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Imazapyr sorption on a macroporous mesoporous natural phosphate rock

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ABSTRACT

The removal of imazapyr pesticide from aqueous solutions, using a macroporous natural phosphate rock (PR) as adsorbent, is studied. The adsorption equilibrium, isotherms and kinetics for imazapyr are studied and the data was fitted into various mathematical models and Langmuir and Freundlich isotherms. Experiments performed by the batch method showed that the sorption process occurs by a monolayer deposition of imazapyr pesticide according to a second order reaction.

Keywords: Phosphate rock; Imazapyr; Adsorption, Isotherm; Kinetics

INTRODUCTION

The removal of pesticides from wastewater is an extremely complex problem due to the wide range of pesticides chemical structures and properties [1]. Nevertheless, adsorption processes using suitable adsorbent have shown high removal efficiency and many economical, ecological and technological advantages [2]. Based on their adsorption performance, activated carbon is the most used adsorbent due to its extreme capacity of adsorption of organic materials [3, 4]. However, this adsorbent has a high cost and remains difficult to regenerate for multiple uses. The search of another efficient and less expensive adsorbent is an interesting task. In this context, the utilization of natural phosphate rock as an adsorbent has a great interest due to its efficiency and availability.

In this work, the adsorption capacity of Imazapyr pesticide was determined using local phosphate rock, which is a natural and available adsorbent in Benguerir. The parameters that influence adsorption such as pesticide initial concentration, contact time, adsorbent mass, and solution pH were investigated. The description of the adsorption of the isotherm was done by applying linear transformations of two isotherms: Langmuir and Freundlich models.

MATERIALS AND METHODS

2.1. Reagents and equipment's

Imazapyr, purity 99.9% was purchased from Riedel-de Haën- PESTANAL, its chemical structure was presented in figure 1.

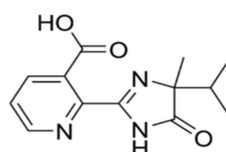


Figure 1: Chemical structure of imazapyr

The phosphate rock sample used in this work was from the Benguerir region (Morocco). The sample was washed by ultrapure water and then sieved to give a 100-400µm size fraction.

Elementary and quantitative analysis identifies the components of natural phosphate. Calcium and phosphorus were measured using ICP-AES spectrometer. Fluorine was assayed by selective electrode potentiometer. The results of chemical analysis were summarized in Table 1 and Figure 2.

Table1 : chemical composition of the rock phosphate.

Elements	Ca	P	Si	F	Ca/P
%mass	37.8	15.02	1.65	3.01	1.97

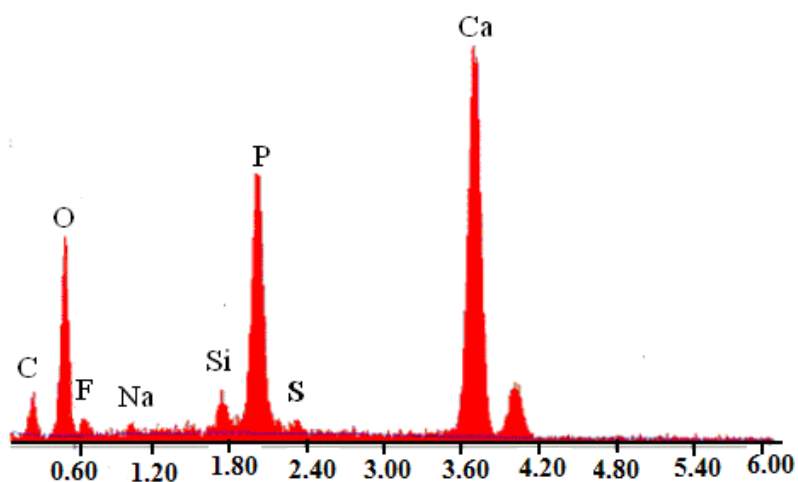


Figure 2: energy-dispersive x-ray spectroscopy of X-rays (EDAX) constituent chemical elements of rock phosphate

The kinetic experiments were performed by following the disappearance of imazapyr pesticide by means of UV-visible spectrophotometer working at 260 nm.

