

Adsorption of Raw Phosphate and Doped Phosphate by Titanium Oxide

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Abstract

Several studies have been done to help reduce the impact of pollution on our ecosystem. In this context, we have developed a support consisting of a phosphate doped with titanium oxide (TiO_2) for use in the treatment of colored effluents. Thereby, the phosphate doped with 20% of titanium is suspended in an aqueous solution with a concentration of 10 mg/l for the methylene blue and 4 mg/l for methyl orange. The analysis of the results indicates that the Freundlich isotherm applies to adsorption of both phosphates. In addition the reaction tests discoloration of methylene blue and methyl orange showed a higher degradation with doped phosphate.

Key words: raw phosphate, doped phosphate, TiO_2 , methylene blue, methyl orange, adsorption kinetics, adsorption isotherm.

1. Introduction

The industrial, agricultural and domestic sources effluents are often responsible for low or non-biodegradable pollutants [1]. Their impact on the flora and fauna is very harmful. In aerobic conditions, the model dyes are not readily biodegradable because of the complexity of the chemical structures and the presence of aromatic rings [2-4]. While under anaerobic conditions, azoic dyes can be reduced to carcinogens [5].

The adsorption of pollution on phosphate has a significant catalytic activity [6]. The efficiency of adsorption depends on many factors including surface, pore distribution, polarity and functional groups of the adsorbent [7, 8].

This study is to verify the ability of raw and doped phosphate by titanium oxide to adsorb organic molecules, particularly dyes. We chose

methylene blue (MB) as a cationic dye because of its strong adsorption on solids [6, 9], and methyl orange (MO) as anionic dye. This process could be an alternative to other more expensive and less adsorbent available.

2. Materials and methods

a. Characterization of raw phosphate

The material used in this study is the phosphate of Khouribga city.

Sample was characterized by scanning electron microscope SEM (Zeiss DSM950) to determine the morphology of materials. The specific surface area was determined by the BET method using a Micromeritics ASAP2420. The size of the porous media was determined by the laser particle size Cilas. Table 1 summarizes the results:

Table 1 : Characterization of draining materials

Settings	Phosphate
Dm (Åm)	238,30
D10 (Åm)	136,86
D90 (Åm)	358,61
Uniformity coefficient	2
SEM	irregular or rounded grains
Surface area (m^2/g)	12,74

The sample of phosphate is characterized by x-ray diffraction using a diffractometer X'Pert Pro MPD Panalytical and X-ray fluorescence spectrometry using a sequential spectrometer Axios brand Panalytical with a measuring channel based on a single goniometer covering complete measuring range B to U. Table 2 summarizes the results of Chemical composition of the raw phosphate.

Table 2 : Chemical composition of the raw phosphate analyzed by x-ray fluorescence

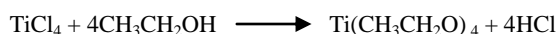
Compound	Conc. (%)	Compound	Conc. (%)
CaO	48.64	Al ₂ O ₃	0.2971
P ₂ O ₅	37.97	SrO	0.1644
SiO ₂	4.797	Fe ₂ O ₃	0.1268
F	3.583	Cl	0.09598
MgO	1.359	NiO	0.02695
Na ₂ O	1.176	Y ₂ O ₃	0.02181
SO ₃	0.7435	P.a.F	1

Table 3 : Chemical composition of the doped phosphate analyzed by x-ray fluorescence

Compound	Conc. (%)	Compound	Conc. (%)
CaO	41.64	Cl	0.65
P ₂ O ₅	33.64	SO ₃	0.54
TiO₂	10.17	Al ₂ O ₃	0.20
SiO ₂	5.29	SrO	0.14
F	2.22	Fe ₂ O ₃	0.10
MgO	1.04	BaO	0.06
Na ₂ O	0.98	Y ₂ O ₃	0.02

b. Doping phosphate by titanium oxide

Phosphate is softly moistened with magnetic stirring by an entity of Ti(CH₃CH₂O)₄. This impregnation is carried out by complete dissolution of titanium tetrachloride in ethanol according to the following equation:



XRD analysis of doped phosphate (Figure 2) indicates the formation of new phases not recorded in the spectrum of the raw phosphate (Figure 1), confirming the insertion of titanium anatase in the matrix.

