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Retention and selectivity of phosphate and fluoride from single and industrial aqueous solutions using purified and surfactant modified Tunisian clay

Kawthar Yahya[a,b], Imed Msadok[b,c], Ammar Mlayah[d], Ezzedine Srasra[b], Noureddine Hamdi[a,b,*]

[a]*Higher Institute of Water Sciences and Techniques of Gabes, University of Gabes, Zrig 6072, Tunisia, emails: nouryhamdi@gmail.com (N. Hamdi), Kawther.y@yahoo.com (K. Yahya)*
[b]*National Center of Research in Materials Sciences, Borj Cedria Technopole (CNRSM) 95-2050, Tunisia, emails: imedmsadok.fsg@gmail.com (I. Msadok), srasra.ezzedine@gmail.com (E. Srasra)*
[c]*Faculty of Sciences of Gabes, University of Gabes, Rue Omarr Eben khattab Zerig, 6029 Gabes*
[d]*Water Researches and Technologies Center Borj-Cedria (CERTE), BP 273 Soliman 8020, Tunisia, email: ammarmlayah17@gmail.com*

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ABSTRACT

Wastewater coming from the manufactory of the phosphoric acid fabrication is one of the most significant environmental problems throughout the Gabes region in Tunisia. This wastewater is very loaded with fluoride (F^-) and phosphate (PO_4^{3-}) and have an acidic pH (pH = 3.2; [F] = 1,840 mg L^{-1}; [P] = 1,420 mg L^{-1}). In this work, a smectitic clay mineral from the region (Jebel Haidoudi, Gabes) was tested for the removal of phosphate and fluoride ions from aqueous solutions. The clay samples are first purified and modified using cationic surfactant (hexadecylpyridinium ($HDPy^+$)) at different concentrations (1.0 to 3.0 CEC of clay CEC – cationic exchange capacity) then characterized by X-ray diffraction and Fourier-transform infrared spectroscopy. A series of batch adsorption experiments were carried out. Three parameters were investigated including the effect of pH, contact time and initial fluoride and phosphate single concentrations. The experimental results show that most of the adsorption took place during the first 5 h and the optimum pH value ranged from 3 to 4. The pseudo-second-order kinetic model described better the (F) and (P) adsorption. Thus, the isotherm studies showed that the best linear-fit was obtained with the Langmuir isotherm. The adsorption selectivity of (P and F) ions in the wastewater solution by the treated clays show that the fluoride is more selective in the acid pH. Finally, organoclay (3 CEC) is the best adsorbent and could be considered as an efficient and cost-effective adsorbent.

Keywords: Clay; Fluoride; Organoclay; Phosphate; Removal; Selectivity

1. Introduction

Water is the most important compound for life and it is a major global challenge for the 21st century to keep it. Due to the exponential increase of health and environmental problems related to water pollution, public authorities are releasing more strict standards for water discharges specially coming from industries. Among, these minerals pollutants, there are phosphate and fluoride.

Phosphorus (P) and fluoride (F) are indeed essential nutrients for animals and plants. But, they are considered harmful when their concentration exceeds 0.2 and 1.5 mg L^{-1} respectively [1]. The Literature reported that

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[*] Corresponding author.

phosphate and fluoride contamination in water owed to industrial activities has been recognized as one of the major problems worldwide imposing a serious threat to the environment and human health [2–5]. The existence of phosphate in water with excess amounts causes eutrophication manifested in the existence of oxygen deficiency, decrease in aquatic species, and deterioration of water [6]. As far as fluoride is concerned when its concentrations between 1.5 and 5 mg L^{-1} result in dental fluorosis while at higher concentrations (5–10 mg L^{-1}) dental fluorosis progresses to skeletal fluorosis [7].

Wastewater of the mining industry has to be treated before discharge into the environment, various techniques have been used for the elimination of phosphate and fluoride such as chemical precipitation [8], adsorption using special materials relatively expensive [9] and biological treatment [10] for phosphate. However, in the case of fluoride most techniques used are adsorption [11], oxidation [12], precipitation [13] and electrodialysis [14]. These methods can be effective, but unfortunately non-affordable for developing countries, because of their high investment and high operational costs. Adsorption using abundant local clay is from one side very cost-effective and from the other side very effective and also generates relatively less waste. Clay is one of the important groups of geomaterials. It is widely used in various industries fields. Several studies have shown the anti-pollutant role of clays [15]. This attention to the remediation is due to the high specific surface area of this material, the presence of negative charges on their surface, their ability to exchange cations, their high availability in deposits and mining soils, their low sensitivity, their non-toxic nature and their water adsorption capacity [16,17]. A lot of work has already been done on the adsorption of cationic pollutants by natural clays [18]. However, few researchers have been interested in the adsorption of anionic pollutants on clays. The reason is probably related to the difficulty of anions adsorption on clay. In fact, in nature clays carry negative overall charges thus attracting cations than anions. Therefore, anions such as phosphate and fluoride could only be repelled by these negative charges. For that reason, diverse studies try to ameliorate this situation, by the modification of the clay surface in order to turn it into suitable materials for anions adsorption [19–21]. Nowadays, several pathways can be used to modify clays [22]. Schoonheydt and Johnston [23] indicated that the surface modification of clay minerals by surfactants can modify the surface properties. Thus, lots of studies have indicated that clay minerals modified by surfactants turn into suitable materials for anions adsorption [24–26].

Among the clay minerals, smectite has been commonly used for the preparation of organic clays due to their special properties, as their high cations exchange capacity, retention properties, swelling behavior and wide surface area [27]. Additionally, several studies demonstrate the efficacy of surfactant-modified smectite adsorbs the anions such as nitrate and vanadium [24,28].

In this paper, the defluoridation and dephosphatation capacity of a purified and surfactant modified clay mineral from Tunisia were studied in batch simulation tests. The effect of adsorption parameters including the time of contact, pH, and concentration, on F and P adsorption, onto clay and prepared organoclay was evaluated. In addition, the equilibrium isotherms were used to determine the adsorption capacity and to elucidate the mechanism for anions (F and P) adsorption on organoclay for the first time using Tunisian illite-smectite clay. The adsorption selectivity of both anions (F and P) from the industrial wastewater was investigated in order to evaluate the performance of synthesized organoclay.

