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Kinetics of cadmium adsorption by smectite of Oued Tfal (Gafsa Basin)

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ABSTRACT

Metals are quickly trapped in the soil and, in particular, in clays, which generally behave as reservoirs of these toxins. This retention is due to the adsorption properties and cation exchange capacity of clays, and we have to control this in order to limit their transport in the biosphere. This will be the subject of the study: the characterization of smectite of the Oued Tfal region in Gafsa (Tunisia) in one hand, and its application in the retention of cadmium through the new method of adsorption, and the study of factors affecting the adsorbability of the metal (nature of clay, ligands, initial concentration, etc.) on the other hand. The total surface area, determined by the methylene blue method, for the raw and purified samples was 556 and 783 m^2/g, respectively. The adsorption kinetics depend on several parameters. The adsorption capacities of Cd(II) by raw and purified clays are 971 and 1,005 mg/g, respectively in the single element system, confirming the close correlation between the physicochemical properties of the adsorbent and its removal capacity. Cd (II)-clay obeys the Langmuir and Freundlich adsorption isotherms with high regression coefficients. The use of this adsorbent notably decreases the cost of treatment.

Keywords: Clay; Adsorption; Membrane; Kinetics; Cadmium

1. Introduction

Extensive use of heavy metals in various fields [1–3] means that large quantities of aqueous effluents contaminated by these metals are released into the environment. These heavy metals are characterized by high toxicity and high storage capacity in aquatic and terrestrial environments where they remain for long periods of time. Contamination of soil and water by heavy metals is a major environmental problem that needs to be solved. Many methods can be applied for the removal and/or recovery of metals from industrial effluents [4–6]. Furthermore, conventional techniques of depollution, which are very effective for organic contaminants, have proved to be cumbersome, expensive, or unsuitable for heavy metals which are, by definition, poorly degradable. Among toxic heavy metals, cadmium, in particular, is considered to be an extremely dangerous pollutant for human health and which also poisons the environment. This is due to its high toxicity even at low concentrations and due to a very high water solubility [3,7]. Due to these legislative

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requirements in one hand, and the harmful consequences of effluents containing cadmium both for humans and for the environment on the other hand, treatment of wastewater contaminated with heavy metals and especially with cadmium, has become a high priority. Cadmium is adsorbed by clays, organic materials, and by the attenuation of metals downstream at waste disposal sites [8–11]. The adsorption of metals by clays has been widely studied. Classical methods studied involve mixing a volume of metal solution with a mass of clay and then subjected to an agitation and centrifugation cycle, the supernatant is then determined through atomic absorption in order to determine the concentration adsorbed by the clay. However, this preparation has several disadvantages. Since, these methods require several constraint adsorption conditions of pH, agitation, and centrifugation, the extract may contain impurities in suspension which can yield wrong analysis results. In this study, we optimized an adsorption through a membrane method which is similar to natural adsorption.

2. Experimental

2.1. Materials

Local clay from Oued Tfal was characterized in an earlier study [12]. Natural clay from Oued Tfal was ground in an agate mortar and sieved through a 100 μm mesh to obtain fine grains. The resulting clay powder was dried at 60˚C. The smaller than 100 μm powder was purified through repeated cation exchange with a NaCl solution (1 M) followed by washing, sedimentation, and dialysis [13]. The raw sample before purification was referred to as OT3 and the purified product as OT3Na. The cation exchange capacities (CEC) as well as the total surface areas (SSA) were determined by the adsorption of methylene blue (MB) from aqueous solutions. The mineralogy was characterized by X-ray diffraction (Philips goniometer, PW1730/10, using the CuKa, 40 KV, 40 mA). The cadmium and the cation concentrations in the solution were measured by atomic absorption spectrometry (spectrometry, Specta-Span III). The amount of cadmium adsorbed was calculated as the difference between the initial and final concentrations. The descriptions of the used membrane (SPECTRA/POR 1 6-8K MWCO 50MM 30M/PKG) were: filtration, dialysis, ultrafiltration, microfiltration, and membranes and microbiology transfer tube. Microscopic analysis was performed using an environmental scanning electron microscope (ESEM) FEI Quanta 200. This device can provide rapid information on the morphology and chemical composition of a solid object.

2.2. Adsorption procedures

The study of retention of cadmium by clay was carried out under conditions as close as possible to those of natural soil adsorption: at room temperature and with a moderately acid pH. The retention kinetics of different forms of cadmium by the clay depends on the speed required to establish interactions with the solid-solution interface and on the limitations in the transfer of matter. To control the speed of mass transfer, the stirring speed of the pump was set to 250 rpm throughout the experiment. Cadmium is adsorbed by the clays through a filtration membrane. This membrane is a thin wall separating two different media with the following characteristics: permeability, porosity, organic, homogeneity, and selective. The reagents used to prepare the test solutions were $CdCl_2{\cdot}H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$. The initial concentrations of Cd (II) metal solution were either 1,028 or 10,282 mg/L. The method (Fig. 1) consisted in preparing an aqueous solution of 5 wt.% clay. This solution was then put in a cylindrical porous membrane. The membrane was then placed in a flat-bottomed container containing two liters of metal solution. To follow the adsorption kinetics, 20 mL of the solution was taken at regular time intervals to determine the amount of adsorbed cadmium and other ions released into the solution. The pH of each test was measured. The amount of adsorbed metallic ions in the clay was expressed as follows:

