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Kinetic and thermodynamic study of the adsorption of As(III) from aqueous solutions by naturally occurring and modified montmorillonites

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ABSTRACT

Adsorption of As(III) from aqueous solutions using naturally occurring and modified Algerian montmorillonites was investigated as a function of contact time, pH and temperature. Kinetic studies reveal that uptake of As(III) ions is rapid within the first 3 hours and it slows down thereafter. Equilibrium studies show that As(III) shows the highest affinity towards Acidic-montmorillonite even at very low concentration of arsenic. A pseudo-second-order chemical reaction model was obtained for As(III). Adsorption isotherms of As(III) fitted the Langmuir and Freundlich isotherm models well. From the thermodynamic parameters, it is concluded that adsorption is exothermic, spontaneous and favorable. The results suggest that M_1, M_2 and Acidic-M_2 could be used as effective filtering materials for removal of arsenic from water.

Keywords: *adsorption; clay; ion exchange; arsenic; montmorillonite.*

1. INTRODUCTION

Arsenic (As) is a notoriously toxic element which is ubiquitous in the environment [1, 2]. Arsenic has been classified as a carcinogen agent who poses a high risk to human health if it is released to the environment. [3]. The main source for people's exposure to As is the contact with water, especially groundwater, which contains As. Arsenicosis is a serious disease mainly caused by drinking As-contaminated groundwater [4]. Many studies have shown that As can also be accumulated in seafood [5-7]. Chronic exposure of humans to high concentrations is associated with skin lesions, peripheral vascular disease, hypertension, blackfoot disease and high risk of cancers [8, 9]. A wide range of physical and chemical treatment technologies have been applied for the removal of As from contaminated water, such as coagulation, ultrafiltration, ion exchange, lime softening, adsorption on iron oxides or activated alumina, and reverse osmosis [10]. All these treatments present two main disadvantages. Firstly, a deposited sludge of As compounds is obtained. Secondly, the operational costs of these treatments are high. Consequently there is growing interest in using low-cost materials to remove As from water [11]. Among many other kinds of identified low-cost natural sorbents, clay, kaolinite, bentonite, montmorillonite, goethite, spodic, and aquifer materials have high adsorption capacities for As [12-15]. The adsorption capability of clays is usually determined by their chemical composition and pore structure, but also by the pH of the medium the

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adsorbent is in contact with arsenic ions [16]. The aim of this work is to investigate the adsorption capacity of two Algerian natural montmorillonites and an acid-modified montmorillonite for As(III) ions from aqueous media solutions. The optimum conditions, equilibrium data and adsorption kinetics for As(III) were obtained. The effects of different variables, like As(III) concentration, pH and temperature have been analyzed. Equilibrium experimental data were fitted to Langmuir and Freundlich isotherm models and a kinetic study has also been performed.

2. EXPERIMENTAL SECTION

2.1. Reagents. Arsenic(III)-containing solutions with concentration ranging from 1 to 2500 (mg.L^{-1})were prepared from analytical grade As_2O_3 (Merk) dissolved in double-distilled water in a 0.1 M NaOH solution. The pH was adjusted to the required value by adding appropriate amounts of 0.1 M HNO_3 solution.

2.2. Preparation of adsorbents. Two clays were obtained from Algeria: a sodium montmorillonite from Telmcen (M_1) and a no-sodium montmorillonite from Mostaganem (M_2). The clay samples were washed with distilled water to remove impurities; the raw-montmorillonites 20 g were crushed for 20 min using a Prolabo ceramic balls grinder. They were then dried at 423 *K* for 2 h and stored in tightly stopered glass bottles for later use (samples M_1 and M_2). The M_2 sample was activated in acid (acidic-M_2) by the procedure of Belbachir et al. [17]. Briefly, this procedure consists on refluxing 20 g of montmorillonite (M_2) in 200 mL of 0.25 M H_2SO_4 for 3 h. The resulting acidic activated clay was centrifuged and washed with water several times until it was free of SO_4^{2-} and the pH of the washing was 6.8. Finally the sample was dried at 378 *K* in air until constant weight. This acid activation also removes sodium from its composition. The chemical composition of the three different clays is included in Table 1.

