

Solid-State Synthesis of Organoclays: Physicochemical Properties and Application for Bisphenol A Removal from Aqueous Solutions

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Abstract

The solid-state intercalation of organoclays, by using surfactants bromide salts (n -C₁₂H₂₅(CH₃)₃NBr, n -C₁₄H₂₉(CH₃)₃NBr, n -C₁₆H₃₃(CH₃)₃NBr and n -C₁₂H₂₅)₂(CH₃)₂NBr) at different levels of the cation exchange capacity (CEC), was reported. According to XRPD data, the basal spacing of the smectite phase unit cell increased systematically up to >38 Å at 2.0-CEC of surfactants loading, indicating that they entered into the smectite interlayers and were arranged parallel to the layers at low concentrations and nearly vertical at high ones. Organoclays FTIR spectra showed a drop in the water band intensities at around 1630 and 3400 cm⁻¹, and new specific bands close to 2920 and 2850 cm⁻¹ were assigned to the asymmetric and symmetric stretching of the surfactants CH₂ groups, respectively. Various factors, impacting bisphenol A (BPA) removal from water, were estimated in batch studies. It is shown that both physisorption and chemisorption describe the BPA sorption, and the pseudo-second-order kinetics and Langmuir isotherm fit better the BPA sorption results. The adsorption capacities of the organoclays are ranged from 88 to 127 mg/g at ambient temperature and in acidic solution. The effect of pH on the adsorption showed a remarkable drop in the quantity of adsorbed BPA when the pH is greater than 10 (pH ≥ 10).

Keywords: organosmectites, surfactant, bisphenol a, adsorption, batch studies

1. Introduction

Endocrine disrupting chemicals (EDCs) are chemical pollutants that can affect the endocrine (hormonal) system and intrude on important developmental processes in humans and wildlife (World Health Organization, 1996). EDCs include natural estrogens (estrone: E1, 17β-estradiol: E2, estriol: E3), synthesized estrogen (ethinylestradiol: EE2), and artificial composites (bisphenol A: BPA, polychlorinated biphenyls: PCBs, polybrominated biphenyls: PBBs, and dioxins). EDCs are

dichlorodiphenyltrichloroethane (DDT) from pesticides and vinclozolin from fungicides [1, 2]. Among these chemicals that are cited, BPA is produced in high volumes than the other ones and it can be found worldwide. Centers for Disease Control reported that BPA is present in the urine of 92.6% of over 2500 Americans [3, 4] and this indicates a general exposure to this chemical. Stockholm Convention has regulated the manufacturing and the utilization of DDT, PCBs, PBBs, and dioxins (Stockholm Convention on Persistent Organic Pollutants, 2009), and this agreement limited the exposition to these composites compared to BPA which is not regulated in all countries. A lot of studies reported that there was arising substantiation for adverse reproductive issues (fruitfulness, cancers, deformations) from exposure to EDCs, and there was also mounting substantiation of these chemicals on thyroid function, brain function, obesity and metabolism, and insulin and glucose homeostasis (Stockholm Convention on Persistent Organic Pollutants, 2009). Former studies reported the presence of BPA in wastewater, surface and ground waters, and indeed drinking water [5]. This urged major enterprises over endocrine-disrupting chemicals by scientists in recent years. The pollution of the environment by these chemicals is mainly via industrial activities [5]. Predominantly, it's used in the manufacturing of polycarbonate plastics and epoxy resins [6]. Also, dental securities, foods and potable barrels, polycarbonate tubes, cleansers, care products, etc., are listed as exposition sources (World Health Organization 1996). The United States Environmental Protection Agency has defined a daily dose of 50 mg of BPA/kg of body weight/day for BPA [6]. Although there is no database on BPA pollution in an aqueous environment in Burkina Faso, its presence could be supposed in wastewater, surface, and ground waters, due to numerous original factories and diligence whose products clearly lead to a general exposition of the population to BPA. The absence of legislation in many countries makes it urgent to develop simple and effective methods for BPA remediation in aqueous matrixes. Numerous procedures including adsorption, chemical advanced oxidation, membrane filtration, and electrochemical mineralization were utilized for BPA removal from water [2, 3, 7–13]. Among the listed procedures, adsorption seems to be appropriate due to its high effectiveness, ease of implementation, and low cost of the process due to the usefulness of various adsorbents. Numerous adsorbents including organo-montmorillonites [7, 8, 10–12, 14, 15], inorganic-organoclays [16], surfactant modified vermiculites [17], surfactant modified sepiolite [18], surfactant modified palygorskite [19], polymer based on kaolinite [20], chitosan [21], surfactant modified zeolite [2, 22, 23], graphene [9], etc., have been used for BPA removal from water.

Clay modification is widely done in aqueous solution via cation exchange or solid-state reactions. Organic molecules are inserted in dried clay interlayers by solid-state responses without washing with solvent and this makes the synthesis environmentally friendly and more favorable for industrialization [24]. Generally, the publication in this topic reported the organoclays synthesis using various procedures and chemicals, numerous type of clays, and diverse surfactants as reviewed elsewhere [24]. To obtain organoclays with hydrophobic properties, quaternary alkylammonium salts are the most frequently used, but n-alkyl-pyrrolidones, maleic anhydride, biomolecules, polymeric quaternary alkylammonium, alkyl-imidazolium, and phosphonium salts are also employed to the accomplishment of this outcome [24]. The field of application of organoclays is very large and this includes nanocomposites, adsorbents of organic and inorganic pollutants in soil, water, air, etc. [8, 24, 25]. Clays and organically modified clays are considerably employed in adsorption processes for the removal of organic pollutants due to their low cost and environmental friendly [3, 7, 8, 10, 21, 26].

Smectites are generally utilized due to their high cation exchange capacity (CEC), swelling aptitude, and high specific surface areas leading to high adsorption/absorption capacities [3, 7, 8, 10]. From the literature, it is known that organoclays employed for BPA removal from water are synthesized by liquid-state insertion of surfactants into the clay layers [16, 21, 26]. In the present investigations, the organoclays utilized to study the BPA sorption from water have been synthesized via a solid-state insertion methodology. The synthesis occurs via solid-state intercalation reaction by using two natural local clays (denoted AH and DI) and four cationic surfactants (dodecyl trimethylammonium, $n\text{-C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{N}^+$ denoted C_{12} ; tetradecyltrimethylammonium, $n\text{-C}_{14}\text{H}_{29}(\text{CH}_3)_3\text{N}^+$ denoted C_{14} ; hexadecyltrimethylammonium, $n\text{-C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$ denoted C_{16} and didodecyl dimethylammonium, $(n\text{-C}_{12}\text{H}_{25})_2(\text{CH}_3)_2\text{N}^+$ denoted 2C_{12}).

The present work investigates: (i) the solid-state intercalation of three alkyltrimethyl-ammonium and one di-alkyldimethylammonium cation into two natural clays, and the subsequent changes in structure and physicochemical properties; (ii) the efficiency of organoclays prepared via solid-state methodology for BPA removal from water; (iii) various parameters such as kinetics (pseudo-first-order model and pseudo-second-order model), isotherm (Freundlich and Langmuir models) and thermodynamic parameters (standard enthalpy (ΔH), standard entropy (ΔS), and standard free energy (ΔG)) on BPA adsorption from water.

2. Characterization of synthesized organoclays

The organoclays synthesis and their characterization using various techniques have been published elsewhere [27].

2.1 X-ray diffraction of raw clays and organoclays

The **Figures 1a, b** and **2a–f** show the XRPD diffractograms of the AH and DI raw clays and the organoclays loaded at various loading levels (0.5 CEC, 1.0 CEC, 1.5 CEC and 2.0 CEC) of the C_{12} , C_{14} , C_{16} , and 2C_{12} surfactants. **Figure 1** shows that AH and DI clays contain quartz, montmorillonite, kaolinite, hematite, rutile, orthoclase, and anorthite only for DI clay.

From **Figures 1** and **2**, it can be seen that the d_{001} basal spacing raises when the surfactant loading level increases. This increase indicates that the surfactant molecules are inserted into the mineral clay layers. It is also seen that an increase in the length of the long alkyl chain (C_{12} , C_{14} , and C_{16}) and the number of long alkyl chains (C_{12} and 2C_{12}) provokes an increase in the d_{001} value (**Figures 1** and **2**). Furthermore, the increase in the d_{001} values seems to take place in steps with preferred intervals, **Figures 1** and **2**.

As a matter of fact, the d_{001} basal spacing value of the organoclays loaded at 2.0 CEC is 25 Å for the C_{12} surfactant (2.0 CEC- C_{12} -AH and 2.0 CEC- C_{12} -DI) < 32 Å and 28 Å for the C_{14} surfactant (2.0 CEC- C_{14} -AH and 2.0 CEC- C_{14} -DI, respectively) < 38 Å for the C_{16} and 2C_{12} surfactants (2.0 CEC- C_{16} -AH and 2.0 CEC- C_{16} -DI, 2.0 CEC- 2C_{12} -AH and 2.0 CEC- 2C_{12} -DI). In a previous study, Park reported that at 0.5 CEC loading level, a marginal increase of the basal spacing (d_{001}) is observed when the long alkyl chain length increases: C_{12} (14.1 Å), C_{14} (14.3 Å), and C_{16} (14.4 Å) at a XRPD step size of 0.0167° for 2θ [28]. As a matter of principle, similar observation should be made in the present study for the d_{001} spacing for all prepared organoclays

