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Study of the Paranitrophenol Adsorption on the Commercial Bentonite

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Abstract
This work focuses on the study of the behavior of commercial yellow bentonite (BTJ) vis-a-vis paranitrophenol (PNP). Before beginning the study of adsorption, we realized the physiquo-chemical characterization of clay by FTIR, BET and XRD technical. The surface area of the bentonite is calculated by BET 35 m^2/g. The adsorption of para-nitrophenol is carried out at room temperature and at a controlled pH. The kinetic study showed that the equilibrium time is 5h. The kinetic model was a pseudo second order. Adsorption isotherm was the Langmuir model. The adsorption capacity was about 0.37 mg / g.
Keywords: Yelow bentonite, paranitorphénol, adsorption, optimisation.

1. Introduction

Since the era of industrialization, pollution has been inereasing, causing thus harm to large extents on the receiving environment (air, water and soil). Currently, it is the center of intense debate, because of the negative impact felt in our daily lives. It is therefore necessary to contribute to the preservation of our environment before its degradation was irreversible. In this sense, laws are established by imposing both discharge standards for harmful pollutants and construction on sites of treatment stations [1-4].

In spite of the precautions developed, the rate of spilled releases remain above the accepted standards, which involves researchers to find adequate and cheaper solutions to bring the values of concentrations of each pollutant applied to the standards[5-7].

The paranitrophenol (PNP) is generally considered one of the most harmful organic pollutants. Its main sources vary such as the paint industry, pesticides used in agriculture, coal conversion, olive presses and more frequently in the oil refining. It can also be found in human and animal waste, and in the decomposition of organic matter. It is very soluble in water, oils, and in many organic solvents. According to the European standard, its concentration in water should not exceed 0.002 mg / l, as it is harmful to organisms at low concentrations [8-10]. Its adverse effects on human health are counted and relate mostly irritation of eyes, skin and inflammation of the respiratory system. It may interact with blood to form the metha-hemoglobin which is responsible for confusion and unconsciousness. When ingested, it causes abdominal pain and vomiting. Prolonged skin contact may cause an allergic reaction. For example, it was estimated that about 584,000 persons in the United States are exposed every year to the PNP in work [11-15].

Because of the toxicity of PNP, their elimination from water is a vital question. Therefore, during the last years has been an increasing interest in the creation of processes for the elimination of these compounds from water. In this sense, different methods, as: oxidation with UV radiation and ozone/hydrogen peroxide [16], UV radiation and hydrogen peroxide [17], membrane filtration [18], reverse osmosis [19], photocatalytic [20] and sonocatalytic [21] degradation, electrochemical oxidation [22] and adsorption [2, 23-26] have been applied for the elimination of organic products in general and phenolic compounds in particular. However, adsorption is frequently the chosen separation process.

The aim of present study was to investigate the use of bentonite as a low – cost adsorbent for the removal of toxic solvent such as para-nitrophenol from aqueous solutions. The kinetics and mechanism of para-nitrophenol

uptake by the clay was investigated.

2. Expérimentale

The bentonite used as an adsorbent for the nitrophenol is in the form of very fine yellow powder, purchased from LOBA Chemicals and the PNP used is a yellow solid crystalline, purchased from Fluka. The adsorption experiments were carried out at constant temperatures. A mass of 0.2 g of bentonite is contacted with 20 mL of the solution pranitrophénol with initial concentration C_0. The assembly is subjected to a stirring of 500 tours per minute for a period t adsorption. The pH of the solutions was adjusted during the adsorption with NaOH or HCl. After the adsorption time t, the solutions were filtered and the residual solution of nitrophenol was analyzed by UV / Visible.

3. Results and discussions

3.1. Characterization of adsorbent support: the bentonite

3.1.1 Measurement of specific surface: BET method

The specific surface of the bentonite is estimated from the amount of nitrogen adsorbed according to its relative pressure P / P ° at the temperature of liquid nitrogen. The relationship of BET below allows the calculation of the amount of nitrogen adsorbed q_m, which corresponds to the formation of the monolayer.

$$\frac{P}{q_T\left(P^\circ - P\right)} = \frac{1}{C.\ q_m} + \frac{(C-1)}{C.\ q_m}\cdot\frac{P}{P^\circ}$$

C: A constant which defined the shape of the isotherm.