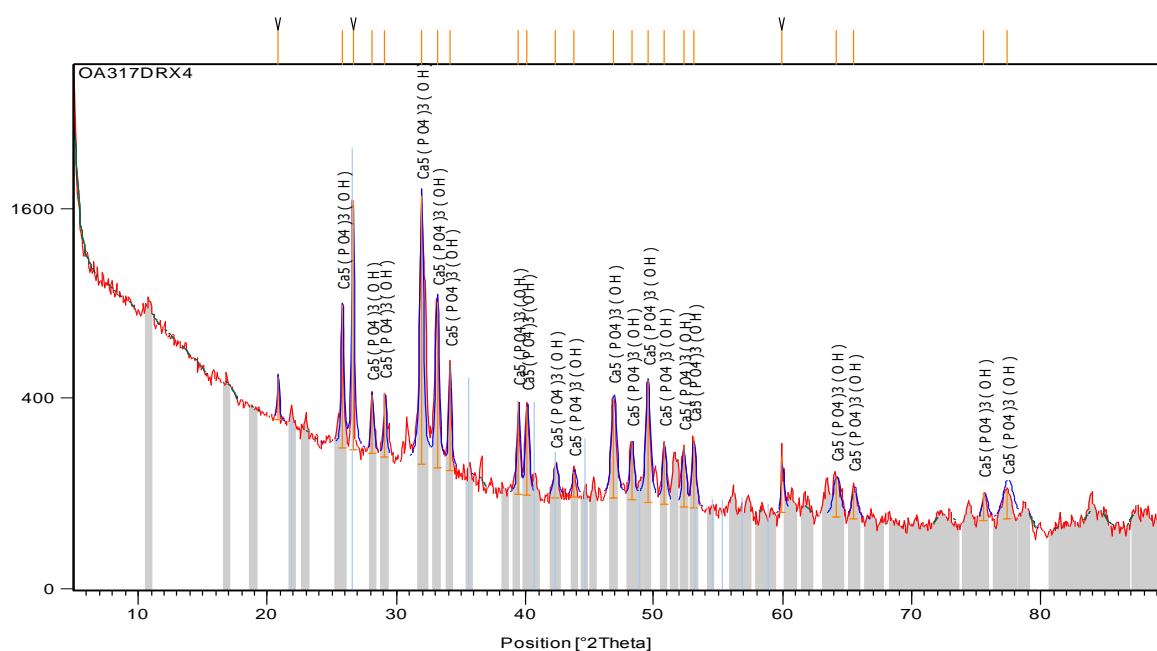
In addition, the chemical composition of doped phosphate (Table 3) analyzed by x-ray fluorescence reveals a change in the weight percentages of the oxides and the appearance of TiO₂, which affirms the doping phosphate titanium oxide.

c. Kinetic Study

Concentrations were determined by UV-Visible absorbance according to the calibration method, using UV-Visible spectrophotometer Perkin Elmer UV / Vis Spectrometer Lambda 20. The wave lengths of maximum absorption of the MB and MO are respectively 664 and 467 nm.

The adsorption kinetics was performed using 500 ml of an aqueous solution with a concentration of 10 mg/l for MB and 4 mg/l for MO, and a mass ratio of 1g/l for the tow dyes. The mixture is kept in suspension by magnetic stirring. The samples were filtered through a membrane of 0.45 μm, before reading in the spectrophotometer.

The adsorption isotherms were studied with the same mass ratios. They were compared with Langmuir and Freundlich model.