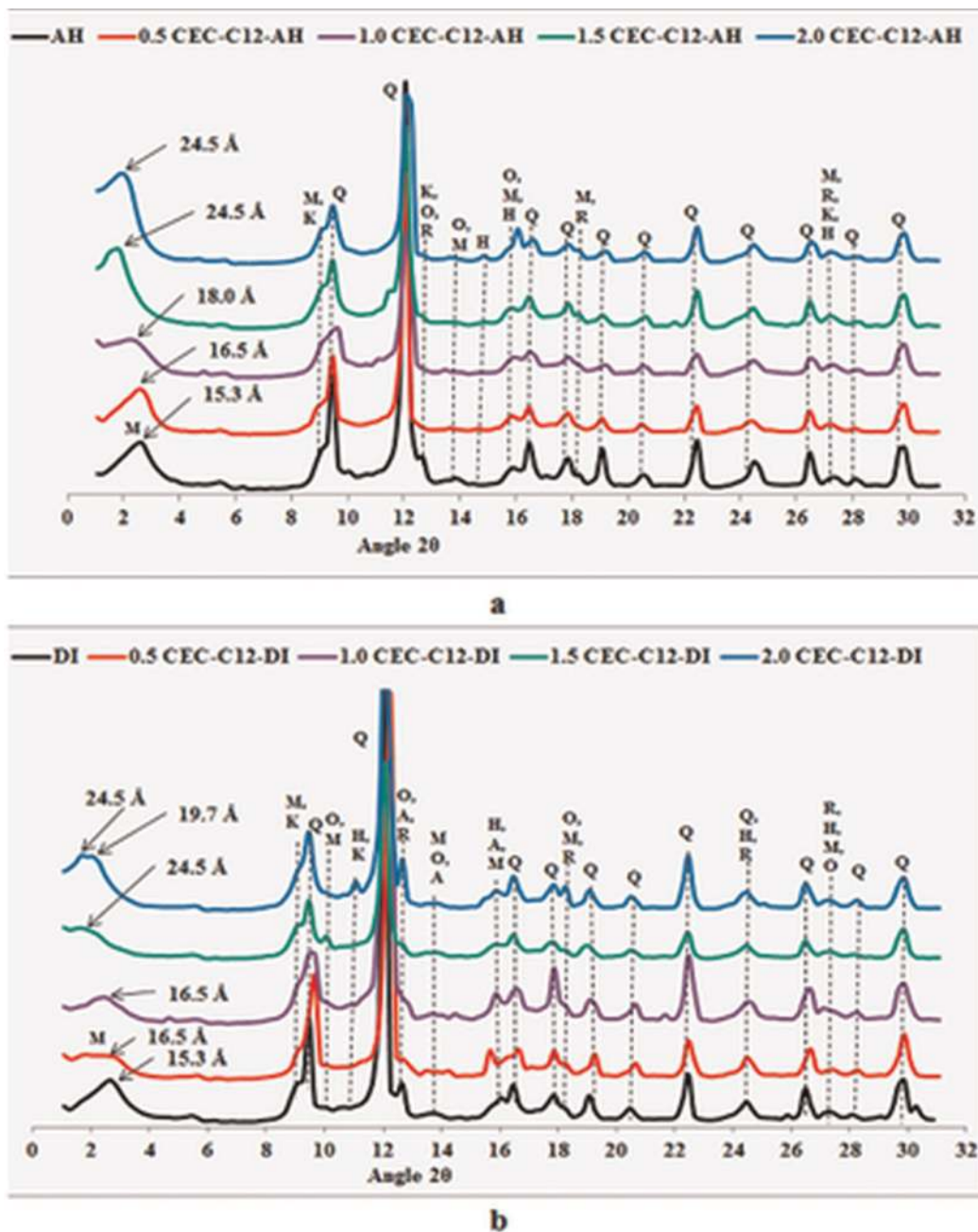


Figure 1. X-ray powder diffraction patterns of AH, DI clays and C₁₂-AH, C₁₂-DI organoclays. Q = quartz, M = montmorillonite, K = kaolinite, H = hematite, R = rutile, O = orthoclase, and A = anorthite.

loaded at 0.5 CEC, **Figures 1** and **2**. This is related to the fact that at low loading level, the long alkyl chains are oriented parallel to the sheets, **Figures 3a** and **b**. The increase of the loading level, the length and the number of long alkyl chains in the quaternary alkylammonium cations increases the d_{001} basal spacing, **Figures 1a, b** and **2a-f**. The obtained results indicate that the orientation of the inserted quaternary alkylammonium cations varies from being parallel with the sheets to turn to more and more upright when the loading level increases (**Figure 3**).

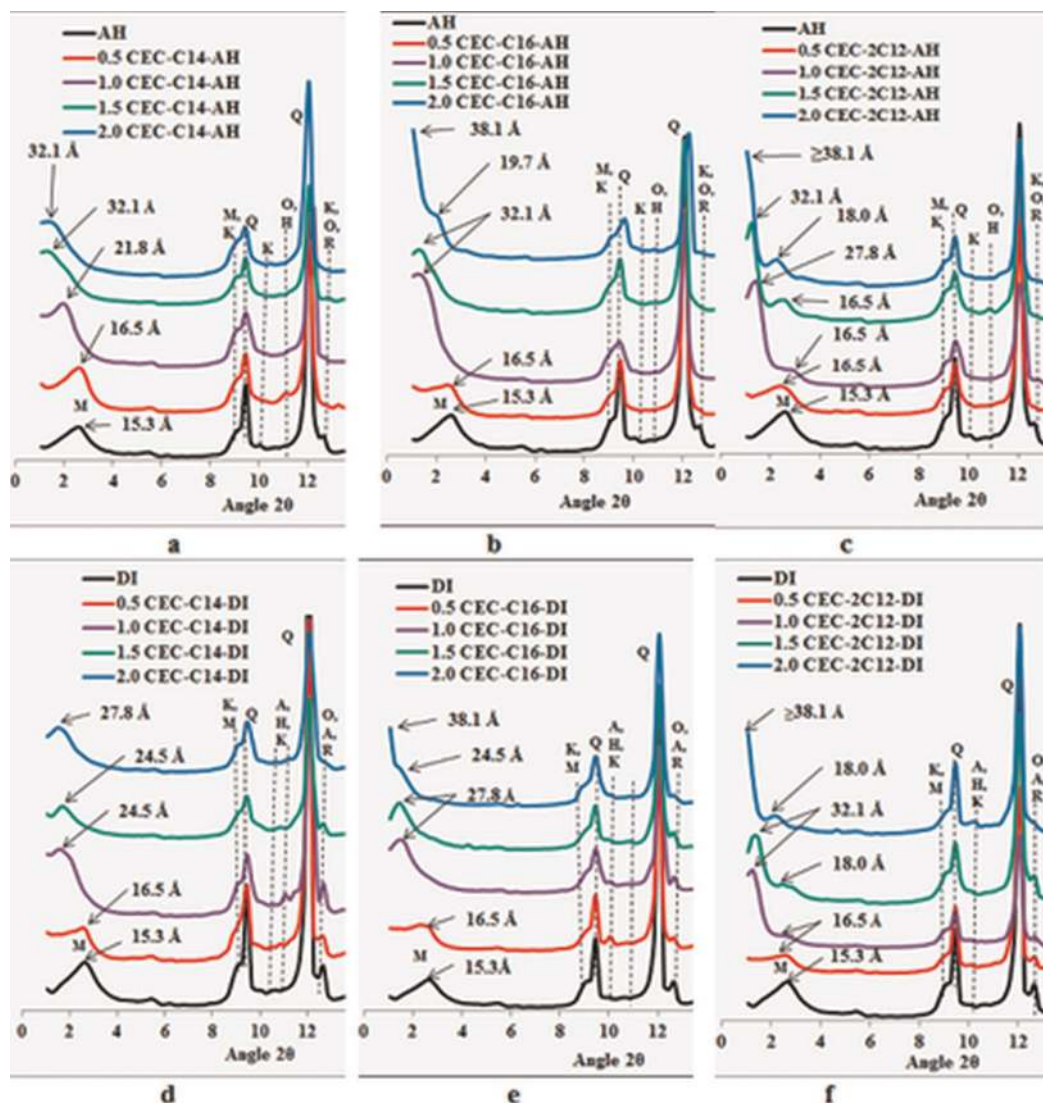


Figure 2. X-ray powder diffraction patterns of AH, DI clays and C_{14} -AH, C_{14} -DI, C_{16} -AH, C_{16} -DI, $2C_{12}$ -AH, and $2C_{12}$ -DI organoclays. Q = quartz, M = montmorillonite, K = kaolinite, H = hematite, R = rutile, O = orthoclase, and A = anorthite.

The increase of the quaternary alkylammonium cations loading level from 0.5 CEC to 2.0 CEC levels causes the expansion of the montmorillonite interlayers to 6.8 Å, 8.3 Å, 10.0 Å, 12.1 Å, 14.8 Å, 18.1 Å, 22.4 Å and higher than 28.3 Å and these expansion values depend on the clays (AH or DI) and/or on the surfactants (C_{12} , C_{14} , C_{16} , and $2C_{12}$) used (Figure 3). Regarding the quaternary alkylammonium cations sizes, 8.3 Å and 10.0 Å as interlayer's expansions are attributed to a bilayer arrangement of the quaternary alkylammonium cations with an angle depending on the interaction between the quaternary alkylammonium cations and the clay layers, the chemical composition of the clay and the structure of the quaternary alkylammonium cations. This arrangement is expected for 18.0 Å and 19.7 Å as d_{001} basal spacing. The pseudo-trilayer arrangement is expected for 12.1 Å and 14.8 Å as basal spacing expansion and the long alkyl chain of the surfactants are orientated in

