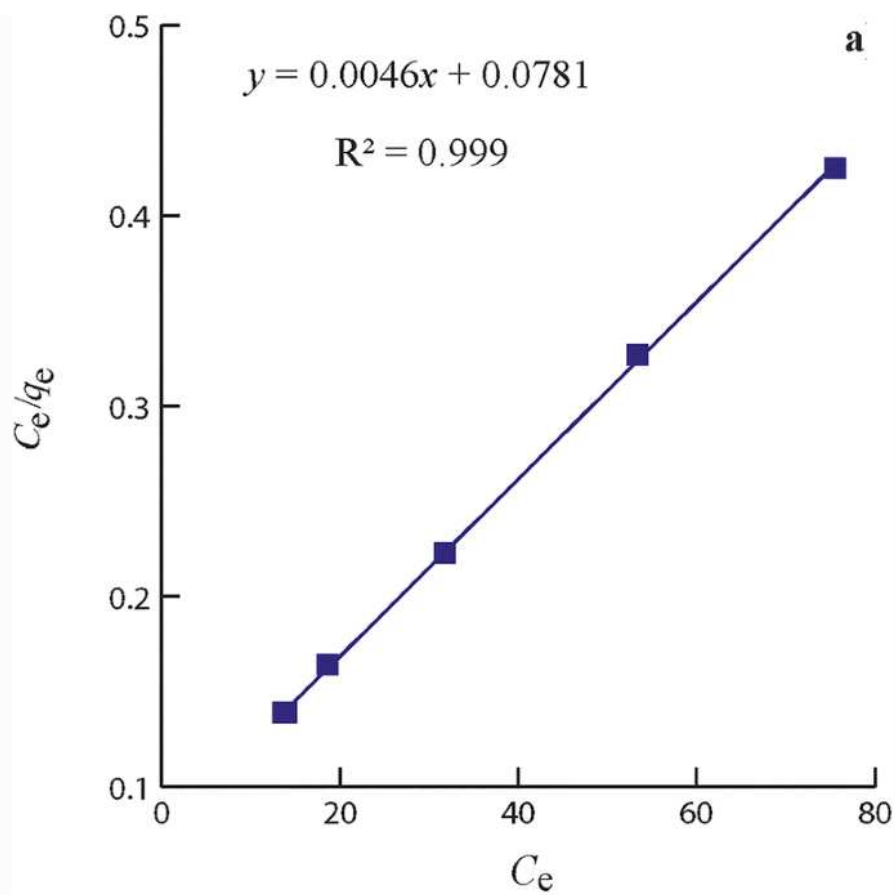


Fig. 6 : Plots of **a** Langmuir and **b** Freundlich isotherm models for BPA adsorption onto HMH

Table 5. Adsorption isotherm parameters for BPA adsorption by HMH

Isotherm	Equation	R ²	Constant value
Langmuir	$C_e/q_e = 0.0046 C_e + 0.0781$	0.999	$q_{\max} \text{ (mg/g)} = 217.39$ $K_L \text{ (L/mg)} = 0.0156$ $R_L = 0.38$
Freundlich	$\ln q_e = 0.3483 \ln C_e + 3.6982$	0.985	$K_F \text{ (mg/g(L/mg)}^{1/n}) = 45.42$ $n = 2.8$

Adsorption Thermodynamics

Thermodynamics were investigated for greater insight into the adsorption mechanism. The experimental data of the BPA adsorption onto HMH, obtained at different temperatures ranging from 296 to 328 K, were exploited to evaluate the thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°), and Gibbs' free energy (ΔG°) using the following equations:

