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Removal of Paranitrophenol by Adsorption on Intercalated Natural Clay

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The present work aims to the valorization of locally available clay for water remediation. The used raw material is a clay soil from the region of Guelma (Algeria). Several physico-chemical treatments have been realized in order to obtain purified clay. The characterization of the sample clay, performed using XRD, FT-IR, DTA and SEM, showed its morphology and its texture. Furthermore, the results correlated to the structural analysis, demonstrated that this clay is a disordered kaolinite of type 1:1. The adsorption experiments of parnitrophenol (PNP) in aqueous medium have been carried out using the raw kaolinite and the urea-intercalated kaolinite. The results showed that the capacity of PNP adsorption on the intercalated kaolinite is more important than that of raw material, where it is 11.06 $\mathrm{mg \cdot g^{-1}}$ and 7.90 $\mathrm{mg \cdot g^{-1}}$ for the urea-intercalated kaolinite and the raw kaolinite respectively. The evaluated experimental values of the adsorption isotherms are in agreement with Langmuir and Freundlich models. In all cases, the adsorption kinetics follows the mechanism of pseudo-second order. In addition, the thermodynamic study indicates that the adsorption of PNP on raw kaolinite and urea-intercalated kaolinite is a spontaneous process.

Keywords: Soil, Characterization, Kaolinite, Intercalation, Adsorption, Paranitrophenol.

1. INTRODUCTION

Phenolic compounds are common contaminants in wastewaters, usually generated from the petrochemical industries. Frequently, paranitrophenol (PNP) is applied for the production of pesticides, dyes, explosives and as a fungicide to protect leather against mildew and Fungus.[1,2] The exposition to PNP may lead to kidney disease, liver failure, skin and eyes alteration and systemic poisoning.[3] Therefore, the removal of PNP from wastewaters is necessary before being discharged into the environment. Many processes are available for removing of soluble chemical species from water such as adsorption, oxidation and filtration. The choice of the technique depends on its cost as well as the type of pollutants to be removed. Adsorption process is an economical process which mainly used for wastewater treatment.

Several studies of adsorption have been performed for removing of paranitrophenol from water using granular activated carbon and a variety of natural materials including kaolinite, montmorillonite and zeolites.[4–11]

Usually, natural clays are not directly applied for water and wastewater treatments. Prior to use them, various physico-chemical modifications are preferable in order to improve their adsorptive capacities. Among them, intercalation of natural clays by organic molecules can increase the interlayer space and also creates new adsorptive sites.

Natural kaolinite (clay of type 1:1), which is very available on the crust, is often used as a host matrix of molecules such as urea, formamide, potassium acetate and dimethyl sulfoxide.[12–17]

In the present work, we studied the adsorption of PNP using a local raw kaolinite and urea-intercalated kaolinite. These materials have been characterized using XRD, IR, DTA and SEM. Different operating parameters have been investigated followed by a thermodynamic kinetic study.

2. MATERIALS AND METHODS

2.1. Materials

The raw material used in this study, which comes from a local clay soil, is applied in the manufacturing of red

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products. It is a characteristic deposit located at the region of Mont Maouna, Guelma (Algeria). A chemical purification of this material has been performed according to the protocol described by Robert and Tessier.[18] The clay intercalation by urea was carried out employing a solid–solid reaction according to the method described by Sadok et al.[13] A mixture of 8 g of urea and 5 g of purified clay was subjected to a manual sanding for 3 h, followed by a mechanical grinding during 15 min at ambient temperature, and then washed with isopropanol in order to eliminate the excess of urea. The intercalated clay was dried at a temperature of 800 °C, and then stored in a glass vial before analysis and uses.

The XRD analysis of clay sample was realized on a diffractometer AT V3.1 Siemens Instrument associated to a graphic program EVA. This diffractometer applied a monochromatized CuKa radiation, with an accumulation time of 5 s/° and a resolution of 0.03°.

The thermal analysis was performed using a DTA 2050 Thermogravimetric Analyze TA Instruments at a heat rate of 10 °C/min from 30 to 700 °C under air atmosphere. The mass of examined samples varies from 15 to 20 mg by using aluminum caps cooled by circulation of argon. The losses in weight during the heating were calculated by an associated program.

Fourier transform infrared (FT-IR) analysis was recorded to identify the functional groups of kaolinite sample in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} using FTIR spectrometer (8400S SHIMADZU). The samples are conditioned in the form of dispersion in a pellet of KBr (1/200 in weight).

The morphology of kaolinite samples was observed by Scanning Electron Microscopy (JEOL6400F).

2.2. Methods

The paranitrophenol (PNP) is a phenolic compound which contains nitro group in its structure. Its molecular formula is $HOC_6H_4NO_2$. The analysis of PNP during adsorption experiments was realized using a spectrophotometer Techompuv/screws 8500 Double-Beam at a maximal wavelength of $\lambda = 317$ nm. The pH solution was monitored by pHmeter HANNA HI 9812-5.

