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Ability of Moroccan Natural Phosphates to Remove Textile Dyes from Aqueous Solutions

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Abstract

The paper reports on the adsorption of Dyes from aqueous solution onto treated and Natural Moroccan Phosphates. Adsorption tests were realized in static mode .The adsorption of both Dyes, Reactive Yellow 4 (RY4) and direct Yellow 28 (DY28), from aqueous solution onto phosphate rocks of Khouribga and Oued-Zem regions was investigated. Phosphate rocks before and after activation was characterized using X-ray powder diffraction XRD, X -ray fluorescence (XRF), point of zero charge (pH PZC) and Infrared absorption spectroscopy FT-IR. The experimental data were analyzed by using three kinetic models: the pseudo first order, pseudo second order and intraparticle diffusion models. The kinetic study shows that equilibrium is quick. The kinetic data were best described by the pseudo second-order model ($R2 \geq 0.9999$). The amount of the dye adsorbed increases with the mass of adsorbent. The adsorption process was pH-dependent with a high adsorption capacity at pH 4.

1. Introduction

The textile industry consumes a lot of water and generates an important quantity of effluents highly charged with pollutants which constitute a serious threat for the environment. It is considered that the textile industry is responsible for 15% To 20% of the global water pollution [1]. The textile industries discharge a huge amount of dyes in water that are difficult to remove. The removal of colour from wastewater becomes a challenging problem because these species are extremely damaging to the environment [2]. In recent years, the removal of the contaminants from wastewater has been extensively studied using various physicochemical and biological techniques [3-6]. Although various treatment methods, such as coagulation precipitation [7], electroflotation [8], membrane separation [9], oxidation [10] and adsorption processes [11-12] can be used to reduce the quantity of toxic substances present in textile wastewater. Among of these processes, adsorption is one of the most effective methods and this process has aroused considerable interest during recent years. Activated carbons are very efficient and have been preferentially used for the adsorption of dyes [13], but their use is restricted due to high cost. Therefore, there is growing interest in using alternative adsorbents that are cheaper and commercially available. Taking Into account their availability and its low cost, Moroccan Phosphate rock (MPR) Constitutes a possible alternative of adsorbent that could be used for the removal of dyes from textile wastewater and, more generally, in industrial wastewater.

Numerous studies have shown that phosphate minerals, both natural and active, have the potential to adsorb heavy metal ions from aqueous solutions [14-19].However, to our knowledge, few studies have been published on the removal of textile dyes by natural phosphates [20-21]. Recently Bouyarmane et al [22] tested the rock phosphate as an adsorbent to remove phenol and pyridine. In our case, we are interested in removing dyes by Moroccan Phosphate Rock (MPR) in view of a possible recovery. In this context, we sought to determine the adsorption capacity of phosphate rocks of Khouribga and Oued-Zem regions. In the present investigation, rock phosphates are characterized and evaluated for the adsorption of both dyes, Reactive Yellow 4 (RY4) and direct Yellow 28 (DY28). The pH, mass of adsorbent, and contact time were studied.

2. Materials and Methods

2.1. Adsorbent

2.1. 1. Phosphate rocks

The Samples of phosphate rocks chosen for this study came from the regions of Khouribga (Oulad Abdoun Plateau) and Oued-Zem (Morocco). The samples were provided by the staff of the Office Cherifien of Phosphate (OCP). They are in the form of a beige powder. The powder was washed with distilled water to remove the impurities dried in an oven at 105°C and crushed.

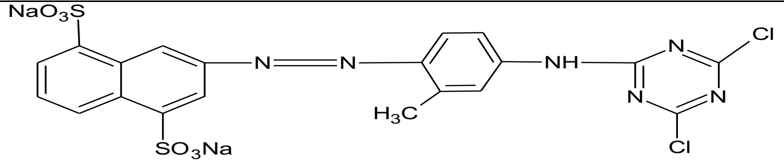
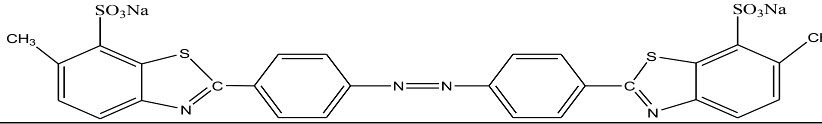
2.1. 2. Phosphate rocks activated

Phosphate Rocks are activated by nitric acid and sodium hydroxide: 50 g of phosphate was added to 200 ml of a solution of NaOH (1M). After stirring for two hours the mixture was filtered, washed with distilled water and then we have added 200 ml of a solution of HNO_3 nitric acid (1M) and stirred for two hours again. The sample was finally filtered, washed with distilled water then dried at 105°C and crushed.

2.2. Adsorbate

The both dyes (RY4 and DY28) were obtained from a textile firm as a commercially available dye formulation and were used without further purification. The structure and characteristics of these dyes are illustrated in Table1. The solutions ware prepared by dissolving the required amount of dye in distilled water .The concentration of the RY4 and DY28 was determined at 385nm and 396nm respectively, using UV spectrophotometer ("UV-2005", Selecta, Spain).

Table 1: Structure and characteristics of RY4 and DY28.