$$q_e = (C_0 - C_e)(V - 0.02n)/W \quad (1)$$

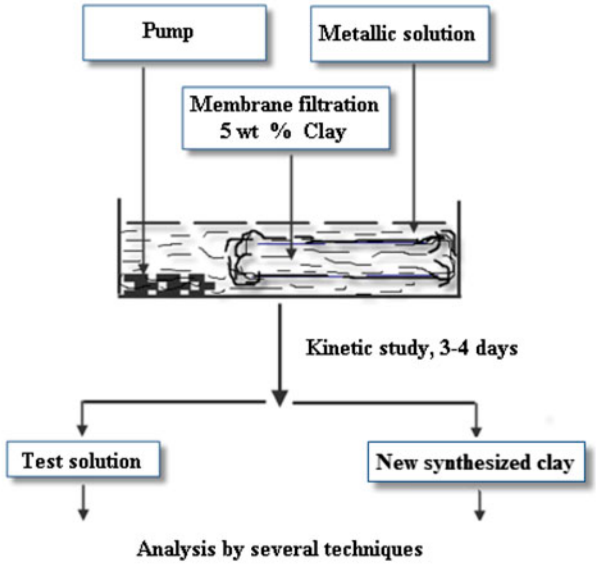


Fig. 1. Protocol of the new method of adsorption through a filtration membrane.

where q_e is the amount (mg/g) of adsorbate adsorbed per unit mass of adsorbent, C_0 and C_e—the initial and the equilibrium concentrations (mg/L) of Cd(II) in solution, respectively, V—volume (L) of solution, n—the test number and W (g)—mass of the adsorbent in the solution. The ions initially present in the clay interlayer space were almost entirely replaced by other metal ones, which led to a new ionic matrix.

Assuming that the clay is a semipermeable membrane, the locations of negative charges will retain cations on one side and release ions from the other and vice versa. Ions released from the clay in the metal solution were: (Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, and K^+). The physicochemical properties of new clay matrices, resulting from the cation exchange, were studied by different techniques.

3. Results and discussion

3.1. Characterization of adsorbents

Clays at Oued Tefal (Gafsa Basin) were smectite mixed with raw calcite and quartz as demonstrated [12]. The reflections from the calcite, quartz, and other impurity phases were relatively attenuated. This proves the importance of purification. The 001 reflection seen on the diffractograms of the OT3Na purified sample (Fig. 2) shows a maximum between 1.54 and 1.31 nm. This is interpreted to be a reflection of smectite in the varying states of hydration that depend on: the nature of the layers, exchangeable cations, and the relative ambient humidity [14–16]. Treatment with ethyl glycol showed a shift of line 001 to 1.7 nm, meaning that these clays are swelling and belong to the smectite family. Heating the sample to 550˚C made the interlayer spacing decrease to 1 nm due to the evaporation of the hydration water of the interfoliaceous ions leads to a reduction in the distance between the layers. Said distance becomes similar to that of micas, where layers are bound by anhydrous ions [17]. The results (Table 1) obtained by the method of the MB show a variation of the CEC for the raw and purified samples. The raw sample OT3 presents the lowest value for the CEC which can be explained by the high amount of calcite in the clay. After purification, the cation exchange capacity of the purified sample (OT3Na) increased greatly and became comparable to that of the smectite [18]. The specific surface area of the purified clay is similar to that of a pure montmorillonite (400–800 m^2/g) [19]. This result shows the influence of particle shape (in sheet) in increasing the specific surface area [20].

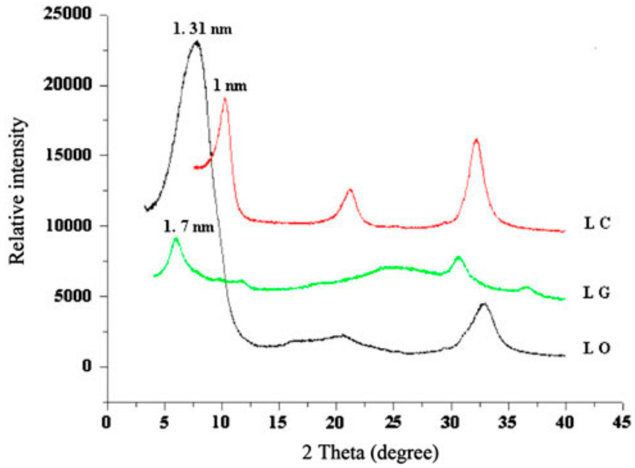


Fig. 2. X-ray diffractograms for: OTNa (LO): Na-exchanged; OTNa (LG): glycolated for 1 h; OTNa (LC): heated for 1 h at 550˚C.

3.2. Adsorption of Cd(II) onto smectite

The adsorption isotherms are graphic representations of the stability data at constant temperature. This aims to follow the variation of metal concentrations in solution as a function of metal content adsorbed by

Table 1
Cation exchange capacity, total surface area and BET of the OT3 raw and OT3Na purified clays

	CEC (meq/100 g)		BET (m^2/g)	SSA (m^2/g)
Clays	Hydrated	Calcined		
OT3	56	71	59	556
OT3Na	82	100	108	783

