Research paper

Removal of paraquat from water by an Algerian bentonite

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ABSTRACT

The sorption–desorption of the cationic pesticide 1,1′-dimethyl-4,4′-bipyridinium dichloride (paraquat) on a bentonite from Maghnia (Algeria) desiccated at 110 °C (M), and calcined at 400 °C (M400) and 600 °C (M600) from aqueous solution at 25 °C has been studied using batch experiments. A complete characterization of the natural and heat activated bentonite samples has been carried out through the following techniques: X-ray fluorescence spectroscopy, FTIR, X-ray diffraction, thermogravimetric and differential thermogravimetric analysis and surface analysis. In order to have a better understanding of the variables affecting the sorption of this herbicide, factors such as the working temperature or the ionic strength of the solution have been investigated. The sorption experimental data have been fitted to the Langmuir equation in order to calculate the maximum sorption capacities (X_m) of the samples. The results show that the sorption capacity of the calcined samples greatly decreased with heat treatment. On the other hand, the sorption process is hardly affected by the working temperature, whereas the higher electrolyte concentration, the lower sorption of this pesticide. In addition to batch experiments, a decontamination continuous process (DCP) was designed by the authors using the natural clay to evaluate the potential application of this adsorbent for removing paraquat from water.

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1. Introduction

The use of pesticides has become a prerequisite aspect of agriculture and public health. Versatile use of pesticides had resulted in contamination of all basic necessities of life, i.e. air, water and food. Amongst various pesticides, paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) along with glyphosate, is one of the most widely used herbicides in the world (Péguy Nanseu-Njiki et al., 2010). This compound is a non-selective contact herbicide which destroys plants by inhibiting photosynthesis (Péguy Nanseu-Njiki et al., 2010; Tsai et al., 2005). Unfortunately, paraquat is known to display some harmful effects such as pulmonary fibrosis, which results from the transformation by paraquat of the oxygen available in the lungs into free radicals. Once paraquat enters the soil environment, it is rapidly and strongly bound to clay minerals and organic matter and becomes biologically inactive (Ricketts, 1999). The risk of contamination by paraquat is enhanced by its high water solubility (620 g/L) (Tomlin, 2009), having been detected in surface and drinking waters (Hadi et al., 2005; Zhou et al., 2009). For European standards, the maximum permissible concentration for individual pesticides (including paraquat) in drinking water is 0.1 $\mu g \cdot L^{-1}$ and 1–3 $\mu g \cdot L^{-1}$ for surface waters (Mojović et al., 2009). Thus, the necessity

to reduce the concentration of paraquat in water is a worldwide challenge as far as water pollution is concerned. In this sense, the sorption/desorption phenomena of pesticides in soils are of great importance from the environmental point of view, as pesticide sorption affects other processes like transport, degradation, volatilization and bioaccumulation of these compounds in the soil (Kumar and Philip, 2006). Furthermore, other authors have reported the strong relationship between the desorption process and the potential mobility of pesticides in soil (Haung and Weber, 1998).

Different materials have been investigated for this purpose, such as diatomite, phillipsite–faujasite tuff (faujasite), zeolite covered with alkylsilane, and methacrylic acid-modified rice husk (Hadi et al., 2005; Khalil and Haneen, 2009; Shih-Tong and Ting-Chung, 2007; Tsai et al., 2005), the majority being the results of the synthesis or transformation of natural products.

Clay minerals are good adsorbents owing to their high cation exchange capacity and high specific surface areas associated with their small particle sizes, and have the advantage of being abundant and inexpensive. Thus, their surface reactions have strong biochemical and ecological effects in soils and waters, and these materials are being used for decontamination and remediation treatments (Quintelas et al., 2011; Sánchez-Jiménez et al., 2011). For this study, we have used a natural Algerian bentonite, which has been widely used in catalysis, sorption of dyes, pesticides, metals and drilling of oil wells for its rheological properties (Abollino et al., 2003; Cheng-Cai et al., 2004; Sankarasubbier and Kiranmayi, 2000; Wang and Wang, 2008). A review of relevant

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literature reveals that there are no complete studies of the physico-chemical characterization of this clay, therefore, this aspect has been considered as part of this study and is detailed in this paper.

On the other hand, given that sorption capacity may be enhanced by thermal or chemical modifications, the present study was aimed at investigating the behavior of the Algerian bentonite as adsorbent after thermal treatment.

In addition, interactions involving divalent organic pesticides, such as paraquat, and clays, depend on environmental conditions such as ionic strength or temperature so, taking into account the above stated; the aims of the present study were therefore: (1) to carry out a complete characterization of the Algerian bentonite, (2) to analyze the effect of calcination temperatures in the sorption capacity of the activated samples, (3) to quantify the sorption/desorption of paraquat on the Algerian bentonite by using batch experiments in an aqueous and saline medium with different values of ionic strength at 25 °C, (4) to evaluate the effect of the working temperature in the sorption process and (5) application of a continuous dynamic system which permits a total removal of paraquat in potential contaminated waters with this herbicide by using a single process.