Name	**RY4 (C.I. Reactive Yellow 4).**
Chemical structure	
Molecular formula	$C_{20}H_{12}Cl_2N_6Na_2O_6S_2$
Other name	disodium 3-[[4-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-o-tolyl]azo]naphthalene-1,5-disulphonate
Molecular weight(g/mol)	613.36
Name	**DY28 (C.I. Direct Yellow 28).**
Chemical structure	
Molecular formula	$C_{28}H_{18}N_4O_6S_4.2Na$
Other name	disodium 5-(5-methyl-1,3-benzothiazol-2-yl)-2-[4-(5-methyl-1,3-benzothiazol-2-yl)-2-sulfonato-phenyl]azo-benzenesulfonate
Molecular weight(g/mol)	680.72

2.3. Adsorbent Experimental Protocol

To study the kinetics of adsorption of the dye at 298K, a volume of 10ml of solution concentration 100 mg/L of dye was placed in contact with adsorbent in a test tube. The mixture was stirred at constant speed (500 rpm) for one minute and then placed in a water bath at 298 K. After, the solid was separated from the mother solution by filtration through a sintered glass and the dye concentration was determined using the UV–vis spectrophotometer. The amount of adsorption at equilibrium, Q_t (mg/g), was given by the following equation:

$$Q_t = \frac{(C_0 - C_t)V}{m}$$

Where C_0 and C_t are the liquid phase concentrations of dye at the initial and equilibrium conditions, respectively, V is the volume of solution (L) and m is the mass of adsorbent used (g).
The percentage of dye removal was calculated from the relation-ship: **% of dye removal = $(C_0-C_t)/C_0*100$**

where C_o is the initial dye concentration and C_t (mg/L) is the concentrations of dye at equilibrium.

3. Results and discussion

3.1. Characterization of the Adsorbent

3.1.1.Infrared absorption spectroscopy FT-IR:

The Analysis by IR spectroscopy of phosphate rocks (Fig.1 and Fig.2) shows a fluor-apatite carbonate type B [23, 15]. In addition, the strips situated towards 3300-3700 cm^{-1} correspond to water molecules [24] .we also note the presence of absorption bands at 2918.2 and 2850.6 cm^{-1} due to the CH bond of organic matter. In addition, bands were observed around 2360 cm^{-1} which may be due to the adsorption of CO_2 carbon during sample preparation dioxide [23,25]. The IR spectra of phosphates activated (Figure 1.b) and Figure 2.b)) show that the frequencies of most of the observed bands have been slightly modified in comparison with those observed for phosphate rocks (Figure 1.a) and Figure 2.a)).

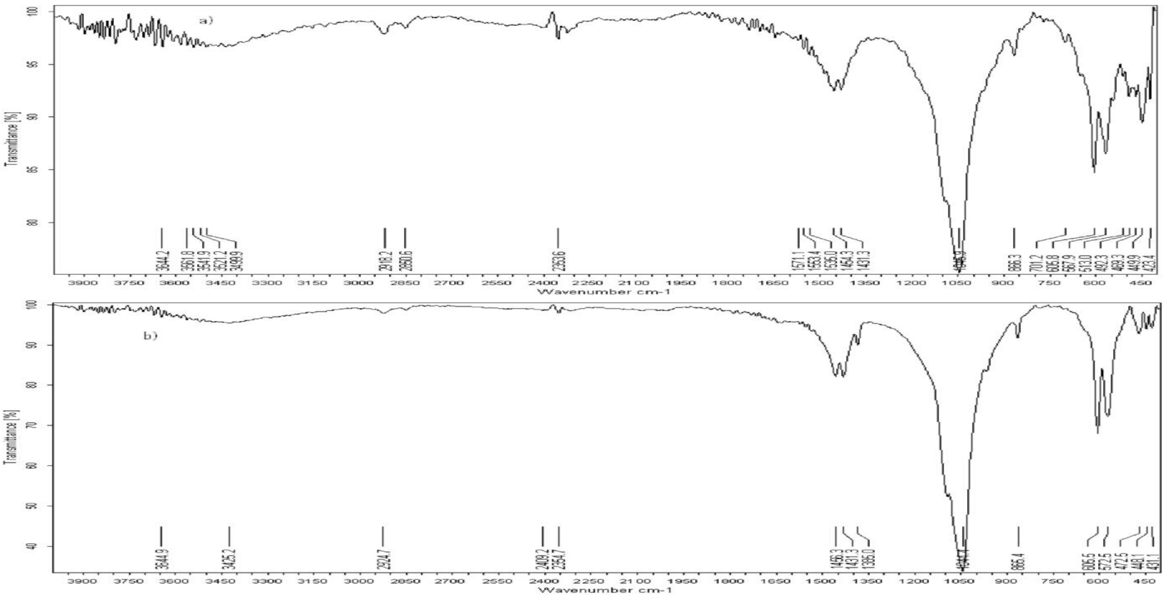


Figure 1: FTIR spectra of: a) Phosphate rock of Khouribga (PRK) and b) Activated phosphate rock of Khouribga (APRK).

3.1.2.X-ray diffraction

The Analyses were conducted using an X-ray diffractometer X'PERT. Figure.3 shows the graphs of X-ray diffraction of phosphates before and after activation. It is observed that the main components of the samples are carbonate fluorapatite (JCPDS No. 15-0876) and calcite (JCPDS No. 15-0876) [15] . In the case of phosphates activated, no modification was observed in the X-ray diffraction pattern.