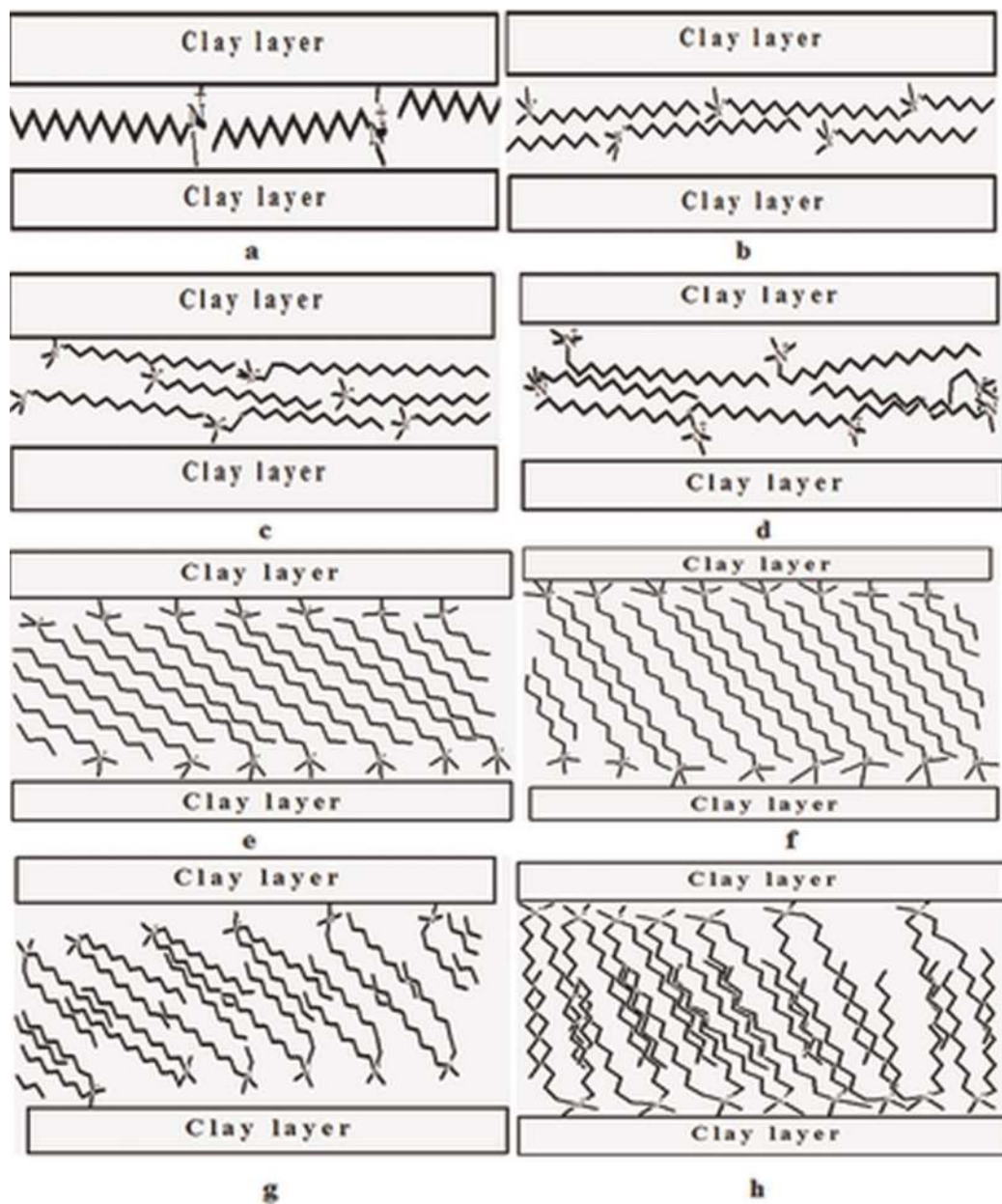


Figure 3. Surfactant molecules orientations into the interlayer space: Arrangements (a) monolayer, (b) bilayers, and (c, d) pseudo-trilayers and (e, f and g, h) paraffin-type for one and two long alkyl chains respectively.

an oblique plan. For 18.1 Å, 22.4 Å and 28.4 Å as expansions, the long alkyl chain are arranged in a paraffin-type and their orientation approaches to the alternate anti-parallel packing in the clay interlayers as described in the crystal structures of the pure surfactants C₁₂, C₁₄ and C₁₆ [29]. This paraffin-type arrangement is expected when the d_{001} basal spacing values reach 27.8 Å, 32.1 Å or are higher than 38 Å. Therefore, the angle between the clay layers and the plane of the surfactant long alkyl chains approaches 90°. These proposed arrangements of the long alkyl chains in the organically modified clays interlayers are analogous to the arrangements reported by Lagaly et al. [30].

2.2 Fourier transform infrared (FTIR) spectroscopy of organoclays

Figures 4–7 represent the FTIR spectra of the raw clays, the organoclays loaded at 0.5 CEC, 1.0 CEC, 1.5 CEC and 2.0 CEC loading level of C_{12} , C_{14} , C_{16} and $2C_{12}$ surfactants, and pure surfactants.

The bending bands of the H-O appear at around 1600 cm^{-1} on the FTIR spectra of the raw and modified clays. The stretching vibrations of the structural hydroxyl (OH) is observed at 3622 cm^{-1} for the raw clays, and the band around 3420 cm^{-1} is attributed to the hydroxyl of water molecules contained in the clay layers. According

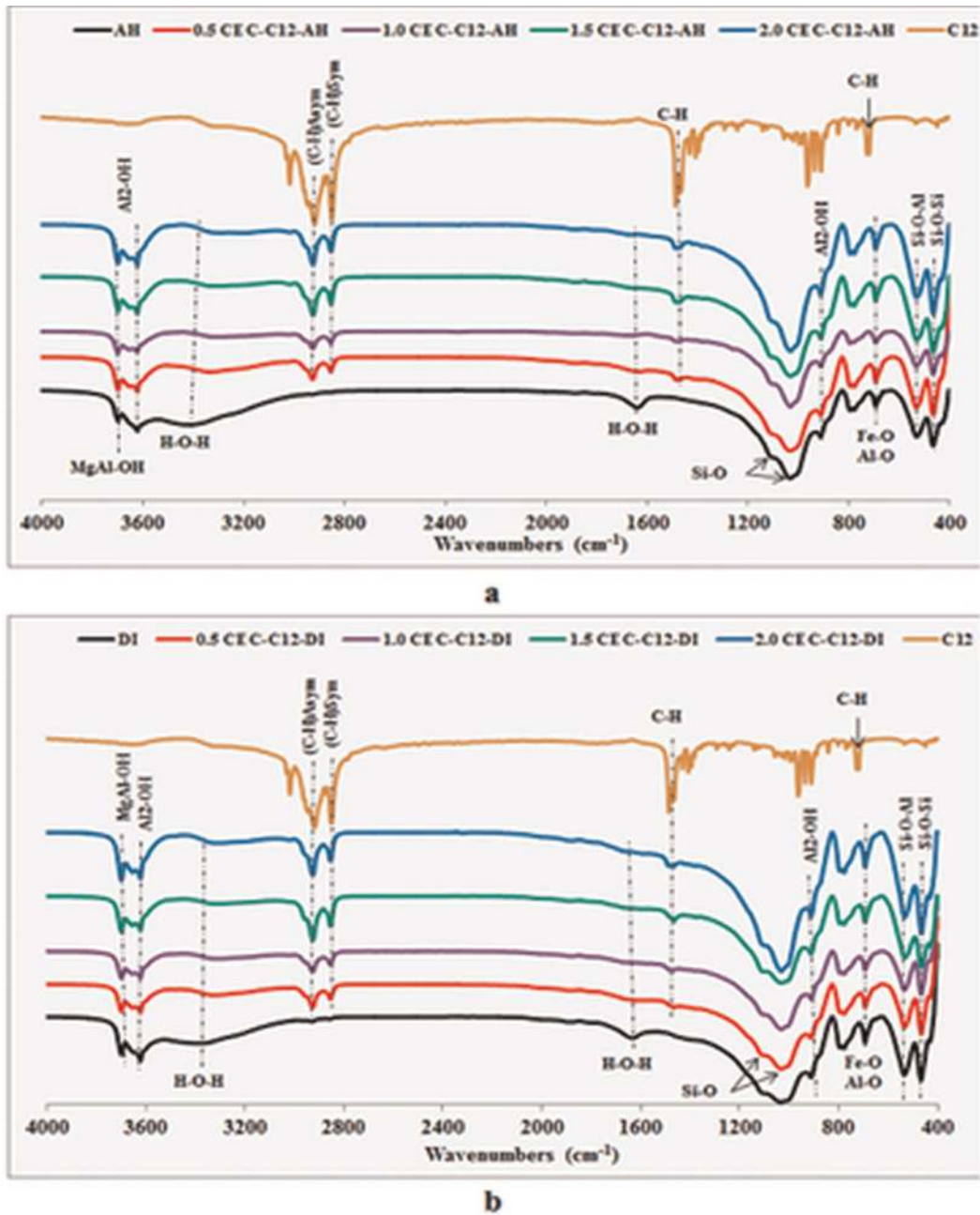


Figure 4. FTIR spectra of AH and DI raw clays, pure C_{12} surfactant and C_{12} -AH and C_{12} -DI organoclays.

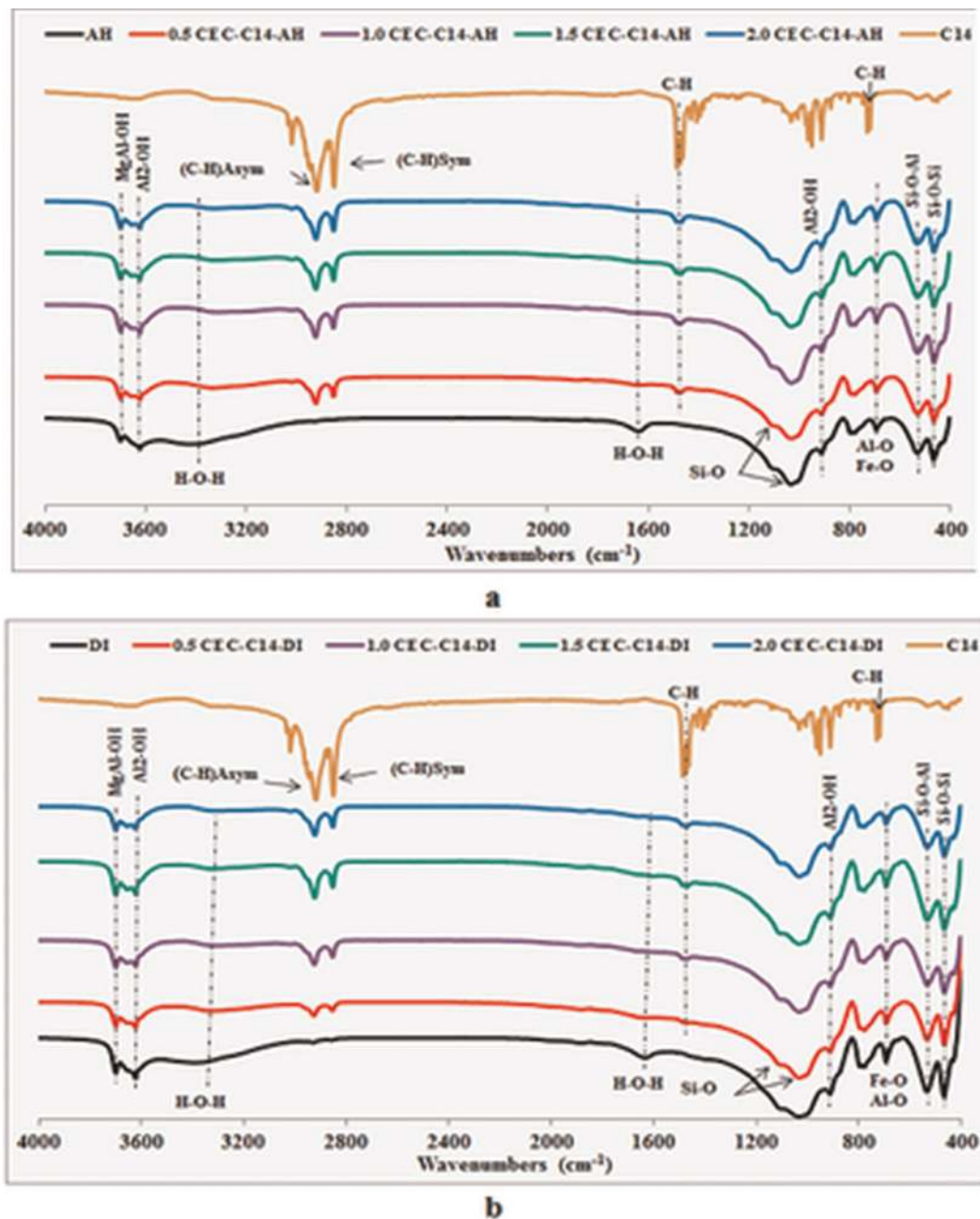


Figure 5. FTIR spectra of AH and DI raw clays, pure C_{14} surfactant and C_{14} -AH and C_{14} -DI organoclays.