2. Materials and methods

2.1. Materials

A montmorillonite-rich material originating from the Hammam Boughrara deposit (Maghnia, Algeria), and industrially treated with sodium carbonate, was supplied by ENOF Ltd. (Algeria). The material was not ground because it was already in an adequate grain size (<60 μm) and was only air dried first and then at 110 °C. This bentonite will be designated M in the following.

Heat treatment of the natural bentonite was carried out by heating samples at 400 °C and 600 °C for 24 h. The products so obtained are labeled in the text as M400 and M600, respectively.

Analytical grade paraquat (1,1′-dimethyl-(4,4′-bipyridilium dichloride)), purchased from Sigma-Aldrich (Supelco, Spain) was used as adsorbate in this study.

2.2. Characterization

The cation exchange capacity (CEC) and the exchange acidity of the samples were determined by the $BaCl_2$-triethanolamine procedure and the carbonate content by using the Bernard calcimeter (Primo-Yúfera and Carrasco Dorrién, 1981).

Specific surface areas (S_{BET}) were obtained from N_2 sorption isotherms at 77.4 K, in a volumetric sorption system, Gemini II-2375 (Micromeritics). A value of 16.2 Å was adopted for the cross-sectional area per nitrogen molecule and the relative pressure interval used $0.02 < P/P_0 < 0.2$. The nitrogen used was 99.998% pure. The samples were degassed previously at 210 °C for 24 h.

The chemical composition of the natural and heat treated bentonite samples was determined by X-ray fluorescence spectroscopy with a MagiX PANalytical equipment.

XRD patterns of bentonite (before and after activation) were collected on a XPERT PRO DE PANALYTICAL diffractometer using graphite-monochromated Cu K_α radiation.

Thermal properties and stability of samples were analyzed using a TGA Q50 thermogravimetric analyzer (TA Instrument). The analyses were conducted at atmospheric pressure under an air flow (100 mL·min^{-1}) with a heating rate of 10 °C·min^{-1} and a temperature limit of 900 °C.

The FTIR spectra of the clay samples were recorded using KBr pellets on an ATI Mattson spectrometer over a range of 4000–400 cm^{-1}.

FTIR spectrum of the natural clay saturated with paraquat was also obtained through the following procedure: an aqueous pesticide solution (25 mL) with a concentration corresponding to the maximum used in the sorption experiments was added under continuous stirring to 0.05 g of the adsorbent in 100 mL conical flasks. These flasks were shaken for the equilibrium time at 25 °C. Following the equilibration period, the samples were centrifuged and the supernatant concentration measured. Another 25 mL portion of the same pesticide solution was added and the process was repeated until the supernatant concentration was constant. The remaining solids were then air-dried without washing and pressed into potassium bromide pellets.

2.3. Sorption experiments

Sorption isotherms were determined by batch equilibration of 0.05 g of each clay sample with 25 mL of pure water solutions of paraquat of varied initial concentration (50 mg·L^{-1}–300 mg·L^{-1}). Experiments were carried out in a thermostatic shaker bath at 25 °C. Preliminary investigations on the sorption rate by using the clay adsorbent indicated that the process occurred rapidly. After a period of 45–60 min, a gradual approach to the sorption capacity was observed, so the sorption equilibrium time used in the experiments was 24 h.

After equilibration, the dispersions were centrifuged, filtered through 0.45 μm nylon filters and the pesticide concentration measured in the supernatant solution (C_e) by absorption at 257 nm (the wavelength corresponding to its maximum absorbance), using a Shimadzu UV-1700 spectrophotometer. The amount of paraquat adsorbed (X) was calculated from the difference in concentration between the initial (C_i) and final (C_e) solutions. Blanks containing no paraquat, and two replicates of each sorption point were used for each series of experiments.

The effect of ionic strength on the sorption capacity of the original clay was studied by using 0.01 and 0.1 M KCl solutions of paraquat of varied initial concentrations (30 mg·L^{-1}–280 mg·L^{-1}). In the same way, sorption experiments were carried out at 15 °C and 35 °C in order to study the influence of the working temperature in the sorption process.

2.4. Desorption experiments

Desorption experiments were carried out with the original clay as this sample showed the higher sorption capacity.

Once the sorption process had finished after 24 h, the volume of the liquid phase in each centrifuge tube corresponding to the higher concentration of paraquat used in the experiment, was removed and replaced with an identical volume of solution (water or 0.01/0.1 M KCl solutions) containing no herbicide and the solution was processed as described above, with the procedure being repeated until the amount of pesticide desorbed remained constant. Desorption data are given as percentages of the initial amounts adsorbed. All measurements were made in duplicate.