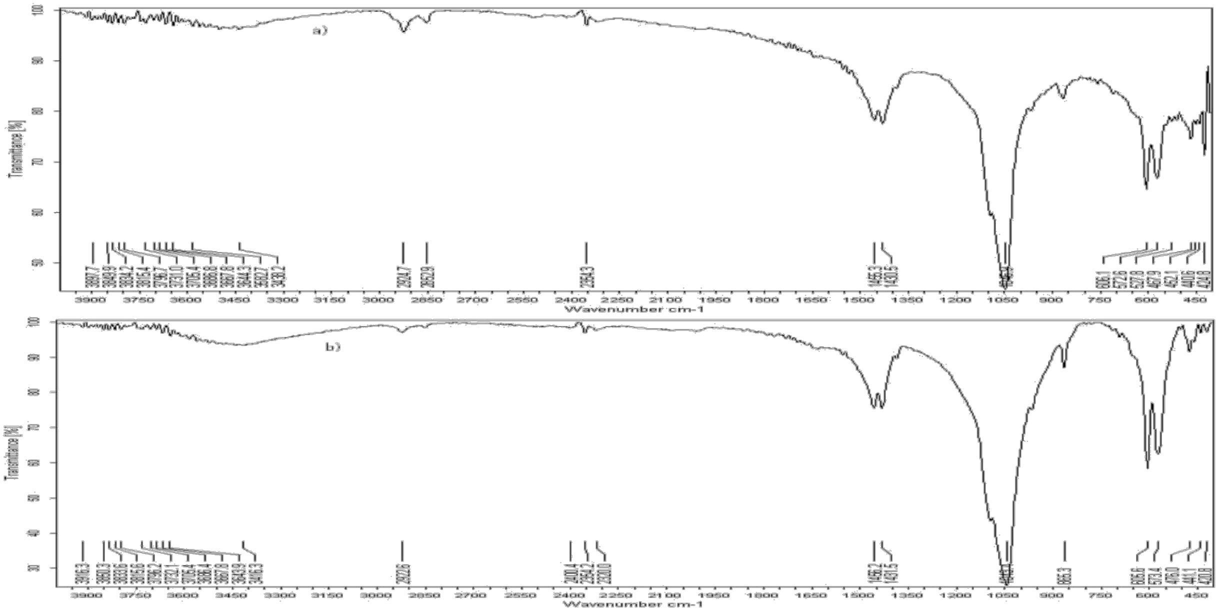


Figure 2: FTIR spectra of: a) Phosphate rock of Oued-Zem (PRO) and b) Activated phosphate rock of Oued-Zem (APRO)

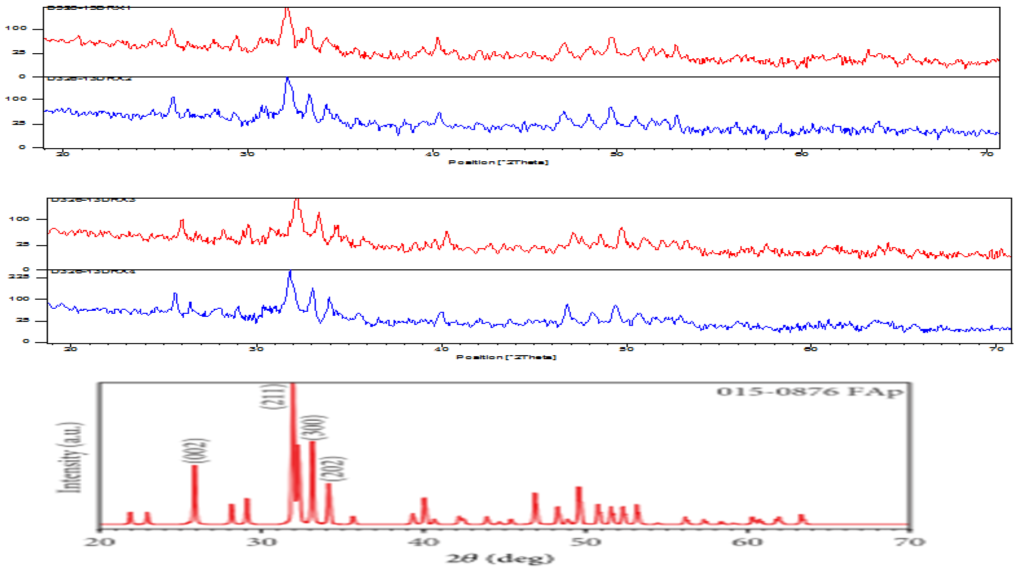


Figure 3: XRD patterns of: (1) Phosphate rock of Khouribga (PRK) (2) Activated phosphate rock of Khouribga (APRK) (3) Phosphate rock of Oued-Zem (PRO) (4) Activated phosphate rock of Oued-Zem (APRO) and (5) FAp standard (JCPDS n ° 15-0876).

3.1.3. Determining the point of zero charge (pH PZC)

The evolution of pH = [pH (final) - pH (initial)] according to the initial pH adjusted to each case of the phosphates studied gives the pH of zero charge (pHz) (Fig .4). The pHz of phosphate of Khouribga, phosphate of Oued-Zem, activated Phosphate of Khouribga and activated Phosphate of Oued –Zem is 8.3, 8.32, 8.23 and 8.22, respectively.

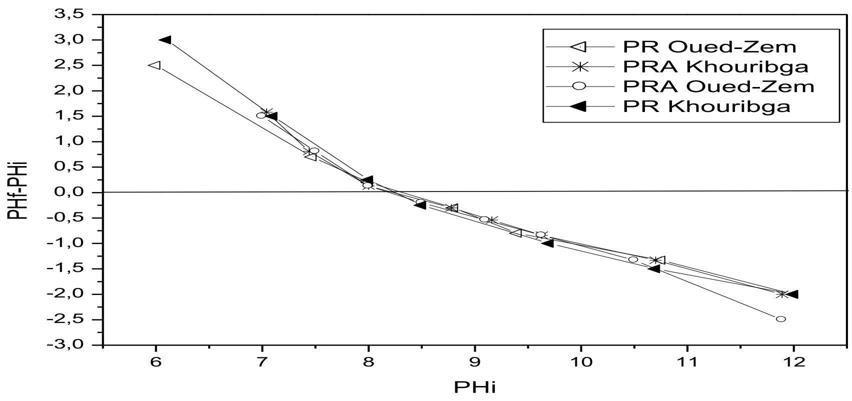


Figure 4: Point of zero charge (PZC) of phosphate rocks.