to Madejová et al., the bands seen at around 3694 and 3620 cm^{-1} are associated to the stretching vibrations of the structural hydroxyl in AlMgO-H and $\text{Al}_2\text{O-H}$ of montmorillonite or kaolinite, respectively [31, 32]. In addition, the band observed at 3620 cm^{-1} on the spectra of raw clays and organoclays are characteristic of smectites containing high amount of Al in the octahedra sheet [31]. The Si-O stretching band is observed at 1100 cm^{-1} and the Si-O in-plane bending appears at 470 cm^{-1} in all FTIR spectra [32]. The Al_2OH bending vibration and the Al-O-Si deformations bands are observed at 913 and 536 cm^{-1} , respectively [32]. The Fe-O or Al-O out of plane bending vibrations appear at around 694 cm^{-1} [33].

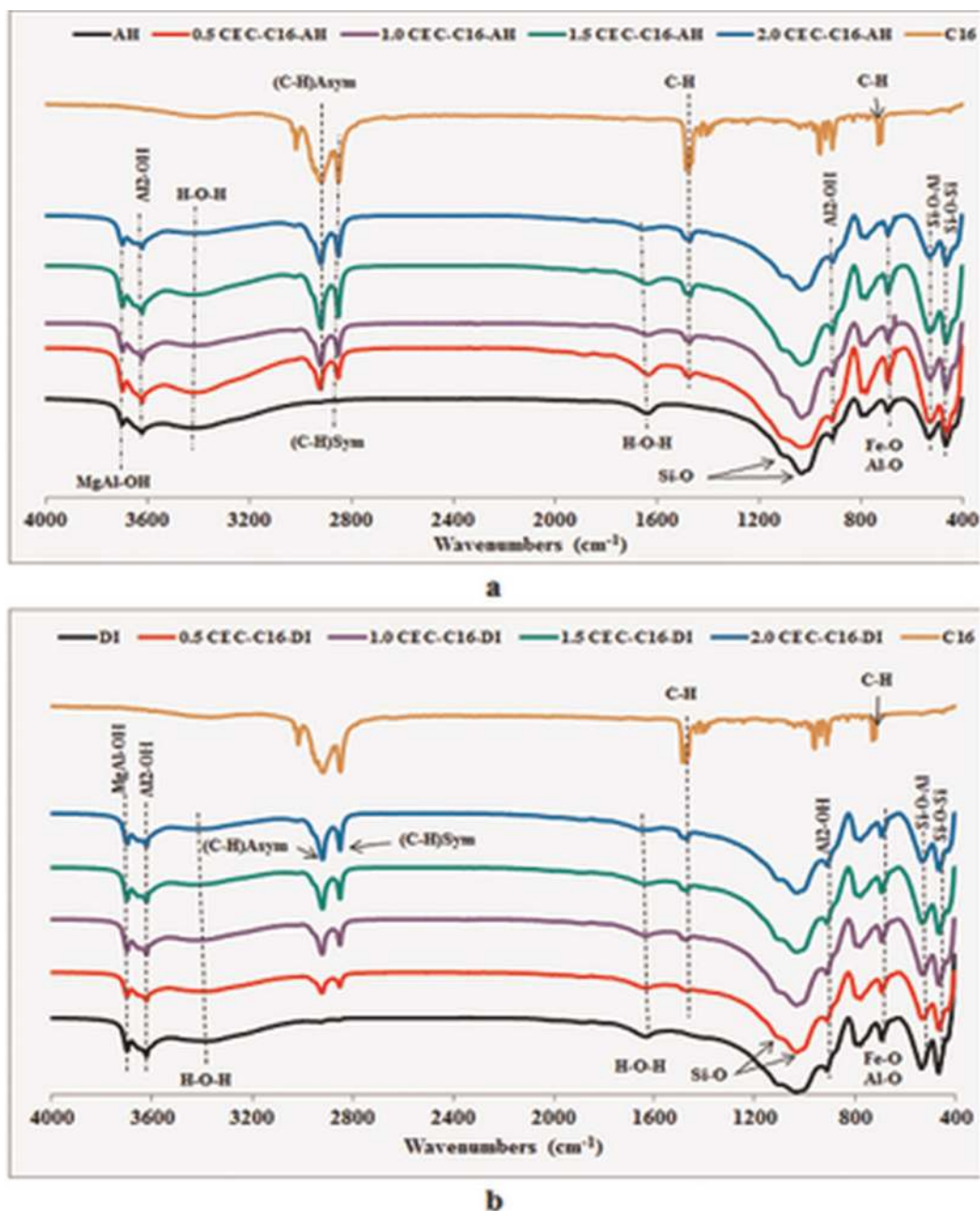


Figure 6.
FTIR spectra of AH and DI raw clays, pure C_{16} surfactant and C_{16} -AH and C_{16} -DI organoclays.

The asymmetric stretching bands of the CH_2 group shift slightly from 2927 to 2920 cm^{-1} depending on AH or DI raw clays, and surfactant loading, 0.5 to 2.0 CEC level due to the insertion of the C_{12} , C_{14} , C_{16} , and $2C_{12}$ surfactants. Likewise, the wavenumbers of the CH_2 symmetric stretching vibrations shift from 2855 cm^{-1} to 2850 cm^{-1} with increasing surfactant loading levels (Figures 4–7). The wavenumbers of asymmetric and symmetric CH_2 stretching bands of surfactants in the modified clays increase with the surfactant loading level's increase and approach the wavenumbers of the pure surfactant. This further sustains that the long alkyl chains are packed identically in clay layers as in the pure quaternary alkylammonium

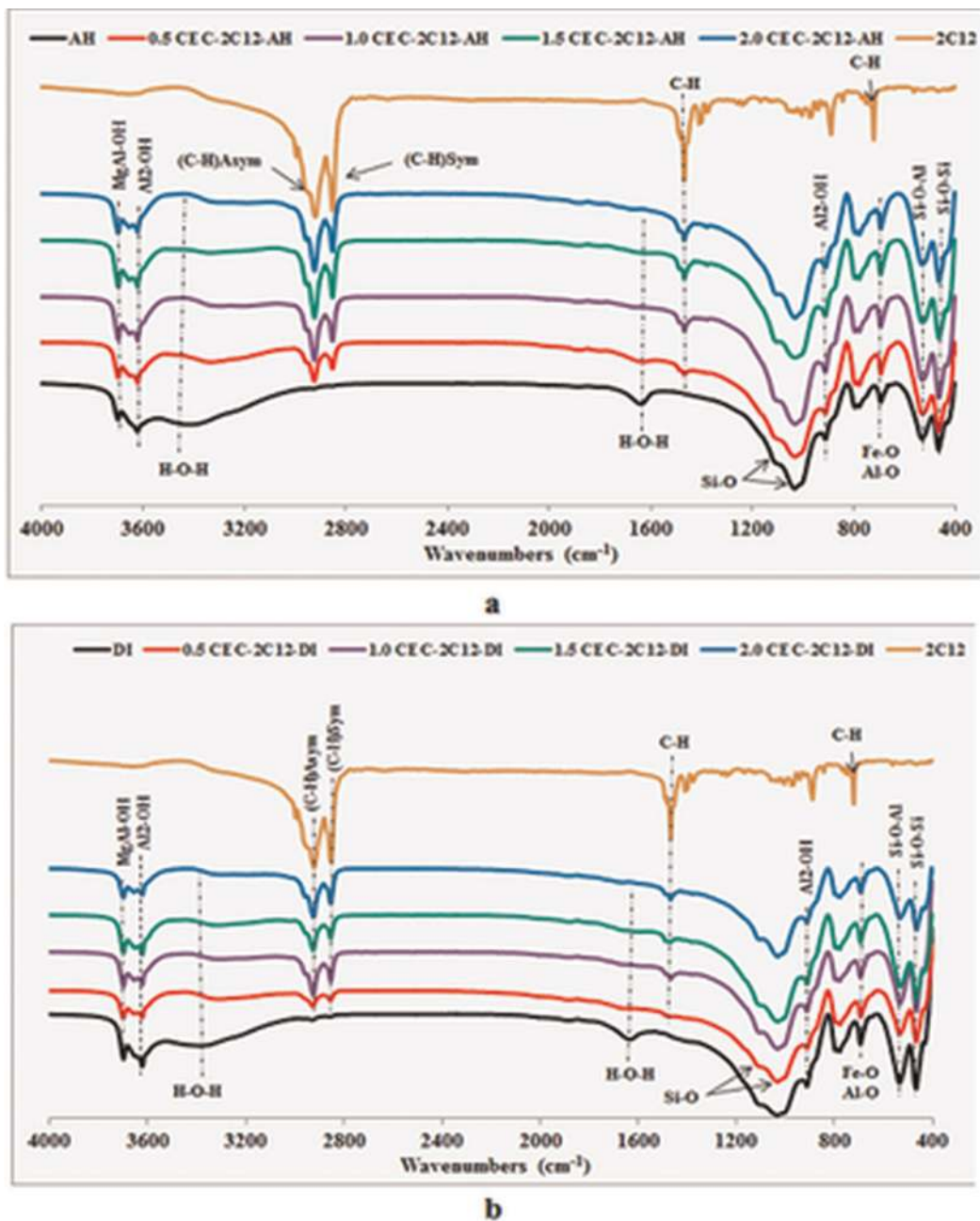


Figure 7. FTIR spectra of AH and DI raw clays, pure $2C_{12}$ surfactant and $2C_{12}$ -AH and $2C_{12}$ -DI organoclays.

bromide salts when the loading level tends to saturation. In fact, Kamitori et al. [29], Silva et al. [34] and Campanelli and Scaramuzza [35] reported that the surfactants (C_{12} , C_{14} , and C_{16}) are arranged in parallel planes inside a sheet and antiparallel as layers which alternate in the pure surfactant compound. The IR spectra of the organoclays support that the long alkyl chains orientation in the montmorillonite clay interlayers evolves progressively from a parallel orientation with clay sheets at lower loading level of surfactant to a standing position at higher loading level as reported in the literature [28, 36, 37].