Table 1: Composition (wt%) of sodium montmorillonite (M_1), no-sodium montmorillonite (M_2) and acid activated montmorillonite (acidic-M_2).

Composition (wt%)	SiO_2	Al_2O_3	MgO	Fe_2O_3	K_2O	TiO_2	Rb_2O	ZrO_2	SO_3	CaO	Na_2O	P_2O_5
M_1	64.45	16.77	3.37	2.45	2.28	0.17	0.03	0.01	–	0.01	10.40	–
M_2	74.43	15.95	1.91	2.81	2.31	0.14	0.02	0.01	0.11	1.88	–	0.33
Acidic-M_2	75.62	17.96	2.87	1.78	1.60	0.12	–	0.01	0.05	–	–	–

2.3. Characterization of the clay adsorbents. The porous texture of all samples was determined by physical adsorption of gases (N_2 at 77 *K* and CO_2 at 273 *K*) using an automatic adsorption system (Autosorb-6, Quantrachrome Corporation) after sample out-gassing at 383 *K* under vacuum for 4 h. The experimental details are reported elsewhere [18]. From gas adsorption isotherms the BET specific surface area, S_{BET}, the volume of mesopores, V_{meso}, and both the total volume of micropores (below 2nm in diameter), $V_{DR}(N_2)$, and the volume of the narrowest micropores (below 0.7 nm in diameter), $V_{DR}(CO_2)$ were worked out for all three adsorbent materials [19-21]. Porous texture characterization data are summarized in Table 2. These data indicate that the clays are basically mesoporous materials with some amount of micropores. In the case of adsorbate nitrogen analysis, the acidic modification of M_2-type montmorillonite gives rise to a significant increase in S_{BET} and in the volume of both mesopores and total micropores, whereas the number of narrowest micropores remains unchanged in the case of adsorbate CO_2 analysis. This result has been attributed to a change from the laminar structure of the pristine clay to a delaminated structure, as revealed by transmission electron microscopy images [18]. Also, the increase in the volume of meso- and micro-pores was associated with the dissolution of exchangeable cations like Na and the partial dissolution of structural cations, like Fe^{3+} and Mg^{2+}, in accordance with X-Ray fluorescence measurements [18].

Table 2: Textural characterization of sodium montmorillonite (M_1), no-sodium montmorillonite (M_2) and acid activated montmorillonite (acidic-M_2).

Samples	S_{BET} (m^2/g)	$V_{DR}(N_2)$ (cm^3/g)	$V_{DR}(CO_2)$ (cm^3/g)	V_{meso} (cm^3/g)
M_1	32.1	0.1	0.01	0.16
M_2	24.6	0.1	0.01	0.16
Acidic-M_2	140.1	0.2	0.01	0.68

2.4. Adsorption experiments. The clay samples were dried at 80 °C under vacuum for 24 h before adsorption. Then, 0.5 g of adsorbent was put in contact with 50 mL of an aqueous solution of As(III) with metal concentration ranging from 1 to 2500 ($mg.L^{-1}$) at 25 °C for 24 h. Each adsorption experiment was replicated two times. The pH of the As(III) initial solution ranged from 3 to 12. The concentration of As(III) in the solution was determined by inductively-couple plasma atomic absorption spectroscopy (ICP-AAS, Perkin-Elmer 7300-DV). As(III) concentration was also determined at different contact times for adsorption kinetics studies.