2.2. Adsorption and kinetic studies

The sorption process of imazapyr pesticide was insured by the putting in contact of 0.2 g of the natural phosphate rock studied in 100 mL of the wished solution to a temperature of 25 °C. After agitation of this mixture, pesticide residual were determined by UV-visible spectrophotometer.

The quantity of imazapyr adsorbed (C_a) (mmol/g) by the natural phosphate rock (PR) was determined by the following literal expression:

$$C_a = \frac{C_0 - C_e}{m} \cdot V$$

Where:

- C_a is the amount ($\text{mg}\cdot\text{g}^{-1}$) of adsorbed pesticide at time t ,
- C_0 and $C(t)$ are the concentrations ($\text{mg}\cdot\text{L}^{-1}$) of pesticide in solution at $t = 0$ and $t = t_e$,
- V is the volume (L) of pesticide solution,
- m is the weight (g) of the adsorbent.

RESULTS AND DISCUSSION

3.1. Effect of quantity of adsorbent and contact time

The kinetic study of adsorption is an important step to evaluate the contact time necessary for reaching the equilibrium. The kinetics is achieved at initial pH of the solution for an initial concentration of 10 mg/L, with a mass of PR of 2 g/L and at $T = 24^\circ\text{C}$. The variation of the quantity adsorbed by the pollutant as function of time is illustrated in Figure 3.

It is clear from Figure 3 that the amount of imazapyr pesticide adsorbed, Q_{ads} increased with time. The equilibrium adsorption was achieved in 120 min.

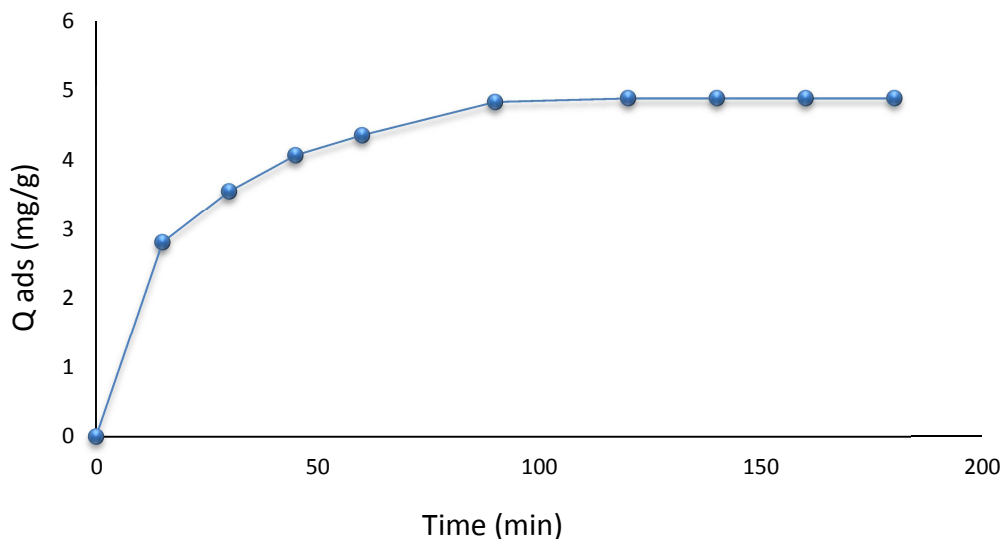


Figure 3: Effect of contact time on the uptake of imazapyr on Phosphate Rock (temperature: 25 °C, initial concentration: 10 mg/L)

The effect of adsorbent dose on the imazapyr removal was studied by varying the dose of adsorbent from 0.5 to 10 g/L. The experiment was carried out at fixed pesticide concentration at 10 mg/L, at a fixed temperature of 25°C and a time of 30 min. It could be seen from Figure 4 that initially the percentage removal of imazapyr pesticide was not influenced by the increase in adsorbent dosage.