Surfactants and wavenumbers (cm ⁻¹) of symmetric and asymmetric CH ₂ stretching								
Loading level	C ₁₂		C ₁₄		C ₁₆		2C ₁₂	
	CH ₂ Sym	CH ₂ Asym	CH ₂ Sym	CH ₂ Asym	CH ₂ Sym	CH ₂ Asym	CH ₂ Sym	CH ₂ Asym
AC clay								
0.5 CEC	2855	2926	2853	2923	2852	2923	2854	2925
1.0 CEC	2854	2926	2852	2923	2851	2921	2854	2924
1.5 CEC	2854	2925	2852	2922	2851	2920	2853	2924
2.0 CEC	2854	2925	2851	2921	2850	2920	2853	2921
DI clay								
0.5 CEC	2855	2926	2854	2926	2852	2923	2855	2927
1.0 CEC	2855	2926	2853	2924	2851	2922	2855	2925
1.5 CEC	2854	2924	2852	2923	2851	2921	2854	2925
2.0 CEC	2854	2924	2852	2922	2851	2920	2854	2924
Pure surfactants	2850	2918	2849	2918	2849	2919	2853	2921

Table 1.
 Change in CH₂ symmetric and asymmetric stretching vibration frequencies depending on the surfactant loading level and/or AH and DI clays.

The CH₂ asymmetric and symmetric stretching vibration bands frequencies in the pure surfactant molecules and the modified clays are summarized in **Table 1**. Contrary to the CH₂ asymmetric and symmetric stretching frequencies, the CH₂ scissoring and rocking vibrations frequencies observed at 1473 and 731 cm⁻¹, respectively [33], seem to be independent of the length of alkyl chain and level of loading.

Figures 4–7 show that the intensities of the band attributed to the hydroxyl of absorbed water seen at 3420 and 1635 cm⁻¹ turn down progressively when the surfactant loading level increases and this behavior is certainly related to the change of the raw clay properties from hydrophilic to hydrophobic ones [33, 38]. The FTIR spectra support the model of insertion of the quaternary alkylammonium cations into mineral clay interlayers as described below, **Figure 3**.

3. Influence of various factors in batch studies of bisphenol A removal

In the present work, various factors such as the adsorbents dose (clays and organoclays), the agitation time, the initial concentration, the pH, the surfactants loading level, and the temperature have been studied in order to elucidate the BPA sorption process. The methodologies used for all adsorption experiences are described elsewhere [39].

3.1 Effect of the agitation time on the BPA adsorption and kinetics

3.1.1 Effect of the agitation time on the BPA adsorption

Figure 8a–d represent the amount of BPA removed as a function of the agitation time for 200 mg as raw clays and organoclays dose. From **Figure 8a–d**, the BPA

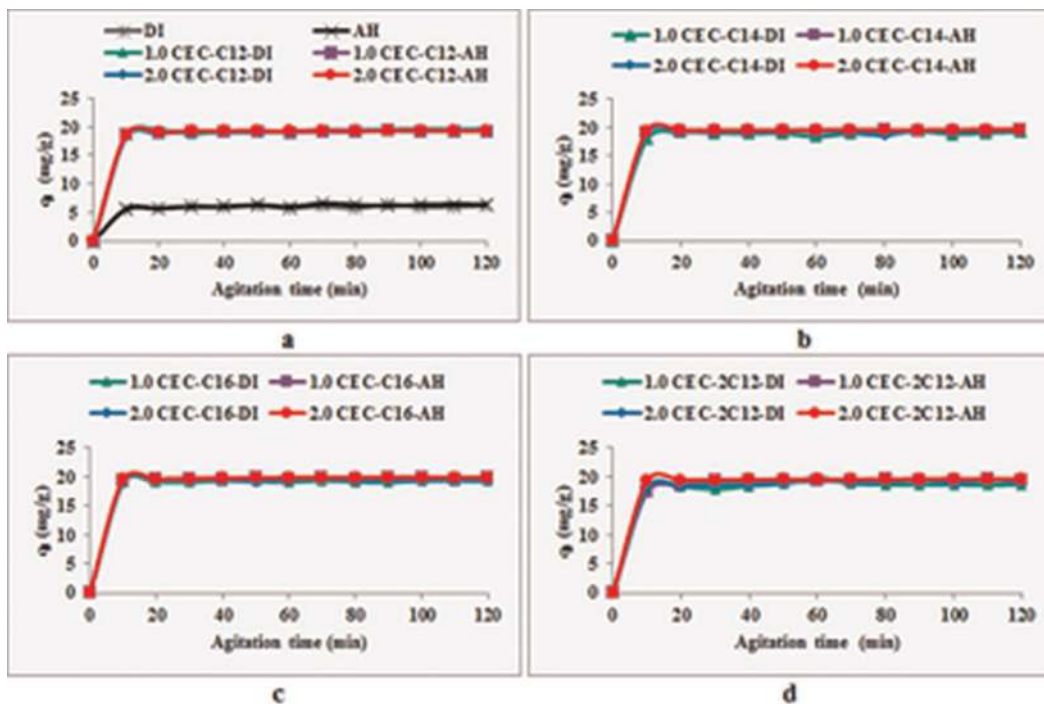


Figure 8. Effect of agitation time of BPA adsorption on the raw clays and organoclays: AH, DI, C₁₂-AH, C₁₂-DI (a), C₁₄-AH, C₁₄-DI (b), C₁₆-AH, C₁₆-DI (c) and 2C₁₂-AH, 2C₁₂-DI (d).

sorption depends on the duration of the agitation. In fact, it is seen that the amount of BPA removed from the aqueous solution by the raw and modified clays increases during the first 10 minutes and attains the equilibrium concentration within 20 minutes (**Figure 8a–d**).

Moreover, after 20 minutes as duration of agitation, no significant difference is observed according to the types of surfactants, the surfactant loading levels and the clays types (**Figure 8a–d**). This finding is unlike to those reported by Zheng et al. [10], where the quantity of BPA removed per unit of mass increases with the surfactant chain longer (C₁₂ to C₁₆). The agitation time required to reach the equilibrium is low and this suggests that the physisorption process is involved in the BPA removal [40]. It is also seen that the number of the surfactant long alkyl chain (C₁₂ and 2C₁₂) does not enhance the BPA adsorption and this results is unlike the results obtained by Park et al., where the quantity of BPA adsorbed increases with the increase of the number of long alkyl chain (C₁₂ and 2C₁₂) [8]. The ranking of the q_e values are from 18.7 to 19.8 mg of BPA/g of adsorbent for 200 mg as adsorbent dosage and 100 mg/L as BPA initial concentration for all the organoclays after 120 min as agitation time.

3.1.2 Kinetics

The constants of the pseudo-first and the pseudo-second kinetics have been evaluated by using the result of the effect of agitation time on BPA sorption and the obtained parameters are summarized into **Table 2** [39].

According to the high determination coefficients obtained ($R^2 > 0.98$) in the case of the pseudo-second order kinetic model when compared to those of the pseudo-

Clays or organoclays	Pseudo-first order			Pseudo-second order		
	K_1 (min^{-1})	q_{e1} (mg/g)	R^2	K_2 (min^{-1})	q_{e2} (g/mg.min)	R^2
AH	0.0145	0.958	0.6042	0.05	5.74	0.9831
DI	0.0065	0.683	0.2835	0.07	5.77	0.9871
1.0 CEC-C ₁₂ -AH	0.0053	0.701	0.5089	0.14	19.34	0.9999
2.0 CEC-C ₁₂ -AH	0.0062	0.427	0.3684	0.30	19.34	0.9999
1.0 CEC-C ₁₂ -DI	0.0064	1.055	0.5983	0.05	19.72	0.9998
2.0 CEC-C ₁₂ -DI	0.0110	0.412	0.6269	0.06	19.57	0.9999
1.0 CEC-C ₁₄ -AH	0.0053	0.701	0.6828	0.17	19.49	1.0000
2.0 CEC-C ₁₄ -AH	0.0062	0.427	0.7616	0.20	19.72	1.0000
1.0 CEC-C ₁₄ -DI	0.0064	1.055	0.2460	0.08	19.23	0.9993
2.0 CEC-C ₁₄ -DI	0.0110	0.412	0.2639	0.42	19.38	0.9991
1.0 CEC-C ₁₆ -AH	0.0225	0.554	0.2877	0.26	19.76	0.9998
2.0 CEC-C ₁₆ -AH	0.0330	0.571	0.7684	0.15	19.96	1.0000
1.0 CEC-C ₁₆ -DI	0.0031	0.854	0.2951	0.17	19.34	0.9998
2.0 CEC-C ₁₆ -DI	0.0308	1.263	0.4490	0.13	19.65	0.9998
1.0 CEC-2C ₁₂ -AH	0.0122	1.405	0.4870	0.05	19.69	0.9999
2.0 CEC-2C ₁₂ -AH	0.0062	0.598	0.8406	0.16	19.69	1.0000
1.0 CEC-2C ₁₂ -DI	0.0043	1.377	0.3742	0.13	18.76	0.9998
2.0 CEC-2C ₁₂ -DI	0.0112	0.848	0.4506	0.06	19.34	0.9989

Table 2.
 Kinetic constants of BPA removal on raw and modified clays.

first-order kinetic model ones ($R^2 < 0.85$) (Table 2), it can be concluded that the removal of BPA is better described by the pseudo-second-order kinetic model than the pseudo-first order kinetic model (Table 2). According to the literature, the pseudo-second-order kinetic model suggests that the chemisorption is the limiting step during the adsorption process [8, 16]. This result is like those reported previously on BPA removal using different adsorbents, such as graphene [9], C₁₆-palygorskite [19], surfactant-modified zeolite [26], organo-montmorillonites [3, 7, 8, 10, 16]. Generally, BPA removal from water using organoclays is better described by the pseudo-second-order kinetic than the pseudo-first order kinetic [7, 8, 10, 11, 16, 21].