**Figure 1 : XRD analysis of raw phosphate**

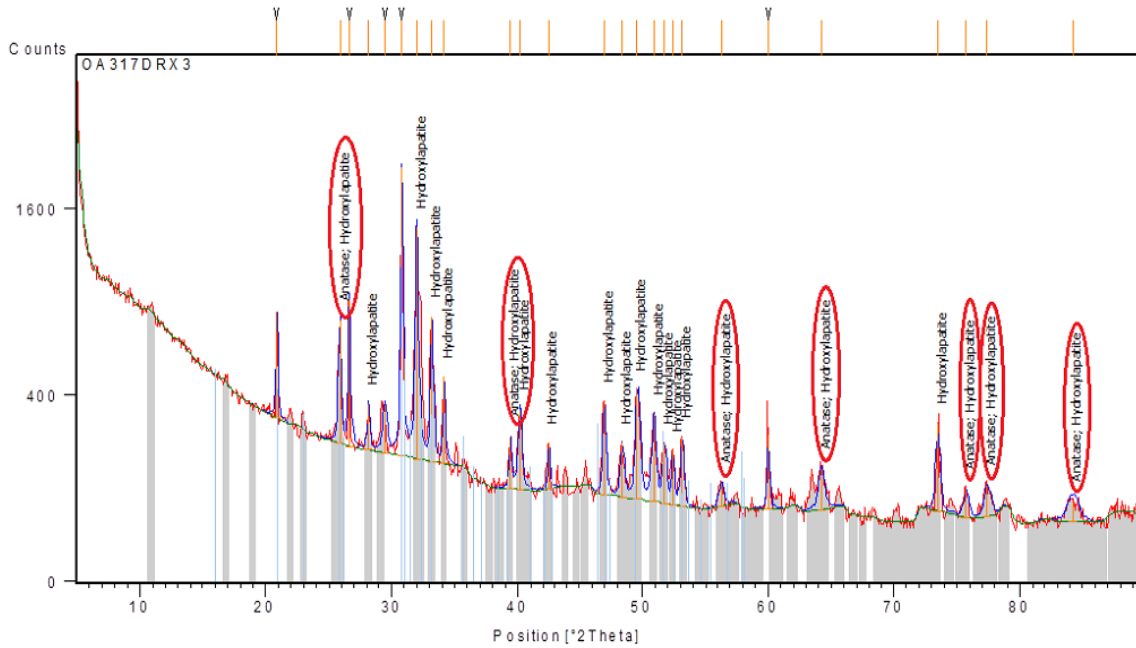


Figure 2 : XRD analysis of doped phosphate

3. Results and discussion

a. Doped phosphate

To determine the rate of titanium oxide required for doping phosphate we studied the variation of the adsorbed quantity depending on the amount of TiO₂. Figure 3 shows the results, where we note that the phosphate doped by 20% of titanium oxide gives the best results.

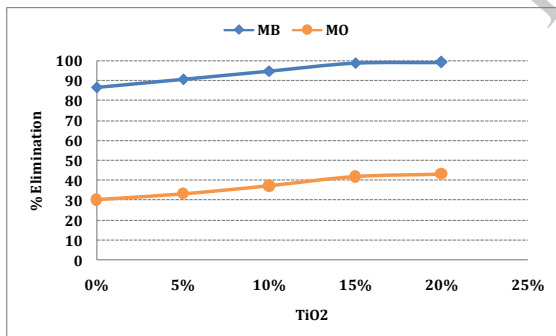


Figure 3 : Variation in the rate of removal dyes according to the concentration of TiO₂

b. Adsorption kinetics

The amount of adsorbed dye per liter of solution is determined by the difference between the initial concentration C_i and the equilibrium concentration C_e. The experimental results of adsorption kinetics on a raw and doped phosphate for both dyes are presented respectively in Figure 4 and Figure 5, where $Q_e = (C_i - C_e) / m$

