



Diclofenac potassium removal from water by adsorption on natural and pillared clay

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Received 13 February 2014; Accepted 8 December 2014

ABSTRACT

This study explores the removal of Diclofenac potassium, an example of hazardous pharmaceutical pollutant, from aqueous solution. Pharmaceutical pollutants are a group of emerging contaminants that contain different groups of human and veterinary medicinal compounds that are widely used all over the globe. Pharmaceutical pollutants have been considered as an emerging environmental problem. In this work, the removal of diclofenac potassium by the use of iron-pillared clays as adsorbents, in comparison with their starting material (a natural clay mineral) was studied. The aim of this study is to improve diclofenac potassium removal by an adsorption process, using modified clays instead of the natural clay mineral. The pillared clays were synthesized from a natural clay mineral from Algeria, by using iron oligocation. The samples were characterized by several techniques (emission scanning electron microscopy and Fourier transform infrared spectroscopy), remarking that some structural and textural changes were produced during the pillaring process. The pillared samples showed a considerable increase in their adsorption capacity in comparison to the natural clay mineral. This effect can be related to the textural and structural changes produced during the pillaring process. Consequently, iron-pillared clays could be the new material to be used in the studied environmental process.

Keywords: Diclofenac potassium; Pharmaceutical pollutant; Adsorption; Clay; Bentonite; Removal efficiency

1. Introduction

Pollution in the aquatic environment is an important issue to consider and study [1,2]. New pollutants are found everyday and the conventional methods of water treatment seem to be insufficient in the removal

of these contaminants. In the last years, especially concerning are the frequent detection of pharmaceutical compounds in surface, ground, and waste waters [3,4]. As per literature reports, diclofenac potassium is one of the most detected pharmaceuticals in water sources; it can be detected in influents and effluents from water treatment plants at concentrations of up to $\mu\text{g/L}$ level [5,6]. Chemically diclofenac potassium is

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Presented at the 3rd Annual International Conference on Water (CI.EAU2013), 18–20 November 2013, Algiers, Algeria

2-[(2, 6-dichlorophenyl) amino] benzene acetic acid, monopotassium salt. Therapeutically, diclofenac potassium is used for treatment of primary dysmenorrhea, relief of mild to moderate pain, relief of the signs and symptoms of osteoarthritis, and for relief of the signs and symptoms of rheumatoid arthritis. Diclofenac potassium is a non-steroidal anti-inflammatory drug [2,7–10].

Various physical, chemical, and biological treatment methods have been used for the treatment of these effluents. However, these methods have certain disadvantages such as high capital cost and operational costs. Instead of these methods, the adsorption technique can be applied to remove these kinds of effluents. Adsorption offers significant advantages over traditional treatment methods especially environmental point of view [11,12]. Although activated carbon is widely used as an adsorbent owing to its excellent adsorption abilities, it has a high price, which limits usage [13,14]. Photocatalytic degradation process, photocatalytic ozonation, irradiation technology, biological processes, hydrodynamic cavitation and UV treatment, and diclofenac removal are using strong-base anion-exchange polymer resins. Hence, an alternative low-cost, novel, locally available adsorbent is currently used for the removal of diclofenac potassium from aqueous solutions such as zeolite [15,16], montmorillonite [17,18], smectite [19,20], and bentonite [13,14,21,22] can be used in these respects [23].

The wide applications of these kinds of clay are a result of their abundance in nature, low-cost, high-specific surface area, their high chemical and mechanical stability, and a variety of surface and structural properties. The chemical nature and pore structure of clays generally determine their adsorption ability [24]. Moreover, they are easy to modify and are efficient materials designed for various purposes including adsorption.

Modifying clay minerals via pillaring currently constitutes an important and broad field of materials and surface science research. Pillared clay minerals were proved very effective in the adsorption and organic contaminants due to geometrical compatibility between the structural pores and molecular dimensions of the chemicals, in addition to their specific interactions with the pillars and layers of the clay mineral [25,26].

Introducing inorganic pillars, in addition to improving clay mineral strength and stability, increases microporosity and provides greater surface area on the solid, thereby facilitating reagents' access to potentially active sites for the catalysis of some reactions. The synthesis of pillared clays has been widely described in the literature [27–29].

The equilibrium adsorption isotherm is basically important in the design of adsorption systems. Equilibrium studies give the capacity of the adsorbent and describe the adsorption isotherm by constants, whose values express the surface properties and affinity of the adsorbent [30–32].

The purpose of this study is to report a relatively novel method for the removal of diclofenac potassium by natural bentonite and pillared clay, and to investigate adsorption kinetics and the mechanism of adsorption of diclofenac potassium onto Na-bentonite and iron-pillared bentonite. The experimental data were fitted into Langmuir and Freundlich equations to determine which isotherm gives the best correlation to experimental data.

2. Experimental

2.1. Materials

The clay was obtained from the ENOF (Clay Mineral Society, Algeria) and was purified by sedimentation method to obtain the fraction less than 2 μm [2]. Bentonite was characterized with respect to cation-exchange capacity, which was 950 mmol/kg.