$$K_d = q_e / C_e \quad (9)$$

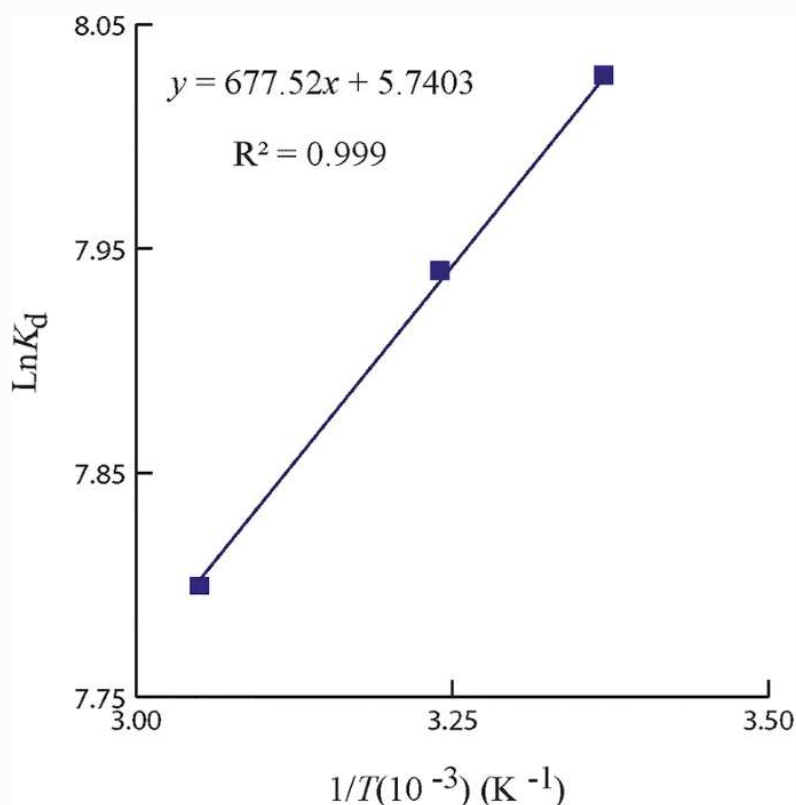
$$\ln K_d = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (10)$$

$$\Delta G^\circ = -RT \ln K_d = \Delta H^\circ - T \Delta S^\circ \quad (11)$$

where R is the ideal gas constant (8.314 J/mol K) and T is the temperature in Kelvin. K_d is the distribution coefficient for the adsorption. In order for Eq. 10 and 11 to be valid, $K_d = K_{eq}$, the true thermodynamic equilibrium constant, which is true only if the relevant activity coefficients either cancel one another or are equal to unity. For the purposes of the present study, the latter was assumed. As demonstrated previously (Milonjic 2007; Salvestrini et al. 2014; Najafi et al. 2015), K_d is dimensionless. Consequently, when q_e is used in mg/g, the equilibrium concentration of BPA in the solution at equilibrium (C_e) should be expressed in mg/mL. The values of q_e , C_e , and K_d as a function of temperature (Table 6) indicated that the distribution coefficient increased with increasing temperature. The variation of $\ln K_d$ vs. $1/T$ (Fig. 7) yielded a straight line from which and according to Eq. 10 the values of ΔH° and ΔS° (Table 6) were determined from the slope and intercept of the plot, respectively.

Table 6. Thermodynamic parameters for the BPA adsorption by HMH

Temperature (K)	C_e (mg/mL)	q_e (mg/g)	K_d	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.K)
296	0.053	162.3	3068.05	-19.75	-5.63	47.72
303	0.054	153.3	2810.26	-20.42		
328	0.057	140.6	2454.27	-21.28		

**Fig. 7 :** Estimation of thermodynamic parameters for BPA adsorption onto HMH

The negative values of ΔG° calculated by Eq. 11 (Table 6) implied that the BPA adsorption was spontaneous, and more favorable at high temperature. Similar results were obtained by Li et al. (2014). The negative value of ΔH° suggested that BPA adsorption onto HMH was exothermic. The exothermic nature was also proved by the decrease in the amount adsorbed with increasing temperature. Based on the ΔH° value, the adsorption process is taken to be physical, if $\Delta H^\circ < 25$ kJ/mol, or chemical, when $\Delta H^\circ > 40$ kJ/mol (Krishna et al. 2000). The value of ΔH° was equal to -5.63 kJ/mol, indicating, therefore, that the adsorption of BPA onto HMH was a physisorption process, which implied the easy regeneration of the saturated HMH. The positive values of ΔS° suggested that the state of the adsorbed BPA molecules was less ordered than in solution (Bereket et al. 1997).

Comparison of BPA Adsorption Capacity with other HDTMA-modified Clays

The BPA adsorption capacity values of various modified commercial clays (Table 7) proved that the HMH prepared in the present study has one of the largest adsorption capacities for BPA. Only palygorskite can rival it. HMH can, therefore, be employed successfully as a cheap and environmentally friendly adsorbent for the treatment of wastewaters polluted by BPA and probably other phenolic compounds.

