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Natural clay (el-Hicha) from Gabès (Tunisia) as adsorbent for the efficient removal of ciprofloxacin from wastewater.

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Abstract.

The presence of Ciprofloxacin in wastewater and surface water has been widely reported, is becoming a growing concern due to its toxicological effect on aquatic species and has been efficiently removed from wastewater by adsorption using natural clay collected from Gabes region (Tunisia). The textural, chemical-surface, structural, and morphological properties of the clay-based adsorbent was examined, finding low-moderate specific surface area value (18.1 m^2 g^{-1}) and a structure coincident with the smectite phase. Adsorption kinetic study revealed that clay reached the equilibrium in (420 min) ~ 7 h, achieving a CIP removal percentage of 80 %. Pseudo-second-order kinetic model describes well the kinetic adsorption experimental data. The equilibrium adsorption capacity (q_e = 177.8 mg g^{1}) was obtained for clay el-Hicha. The Freundlich adsorption model led to the best-fitting results, suitable for heterogeneous adsorptive systems. From pH studies, considering the dissociation constants of the CIP molecule, working at solution pH = 6 led to the best adsorption results.

Keywords: Adsorption; Ciprofloxacin; CH:clay el-Hicha; Wastewater.

1 Introduction

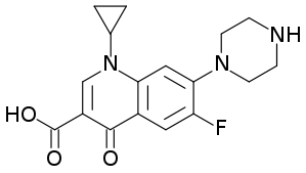
The pharmaceutical sector could produce antibiotic wastes with a high concentration and release them into the environment. The pharmaceuticals are discharged directly into surface water.[3,4].Ciprofloxacin (CIP) is one of the most representative broad-spectrum fluoroquinolone antibiotics, has been usually used for the treatment of infectious diseases in humans and animals [5–6]. In addition, ciprofloxacin in water above certain concentration limits could cause several diseases, such as liver problems, carcinogenesis, etc. [7]. For this reason, several wastewater treatments have been proposed to remove organic pollutants efficiently [8–9]. So, last years, different treatments have been accomplished to remove ciprofloxacin in wastewater. Among others, ozonation, catalytic wet peroxide oxidation (CWPO), photo-Fenton, extraction, and adsorption processes [10,11] . Among these technologies, adsorption is one of the most popular since it is considered adequate, efficient, economical and used in many real wastewater purification systems.So, considering these statements, treating micropollutants by clay adsorption has been considered an excellent alternative to activated carbon. Thus, natural clays is inexpensive materials that can be found in many continents worldwide and show relatively high specific surface area values, leading to relevant adsorption capacities [12]. These characteristics indicate that they are good candidates as adsorbents. Many clays, such as kaolinite, montmorillonite, sepiolite, bentonite, etc., have been efficiently used as adsorbents[13].

2. Materials and Methods

2.1.Ciprofloxacin

Principal caracteristics of ciprofloxacin are presented in table 1

Table 1. Characterization of ciprofloxacin.

Chemical	Structure	Supplier	Purity (wt. %)
Ciprofloxacin, CAS nº 85721-33-1		Sigma-Aldrich	≥ 98.0

2.2. Adsorbents preparation and characterization

The raw clay was collected in the region of Gabès (in the south of Tunisia). It was ground using an agate mortar and sieved, recovering the particle size fraction below 125 µm. Then, about 50 g of clay is added to 1 L of ultrapure water, and the mixture was kept under constant stirring (500 rpm) in a rotary blade stirrer for 60 min. Then the mixture was allowed to stand in a graduated cylinder for several hours. Subsequently, the upper fraction containing the purified clay was then recovered by centrifugation and then rewashed four times with ultrapure water until reaching a neutral pH in the washing water. Finally, the purified clay was oven-dried at 90°C overnight before being reused.

2.3 Adsorption experiments

Batch adsorption experiments was accomplished by putting in contact the CIP solution (C_0 = 50 mg L^{-1}, 25 mL) with the adsorbent in glass vessels, using a LabMate orbital shaker at a constant stirring speed (250 rpm) and a controlled temperature (T = 25ºC). Samples were collected and filtered for further analysis using 0.45 µm PTFE filters. The CIP concentration was measured in an Agilent HPLC 1260 Infinity II chromatograph with a "*diode array*" detector using a Poroshell 120 EC-C18 column (4.6 × 150 mm; 4 µm).