Analytical-grade inorganic chemicals: NaCl, AgNO₃, Al(NO₃)₃·9H₂O, BaCl₂·2H₂O, NaOH were purchased from Merck; MgSO₄·7H₂O and Fe(NO₃)₃·9H₂O were obtained from Fluka.

Deionized water was used to prepare all solutions.

UIPAC chemical name of diclofenac potassium is 2-[(2, 6-dichlorophenyl) amino] benzene acetic acid, monopotassium salt. Fig. 1 shows its chemical structure.

2.2. Material characterization

The chemical analysis of bentonite was determined using an energy-dispersive X-ray spectrometer (EDX-LINK ISIS 300) attached to a scanning electron microscope (SEM-Cam Scan S4).

Fourier transform infrared spectroscopy (FTIR) spectra for Na-bentonite and Fe-pillared bentonite

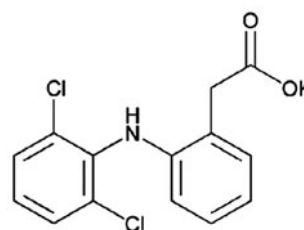


Fig. 1. Chemical structure of potassium diclofenac.

were obtained (KBr) on a *Perkin–Elmer* FT/IR Fourier transform infrared spectrometer to confirm the surface modification.

The concentration of diclofenac in the mg/l range was determined by using a *Jasco V- 530*. UV Visible spectrophotometer was employed for all spectral measurements. Absorption spectra were recorded between 230–330 nm. Analytical wavelength was 275 nm. Samples were shaken using *Jouan and VELP (scientifica)*. The samples were centrifuged in a *niive NF 200*.

2.3. Preparation of adsorbents

2.3.1. Purification of bentonite

The Na-exchanged form of bentonite was prepared by stirring samples for 24 h with 1 N NaCl. This was followed by several washings with distilled water and filtrations to remove the excess NaCl and other exchangeable cations from the clay. The clay was then resuspended and filtered until a negative chloride test was obtained with 0.1 M AgNO₃ [33,34].

2.3.2. Preparation of pillared clay minerals

Iron nitrate solution was hydrolyzed by titration with 0.75 M NaOH with a discontinuous flow of 1 ml/mn. The OH/Fe molar ratio was 2.0. These pillaring solutions were aged for 10 d. Then, 10 g of Na-montmorillonite was dispersed in 250 ml water, and the pillaring solutions in a ratio of 8 mmol Fe/g Na-montmorillonite were added slowly with a peristaltic pump. The final clay mineral content was 0.5% (w: w). The dispersions were stirred for 24 h. Finally, the powder clay minerals were dried for 24 h at 60°C under nitrogen atmosphere [25].

2.3.3. Adsorption kinetics and isotherm studies

Batch adsorption experiments were carried out for solutions of diclofenac potassium in the concentrations range 50–1,000 mg/l. Experiments were performed in 250 ml Erlenmeyer flasks containing 0.100 g of clay; 100 ml of diclofenac potassium solutions with known initial concentration were then introduced to each flask. The flasks were shaken in an electric shaker VISE STIR MS-MP8 with 200 rpm for 3 h at room temperature; then the content of each flask was centrifuged for 5 min and filtered using a 0.45 µm Millipore filter. The equilibrium concentration of diclofenac potassium was then obtained spectrophotometrically. The amount of diclofenac potassium adsorbed by the montmorillonite (q_t , mg diclofenac potassium /g clay)

was determined by the difference between the initial concentration of C_o and that of the supernatant in equilibrium C_e .

In order to study the adsorption isotherms, 0.1 g of adsorbent was kept in contact with 100 ml of diclofenac potassium solution at various concentrations for 3 h to allow attainment of equilibrium at room temperatures [31,35].

$$q_t = (C_o - C_e) \times V/m \quad (1)$$

where, q_t : amount of diclofenac potassium/of adsorbent (mg/g), C_o : Initial concentration of diclofenac potassium (mg/l), C_e : residual equilibrium concentration (mg/l), V : volume of solution (l), m : weight of adsorbent (g).

2.4. Optimization of adsorption parameters

2.4.1. Contact time

For the adsorption experiments prepared with 1 g/l of clay and diclofenac potassium concentration (100 mg/l), equilibration times of 3 h were tested.

2.4.2. Adsorbate/adsorbent relationship

The amounts of clay chosen were 100, 300, 500, 700, 900, and 1,000 mg/l with 100 mg/l of diclofenac potassium solution.

2.4.3. Effect of pH

The pH of the suspension analyzed was within the range of 2–10, with 50 mg/l of diclofenac potassium solution. Clay concentration used was 100 mg/l.

2.4.4. Effect of the initial concentration of diclofenac potassium solution

The initial concentrations of diclofenac potassium solution chosen were 10, 20, 50, 100, and 120 mg/l with 100 mg of clay.