Table 7. Adsorption capacity for BPA by HMH in comparison with other HDTMA-clays

Nature and origin of clay	q_m (mg/g)	Temperature (K)	Reference
Nanhai, Guangdong province, China	74.55	303	Liu et al. (2016)
Pure MMT, Sigma-Aldrich, Germany	114.94	296	Park et al. (2014)
Pure Ca-montmorillonite, clay mineral repository, Arizona, USA	151.52	297	Zheng et al. (2013)
Palygorskite, Golden Stone Palygorskite, Research and Development Center (Jiangsu, China)	219.30	303	Zhao et al. (2014)
Bentonite, commercial supplier mined at Bhuj, Gujarat, India	50.97	298	Lee et al. (2016)
Local clay (India)	19.58	298	Lee et al. (2016)
Bentonite, Weifang Huawei Bentonite Co., Ltd. (Shandong, China)	10.44	298	Li et al. (2015)
Natural clay, El Hicha deposit, Gabes, Tunisia	217.39	296	Present study

Conclusions

Conventionally, clay modification is carried out by heating a mixture of the clay and the surfactant solution for 2 to 24 h at 60–80°C. In order to reduce the heating time to a few minutes (and to reduce energy consumption), a domestic microwave oven was used. The microwave technique provided a uniform heating rate, allowing the preparation of the unique material more quickly. Without acid activation or sodium exchange, the natural Tunisian clay was modified successfully with HDTMA

using microwave irradiation at optimal conditions of 100 W for 2 min with an activation ratio of 0.3, and a solid:liquid ratio of 5%. The success of the HDTMA intercalation between the clay layers was proven by BET, SEM, FTIR, and XRD analysis. The study of BPA adsorption by the organo-clay prepared here revealed that the amount of BPA adsorbed increased when its initial concentration, the dose of adsorbent, and the contact time increased, and decreased slightly when the temperature increased. The impact of the pH variation between 2.6 and 10 was not significant. The kinetics of adsorption followed well the pseudo-second order kinetics model, and the Langmuir model followed the experimental data better than the Freundlich model, giving a maximum monolayer adsorption capacity of 217.39 mg/g. The adsorption of BPA onto HMH was spontaneous, exothermic, and not controlled solely by intraparticle diffusion. In conclusion, the Tunisian natural clay may be used successfully, following intercalation by HDTMA, as a cheap and environmentally friendly adsorbent for the removal of BPA (and possibly other organic pollutants) from wastewaters.

References

- Bautista-Toledo, I., Ferro-García, M. A., Rivera-Utrilla, J., Moreno-Castilla, C., & Vegas Fernández, F. J. (2005). Bisphenol A removal from water by activated carbon. Effects of carbon characteristics and solution chemistry. *Environmental Science and Technology*, 39, 6246–6250.
- Bereket, G., Arog, A. Z., & Özel, M. Z. (1997). Removal of Pb(II), Cd(II), Cu(II), and Zn(II) from aqueous solutions by adsorption on bentonite. *Journal of Colloid Interface Science*, 187, 338–343.
- Bergaya, F. & Lagaly, G. (2011). Intercalation processes of layered minerals. In: *Layered Mineral Structures and their Application in Advanced Technology* (M.F. Brigatti and A. Mottana, editors). EMU Notes in Mineralogy, European Mineralogical Union and the Mineralogical Society of Great Britain & Ireland, London, pp. 259–284.
- Bergaya, F., Detellier, C., Lambert, J.F., & Lagaly, G. (2013). Introduction on clay polymer nanocomposites (CPN). *Handbook of Clay Science (2nd edition ed., Vol. 5A)*. (F. Bergaya & G. Lagaly, editors). Developments in Clay Science, Elsevier.
- Bing-zhi, D., Hua-qiang, C., Lin, W., Sheng-ji, X., & Nai-yun, G. (2010). The removal of bisphenol A by hollow fiber microfiltration membrane. *Desalination*, 250, 693–697.
- Careghini, A., Mastorgio, A. F., Saponaro, S., & Sezenna, E. (2015). Bisphenol A, nonylphenols, benzophenones, and benzotriazoles in soils, groundwater, surface water, sediments, and food: a review. *Environmental Science and Pollution Research*, 22, 5711–5741.
- Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*, 97, 1061–1085.
- Erdem, B., Özcan, A. S., & Özcan, A. (2010). Preparation of HDTMA-bentonite: Characterization studies and its adsorption behavior toward dibenzofuran. *Surface and Interface Analysis*, 42, 1351–1356.

