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Adsorption of water organic pollutants over a new zincophosphate material

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Abstract

A novel hybrid material zincophosphate was hydrothermally synthesized using l-methionine as a structure directing agent. The new material has been characterized by X-ray diffraction powder, scanning electronic microscopy, and infrared spectroscopy to find out the cell parameters, the shape of the obtained crystals, and to confirm the existence of the amino acid in the framework. It is used for polluting organic molecules fixation. The new adsorbent is a hybrid zincophosphate-methionine. It is promising for fixing the Red Telon (RT) and Red Bemacide (RB) dyes used by an Algerian textile company. A modeling study has allowed a glimpse of the adsorption phenomena and highlight interactions. The chosen adsorption models are the Freundlich and Sips. The best correlation factors are obtained in the case of the Sips model for the RB-zincophosphate system.

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1. Introduction

Environmental protection has since a long time become a major economic and political issue. Among the priorities is safe guarding water resources. The disparity between needs and water availability request, lead to provide new routing and processing means to increase the availability of resources. It is essential to protect water [1]. Among the most cited water pollutants are textile dyes since they consist of highly resistant molecules and harmful to the environment [2-5]. Adsorption is a very clean and less expensive tool, hence the wide use of this process [6-7]. Zeolites are, thanks to their very particular structures, the most widely used adsorbents to fight against pollution [8]. The similarities of chemical affinity, size or shape between a molecule and the porosity of different zeolites allow the latter to be used as molecular sieves in separation and selective adsorption of molecules. Their high adsorption capacity is due to their excellent external surface and molecules selectivity. Alongside the zeolites, other zeolites related families begin to take the field and replace the zeolites in various applications, including adsorption. The zincophosphates are one of zeolites related materials that have very intimate similarities with the zeolites of the structural point of view and applications [9-10]. These materials have the advantage of being directly linked to organic molecules, there by forming the organic-inorganic hybrid materials. In fact, a synergistic effect enclosing the remarkable properties of the porosity of the organic matter and molecular interactions properties of the organic material [11]. The aim of this study is the use of a novel hybrid zincophosphate-methionine [12], for the adsorption of two textile dyes.

2. Materials and methods

2.1. Experimental section

2.1.1. Adsorbent

The adsorbent used is a new hybrid material composed of an inorganic framework built up with ZnO_4 and PO_4; and an organic molecule; the methionine, synthesized in the laboratory by a hydrothermal method using the following reagents: ZnO, P_2O_5, Methionine, H_2O, for 3 days at 100 ° C [12].

2.1.2. Dyes

The dyes used for the fixation of water organic polluants are Red Telon "RT" and the Red Bemacide "RB", they are used in the textile industry of the company (SOITEXTM) at the Wilaya of Tlemcen in the Northwest of Algeria. Both dyes are marketed in powder form, soluble in water and they produce a red color in aqueous solution with an initial pH of about 5.98 and 6.2 for the RT and RB dye, respectively.

2.2. Characterization

2.2.1. X-ray diffraction

The Figure 1 shows the X-ray diffraction pattern of the new material that has been used as adsorbent. The diffraction peaks of the new material can easily be indexed using the TREOR algorithm, in the orthorhombic system with the following lattice parameters: a= 5.2210 (2) Å, b=9.1889 (4) Å, c=22.1559 (10) Å, α= β= γ =90 (0) °, Z=4, V = 1062.93 (8) $Å^3$. The compound consists of a network of ZnO_4 and $(HO)PO_3$tetrahedrathatformladder-likechains of edge-fused $Zn_2P_2O_4$ rings propagating parallel to [100]. The chains are decorated on each side by zwitterionic l-methionine ligands, which interact with the inorganic framework via Zn—O coordination bonds.

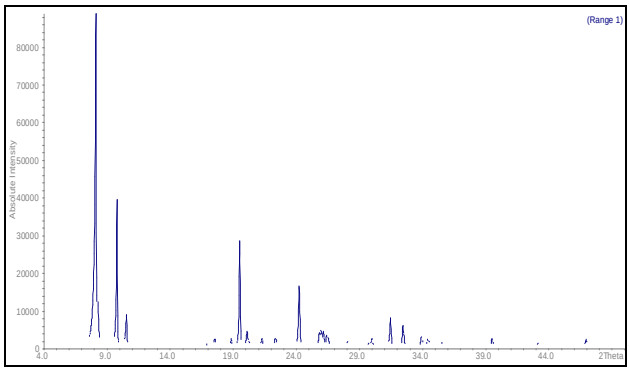

Figure 1. Powder diffraction pattern of the new zincophosphate-methionine.