The isotherm obtained Figure (1) shows that the adsorption and desorption curves are shifted, having a hysteresis which reflects the existence of pores in the bentonite and that the specific surface is 35 m^2 / g (Table 1). Its shape is of type IV according to the IUPAC classification (International Union of Pure and Applied Chemistry). The shape of the hysteresis corresponds to parallel fonts pore. Their size, estimated at 50 Å, indicates that the solid is mésoporeux [27-29].

3.1.2 X-ray diffraction characterization

The X-ray diffraction characterization of bentonite figure (2), obtained by the device type X'PERT MPD_PRO anticathode emitting copper Kα radiation = 1.5406 Å and nickel filter contains several lines of diffraction. The indexing of the spectrum shows that the bentonite is composed of quartz ($Si\ O_2$), beidellite ($Na_{0.3}\ Al_2\ (Si, Al)_4\ O_{10}\ (O\ H)_2, 2\ H_2O$) and kaolinite ($Al_2\ Si_2\ O_5\ (O\ H)_4$. The most intense line at $2\theta = 7.11°$ corresponds to the (100) plan [30-31].

3.1.3 Characterization by FTIR

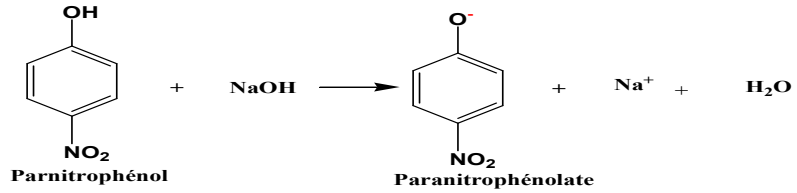
Spectrophotometer used in this study is Fourier transform (FTIR), type JASCO 4100, with a sensor (TGS) and a ceramic source, separated by an optical system using an interferometer Mechelson.

The FTIR spectrum of BTJ is shown in figure (3). The main absorption bands observed are given in Table (2) [32-34]

4. Study of the adsorption of PNP on yellow bentonite BTJ

4.1 Effect of pH on the adsorption of PNP

Adsorption of nitrophenol on commercial bentonite has been studied in acidic media (pH 4) and basic media (pH = 8.5). Analysis by UV / Visible shows that in basic middle there is an increase and displacement of the peak intensity caused by conversion of PNP molecule to paranitrophénolate anion according to the reaction below by inducing the bathochromic and hyperchromic effects engendered by the increase of the conjugation within the molecule of paranitrophénolate.



This increase of the peak intensity compared with the peak of the standard solution, makes it difficult to determine the adsorbed amounts of PNP in basic medium. As a consequence of this result, it was decided to carry on the experiments of the adsorption at pH = 4

4. 2 Kinetic study of the adsorption of PNP on BTJ

The objective of this study is to determine the time of the equilibrium established between the adsorbate (PNP) and the adsorbent (BTJ) during the adsorption using the following equation:

$$Q_{ads} = \frac{C_0 - C_{res}}{m_{BTJ}}.M.Vsol \approx \frac{(A_0 - A_{res})}{m_{BTJ}}.M.Vsol$$

With: C_0 and C_{res} (mol/l): initial and residual concentrations of PNP solution. ,
V_{sol} (l): volume of the solution;
m_{BTJ} (g) the mass of bentonite,
M (g / mol) molar mass of paranitrophenol; A_0 and A_{res}: initial and residual absorbance of the peak at λ_{max} = 315 nm

The curve in Figure (4) shows that the kinetics of PNP on the bentonite is initially very fast and then stabilizes after t = 5 h of contact, this is the equilibrium time. The saturation value of the surface is 0.375 mg / g, corresponding to $C_0 = 9.87\ 10^{-5}$ M, with a level of PNP removal of 21%.

4.2.1 Kinetic models

Kinetic models are generally established for comparing the experimental results to determine the kinetic parameters involved in the adsorption process. In the case of the contact solution / solid. From Table (3) the adsorption kinetics of PNP on BTJ obeys the kinetic law of pseudo second ordre [35-36].