3. Results and Discussion

3.1. Characterization of bentonite powders

3.1.1. Chemical composition of bentonite analysis (Fluorescence X)

The chemical composition of natural bentonite, purified bentonite (Na-montmorillonite), and iron-pillared clay obtained by using X-ray fluorescence

Table 1
Chemical analysis by XRF of bentonite (% mass)

Eléments	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	SO ₂	TiO ₂
Natural clay	69.66	14.12	6.58	4.17	4.00	1.23	0.24
Purified clay	71.83	15.13	5.96	2.86	3.79	/	0.43
Iron Pillared clay	26.79	5.01	64.98	1.46	1.76	/	/

analysis, given in Table 1, indicates the presence of silica and alumina as major constituents along with traces of sodium, potassium, iron, magnesium, calcium, and titanium oxides in the form of impurities. The results show that most of the aluminum and silicate are in the form of bentonite. Results also indicated the presence of free quartz in bentonite. It is thus expected that the adsorbate species will be removed mainly by SiO₂ and/or Al₂O₃.

3.1.2. Analysis by X-ray diffraction

X-ray diffraction (XRD) analysis (Fig. 2) revealed that the bentonite consisted of predominantly montmorillonite, and substantial amounts of quartz and feldspar impurities, in addition to minor amounts of illite [33,36–39].

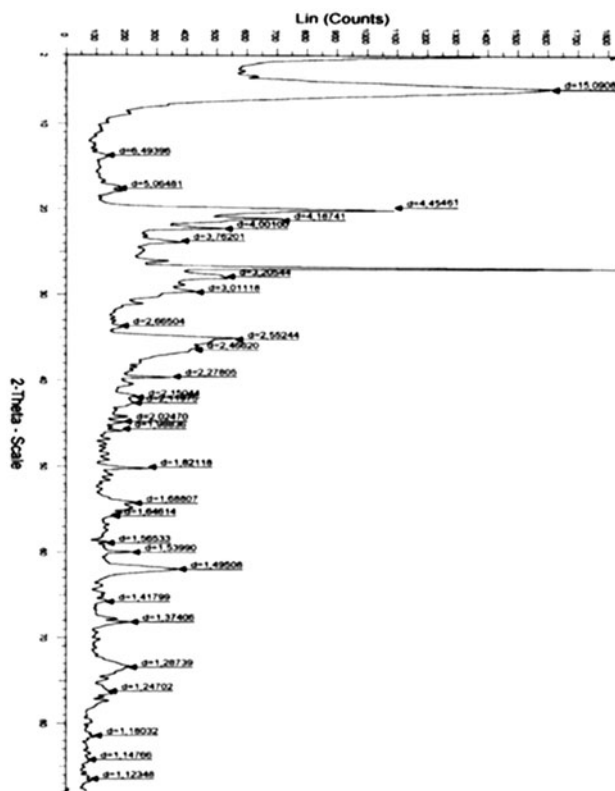


Fig. 2. XRD patterns of natural clay.

XRD analysis revealed the successful purification of bentonite (Fig. 3) and synthesis of pillared clay. The shift of the 001 diffraction maximum (d001 basal spacing) from 15.09 Å (natural clay) to 12.63 Å for Na-montmorillonite (purified bentonite) and 17.21 Å for pillared bentonite (Figs. 2–4) Fig. 4 clearly indicates that the Na-bentonite was pillared with the iron species.

The Na-exchange process lowered d001 bentonite basal spacing from 15.09 Å for the starting bentonite to 12.63 Å, but the clay retained its swelling properties. The pillaring process led to the increase of the d001 spacing according to the type of intercalated iron

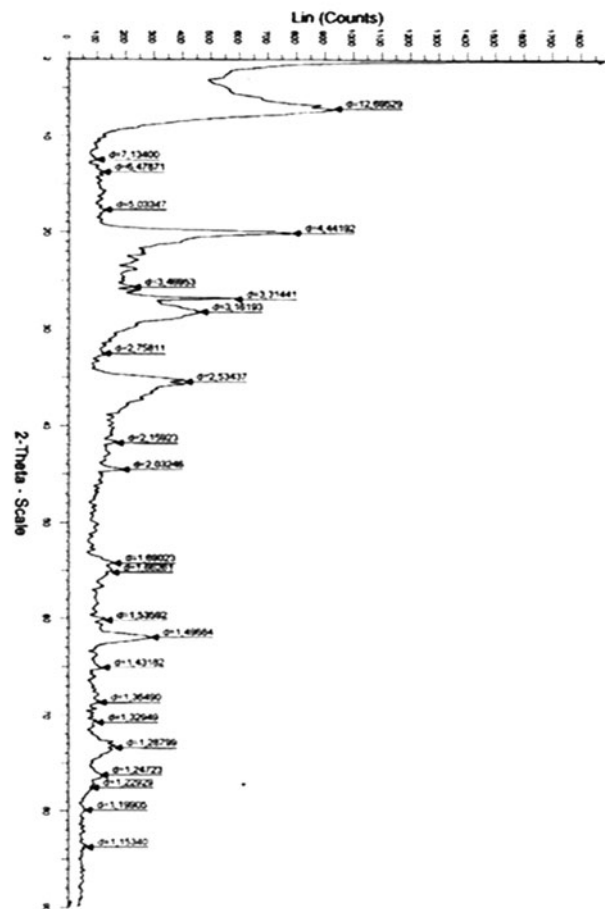


Fig. 3. XRD patterns of purified bentonite.

