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REMOVAL OF BASIC TEXTILE DYE FROM AQUEOUS SOLUTION BY ADSORPTION ON RELEASES OF ALGERIAN NATURAL PHOSPHATES

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ABSTRACT: The dyes, present in the rejections of textile industry, represent a true danger to human being and its environment, because of their stability and their low biodegradability. Our work is focused on the use of releases of rock phosphates of Djebel-Onk (Algeria) for elimination of a basic dye, Bezacryl Yellow (BY). The study of the influence of some parameters on the capacity of adsorption of the dye by phosphate revealed that the favorable conditions for obtaining a maximum rate of discoloration are: Concentration of the phosphate suspension R=4g/L; pH of the dye solution=6; stirring velocity ω=300 trs/min; temperature of reactional medium T=25°C. The modeling of the experimental values by different kinetic models showed that the kinetics is governed by the second-order model. Starting from the values of the various parameters of the mathematical models calculated, the results obtained revealed a good correlation between the experimental data and the values predicted by the Langmuir model. The value of the calculated ΔH is lower than 50 kJ/mol and positive, suggesting that the adsorption process is endothermic and of physical nature.

Keywords: *Phosphate; Environment; Bezacryl Yellow; Adsorption; Kinetics.*

INTRODUCTION:

The effluents containing pollutants are increasing in natural streams due to industrialization. The main contaminants found in wastewater include biodegradable, volatile and recalcitrant organic compounds, toxic metals, suspended solids, pathogens, parasites and dyes (Gürses, 2006, Allen, 2005). The water quality is degraded by the presence in the effluents of these toxic organic and inorganic substances.

Organics dyes constitute one of the largest groups of pollutants in wastewater released from textile and other industries. Among 7×10^5 tons and approximately 10,000 different types of dyes and pigments produced worldwide annually, it is estimated that 1-15% of the dye is lost in the effluents during the dyeing process (lmoubarki, 2015). Most of these dyes are toxic, mutagenic and carcinogenic. Moreover, they are very stable to light, temperature and microbial attack, making them recalcitrant compounds. From an environmental point of view, the removal of synthetic dyes is of great concern. Several physical or chemical processes are used to treat water charged with dyes. These include flocculation, precipitation, ion exchange, membrane filtration, electrochemical destruction, irradiation and ozonation (Gürses, 2006, Karim, 2009). However, these processes are often expensive and lead to the generation of sludge or to the formation of byproducts (Karim, 2009). For this purpose, adsorption is one of the most effective methods to remove dyes from waste water (Crini, 2006, Allen, 2005, Karim, 2009).

Activated carbon is the most widely used adsorbent for dyes removal, but it is too expensive and difficult to regenerate (Gürses, 2006, Crini, 2006, Karim, 2009). Over the last years, there has been a continuous search for effective and inexpensive adsorbent materials to replace activated carbon. The removal of colored organic molecules by adsorption onto low cost materials such as natural materials, organic adsorbents and waste materials from industry and agriculture has been reported by several authors. Some adsorbents include peat (Ramakrishna, 1997), chitin, chitosan (Ulzin, 2006), silica, perlite (Dogan, 2000), titania (Bavykin, 2010), some agricultural wastes (Namasivayam, 2002), natural phosphates (Barka, 2009, Bezzi, 2012, Graba,2015) and hydroxyapatite (Del Rio, 2004, Barka, 2008).

The phosphate industry utilizes about 80% of this material in the manufacture of fertilizers and phosphoric acid. However, phosphate valorization in other fields should constitute a new approach to expand its potential applications. For instance, phosphate was applied in environmental remediation although most of these studies focused on the removal of heavy metal ions from aqueous solutions (Saxen, 2008, Cao, 2004, Elouear, 2008, Aklil, 2004, Mouflih, 2006, Sariogli , 2005, Keles, 2010). To the best of our knowledge, there are only a few studies on the removal of organic pollutants using phosphates (Malash , 2010, Bellir, 2012, Eren , 2009). Given that Algeria has significant reserves of phosphates, mainly in the Djebel-Onk,

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located 100 km from Tébessa, there is a great potential for its utilization for waste water treatment.

In this paper, we investigated the efficacy of phosphate as an adsorbent for the removal of an organic pollutant, the Bezacryl Yellow (BY). This study not only represents an appealing approach to phosphate exploitation and valorization in industry, but also to reduce the environmental impact caused by this dye. The main objective of this study is to optimize the main experimental parameters of the adsorption process (concentrations of the dye solution and phosphate rock, stirring rate, pH and temperature of the reaction medium) in order to define the most appropriate scheme for water treatment contaminated with BY.

MATERIALS AND METHODS:

Bezacryl yellow (by) dye

The basic dye used as an adsorbate in the present study is the cationic, Bezacryl Yellow (BY). It was provided by the textile company ALCOVEL Akbou (Bejaia, Algeria). The chemical structure and physico-chemical characteristics of the dye are given respectively in Fig.1 and Table 1.

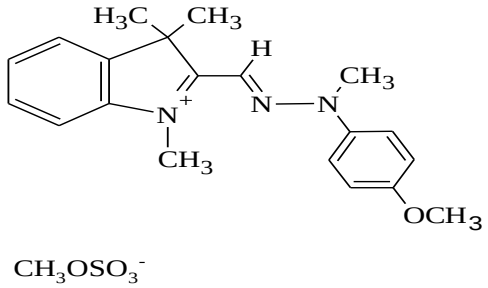

Fig.1. Chemical structure of Bezacryl Yellow(BY) dye.