2.5. Dynamic sorption experiments

The dynamic sorption study was carried out by using a column system designed by the authors (Fig. 1). The column experiments were only carried out with the natural clay since, as will be seen below, the sorption capacity of this sample is higher than the other clay samples. The system was constructed using two glass columns of 15 mm inside diameter by 250 mm in length, with tap and frit filter. At the top and bottom of both columns, glass wool was placed to prevent the blockage of the column. Some glass marbles were used at the bottom of the columns to facilitate a better contact between the paraquat and clay solutions. The experiment was carried out as follows: a paraquat aqueous solution and a clay dispersion were each passed through the bottom of the first column at a fixed flow using a pump working with a steady flow. The use of a second column allows the prolonging of the contact time between the clay and the herbicide. The study was conducted using different flows (Q) for both solutions (0.75, 1.5 and 3 mL·min^{-1}) and varying the concentration of the clay dispersion used (0.8, 1.4, 2.1 and 3.5 g·L^{-1}).
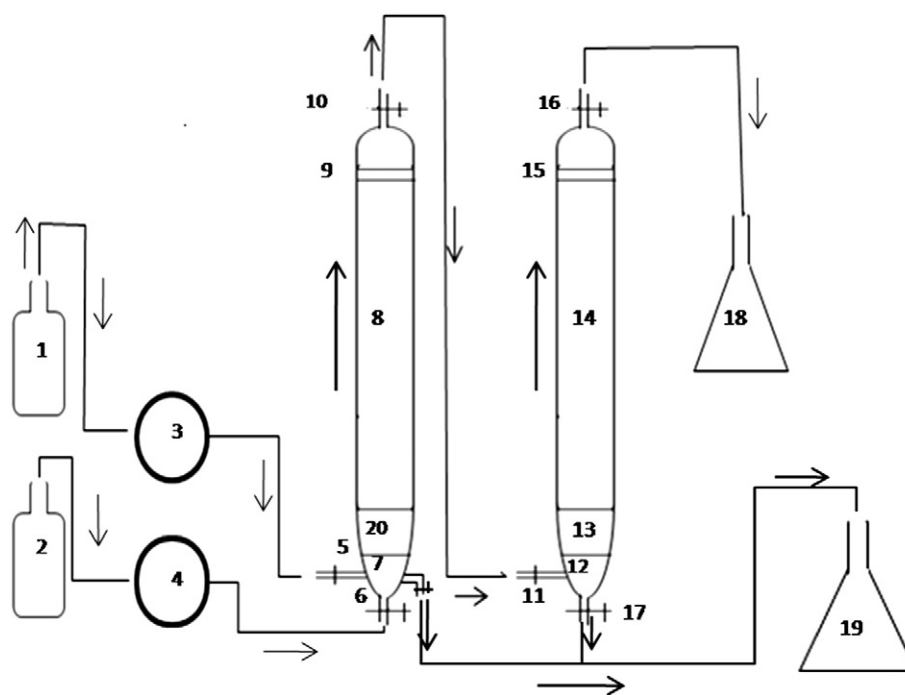
Fig. 1. Dynamic system for decontamination of paraquat onto natural bentonite. 1. Paraquat solution. 2. Agitated clay suspension. 3 and 4. Pumps. 5. Paraquat solution input. 6. Clay suspension input. 7, 9, 15, and 12. Glass Wood. 8 and 14. Glass columns. 10. Output of the first column 11. Input to the 2nd column. 13 and 20. Glass marbles. 16. Exit for decontaminated solution. 17. Exit of saturated clay solution 18. Clean solution. 19. Solution of paraquat saturated clay.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The X-ray pattern of the Algerian clay shows the characteristics reflection bands of this type of clay (Brnardic et al., 2008; Wang and Wang, 2008). Montmorillonite is the major component in the sample, the diffraction maximum being located at 2θ equal to 7.05 which is equivalent to basal spacing d_{001} of 12.53 Å. Other bands observed are, the strong and sharp reflection at 4.48 Å corresponding to the spacing d_{110} and the less asymmetric reflection centered at 2.49 Å corresponding to the spacing d_{200}. The parent clay, apart from montmorillonite, also contained: feldspar (4.25, 3.22, 2.99 and 2.46 Å), a kaolin mineral (7.2 Å) and quartz (4.25, 3.35, 2.46 Å) and calcite (3.03, 2.28, 2.09 Å) impurities (Brnardic et al., 2008; Dixon and Weed, 1989; Khenifi et al., 2009).

In relation to the X-ray patterns of the heat treated samples it can be observed that the heat treatment produces a decrease in the intensity of the characteristic reflection band owing to the loss of water; the value of the basal spacing diminishing from 12.53 Å (M) to 12.46 Å (M400) or 9.81 Å (M600) and that it could be related to a collapse of the crystalline structure as a consequence of the heat treatment (González-Pradas et al., 1991). Characteristics kaolinite peaks were no longer recognized in the patterns of samples heated at 600 °C, suggesting the transformation of kaolinite into metakaolin by effect of the loss of structural OH groups (Rashad, 2013).

The identification of the different mineralogical components was completed with the analysis of the diffraction patterns of the oriented aggregates in ethylene glycol. The results showed the swelling capacity of the natural bentonite and the M400 sample, with a basal spacing of 17.54 Å and 17.66 Å in ethylene glycol, respectively, whereas the M600 sample did not show any swelling.

3.2. Characteristics of natural clay and heat-treated samples

The CEC of the natural bentonite and M400 sample (Table 1), show values similar to those reported by other authors for this type of materials (Didi et al., 2009; González-Pradas et al., 2000). The very low value shown by M600 can be explained taking into account that the thermal treatment produces the loss of the exchangeable cations coordinated to surface and interlayer water molecules (Jozefaciuk and Bowanko, 2002).

The carbonate content (Table 1) for the natural clay can be considered as not very high, this value diminishing, as expected, for the heat treated samples.