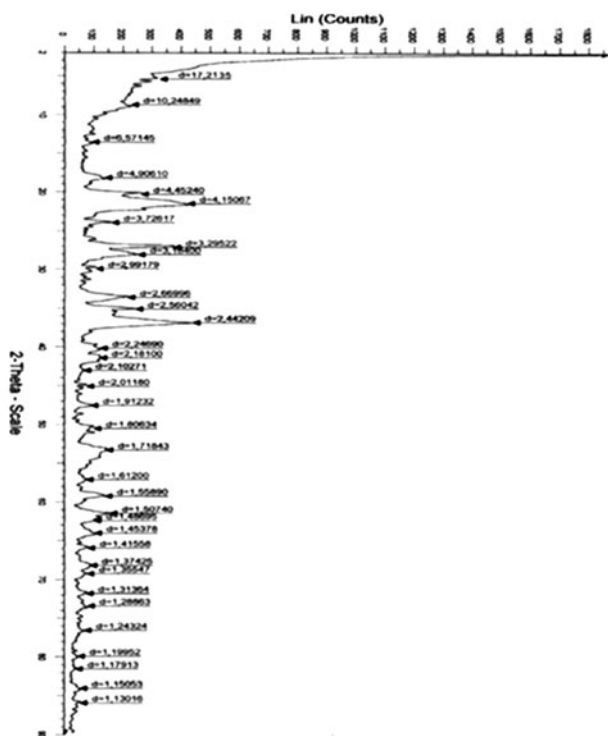


Fig. 4. XRD patterns of iron-pillared clay.

cations. The recorded basal spacing was 17.21 Å for the iron-pillared clay. Hence the exchangeable Na^+ cations from the interlamellar region were replaced by iron cations, increasing the interlayer distance [4,26].

3.1.3. Analysis by SEM

The morphology of natural clay, purified clay, and iron pillared clay was evaluated by SEM (Figs. 5 (a)–(c)), and the micrographs showed the existence of

different size of particles in natural clay (Fig. 5(a)). The morphology of purified clay (Fig. 5(b)) showed that the diameter of particles is lower than 2 μm . Microscopic observation of iron-pillared clay (Fig. 5(c)) indicated that iron-oxide particles are on the surface of the natural bentonite.

3.1.4. Infrared characterization (FTIR)

In order to obtain complementary evidence for the intercalation of iron cations into the silicate lattice, FTIR spectra were recorded in the region 400–4,000/ cm (Fig. 6). A strong band, 795.46/ cm , was observed only in iron pillared-bentonite; this can be assigned to insertion of iron in the bentonite [24]. Montmorillonite is confirmed by the presence of Si–O vibrations of bonds, Si–O, Si–Al^{VI}, Si–Mg^{VI}, and Al–OH.

3.2. Kinetics study

3.2.1. The effect of contact time

The effect of contact time on the amount of diclofenac potassium, adsorbed onto Na–bentonite and iron-pillared bentonite (Fig. 7) was examined at the 100 mg/l concentration of diclofenac potassium, without adjustment of pH (pH = 5.4) and 100 mg of clay. As can be seen from the figures, when the equilibrium time was increased, the amount of adsorption was not drastically increased. The adsorption of diclofenac potassium occurred very quickly from the beginning of the experiments. This may be indicative of chemical adsorption. Maximum adsorption of diclofenac potassium onto Na–bentonite and iron-pillared bentonite was observed at 150 min; it can be said that beyond this there is almost no further increase in the adsorption and it is thus fixed as the equilibrium time.

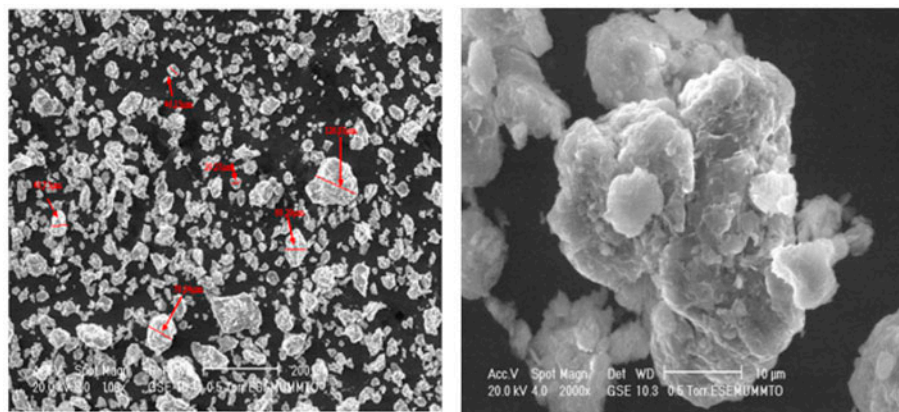


Fig. 5(a). SEM micrographs of particles observed on the natural clay.