Tab. 1.
Physico-chemical characteristics of Bezacryl Yellow dye.

Usual name	Chemical formula	Molecular weight ($g.mol^{-1}$)	Solubility in water	λ_{max} (nm)	pK_a
Bezacryl Yellow	$C_{21}H_{27}N_3O_5S$	433.52	High	437	10.35

Absorption spectra were recorded using SHIMADSU UV-Vis spectrophotometer in a spectrometric quartz cuvette with an optical path of 10 mm. The wavelength range was 400-800 nm.

Adsorbent (releases of rock phosphates) Preparation

The crude phosphate rock (PR) is from the career of Djebel-Onk (Tébessa, Algeria) with a particle size ranging from 1000 to 1200 mm. The PR underwent mechanical treatment to release the mineralogical components and define the interval of suitable granulometry. For this operation, we used a series of sieves of different sizes 100, 250 and 500 µm to separate the different size fractions. In this study, we were mostly interested by the fine fraction (FF) <100 µm, because it represents releases of rock phosphates.

Characterizations

X-ray diffraction (XRD)

X-ray powder diffraction (XRD) was used to identify the phases present in the samples. The measurements were performed using an X-ray diffractometer (X Pet Pro Panalytical) with Cu $K\alpha_1$ radiation (λ = 0.154 nm). Scans were conducted in the 2θ range of 5-70° at a rate of 0.01° min^{-1}.

Fourier transform infrared (FTIR) spectroscopy

Transmission FTIR spectra were recorded using a SHIMADZU 8300 spectrometer with a resolution of 4 cm^{-1} using KBr pellets. Dried powder (100 mg) was mixed with KBr powder (300 mg) in an agate mortar. The mixture was pressed into a pellet under 10t load for 2-4 min and the spectrum was recorded immediately. Thirty-six accumulative scans were collected in the 4000-400 cm^{-1} range. The signal from a pure KBr pellet was subtracted as a background.

Brunauer-Emmett-Teller (BET) measurements

The specific surface area of the phosphate was measured by N_2 adsorption – desorption isotherm using a Quanta-chrome NovaWin2 instrument.

Scanning Electron Microscopy (SEM)

SEM images were obtained on powder samples using an electron microscope FEI CONTA 200 equipped with an energy dispersive X-ray analysis device (EDX analysis).

Point of zero charge determination

The method of determination of the point of zero charge (pH_{pzc}), consists in adding a solution of hydrochloric acid HCl (1 N) or sodium hydroxide NaOH (1 N) to 50 mL of NaCl solution (0.01 N), contained in a chamber thermostated at 25°C [28]. When the pH of the NaCl solution is fixed, 0.05g of phosphate is added. The mixture is stirred for 24 h and then the pH final is recorded. The intersection point of the curve pH (final) versus pH (initial) with the bisector is the pH_{pzc}.

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Adsorption experiments

The adsorption tests were performed for the system adsorbate (Bezacryl Yellow (BY)- adsorbent (fine fraction (FF) <100 µm) to define the optimal operating conditions of the main parameters related to the adsorption process. The adsorption experiments were realized in Erlenmeyers covered by corks to avoid the contamination of the solutions by other elements and pH modification. The Erlenmeyer was immersed in a water bath to stabilize the temperature. For every time of contact, a certain quantity of phosphate is introduced into an Erlenmeyer with 50 mL of the solution of BY of a given concentration C_0 (mg/L). The heterogeneous mixture is subjected to a permanent magnetic agitation by means of a magnetic bar, on a heating plate, to assure the contact between the adsorbate and the adsorbent. After a given time of agitation, a certain volume of the solution is taken out and centrifuged at 5000 trs/min during 4 min. The residual concentration of the dye in solution is determined by UV-Visible spectrophotometry.

The amounts of waste adsorbed in mg per gram of adsorbent at time t (q_t), and at equilibrium time, t_e (q_e), are respectively calculated according to the relations (1) and (2).

$$q_t = \frac{(C_0 - C_t) \times V \times 10^{-3}}{m} \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V \times 10^{-3}}{m} \quad (2)$$

The dye removal percentage at time t, and at equilibrium time t_e, are respectively calculated according to the relations (3) and (4).

% elimination at time t: $\left(\frac{C_0 - C_t}{C_0}\right) x100$ (3)

% elimination at equilibrium time $= \left(\frac{C_0 - C_e}{C_0}\right) \times 100$ (4)

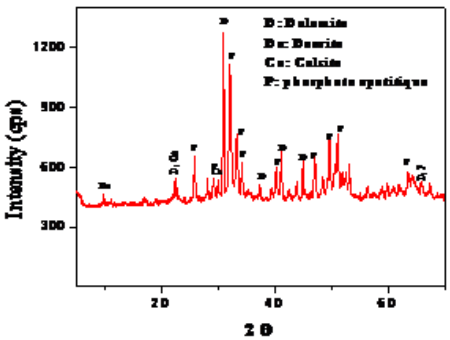
Where C_0 (mg.L^{-1}) is the initial concentration of dye, C_t (mg.L^{-1}) is the residual concentration of dye at the time t, C_e (mg.L^{-1}) is the residual concentration of dye at equilibrium time, V (mL) is the volume of the solution and m(g) is the mass of the adsorbent.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Fig.2 shows the X-ray diffraction pattern of the phosphate adsorbent investigated in this work. It comprises intense dolomite peaks and apatitic phosphate elements, along with minor contributions of calcite and deerite phases. Table 2 illustrates the identified mineralogical phases.