2. Experimental

2.1. Raw material

The studied natural Haidoudi clay (N-Haidoudi) material is collected from the region of Gabes located on the Southeast of Tunisia, exactly from the top of Aleg formation (Maider II) in the Coniacian-Santonian outcroppings, widely exposed in Jebel Haidoudi [29]. In the present study, a representative clay sample of the Aleg formation was done for laboratory assessment including characterization study and adsorption tests. After extraction, it is initially dried at 80°C. The material was purified through classical methods. Firstly, the raw material was treated with dilute HCl (0.5 N) solution to eliminate carbonates [30] and treated with H_2O_2 to remove any organic matter. After that, the sample was washed five times with 1 N NaCl solution. The purified clay fraction (Na-Haidoudi) was separated by centrifugation and was dried at 60°C according to the method of Churchman et al. [17].

2.2. Modified material

In this study, modified clay using the surfactant hexadecylpyridinium (HDPy) bromide ($C_21H_{38}NBr$) (HDPy-Haidoudi) was synthesized based on the work of Hamdi and Srasra [27]. HDPy is a cationic surfactant with a critical micelle concentration (CMC) of 0.7 mM and it has an average molecular weight of 384.44 g mol^{-1}. Three organoclays were prepared. In each case, 6 g of Na-Haidoudi clay are mixed with 300 mL of HDPy surfactant solutions at a different initial amount equal to 1, 2 and 3 times the cationic exchange capacity (CEC). These solutions were stirred for 24 h on a mechanical shaker at 2,700 rpm. Then they were left to stand and separate modified clay from the liquid phases. This separated modified clay (HDPy-Haidoudi) was washed with bi-distilled water repeatedly to remove the excess surfactant. The product (organoclay) was dried at 80°C for 24 h and sieved. The resulting organoclay was identified by a prefix stating and the concentration of HDPy were added, for example, HDPy1-Ha identifies an organoclay where the concentration of HDPy added equal to 1.0 time the CEC of Na-Ha., the others were denoted in a similar way.

2.3. Chemicals

The pollutants elements studied in this work were phosphate and fluoride. These pollutants can be provided by several Tunisian industries such as the Gabes chemical group (manufacturing of phosphoric acid). A 1,000 mg L^{-1} phosphate and fluoride stock solution was prepared by dissolving NaF and KH_2PO_4, respectively in bi-distilled water.

Phosphate and fluoride working solutions with different concentrations were obtained by diluting the stock solution with bi-distilled water. The industrial wastewater has an acidic pH of about 3.2 and is heavily loaded with fluoride and phosphate ([F] = 1,840mg L^{-1}; [P] = 1,420 mg L^{-1}) in addition to other ions such as chloride, sulfate, sodium and calcium.

2.4. Characterization methods

Characterization of the clay fraction with X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) was performed before and after the surfactant modification in order to verify the intercalation in the interlayer.

XRD was used to determine the interlayer $d_{(001)}$ spacing, of the surfactant-treated clay and, the starting clay was obtained using an X-ray (PANalytical X'Pert) diffractometer with Cu-Kα radiation, over the (2θ) range 2°–30°, at the scanning speed of 2°min^{-1} and a wavelength λ = 0.154056 nm. The diffractograms are analyzed using "HighScore plus" processing software.

The infrared analysis was carried out using a Perkin-Elmer FTIR (model 783) spectrometer (USA). The spectra were recorded in the region from 400 to 4,000 cm^{-1} by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm s^{-1}. KBr pellets were prepared by mixing 1 wt.% clay with 99 wt.% KBr and by pressing.

The point of zero net charge (pHzpc) was determined according to the methodology given by Hamdi and Srasra [27].

2.5. Batch adsorption studies

The adsorption of phosphate and fluoride on both adsorbents (Na-Haidoudi and HDPy-Haidoudi) was investigated in an aqueous solution by batch experiments. The experiments were performed at room temperature, with a constant volume (V = 25 mL) and with a mass of adsorbent equal to 0.05 g. The flasks were agitated on a mechanical shaker for a given time to ensure that the equilibrium was reached. The reaction mixture was centrifuged and the supernatant was analyzed using liquid chromatography of ions. The amounts of phosphate and fluoride adsorbed by the sorbent were calculated using the following mass balance relationship:

$$Q_{\text{ads}} = \frac{\left(C_0 - C_e\right)V}{m} \tag{1}$$

where C_0 (mg L^{-1}): initial concentration of phosphate and fluoride solution; C_e (mg L^{-1}): equilibrium concentration of the phosphate and fluoride solution; V (mL): volume of solution and m (g): a mass of sorbent.

First, the pH effect was studied to find out the optimum pH for the process. To test the solution pH effect on phosphate and fluoride, the experiments were carried out by adjusting the solution's initial pH to 3.5; 5; 8 and 10. During these tests, the initial phosphate and fluoride concentration and the adsorbent dosage were fixed at 100 mg L^{-1} and 2 g L^{-1}, respectively. In order to determine the required adsorption equilibrium time of phosphate and fluoride into Na-Haidoudi and HDPy-Haidoudi as well as the probably involved mechanisms, a kinetic study was elaborated for contact times varying from 30 min to 24 h for an initial phosphate and fluoride concentration of 100 mg L^{-1}, an adsorbent dose of 2 g L^{-1} and a pH of 3.5. Finally, the effect of concentration was studied by varying the concentration of the phosphate and fluoride synthetic solution from 4 to 100 mg L^{-1}, with a constant contact time of 5 h and pH (3.5), this contact time and pH were determined on the basis of preliminary tests.

2.6. Theoretical foundation of kinetic and isotherm adsorption modeling

In literature, several theoretical models were used to fit the adsorption kinetics and adsorption isotherm. In this study, the kinetics of phosphate adsorption was investigated using four models (the first-order, second-order, intraparticle, and film diffusion). The four used isotherms models are Langmuir, Freundlich, Temkin and Dubinin–Radushkevich. Table 1 illustrates the corresponding original and linear equations as well as the related plots of the different models.