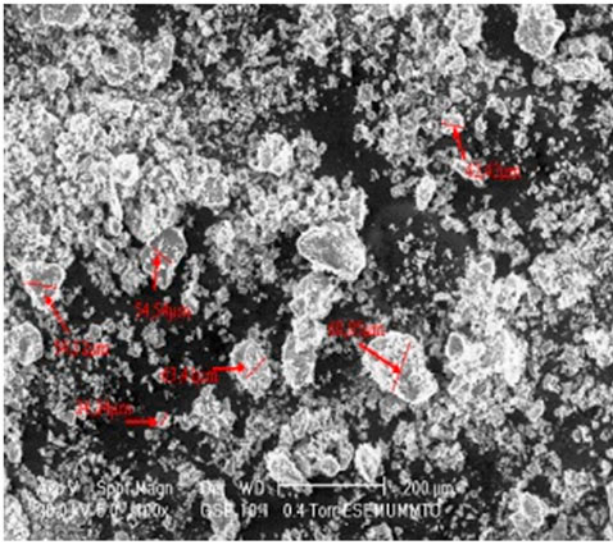


Fig. 5(b). SEM micrographs of particles observed on the purified clay.

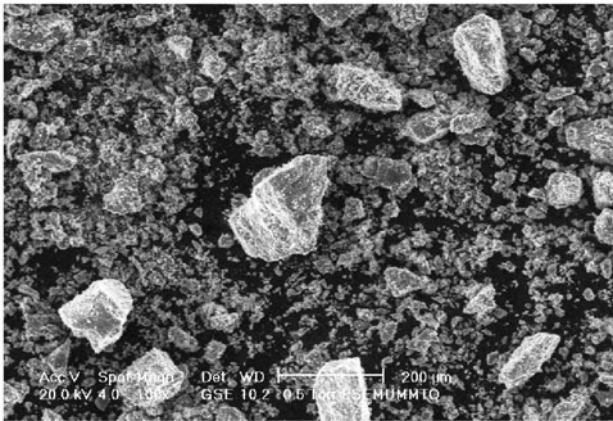


Fig. 5(c). SEM micrographs of particles observed on the Iron pillared clay.

3.2.2. Influence of the initial concentration of diclofenac potassium

The effect of the initial concentration of diclofenac potassium in the adsorption onto Na-bentonite and iron-pillared bentonite (Fig. 8) was examined with 100 mg of clay. As can be seen from the figures, the elimination of diclofenac potassium occurred very quickly with increasing concentration of diclofenac potassium. Maximum adsorption of diclofenac potassium onto Na-bentonite and iron-pillared bentonite was observed at the concentration 100 mg/l of diclofenac potassium with iron-pillared bentonite; it can be said that the intercalation of metals into the clay, thus ensuring uniform porosity with a high interlayer and

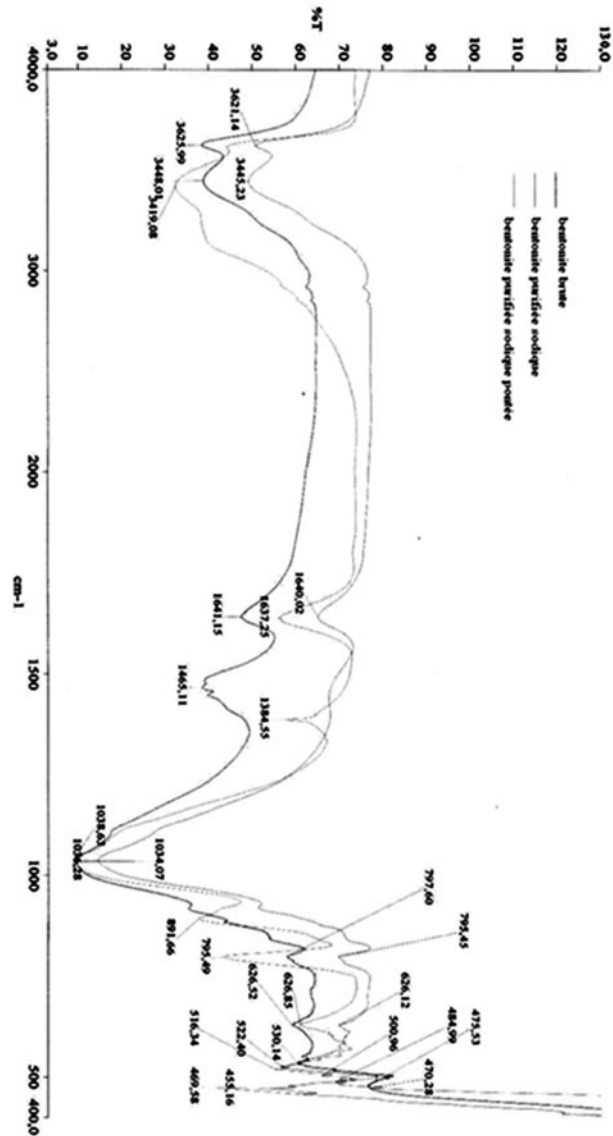


Fig. 6. FTIR spectra of natural bentonite, purified bentonite and iron-pillared bentonite.

better insertion of diclofenac potassium and its elimination.