The amount of adsorbed As(III) at any time, q_t ($mg.g^{-1}$) was calculated according to the expression:

$$q_t = \frac{(c_0 - c_t)V}{m} \qquad (1)$$

Where q_t ($mg.g^{-1}$) is the amount of As(III) adsorbed at time t, c_0 and c_t are the initial concentration and concentration at time t ($mg.L^{-1}$), V the volume of solution (L), and m the weight of the montmorillonite (g). When sufficient time has elapsed to reach equilibrium the measured concentration is the equilibrium concentration, c_e, and Equation (1) yields the amount of As(III) adsorbed at equilibrium, q_e.

3. RESULTS SECTION

3.1. Effect of contact time on the adsorption of As(III). Figure 1 shows the adsorption kinetics of a 2500 ($mg.L^{-1}$) As(III) solution on M_1, M_2 and Acidic-M_2 at pH = 5. The adsorption rates (the slope of the plot) of As(III) were fairly high at the beginning of these experiments, and declined throughout the time investigated. After 120 min the amount of adsorbed As(III) remains nearly unchanged, thus indicating that adsorption approaches equilibrium. In order to determine the adsorption kinetics of As(III) ions, first-order and second-order kinetics models were checked. The first-order rate expression [22] is expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (2)$$

Where q_e and q_t are the amounts of As(III) adsorbed onto the montmorillonite ($mg.g^{-1}$), at equilibrium and at time t, respectively, and k_1 is the first-order rate constant (min^{-1}). After integration from $t = 0$ to t and from $q_t = 0$ to q_e, it becomes the Lagergren's rate equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

A pseudo-second-order rate law expression was also used; the kinetic rate equation is expressed as [23-25]:

$$\frac{dq_i}{dt} = k_2(q_e - q_t)^2 \qquad (4)$$

Where k_2 is the second-order rate constant (g.mg^{-1}.min^{-1}). At boundary conditions from $t = 0$ to t and from $q_t = 0$ to q_e [26, 27], the rate law becomes:

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{t}{q_e} \tag{5}$$

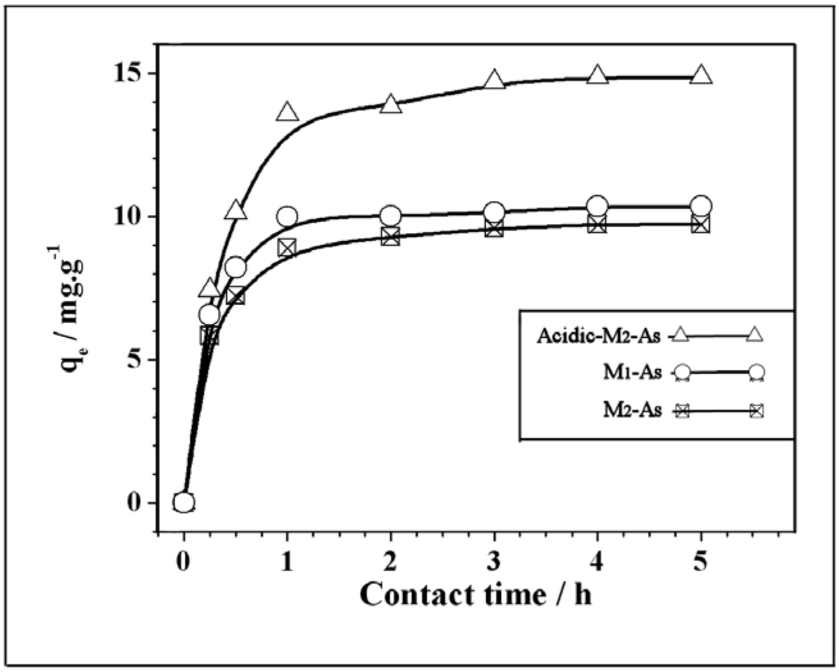

Figure 1: The adsorption of As(III) by M_1,M_2 and Acidic-M_2 as a function of contact time at 2500 mg.L^{-1} As(III) concentration and pH = 5.