The adsorption capacity at giving time can be determined according to Equation 1:

$$qt = \frac{C_{CIP,0} - C_{CIp,t}}{m_{ads}} \quad (1)$$

where q_t (mg g^{-1}) is the adsorption capacity at time t; $C_{CIP,0}$ and $C_{CIP,e}$ (mg L^{-1}) are the initial and time t CIP concentrations, respectively; and m_{ads} (g L^{-1}) is the adsorbent dose used in the adsorption experiments. At equilibrium time, Ct became Ce and qt became qe

3. Results and Discussion

3.1. Adsorbents characterization

3.1.1. Chemical composition.

The chemical composition of clays may vary depending on their geological source and formation process. Generally, it was mainly composed of hydrated aluminium silicate and other minor elements, such as iron or alkali and alkaline-earth metals [14,15].

As can be observed in Table 2, the chemical composition of el-Hicha clay is predominantly oxygen (30.22 wt.%), silicon (13.41wt.%), aluminium (5.33 wt.%),

and iron (4.70 wt.%). Additionally, calcium is a one of major elements (2.67 wt. %), while phosphorus content is significant (2.73 wt.%). The sodium concentration is high percentage (1.53 wt. %).

Table 2 . Chemical composition of the tested CH-based adsorbent.

element	O	Si	Al	Ca	Fe	P	Na	Others, Σ
%	30,22	13,41	5,33	2,67	4,70	2,73	1,53	

As can be observed from Table 3, the surface erea value was 18.1 $m^2\ g^{-1}$ with the total pore volume value of 0.11 $cm^3\ g^{-1}$ and the verage pore (D_{avg}) of 15.8 nm.

Table 3. Textural properties of the tested clay-based adsorbents.

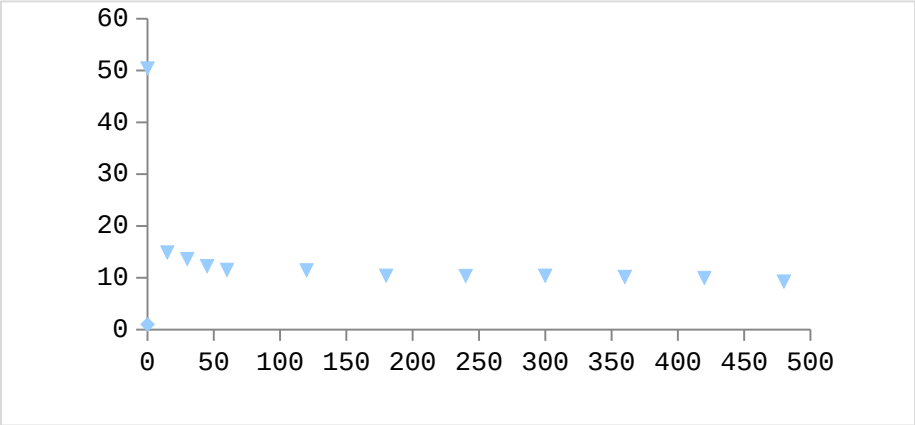
Parameter	Clay el-Hicha
S_{BET} ($m^2\ g^{-1}$)	18.1
V_{Micro}·$x10^3$ ($cm^3\ g^{-1}$) [a]	0.72
V_{Meso} ($cm^3\ g^{-1}$) [b]	0.11
V_{Total} ($cm^3\ g^{-1}$) [c]	0.11
V_{Micro}/V_{Total} (%)	0.68

[a]Calculated by Dubinin-Radushkevich equation; [b]Calculated from V_{Micro} and V_{Total} values; [c]Pores volume at $P/P^0 = 0.99$; [d]D_{avg} at adsorption average pore width (4 V/ A by BET).

3.2.Adsorption Study

3.2.1. -Time effect

The variation of [Cip] in function of time is illustrated in figure2



Limit to 500 min

Fig2. Variation of CIP concentration versus time
([Cip] =50mg/L, T=30°C, pH=6, adsorbent dosage = 1g/L)

Figure 2 revealed that CH reached the equilibrium in (420 min) ~7h, achieving a CIP removal percentage of 80%.
We noticed that concentration of CIP decreades with an increase in time. We can say that 420 min is the optimal time.

3.2.1.2. Dose adsorbent effect

. Figure 3 shows the variation of the CIP concentration as a function of the clay dose applied range from 0.052 to 2.40

.We noticed that concentration of CIP decreased with increasing clay dosag until 1.2 g/L. Within this value, the CIP concentration stilled almost constant. We can say that 1.2 g/ is the optimal dosage.