3.2.3. Effect of pH

The pH is the most important factor affecting the adsorption process [23]. To study the influence of pH on the adsorption capacity of natural bentonite, Na-bentonite, and iron-pillared bentonite, experiments were performed using various initial pH varying from 2 to 10. The uptake of diclofenac potassium decreased with increasing pH (Fig. 9). It was observed that the

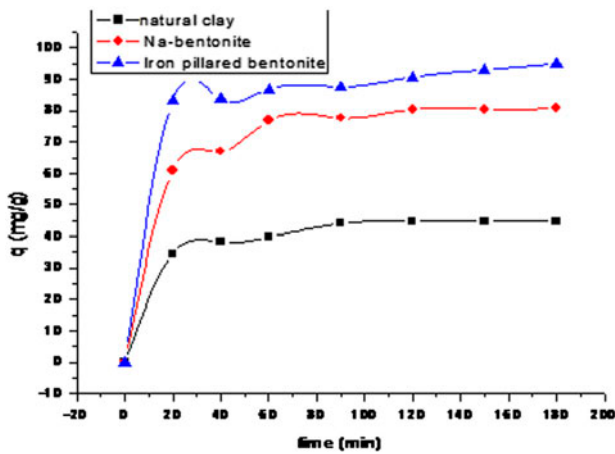


Fig. 7. Effect of contact time for the adsorption of diclofenac potassium onto natural bentonite, purified bentonite and iron pillared bentonite.

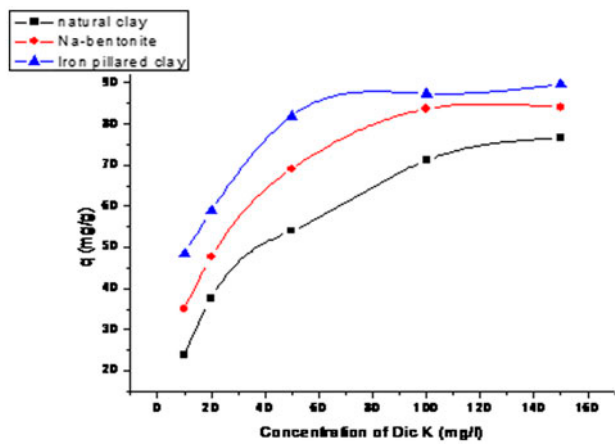


Fig. 8. Influence of the initial concentration of diclofenac potassium adsorption (100 mg of clay. pH 6).

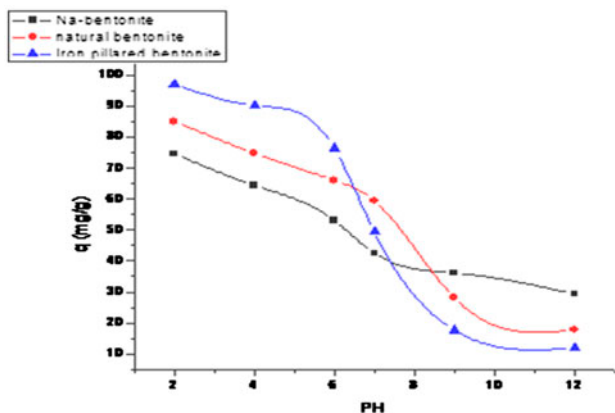


Fig. 9. Influence of pH on the adsorption of diclofenac potassium (100 mg of clay. 100 mg/l of diclofenac potassium).

adsorption is highly dependent on the pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. At lower pH more protons will be available; thereby increasing electrostatic attraction between negatively charged diclofenac potassium and positively charged adsorption sites and causing an increase in diclofenac potassium adsorption [40].

Maximum removal of diclofenac of potassium with Na-bentonite and iron-pillared bentonite was at acidic pH 2. When the pH of the solution is increased, the positive charge on the oxide or solution interface decreases and the adsorbent surface becomes negatively charged. On the other hand, a lower adsorption at higher pH (at basic conditions) may be due to the abundance of OH^- ions and consequently the ionic repulsion between the negatively charged surface and the diclofenac potassium molecules, and also there are no exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently the adsorption decreases [41,42].

3.2.4. Effect of adsorbent

It is evident from the figure that as the amount of adsorbent dosage increases up to 1 g (Fig. 10), the maximum of diclofenac potassium removal was attained with this amount and it was used for further experiments. It can be said that by increasing the mass of adsorbent, the surface area of the adsorbent increases, thus ensuring elimination of diclofenac potassium.

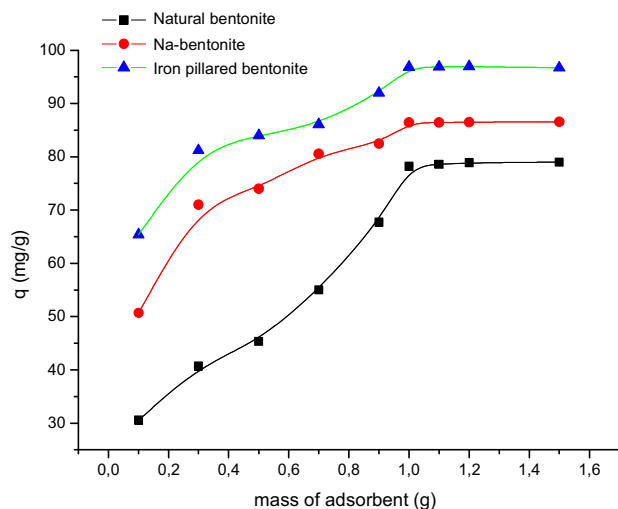


Fig. 10. Influence of the mass of adsorbent in the adsorption of diclofenac potassium (100 mg/l of diclofenac potassium. pH 6).