Specific surface area of the samples available to the N_2 molecules was calculated by applying the Brunauer, Emmett and Teller equation (BET) to the experimental data points obtained in the N_2 sorption process at 77.4 K and are shown in Table 1. The low values obtained, might be explained according to the model proposed by Kaufhold et al. (2010); this model supposes that when the predominant exchangeable cation is Na^+, as in our samples, a higher number of cations would be required to compensate the permanent negative charge, blocking in this way, most of the N_2-accesible sites at the layer edges.

Table 1
Physical and chemical characteristics of the Maghnia bentonite and heat treated samples.

Sample	CEC (meq/100 g)	Carbonate content (%)	BET surface area (m²/g)
M	59.37	7.1	8.69
M400	41.87	5.1	8.07
M600	9.37	1.3	6.13

Table 2
Chemical composition of the Maghnia bentonite and heat treated samples.

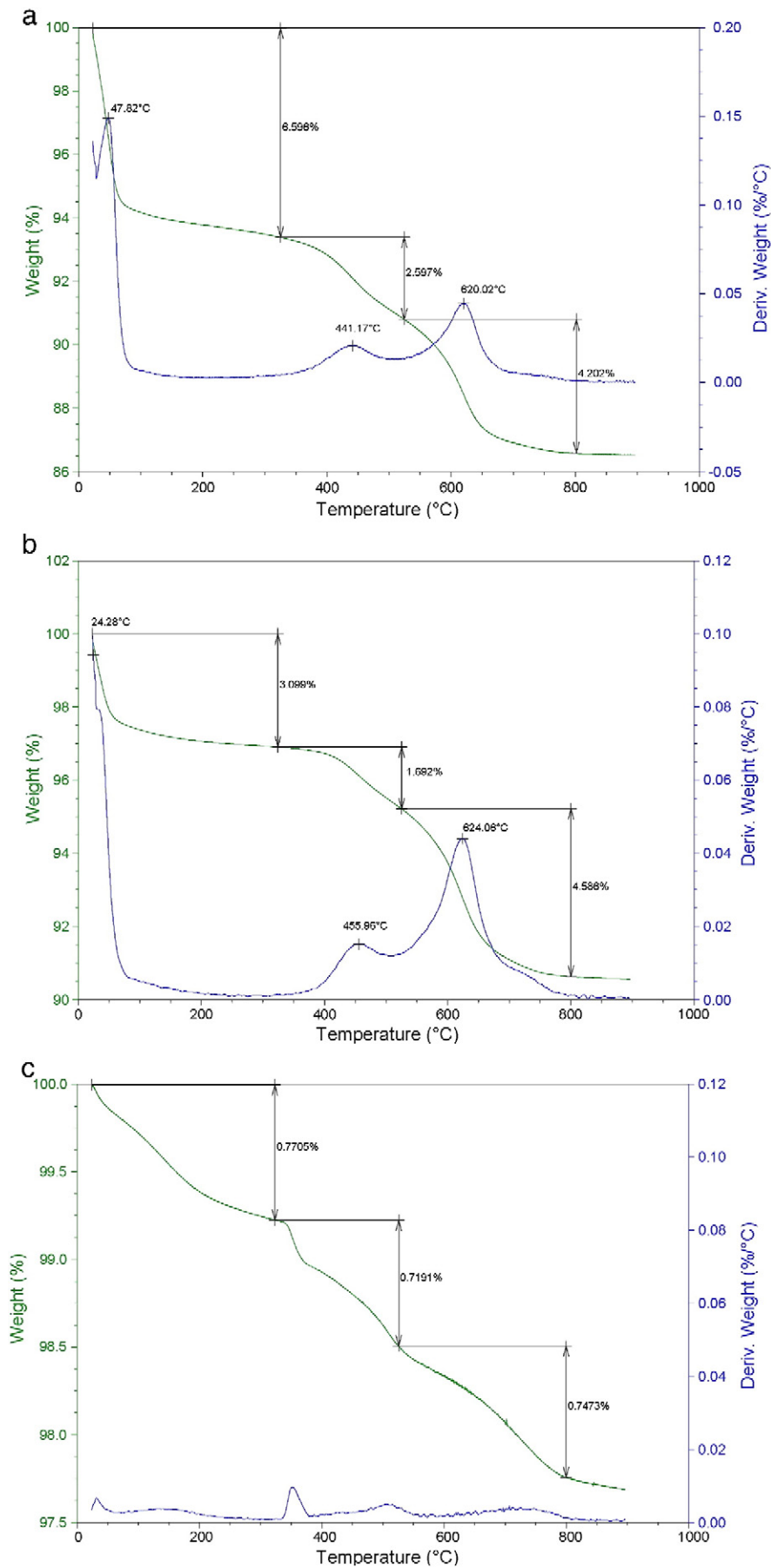| Sample	SiO₂ (%)	Al₂O₃ (%)	Fe₂O₃ (%)	CaO (%)	TiO₂ (%)	MnO (%)	K₂O (%)	MgO (%)	P₂O₅ (%)	Na₂O (%)	LOI[a]
M	53.29	20.03	1.58	2.72	0.04	0.03	0.92	2.95	0.01	3.94	14.12
M400	55.21	20.75	1.62	2.75	0.04	0.03	0.96	3.04	0.01	4.02	11.29
M600	60.63	22.85	1.77	3.04	0.04	0.03	1.05	3.36	0.01	4.16	2.94

[a] Loss on ignition at 950 °C.