3.2 Effect of pH on BPA adsorption

Figure 9 represents the amount of BPA removed when the pH increases from 2 to 12. It is seen that from acidic pH up to pH 8, the amount of BPA removed on all organoclays stays relatively constant (Figure 9a-d). For pH values ranging from 2 to 8, the q_e values ranged from 19.4 to 19.8 mg/g for all modified clays. This is followed by a decrease in the efficiency of organoclays in BPA sorption from aqueous solution having $\text{pH} \geq 8$. In fact, the q_e values decrease slightly from 19.8–19.4 mg/g to 19.6 – 16.6 mg/g when the pH value increases from 8 to 10. The q_e values turn down remarkably when the pH becomes higher than 10 for all the organoclays with higher

decrease for those loaded at 1.0 CEC. In fact, it is seen that the q_e values for all modified clays are ranged between 18 to 9.0 mg /g when the pH varies from 10 to 12. For pH = 12, the organoclays loaded at 2.0 CEC loading level give higher q_e values (9.2 to 18.5 mg/g) compared to those loaded at 1.0 CEC (9.0 to 13.9 mg/g). In addition, higher q_e values are obtained for the organoclays based on AH clay loaded at 2.0 CEC than the ones based on DI clay loaded at 2.0 CEC and only for C₁₄, C₁₆ and 2C₁₂ surfactants at a pH = 12. An opposite effect is observed for C₁₂ surfactant because the C₁₂-DI organoclays yielded high q_e values than the C₁₂-AH ones at 2.0 CEC loading level. This result which is obtained in the case of high pH value (pH = 12) seems to be linked to the high ability of AH clay to insert more quaternary alkylammonium cations than the DI clay one, due to the fact that AH clay has a high CEC value than the DI clay. The BPA molecules ionization degree depends on the pH of the aqueous solution and this seems to be another reason for the decrease in the q_e values when the pH reached 8 [2, 8, 9]. In fact, BPA molecules remain predominantly in their neutral form when pH ≤ 8, in their mono-ionized form when 8 ≤ pH ≤ 10 (pKa₁ = 9.6) and in the di-ionized form when pH ≥ 10 (pKa₂ = 11.3). Thus, the adsorption capacity's decrease of the modified clays seen in the case of alkaline pH range can be explained by the electrostatic repulsions existing between the negative charges of the clay's surface and those bisphenolate anions [9]. In the present work, the efficiency of organoclays to sorb BPA in alkaline solution (pH ≥ 8) is less influenced for organoclays loaded at 2.0 CEC than those ones loaded at 1.0 CEC. This result sustains that the modified clays loaded at 2.0 CEC maintain high affinity toward the mono-ionized and the di-ionized forms of BPA at high pH values. Rathnayake et al. reported a possible retention of surfactant molecules onto the clays surface, which provides sites having hydrophobic character for BPA removal [16]. **Figure 9** shows that in the case of a solution with

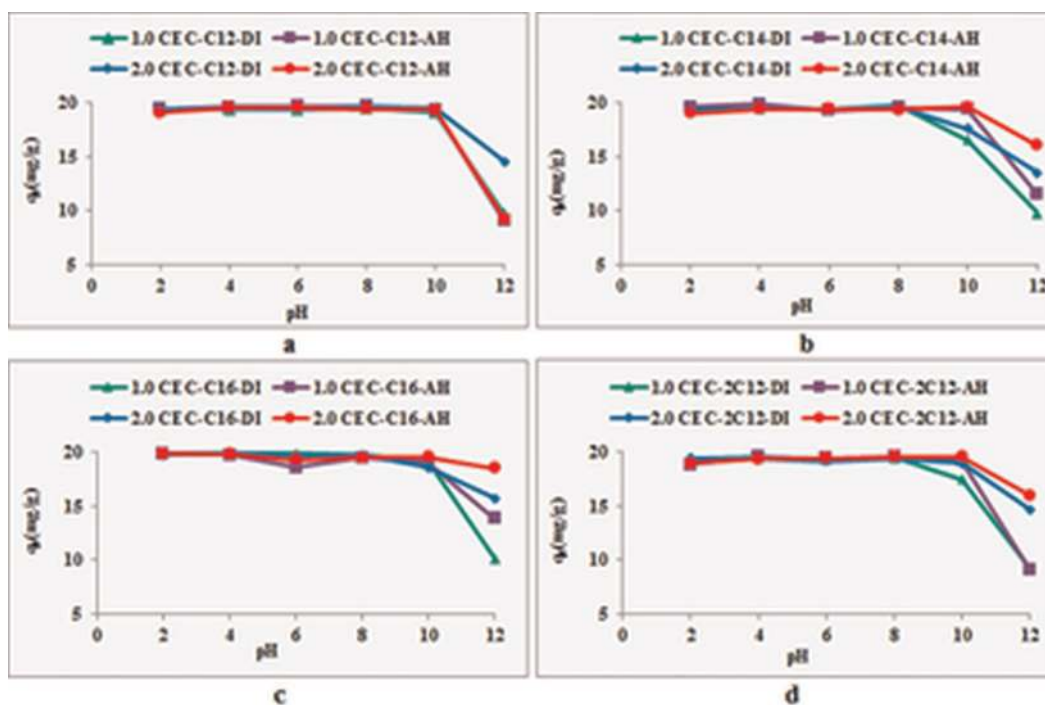


Figure 9. Effect of pH on the adsorption of BPA by organoclays: C₁₂-AH and C₁₂-DI (a), C₁₄-AH and C₁₄-DI (b), C₁₆-AH and C₁₆-DI (c), 2C₁₂-AH and 2C₁₂-DI (d).

pH \leq 8, 1.0 CEC as loading level is sufficient to get organoclays having high removal capacities for BPA, whereas in the case of a solution with pH value \geq 8, 2.0 CEC as loading level is required to get organoclays having high removal capacities toward BPA. Particularly, when the pH reaches 12, we recommend the employment of either 2.0 CEC- C_{14} -AH, 2.0 CEC- C_{16} -AH, 2.0 CEC- $2C_{12}$ -AH organoclays, or 2.0 CEC- C_{12} -DI organoclay.

3.3 Effect of BPA initial concentration on BPA adsorption and isotherms

3.3.1 Effect of BPA initial concentration on BPA adsorption

Figure 10a-d represent the amount of BPA removed as a function of the initial concentration for 12 hours as agitation duration.

It is seen that the quantity of BPA removed from the aqueous solution increases rapidly up to 200 mg/L as initial concentration. Figure 10a-d show that the equilibrium adsorption capacity of BPA on modified clays increases when the initial concentration increases and this until to the saturation of available reactive sites [11]. As shown in Figure 10a-d, all curves on the effect of initial concentration on BPA adsorption onto the organoclays are almost relatively linear up to 200 mg/L and become parabolic after that value. As a result, the removal of BPA onto the organoclays is affected by its initial concentration. This can be explained by the fact that before 200 mg/L is BPA initial concentration, there are more available active sites onto the organoclays which causes a better elimination rate of BPA. However, the number of active sites decrease gradually after 200 mg/L and this induces less efficient adsorption. As reported in previous studies, the present work shows that the

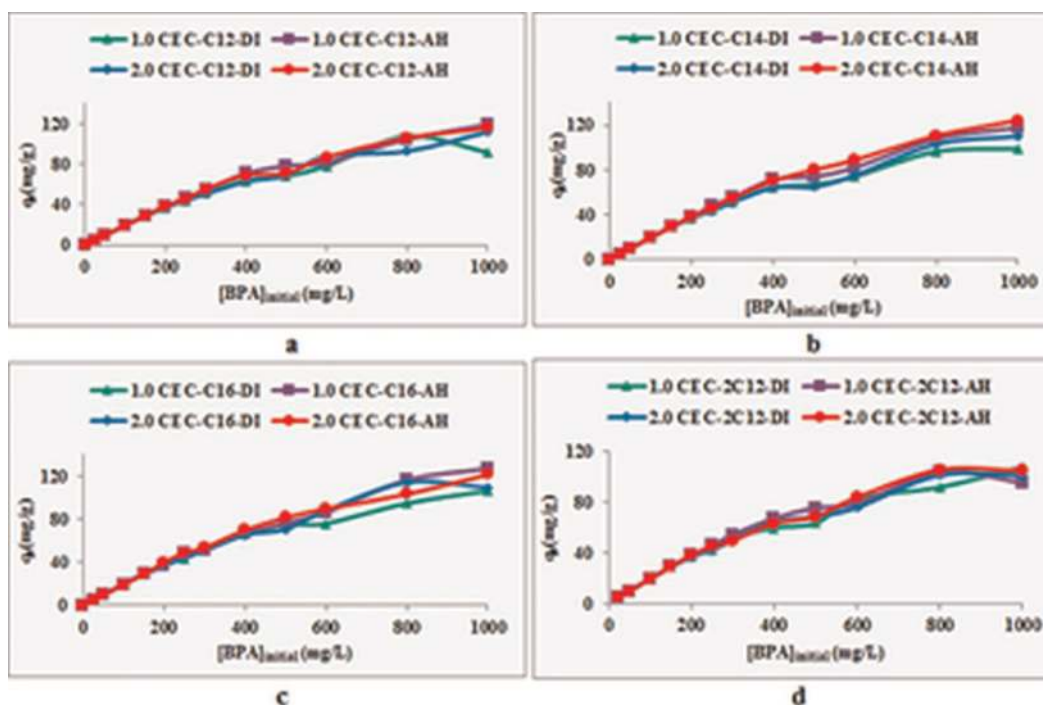


Figure 10. Initial concentration effect on BPA adsorption by organoclays: C_{12} -AH and C_{12} -DI (a), C_{14} -AH and C_{14} -DI (b), C_{16} -AH and C_{16} -DI (c), $2C_{12}$ -AH and $2C_{12}$ -DI (d).

increase of BPA initial concentration causes an increase in the q_e value. For example, for 200 mg as adsorbent dose, when we increase the initial concentration from 25 to 1000 mg/L, the q_e values increase from 4.8–4.9 mg/g to 88–127 mg of BPA/g of adsorbent for all the organoclays.