2.2.2. Scanning electronic microscopy

The Figure 2 represents the SEM images of the new material. These micrographs show the presence of large crystals isolated as needles having a very substantial size of about 100 microns.

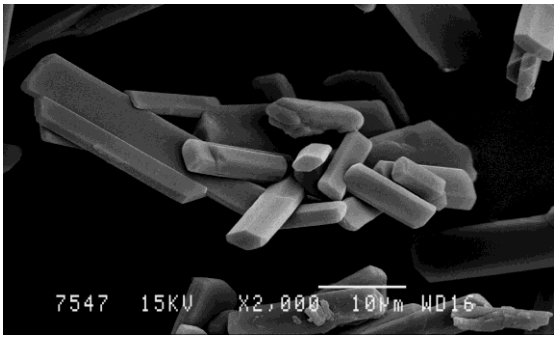

Figure 2. Scanning electronic microscopy of the new zincophosphate-methionine.

2.2.3. Infrared spectroscopy

The Figure 3 represents IR spectrum of the new zincophosphate-methionine. The methionine vibration bands occur primarily by the vibrations of the -CH2- groups observed between 2700 to 2900 cm^{-1}, CO_2^- group of the stretching vibration bands and -NH_3 occur at 1412 cm^{-1} and 1624 cm^{-1}

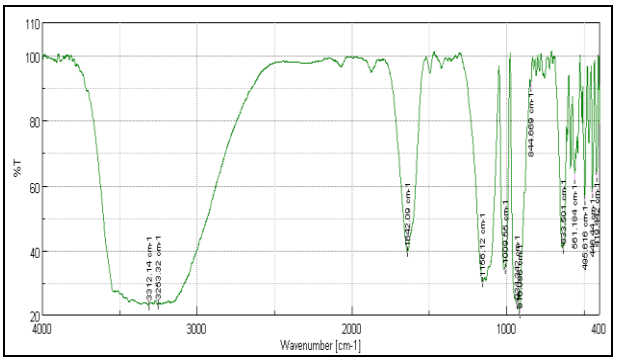

Figure 3. IR spectrum of the new zincophosphate-methionine.

The deformations of the NH_3 groups and carboxylate group are observed at 1513 cm^{-1} and 1579 cm^{-1}, respectively. Broadband between 2400-3500cm^{-1} is attributed to OH and NH bonds inter- and intra-molecular (NH bonds and the free OH to absorb towards 3500-3600 cm^{-1}) of methionine which is in the form of zwitterion, and that masks CH_3 and CH_2 vibrational bands of the amino acid that absorbs between 2800-3000 cm^{-1}. At 1159 cm^{-1}, a NH_3^+ stretching

vibration band is assigned. A stretching vibration band of C-S-C symmetrical is 750-717 cm^{-1}. On the spectrum of the new phase, one almost finds the same vibration bands of methionine, which corroborates the results of the structural resolution which show that the molecule is intact in the frame. However, we found additional bands occur primarily to 900-1000 cm-1, corresponding presumably to the asymmetric and symmetric vibrations of P-O bonds

2.2.4. UV – Visible spectroscopy

Spectrophotometr-vis the technique used for dosing the dye. The apparatus used for the assayis a UV - Visible monochromatic type SPECORD 210. To know the cyclical nature of an organic product, scanning between 200 and 400 nm isnecessary. Figure 4 canraise an absorption band at 320 nm for both dyes RT and RB.

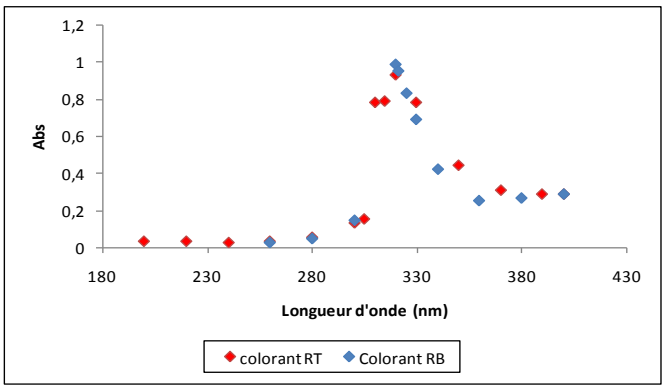

Figure 4. UV-visible spectra of the two dyes RT and RB: determining the cyclical nature.