Fig.2. X-ray diffractogram of the phosphate sample studied.



Tab. 2.
Mineral species identified in the phosphate sample studied.

Chemical formula	Mineral
$CaCO_3$	Calcite
$Fe_6Fe_3O_3(Si_6O_{17})(OH)_5$	Deerite
$CaMg(CO_3)_2$	Dolomite

Infrared spectroscopy analysis, carried out on the phosphate sample (Fig.3), revealed several bands, in particular those attributable to carbonates, phosphates and OH^- hydroxide ions of apatite. The characteristic peaks of the phosphatic elements and the apatitic carbonates are not very intense, suggesting that the phosphate sample is not rich in phosphate.

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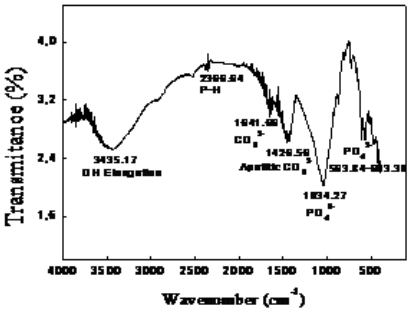

Fig.3. FTIR spectrum of the studied phosphate sample.

Tab. 3.
Position and identification of bands observed by IR of the samples studied

Position(cm^{-1})	Identified species	Intensity
563.84-603.30	PO_4^{2-}	Low
720.91-730.20	P-O-C	Low
867.92	P-OH Elongation in HPO_4^{2-}	Low
883.00	CO in CO_3^{2-}	Low
1034.27	PO_4^{3-} ions	Strong
1426.56	ApatiticCO_3^{2-}	Medium
1641.66	CO_3^{2-}	Low
2366.64	P-H	Low
3435.17	OH	Broad

The morphology of the phosphate adsorbent was analyzed by scanning electron microscopy (SEM). Fig.4 shows mostly dolomitic crystals and fine phosphated elements.

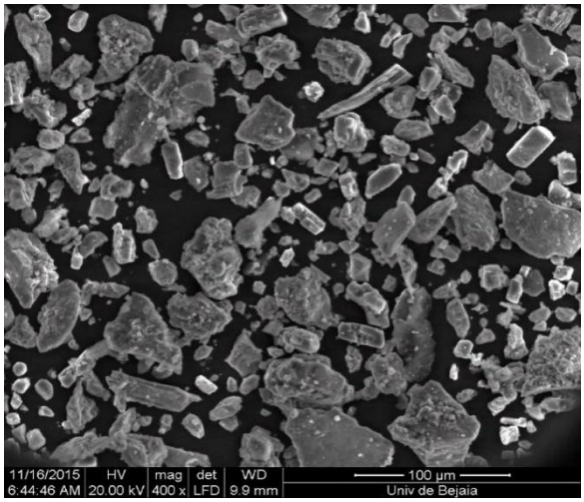

Fig.4. SEM micrograph of the phosphate sample studied.

Figure 5 displays the nitrogen adsorption-desorption isotherm of the adsorbent sample. It is marked by the presence of an hysteresis loop and matches the type IV isotherm, according to the classification of Sing *et al, 1985*. This isotherm is typical of mesoporous materials (Bezina, 1990). Thus, the active pores of the site of adsorption of the adsorbing solid investigated vary from 25 to 500 Å. In addition, the isotherm exhibits an H_3 type hysteresis at high relative pressure, characteristic of the branches of adsorption and desorption which are not parallel, observed for the solids made up of aggregates or having a non rigid texture which inflates in liquids

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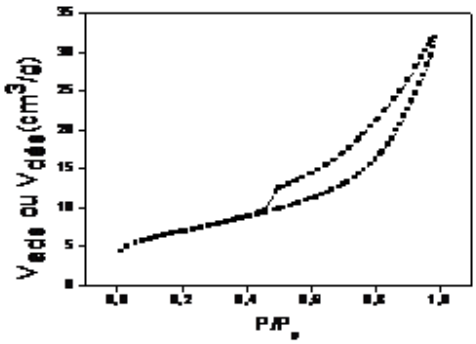

Fig.5. Isotherm of adsorption-desorption of nitrogen.

The specific surface S_{BET} and the total pore volume, Vp of the phosphate sample studied were determined by the BET method. They are respectively equal to 27.05 m^2/g and 0.06 cm^3/g. The point of zero charge (pH_{pzc}) of the phosphate studied is 8.15 (Graba, 2015). Below pH_{pzc} value, the surface of phosphate is generally positive and above it is negative.

Influence of adsorption parameters

Influence of contact time

The effect of contact time on the adsorption of Bezacryl Yellow (BY) is depicted in Fig.6. The choice to study the influence of contact time on adsorption of BY dye by our adsorbent as the first parameter is to determine the time required for equilibrium establishment as well as the optimal dye concentration. The study was performed for dye concentrations of 40, 60, 80 and 100 mg/L.