3.1.4. Mineralogical Analysis of Phosphate Rocks

The mineralogical composition of phosphates activated or not activated of Khouribga and Oued-Zem used in this study is given in Tables 2 and 3.

3.2. Study of the Adsorption

3 .2.1. Effect of the mass of solid

We represented the change in the percentage removal of two dyes depending on the mass of used phosphate rocks (fig.5 and 6). As shown in both figures, for 0.5 g of phosphate rock of Khouribga (PRK), phosphate rock of Oued Zem (PRO), phosphate rock activated of Khouribga (PRAK) and phosphate rock activated of Oued Zem (PRAO) respectively , can eliminate 47.57 , 51.92 , 81.93 and 83.77 % of reactive yellow 4 (RY4) and 40 , 48.4 , 80 and 81.43 % of Direct Yellow 28 (DY28) . The percentage values removal of dyes removed increases with increasing in amount of adsorbent and reaches up to 2g. However, after a mass of 2g, there is no significant change in the percentage removal of the two dyes.

Table 2: Chemical composition analysed by x-ray fluorescence of phosphate rocks of Khouribga.

Compound		**CaO**	**P_2O_5**	**SiO_2**	**F**	**Al_2O_3**	**SO_3**	**Na_2O**	**MgO**	**Fe_2O_3**	**K_2O**
Conc %	**PRK**	38.1	29.9	9.06	7.66	2.93	1.55	0.944	0.776	0.398	0.169
	PRAK	41.5	30.5	6.29	5.98	1.83	1.54	0.955	0.651	0.328	0.093

Element		**O**	**Ca**	**P**	**F**	**Si**	**C**	**Al**	**Na**	**S**	**Mg**	**Fe**	**K**
Conc %	**PRK**	41.5	27.3	13.1	7.66	4.23	2.18	1.55	0.7	0.623	0.468	0.278	0.14
	PRAK	42.1	29.6	13.3	5.98	2.94	2.73	0.97	0.708	0.618	0.393	0.23	0.0777

Table 3 : Chemical composition analysed by x-ray fluorescence of phosphate rocks activated of Oued - Zem.

Compound		**CaO**	**P_2O_5**	**SiO_2**	**F**	**Al_2O_3**	**SO_3**	**Na_2O**	**MgO**	**Fe_2O_3**	**K_2O**
Conc %	**PRO**	37.3	30.8	6.96	12.4	1.89	1.53	0.832	0.622	0.34	0.128
	PROK	36.7	31	6.1	13.7	1.64	1.52	0.761	0.586	0.36	0.102

Element		**O**	**Ca**	**P**	**F**	**Si**	**C**	**Al**	**Na**	**S**	**Mg**	**Fe**	**K**
Conc %	**PRO**	39.2	26.6	13.4	12.4	3.26	1.91	1	0.617	0.612	0.375	0.238	0.102
	PRAO	38.6	26.2	13.5	13.7	2.85	1.91	0.865	0.565	0.609	0.354	0.252	0.0845

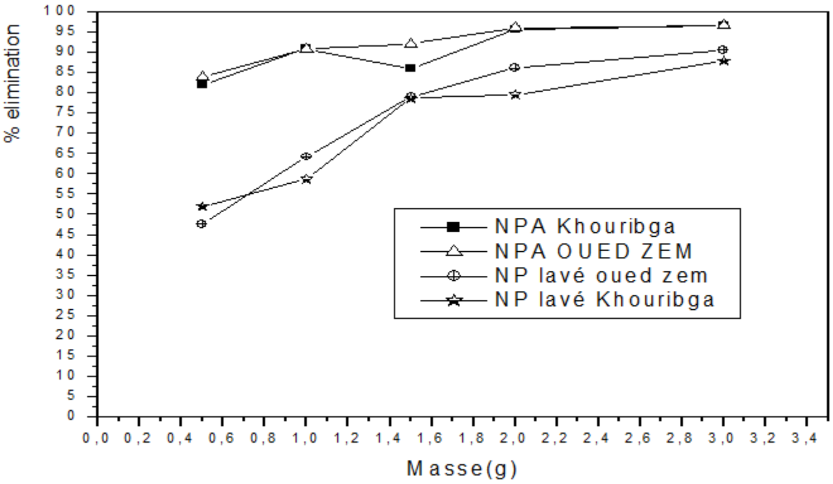


Figure 5: Percentage of elimination of RY4 according to the mass of phosphate rocks (pH = 5.69, C = 100 mg/L).

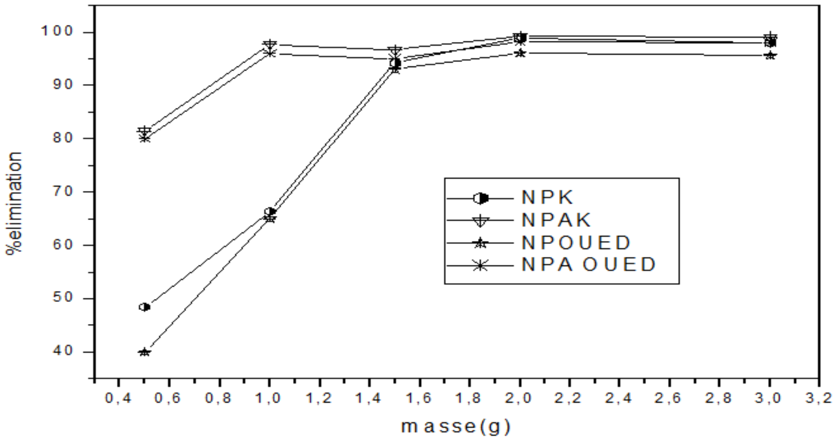


Figure 6: Percentage of elimination of DY28 according to the mass of phosphate rocks (pH = 5.93, C = 100 mg/L).