Table I. Main physico-chemical characteristic of clay material.

Chemical composition	Mass rate	Physical parameters
SiO_2	52.18	pH of solution: 7.72
Al_2O_3	29.35	Granulometry: 15% < 100μm
Fe_2O_3	8.08	Humidity = 6.31%
MnO	0.03	BET specific surface area: 5.3 m^2/g.
MgO	0.40	
CaO	0.15	
K_2O	0.22	
Na_2O	0.14	
Loss of ignition	9.45	

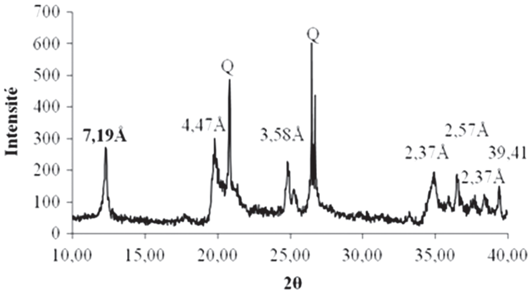

Fig. 1. Diffractogram of clay material, *Q* (quartz).

3. RESULTS AND DISCUSSION

3.1. Characterization of Materials

The results of physico-chemical composition of this clay material are reported in Table I. From this table, we note that the content rate of iron is relatively high. Furthermore, the content of silica (SiO_2) and alumina (Al_2O_3) are predominant which is characteristic of a clay soil composition. The importance of the loss on ignition may be explained by the natural character of this powder and may contain particularly some organic residues.[19]

Figure 1 represents the diffractogramme of clay sample. The analysis of this latter was carried out using data of JCPDS (012-0447) of standard kaolinite (Table II). It is important to note that the sample clay is composed mainly of associated minerals of quartz and kaolinite, together with the presence of traces of other minerals. The amount of quartz is not negligible compared to that of kaolinite. Therefore, peaks at 2θ: 12.35, 20.81 and 24.80 are clearly characteristics of a kaolinite.[20] In addition, it can be seen that most of peaks are wide which suggests that there is a disorders in the kaolinite crystalline.[21, 22]

The DTA curve of raw kaolinite sample presents weight loss in two stages (Fig. 2(a)). The first stage until 85 °C corresponds to a weight loss of physisorbed water. The second which is more important (6.046%) is due to desorption of adsorbed water of structure where the observed endothermic peak between 450 and 700 °C is characteristic of kaolinite dehydroxylation.[23] The reaction of dehydroxylation of kaolinite can be written as following:

$$Al_2Si_2O_5(OH)_4 \xrightarrow{470\ °C\text{–}700\ °C} Al_2O_3 + 2SiO_2 + H_2O$$

Table II. Standard list of XRD peak intensities of kaolinite material.

Kaolinite (JCPDS 012-0447)				Kaolinite material	
hkl	d (Å)	Intensity	2θ	d (Å)	2θ
001	7.15	50	12.39	7.19	12.35
020	4.46	75	19.91	4.47	19.79
110	4.34	65	20.46	4.26	20.81
002	3.56	50	25.01	3.58	24.80
111	3.37	12	26.45	3.36	26.84
$11^{-}3$	2.33	95	38.61	2.37	38.61
$^{-}202$	2.28	65	39.41	2.28	39.45