3. Results and discussion

3.1. Adsorbent characterization

The XRD patterns of purified clay (Na-Haidoudi) and modified clay (HDPy-Haidoudi) are shown in Fig. 1. The XRD analysis of pure clay indicates the presence of smectite at 12.62 Å. Also, the d_{001} = 7.21 Å reveals the presence of kaolinite. After treatment by a surfactant (HDPy1, HDPy2 and HDPy3) the d_{001} = 12.62 Å moved to 20.12, 43.21 and 43.21 Å respectively. As a result, the addition of HDPy increases the expansion of the interlayer space distance of the clays. The cationic surfactant was intercalated by different arrangements in the basal spacing of the smectite. This arrangement can be procured by comparing the interlayer distance and the size of the surfactant molecule [33]. According to the literature, the thickness of the phyllosilicates 2:1 (TOT) is 9.7 Å [34] and the molecular size of HDPy is 23.1 Å in length and 4.6 Å in height [35]. At low surfactant concentration (1 CEC), the d_{001} = 12.62 Å of HDPy1-Haidoudi was 20.12 Å which indicated the formation of lateral bilayer arrangement in the interlayer space. At high surfactant concentration (2 CEC and 3 CEC) the d_{001} = 12.62 Å increase double compared to HDPy1-Haidoudi with the value at 44.51 Å. That proved the formation of a paraffin-type bimolecular arrangement. This result is in accordance with other studies [24,36].

The FTIR spectra of Na-Haidoudi and HDPy-Haidoudi are shown in Fig. 1. The bands of absorbance from the different samples appeared approximately at similar wavenumbers, however, their intensity and width exhibit distinct differences. Examining the spectra of HDPy-Haidoudi comparing to the Na-Haidoudi;

- Similar band between Na-Haidoudi and HDPy-Haidoudi, for example, the bands at 3,425 cm^{-1} (H–O–H stretching), and 1,639 cm^{-1} (H–O–H bending) indicate the presence of adsorbed water. Thus, the band at 3,425 cm^{-1}

Table 1
Used models for the kinetic and isotherm studies

Model	Equation	Linear form	Plot	References
Kinetic models				
First-order	$\frac{dq_t}{dt}=K_1\left(q_e-q_t\right)$	$\ln\left(q_e-q_t\right)=\ln q_{e\text{I}}-K_1t$	$\ln\left(q_e-q_t\right)\text{vs.}\ t$	[31]
Second-order	$\frac{dq_t}{dt}=K_1\left(q_e-q_t\right)^2$	$\frac{t}{q_t}=\frac{1}{K_2q_{e\text{II}}^2}+\frac{1}{q_{e\text{II}}}t$	$\frac{t}{q_t}\text{vs.}\ t$	[31]
Film diffusion	–	$\frac{q_t}{q_e}=6\frac{D_f^{1/2}}{\pi a^2}\sqrt{t}$	$\frac{q_t}{q_e}\ \text{vs.}\ \sqrt{t}$	[31]
Intraparticle diffusion	–	$\ln\left(1-\frac{q_t}{q_e}\right)=\ln\left(\frac{6}{\pi^2}\right)-\left(\frac{D_{\text{ip}}}{a^2}\pi^2\right)$	$\ln\left(1-\frac{q_t}{q_e}\right)\text{vs.}\ t$	[31]
Isotherms				
Langmuir	$q_e=\frac{q_{\max,L}K_lC_e}{1+K_lC_e}$	$\frac{C_e}{q_e}=\frac{1}{K_Lq_{\max,L}}+\frac{1}{q_{\max,L}}C_e$	$\frac{C_e}{q_e}\ \text{vs.}\ C_e$	[32]
Freundlich	$q_e=K_fC_e^{1/2}$	$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e$	$\ln q_e\ \text{vs.}\ \ln C_e$	[32]
Dubinin–Radushkevich	$q_e=q_{\max,\text{D-R}}\exp\left(-\beta\varepsilon^2\right)$	$\ln q_e=\ln q_{\max,\text{D-R}}-\beta\varepsilon^2$	$\ln q_e\ \text{vs.}\ \varepsilon^2$	[32]
Temkin	$q_e=\frac{RT}{b}\ln\left(AC_e\right)$	$q_e=\frac{RT}{b}\ln\left(A\right)\frac{RT}{b}\ln\left(C_e\right)$	$q_e\ \text{vs.}\ \ln\left(C_e\right)$	[32]

K_1 (min^{-1}) and K_2 (min^{-1}) first- and second-order kinetic constants, respectively, $q_{e\text{I}}$ and $q_{e\text{II}}$ (mg g^{-1}) first and second-order theoretical adsorbed amounts of phosphate and fluoride, respectively, D_f and D_{ip} (m^2 s^{-1}) diffusion film and intraparticle diffusion constants, respectively, K_L (L mg^{-1}) and K_F (mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}) Langmuir and Freundlich constants, respectively, n adsorption intensity, β Dubinin–Radushkevich isotherm constant (mol^2 kJ^{-2}), ε potential energy constant

band corresponding to the isolated Si–OH group and the linked Si–OH group.

- Absorption band at 1,026 cm^{-1} was assigned to the stretching mode of Si–O (650 cm^{-1}). The bending bands are at 528 cm^{-1} for Si–O–Al and 469 cm^{-1} for Si–O–Si [37].
- Additional bands at 1,473 and 1,639 cm^{-1} in organoclay, indicate the presence of C–N vibrations in tertiary amines and of C–H stretching bands of CH$_2$ and aliphatic C–H stretching bands at 2,920 and 2,850 cm^{-1}, respectively.
- For all organoclays, it was noted that the frequency and the intensity of asymmetric and symmetric stretching bands of CH$_2$ changed with the amount of intercalated surfactant. These frequencies are extremely sensitive to the conformational ordering of the chain of cationic surfactant onto clay [36]. With the increase of surfactant loading from 1 CEC to 3 CEC, the frequency of υ as (CH$_2$) shifted from 2,930 cm^{-1} for N-HDPy$_1$ to 2,920 cm^{-1} for N-HDPy$_3$.

All these observation show the success of the interaction of HDPy with Haidoudi clay.

The pH$_{\text{pzc}}$ values of Na-Haidoudi and HDPy3-Haidoudi were found to be 6 and 8.2 respectively. The modification of raw smectite clay with HDPy increases the pH$_{\text{pzc}}$ value, which indicates that the acidic region of organoclay increased [36].