3.3. Adsorption isotherm studies

Diclofenac adsorption isotherm data starting at different initial diclofenac potassium concentrations were investigated to fit the models of Langmuir and Freundlich. These data were obtained by diclofenac potassium concentration measurement after adsorbent/adsorbate contact periods equal to the equilibrium times

The well-known expression of the Langmuir model is

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (2)$$

where q_e is the equilibrium of diclofenac potassium concentration on adsorbent (mg/g), C_e is the

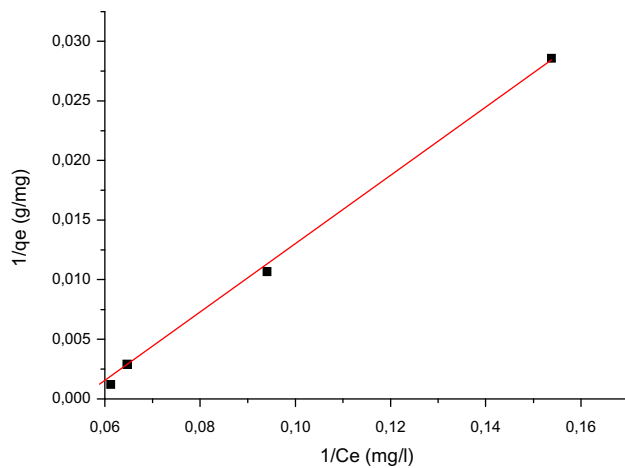


Fig. 11. Langmuir plots for the adsorption of diclofenac potassium onto natural bentonite.

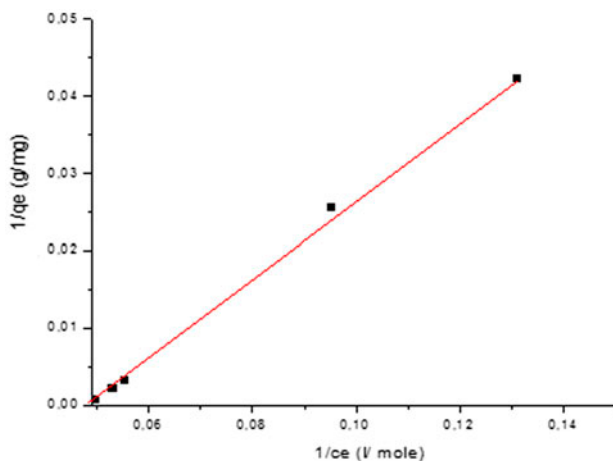


Fig. 12. Langmuir plots for the adsorption of diclofenac potassium onto Na-bentonite.

equilibrium diclofenac potassium concentration in solution (mg/l), q_{\max} is the monolayer capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant (l/mg) [43]. A plot of C_e/q_e vs C_e gives a straight line of slope $1/q_{\max}$ and intercept, $1/q_{\max} K_L$. The Langmuir equation is applicable to homogeneous sorption, where the sorption of each sorbate molecule onto the surface has equal sorption activation energy [44].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where q_e is the equilibrium diclofenac potassium concentration on adsorbent (mg/g), C_e is the equilibrium diclofenac potassium concentration in solution (mg/l), and K_F (l/g) and n are the Freundlich constants

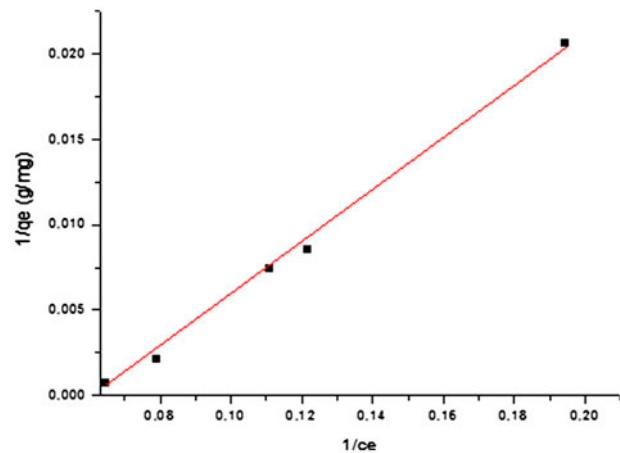


Fig. 13. Langmuir plots for the adsorption of diclofenac potassium onto iron-pillared bentonite.

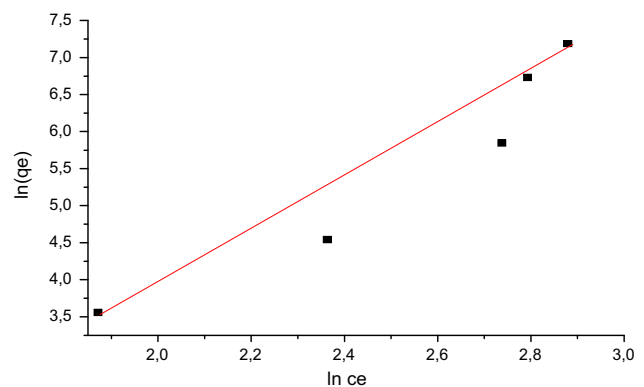


Fig. 14. Freundlich plots for the adsorption of diclofenac potassium onto natural bentonite.

characteristic of the system, indicators of adsorption capacity and adsorption intensity, respectively.