4.3 Adsorption isotherm

The experimental curve of the adsorption isotherm Q (ads) i = f (Cres) i is drawn in figure (5), then represented by Langmuir and Freundlich models. Modeling the experimental isotherm curve from the theoretical equations of these models does not clearly decide between one of them, however, drawing their linear from allows the distinction.

4.3.1 Langmuir model

Equation that governs this model is as follows:

$$Q_{ads} = \frac{Q_0 . K_L . C_{res}}{1 + K_L . C_{res}}$$

The linearization is used to determine the constants Q_0 and K_L, either:

$$\frac{C_{res}}{Q_{ads}} = \frac{1}{K_L \cdot Q_0} + \frac{C_{res}}{Q_0}$$

With: Q_{ads}: the amount adsorbed at equilibrium (mg / g); Q_0: the maximum amount of adsorbate (mg / g); KL: constant relative to the Langmuir adsorption energy (in L / g).

4.3.2 Freundlich model

The main assumption of this model is the heterogeneity of the solid adsorption sites. The empirical equation established by Freundlich equation is as follows:

$$Q_{ads} = K_F . C^{1/n}$$

Where K_F and n are the Freundlich constants which express the adsorption capacity and its intensity. The application of this equation in its logarithmic form to experimental data leads to the values of these constants.

$$\ln(Q_{ads}) = \ln(K_F) + \frac{1}{n} . \ln(C_{res})$$

The graphical representation of the equation of Langmuir and Freundlich linearized is given in Figure (6). It can be seen that the experimental points verify the Langmuir model, they follow a straight line with a regression coefficient $R^2 = 0.9987$ very close to 1. The results show that the Freundlich model is not suitable to describe the adsorption of PNP on BTJ [37-39]. The parameters of these two models are shown in Table (4).

4.4 Adsorption mechanism.

The adsorption of PNP on BTJ can be explained by the presence of H^+ protons that give a positive charge to the PNP molecules ($R\text{-}OH^{2+}$) that interact with the negative charges of the surface of BTJ [36,40,41].

5. Conclusion

This study focused on the adsorption of a highly toxic pollutant model, namely the paranitrophenol on commercial yellow bentonite. It has allowed to determine the optimal experimental conditions for the removal of this pollutant. Thus, it was found that the contact BTJ low mass (m = 0.2 g) with ongoing solution of PNP seems to favor its adsorption at acidic pH and at room temperature. Spectroscopic techniques (FTIR, XRD) characterization showed that BTJ used a mesoporous alumino-silicate clay structure (BET). The adsorption kinetics of PNP obeys a second-order kinetics and adsorption isotherm obeys a Langmuir model.

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Table 1: Textural characteristics of BTJ.

	B.E.T		
	Specific area (m^2/g)	Volume (cm^3/g)	Diameter (Å)
BTJ	35	0,044	50,181

Table 2: IR bands of yellow BT Commercial.

Fréquency (cm^{-1})	Identification
3696	Stretching vibration OH (Fe, Mg ou Al)
3620	Stretching vibration OH (Fe, Mg ou Al)
3443	Stretching vibration OH in H_2O interfoliaire
3270	Vibration OH bound by connected hydrogenates
1637	Bending vibration bonding O-H de H_2O interfoliar;
1033	Stretching vibration of grouping Si-O
913	Stretching vibration O-H (Fe; Mg)
525	Bending vibration outside plan of Si-O-M (M=Al,Mg ou Fe)
470	Bending vibration outside plan of Si-O dans Si-O-Si
421	Bending vibration outside plan of Si-O-M (M=Al,Mg ou Fe)

Table 3: Kinetic parameters of adsorption of PNP on BTJ

Lagergren (1^{er} ordre)			Kannan(1^{er} ordre)			Ho et coll (2^{eme} ordre)		
k_1 (min^{-1})	Q_e (mg/g)	R_1^2	k'_1 (min^{-1})	Q_e (mg/g)	$R_1^{2'}$	k_2 (g/mg.h)	Q_e (mg/g)	R_2^2
0,03069	0,0599	0,5887	0,126184	0,3841	0,85613	144,314	0,37283	0,999

Table (4): The parameters of the linear Langmuir and Freundlich equations for the adsorption of PNP.