3.2. Sorption study of fluoride and phosphate

3.2.1. Effect of pH

The effect of pH on phosphate and fluoride sorption capacity of both adsorbents is summarized in Fig. 2a. Comparing the adsorption of phosphate and fluoride ions onto Na-Haidoudi and HDPy3-Haidoudi at different pH shows that the maximum of adsorption is obtained in an acid medium (pH = 3.5). These results can be explained by the high positive surface charge of raw clay and organoclays at low pH < pH$_{\text{pzc}}$ [20,38]. Thus, the experimental results showed that the removed amount of phosphate and fluoride increases with the decrease pH value. Earlier works reported that P and F adsorption decreased with an increase in the pH [31,39–41]. Indeed, for a constant initial aqueous concentration of 100 mg L^{-1}, the phosphate and fluoride adsorption was evaluated to be equal to 2.1 and 3.5 mg g^{-1} by Na-Haidoudi and 10.8 and 10.9 mg g^{-1} by HDPy3-Haidoudi, respectively at pH of 10. These amounts increased up to 6.2 and 8.5 mg g^{-1} by Na-Haidoudi and

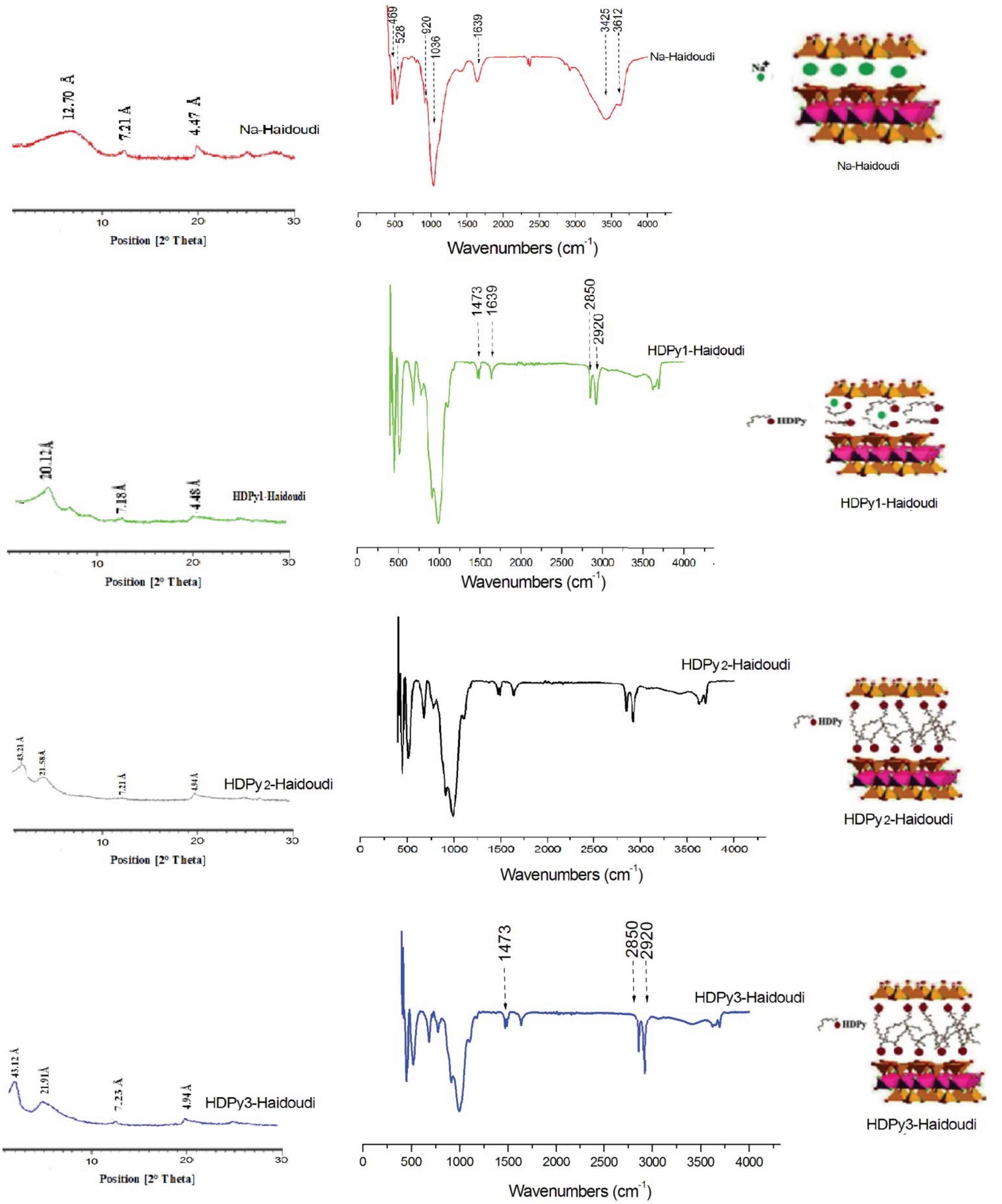

Fig. 1. X-ray diffraction patterns, infrared spectra of purified and modified clays and illustration of a configuration of intercalated surfactant molecules in the interlayer space.