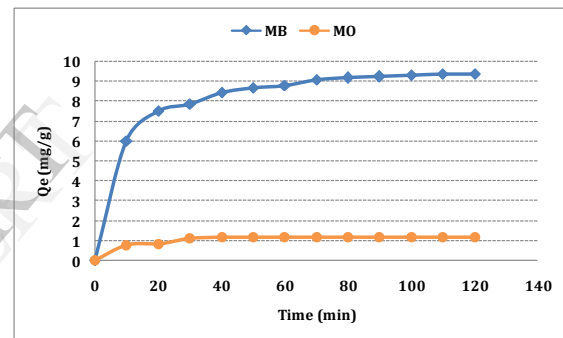


Figure 4 : Adsorption kinetics on a raw phosphate

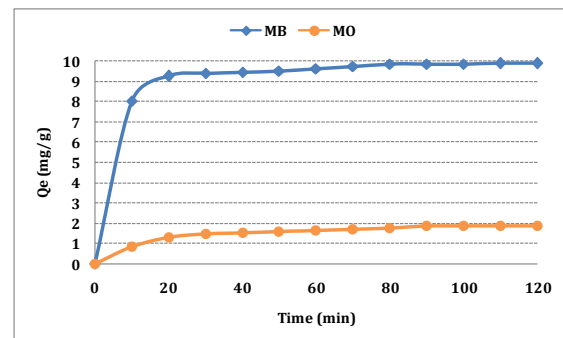


Figure 5 : Adsorption kinetics on a doped phosphate

Adsorption is rapid during the first period but becomes slower with increasing contact time. The equilibrium time of the three dyes is 110 min for MB and 90 min for MO. The adsorption capacity of MB is much greater than that of MO. This could be due to the difference of interactions between the dye and the particle surface rock phosphate [6, 10]. The adsorption rate constants were determined using the pseudo first-order equation of Lagergren [6, 11].

$$\log_{10} (q_e - q) = \log_{10} q_e - (k_1 / 2.303) t$$

With q_e (mg/g) quantity of dye adsorbed at equilibrium, q (mg/g) quantity of dye adsorbed at time (t), k_1 (min^{-1}) the constant of the reaction rate of adsorption pseudo-first order. K_1 values were calculated from the slopes of the plots of $\log_{10} (q_e - q)$ versus time. Table 4 summarizes the results:

Table 4 : constants adsorption kinetics

Phosphate	Days	K_1	R^2
Raw	MB	0,010	0,987
	MO	0,019	0,983
Doped	MB	0,046	0,982
	MO	0,035	0,996

c. Adsorption isotherms

The quantities adsorbed according to equilibrium initial concentrations for each dye are shown in following figures:

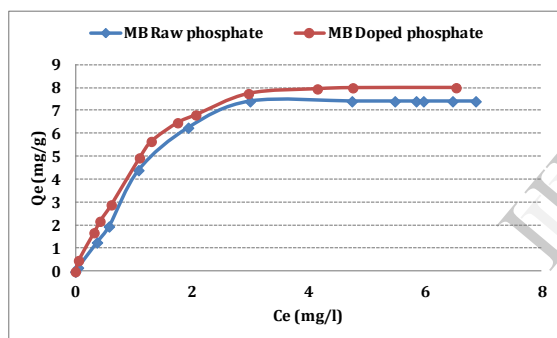


Figure 6 : The amount of MB absorbed as a function of the initial concentration

The isotherm corresponding to the adsorption of MB indicates a significant adsorption at low concentrations. The isotherm is of type L according to Giles classification [12-15] characterizing a typical monolayer adsorption, or corresponding to the filling of micropores with saturation when the available volume is completely filled. This type of isotherm is characteristic of adsorption on microporous carbons and zeolites [16].

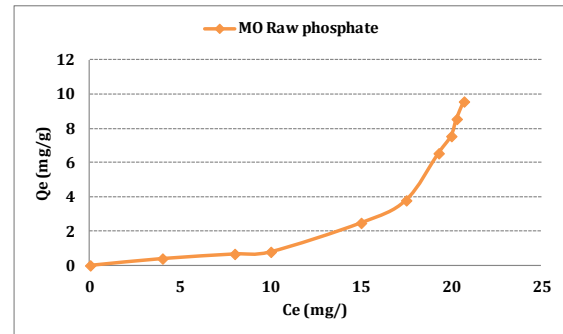


Figure 7 : The amount of MO absorbed as a function of the initial concentration

The isotherm of the MO adsorbed on a raw phosphate is Type S; it characterizes a cooperative adsorption, where the adsorbed molecules favor the subsequent adsorption of other molecules [14]. This behavior is observed when the binding energy of the first layer is lower than the binding energy between water molecules. This could be due to the anionic character that has the same charge as the phosphate [10].