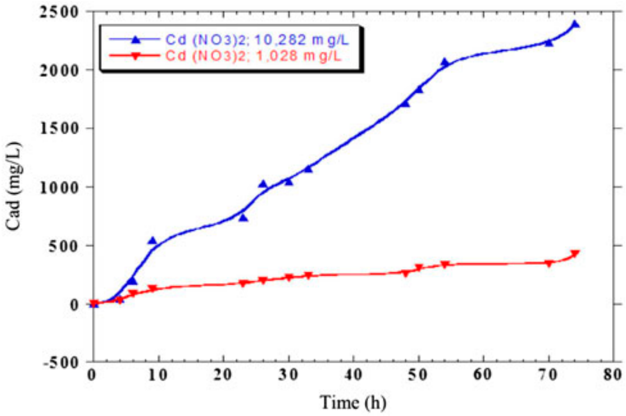


Fig. 3. Evolution of the concentration of cadmium adsorbed by the OT3Na purified sample at two concentrations: 1,028 and 10,282 mg/L.

the clay. The adsorption isotherms (Fig. 3) obtained were *S*-shaped as demonstrated [21,22]. The S-shape reflects a strong competition for the adsorption sites between the clay and the ions being studied. It is worth noting that the positive concavity equated with this type of isotherms suggests that the adsorption takes place in a multilayer adsorption mechanism [23]. Moreover, the adsorbed ions are perpendicularly sited at the adsorbent surface.

The kinetics experiments involved several cycles. Each cycle strongly indicates that the adsorption of cadmium metal ions by clay is a two-step process: a rapid adsorption of metal ions by the external surface followed by a possible slow intraparticle diffusion. This two-stage process can also be due to the fact that adsorption occurs onto two different types of binding sites on the adsorbent particles. Similar results have also been obtained by other researchers [24–26]. The metal forms several, almost irreversible, strong links to internal binding sites. The results of the work on the kinetics of binding Cd (II), Cu (II), and Ni (II) with an initial concentration of 100 mg/L of natural clinoptilolite clay [27], showed that the time to reach equilibrium was reached after 60 min for all concentrations studied. Various studies of heavy metals, such as copper, zinc, lead, cadmium, and nickel confirm the fast retention reactions of these elements in soils [28,29]. By examining the different results we can deduce that the binding kinetics of cadmium in the clay is quite long. The equilibrium time ranges from 74 to 75 h. This result disagrees with the available literature dealing with batch adsorption trials. The comparison of conventional adsorption (batch method) with the new one explains the large variation in equilibrium time between the two methods. The adsorption capacity becomes constant after the equilibrium time is reached.

3.2.1. Factors affecting the mobility of cadmium

The transfer process between the solid and liquid phase are manifold and depend greatly on the nature of the link between the metals and the solid phase (which is also known as a carrier or retention phase), as well as on the physical-chemical conditions prevailing in the soil. These aspects will be dealt separately in order to explain the mobility of heavy metals.

3.2.2. The effect of the nature of the ligand and the adsorbent state

To highlight the selective role of such ligand, we chose to introduce the metals in a solution in the form of nitrates and chlorides to observe the effect of the ligand in minimizing the formation of mineral complexes in solutions and how it encourages the adsorption of metal clay. The adsorption selectivity (Table 2) for a fixed concentration 1,028 mg/L, was in descending order as follows: Cd (NO_3^-) > Cd (Cl^-), which showed a better competition between the adsorption sites of the clay and the nitrate ligand. Introducing the metal in solution in the form of nitrates minimizes the formation of mineral complexes in solution. The slight decrease in adsorption with ligand nitrates compared to that of chlorates when the metal concentration increases, is insignificant. Furthermore, it should be noted that the adsorption for the divalent cation Cd(II), is better for OT3Na the purified sample than for OT3 the raw sample. This is due to the impurities in the matrix which hinder the adsorption in some cases.

3.2.3. Effect of initial Cd(II) ion concentration

These results (Table 2) show that increasing the concentration (in other words increasing the ionic strength) favors the ion exchange [30]. The links of the outer sphere, based on electrostatic interactions, are more sensitive to ionic strength [31], thus sensitivity to ionic strength is often considered an indicator of outer-sphere complexation [32]. Replacement power increases qualitatively with atomic number for ions of the same valence; in other words, replacement power tends to increase when the size of the ion increases. Smaller ions are retained less than large ones. The change in adsorbability depends on the nature of the raw or purified clay, the nature of metal and its initial concentration. These variations can be attributed to differences in the binding energy of the metal-clay silt and the recess parameters: temperature, ionic strength, and pH, which are fixed. Ghorbel-Abid et al. [33,34] proved that the effect of increasing the equilibrium concentration could cause changes in the edge of the surface of the clay such as energy distribution of adsorption sites and the loading of particle size.

Table 2
Effect of concentration and nature of the ligand on the adsorbtion of cadmium by OT3 and OT3Na clays

Concentrations of Cd^{2+} (mg/L)	1,028		10,282	
Nature of the ligand	Cl^-	NO_3^-	Cl^-	(NO_3^-)
Samples	Q_{max} (mg/g)		Q_{max} (mg/g)	
OT3	12	148	917	803
OT3Na	42	150	1,005	842