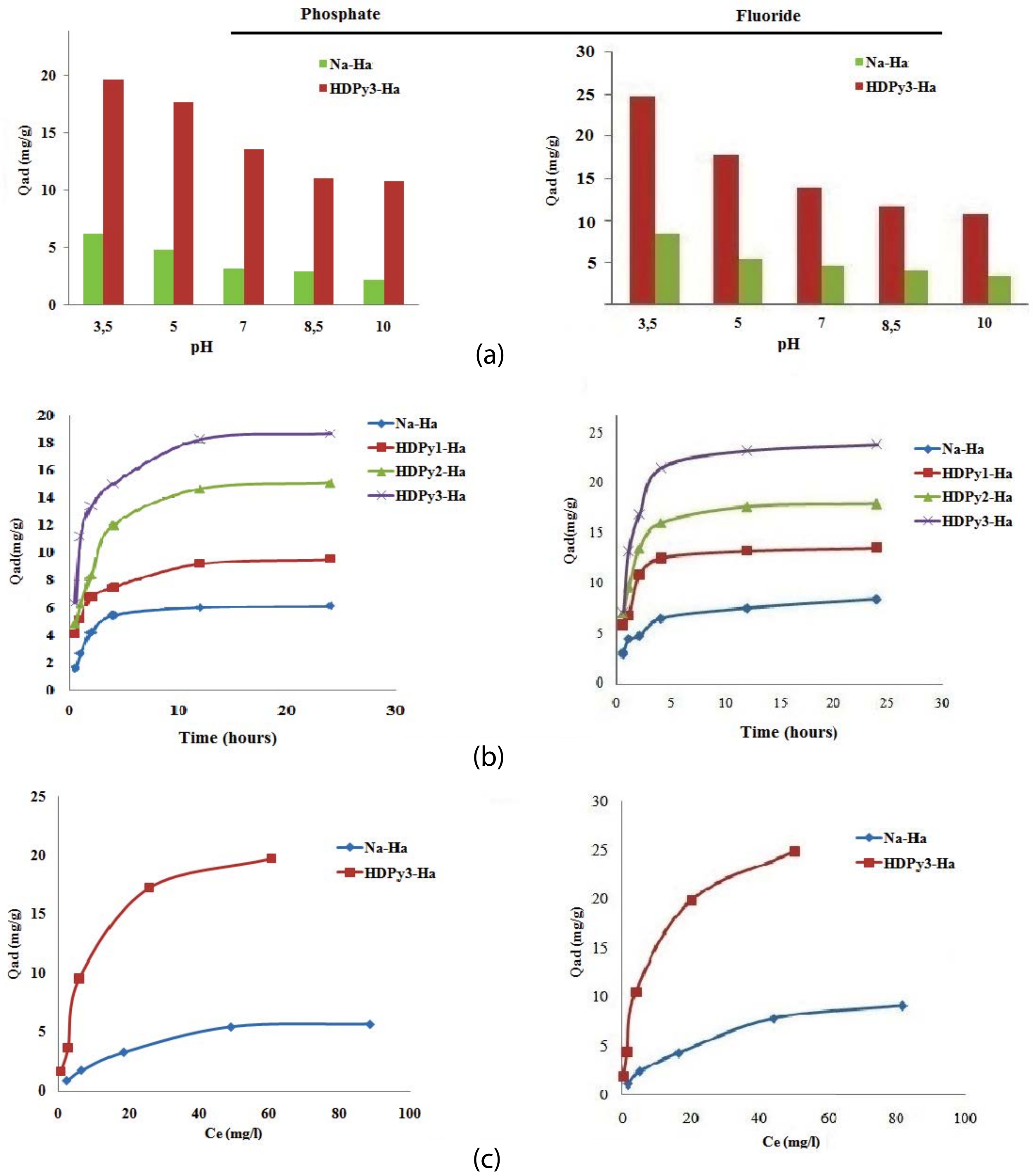

Fig. 2. Effect of (a) pH, (b) contact time, and (c) initial phosphate and fluoride concentrations on Na-Haidoudi and HDPy-Haidoudi.

19.56 and 24.8 mg g^{-1} by HDPy3-Haidoudi respectively at pH of 3.5. This increase could be explained by the effect of pH of the medium, attractive charge at lower pH ($<pH_{pzc}$) and repulsive at higher pH. This means that the increase in the amount of OH$^-$ in solution decreased the phosphate and fluoride adsorption. This result inferred that there were exchange competitions between OH$^-$ and phosphate and fluoride anions. This result is consistent with other phosphate and fluoride adsorption studies using natural and modified clay [42–45].

3.2.2. *Effect of contact time (P and F adsorption kinetics)*

In an illustrated in Fig. 2b, it is obvious that experimental results show that the phosphate and fluoride adsorption process is clearly time-dependent. For example, for a contact time of 30 min, the phosphates and fluoride adsorption rate are lower than 50%. This adsorption rate increases significantly by increasing contact times for all media. From these results, it can be determined that adsorption takes place in three stages depending on the slope. During the first step (30 min–2 h) the slope is very important as well the adsorption is relatively fast; this can be interpreted by the fact that at the beginning of the adsorption, the number of active sites available on the clay surface is considerable, consequently the sticking probability was large and adsorption proceeds with a high rate. At the second step (2–5 h) the slope is lower than the first step. At this level, the active sites are gradually filled up by phosphate and fluoride. So a decrease in adsorption rate is noted. This decrease is due to the decrease in the number of sites available for adsorption. In the third step (>5 h), the slope is zero, this is explained by the stability of the adsorption capacity and thus the equilibrium of the system is reached. This is probably due to the occupation of the almost total of available adsorption sites. These steps adsorption process have been observed in previous studies on various pollutants adsorption on different adsorbents [46,47]. The time required to reach this state of equilibrium was estimated at about 5 h. This finding is in concordance with previous studies, where the anion adsorption by organoclay and raw clay attains an equilibrium state at about 5 and 6 h [24,42].

In order to find the effective processes regarding phosphate and fluoride adsorption onto purified and modified clays, four kinetic equations were examined: pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. The parameters of the four models are presented in Table 2. The results show that data are best fitted by the pseudo-second-order model as evidenced by high correlation coefficients (Table 2).

For, pseudo-first-order model the correlation coefficients were not close to 1 which suggests the adsorption kinetic is not a pseudo-first-order process. Besides, for the second-order model, the correlation coefficients were very close to 1 and the calculated adsorbed rate (q_{eII}) values, agree very well with the experimental ones. However, results indicate that the pseudo-second-order model is the most adequate to fit the experimental results of all samples. The values of diffusion coefficients given in Table 2 indicate that the intra-particle diffusion coefficients are greater than those of the film diffusion through the boundary layer for Na-Haidoudi and HDPy-Haidoudi. This finding confirms that in case of the tested adsorbents, the film diffusion process controls significantly the rate of adsorption of phosphate and fluoride. The same outcomes were reported by [31] when investigating the phosphate removal by powdered marble.