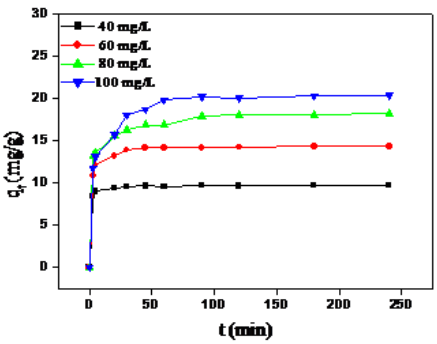

Fig.6. Evolution of the amount of BY dye adsorbed as a function of the contact time (pH=6, m=0.2g, ω=300trs/min, V=50 mL and T=25 °C).

From the curves in Fig.6, it appears that the rate of adsorption of BY dye by phosphate is very fast at the beginning of the adsorption process (about 20 min for a concentration of 20 mg/L) and around 90 min for the other concentrations, and then reaches a plateau. The latter corresponds to the establishment of a balance between the adsorbate in aqueous solution and the adsorbate fixed by the solid. In order to ensure that equilibrium is achieved and that there is no desorption of the adsorbed BY dye, we set the adsorbent-adsorbate contact time for 3 h for all experiments. The rapid adsorption kinetics observed during the first few minutes can be explained by the availability of a large number of active sites on the surface of the adsorbent at the beginning of the adsorption process. The decrease in the rate of adsorption over time is due to the occupation of the remaining vacant sites and the appearance of repulsive forces between the adsorbed dye molecules and those in solution.

The amount of adsorbed BY and the equilibrium time increase with the increase of initial concentration, this is due to the presence of a strong solute concentration gradient between the solution and the surface of the solid (Önal, 2007).

Effect of initial dye concentration on adsorption process

Figure 7 depicts the effect of the initial concentration (C_0) of dye on the adsorbed amount. It is evident from this figure that the adsorption capacity of phosphate increases with increasing initial dye concentration; there is no plateau in the range of concentrations investigated. This means that the saturation rate is not yet reached and that the phosphate could adsorb larger amounts of BY dye.

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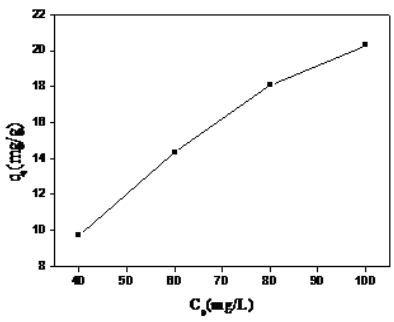

Fig.7. Influence of the initial concentration of adsorbate on the amount fixed at equilibrium (pH=6, m=0.2g, ω=300trs/min, V=50mL, t_e=180min and T=25°C).

Effect of the phosphate suspension on the rate elimination

Figure 8 displays the evolution of the BY dye removal rate as a function of the concentration of the phosphate suspension (R(g/L)). It is clear that the rate of BY dye removal increases as the concentration of the phosphate suspension increases and reaches a plateau at 8 g/L.

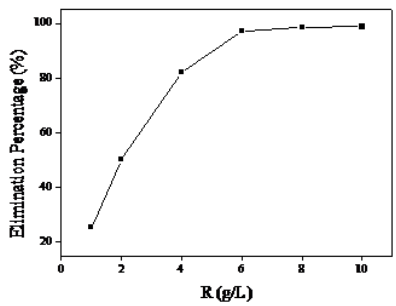

Fig.8. Evolution of the amount of BY dye adsorbed as a function of the concentration of the phosphate suspension (pH=6,ω=300trs/min, V=50mL, C_0=100mg/L, t_e=180min and T=25°C).

The maximum elimination rate (98.6%) is reached for a phosphate concentration of 8 g/L. The increase in the phosphate mass causes an increase in the number of active sites, responsible of the enhanced rate of discoloration. When the phosphate concentration exceeds 8 g/L, the elimination yield becomes constant; above 9 g/L, it is likely that phosphate aggregation occurs, reducing the available surface active area and thus dye removal (Barka, 2008).

Effect of ph solution on dye adsorption

The pH is an important factor in the adsorption process as it can influence at the same time the structure of adsorbent, adsorbate as well as the mechanism of adsorption. Fig. 9 shows the wavelength variation (absorption maximum) as a function of pH. It is clearly seen that the absorption maximum is not affected by the pH variation.

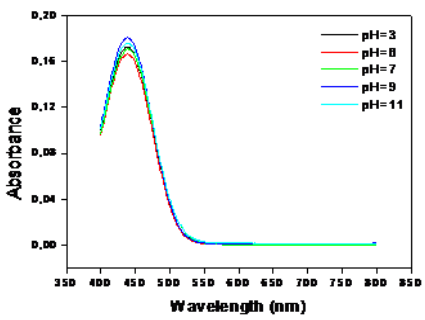

Fig.9. Evolution of the wavelength of BY dye with pH.

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The point of zero charge of our phosphate sample is 8.15. The capacity of an adsorbent to remove dye from the aqueous solution depends on the material surface charge and pH of the solution (Viraraghavan, 1999, Barka, 2008). The influence of the pH on the BY adsorption on the phosphate was carried out by bringing into contact 50 mL of dye solution of concentration 100 mg/L with 0.4 g of phosphate at 25°C and stirring speed of 300 trs/min. The experiment was conducted at different pH values from 2 to 12 and the results are displayed in Fig.10.