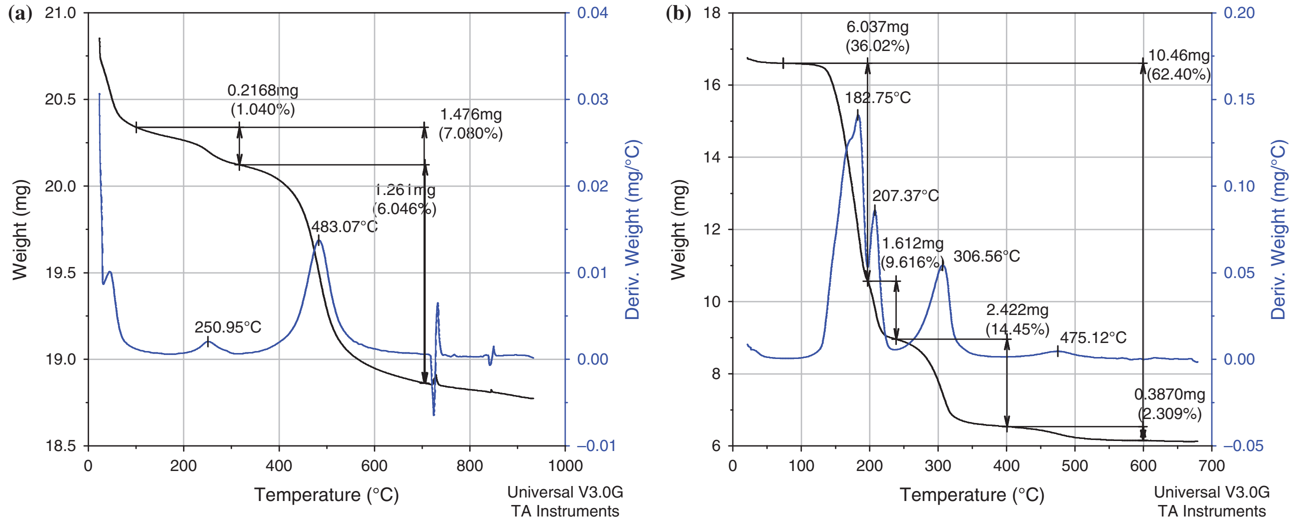

Fig. 2. DTA curves (a) raw kaolinite (b) urea-intercalated kaolinite.

In the case of urea-intercalated kaolinite (Fig. 2(b)), DTA curve presents three weight loss stages. The first until 75 °C is due to surface water evaporation. The second (182–207 °C) may be assigned to the decomposition of urea molecules in the kaolinite surface. The third stage between 182 and 207 °C, which corresponds to an important weight loss of 14.45% at 306.5 °C, can be explained by the decomposition of intercalated urea in the interlayer species of kaolinite. This latter important loss in mass allows us to confirm effectively the intercalation of kaolinite by urea molecules.

Furthermore, the results of FT-IR analysis (Fig. 3) confirm the results obtained by DTA. Similar research studies achieved by other researchers,[14] for the case of pure kaolinite intercalated by urea, have shown that the principal peak at d_{001} increases and passes from 7.2 to 10.7 Å.

The FT-IR spectrum of raw kaolinite (Fig. 3(a)) allowed us to know the assignments of OH and different functional groups. Bands of hydroxyls at 3695, 3669, 3652 and 3619 cm^{-1} are characteristics of the kaolinite. In the case of our kaolinite sample, there are three major vibration bands at 3697, 3649 and 3620 cm^{-1} which indicate that the used clay soil has a disordered structure.[24] In general, clay is characterized by bands of elongation vibrations at 3649 and 3697 cm^{-1}, assigned to hydroxyl groups in the interlayers. Their intensities and their positions are usually susceptible for the intercalation of organic molecules. Another characteristic band at 3620 cm^{-1} could be attributed to external hydroxyl sheets which are not susceptible for the intercalation process.

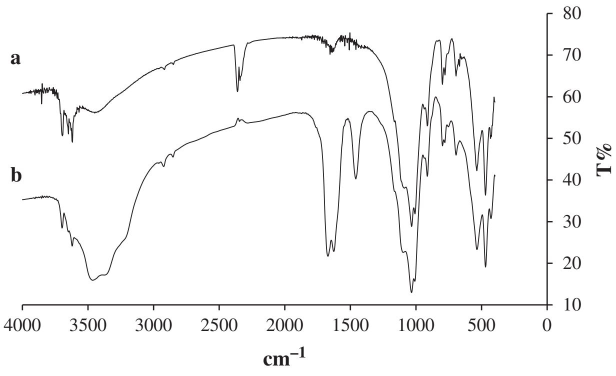

Fig. 3. FT-IR spectrum (a) raw kaolinite (b) urea-intercalated kaolinite.

In the case of the urea-intercalated kaolinite (Fig. 3(b)), the intensities of bands at 3649 and 3697 cm^{-1} have undergone a significant decrease due to interactions of OH external with the carbonyl of the urea.[25] Band of vibration at 1099 cm^{-1} may be attributed to anti-symmetric elongation of C–N group. Bands at 1030 and 1010 cm^{-1} correspond to the deformation vibrations of Si–O–Si groups. Bands of deformation vibrations of Al–O and Al–OH are respectively at 694 and 752 cm^{-1}. Carbonyl group C═O of urea is represented by the vibration band at 1670 cm^{-1}. It is important to note that a new vibration band was appeared at 1627 cm^{-1} which could be attributed to hydrogen bonding of NH_2 with oxygen atom of tetrahedral sheet of O–Si–O.[26, 27]

SEM image, at different scales (Fig. 4), shows that the basal space of material particles is in order of a few micrometers for a thickness less than 100 nm. On the other hand, the hexagonal shape of the basal space is characteristic of the typical texture of a kaolinite particle.

3.2. Effect of Adsorbent Mass on the PNP Adsorption

In order to compare the efficiency of raw and intercalated kaolinite samples, experiences with the same concentration of PNP were performed by the use of different masses of both adsorbents. The results of mass optimization show that 0.2 g of raw kaolinite and 0.1 g of urea-intercalated kaolinite are enough to obtain the adsorption equilibrium of PNP at an initial concentration of 100 $\text{mg}\cdot\text{L}^{-1}$.