	Langmuir			Freundlich		
	R^2	K_L(L/mg)	Q_m(mg/g)	R^2	n	K_F(L/mg)
BTJ	0,9987	$4{,}08.10^{-1}$	0,29	0,92364	2,43	$8{,}38\ 10^{-2}$

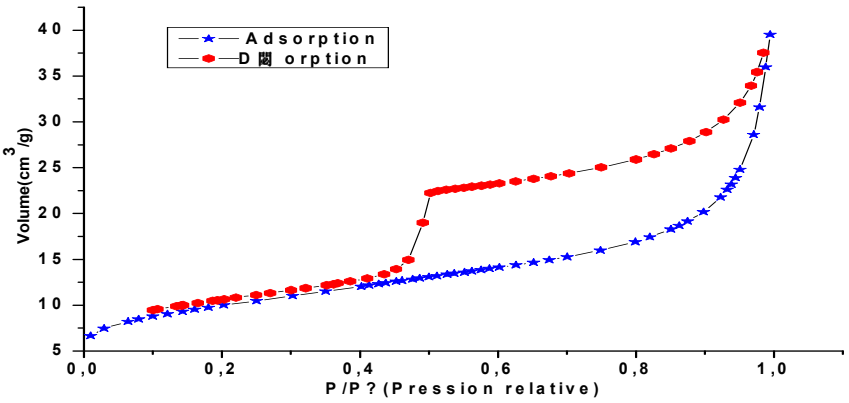

Figure 1: isothermal adsorption / desorption of N2 on BTJ.

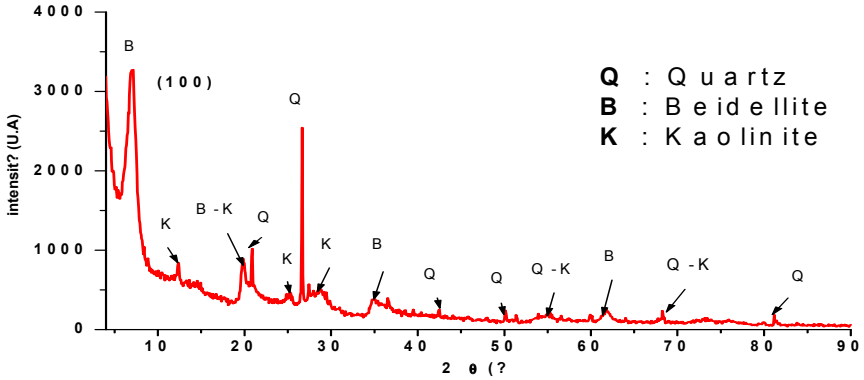

Figure 2: Diffractogramme of BTJ.

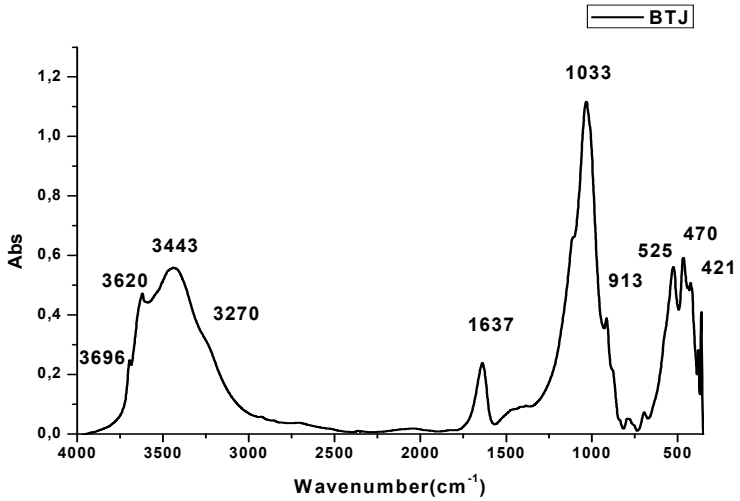

Figure 3: Specter IR of BTJ.