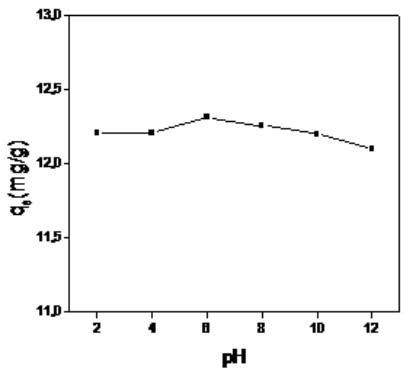

Fig.10. Evolution of the amount of BY dye adsorbed as a function of pH (m= 04g, ω=300 trs/min, V=50 mL, C_0=100 mg/L, t_e=180 min and T=25°C).

The results indicate that the removal rate and the amount of adsorbed BY increase with increasing pH from 2 to 6 and then decrease. The maximum values are reached at pH 6, they are respectively equal to 98.33% and 12.32 mg/g.

At pH < 6, the adsorbent is positively charged and the adsorbate is in two forms: cationic and molecular, the latter is fixed on the surface of the adsorbent thanks to Van der Waals type bonds. For pH values between 6 and 8.13 (pH_{pzc}), the decrease of the amount of adsorbed dye molecules is prevented by the repulsive electrostatic forces existing between the positive charged surface of phosphate and cations of dye groups predominant in this range. At pH >8,13, the adsorbent is negatively charged, the decrease in retention can be explained by the excess of OH^- ions which surround the dye (cation) by electrostatic attraction which prevents them from being retained on the anionic sites of the adsorbent, or by the repulsive electrostatic forces existing between the negatively charged surface of phosphate and $CH_3OSO_3^-$ groups of the dye which is predominant in this range.

Effect of agitation speed

To study the effect of agitation speed on dye adsorption, 0.5 g of adsorbent was agitated for 3 h with 50 mL of the solution (dye concentration = 100 $mg.L^{-1}$) at 25°C. The experiment was conducted at different speed agitations values from 100 to 500 turns per minute at pH 6. The stirring speed is a very important parameter in any process involving a transfer of material; it has the effect of homogenizing the solution and reducing the thickness of the boundary layer which surrounds the adsorbent grains, thus favoring the adsorption of the dye. However, the strong agitation forces the grains of the suspension against the walls of the reactor, which causes the decrease of the free surface area. This is remarkable in the case where the elimination rate and the adsorbed quantity qe increase with the increase of the stirring speed until reaching respectively a maximum of 98.53% and 12.32 mg/g at a rate of 300 rpm from which we see a decrease (Fig.11).

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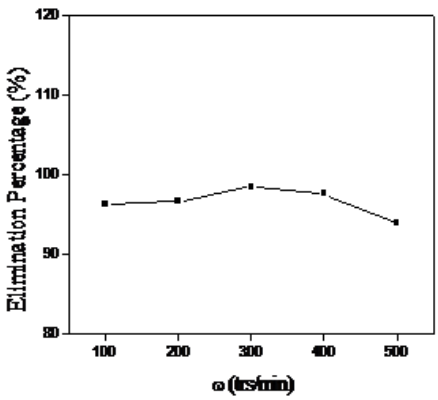

Fig.11. Influence of stirring rate on adsorption of BY dye (pH=6, m=0.4 g, V=50 mL, C_O=100 mg/L, te=180 min and T=25 °C).

Effect of temperature on adsorption process

The influence of the temperature on the amount of adsorbed BY was investigated at different temperatures (28, 36, 50 and 60 °C) by bringing into contact 50 mL of coloring solution of initial concentration of 100 mg/L at pH 6, with an adsorbent mass of 0.4 g. The stirring speed of the mixture was maintained at 300 rpm. Fig.12 depicts the rate of BY dye removal as a function of the temperature of the reaction medium. These results show that the temperature has no significant effect on adsorption of BY under our experimental conditions.

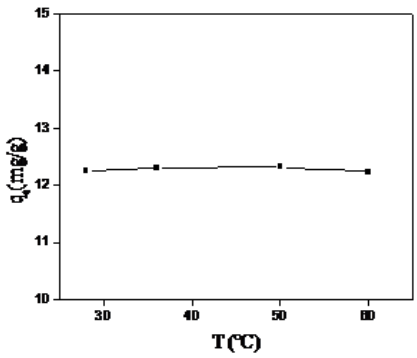

Fig.12.Influence of temperature on BY dye adsorption (pH=6, m=0.4g,ω=300 trs/min, V=50 mL, C_0=100 mg/L and t_e=180 min).

The thermodynamic study made it possible to determine the thermodynamic quantities such as the standard variations of enthalpy (ΔH°), free energy (ΔG°) and entropy (ΔS°) for the YB dye adsorption by the phosphate adsorbent. These parameters are calculated from the relationships (5-8) and the values are summarized in Table 4. The equilibrium constant (k_d) of the adsorption process is equal to qe/Ce. The variations of the exchanged enthalpy (ΔH°) and the entropy (ΔS°) for our adsorbent are determined starting from ln(k_d) as a function of (1/T).

$$K_d = \frac{q_e}{C_e} \quad (5)$$

$$K_d = \frac{(C_0 - C_e)}{C_e} \cdot \frac{V}{m} \quad (6)$$

$$\Delta G^0 = \Delta H° - T.\Delta S° = - RT \ln k_d \quad (7)$$

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (8)$$

Tab. 4.
hermodynamic parameters calculated in the studied temperature range.