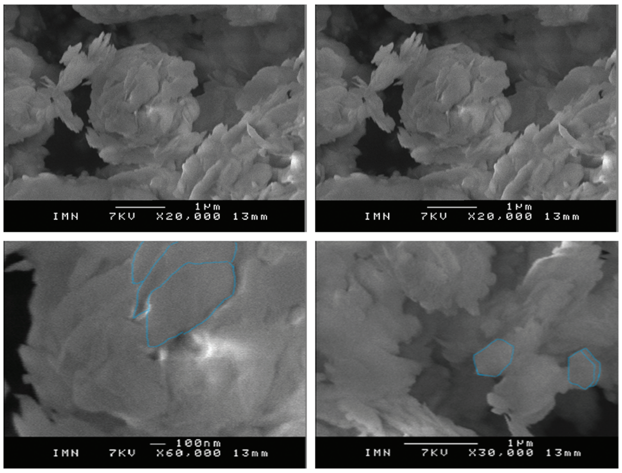

Fig. 4. SEM image of clay material.

3.3. Determination of Equilibrium Time

The optimized time for the elimination of PNP by raw kaolinite and urea-intercalated kaolinite was studied (Fig. 5). The solutions were prepared in Pyrex tubes containing a given mass of adsorbent with a solution of PNP at 100 $\text{mg} \cdot \text{L}^{-1}$ under magnetic stirring at 60 rpm. The obtained results demonstrate that the equilibrium time is reached after 20 min for raw kaolinite and 60 min for urea-intercalated kaolinite.

3.4. Effect of pH

In general, the effect of pH solution is an important parameter for the adsorption process. It can affect both the ionization of adsorbent surface and adsorbate species in the solution. Adsorption experiments of a series of 50 mL flasks containing solutions of PNP at a concentration of 100 $\text{mg} \cdot \text{L}^{-1}$ with different pH values at 2–11 range were operated. The experimental results show that the adsorption of PNP by raw kaolinite is favorable at pH 6 (Fig. 6). The increase in the adsorption capacity in acidic medium may be due to the increase of H^+ ions which affect the ionization degree of PNP. Hence, different PNP structures can be presented in the mixture that can inter-react with the clay support. However, in acidic medium, the adsorption is unfavorable which can be explained by the presence of OH^-. These species can react with hydroxyls of the kaolinite surface. These interactions clay-ions increase the negative charge of material surface leading to a strong electrostatic repulsion between kaolinite surface and PNP molecules.[9,28,29] In the case of urea-intercalated kaolinite, the adsorption of PNP is favorable with pH increasing, and then it remains constant which is due to different interactions in the medium.

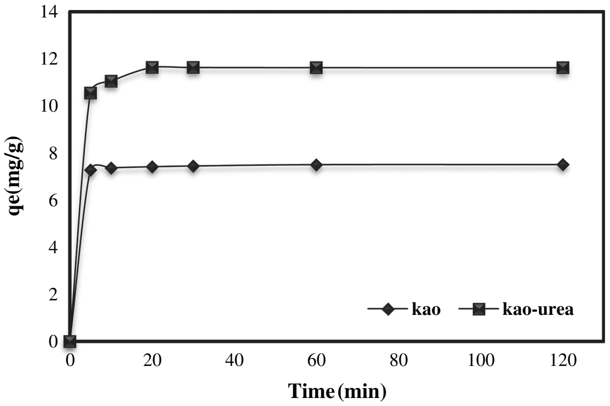

Fig. 5. Adsorption kinetics of PNP on raw kaolinite and urea-intercalated kaolinite.

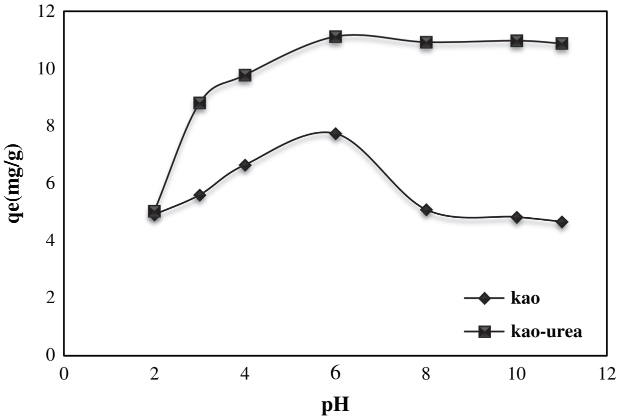

Fig. 6. Effect of pH on PNP adsorption on raw kaolinite and urea-intercalated kaolinite.