Table 3 includes the relevant kinetic parameters, together with the correlation factor R^2 from the adsorption kinetics for a 2500 (mg.L^{-1}) As(III) solution, obtained after applying the two models mentioned above. It can be observed that the pseudo-second-order model provides a better correlation to the kinetic data, with correlation coefficients of 0.99. A pseudo-second-order model for arsenic adsorption process has also been reported previously [26-28].

Table 3. Comparison of the first- and second-order adsorption rate constants, for calculated ($q_{e,cal}$) and experimental ($q_{e,exp}$) values at 2500 mg.L^{-1} As(III) concentration and pH = 5.

Adsorbent	$q_{e.Exp}$ (mg.g^{-1})	First-order kinetic model			Second-order kinetic model		
		k_1 (min^{-1})	$q_{e.Cal}$ (mg/g)	R^2	$k_{2.ads}$ (g/mg.min)	$q_{e.Cal}$ (mg/g)	R^2
M_1	10.34	0.0196	4.33	0.77	0.0115	10.77	0.99
M_2	9.71	0.0188	5.60	0.94	0.0098	10.08	0.99
Acidic-M_2	14.84	0.0225	10.07	0.93	0.0045	15.17	0.99

3.2. Effect of pH on the adsorption of As(III). The pH of the aqueous solution is an important controlling parameter in the adsorption process [29]. Thus, the effect of pH of the solution ranging from 3 to 12 was examined. The effect of pH on the adsorption of As(III) is summarized in Figure 2. It seems that pH has little effect on the adsorption of As(III) under acidic conditions. This is probably because arsenic ions exist in the form of H_3AsO_3 in the pH range 0–9 [27], and therefore there is a lack of electrostatic interaction between As(III) and the adsorbent surface. Decreased As(III) retention at pH > 9, is also likely due to increased electrostatic repulsion between negatively charged arsenic species and the montmorillonite surface. Thus, it can be postulated that at least within the range $0 < pH < 9$, As(III) is adsorbed through pH-independent complexation reactions on surface hydroxyl sites [27]. Similar phenomena have been observed in previous studies of the removal of arsenic from water [28]. To obtain the optimal removal rates, a pH of 5 for As(III) were used in subsequent experiments.