The result of a kinetic study was given a clear idea of the adsorption capacities of modified clays comparing to purified clay. The equilibrium adsorption quantity of fluoride and phosphate by the absorbents samples show this order; Na-Haidoudi < HDPy1-Ha < HDPy2-Ha < HDPy3-Ha (Fig. 3). These results are confirmed by Xi et al. [48] who found that the intercalation of cationic surfactants increases greatly the anion's adsorption capacity especially when surfactant loading exceeds the CEC of clay. In addition, the adsorption of fluoride is higher than phosphate which is explained by the steric phenomena (the fluoride has a small size comparing to phosphate). The adsorption capacity by HDPy3-Ha modified clay is about 3 times more efficient than sodium clay (Fig. 3).

3.2.3. Effect of concentrations (P and F adsorption isotherm)

As seen from Fig. 2c the phosphate and fluoride uptake increased with their initial concentration. In fact, when raising initial aqueous phosphate and fluoride concentrations from 4 to 100 mg L^{-1} the adsorption capacities increase from 0.8 to 5.65 mg g^{-1} (Na-Haidoudi) mg g^{-1} and from 1.65 to 19.7 mg g^{-1} (HDPy3-Ha) for phosphate, and from 1.13 to 9.15 mg g^{-1} (Na-Haidoudi) and from 1.865 to 24.87 mg g^{-1} (HDPy3-Ha) for fluoride. This tendency could be explained by the fact that for high initial aqueous single phosphate and fluoride solution concentrations, the contact probability between phosphates and fluoride contained in the aqueous phase and the adsorbent might be more privileged. Hence, when the concentration

Table 2
Kinetic rate parameters of the adsorption of phosphates and fluoride onto Na-Haidoudi (Na-Ha.) and HDPy-Haidoudi (HDPy-Ha.) (pH = 3.5; adsorbent dosage = 0.05 g L^{-1}; C_0 = 100 mg L^{-1}; temperature = 25°C)

		Phosphate				Fluoride			
		Na-Ha.	HDP1-Ha.	HDPy2-Ha.	HDPy3-Ha.	Na-Ha.	HDPy1-Ha.	HDPy2-Ha.	HDPy3-Ha.
$q_{e,\exp}$, (mg g^{-1})		6.1	9.52	15.08	18.66	8.41	13.52	17.93	23.91
Pseudo-first-order	q_{eI}, (mg g^{-1})	3.90	5.31	10.91	11.15	4.74	4.77	11.12	12.75
	K_1, (min^{-1})	0.30	0.23	0.27	0.27	0.23	0.13	0.31	0.02
	R^2	0.92	0.98	0.97	0.97	0.90	0.87	0.93	0.87
Pseudo-second-order	q_{eII}, (mg g^{-1})	6.45	9.9	16.12	19.60	8.77	13.88	19.23	25
	K_2, (min^{-1})	0.13	0.10	0.04	0.05	0.08	0.15	0.04	0.04
	R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
Film diffusion	D_f, (m^2 s^{-1})	2.67E-19	3.13E-19	4.53E-19	4.92E-19	9.64E-18	1.67E-17	1.39E-17	5.60E-17
	R^2	0.89	0.76	0.87	0.90	0.69	0.68	0.68	0.85
Intraparticle diffusion	D_{ip}, (m^2 s^{-1})	1.21E-12	9.4E-12	1.09E-12	1.1E-12	5.72E-12	1.052E-12	9.52E-13	1.27E-12
	R^2	0.92	0.98	0.99	0.97	0.90	0.8	0.93	0.87

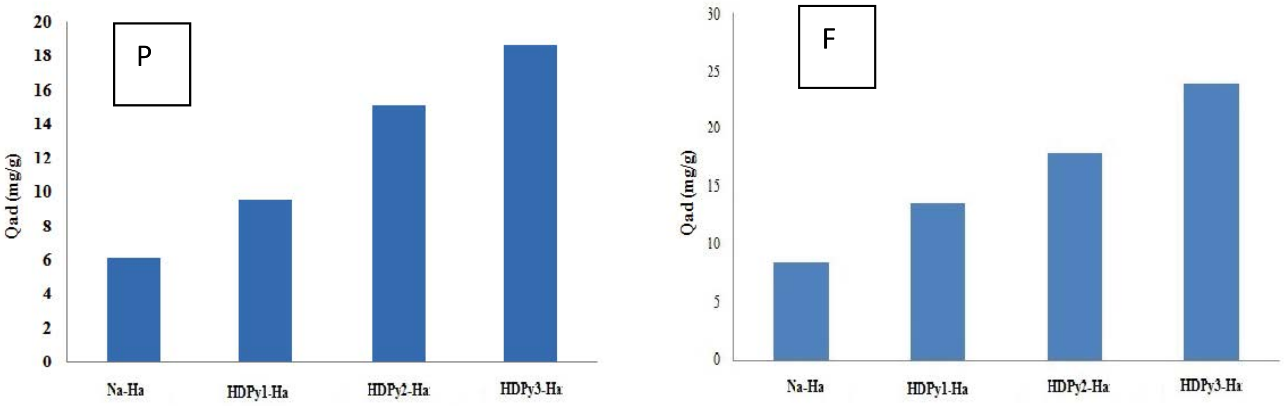

Fig. 3. Effect of surfactant intercalation in the interlayer of purified clay.

gradient between the aqueous solution and the solid phase is higher, it results in more important diffusion rates [49].

In order to understand the adsorption phenomena of fluoride and phosphate onto Na-Haidoudi and HDPy-Haidoudi clays four, isotherms models were used (for multilayer and monolayer adsorption surfaces) and were examined (Table 1). The linear isotherms constants with corresponding correlation coefficients (R^2) of the four used models are given in Table 3.