3.2.4. Influence of pH

The pH is a factor with a crucial role in the mobility of metallic ions, as it affects the number of negative charges that can be placed in solution; the increase in soil pH favors the adsorption of metals [35,36]. In general, when the pH increases, the cations are less soluble and the anions are more soluble [37–40]. In addition, the increase in pH often induces the formation of precipitated species that may limit the solubility and bioavailability of all ionic species. However, it also leads to organic matter dissolution and the subsequent formation of more soluble organometallic complexes [41]. Changes in pH are, therefore, complex and sometimes have opposing effects on the mobility of heavy metals, especially in the presence of organic and inorganic ligands. Under acidic conditions, the metal remains in the form of free cations and the percentage of adsorption by a colloid is low. With increasing pH, the concentration of hydroxide metallic cations increases and the percentage of metallic cations bound to the colloid increases sharply. In the case of cadmium, the slight decrease in the adsorption is explained by the initial acidic pH (5–6) conditions (Fig. 4). The active sites of the clay are saturated from the beginning of the treatment with excess protons located in the aqueous solution, which may limit the fixation of Cd^{2+} cations in the pores and surface of the clay. Cadmium is found in various free cationic forms (Cd^{2+}), hydrated Cd $(H_2O)_6^{2+}$ or hydroxy Cd $(OH)^+$. Treatment of the adsorbent by acid can liberate divalent (Fe^{2+}, Ca^{2+}, Mg^{2+}) and trivalent (Fe^{3+}, Al^{3+}) metal cations through ion exchange with H^+ protons. There will be a competition between the cationic species of cadmium, the metal cations released from the clay, and protons to occupy the active sites on the surface of the clay [42,43]. The H^+ protons are preferentially fixed because of their small size (steric hindrance), high concentrations (the phenomenon of mass transfer), and the weak electrostatic repulsion with the occupied sites on the surface of the clay. From our experience, this explains well the lowest removal efficiency of cadmium. This result is consistent with the work of Achour and Xu [44,45] which showed that the greater removal efficiency of cadmium on two bentonite clays from Algeria (bentonite and Maghnia Mostaghanem) reached a maximum at a pH between 9 and 10.

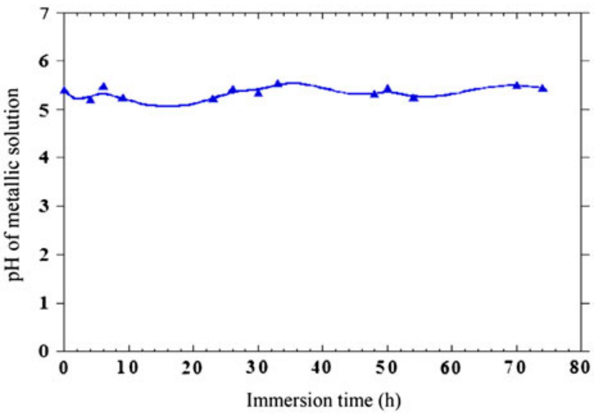


Fig. 4. The pH value of a metallic solution as a function of immersion time.

3.3. Kinetics of ions released from the clay in the metal solution

Assuming that the clay is a semipermeable membrane, it does not remain inert to the surrounding environment. When in contact with a solution, exchange between the two phases occur until a balance is reached. A change in the composition of the solution (concentration of pollutants) may cause a redistribution of chemical species between the two phases with the consequent retention of the pollutant. This is one of the reasons why clays are considered to be a constituent of the highest order for containment barriers. For this reason, we carried out an additional analysis to identify the ions released from the clay in the supernatant solution. Analysis of this solution (Fig. 5) shows an increase in the concentration of the ions: sodium, calcium, and magnesium. This could be explained by an affinity between the Cd^{2+} ion adsorbed by the clay and the Ca^{2+}, Mg^{2+}, and Na^+ ions released into the solution. The stability of the concentrations of some elements, such as iron and aluminum is explained by the exchange in the interlayer space and does not affect the structure of the clay.

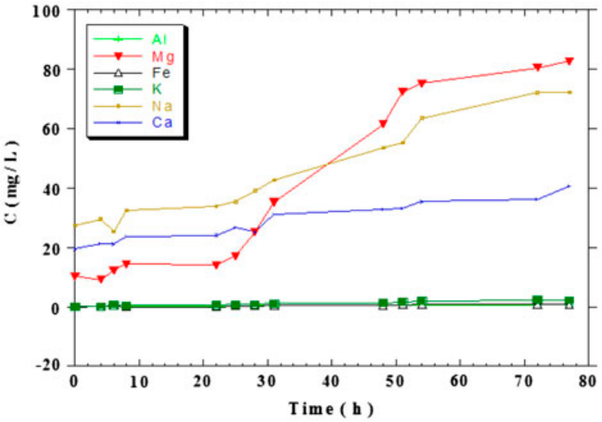


Fig. 5. Evolution of the concentration of cations released by the purified clay in the metallic solution: Cadmium treated with 10,282 mg/L.

3.4. Characterization of new synthesized matrices

This part concerns the study of physicochemical properties of new synthesized clay matrices after treatment with cadmium through the filtration membrane.

3.4.1. Cation exchange capacity and specific surface area

A comparative study of these values (Table 3) and the results found through the adsorption of cadmium show a decrease in all sizes. In fact, this reduction differs depending on the state of the raw or purified clay. We can show complementary results: raw or purified clays, which have a better adsorbability of cadmium, with a low adsorption of MB. However, the purification of clay with distilled water and sodium suggests an adsorption selection of metals. Indeed matrices saturated with cadmium do not have the same affinity for MB: the sudden drop in the CEC value for the matrix (OT3, $Cd(NO_3)_2$, and 1,028 mg/L) compared to the same untreated OT3 sample, shows that the adsorption of (MB) was enhanced, when the clay adsorbed less cadmium. On the other hand, the comparison of the same matrix treated with two different ligands showed a greater adsorption of the (MB) molecule for matrices richer in Cl^- than in NO_3^- at a high concentration. Based on the results found, there are indications that the adsorption of the (MB) is enhanced when the clay adsorbs less cadmium, and depends on the initial concentration of the metal and the nature of the raw or purified clay.