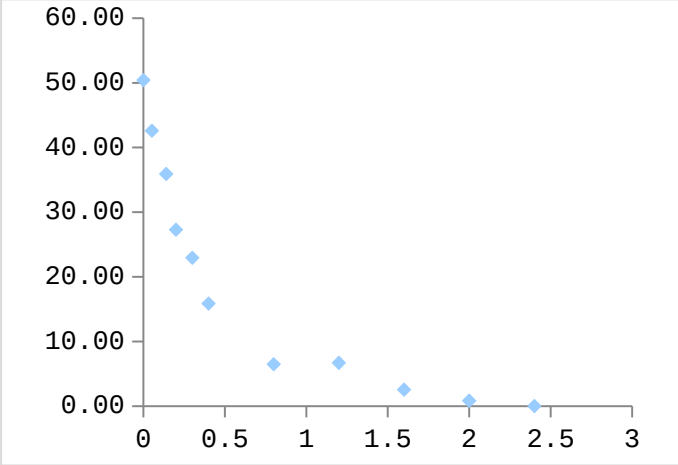


Fig3. Dose adsorbent effect ([Cip] =50mg /L, T=30°C, pH=6)

An adsorbent dose range from 0.052 to 2.40 g L^{-1} was used in the equilibrium adsorption experiments. In this case, WHEN the optimal dose is 1 g/L .

3.2.2. Kinetic studies

In terms of adsorption kinetic, CH is showed a very high pharmaceutical removal percentage (~80%). Thus, the industrial application of these material requires a trade-off between kinetic and equilibrium adsorption. For the kinetic modeling, two well-known kinetic models have been considered, including Pseudo-First Order or "PFO" (eq. 2), Pseudo-Second Order (eq.3).

$$q_t = q_1 \left(1 - e^{-K_1 t}\right) \quad (2)$$

$$q_t = \frac{q_2^2 \cdot K_2 \cdot t}{1 + K_2 \cdot q_2 \cdot t} \quad (3)$$

q_t (mg g^{-1}) is the CIP adsorption capacity at any time t; q_1 (mg g^{-1}) and K_1 (min^{-1}) are the CIP adsorption capacity at the equilibrium time, and the adsorption rate constant, respectively, in PFO model; q_2 (mg g^{-1}) and K_2 (g mg^{-1} min^{-1}) are the CIP adsorption capacity at the equilibrium time and the adsorption rate constant, respectively, in PSO.

The experimental data was fitted using Origin 2021 software, with the Levenberg–Marquardt iteration algorithm (figure 4)

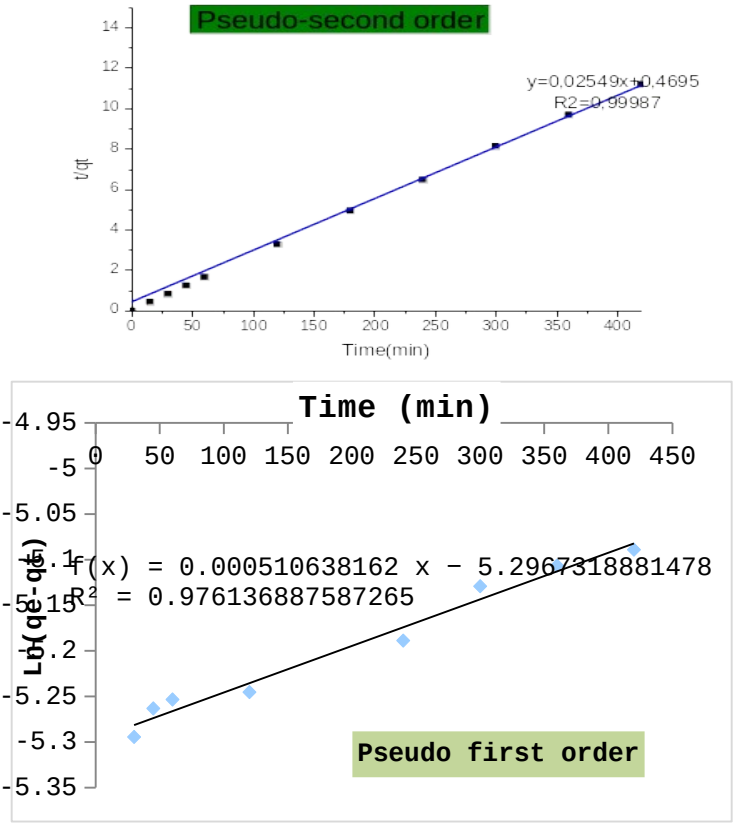


Figure4. Adsorption kinetics of ciprofloxacin at 25 ºC, C_0 = 50 mg L^{-1}, m=1.0 g L^{-1}, V=25 and ultrapure water using the clay-based adsorbent: CH.