3.3.2 Isotherms of BPA adsorption

The effect of the initial concentration has been used to evaluate the Langmuir and Freundlich isotherms parameters [39] and the obtained values are included in **Table 3**. **Table 3** shows that the determination coefficient (R^2) values are better in the case of the Langmuir isotherm ($0.89 \leq R^2 \leq 0.99$) than the Freundlich isotherm ($0.89 \leq R^2 \leq 0.95$) for all the organoclays and this corresponds to a monolayer adsorption of BPA. The above results resemble to those obtained on BPA adsorption using organically modified montmorillonite [7, 10] and amphoteric modified vermiculite [17].

3.4 Effect of surfactant loading level on BPA adsorption

The **Figure 11a-d** represent the q_e values of adsorbed BPA as a function of the surfactant loading level (aqueous solution pH around 5–6). **Figure 11a-d** show high elimination rate of BPA onto AH and DI modified clays compared to the untreated ones. This result states that the intercalation of the quaternary alkylammonium into the clays' interlayers induces a strong removal level of BPA from aqueous solution. As

Organoclays	Freundlich			Langmuir		
	K_F (L/g)	n	R^2	K_L (L/mg)	q_m (mg/g)	R^2
1.0 CEC-C ₁₂ -AH	13.2355	2.5588	0.9136	0.044	114.9	0.9700
2.0 CEC-C ₁₂ -AH	12.4460	2.5208	0.9172	0.047	108.7	0.9745
1.0 CEC-C ₁₂ -DI	10.9968	2.6199	0.9106	0.044	92.6	0.9654
2.0 CEC-C ₁₂ -DI	10.2492	2.4337	0.8963	0.019	113.6	0.8890
1.0 CEC-C ₁₄ -AH	12.0903	2.2188	0.9270	0.046	125.0	0.9756
2.0 CEC-C ₁₄ -AH	10.6440	2.2311	0.9464	0.050	125.0	0.9766
1.0 CEC-C ₁₄ -DI	11.0012	2.6100	0.9060	0.038	97.1	0.9635
2.0 CEC-C ₁₄ -DI	10.8786	2.2750	0.9100	0.036	96.1	0.9460
1.0 CEC-C ₁₆ -AH	12.1521	2.4384	0.9407	0.310	126.6	0.9379
2.0 CEC-C ₁₆ -AH	11.4857	2.3180	0.8853	0.044	119.1	0.9800
1.0 CEC-C ₁₆ -DI	10.5018	2.6157	0.8885	0.046	112.4	0.9579
2.0 CEC-C ₁₆ -DI	10.7585	2.4050	0.9280	0.034	111.1	0.9747
1.0 CEC-2C ₁₂ -AH	10.6867	2.4290	0.8920	0.051	99.0	0.9900
2.0 CEC-2C ₁₂ -AH	10.1757	2.3430	0.8881	0.035	108.7	0.9659
1.0 CEC-2C ₁₂ -DI	11.2105	2.6302	0.9215	0.060	87.7	0.9704
2.0 CEC-2C ₁₂ -DI	10.6515	2.5589	0.9482	0.031	103.1	0.9680

Table 3. Isotherm parameters of BPA adsorption on the organoclays.

a result of the surfactants intercalation, the amount of BPA sorbed per mass of adsorbent (q_e) increases remarkably from 1.4 and 2.5 mg/g for DI and AH raw clays, respectively, to q_e values higher than 19.5 mg/g in the case of organoclays loaded at 2.0 CEC loading level. We notice that the efficiency of the modified clays to remove BPA from aqueous solution is not significantly affected when the surfactant loading level increases from 1.0 to 2.0 CEC for $\text{pH} \leq 8$. The below result is unlike those reported by Park et al. who found that the amount of BPA adsorbed increases when the surfactant loading level increases [8]. According to **Figure 11**, a better elimination rate is obtained in acidic solution when the AH and DI raw clays are loaded at least at 1.0 CEC loading level of the C_{12} , C_{14} , C_{16} , and $2C_{12}$ surfactants, which result is identical to the those obtained by studying the effect of the pH on the BPA sorption.

3.5 Effect of temperature on BPA adsorption and thermodynamics

3.5.1 Effect of temperature on BPA adsorption

The temperature effect on BPA adsorption onto the organoclays was evaluated at different temperatures (303, 313 and 323 K) and the obtained results are presented in **Figure 12a–d**.

Figure 12 shows that the increase of the temperature from 30 to 50°C causes a slight drop of the amount of BPA removed on the organoclays. This result shows that BPA removal is more propitious for lower temperatures. In fact, the ranking of the q_e values obtained are from 19.6 and 18.5 mg of BPA/g of organoclays and this occurs when the temperature increases from 30 to 50°C. This is due to the exothermic nature of the adsorption reaction [41, 42]. This means that the temperature affects weakly

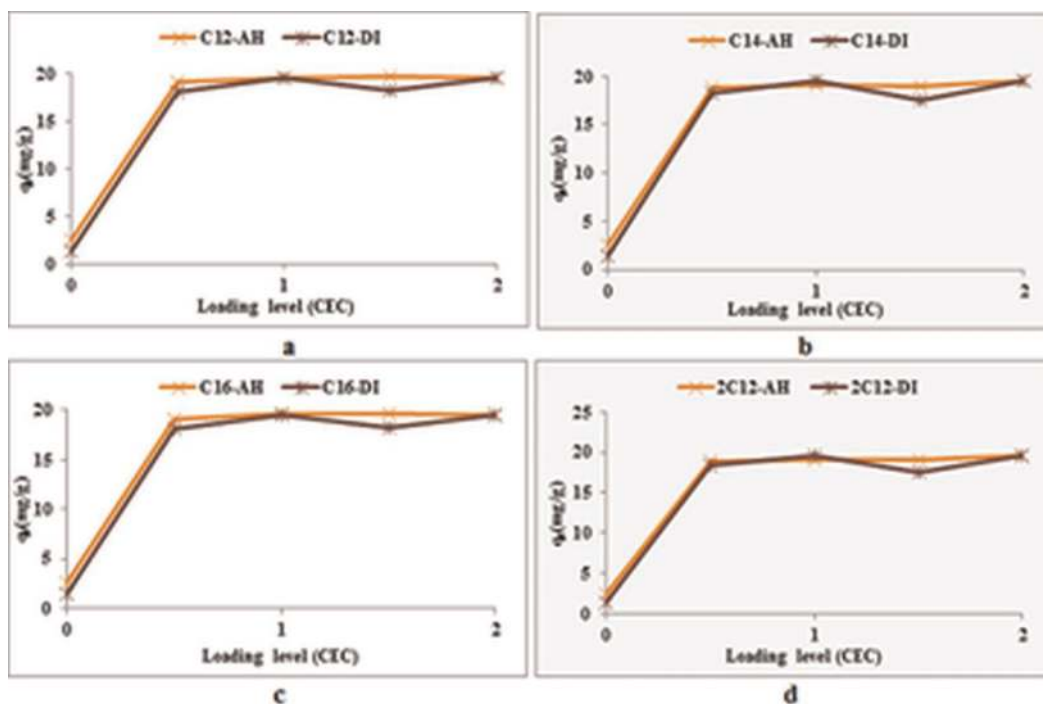


Figure 11.
The C_{12} , C_{14} , C_{16} , and $2C_{12}$ surfactants loading level effect on the BPA adsorption.

the uptake of BPA onto the organoclays. The organoclays maintain high removal level toward BPA molecules at a temperature up to 50°C ($q_e \geq 18.5$ mg/g).

3.5.2 Thermodynamics

Figure 12a-d represent the quantities of BPA removed on the organoclays at different temperatures (303, 313, and 323 K). These figures show that the quantity of BPA removed on the organoclays drop weakly with the increase of the temperature from 30 to 50°C and this results means that the adsorption process is favored at lower temperature.

The results obtained by studying the effect of the temperature on BPA removal have been used to calculate the thermodynamic parameters such as Gibbs free energy (ΔG), enthalpies change (ΔH), and entropy change (ΔS) and the calculated values are included in **Table 4**. All enthalpies change values (**Table 4**) are less than zero ($\Delta H \leq 0$) and this suggests that the uptake of BPA from water using organoclays is exothermic, which is also sustained by the drop of the amount of BPA removed with the increase of the temperature. From the literature, it can be noted that when the values of ΔH are ranged from 2.1 to 20.9, a physisorption is involved in the adsorption process, but chemisorption intervenes for a value ranging from 80 to 200 kJ/mol [43]. In this work, the ΔH values evaluated from the experimental data of BPA sorption onto the organoclays are ranged from -76.5 to -13 kJ/mol. According to the ΔH values, different forces and interactions are supposed to be involved in the adsorption process [19]: between 4 and 10 kJ/mol for Van der Waals interactions, about 5 kJ/mol for hydrophobic interactions, between 2 and 40 kJ/mol for hydrogen bond interactions, around 40 kJ/mol for coordination exchange interactions, between 2 and 29 kJ/