3.4.2. Analysis with an ESEM

Morphological examination via environmental scanning electron microscopy allowed us to follow the evolution of grain size. As an example, in this paper we present studies of matrices synthesized from the raw and purified samples, saturated with cadmium at two concentrations: 10,282 and 1,028 mg/L.

3.4.2.1. Morphological study. The micrographs of the four samples were examined in pairs (Fig. 6). For the low cadmium concentration we found that there is grain growth but with irregular geometric shapes. With 10,282 mg/L concentration, it seems that the grains agglomerate and form large grains of a regular geometric shape. We can argue that the cadmium has a role in the reorganization of the constituents of the clay.

3.4.2.2. Qualitative X-ray microanalysis study. The micrographs of the sample (Fig. 7) confirmed the presence of major elements and cadmium. We maintained the high peak intensity of cadmium to the concentration of 10,282 mg/L. There are significant reduction in magnesium and aluminium peaks indicating a change in the octahedral layer which can change the charge thereof. To confirm this hypothesis, it is therefore essential to map X cadmium.

3.4.2.3. Mapping X. The results that emerged from this analysis confirmed that cadmium had entered the clay grains. Peaks of cadmium (Fig. 8) confirm the importance of this result. The maps show that the clay grains "trap" cadmium; we would therefore be tempted to repeat a systematic study at different concentrations. In this section it has been clearly proved that the clay grains traps cadmium. The clay was found to be an efficient adsorbent for Cd(II) removal in aqueous systems.

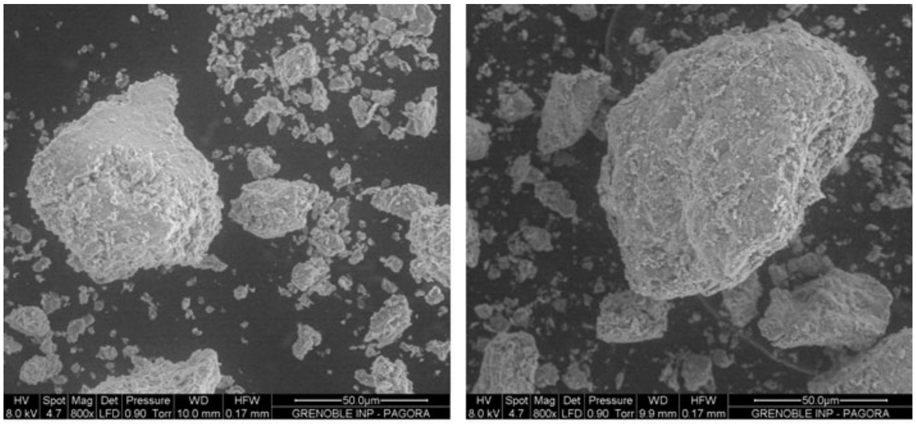
3.5. Kinetics and the modeling of cadmium adsorption isotherms

3.5.1. Kinetic study

In order to approach the actual reaction mechanism as much as possible [46,47], we opted for a second-order kinetic model. These mathematical models were chosen firstly for their simplicity and also for their application in the field of adsorption of inorganic compounds on different adsorbents. In this study we

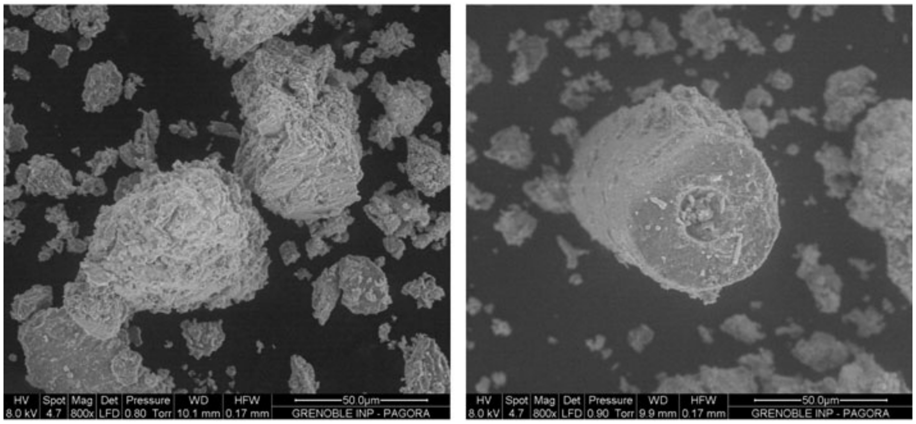
Table 3
Cation exchange capacity and specific surface area determined by the MB method for the cadmium-saturated matrix clay

Samples	Q_{max} (mg/g)	CEC (meq/100 g)	SSA (m^2/g)
OT3	199	56	556
OT3 (Cd $(NO_3)_2$; 1,028 mg/L)	118	33	258
OT3 (Cd $(NO_3)_2$; 10,282 mg/L)	144	41	321
OT3Na	289	82	783
OT3Na (Cd $(NO_3)_2$; 1,028 mg/L)	230	65	509
OT3Na (Cd $(NO_3)_2$; 10,282 mg/L)	178	50	391



OT3Na, Cd(II), 1,028 mg/L

OT3, Cd(II), 1,028 mg/L



(OT3Na, Cd(II), 10,282 mg/L)

(OT3, Cd(II), 10,282 mg/L)