3.5. Effect of Temperature

The temperature of the solution is a very important parameter in the adsorption process, because it has a considerable influence on the energy of interaction between the adsorbate and adsorbent. Although the effect of temperature on the adsorption process has been studied carefully, no universal law was however found.[30,31] We studied the effect of temperature on PNP adsorption on clay samples at different values (25, 35 and 45 °C) by conserving the other parameters such as: equilibrium time, pH and adsorbent mass. The obtained results (Fig. 7) show that the adsorption of PNP by kaolinite increases with the increase of temperature. This is can be explained that the adsorption of PNP on this type of solid support follows an endothermic process.

3.6. Adsorption Isotherms

The adsorption isotherms play an important role for the determination of the maximum capacities of adsorption and for the conception of new adsorbents. Therefore, it is important to investigate this point. The adsorbate quantities were determined using the rest method.[32]

$$q_e = \frac{(C_i - C_e)}{m} V \tag{1}$$

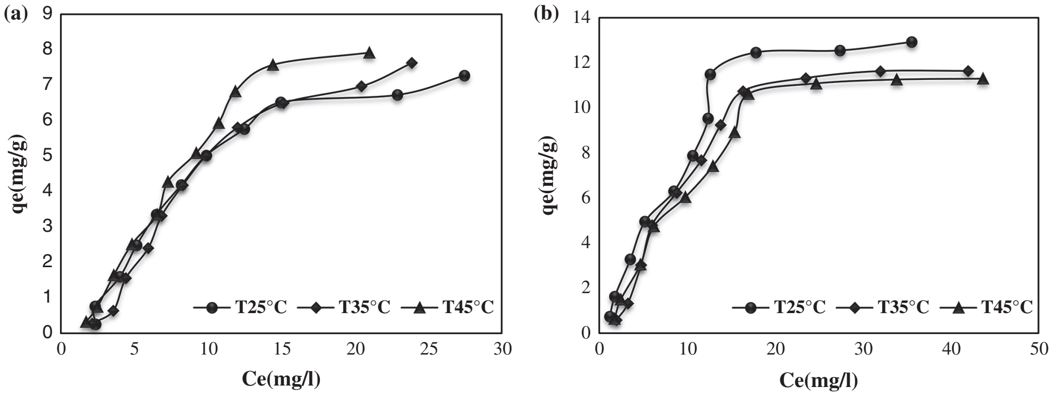

Fig. 7. Effect temperature on PNP adsorption (a) raw kaolinite (b) urea-intercalated kaolinite.

Where, C_i and C_e are the concentrations of initial solution and at the equilibrium respectively ($\mathrm{mg \cdot L^{-1}}$); q_e is the adsorption capacity for the solute ($\mathrm{mg \cdot g^{-1}}$); V is the solution volume (L); m is the adsorbent dose (g).

In our work, we applied two models for studying the adsorption of PNP on raw and urea-intercalated kaolinite samples.

The Langmuir isotherm focuses on the fact that all sites of adsorption are homogeneous and there is no interaction between adsorbed particles on the adsorbent surface which implies, at the maximum adsorption, a saturated monolayer of adsorbed particles on the surface.[33] It is written by the following equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

Where, C_e is the concentration of solution at the equilibrium ($\mathrm{mg \cdot L^{-1}}$); q_e is the adsorption capacity for the solute $\mathrm{mg \cdot g^{-1}}$; $q_{\max}$ is the maximum capacity of adsorption $\mathrm{mg \cdot g^{-1}}$ and K_L is the equilibrium constant.

This equation will be exploited under its linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \tag{3}$$

The Freundlich model (Eq. (4)) is used in the case of the formation of multilayers adsorbed molecules on the surface, with sites sometimes heterogeneous which their energies of fixation are different.[34]

$$q_e = K_F C_e^{1/n} \tag{4}$$

q_e is the adsorption capacity for the solute $\mathrm{mg \cdot g^{-1}}$, C_e is the concentration of solution at the equilibrium ($\mathrm{mg \cdot L^{-1}}$), K_F and $1/n$ are the constants of Freundlich associated to the adsorption and to the affinity.

The linear form of the equation of Freundlich is written as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

Table III presents the constants of adsorption isotherm at different temperature values which were calculated based on Langmuir and Freundlich models. Figure 8 shows that the isotherm linearization of PNP adsorption by raw kaolinite and urea-intercalated kaolinite is satisfactory with good correlation coefficients R^2. We can say that both models of Langmuir and Freundlich give a good description of PNP adsorption isotherm. Hence, the adequacy of both models for the adsorption of PNP on these adsorbents indicates that the adsorption is occurred both in mono and multilayer. The Freundlich constant is a measure of the linearity of the adsorption. On the other hand, the Freundlich constant, n is in the range 1.72–1.96 and 2.28–2.94 respectively for PNP adsorption on raw kaolinite and on urea-intercalated kaolinite which indicates a favorable adsorption of PNP on both materials. Furthermore, the obtained values of n satisfy the condition of heterogeneity ($1 < n < 10$ and $0 < 1/n < 1$) required by the model[11, 35] (Table III).