Fig. 2. DTA/TA curves for the natural bentonite (a) and heat treated at 400 °C (b) and 600 °C (c).

The low values obtained have also been reported by other authors (Kaufhold et al., 2010; Oliveira et al., 2003).

On the other hand, as can be seen, the heat treatment produces a decrease in the surface area values, which may be due to the collapse of the structure as the temperature increases (Ureña-Amate et al., 2008).

3.3. Chemical composition

The chemical composition of the major elements in the natural bentonite and the heat treated samples is indicated in Table 2. The results obtained are in the range reported by other authors (Bacquet et al., 2004; Khenifi et al., 2009), showing a high content in sodium, and that the heat treatment only produces a slight relative increase of the silica content due to the loss of water (Ureña-Amate et al., 2008).

3.4. Thermogravimetric analysis (DTG/TG)

The DTG/TG curves of the natural bentonite and heat treated samples are shown in Fig. 2. The TG curves for samples M and M400 showed three distinct zones of weight loss in the temperature ranges: 25–350 °C, 350 °C–550 °C and 550–800 °C whereas the TG curve of the M600 sample shows, as expected, a more continuous weight loss in the temperature range studied. The transformations observed are the following: (i) the first, due to the removal of interlayer water from the clay mineral with a loss of weight of 6.6% and 3.1% for M and M400, respectively, (ii) the weight loss at ~450–500 °C is mainly due to the dehydroxylation of kaolin mineral (2.6% and 1.7% for M and

M400, respectively) and, to a lesser extent, to dehydroxylation of montmorillonite; and (iii) the loss of structural water of 4.2% for the M sample and 4.6% for M400. It can be noted, that the loss of structural water in sample M400 occurred at higher temperatures than for the untreated bentonite, whereas for the M600 the loss of weight was lower and continuous in the range of temperature studied (Brnardic et al., 2008; Korichi et al., 2009).

3.5. Infrared analysis

The FTIR spectra of the natural and heat treated bentonite samples are shown in Fig. 3. The spectrum of the natural clay (Fig. 3a) shows the characteristic bands of this type of mineral, similar to those appearing in the literature (Boufatit et al., 2007, 2008; Temuujin et al., 2004). Thus, the following bands can be seen as: (a) a small band centered at 3670 cm^{-1} corresponding to a kaolin mineral, (b) a broad band centered at 3450–3622 cm^{-1} ascribed to the stretching frequencies of the OH functional groups of crystallization water molecules, (c) a band centered at 1639 cm^{-1} which might be assigned to the OH deformation because of the presence of some interlamellar water, (d) a broad band at 1481 cm^{-1} due to the calcite impurity (Temuujin et al., 2004), (e) an intense band at 1038 cm^{-1} assigned to the asymmetric stretching vibrations of Si−O−Si, (f) a band corresponding to the hydroxyl bending vibrations centered at 916 cm^{-1} that suggests that the Al^{3+} ions occupy octahedral sites (Gates et al., 2002; Madejova et al., 1998) and that centered at 468 cm^{-1} which might be assigned to the Si−O−Si bending vibrations.
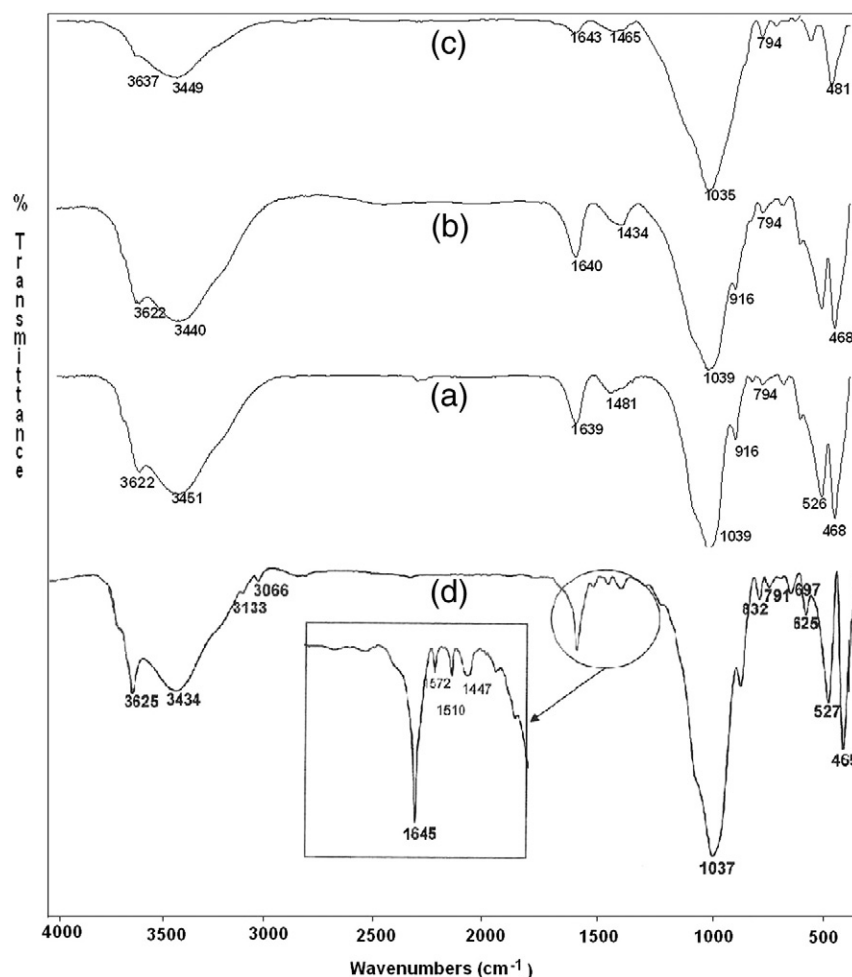