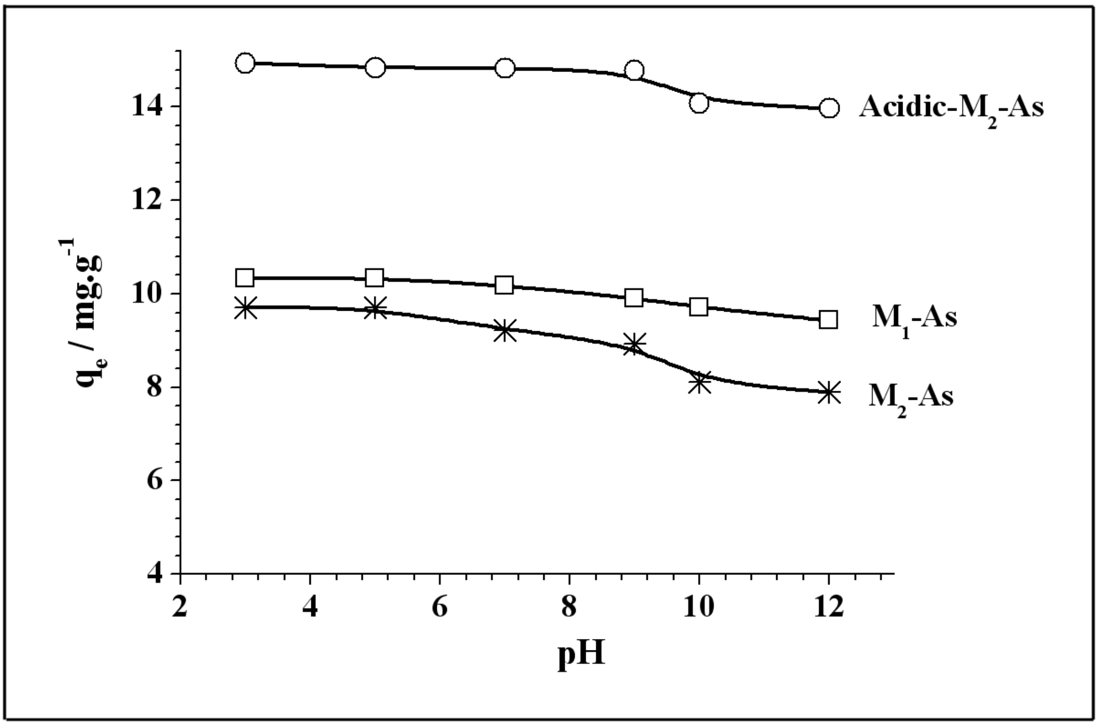

Figure 2: Effect of pH value on As(III) adsorption on M_1, M_2 and Acidic-M_2 at 2500 mg.L^{-1} As(III) concentration and pH = 5

3.3. Adsorption isotherms. Figure 3 presents the adsorption isotherms of As(III) for the three montmorillonites at 25 ºC. Langmuir and Freundlich isotherms were used to analyze the adsorption data. The Langmuir isotherm is based on monolayer adsorption at the active sites of the adsorbent, with no interaction between adsorbate molecules. The linear form of the isotherm given by:

$$\frac{c_e}{q_e} = \frac{1}{q_0.K_l} + \frac{c_e}{q_0} \qquad (6)$$

Where c_e is the equilibrium concentration of As(III) (mg.L^{-1}), q_e is the amount of As(III) adsorbed on the adsorbent (mg.g^{-1}), and q_o and K_l are the adsorption capacity (mg.g^{-1}) and a parameter related to the energy of adsorption (L.mg^{-1}), respectively. Plots of c_e/q_e versus c_e values can be used to determine q_o and K_l [30].

The linear form of the Freundlich isotherm is given by:

$$ln\, q_e = ln\, K_f + \frac{1}{n} ln\, c_e \qquad (7)$$

Where K_f and n are constants related to adsorption capacity and adsorption strenght, respectively, and c_e and q_e have the same meaning as in the Langmuir model. A linear plot of ($ln\ q_e$) versus ($ln\ c_e$) yields K_f and n.

The fitted constants for the Langmuir and Freundlich models are shown in Table 4. R^2 in the table is the regression coefficient. Notably, the experimental data fit both models well ($0.93 > R^2 > 0.98$ for Langmuir and $0.88 > R^2 > 0.93$ for Freundlich). This suggests that the adsorption of As(III) on montmorillonites occurs at the monolayer level. Also, the Langmuir adsorption capacity increases in the order $M_2 < M_1 <$ acidic-M_2, in complete agreement with the observed BET surface areas and porosity of the clays, The value of the *n* parameter in the Freundlich isotherm lies between 1 and 10, as it corresponds for a favorable adsorption process [18].