T(K)	AH° (J/mol)	AS° (J/mol/K)	AG° (KJ/mol)
301	10,61	46,08	-13,86
309			-14,23
323			-14,87
333			-15,33

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The results in Table 4 show that:
- The negative values of ΔG° mean that the adsorption process is spontaneous;
- The positive sign of ΔH° demonstrates the endothermic nature of the reaction and its value (10.61 J/mol) <50 kJ/mol) suggests that it is a physical adsorption.
- The positive sign of ΔS° signifies an increase in the molecular disorder of the dye molecules by passing from the dye solution to the surface of the phosphate adsorbent.

Study of the adsorption isotherm

In general, the adsorption isotherms deal with the distribution of adsorbate molecules between the solution and the surface of the adsorbent material. This sharing obeys precise relationships that represent the amount adsorbed as a function of equilibrium concentration. In order to define the type of adsorption isotherm, we determined the quantity of the dye adsorbed at equilibrium as a function of the concentration of the equilibrium dye solution. The results are displayed in Fig.13, and compared to the adsorption isotherms according to the classification of Giles *et al.* They confirm the type L, which is relative to the adsorption of molecules from an aqueous solution on the solid in a linear form. This means that there is no competition between the dye molecules and the aqueous solution for the occupation of sites of adsorption.

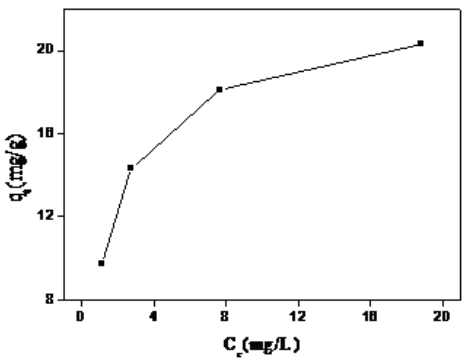

Fig.13. BY dye adsorption isotherm (pH=6, m=0.4g,ω=300 trs/min, V=50 mL, t_e=180 min, and T=25°C).

Modeling of adsorption isotherms

Many classical mathematical models can be applied in the case of the adsorption phenomena. The most commonly used are the Langmuir, Freundlich and Temkin models.

a) Langmuir model is valid for monolayer coverage of adsorption i.e. each dye molecule occupies a site and no further adsorption can take place at that site. The form of Langmuir model is given by:

$$q_e = \frac{q_m.K_L.C_e}{1+K_L.C_e} \quad (9)$$

The linear transform of this model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m.K_L} + \frac{C_e}{q_m} \quad (10)$$

Where q_m (mg/g) is the monolayer adsorption capacity, K_L ($L.mg^{-1}$) is the Langmuir constant, C_e ($mg.L^{-1}$) is the equilibrium dye concentration in the solution and q_e ($mg.g^{-1}$) represents the amount of dye adsorbed on adsorbent at equilibrium. The plot $\frac{C_e}{q_e}$ versus C_e was employed to allow the determination of the two equilibrium parameters of the equation qm and K_L. The essential characteristics of Langmuir adsorption isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L [42], defined as:

$$R_L = \frac{1}{1+K_L.C_0}$$

Where C_0 is the initial concentration of the dye. The value of R_L indicates the type of isotherm to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1) or unfavorable (R_L>1). The modeling of the experimental results by the Langmuir model, exploited in its linear form, is shown in Fig.14.

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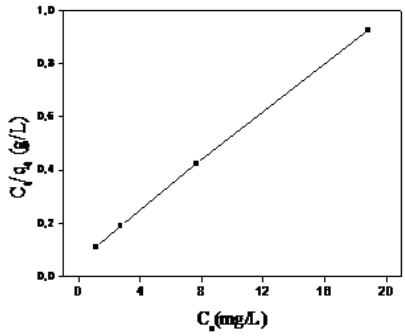

Fig.14. Modeling experimental results by the Langmuir model (pH=6, m=0.2 g, ω=300 trs/min, V=50 mL, t_e=180 min and T=25°C).

The results of the Langmuir transform showed good linearity. Table 5 summarizes the values of the Langmuir parameters, calculated from the slope and the intercept at the origin of the line observed on the graph and the R_L values.

Tab. 5.
Values of the constants of the Langmuir model.

T (C)	q_m (mg/)	K_L (L/m)	R_L(mg/L)				R^2
			40	60	80	100	
25	21,786	0.700	0.034	0.023	0.017	0.014	0.999

The value of the obtained correlation coefficient (R^2= 0.9999) suggests that BY adsorption on our phosphate adsorbent can be described by the Langmuir model. The values of R_L calculated according to equation 11, are between 0 and 1, which means that the adsorption of the BY dye over the phosphate adsorbent is favorable.

b) Freundlich model assumes that adsorption takes place on heterogeneous surfaces. Freundlich model, can be expressed as:

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (12)$$

Where K_F is the relative adsorption capacity of adsorbent $(mg.g^{-1}).(mg.L^{-1})^{1/n}$, n is a constant related to adsorption intensity (dimensionless).
The linear transform to verify the validity of this equation is in the form:

$$\ln qe = \ln K_F + 1/n \ln Ce \qquad (13)$$

The shape of the isotherm will depend on the value of 1/n, which represents the adsorption intensity and gives crucial information on the mechanisms governing the adsorption of the compound on the adsorbent. According to the value of 1/n, the following cases are distinguished:
1/n=1: the isotherm is linear of type C;
1/n>1: the isotherm is convex of type S;
1/n<1: the isotherm is concave type L;
1/n<<1: the isotherm is of type H;
n is between 2 and 10, the adsorption is good (easy);
n is between 1 and 2, the adsorption is moderately difficult.
n is less than 1, the adsorption is small. In this case, a large mass of adsorbent is used to recover an appreciable fraction of the solute. The plot of ln q_e versus lnC_e is displayed in Fig.15. The latter allows us to calculate the Freundlich constants K_F and 1/n.