The calculated parameters from the slope and the intercept of the obtained straight line for the two kinetic models are summarized in Table 4, and depicted in Figure 5at the non linear form.

Table 4. Kinetic model parameters for the ciprofloxacin adsorption onto the clay-based adsorbents.

Model	Parameter	Value
	q_{exp} (mg g^{-1})	**36.84**
PFO	q_1 (mg g^{-1})	34.74

PSO	q_2 (mg g^{-1})	35.25

As shown in Table4 , the best fitting among the tested adsorption kinetic models has been by the pseudo-second order (PSO) model [18].

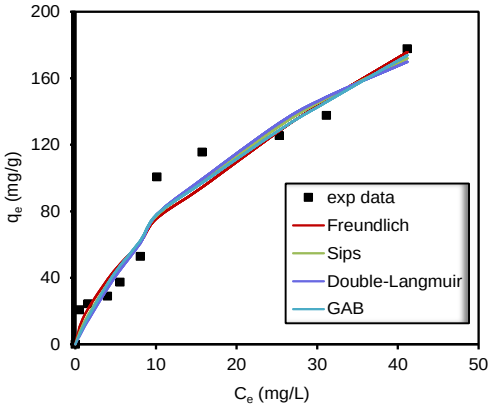


Figure 5. Adsorption isotherms of ciprofloxacin at 25 ºC ,C_0 = 50 mg L^{-1}, m=1.0 g L^{-1} , V=25 and ultrapure water using the clay-based adsorbents: CH **(c)**

3.2.2. isotherm models

Two models were tested to model the experiment data obtained at equilibrium ,namely :Freundlich and Langmiur.

Freundlich isotherm is an empirical model that can be used for multilayer adsorption on heterogeneous active sites. The mathematical model can be shown as:

$$q_e = K_F \cdot C_e^{1/n_F} \quad (4)$$

Where, q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_e (mg L^{-1}) is the equilibrium adsorbate concentration in the aqueous phase, K_F (L mg^{-1}) is the Freundlich model adsorption capacity, and $1/n_F$ is a parameter related to the adsorption intensity or the adsorbent surface heterogeneity; thus, when, n_F>1, the adsorption process could be considered as favourable.

Dual-site Langmuir model, usually used for multilayer (bilayer) adsorption systems, can be described by the following equation:

$$q_e = \frac{q_{sat1} \cdot K_1 \cdot C_e}{1 + K_1 \cdot C_e} + \frac{q_{sat2} \cdot K_2 \cdot C_e}{1 + K_2 \cdot C_e} \quad (6)$$

where q_{sat1} and q_{sat2} (mg g^{-1}) are the maximum adsorption capacity values on each monolayer, and K_1 and K_2 (L mg^{-1}) are the adsorption equilibrium constants related to the affinity of the adsorbate molecule towards the adsorbent surface.

As can be seen from Table5, the Freundlich adsorption model led to the best fitting results (with R^2 value of 0.978), concluding that the active sites in the adsorbent are non-uniform, characteristic of heterogeneous system.

Model	Parameter	Clay 3
	q_{exp} (mg g^{-1})	177.80
Freundlich	K_F (L mg^{-1})	15.946
Dual-site Langmuir	q_{sat1} (mg g^{-1})	266.12

4. Conclusions

Natural clay collected from Gabes used as alternative adsorbent was revealed as efficient adsorbents of CIP from the aqueous medium, including environmentally-relevant water matrices. The textural characterization showed material with low-moderate specific surface area, characteristic of clay material. The Pseudo-second-order kinetic model best fit the experimental kinetic data. Moreover, the equilibrium adsorption capacity value (q_e = 177.7 mg g^1) was found for clay el-Hicha, with multilayer profile adsorption isotherms that best fitted the Freundlich adsorption model. It was also shown that CIP cationic species possess significant adsorption affinity compared to zwitterionic and anionic forms, observing a favoured adsorption

process at solution pH = 6.0.

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