Fig. 3. FTIR spectra of the natural bentonite (a) heat treated sample at 400 °C (b) heat treated sample at 600 °C (c) and the paraquat-adsorbent complex (d).

No significant differences were observed in the FTIR spectrum obtained for the M400 (Fig. 3b) sample whereas for the M600 (Fig. 3c) some modifications can be indicated. The band at 3670 cm^{-1} disappears, owing to the decomposition of the kaolin mineral; the representative band of the OH stretching vibrations is smaller due to the loss of water molecules and the disappearance of the band centered at 916 cm^{-1} can also be observed and a significant decrease of the intensity of the band centered at 1639 cm^{-1}, which is also due to the loss of water. The band at 794 cm^{-1} associated with quartz impurity remains and intensifies in this sample whereas that at 1481 cm^{-1}, corresponding to the presence of calcite, confirming the above indicated in the X-ray studies.

Fig. 3d shows the FTIR spectra of the paraquat–adsorbent complex. The FTIR spectrum of the paraquat–adsorbent complex (Fig. 4a) exhibits band characteristics of this herbicide centered at 3066 and 3133 cm^{-1}, assigned to the C–H stretching mode of the methyl groups on the aromatic ring in the paraquat molecule (Haque and Lilley, 1972). A characteristic set of bands can also be seen between 1200 and 1600 cm^{-1} that may be assigned to the C–C stretching mode and the C–H deformation mode in the aromatic ring plane (Brienne et al., 1995; Haque and Lilley, 1972). Furthermore, the band corresponding to the stretching mode of –C=N– bond at 1561 cm^{-1} in the paraquat molecule is slightly upshifted to 1572 cm^{-1} in the paraquat–clay complex. These findings can be related to the mechanism of the sorption of this pesticide which will be discussed later, where Coulombic forces play an important role as demonstrated in the IR spectra (Rytwo et al., 1996) but also a possible intercalation of the paraquat molecules into the aluminosilicate interlayers with flat configuration (Yang-Su et al., 2010).

3.6. Sorption/desorption experiments

Fig. 4 shows the sorption isotherms of paraquat on the bentonite samples. According to the slope of the initial portion of the curves, these isotherms may be classified as H-type of the Giles classification (Giles et al., 1960). This suggests that the Algerian bentonite has a high affinity for this herbicide, being strongly sorbed on the samples, and that there is no competition from the solvent for sorption sites. However, it is noteworthy that for a given equilibrium concentration, the amount of paraquat sorbed on the heat-treated sample at 600 °C is much smaller than that corresponding to the natural bentonite and that treated at 400 °C, the latter being in the same order as that for the natural clay.

On the other hand, the sorption isotherms in Fig. 4 tend to define a plateau. Therefore it seems reasonable to suppose that, in the experimental conditions used, the formation of a complete monolayer of paraquat molecules covering the natural and heat-treated bentonite surface (isotherms belonging to sub-group II of the Giles classification) is possible; that is to say, the curves tend to a constant value of X and, also according to Giles et al., saturation of the surface by paraquat molecules seems to be reached.
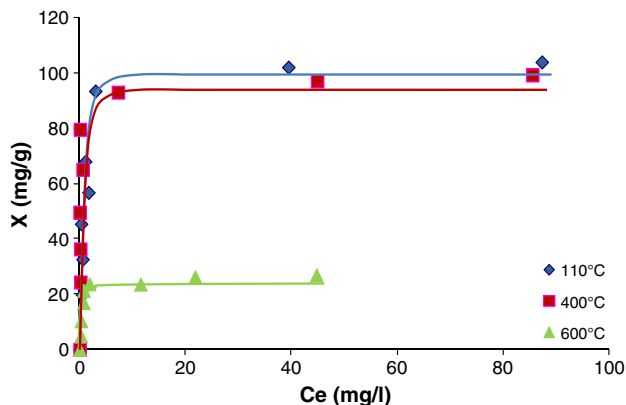

Fig. 5. Adsorption isotherms of paraquat from aqueous solution onto natural bentonite at 15 °C, 25 °C and 35 °C.

Fig. 5 shows the sorption isotherms of paraquat on the natural clay sample at 15 °C, 25 °C and 35 °C in pure water solution. As can be observed, there is no significant influence of temperature in the paraquat sorption process, at least in the range studied.