3 .2.2. Adsorption kinetics

The adsorption kinetics of the two dyes was performed with solutions of initial dye concentration of 100 mg /L. the evolution of adsorbed amounts as a function of time (Figure 7 and 8) shows that the adsorption kinetics of the two dyes characterized by high adsorption from the first few minutes of contact. Equilibrium is reached quickly showing that the phosphates used are highly effective in a very short time for these dyes. The maximum adsorption is observed in a short time, indicating of the active sites at the surface of the phosphate at the beginning of the adsorption relative to the remaining sites after some time.

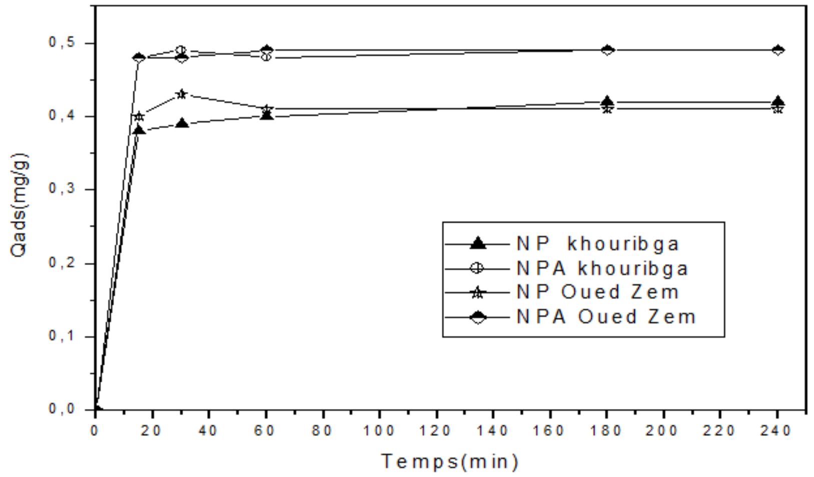


Figure 7: Kinetics of adsorption of RY4 on the phosphate rocks used (pH = 5.69, C = 100 mg/L)

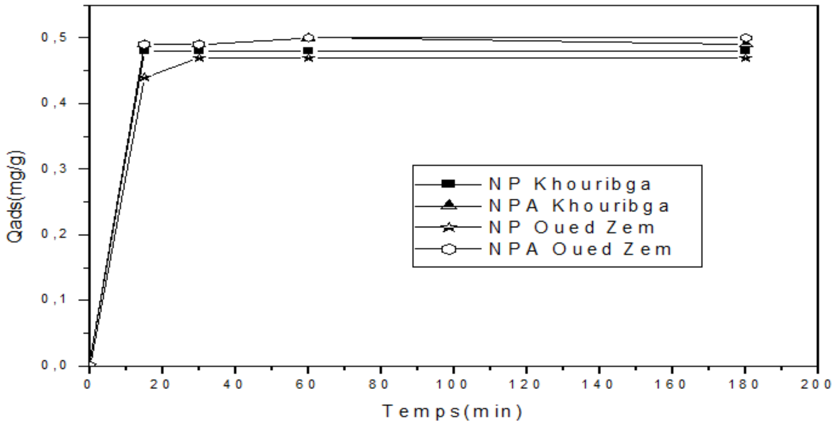


Figure 8: Kinetics of adsorption of DY28 on the phosphate rocks used(pH = 5.93, C = 100 mg/L).

The adsorption constants were determined from experimental kinetic data of adsorption of Reactive Yellow 4 and Direct Yellow 28 on various phosphates, for the first-order, pseudo-second-order, second-order and intra-diffusion particle, using linear regression. The pseudo first order equation was represented by Lagergren [26]:

$$\mathbf{Log(Qe-Qt)=Log(Qe)-K_1/2.3t}$$

The pseudo second order [27-28] model has been examined to find out the adsorption mechanism, for the pseudo second order rate constant K_2 is given by the following equation:

$$\mathbf{t/Qt=1/2K_2Qe^2+t/Qe}$$

For the second order rate constant K3 is given by the following equation:

$$\mathbf{1/(Qe-Qt)=1/Qe+K_3t}$$

where Qe is the amount of adsorbate at equilibrium per gram of adsorbent (mg .g−1), t contact time (min), K_1, K_2 and K_3 are rate constants of adsorption, respectively, for the pseudo first order (min−1), the pseudo second order (g/mg .min) and the second order (min−1. g/mg).

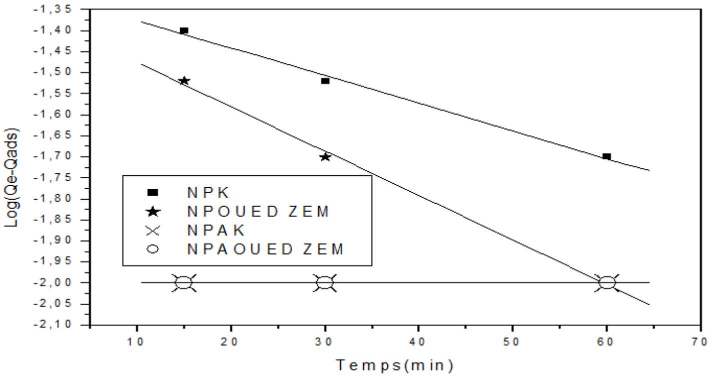


Figure 9: Constants of pseudo-first-order of adsorption of RY4 on the phosphate rocks.