3.7. Study of Adsorption Kinetics

In order to study the adsorption kinetics of PNP on both materials, experiments have been realized using the optimized parameters including adsorbent mass, pH and temperature. The pseudo-order reaction is estimated by the kinetic model of Lagergren and Blanchard.[36, 37] The model of pseudo-first order of Lagergren is

Table III. Determination of the parameters of adsorption models of Langmuir and Freundlich.

Langmuir					Freundlich	
	R^2	$q_{\max}$	K_L	R^2	K_F	n
T.C°	Kao					
25	0.992	19.60	0.063	0.963	0.43	1.96
35	0.976	21.27	0.039	0.952	0.30	1.72
45	0.987	45.45	0.052	0.982	0.42	1.81
T.C°	Kao-urea					
25	0.995	50	0.021	0.987	1.035	2.28
35	0.988	32.25	0.033	0.992	1.16	2.57
45	0.969	18.18	0.054	0.978	1.32	2.94

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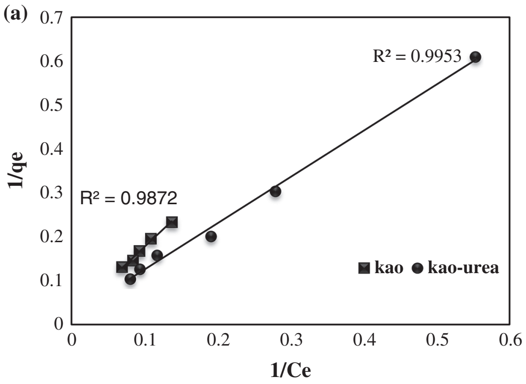

Fig. 8. Isotherms of PNP adsorption based on Langmuir (a) and Freundlich (b) models.

represented by Eq. (6).

$$\frac{dq}{dt} = k_1 \times (q_e - q) \tag{6}$$

Where, K_1 is the apparent rate constant (min^{-1}), q_t is the PNP adsorbed quantity ($\mathrm{mg \cdot g^{-1}}$) at a time t, q_e is the PNP adsorbed quantity at the equilibrium ($\mathrm{mg \cdot g^{-1}}$).

The integration of Eq. (6) in boundary conditions: ($t = 0 \rightarrow t$ and $q_t = 0 \rightarrow q_e$)

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{7}$$

The model of pseudo-second order of Blanchard is represented by Eq. (8).

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{8}$$

Where, q_t and q_e are the PNP adsorbed quantity ($\mathrm{mg \cdot g^{-1}}$) at a time t and at the equilibrium respectively ($\mathrm{mg \cdot g^{-1}}$), K_2 is the apparent rate constant (g.mg^{-1}.min^{-1}).

The integrated form of Eq. (9) becomes:

$$\frac{t}{dt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{9}$$

The kinetic parameters calculated by the linear regression (Fig. 9) are recorded in Table III. From these results, it can be concluded that the correlation coefficients R^2 for the kinetic model of pseudo-first order are lower than that of pseudo-second order which proves that the model of pseudo-second order best describes the PNP adsorption process on both materials. On the other hand, it can be seen that the process governing the PNP adsorption on both adsorbents would be chemisorption which involves electrostatic forces and electron exchange between adsorbent and adsorbate. This hypothesis has been described by several authors in the case of pseudo-second order kinetics.[38, 39]

Table IV. Values of kinetic parameters and correlation coefficient (R^2) of PNP adsorption on raw kaolinite and urea-intercalated kaolinite.

		Pseudo-first order			Pseudo-second order		
	$q_{\mathrm{eexp}\ (mg \cdot g^{-1})}$	K_1	$q_{\mathrm{e}\ (mg \cdot g^{-1})}$	R^2	K_2	$q_{\mathrm{e}\ (mg \cdot g^{1})}$	R^2
Kao	7.90	0.15	3.50	0.851	0.10	8.26	0.9998
Kao-urea	11.07	0.24	5.65	0.846	0.01	25.44	0.9997

3.8. Thermodynamic Parameters

The quantity of adsorbed PNP on raw kaolinite and urea-intercalated kaolinite was measured at different applied temperatures 25, 35 and 45 °C.