- Farmer, V. C., & Russell, J. D. (1964). The infrared spectra of layer silicates. *Spectrochimica Acta*, 20, 1149–1173.
- Farmer, V.C. (1974). *The Infrared Spectra of Minerals*. Monograph 4. Mineralogical Society, London, 539 pp.
- Freundlich, H. M. F. (1906). Über die adsorption in losungen. *Zeitschrift für PhysiKalische Chemie*, 57, 385–470.
- Gupta, V., & Rastogi, A. (2008). Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies. *Journal of Hazardous Materials*, 152, 407–414.
- He, H., Zhou, Q., Martens, W. N., Kloprogge, T. J., Yuan, P., Xi, Y., Zhu, J., & Frost, R. L. (2006). Microstructure of HDTMA⁺-modified montmorillonite and its influence on sorption characteristics. *Clays and Clay Minerals*, 54, 289–696.
- Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, 34, 451–465.
- Jandegian, C. M., Deem, S. L., Bhandari, R. K., Holliday, C. M., Nicks, D., Rosenfeld, C. S., Selcer, K. W., Tillitt, D. E., Vom Saal, F. S., Vélez-Rivera, V., Yang, Y., & Holliday, D. K. (2015). Development exposure to bisphenol A (BPA) alters sexual differentiation in painted turtles (*Chrysemys picta*). *General and Comparative Endocrinology*, 216, 77–85.
- Karger, J., & Ruthven, M. D. (1992). *Diffusion in Zeolites and Other Microporous Solids* (p. 605). New York: Wiley-Interscience Pubs.
- Kinch, C. D., Ibhazehiebo, K., Jeong, J. H., Habibi, H. R., & Kurrasch, D. M. (2015). Low dose exposure to bisphenol A and replacement bisphenol S induces Precocious hypothalamic neurogenesis in embryonic zebrafish. *Proceedings of the National Academy of Sciences*, 112, 1475–1480.
- Krishna, B. S., Murty, D. S. R., & Prakash, B. S. J. (2000). Thermodynamics of chromium (VI) anionic species sorption onto surfactant-modified montmorillonite clay. *Journal of Colloid and Interface Science*, 229, 230–236.
- Laatikainen, K., Bryjak, M., Laatikainen, M., & Sirén, H. (2014). Molecularly imprinted polystyrene-divinyl benzene adsorbents for removal of bisphenol A. *Desalination and Water Treatment*, 52, 1885–1894.
- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svensk Vetenskapsakademiens Handlingar*, 24, 1–39.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica, and platinum. *Journal of the American Chemical Society*, 40, 1361–1403.