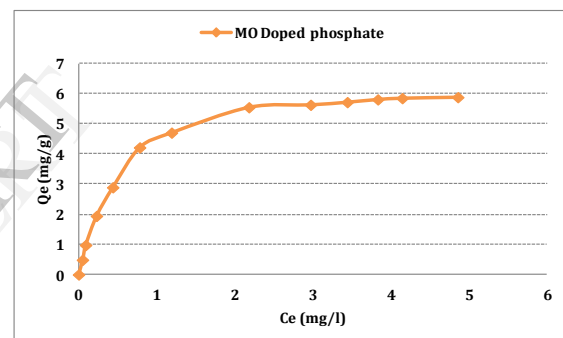


Figure 9 : The amount of MO absorbed as a function of the initial concentration

The isotherm corresponding to the adsorption of MO on doped phosphate is an isotherm type L in the Giles classification. This type of isotherm is usually associated with an ionic adsorption solution at low competition with solvent molecules [12, 15].

The Langmuir equation is used to describe the adsorption behavior of a localized homogeneous surface, forming a monolayer without lateral interaction between adsorbed molecules.

The mathematical expression of Langmuir can be written as follows:

$$Q_e = Q_o K_L C_e / (1 + K_L C_e)$$

Where: Q_e (mg/g) is the amount adsorbed at equilibrium, C_e (mg/l) is the amount of adsorbate in equilibrium, K_L Langmuir equilibrium constant and Q_o (mg / g) maximum amount adsorbed.

The Freundlich equation is well suited to describe the equilibrium aqueous phase. Its empirical formula is:

$$Q_e = K_F C_e^{1/n}$$

Where Q_e and C_e have the same definitions as above, K_F and n are Freundlich constants, indicative of the intensity and the adsorption capacity.

The results of the linear regression analysis are shown in table 5:

Table 5 : Constants models of adsorption isotherms

Phosphate		Raw		Doped	
Days		MB	MO	MB	MO
Langmuir	Q_m	20,83	0,021	1,837	1,980
	k_l	0,284	20,787	1,092	0,931
	r^2	0,9734	0,9366	0,989	0,977
Freundlich	$1/n_F$	0,447	0,374	0,512	0,574
	K_F	5,657	0,002	0,784	0,736
	r^2	0,993	0,986	0,996	0,997

The table shows that the linear correlation coefficients for the Freundlich model are closer to one than the Langmuir model. This implies that the Langmuir equation, which assumes the presence of only one type of adsorption sites, is not suitable for our data. While better correlation results were obtained using the Freundlich isotherm model, which could explain a continuous distribution of adsorption sites. This could be taken as a consequence of the presence of unsaturated sites, several types of sites on the catalyst surface, or change of steric or electrostatic factors when the adsorption rate changes [10]. The catalyst further comprises a support of phosphate doped by TiO_2 which involved in adsorption rate, which influences the adsorption isotherms.

4. Conclusion

Phosphate is capable of removing dyes in aqueous solution. The experimental results showed that; the adsorption capacity of cationic dyes (methylene blue) is higher than that of anionic dyes (methyl orange), and the adsorption capacity of doped phosphate is higher than that of raw phosphate.

The adsorption corresponds to the Freundlich model. This would be a chemical adsorption of the amine groups of BM on positively charged phosphate groups of carbonates which are negatively charged. More hydrogen bonding could occur between the OH groups of phosphate and BM molecules [6, 10]. In addition, the adsorption of MB and MO on the doped phosphate is favorable because of the Freundlich constant $1/n_F$ is less than 1. This means that the adsorption is higher for low concentrations [17].

5. References

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