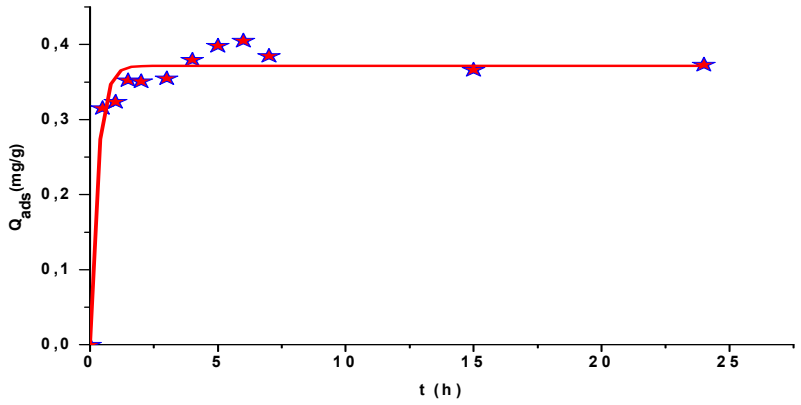

Figure 4: Kinetics of Adsorption of PNP (C0 = 10^{-4} M) on bentonite

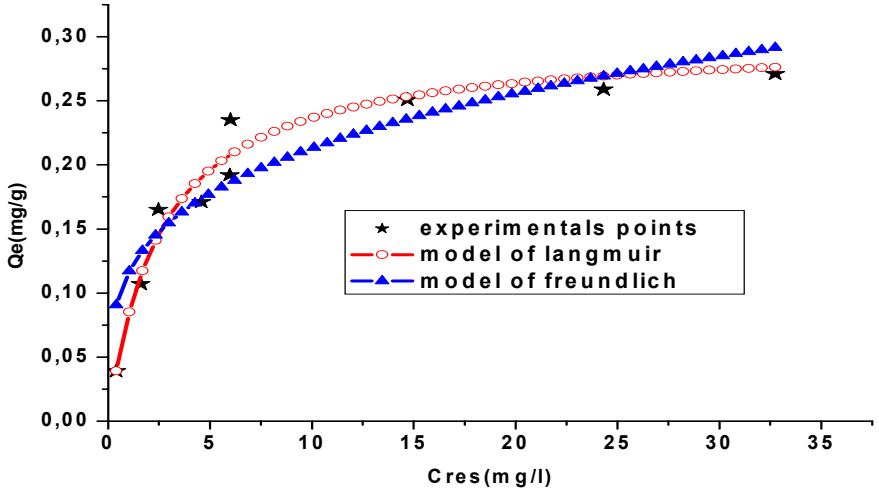

Figure 5: para-nitrophenol adsorption isotherm on BTJ (t = 5 hours).

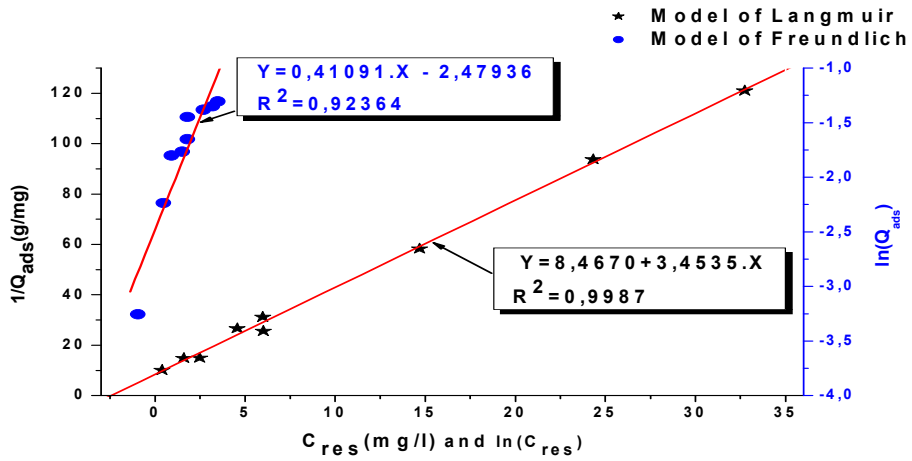

Figure 6: Graphical representation of the equations of Langmuir and Freundlich adsorption linearized for PNP on BTJ.