- Lee, S. M., Thanhmingliana, & Tiwari, D. (2016). Hybrid materials precursor to natural clay in the attenuation of bisphenol A from aqueous solutions. *Journal of Water Process Engineering*, *11*, 46–54.
- Li, Z., Burt, T., & Bowman, R. S. (2000). Sorption of ionizable organic solutes by surfactant-modified zeolite. *Environmental Science and Technology*, *34*, 3756–3760.
- Li, J., Zhan, Y., Lin, J., Jiang, A., & Xi, W. (2014). Removal of bisphenol A from aqueous solution using cetylpyridinium bromide (CPB)-modified natural zeolites as adsorbents. *Environmental Earth Sciences*, *72*, 3969–3980.
- Li, Y., Jin, F., Wang, C., Chen, Y., Wang, Q., Zhang, W., & Wang, D. (2015). Modification of bentonite with cationic surfactant for the enhanced retention of bisphenol A from landfill leachate. *Environmental Science and Pollution Research*, *22*, 8618–8628.
- Liang, L., Zhang, J., Feng, P., Li, C., Huang, Y., Dong, B., Li, L., & Guan, X. (2015). Occurrence of bisphenol A in surface and drinking waters and its physicochemical removal technologies. *Frontiers of Environmental Science and Engineering*, *9*, 16–38.
- Liu, G., Ma, J., Li, X. C., & Qin, Q. D. (2009). Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments. *Journal of Hazardous Materials*, *164*, 1275.
- Liu, C., Wu, P., Zhu, Y., & Tran, L. (2016). Simultaneous adsorption of Cd²⁺ and BPA on amphoteric surfactant activated montmorillonite. *Journal of Chemosphere*, *144*, 1026–1032.
- Meera, K. M., Sankar, R. M., Murali, A., Jaisankar, S. N., & Mandal, A. B. (2012). Sol-gel network silica/modified montmorillonite clay hybrid nanocomposites for hydrophobic surface coatings. *Colloids and Surfaces*, *90*, 204–210.
- Milonjic. (2007). A consideration of the correct calculation of thermodynamic parameters of adsorption. *Journal of Serbian Chemical Society*, *72*, 1363–1367.
- Najafi, F., Moradi, O., Rajabi, M., Asif, M., Tyagi, I., Agarwal, S., & Gupta, V. K. (2015). Thermodynamics of the adsorption of nickel ions from aqueous phase using graphene oxide and glycine functionalized graphene oxide. *Journal of Molecular Liquids*, *208*, 106–113.
- Neel, D. & Bowman, R.S. (1992). Sorption of organics to surface-altered zeolites. In: *Proceedings of the 36th Annual New Mexico Water Conference*, 7–8 November 1991, Las Cruces, New Mexico, p. 57–61.
- Okugbe, E. O., & Songhe, Z. (2019). Endocrine disrupting effects of bisphenol A exposure and recent advances on its removal by water treatment systems. *A review. Scientific African*, *5*, e00135.
- Park, Y., Sun, Z., Ayoko, G. A., & Frost, R. L. (2014). Bisphenol A sorption by organo montmorillonite: Implications for the removal of organic contaminants from water. *Chemosphere*, *107*, 249–256.

- Salvestrini, S., Vincenzo, L., Pasquale, I., Silvana, C., & Sante, C. (2014). Considerations about the correct evaluation of sorption thermodynamic parameters from equilibrium isotherms. *Journal of Chemical Thermodynamics*, 68, 310–316.
- Sassi, H., Lafaye, G., Amor, H. B., Gannouni, A., Jeday, M. R., & Barbier, J. (2018). Wastewater treatment by catalytic wet air oxidation process over Al-Fe pillared clays synthesized using microwave irradiation. *Frontiers of Environmental Science and Engineering*, 12, 2.
- U.S. Environmental Protection Agency (2010). Bisphenol A Action Plan. <https://canvas.uw.edu/courses/1220635/files/50902839>. Retrieved September 24, 2018.
- Weber, J.C. & Morris, W.J. (1962). Advances in water pollution research: removal of biologically resistant pollutant from waste water by adsorption. In: *Proceedings of International Conference on Water Pollution Symposium*, Pergamon Press, 2, 231–266.
- Zhang, L., Zhang, B., Wu, T., Sun, D., & Li, Y. (2015). Adsorption behavior and mechanism of chlorophenols onto organo-clays in aqueous solution. *Journal of Colloids and Surfaces A: Physicochemical Engineering Aspects*, 484, 118–129.
- Zhao, Z., Fu, D., & Ma, Q. (2014). Adsorption characteristics of Bisphenol A from aqueous solution onto HDTMA-modified palygorskite. *Separation Science and Technology*, 168, 1590–1594.
- Zheng, S., Sun, Z., Park, Y., Ayoko, G., & Frost, R. L. (2013). Removal of bisphenol A from wastewater by Ca-montmorillonite modified with selected surfactants. *Chemical Engineering Journal*, 234, 416–422.
- Zhu, R., Zhu, L., Zhu, J., Ge, F., & Wang, T. (2009). Sorption of naphthalene and phosphate to the CTMAB-Al13 intercalated bentonites. *Journal of Hazardous Materials*, 168, 1590–1594.

Acknowledgments

The authors are grateful to the PHC-Maghreb project (16/MAG 11), University of Gabes, Tunisia, and the University of Poitiers, France, for financial support of the Research Project.