2.2.4.1. Maximum wavelength

The study of the visible spectrum of a 100 ppm solution of both dyes Red Telon "RT" and Red Bemacide "RB" in wavelengths between 400 and 650 nm was used to determine the wave length corresponding to the maximum of absorption; it is of the order of 497 nm for the RT and 506 nm for the RB. The spectrum is given in Figure 5.

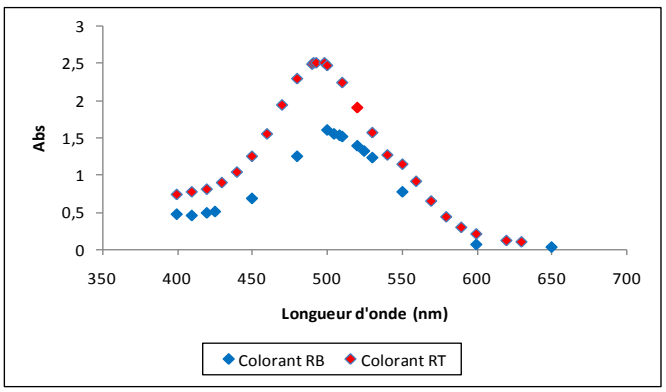

Figure 5. Determination of the maximum wavelength of the two dyes RT and RB.

2.2.4.2. Procedure

For securing the mass of zincophosphate which will be used throughout this study, a series of experiments has been developed by introducing an amount of 0.05 g of dye in a volume of 100 ml of distilled water to prepare an aqueous solution of 500 ppm. Several dilutions are made for adsorption, the time chosen for these experiments is 30 minutes. Adsorption is made stirring under static conditions. The adsorbed amount is calculated as follows:

$$Q_{ads} = (C_0 - C_{eq}) * \frac{V(l)}{m}$$

C_0: Concentration of Red Telon solution in ppm.

C_{eq}: equilibrium concentration after agitation.

2.2.4.3. Calibration

The calibration curves of the RT and RB dyes has been conducted by preparing a stock solution of 500 ppm with dilutions of 20 to 100 ppm.

3. Results and Discussions

C_0 concentration set at 100 ppm, the adsorbedamountsdetermined by UV-Visible spectroscopy are given in Table 1:

Table 1. Dyes adsorbedquantities on the new zincophosphate.

Adsorbate	Temperature	Stirring time	Q ads
RT	25°C	30 mn	/
RB	25°C	30mn	3,4

From the results shown in Table 1, it appears that the zincophosphates prepared in the presence of amino acids have remarkable adsorption properties, despite the fragility of these materials which considerably reduces their scope. RT does not adsorbalmost on the new zincophosphate. This canbeexplainedassumingthat the methionine in this case is linked to the framework through strong bonds.

3.1. Modelization

To set the results, we found it useful to make a preliminary study of the adsorption isotherm of the RT and RB dyes on the new zincophosphate. In order to plot the isotherm of adsorption of the dyes (liquid phase), we selected several initial concentrations ranging from 20 to 150 ppm. All operationswerecarried out at constant temperature T = 25 ° C.

$$Q_{ads} = f(C_{eq})$$

The isotherms are shown in Figure 6. The Figure 6 shows that the adsorption isothermis type II. This reflects the fact that the adsorption takes place in a heterogeneous surface with a strong interaction between the adsorbent and the adsorbate. Adsorption is far from the Langmuir model which assumes a homogeneous surface without interactions. Consequently, among the models thatcould fit this type of isotherm models are Freundlich and Sips.

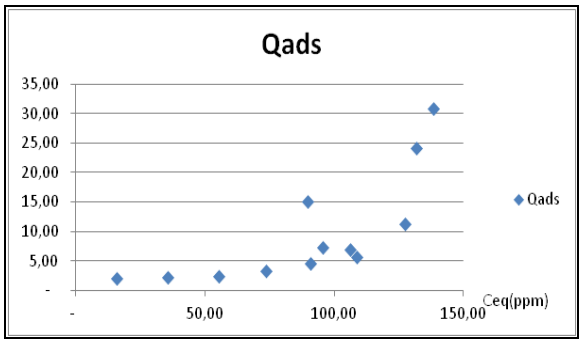

Figure 6. Isothermal adsorption of the dye on the RB-zincophosphate system.