Fig. 6. Morphology of raw and purified samples treated with cadmium at two concentrations: 1,028 and 10,282 mg/L.

have used the laws of pseudo-second-order kinetics, which are described by the mathematical equation:

$$t/q_{\mathrm{t}} = 1/2K + t/q_{\mathrm{e}} \tag{2}$$

where k is the pseudo-second-order rate constant of adsorption (g min/mg), q_{e} and q_{t} are the amount (mg/g) of cadmium adsorbed at equilibrium and at time t, respectively. In the previous section, it was noted that the adsorption of metals happens in cycles that repeat in time; for this reason, we studied the adsorption isotherms at appropriate intervals. The kinetic plots of t/q_{t} vs. t for Cd(II) ions adsorption are presented in Fig. 9. The k values were calculated from the gradient of the linear plot of (t/q_{t}) vs. time for the metal Cd(II). The relationships were linear and the values of the correlation coefficient (R^2) suggest a strong relationship between the parameters, and also explain that the process of adsorption of ion follows pseudo-second-order kinetic model. From Table 4, it can be seen that the correlation coefficient has an extremely high value ($R^2 > 0.98$). Cd^{2+} metal ions are not adsorbed on the clay in the same way because the initial concentration of the metal greatly affects the rate of adsorption. We found that the amount adsorbed at equilibrium is greater at high concentrations. The pseudo-second-order model gives a better description of the reaction kinetics of adsorption of cadmium by raw and purified clay. These results suggest that the adsorption of metals by clays is controlled by the physisorption process (or physical adsorption). Several studies [48,49] found that the kinetics of adsorption of metals by clay materials obey the pseudo-second order. [50,51] have shown that the adsorption kinetics are rapid during the first minutes of contact. This can be interpreted by the fact that, at the beginning of adsorption, the number of active sites available on the surface of the adsorbent material is much greater than those remaining after a certain amount of time.

3.5.2. Langmuir and Freundlich isotherm models

Adsorption isotherms are often used as empirical models, which do not make statements about the

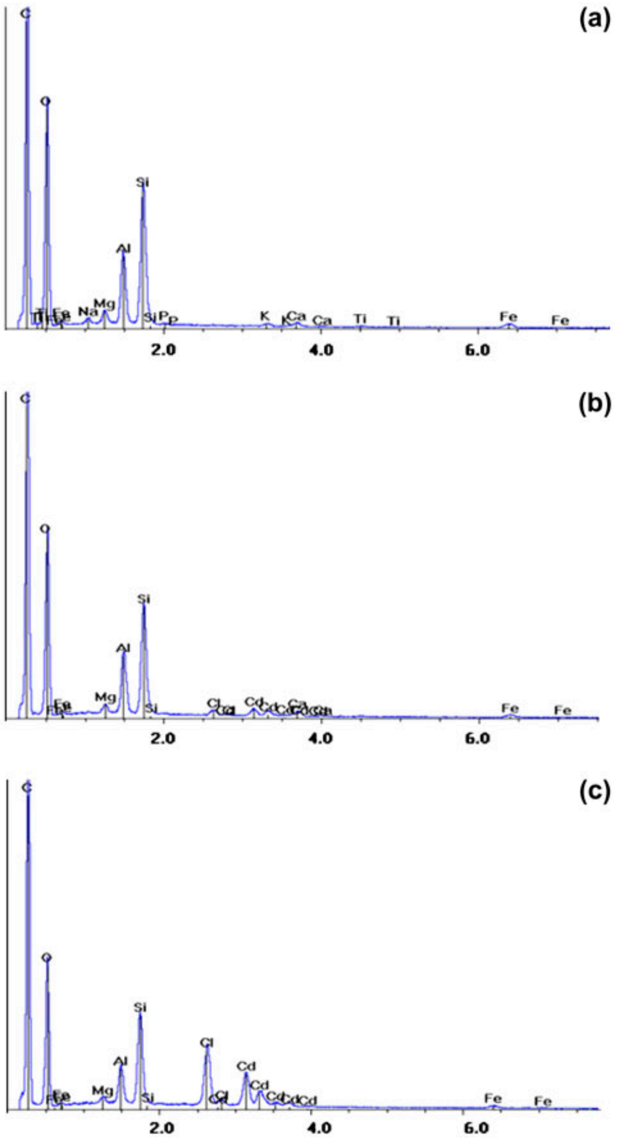


Fig. 7. X-microanalysis of OT3Na purified treated with $CdCl_2$ at two concentrations, (a): OT3Na purified untreated, (b): 1,028 mg/L, (c): 10,282 mg/L.

underlying mechanisms and measured variables. They are obtained from measured data by means of regression analysis. The most frequently used isotherms are the Freundlich, and the Langmuir models. They are mathematically expressed as:

$$q_e = Q_m\, b\, C_e/(1 + b\, C_e),\quad \text{the Langmuir monolayer isotherm} \tag{3}$$