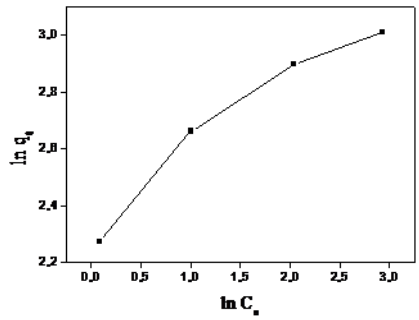

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Fig.15. Modeling of experimental results by the Freundlich model (pH=6, m=0.2, ω=300 trs/min; V=50 mL, t_e=180 min and T=25°C).

The results and the correlation coefficient are reported in Table 6.

Tab. 6.
Freundlich constant values.

$K_F(mg.g^{-1}).(mg.L^{-1})^{1/n}$	n	1/n	R^2
10,2267	3.9262	0.2547	0.9703

The results in Table 6 reveal that:

The value of the correlation coefficient obtained according to the Freundlich model is lower than that of the Langmuir model, which means that the adsorption of the YB dye is better described by the Langmuir model.
The value of the parameter 1/n is less than 1; the isotherm is then of type L.
The value of n is between 2 and 10, thus the adsorption of the BY dye on the sample of phosphate is favored.

c) **Temkin isotherms** assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. Temkin model, can be expressed as:

$$q_e = \frac{RT}{b} Ln(A.C_e) \quad (14)$$

With $B = \frac{RT}{b}$ (15)

Where, R is the ideal gas constant, A is the Temkin isotherm constant ($L.mg^{-1}$) corresponding to the binding energy maximum, B is a constant related to Temkin adsorption heat ($J.mol^{-1}$). The constants A and B are determined from the slope and intercepts of the plots obtained by plotting q_e versus lnC_e. All results are summarized in Table 7.
The application of the Temkin model in its linear form equation (14), that is to say by plotting qe as a function of lnC_e is depicted in Fig.16.

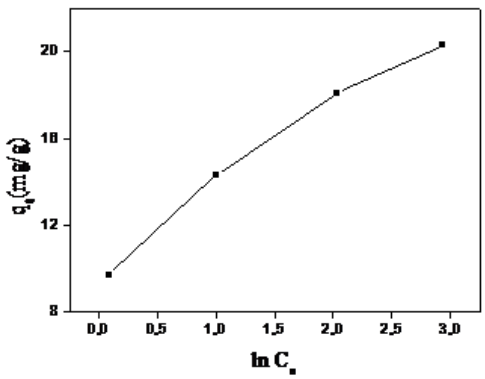

Fig.16. Modeling of experimental results by the Temkin model (pH=6, m=0.2 g, ω=300 trs/min, V=50 mL, t_e=180 min and T=25°C).

The values of the Temkin parameters are reported in Table 7.

Tab. 7.
Values of Temkin constants.

Adsorption	T (°C)	B (kJ/mol)	A (L/mg)	R^2
FF	25	.7057	14.8569	0.9893

The values of the correlation coefficient obtained according to the three models show that the adsorption obeys more to the Langmuir model than to the Freundlich and Temkin models.

Adsorption of BY dye was found to be consistent with the Langmuir model suggesting that:
- The adsorption sites on the surface of the solid are all energetically equivalent;
- Each site can only fix one molecule;

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- There is no interaction between the adsorbed molecules;
- The adsorption takes place as a monolayer.

Modeling adsorption kinetics

To find out the mechanism limiting the kinetics of the adsorption process, correlations between adsorbed quantities and time are established using three models of which the first order, the second order and the model of intra-particle diffusion were applied. The applicability of these models is tested by the construction of linear shapes for each.

Models based on the reaction

Kinetic model of first order

It is the oldest of the kinetic models proposed by Lagergren in 1898. This model considers the adsorption as limited by the formation of the bond between solute and active sites. The differential Lagergren equation that governs first-order adsorption kinetics is:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (16)$$

The integration of equation (16) between 0 and t, leads to equation (17):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (17)$$

The study focused on the variation of $\ln(q_e\text{-}q_t)$ as a function of time. In Fig.17, the kinetic model of first order is represented. The points in Fig.17 do not correspond to straight lines, which indicates that the kinetic model of first order is not applicable in this case. Therefore, the adsorption kinetics are not first order.

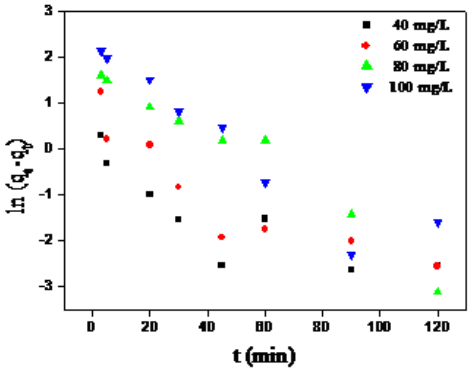

Fig.17. Graphical representation of the adsorption kinetics according to the model of first order for different concentrations of BY dye (pH=6, m=0.2g, ω=300 trs/min,V=50 mL, t_e=180 min and T=25°C).