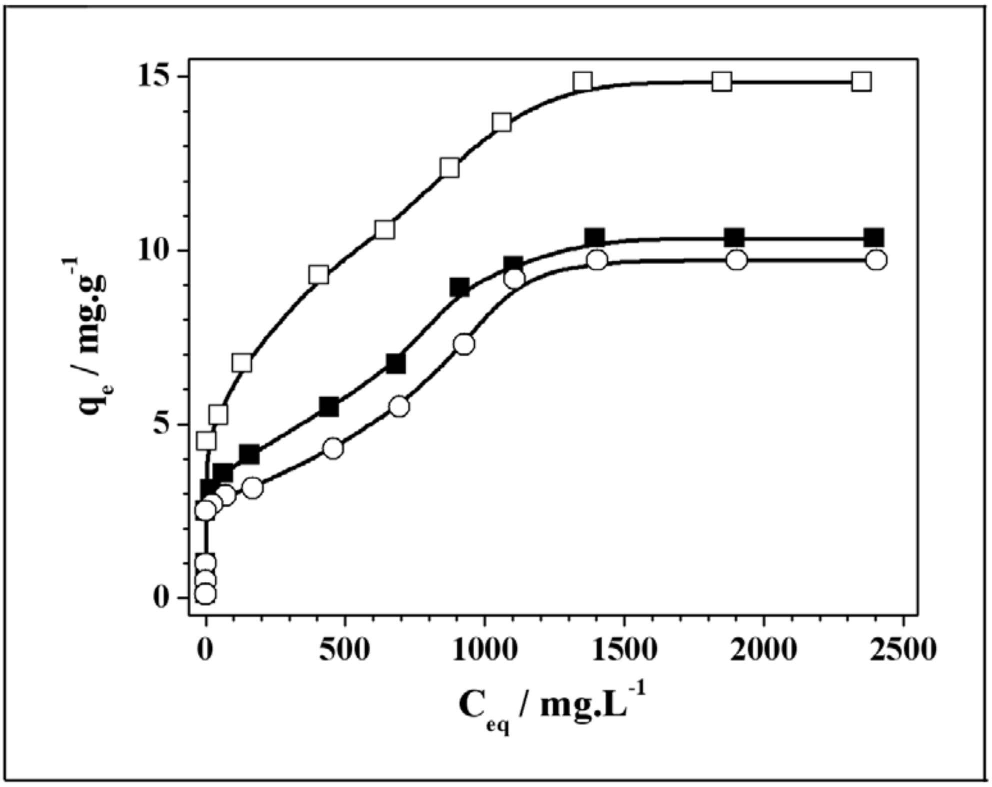

Figure 3: As(III) adsorption isotherm on M_1, M_2 and Acidic-M_2 at pH = 5.

Table 4: Freundlich and Langmuir coefficients obtained from the adsorption isotherms of As(III) on the montmorillonite samples at 298*K* and pH = 5.

Adsorbents	Freundlich coefficients			Langmuir coefficients		
	K_f (mg$^{1-1/n}$.L$^{1/n}$/g)	N	R^2	q_0 (mg/g)	K_l (L/mg)	R^2
M_1	1.12	3.45	0.93	10.6	0.008	0.96
M_2	0.28	3.04	0.88	10.21	0.005	0.93
Acidic-M_2	2.60	4.43	0.93	15.03	0.01	0.98

3.3. Effect of temperature. Adsorption experiments were carried out in the temperature range 298 *K* to 328 *K* at an initial arsenic concentration of 2500 (mg.L^{-1}) and a fixed clay dose of 0.5 g. The adsorption time was long enough to ensure that the adsorption of As(III) reached equilibrium. It is observed that the removal efficiency for As(III) falls with the rise in temperature (Figure 4) as it is expected for an exothermic adsorption process (see below).

Thermodynamic parameters such as standard free energy *ΔG*, standard enthalpy *ΔH*, and standard entropy changes *ΔS* can be determined using the equilibrium constant $K_C = \frac{q_e}{c_e}$, which depends on temperature [31, 32]:

$$\Delta G = -RT \ln K_C \qquad (8)$$

$$\ln K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (9)$$

where *R* is the universal gas constant (8.314 J.mol^{-1}.K^{-1}) and *T* is the temperature (*K*).

According to Equation (9), *ΔH* and *ΔS* can be obtained from the slope and intercept, respectively, of the Van´t Hoff plot of (*ln K*) versus (*1/T*).