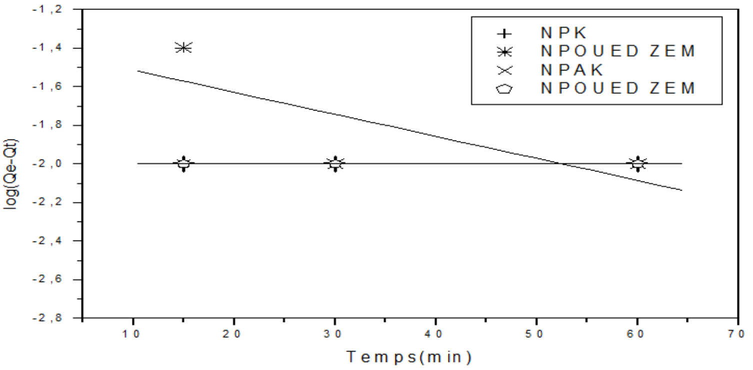


Figure 10: Constants of pseudo-first-order of adsorption of DY28 on the phosphate rocks.

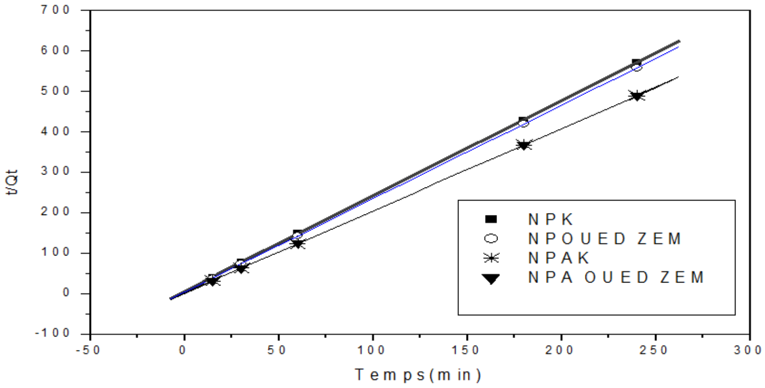


Figure 11: Constants of pseudo-second-order of adsorption of RY4 on the phosphate rocks.

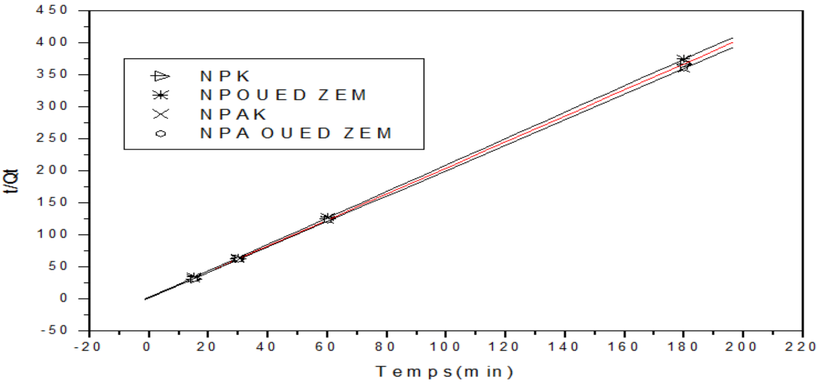


Figure 12: Constants of pseudo-second-order of adsorption of DY28 on the phosphate rocks.

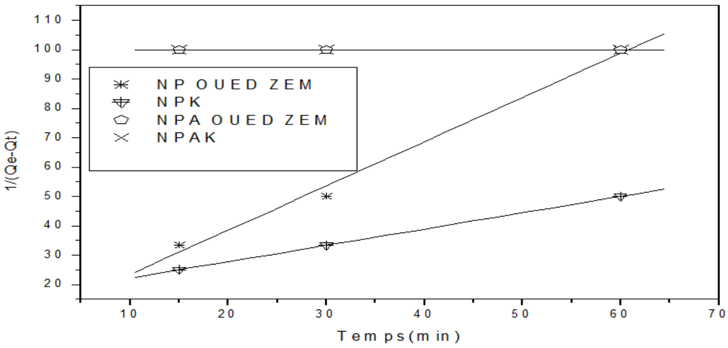


Figure 13: Constants of second-order of adsorption of RY4 on the phosphate rocks.

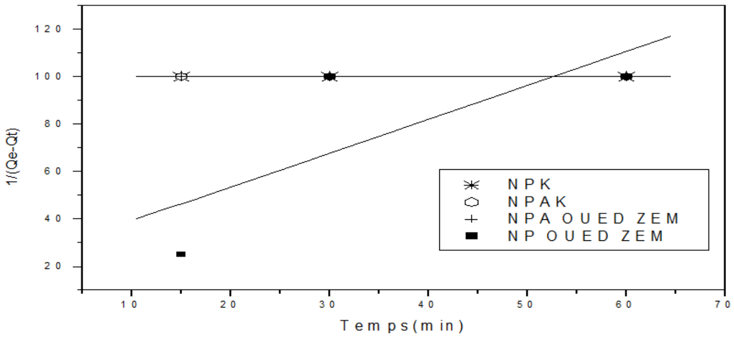


Figure 14: Constants of second-order of adsorption of the DY28 on the phosphate rocks.

The values of constants obtained (Tables 4 and 5) show that the pseudo second-order model (Figures 11 and 12) with good correlation coefficients, is the most suitable.

Table 4: Constant speeds of the pseudo first order, pseudo- second order and second order of RY4.