On the other hand, in order to analyze the influence of the ionic strength in the sorption, Fig. 6 shows together, the sorption isotherms of paraquat on the natural clay from pure water, 0.01 M and 0.1 M KCl solution at 25 °C. As can be seen, the shape of the isotherms from saline solutions is the same shape as that obtained for pure water solution. Nevertheless, it is important to note that for a given equilibrium concentration, the amount of paraquat adsorbed is lower when KCl solution is used in the sorption experiments, the most pronounced effect being when the concentration of KCl is higher.

The sorption capacities of the bentonite samples were obtained by fitting the experimental data points to the Langmuir equation (Adamson, 1982):

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m}$$

where

X   paraquat sorbed per gram or bentonite
C_e equilibrium solution concentration
X_m maximum amount of paraquat that can be adsorbed in a monolayer (sorption capacity)
b   constant related to the energy of sorption.

Langmuir isotherm equation can be linearized and the relative parameters obtained from the plots of C_e/X vs C_e. If the experimental

Fig. 4. Adsorption isotherms of paraquat from aqueous solution onto natural bentonite and heat treated samples at 25 °C.
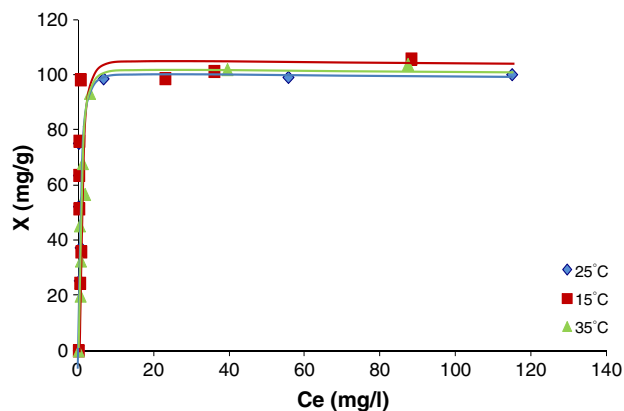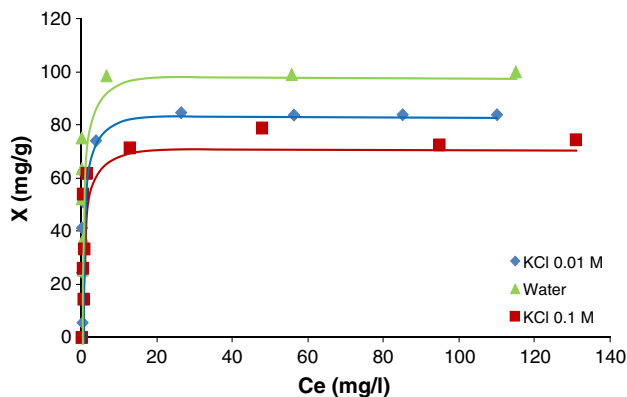

Fig. 6. Adsorption isotherms of paraquat onto natural bentonite from aqueous and saline medium at 25 °C.

data are fitted to this equation, a straight line is obtained whose slope gives X_m and the intercept will provide the b value.

As the applicability of the isotherm equation to describe the adsorption process is judged by the correlation coefficient (r^2), in our study all the coefficients were higher than 0.99 (all correlations were significant at the 0.001 probability level), thus indicating a very good fit.

Langmuir parameters (X_m and b) are summarized, together with the correlation coefficients, in Table 3. The correlation coefficients were in all cases greater than 0.99 (all correlations were significant at the 0.001 probability level). The influence of the heat treatment given to the natural clay shows that the sorption capacity decreases as the calcination temperature increases. If we compare the X_m values obtained with others found in literature, it can be observed that these are higher than those obtained for sorption of this herbicide on other adsorbents such as diatomaceous earth and clays such as bentonite, sepiolite or illite (Seki and Yurdakoç, 2005; Tsai et al., 2005).

The authors consider that the sorption of this herbicide is mainly produced via cation exchange, this fact being supported by the fast decrease in residual paraquat concentration on a short time scale, implying the strong electrostatic interaction between the negatively charged surface and paraquat cation. Hence, the lower results obtained for the M600 sample might be explained, taking into account that the heat treatment releases structural water initially present in the form of structural OH^-, producing the destruction of the octahedral layer and the collapse of the structure (Bojemueller et al., 2001).

Another prominent feature of these results is the difference observed among the X_m values of the different media studied. The sorption of paraquat depends on the ionic strength, so that as the electrolyte concentration increases, the cationic pesticide sorption decreases. This fact might be explained if we consider that ion exchange is primarily an electrostatic process in the sorption system. So, the smaller the solvated radius of the ion, the closer it can approach the negatively charged clay surface and the greater the affinity of the surface for the ion becomes. Therefore, the positively charged paraquat molecules compete with electrolyte ions for sorption sites, so that a decrease in sorption is observed when the ionic strength is increased (Tsai et al., 2003). This trend has also been reported previously by other authors for the sorption of paraquat on other materials (Iglesias et al., 2010; Péguy Nanseu-Njiki et al., 2010).