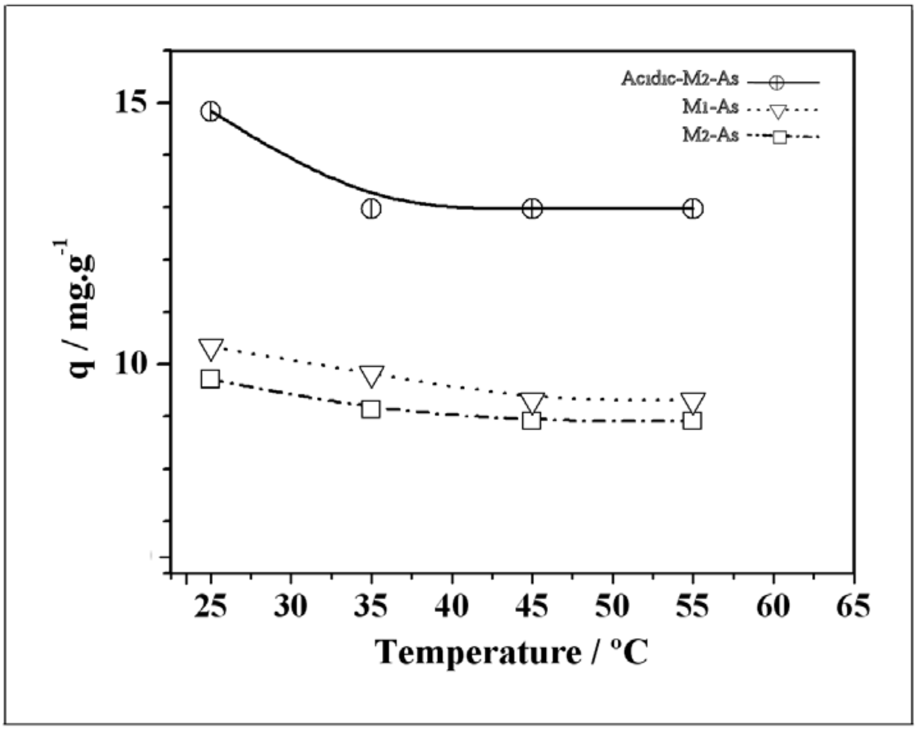

Figure 4: The effect of temperature on the removal rate of As(III) on M_1, M_2 and Acidic-M_2 at 2500 mg.L^{-1} As(III) concentration and pH = 5.

In Table 5. The negative values of *ΔG* indicate that the adsorption of As(III) onto M_1, M_2 and acidic-M_2 is a spontaneous process. When the temperature decreases, the magnitude of free energy change shifts to high negative value for As(III), suggesting that the process is more spontaneous at lower temperature [33-35]. The negative value of the standard enthalpy change *ΔH* for As(III) indicates that the adsorption is exothermic, thereby demonstrating that the process is stable energetically [33-36]. The negative standard entropy change *ΔS* value for As(III) correspond to a decrease in the degree of freedom of the adsorbed species.

Table 5: Thermodynamic constants for the adsorption of As(III) on M_1, M_2 and acidic-M_2 montmorillonites at various temperatures.

Adsorbents	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
M_1	298	-8.47	-20.55	-40.53
	308	-8.07		
	318	-7.66		
M_2	298	-7.03	-18.53	-38.58
	308	-6.64		
	318	-6.26		
Acidic-M_2	298	-10.12	-24.82	-49.31
	308	-9.63		
	318	-9.14		

3.4. Analysis of montmorillonites after adsorption by XRD. XRD patterns of Acidic-M_2 with adsorbed arsenite and raw montmorillonite are shown in Figure 5 the same patterns have been obtained with the other two clays. Table 6 shows the $d_{(001)}$ spacing before and after adsorption for the three clays. For Acidic-M_2 this value is 13.82 (Å), while for of Acidic-M_2-As after the adsorption of As(III) are increased to 15.26 (Å) (Table 6).