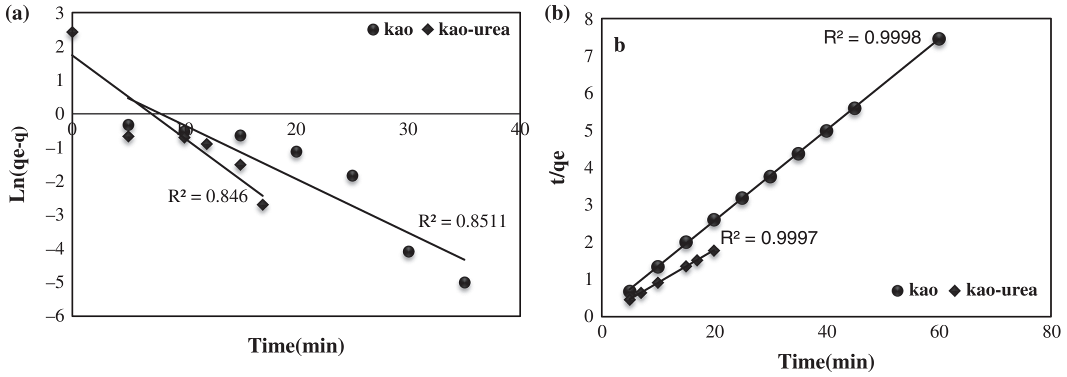

Fig. 9. Linear regressions of PNP adsorption kinetics on raw kaolinite and urea-intercalated kaolinite.

Table V. Results of thermodynamic parameters of PNP adsorption on raw kaolinite and urea-intercalated kaolinite.

	ΔG (kJ. mol^{-1})				
	298 K	308 K	318 K	ΔH (kJ mol^{-1})	ΔS (J.mol^{-1} K^{-1})
Kao	−6.24	−6.58	−8.85	30.71	0.12
Kao-urea	−9.56	−8.73	−7.74	−36.60	−0.09

The equilibrium constant K of the adsorption process for each temperature value is calculated using Langmuir equation.[40]

The thermodynamic parameters ($\Delta H°$, $\Delta S°$ and $\Delta G°$) are useful for the identification of the nature of thermal process (endothermic or exothermic and spontaneity). These parameters can be calculated from the following equations:

$$\Delta G° = -RT \ln K \tag{10}$$

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{11}$$

The values of the enthalpy, the free enthalpy and entropy of PNP adsorption on both adsorbents are represented in Table V.

The positive value of the enthalpy ($\Delta H°$) confirms that the PNP adsorption on raw kaolinite is an endothermic process. However, for the case of urea-intercalated kaolinite, the enthalpy is negative which indicates that the adsorption process on this latter is exothermic.

Generally, for the physisorption, the variation of $\Delta H°$ is <40 kJ.mol^{-1}, however, for the chemisorption, the enthalpy variation is between -80 and -400 J.mol^{-1}.K^{-1}.[41,42] The enthalpy variation is associated to the adsorbed amount at equilibrium which depends on the heterogeneity of adsorption sites kaolinite surface.

The positive value of the entropy variation ($\Delta S°$) shows that the PNP adsorption on kaolinite is accompanied by a medium disorder. Nevertheless, for the urea-intercalated kaolinite, the value ($\Delta S°$) is negative, which means that the PNP molecules in solid-liquid interface are organized more than that of the liquid phase.

The negative values of $\Delta G°$ demonstrate that the PNP adsorption process on these clay supports is spontaneous in the range of studied temperatures.[43]

4. CONCLUSIONS

In the present work, we valorized a local clay soil coming from the region of Guelma (Algeria) for water treatment. The characterization results show that the used material is a disordered kaolinite. In order to enhance the adsorption capacity, this kaolinite was intercalated by urea.

FTIR analysis of urea-intercalated kaolinite shows that the intensity of vibration band of internal OH group (at 3697 cm^{-1}) is displaced and reduced. However, the peak of external OH at 3620 cm^{-1} was not changed during intercalation process.

DTA curves of both clay samples show that the values of different weight losses and their derived temperatures are not the same.

The evaluation of PNP adsorption on raw kaolinite and urea-intercalated kaolinite indicates that the intercalation favors the adsorption of PNP in acidic medium. The increase of temperature leads to increase the adsorption capacity of PNP on the kaolinite (7.90 $\text{mg} \cdot \text{g}^{-1}$), however, in the case of the urea-intercalated kaolinite, is 11.06 $\text{mg} \cdot \text{g}^{-1}$.

The experimental values of adsorption isotherms were estimated using Langmuir and Freundlich models. On the other hand, the results demonstrate that the adsorption kinetics follow the model of pseudo-second order which describes well the PNP adsorption process of the on natural and urea-intercalated kaolinite samples. Finally, the study of thermodynamic parameters indicates that the PNP adsorption on both materials is a spontaneous process.