Adsorption data obtained in the concentration range (50–1,000) mg/l were correlated with the following linear forms of Langmuir (Eq. (2)) [45] and Freundlich (Eq. 3) [46] adsorption isotherm models:

Best-fitted straight lines with high correlation coefficients obtained in case of Langmuir (Figs. 11–13) and Freundlich (Figs. 14–16).

The all isotherm parameters derived from the respective plots are presented in Table 2. The fit of the data for diclofenac potassium adsorption onto natural bentonite, Na-bentonite and iron-pillared bentonite

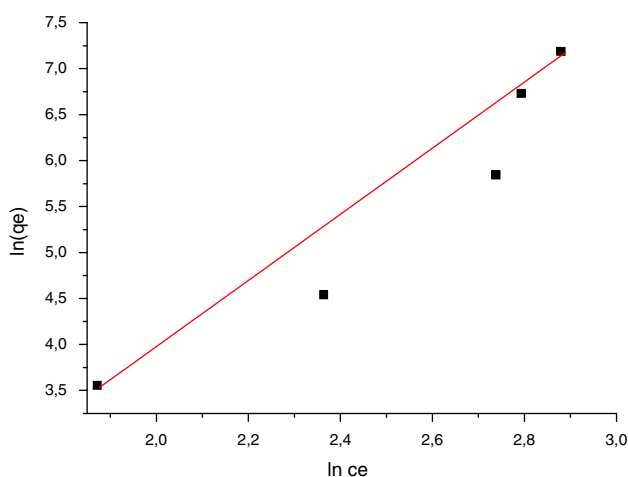


Fig. 15. Freundlich plots for the adsorption of diclofenac potassium Na-bentonite.

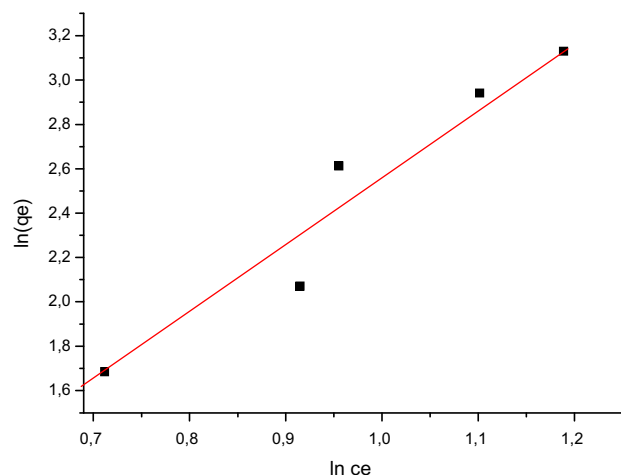


Fig. 16. Freundlich plots for the adsorption of diclofenac potassium onto Iron-pillared bentonite.

Table 2

Langmuir isotherm constants for the adsorption of diclofenac potassium

Sample	q_{\max}	K_L	R
Natural Bentonite	62.50	0.056	0.998
Na-Bentonite	40.00	0.048	0.999
Iron-pillared Bentonite	100.00	0.063	0.992

Table 3

Freundlich isotherm constants for the adsorption of diclofenac potassium

Sample	$1/n$	K_f	R
Natural clay	0.287	0.039	0.923
Purified clay	0.623	0.155	0.945
Iron-pillared clay	0.315	0.547	0.936

suggests that the Langmuir model gave slightly better fitting than that of Freundlich model, as it is obvious from a comparison of the r^2 values in Table 2.

The obtained isotherms are shown in Figs. 11–16 with their corresponding Langmuir and Freundlich fits. The fit correlation coefficients (R^2), the average residues between the experimental data and the models used in the fitting and, the adjustment parameters obtained from Langmuir and Freundlich equations are shown in Tables 2 and 3. According to the R^2 term, the experimental data were appropriately described by both models for all samples.

However, as seen in Figs. 11–13, the natural, purified, and iron-pillared clay isotherms show the best fit for the Langmuir equation. These results indicate that in the natural clay mineral and in the purified and iron pillared samples, the adsorption is reached in homogeneous sites of adsorption.

4. Conclusion

In the present study, a natural clay mineral from Algeria was successfully pillared using iron oligocations. The pillaring process was evidenced by the increase in the basal spacing (d001) and the development of microporous structures, observed by XRD. The diclofenac adsorption studies for the three materials showed a considerable increase in the adsorption capacity of the iron-pillared clay compared to the natural material.

Results showed that this material is a good adsorbent of diclofenac potassium due to the high affinity between adsorbate and adsorbent. Batch studies suggested that the high adsorption capacity of iron-pillared bentonite in acidic solutions is due to the strong

electrostatic interactions between its adsorption site and the anionic diclofenac. The straight lines obtained from the Langmuir and Freundlich models obey to fit well with the experimental equilibrium data, but the Langmuir model gives slightly better fitting than Freundlich model.

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