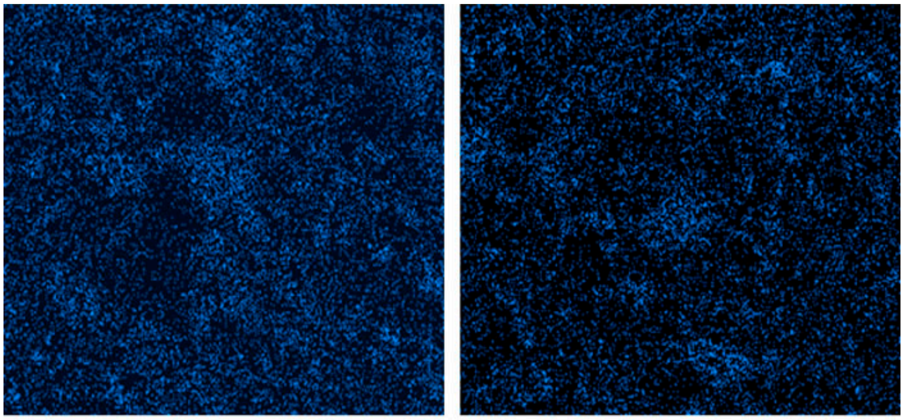
$$C_e/q_e = 1/K_l + (b/K_l)C_e,\quad \text{the linearized forms of (3) [52]} \tag{4}$$

$$q_e = K_f\, C_e^{1/n}, \text{Freundlich isotherm [53]} \tag{5}$$

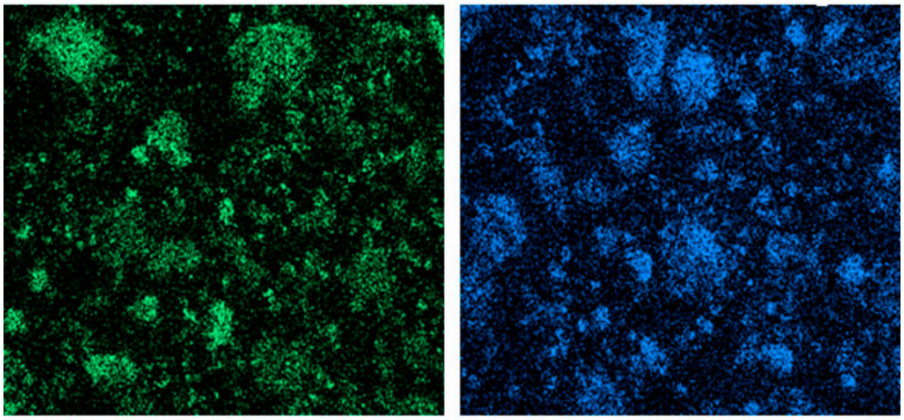
$$\ln q_e = \ln K_f + 1/n \ln C_e,\quad \text{the logarithmic forms of (5)} \tag{6}$$

$$\Delta G^\circ = -RT \ln K_l,\quad \text{the changes of the Gibbs free energy} \tag{7}$$

where q_e is the adsorption density (mg/g) at equilibrium of Cd(II), Q_m is the monolayer adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L) of Cd(II), (b, K_l) and (K_f, n)—Langmuir and Freudlich parameters, respectively, T (K) refers to the temperature, R (8.314 J/mol K) is the gas constant. We found a good agreement between these isotherms and experimental results of the linearization for the models studied (Fig. 10). Furthermore, the high coefficients of determination, further confirmed that our experimental data fit these models. The adsorption isotherm of Cd(II) on all the four adsorbents was also fitted well in the Freundlich isotherm model and the adsorption capacity (K_f) of adsorbents for Cd (II) was increased in the order OT3Na (Cd, 1,028 mg/L) < OT3 (Cd, 1,028 mg/L) < OT3 (Cd, 10,282 mg/L) < OT3Na (Cd, 10,282 mg/L). The constant adsorption capacity K_f increases with increasing initial metal concentration. The values of $1 < n < 10$ indicate favorable adsorption conditions [54,55]. Results of the OT3 (Cd, 1,028 mg/L) matrix (Table 5) were not consistent with the Freundlich model ($n > 10$, $R^2 < 97$), since it showed a monolayer adsorption. Langmuir theory is applicable in the case of localized adsorption sites, which are homogeneous and of equal energy without lateral interactions between adsorbed particles. For the matrix OT3 (Cd, 10,282 mg/L), the experimental data fit the linearized Freundlich isotherms well. The effectiveness of the Freundlich equation in describing metal adsorption was also reported by others [56–58]. We also found that these models have good adsorbability in the case of clay. This suggests that the adsorption through the membrane of cadmium by smectite of Oued Tfal is controlled by several processes. The Gibbs free energy change, ΔG°, is the fundamental criterion of spontaneity. The negative values of ΔG° increased in the order OT3 (Cd, 1,028 mg/L) < OT3Na (Cd, 1,028 mg/L) < OT3 (Cd, 10,282 mg/L) < OT3Na (Cd, 10,282 mg/L) indicate that the adsorption was more spontaneous on OT3Na (Cd, 10,282 mg/L). The obtained negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of the adsorption processes with preference towards Cd(II) ions.



(OT3Na, Cd(II), 1,028 mg/L) (OT3, Cd(II), 1,028 mg/L)



(OT3Na, Cd(II), 10,282 mg/L) (OT3, Cd(II), 10, 282 mg/L)

Fig. 8. Mapping X of cadmium on different samples treated at two concentrations: 1,028 and 10,282 mg/L.