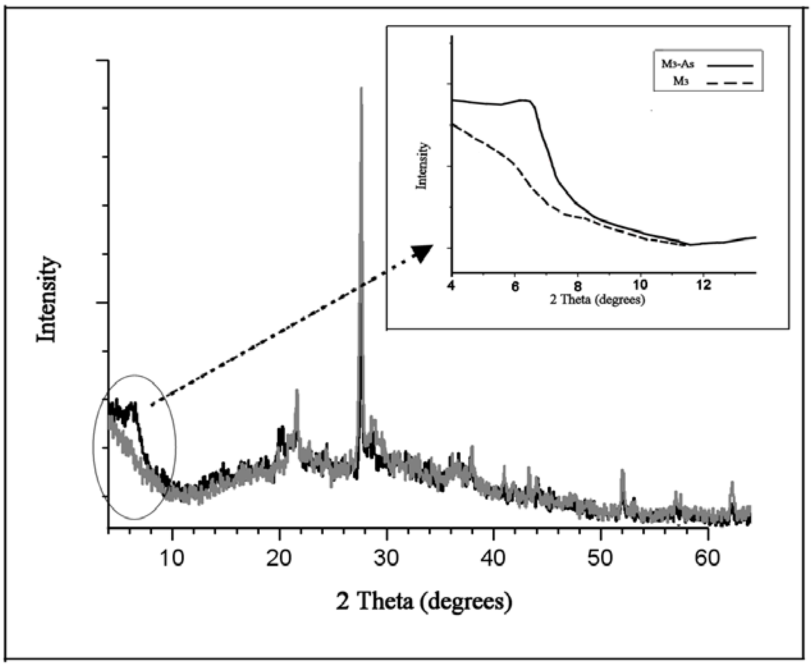

Figure 5: Powder XRD patterns of Acidic-M_2 after and before adsorbed As(III) concentration and pH = 5.

The $d_{(001)}$ pattern has been increased after the adsorption of As(III), suggesting that arsenic species enters into the interlayer of montmorillonite during the adsorption process. Because of the introduction of polyhidroxy cations into the interlayer space, many active hydroxyl groups are formed. The increase of the interlayer space of montmorillonite could be due to the complexation of arsenic with these active hydroxyl groups.

Table 6: Peak maximum, d-spacing and deference intensity peak of M_1, M_2 and acidic-M_2 montmorillonites before and after loading with arsenic.

Adsorbents	Peak maximum, $2\theta_{max}$ (deg)		Basal spacing, $d_{(001)}$ (Å)		Interlayer spacing$^{(a)}$, Δd (Å)	
	Before	*After*	*Before*	*After*	*Before*	*After*
M_1	6.01	5.74	14.78	15.47	5.08	5.77
M_2	6.15	5.79	14.45	15.34	4.75	5.64
Acidic-M_2	6.43	5.82	13.82	15.26	4.12	5.56

(a) Thickness of a montmorillonite layer = 9.7A°.

4. CONCLUSIONS

Results are presented showing that acidic-M_2 is an efficient material for the removal of As(III) from the aqueous solutions. Experimental parameters such as contact time, solution pH and temperature have been investigated and optimized.The kinetics of As(III) adsorption on all used montmorillonites used is well described by a pseudo-second-order chemical reaction model, which indicates that the adsorption process of these species is likely to be chemisorption. The adsorption isotherms are indicative of monolayer adsorption because the experimental data fit better to Langmuir isotherm. The removal of As(III) is pH-dependent. Optimal adsorption of arsenite is obtained at pH = 5, is indict the adsorption of As(III) is less favorable under acidic conditions. Although none of the montmorillonites used is highly effective in the adsorption of As(III) over a wide range of pH, it still can be economically feasible to be used for the removal of arsenic from waste-waters due to their large specific surface area and low cost. Furthermore, the adsorption capacity is significantly increased by acidic treatment. The negative values of ΔG and ΔH indicate that the adsorption of As(III) onto M_1, M_2 and acidic-M_2 is a spontaneous and exothermic process.

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