Adsorbents	pseudo first order			pseudo second order			second order		
	Qe (mg/g)	k$_1$(min-1)	R^2	Qe(mg /g)	k2 (min -1.g/mg)	R^2	Qe (mg/g)	k3 (min -1.g/mg)	R^2
PRK	0.049	0.01513	0.9972	0.43	0.9389	0.9999	0.0600	0.5556	1
PRO	0.043	0.0243	0.9989	0.41	-3.2258	0.9999	0.1200	1.5080	0.9959
PRAK	0.01	0	-	0.49	4.829	1	0.01	0	-
PRAO	0.01	0	-	0.49	5.2632	1	0.01	0	-

Table5: constant speeds of the pseudo first order, pseudo- second order and second order of DY28.

Adsorbents	pseudo first order			pseudo second order			second order		
	Qe (mg/g)	k1 (min^{-1})	R^2	Qe (mg/g)	k2(min^{-1}.g/mg)	R^2	Qe (mg/g)	k3(min^{-1}.g/mg)	R^2
PRK	0.0398	0.0329	0.7559	0.47	4.2644	0.9999	0.01	0	-
PRO	0.01	0	-	0 .48	-	1	0.04	1.4286	0.7559
PRAK	0.01	0	-	0.49	-5.6883	0.9999	0.01	0	-
PRAO	0.01	0	-	0.50	4.9019	1	0.01	0	-

In addition, the comparison of the values of Qe calculated by this model with those of experimental Qe (Table 6) confirmed that the adsorption kinetics of the two dyes is the pseudo-second-order. This result is consistent with several studies of the kinetics of adsorption of the dyes [29-32].

Table 6: Comparison of the amount of the dyes adsorbed by the used phosphate rocks.

Adsorbents	**Adsorbates**	**Qe (mg/g) experimental**	**Qe (mg/g) calculated Pseudo first order**	**Qe(mg/g)calculated Pseudo second order**	**Qe(mg/g)calculated Second order**
PRK	**RY4**	0.42	0.0489	0.43	0.0600
PRO		0.41	0.0426	0.41	0.1200
PRAK		0.49	0.01	0.49	0.01
PRAO		0.49	0.01	0.49	0.01
PRK	**DY28**	0.48	0.0398	0.48	0.01
PRO		0.47	0.01	0.47	0.04
PRAK		0.49	0.01	0.49	0.01
PRAO		0.5	0.01	0.5	0.01

The data for the adsorption kinetics of the two dyes were processed to determine whether the intra-particle diffusion is the rate limiting step. The model of Weber and Morris [33] is applied; its characteristic equation is:

$$q_t = k_{\text{int}} t^{1/2} + C$$

We plot the adsorbed quantity according to (t) ½, if it passes through the origin, we can conclude that the pore diffusion is the only mechanism limiting the adsorption kinetics [34-35]. In this case, we note that the set of lines plotted (Figures 15 and 16) does not pass through the origin, plus the correlation coefficients are less than 0.999 (Table 7), indicating that the broadcast the two dyes in the pores of the phosphate used is not the only mechanism to limit the adsorption kinetics. The result showed that the adsorption process was complex and involved more than one mechanism.

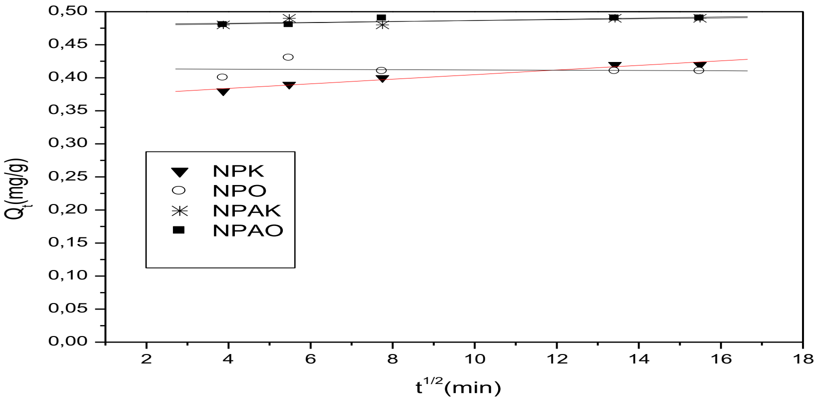


Figure 15: Intra- particle diffusion model for the adsorption of RY4.

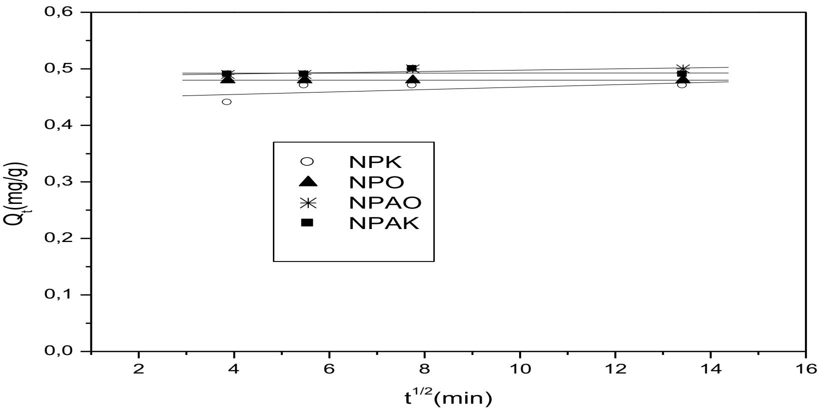


Figure 16: Intra- particle diffusion model for the adsorption of DY28.

Table 7: parameter of the intra-particule diffusion of the both dyes.