References and Notes

1. Z. Aksu and J. Yener, *Waste Manage.* 21, 695 (**2001**).
2. S. Rengaraj, S. H. Moon, R. Sivabalan, B. Arabindoo, and V. Murugesan, *Waste Manage.* 22, 543 (**2002**).
3. Z. Liu, C. Yang, and C. Qiao, *FEMS Microbiol. Lett.* 277, 150 (**2007**).
4. T. Dengyong, Z. Zheng, L. Kui, L. Jingfei, and Z. Jibiao, *J. Hazardous. Mater.* 143, 49 (**2007**).
5. T. S. Anirudhan, S. Jalajamony, and S. S. Sreekumari, *J. Chem. Eng.* 184, 178 (**2012**).
6. C. Muñiz-Lopez, J. Duconge, and R. Roque-Malherbe, *J. Colloid Interface Sci.* 329, 11 (**2009**).
7. P. Yuri, A. A. Godwin, and L. Frost, *Ray. J. Colloid Interface Sci.* 360, 440 (**2011**).
8. K. Hülya, Y. Nuray, S. Uğur, K. Fatmanur, and C. Ayla, *J. Hazardous Mater.* 185, 1332 (**2011**).
9. X. Guanghai, G. Manglai, G. Zheng, L. Zhongxin, and H. Zhaochao, *Chem. Eng. J.* 218, 223 (**2013**).
10. Z. Qin, P. H. Hong, X. Z. Jian, S. Wei, L. F. Ray, and Y. Peng, *J. Hazardous Mater.* 154, 1025 (**2008**).
11. B. Zhanga, F. Lia, T. Wub, D. Sunb, and Y. Lia, *Physicochem. Eng. Aspects* 464, 78 (**2015**).
12. F. Franco and M. D. R. Cruz, *Clay. Miner.* 39, 193 (**2004**).
13. L. Sadok, T. A. Elbokl, and C. Detellier, *J. Colloid Interf. Sci.* 302, 254 (2006).
14. M. Éva, K. János, H. Erzsébet, and V. Veronika, *J. Colloid Interface Sci.* 330, 367 (**2009**).
15. P. C. Lopes, A. Dias, Francisco, and L. R. D. da Silva, *Mater. Lett.* 57, 3397 (**2003**).
16. Kh. Nithima, *Appl. Clay Sci.* 50, 414 (**2010**).
17. C. Hongfei, H. Xinjuan, L. Qinfu, L. Xiaoguang, and L. F. Ray, *Appl. Clay Sci.* 109, 55 (**2015**).
18. M. Robert and D. Tessier, *Ann. Agrom.* 25, 859 (**1974**).
19. T. Karfa, B. Philippe, J. Jean-Paul, and G. Moussa, *C. R. Chimie* 10, 511 (**2007**).
20. J. M. Cases, O. Lietard, J. Yvon, and J. F. Delon, *Bull. Minéral.* 105, 439 (**1982**).
21. T. Holtzapffel, Editions des sociétés Géologique du Nord (**1985**)
22. F. Toussaint, J. J. Fripiat, and M. C. Gastuche, *Phys. Chem.* 67, 26 (**1963**).
23. K. Heide and M. Földvari, *Thermochim. Acta* 446, 106 (**2006**).
24. M. Jakub, G. Adam, and B. Krzysztof, *Appl. Clay Sci.* 56, 63 (**2012**).
25. V. A. Drits and C. Tchoubar, 371 (**1990**).

26. A. O. Lawal, J. A. Lori, and E. J. Ekanem, *J. Applied Sci. Research* 6, 1662 (**2010**).
27. T. Slonka, *Mater. Sci. Forum* 91–93, 231 (**1992**).
28. F. Uday Alkaram, A. Abduljabar, H. Mukhlis, and A. Al-Dujaili, *J. Hazard Mater.* 169, 324 (**2009**).
29. S. K. Nadavala, K. Swayampakula, V. M. Boddu, and K. Abburi, *J. Hazard Mater.* 162, 482 (**2009**).
30. N. Jozja, P. Baillif, and J. S. Touray, *Comptes Rendus Géoscience* 335, 729 (**2003**).
31. N. Güngör and S. Karaoglan, *Mater. Lett.* 48, 168 (**2001**).
32. Y. Huang, X. Ma, G. Liang, and H. Yan, *Chem. Eng. J.* 141, 1 (**2008**).
33. I. Langmuir, *J. Am. Chem. Soc.* 38, 272 (**1916**).
34. H. Freundlich, Metheum, London (**1926**).
35. J. Q. Jiang, C. Cooper, and S. Ouki, *Chemosphere* 47, 711 (**2002**).
36. S. Binoy, M. Mallavarapu, X. Yunfei, and N. Ravi, *Chem. Eng. J.* 185–186, 35 (**2012**).
37. Y. S. Ho, *Scientometrics* 59, 171 (**2004**).
38. Y. S. Ho, *Water Res.* 40, 119 (**2006**).
39. Z. Ioannou and J. Simitzis, *J. Hazardous Mater.* 171, 954 (**2009**).
40. P. S. Nayak and B. K. Singh, *Desalinatio* 207, 71 (**2007**).
41. M. B. McBride, Oxford University Press (**1994**).
42. M. J. Jaycock and G. D. Pariftt, Chemistry of Interfaces, Ellis Horwood Ltd., Onichester (**1981**).
43. M. Akcay, *J. Colloid Interface Sci.* 296, 16 (**2006**).