The highest values of R^2 for Na-Haidoudi and HDPy-Haidoudi were exhibited to the Langmuir model. This indicates the homogeneous nature of the adsorbent's surface, that is, the formation of monolayer coverage characterized by uniform functional site occupation by phosphate and fluoride ions on the outer surface [50]. This model assumes that the adsorptive molecules interact with active sites on the Na-Haidoudi and HDPy-Haidoudi surfaces that have identical energy. Furthermore, the values of the Langmuir's coefficients ($R_L = 1/1 + K_LC_0$) is of the order of 0.16 and 0.2 for Na-Haidoudi and 0.1 and 0.05 for HDPy3-Haidoudi. These values are lower than 1, which confirms that the used material is favorable for phosphate and fluoride adsorption. Regarding, the Freundlich model, which describes processes of non-ideal adsorption, multilayer adsorption and assumes the presence of a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface and assumes that the adsorption process is reversible, their calculated determination coefficients were less fitting to the experimental, which excludes the assumption of possible non-uniform adsorption of phosphate and fluoride onto a heterogeneous surface. The calculated values of Freundlich exponent "n" was estimated to be 1.79 (phosphate) and 1.818 (fluoride) for Na-Haidoudi and to be 1.727 (phosphate) and 1.968 (fluoride) HDPy-Haidoudi, respectively. They are in the range between 1–10, indicating favorable adsorption of phosphate and fluoride onto both adsorbents. The D–R isotherm is more general than the Langmuir model because it does not assume a homogeneous surface or a constant sorption potential [51]. This model assumes the presence

Table 3
Adsorption isotherms constants for phosphate and fluoride adsorption onto Na-Haidoudi (Na-Ha.) and HDPy3-Haidoudi (HDPy3-Ha.) (pH = 3.5; adsorbent dosage = 0.05 g L^{-1}; 4 < C_0 < 100 mg L^{-1}; contact time = 5 h)

		Phosphate		Fluoride	
		Na-Ha.	HDPy3-Ha.	Na-Ha.	HDPy3-Ha.
Langmuir	$q_{e,\text{exp}}$, (mg g^{-1})	5,65	19.7	9.15	24.87
	$q_{\max}$, (mg g^{-1})	7.04	23.80	11.36	27.77
	K_L, (L mg^{-1})	0.05	0.09	0.04	0.16
	R^2	0.99	0.99	0.98	0.99
Freundlich	n	1.79	1.72	1.81	1.96
	K_F	2.32	0.55	5.87	1.23
	R^2	0.94	0.96	0.97	0.98
Dubinin–Radushkevich	$q_{\max}$, (mg g^{-1})	4.00	10.02	5.73	15.16
	E, (kJ mol^{-1})	0.5	1.11	0.7	0.5
	R^2	0.62	0.71	0.72	0.65
Temkin	A, (L mg^{-1})	0.84	3.24	3.38	0.71
	b, (J mol^{-1})	560.69	1,697.82	535.61	1,154.55
	R^2	0.94	0.96	0.95	0.94

of a fixed volume of sorption space close to the adsorbent surface and the existence of sorption potential over these spaces. This sorption potential is considered to be temperature independent but it varies according to the nature of sorbent and sorbate [52]. Concerning this isotherm, the estimated R^2 and theoretical maximal adsorption capacity for Na-Haidoudi and HDPy-Haidoudi do not fit well the experimental data (Table 3). The Temkin isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly due to adsorbent–sorbate interactions and that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [53]. The determination coefficients showed that this model does not predict the experimental data very well (Table 3).

3.2.4. Mechanism of anion uptake in organoclays

In general, adsorption onto smectite clay involves two distinct mechanisms: (i) an ion exchange reaction at permanent charge sites, and (ii) the formation of complexes with the surface hydroxyl groups. Li and Bowman [53] indicate the removal of anion seems to be due principally to anion exchange. So it could be supposed that phosphate and fluoride may have been absorbed by anionic exchange with bromide ion from the HDPy molecule which was fixed into the interlayer of smectite by van der Waals hydrophobic interactions. The bond for bromide ion could be an active site for phosphate and fluoride adsorption. When the anionic exchange occurred, the counter-ion bromide was desorbed and replaced by the phosphate and fluoride. Fig. 4 shows the mechanism that involves the ion exchange reaction because it is the most dominant mechanism for the present study.

3.2.5. Comparison with other adsorbents

In order to analyze the HDPy3-Haidoudi efficiency for phosphate and fluoride removal as compared to other adsorbents, a comparison based on Langmuir's adsorption capacity "$q_{\max}$" was performed. The comparison of the phosphate and fluoride adsorption capacity by HDPy-Haidoudi and other materials is given in Table 4. It can be concluded that HDPy3-Haidoudi presents a relatively higher adsorption capacity than that other adsorbent listed in Table 4. Indeed, the phosphate adsorption capacity by HDPy3-Haidoudi was about double than modified bentonite [55,56] which has probably the same characteristics. In addition, the adsorption capacity of our modified clay is very higher than other expensive adsorbents like magnetic iron oxide nanoparticles and almond shell biochar. The fluoride adsorption rates of our adsorbents are very interesting comparing to other modified clay minerals and the cost is very competitive also. It is worth mentioning that HDPy3-Haidoudi could be considered as a promising and attractive material for harmful anions (F and P) removal from aqueous solutions.

3.2.6. Adsorption of phosphate and fluoride ions from industrial wastewater, selectivity study

Basing on the good results of adsorption of fluoride and phosphate found using a single aqueous solution we are very motivated to test the performance of our adsorbents in waste solution and see the competition between both anions (F and P). The adsorption selectivity of phosphate and fluoride ions from the wastewater on both adsorbents (Na-Haidoudi and HDPy3-Haidoudi) was studied and the results are given in Fig. 5. The experimental study was made in the same condition of the precedent work using the wastewater in the place of a single stock solution. Therefore, the results of both adsorbents show low adsorption ability for fluoride and phosphate ions comparing the case of single solutions. In addition, the selectivity of fluoride ions is better than phosphate and with coexisting chloride, sulfate ions and other cations. The adsorption quantity of the fluoride passes from 27.77 mg g^{-1} for the synthetic solution to 24 mg g^{-1} using the wastewater. Although in the case of phosphate the Qad using the wastewater pass to the half comparing to the case of a single solution. This study gives a clear idea of the selectivity of fluoride anion comparing to phosphate in industrial wastewater for the first time and confirm the proposal given by Habuda-Stanić et al. [61].