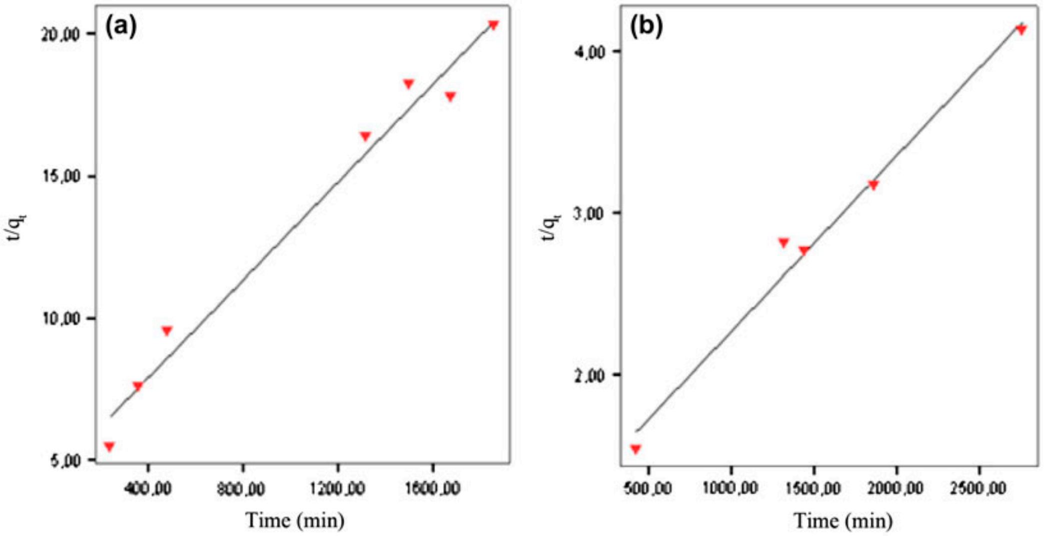


Fig. 9. Determination of rate constants (pseudo-second order) of the adsorption of cadmium by clays, (a): (OT3, Cd, 1,028 mg/L) and (b): (OT3Na, Cd, 10,282 mg/L).

Table 4
Maximum quantity (Q_{max}) and constant speeds of pseudo-second order in the different matrices treated

Metals	Clays	Q_e (mg/g)	K (mg min/g)	R^2
($Cd(NO_3)_2$; 1,028 mg/L)	OT3	100	0.111	0.99
($CdCl_2$; 10,282 mg/L)	OT3Na	1,000	0.420	0.99

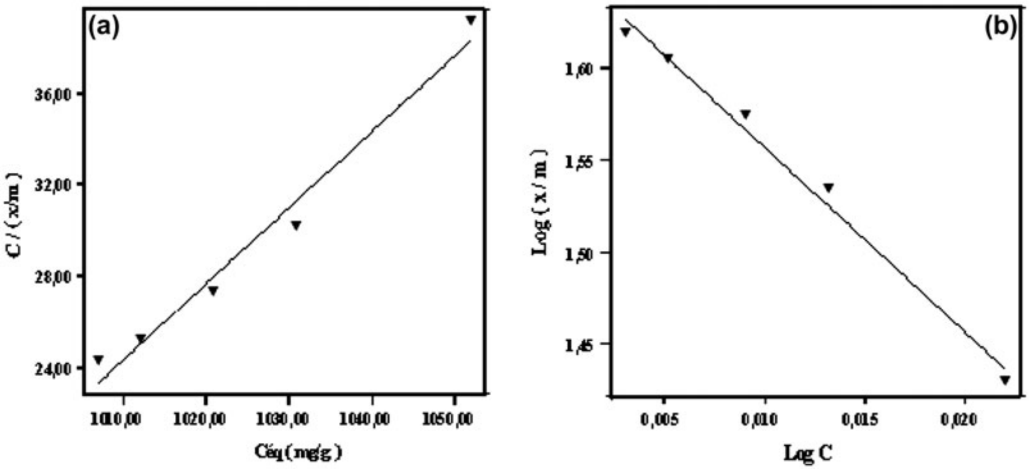


Fig. 10. Isothermal retention of cadmium by the purified clay OT3Na: (a) Langmuir model, x/m: amount of contaminant adsorbed per unit mass, (b) Freundlich model.

Table 5
Isotherm parameters for adsorption of Cd(II) onto clays

Samples	Langmuir			Freundlich		
	K_L (L/g)	ΔG° (kJ/mol)	R^2	K_f (L/g)	n	R^2
OT3 (Cd, 10,282 mg/L)	15.76	−6.822	0.96	1.6×10^8	5.30	0.98
OT3Na (Cd, 10,282 mg/L)	17.40	−7.077	0.98	1.5×10^9	6.22	1.00
OT3 (Cd, 1,028 mg/L)	1.20	−0.452	1.00	9.5×10^3	74.43	0.96
OT3Na (Cd, 1,028 mg/L)	3.20	−2.881	0.98	45.70	10.00	0.99

4. Conclusion

Clay is currently used for the containment of hazardous industrial waste and remediation of industrial water and waste. The physicochemical characterization of OT3 and OT3Na clays deposits from Oued Tfal in the Gafsa region were used to test and compare their adsorbing power vis-a-vis the removal of Cd (II). The adsorption processes followed the pseudo-second-order kinetics. These results suggest that the adsorption of metal by the clay is controlled by the physisorption process (or physical adsorption) and the adsorption takes place in a multilayer. The application of the linearized forms of the models was checked and confirmed that they are applicable with a good correlation of the adsorption isotherms and that the removal efficiencies of metals vary in the same way with these models. In addition, the negative values of ΔG° indicate that the adsorption of Cd(II) onto clays was thermodynamically feasible and spontaneous. It was concluded that clay shows a strong adsorption capacity of Cd(II). This amount adsorbed is high and promising when compared to the other related adsorption studies. The adsorption through a membrane method could be extended for the treatment of effluents containing other metals.

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