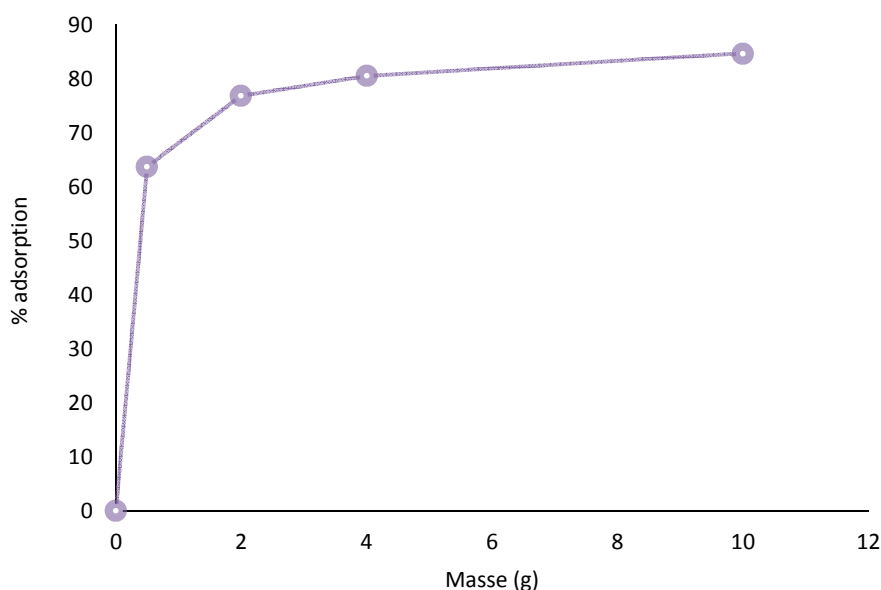


Figure 4: Effect of adsorbent dosage on the uptake of imazapyr on PR (temperature: 25°C, initial concentration: 10 mg/L)

3.2. Adsorption kinetics

The Lagergren's pseudo-first-order [5] and pseudo-second-order [6] models were used to test adsorption kinetics data in order to investigate the mechanism of adsorption. The values of the kinetic parameters as well as the regression coefficients (R^2) are listed in Table 2.

Table 2: Kinetic parameters for Imazapyr on PR

Model	parameters	value
Pseudo first order	K_1 (min^{-1})	0.0428
	$Q_{e,1}$ (mg/g)	3.0853
	R^2	0.9636
Pseudo second order	K_2 (min^{-1})	0.012543
	$Q_{e,2}$ (mg/g)	5.46
	R^2	0.9994

The value of correlation coefficient R^2 for the pseudo-first-order adsorption model is relatively high (>0.95), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo-second-order model are more satisfactory to describe the adsorption kinetics of Imazapyr on natural phosphate rock.

3.3. Modeling of adsorption isotherms

Isotherm data was analyzed with Langmuir and Freundlich models and the results of their linear regression were used to find out the fit model. Values of Langmuir constants q_{\max} and b , Freundlich constants K_F and n , as well as the regression coefficients (R^2) are listed in Table 4. Langmuir model was found fit due to high correlation coefficients for natural phosphate rock –Imazapyr system.

Table 4: Adsorption Isotherm model parameters for Imazapyr on natural phosphate rock

Langmuir			Freundlich		
Q_m	K_L	R^2	K_f	n_f	R^2
25.5102	0.2009	0.9951	5.9061	2.6309	0.8816

The correlation coefficients (R^2) related to the linearity of the adsorption isotherms of the two models. we can conclude that the Langmuir model is more likely to characterize the adsorption of imazapyr on natural phosphate rock.

CONCLUSION

Adsorption study of imazapyr on natural phosphate rock allows us to conclude that:

- The adsorption of imazapyr pesticide process is fast.
- The natural phosphate rock (PR) adsorbent has a higher retention capacity.
- Adsorption of imazapyr obeys to the Langmuir model

Finally, this study has allowed us to demonstrate the effectiveness of phosphate rock to remove organic pollutants in particular imazapyr contained in polluted synthetic solutions. The promising results of imazapyr adsorption phenomenon of natural phosphate seems to be an interesting solution for the future.

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