Kinetic model of second order

The kinetics of adsorption can, in some cases, follow a pseudo-second order model (Mckay, 1999). This model developed by Ho and McKay translated the existence of a balance between species in solution and adsorbed species. The pseudo-second order model follows equation (18):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (18)$$

The integration of equation (18) between 0 and t, leads to equation (19):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (19)$$

The study of second-order kinetics focused on the variation of t/q_t as a function of time. The results obtained are displayed in Fig.18.

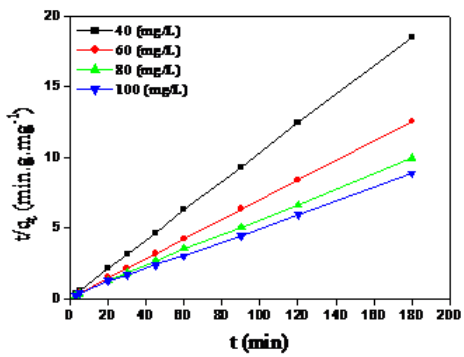

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Fig.18. Graphical representation of adsorption kinetics of the model of second order for different concentrations of BY dye (pH=6, m=0.2g, ω =300 trs/min, V=50 mL, te=180 min and T=25°C).

It should be noted that the set of curves t/q_t, obtained as a function of time, are straight lines. From the slopes, it is possible to deduce the K_2 speed constants. The results are summarized in Table 8.

Tab. 8.
Parameters of second-order kinetics.

C_0 (mg/L)	K_2 ($g.mg^{1}.min^{-1}$)	q_e exp (mg/g)	q_e cal (mg/g)	R^2
40	0.1434	9.7274	9.97399	0.999
60	0.0608	14.3206	14.3988	0.999
80	0.0183	18.0893	18.3553	0.999
100	0.0126	20.2979	20.7598	0.999

We note that the second-order model gives an excellent description of the adsorption kinetics of BY dye on our phosphate sample since the correlation coefficients are very close to 1. Similarly, the values of q_e exp are close to q_e cal.

Dissemination model

Internal or intra-particle diffusion model

Intra-particle diffusion is frequently the limiting step in many adsorption processes. The possibility of intra-particle diffusion can be explored using the Weber and Morris model of intra-particle diffusion [45].

$$q_t = K_d\sqrt{t} \qquad (20)$$

Where, K_d is the coefficient of internal diffusion ($mg.g^{-1}.min^{-1/2}$). By representing q_t as a function of $\sqrt{t}$, the speed constant K_d can be determined, which allows to highlight the different stages of the process. Fig.19 represents the kinetic model of internal diffusion for different dye concentrations.

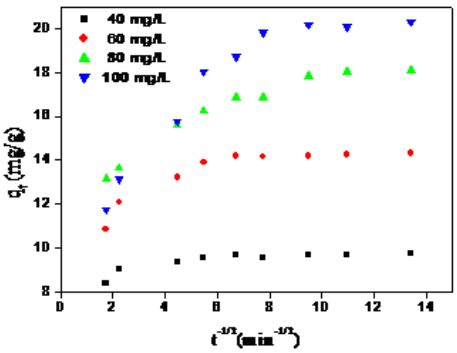

Fig.19. Graphical representation according to the internal diffusion model for different concentration of BY dye (pH=6, m=0.2 g,ω=300 trs/min, V=50 mL, t_e=180 min and T=25°C).

The application of Weber and Morris's equation to the experimental results does not lead to straight portions due to the non-linearity of the experimental points in the time intervals considered, as shown in Fig.20. As a result, kinetic is not governed by internal diffusion. This can be explained by the adsorption of the dye molecules on the outer surface of the adsorbent. We conclude that adsorption kinetics of the dye is governed by the second-order model.

CONCLUSION:

Our study focused on the elimination of the Bezacryl Yellow (BY) dye by fine fraction (FF) phosphates (Djebel-Onk, Algeria) with particle size less than 100 µm. The objective of this work is the valorization of local mineral materials as adsorbents for the treatment of aqueous effluents loaded with organic pollutants. The tests carried out in a closed stirred reactor made it possible to study the influence of several parameters on the adsorption capacity of BY in aqueous solution. We limited this study to the influence of the adsorbent-adsorbate contact time of the initial dye concentration, the mass of the adsorbent, pH of the solution, the stirring speed and the temperature of the reaction medium. The results showed that the amount of the adsorbed BY increases with increasing adsorbate-adsorbent contact time and this regardless of the initial concentration of dye. The increase in the amount adsorbed when C_0 increases, can be explained by the existence of a strong dye concentration gradient

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between the solution and the surface of the adsorbent. The pH of the solution is a very important factor because it affects the surface charge of the adsorbent. We found that the maximum adsorbed dye quantity was achieved at pH 6 and agitation rate of 300 rpm, independent of the temperature (28-60 °C) under our experimental conditions. The study of the influence of the concentration of the adsorbent on the adsorption of the BY revealed that the adsorbed quantity decreases with the increase of the concentration of material, therefore the optimum is obtained for a concentration of 8g/L.

The thermodynamic study revealed that the adsorption process is exothermic and its reaction is spontaneous and of a physical sorption nature. The second-order model is the one that best describes the adsorption phenomenon. Measurements of the equilibrium concentrations for different initial dye concentrations allowed us to plot the adsorption isotherm. The latter is of type L. The application of adsorption models of Temkin, Freundlich and Langmuir to the experimental results showed that the Langmuir model describes better the process of adsorption of Bezacryl Yellow.

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