On the other hand, as can also be seen, the influence of working temperature in the sorption process of paraquat is nearly negligible, at least in the experimental conditions used in this work. These observations are similar to other authors' findings, where it was found that there was no apparent effect of temperature on the sorption of paraquat onto soil particles (Mehdi et al., 2009).

Table 3

Parameters of the Langmuir equation for adsorption of paraquat on the Maghnia bentonite and heat-treated samples.

	$X_m{}^a$ (mg/g)	b	r
Natural bentonite			
Pure water medium			
15 °C	111 ± 0.13	1.5	0.999
25 °C	100 ± 0.12	3.33	0.999
35 °C	111 ± 0.11	1.00	0.999
Saline medium (0.01 M KCl) at 25 °C	91 ± 0.20	1.37	0.998
Saline medium (0.,1 M KCl) at 25 °C	77 ± 0.23	2.17	0.999
Heat treated bentonite			
Pure water medium at 25 °C			
M400	100 ± 0.16	3.33	0.999
M600	28 ± 0.30	1.56	0.999

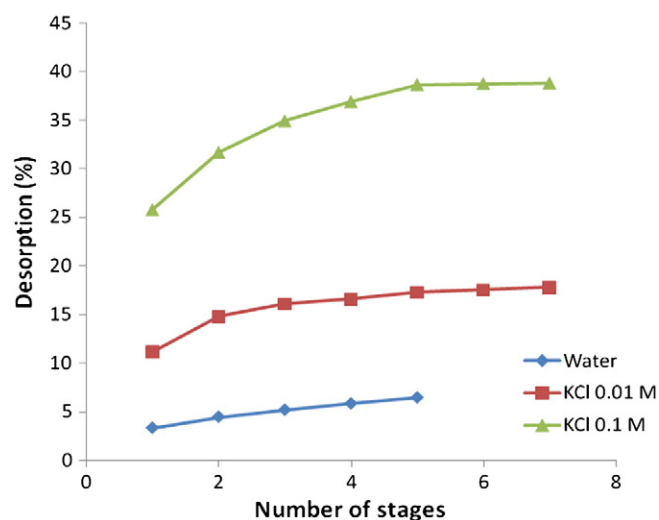[a] These values represent the 95% confidence limits.

Fig. 7. Desorption isotherms of paraquat onto natural bentonite from aqueous and saline medium at 25 °C.

Fig. 7 shows the desorption curves of paraquat from the natural clay sample in the three media studied. As can be seen, the low desorption of paraquat from the bentonite in water (around 6%) shows that paraquat molecules are strongly adsorbed on the clay, confirming the type of isotherm obtained. The presence of KCl in the medium increases this percentage up to 38% in KCl 0.1 M as a consequence of the strong competition between k^+ ions and paraquat cations above indicated.

3.7. Dynamic sorption experiments

Owing to experimental difficulties, fundamentally the small particle size of the natural bentonite, which produces an impermeable mud in contact with the decontaminating solution and the blockage of the column in the experiment we conducted, we used an important feature of this clay, that is, its flocculation when loaded in paraquat.

Various test experiments were performed to optimize the total elimination of paraquat by using this dynamic system. The flow rate was calculated taking into account the area (S) of the column and the different flows used (V = Q/S). So, the best results were obtained when the following conditions were applied: an initial concentration of paraquat of 150 mg·L^{-1}, a clay dispersion of 3.5 g·L^{-1}, and a flow of 1.5 mL·min^{-1}. Thus, the optimum flow rate was 0.85 cm·min^{-1} allowing the final solution to be recovered free of paraquat.

Under these conditions, the contact time between the clay and the herbicide was approximately 60 min (the same as that obtained in the kinetic study), so, the total volume that passed through the column from both solutions was 90 mL.

Taking into account all the above indicated, the amount of paraquat removed per gram of clay in this continuous system was 43 mg·g^{-1}. Although this value is almost half of that calculated by applying Langmuir equation in the batch experiments, this system has some important advantages: (i) the cost of the adsorbent is much lower than others such as activated carbon, (ii) the use of a natural resource of the region, (iii) the bed load occurs continuously and then, it is not necessary to stop the depuration process, and (iv) the saturated clay residue might be reused as matrix in the preparation of controlled release formulations.

4. Conclusions

The effect of heat treatment on the textural and structural properties of a bentonite from Maghnia has shown some physical changes clearly affecting the potential sorption capacity of the Algerian clay. So, these experiments indicate that despite the heat treatment applied to the

Maghnia bentonite, the natural sample is the most effective in removing paraquat from aqueous solution, as shown by the higher sorption capacity obtained from the batch experiments. The range of the working temperature studied hardly affects the sorption process whereas the presence of KCl in the medium seems to decrease the amount of herbicide retained, owing to the competition between the positively charged paraquat molecules and the electrolyte ions for sorption sites. The analysis of FTIR spectrum of the paraquat–adsorbent complex confirmed our hypotheses about the proposed sorption mechanism which might be mainly controlled by cation exchange. Alternatively, the dynamic sorption study carried out with the natural sample could be used as an applicable dynamic method – easy, quick and cheap to design – for carrying out the purification of water contaminated with this herbicide, thus contributing to an environmentally sustainable development.

Acknowledgments

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