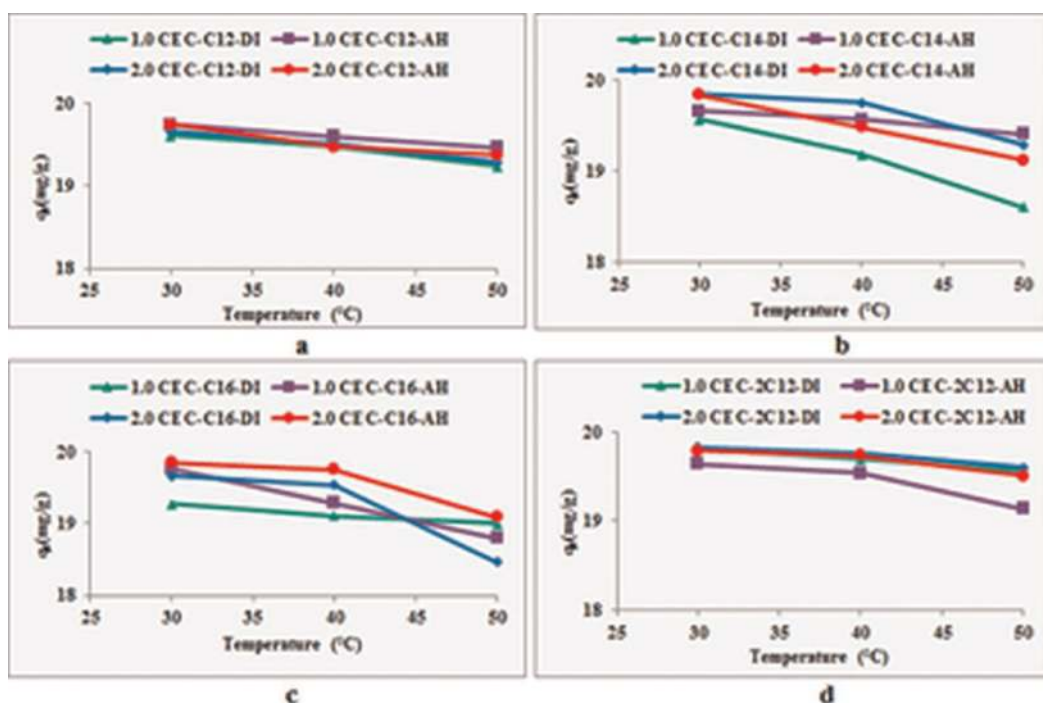


Figure 12. Effect of the temperature on BPA adsorption by the organoclays: C₁₂-AH and C₁₂-DI (a), C₁₄-AH and C₁₄-DI (b), C₁₆-AH and C₁₆-DI (c), 2C₁₂-AH and 2C₁₂-DI (d).

mol for dipole bond, and up to 60 kJ/mol for chemical bond. All ΔH values obtained in the present work are ranged from -76.5 to -13 kJ/mol and this suggests that the following interactions can intervene during the adsorption process: dipole-bonding, coordination exchange, hydrogen bonding and chemical bond. From the lower adsorption efficiency of the raw clays toward BPA molecules, we suggest that the hydrogen bonding contributes weakly to the BPA sorption in the present work [11]. From the obtained results, it can be postulated that both physisorption (Van der Waals forces, hydrogen bonding) and chemisorption (hydrophobic interactions, BPA phenolic rings and alkylammonium group interactions) intervene during BPA sorption onto the organically modified clays. The results obtained in the present work resemble to those reported previously on the adsorption of Rhodamine-B onto activated carbon [44]; adsorption of Acid Red G dye onto C_{18} -montmorillonite [45], adsorption of carbofuran onto biochars [46]. According to previous reported results, adsorption can be due to the intervention of both physisorption and chemisorption and this coexistence is described as the following: (i) a first rapid chemisorption followed by a slow physisorption [47]; (ii) contributions of both processes [48]; (iii) simultaneous occurring of both physisorption and chemisorption with predominant chemisorption [46] or without any predominant process [49].

Table 4 indicates that $\Delta G \leq 0$ and this suggests that the uptake of BPA molecules by the organoclays is spontaneous. The drop of the ΔG values with the increase of the temperature shows that the capacity of the organoclays to sorb BPA molecules is inversely dependent on the temperature [9, 19, 50], which also indicates a spontaneous process at low temperatures. In addition, ΔG decreases with the increase of the temperature (**Table 4**) and this shows that BPA sorption is thermodynamically favored at room temperature than at higher temperatures [51]. Gibbs free energy ranging from -20 to 0 kJ/mol corresponds to physisorption mechanism, while values ranging from -80 to -400 kJ/mol suggest chemisorption mechanism [52]. In the present work, the Gibbs free-energy values are ranged from -11 to -6 kJ/mol (**Table 4**) and this result means that the physisorption intervenes in BPA removal from water. According to previous literature results, when ΔS value is higher than zero ($\Delta S > 0$) the interactions at the solid-liquid interface are aleatory, while value less than zero ($\Delta S < 0$) suggests inverse interactions [50, 53]. In the present work, the ΔS values are all negative ($-30 \leq \Delta S \leq -205$ J/mol) and this suggests a decrease of the disorder at the solid-liquid interface, while ΔG and ΔH negative values indicate spontaneous and exothermic processes of BPA sorption onto the organoclays [8].

Our study highlights the fact that the adsorption is spontaneous ($\Delta G < 0$), exothermic ($\Delta H < 0$) with negative entropy values ($\Delta S < 0$) and these results are in agreement with those previously reported on the adsorption of BPA using organoclays [7, 8, 10], C_{16} -modified palygorskite [19], and surfactant-modified zeolite [22, 54].

4. Conclusion

The solid-state reaction methodology was successfully used to intercalate three cationic alkyltrimethylammoniums ($n-C_{12}H_{25}(CH_3)_3 N^+$, $n-C_{14}H_{29}(CH_3)_3 N^+$ and $n-C_{16}H_{33}(CH_3)_3 N^+$) and one di-alkyldimethylammonium ($(n-C_{12}H_{25})_2(CH_3)_2 N^+$) into two natural clays containing Ca-montmorillonite as main clay type. XRPD shows that the d_{001} basal spacing increases after the intercalation of the cationic surfactants and this proved the swelling of the clays layers. It is observed that at 2.0 CEC as surfactant loading level, the basal spacing (d_{001}) of the prepared organoclays are

Organoclays	Thermodynamics constants					
	Temperature (K)	ΔG (kJ/mol)	R^2	ΔH (kJ/mol)	ΔS (J/mol.K)	R^2
1.0 CEC-C ₁₂ -AH	303	-8.651	0.9899	-31.382	-80.782	0.9830
	313	-8.936				
	323	-9.222				
2.0 CEC-C ₁₂ -AH	303	-8.525	0.9938	-38.429	-103.958	0.9978
	313	-8.806				
	323	-9.087				
1.0 CEC-C ₁₂ -DI	303	-7.557	0.9927	-27.847	-72.486	0.9838
	313	-7.806				
	323	-8.055				
2.0 CEC-C ₁₂ -DI	303	-7.861	0.9893	-31.537	-83.439	0.9976
	313	-8.120				
	323	-8.380				
1.0 CEC-C ₁₄ -AH	303	-8.035	0.9941	-23.714	-57.736	0.9927
	313	-8.300				
	323	-8.566				
2.0 CEC-C ₁₄ -AH	303	-8.445	0.9623	-62.330	-181.278	0.9777
	313	-8.724				
	323	-9.003				
1.0 CEC-C ₁₄ -DI	303	-6.734	0.9756	-49.269	-144.431	0.9993
	313	-6.956				
	323	-7.179				
2.0 CEC-C ₁₄ -DI	303	-9.018	0.9748	-64.258	-185.011	0.9950
	313	-9.316				
	323	-9.613				
1.0 CEC-C ₁₆ -AH	303	-7.897	0.9583	-69.123	-205.322	0.9666
	313	-8.158				
	323	-8.418				
2.0 CEC-C ₁₆ -AH	303	-8.854	0.9737	-76.408	-223.372	0.9989
	313	-9.147				
	323	-9.439				
1.0 CEC-C ₁₆ -DI	303	-6.454	0.9984	-13.375	-30.347	0.9811
	313	-6.666				
	323	-6.881				
2.0 CEC-C ₁₆ -DI	303	-7.216	0.9994	-48.506	-139.467	0.9996
	313	-7.454				
	323	-7.692				

Organoclays	Thermodynamics constants					
	Temperature (K)	ΔG (kJ/mol)	R^2	ΔH (kJ/mol)	ΔS (J/mol.K)	R^2
1.0 CEC-2C ₁₂ -AH	303	-7.514	0.9924	-36.103	-99.726	0.9989
	313	-7.762				
	323	-8.010				
2.0 CEC-2C ₁₂ -AH	303	-9.237	0.9940	-34.668	-90.032	0.9974
	313	-9.541				
	323	-9.846				
1.0 CEC-2C ₁₂ -DI	303	-9.177	0.9867	-34.165	-87.729	0.9911
	313	-9.480				
	323	-9.783				
2.0 CEC-2C ₁₂ -DI	303	-9.398	0.9883	-34.956	-87.305	0.9888
	313	-9.708				
	323	-10.018				

Table 4.
 Thermodynamic constants of BPA adsorption on the modified clays.

25 Å and 32 Å for those treated with C₁₂ and C₁₄ surfactants respectively and up to 38 Å for those treated with C₁₆ and 2C₁₂ surfactants. The appearance of the CH₂ symmetric and asymmetric stretching bands on the IR spectra at around 2850 and 2920 cm⁻¹, respectively, proves successful insertion of the surfactants into clays interlayers. The values of the frequencies related to the CH₂ symmetric and asymmetric stretching bands of the surfactants in organoclays diminish and tend to those of the pure surfactants when the surfactant loading level increases. The hydrophilic and organophobic properties of the raw clays change to hydrophobic and organophilic ones upon the insertion of the surfactants into the clays interlayers. The present work shows that the organoclays synthesized by using AH and DI local clays lead to a high removal efficiency toward BPA molecules in aqueous solutions. In fact, higher values of q_m (from 88 to 127 mg/g) were achieved for BPA adsorption onto organoclays based on AH and DI clays and n-C₁₂H₂₅(CH₃)₃N⁺, n-C₁₄H₂₉(CH₃)₃N⁺, n-C₁₆H₃₃(CH₃)₃N⁺ and (n-C₁₂H₂₅)₂(CH₃)₂N⁺ surfactants. The BPA removal was influenced by the adsorbent dose, the initial concentration, and the agitation time, the surfactant loading level, the pH and the temperature. The organoclays efficiencies to sorb BPA molecules from water decrease significantly when the pH value reached 10. It is also noted that when the level of surfactants is 2.0 CEC, the efficiency of the organoclays to sorb BPA is less influenced in alkaline solution than the one of those loaded at 1.0 CEC. The present work indicates that organoclays loaded at 1.0 CEC level are efficient for BPA removal from acidic solution, and those loaded at 2.0 CEC level are useful to achieve high elimination rate of BPA in alkaline solution. The results obtained from the thermodynamic and kinetic investigations show that both physisorption and chemisorption intervene in the retention of BPA species. The present work strongly sustains that organoclays prepared via solid-state intercalation are effective adsorbents as those obtained via solid-liquid reactions for BPA removal from water.

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Conflict of interest

The authors declare no conflict of interest.


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