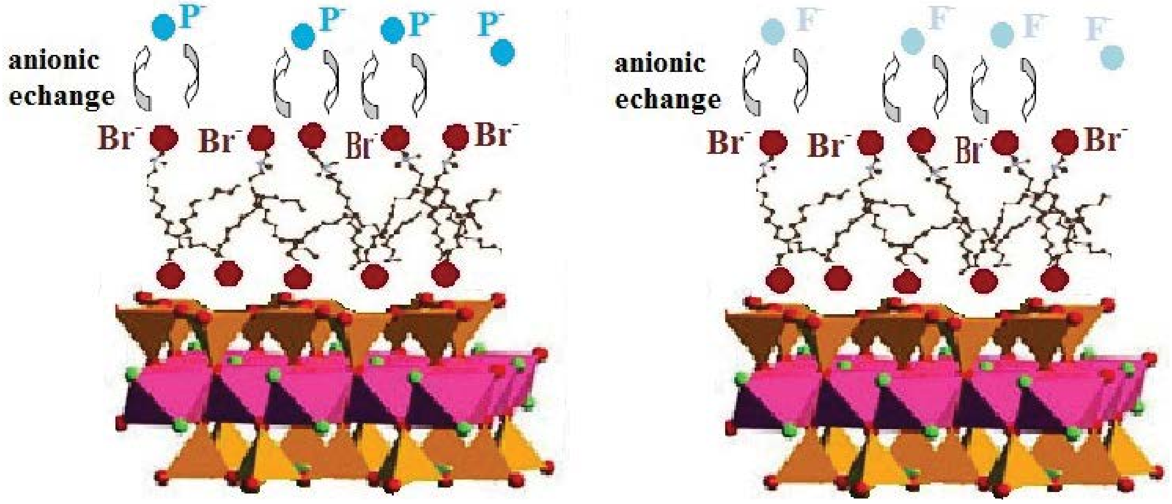

Fig. 4. Mechanism of phosphate and fluoride uptake in organoclays.

Table 4
Comparison of adsorption capacity of phosphate and fluoride onto Na-Haidoudi and HDPy3-Haidoudi with other mineral and organic adsorbents

		Adsorption capacity (mg g^{-1})	References
Phosphate	Modified bentonite	14.33	[54]
	Magnetic diatomite and illite clay	11.9	[55]
	Magnetic iron oxide nanoparticles	5.03	[56]
	Almond shell biochar	7.10	[57]
	Na-Haidoudi	7.04	This work
	HDPy3-Haidoudi	23.80	This work
Fluoride	Aluminum loaded clay	1.30	[58]
	Al^{3+} bentonite	5.7	[59]
	Natural clay (kaolinite)	0.55	[20]
	Synthetic hydroxyapatite with amended aqueous calcium	5.63	[60]
	Na-Haidoudi	11.36	This work
	HDPy3-Haidoudi	27.77	This work

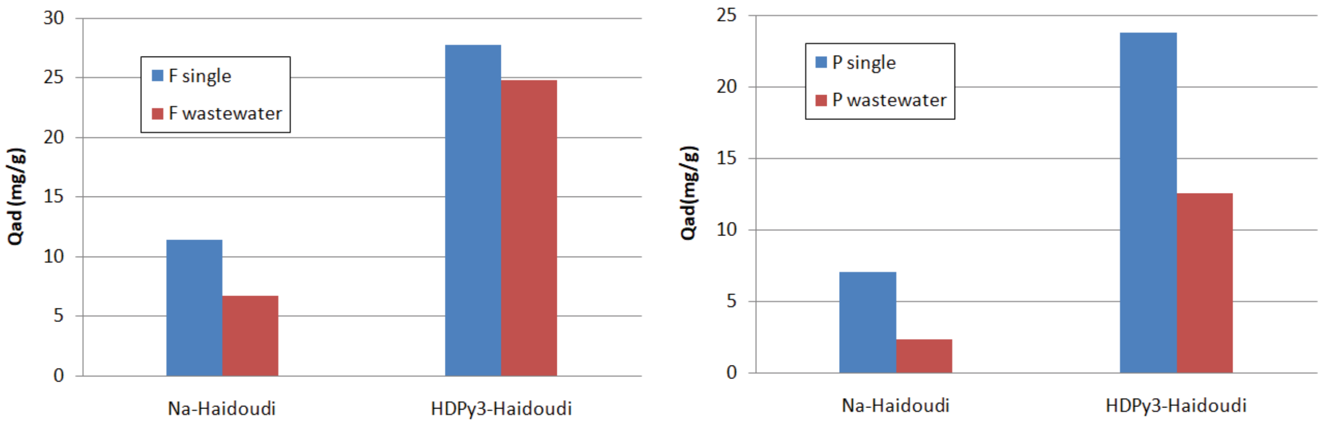

Fig. 5. Adsorption of phosphate and fluoride ions from industrial wastewater, selectivity study.

This good selectivity of fluoride is attributed mainly to steric and charge effects [62] because fluoride is a very small ion it is more strongly hydrated than other monovalent anions because of its high charge density. Especially in this industrial solution when the competition is very higher between fluoride, phosphate, chloride and sulfate and the occupation of the active sites is very limited. The selectivity sequence of anion adsorption coexisting on both adsorbents at pH about 3.3 has been reported to be: fluoride > phosphate > sulfate > chloride.

4. Conclusion

This study investigated the optimization of the modification of Haidoudi clay using the surfactants (HDPy) process for phosphate and fluoride removal from aqueous solutions using the batch method. The modification success of clay was verified by the XRD and FTIR analysis. The treated clay has undergone very important physical and chemical modifications. Based on batch experimental data, modification of Haidoudi clay using surfactants (HDPy) offered an efficient method for adsorbing large amounts of phosphate and fluoride under diverse experimental conditions. Phosphate and fluoride removal from aqueous solutions by these materials increases with the contact time, initial concentration and amount of surfactant intercalated and decreases with increases of pH. Fluoride and phosphate adsorption onto purified and modification Haidoudi clay was a fast process with the initial batch equilibrium being attained within 5 h. Kinetic data follows a pseudo-second-order kinetic model. Adsorption behavior is described by a monolayer Langmuir type isotherm. The maximum adsorption capacities are given by the HDPy3-Haidoudi sample and the values are q_{max} = 23.8 and 27.77 mg g^{-1} for phosphate and fluoride, respectively, which are already three-time higher than the quantity found using the purified clay (clay-Haidoudi). Using industrial wastewater, the removal of fluoride is more selective comparing to phosphate and the modified clay (HDPy3-H) has higher adsorption capacity and can be considered as an attractive material for anions (F and P) removal from aqueous acidic solutions.

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