3.1.1. Freundlich model (1926)

This model applies in the case of an adsorbent with a heterogeneous adsorption surface (energetically different adsorption sites).

$$q_e = K_F * C_{eq}^{1/n}$$

Where K_F and n are constants that must be evaluated for each molecule and for each temperature. The disadvantage of this model is that it is not based on theory. It is an entirely empirical model. The linearization of the model gives:

$$LnQ_{ads} = LnK_F + (\frac{1}{n})LnC_{eq}$$

So by drawing $LnQ_{ads} = f(LnC_{eq})$, there will be a straight if the model isapplied.Application of the model Freundlich adsorption RB on the phase is given in Figure 7. It was noted that the linearity of the line starts from the concentration C_{eq} = 3.5 ppm, and low concentrations do not join the Freundlich model.

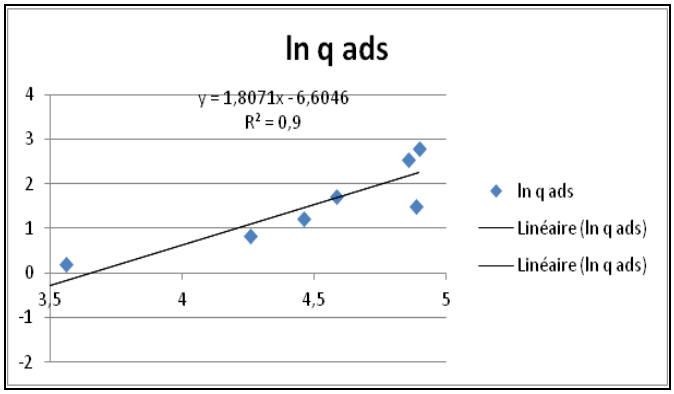

Figure 7. Application of Freundlich model to RB- zincophosphate system.

Similarly, the linearity of the model starts from a concentration C_{eq} = 4.2 ppm. The area selected for application of the model isbetween 4.2 and 5 ppm.

Table 2. Freundlich model parameters.

Phase	Kf	n	R^2
RB-zincophosphate	1,299. 10^{-3}	0,553	0,90

3.1.2. Sips model

This model, valid for localized adsorption without adsorbent-adsorbate interaction, as follows:

$$\theta = \frac{AP^c}{(1 + AP^c)}$$

A and c constants. P: equilibrium pressure. And θ: recovery rate.

The difference with the Langmuir model is that in this model, there is no question of an interaction adsorbate-adsorbate center of type 1: 1 In the low pressure area, this equation reduces to that of Freundlich. If the equation of Sips is verified, we should get in coordibates : $ln\left(\frac{\theta}{1-\theta}\right) = f(ln\,P)$ knowing that the linearization of this model leads to an equation of the type : $ln\left(\frac{\theta}{1-\theta}\right) = ln\,A + c\,ln\,P$.

3.1.2.1. RB dye adsorption

Applying this model to the adsorption of the RB dye on the new material by plotting: $ln\left(\frac{\theta}{1-\theta}\right) = f(lnC_{eq})$, the curve is shown in Figure 8. The Figure 8 shows a good correlation between the model and the adsorption of RB on zincophosphate. However, the scope of the Sips model is reduced to a range of concentrations varying from 3-5 ppm, soonly for intermediate concentrations.

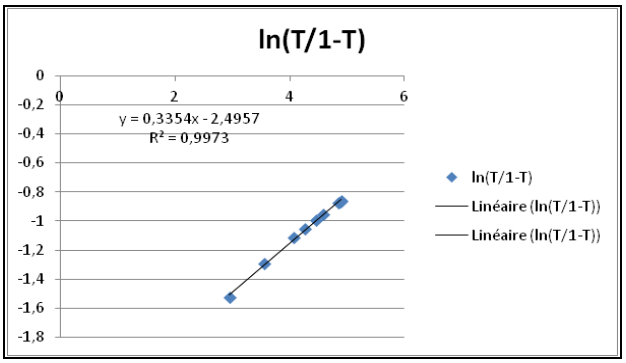

Figure 8. Fit of Sips model on the RB- zincophosphate system.

3.1.2.2. Sips model parameters

Sips model parameters A and c, and the correlation factor are given in Table 3:

Table 3. Sips model parameters.

Phase	A	c	R^2
RB-zincophosphate	0.082	0,335	0,99

A good correlation factor is obtained for the RB-zincophosphate system, reflecting perfectly consistent with the model. Comparing the constant A, which reflects the strength of adsorption, one notices that the RB-zincophosphate system has a great value of constant A, so a large adsorption force. The constant c reflects the distance from the Langmuir.

4. Conclusion

In light of these results, we can conclude that our amino acid zincophosphate hybrid material has out-standing adsorption properties, despite the fragility of its structure and its reduced porosity. The chosen adsorption models were the Freundlich and Sips. The best correlation factors are obtained in the case of the Sips model for the RB-zincophosphate system.

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