Dyes	Phosphate rocks	K_{int} (mg/g.min$^{-1/2}$)	C (mg/g)	R^2
RY4	PRK	0.00348	0.36998	0.9810
	PRO	-2.076.10^{-4}	0.41391	0.09558
	PRAK	6.669.10^{-4}	0.47986	0.61403
	PRAO	8.901.10^{-4}	0.47781	0.81949
DY28	PRK	0.00216	0.44604	0.60036
	PRO	0	0.48	-
	PRAK	2.2945.10^{-5}	0.49232	0.01916
	PRAO	0.00113	0.48638	0.81723

3 .2.3.The effect of pH on the adsorption of dyes

The pH of de medium is the most critical parameter affecting the adsorption processes in the removal of dyes. The influence of pH on dyes removal was studied by varying the initial pH of dye solutions from 3 to 11 using 0.1N HCl or NaOH solutions, with the initial dyes concentration fixed at 400 mg/l. Figures 17 and 18 show the effect of pH on the adsorption of Reactive Yellow 4 (RY4) and Direct Yellow 28 (DY28) by the adsorbents used, It notes that the adsorption is strongly dependent on the pH of the solution. The adsorption in this case of Reactive Yellow 4 (RY4) and Direct Yellow 28 (DY28) decreases as the pH increases. This observation can be interpreted by the point of zero charge (PH_Z) of Natural Phosphate of Khouribga, Natural Phosphate of Oued - Zem, Natural Phosphate activated of Khouribga and Natural Phosphate activated of Oued Zem is 8.3, 8.32, 8.23 and 8.22, respectively.

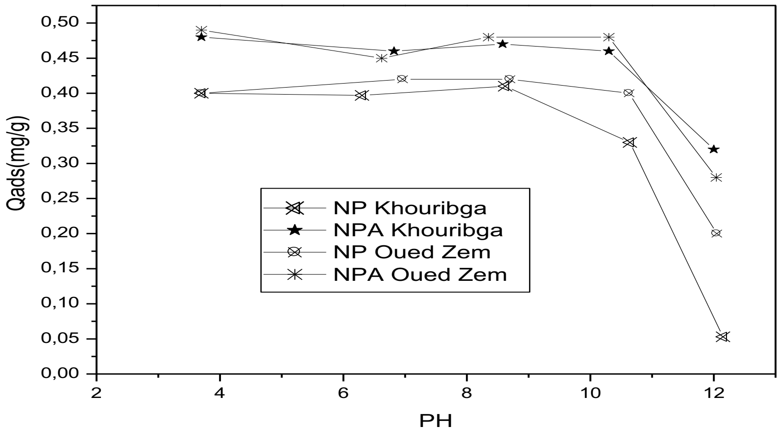


Figure 17: Effect of pH on the adsorption of RY4(C = 100 mg/L).

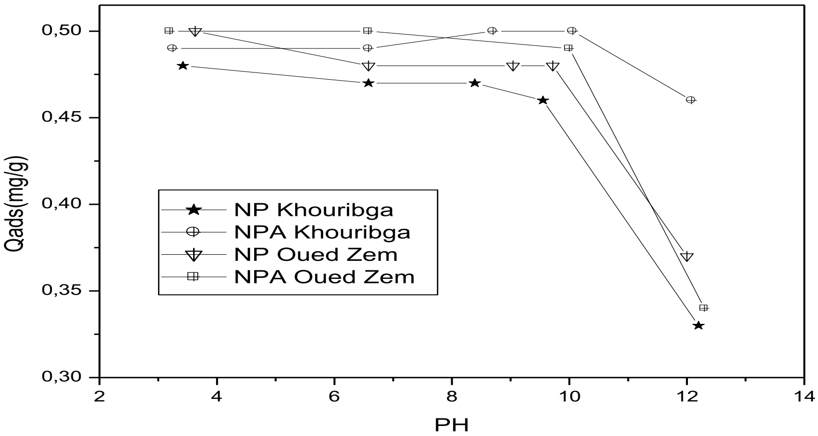


Figure 18: Effect of pH on the adsorption of DY28 (C = 100 mg/L).

For pH values of greater than pH_Z of phosphate, the particle surface of the phosphate used is negatively charged. For lower pH values, it becomes positively charged. Therefore, the absorbent-adsorbate interactions for the reactive yellow 4 (JR4) and Direct Yellow 28 (JD28) with the negatively charged phosphate particles gradually become significant at pH values less than large PH_Z. Whereas, in the environments of pH higher than PH_Z, the adsorption is disadvantaged by the repulsive forces between the φ - SO^{3-} groups of dye molecules and the surface of phosphates which is negatively charged. This explains the decrease in adsorbed amounts. Similar behavior was observed by Mourabet et al [36] and el boujaady et al [37-38].

Conclusion

The study of the adsorption of the two dyes, Reactive Yellow 4 and Direct Yellow 28, under static conditions, on the Natural Phosphate of Khouribga, Natural Phosphate of Oued-Zem, Natural Phosphate Activated of Khouribga and the Natural Phosphate Activated of Oued-Zem and the influence of certain parameters were studied.The Experimental results show that the adsorption kinetics of the two dyes (Reactive Yellow Direct Yellow 4 and 28) may be considered as the pseudo second order. The kinetics are rapid, equilibrium is reached after a few minutes of contact. The adsorption is strongly dependent on the pH of the solution. The maximum of adsorption is observed at pH=4. The adsorption of two dyes (Reactive Yellow Direct Yellow 4 and 28) is greater on activated natural phosphate. This study reveals that Moroccan phosphate material can be used as an environmental reactant in wastewater treatment.

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