

Evaluation of the adsorption capacity of Natural Phosphate to remove Remazol Brilliant Blue R dye in aqueous solution

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Abstract

In this study, natural phosphate (NP) was used as adsorbent to remove Remazol Brilliant Blue R dye (RBBR) from aqueous solution. The effects of different factors that influence the uptake onto adsorbent such as pH of dye solution, contact time and initial dye concentration has been investigated. The experimental results show that the maximum adsorption occurred at the pH value of 11. The test of the kinetic models shows that the adsorption process of RBBR on NP follows the pseudo-second order kinetic. The adsorption isotherms data are found agree Freundlich model. The amount of dye adsorbed increases with the decrease of the amount of NP. The dye removal rate reaches 50% for the mass ratio NP/RBBR of 0.3.

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1. Introduction

The aqueous effluents containing dyes from certain industries (printing, cosmetics, textile, etc.) are important sources of water pollution. The dyeing process of textile fiber, for example, is the cause of not negligible amount of release (10-15 %) of dyes involved in the wastewater [1-3]. The color of wastewater is the first indicator of pollution. Indeed, the presence of dyes in water, even in very small amount, might be harmful to human beings and seems hazardous to aquatic organisms. Dyes can cause allergic dermatitis and skin irritation. Many dyes and pigments contain aromatic cycles in their structures, which make them toxic, non-biodegradable, carcinogenic and mutagenic for aquatic systems (eutrophication, under- oxygenation) and human health [4]. The presence of dyes greatly reduces the passage of light through the water and therefore can have a negative impact on aquatic diversity. Many different techniques, such as, chemical, electrochemical processes, electrocoagulation and adsorption has been used for the removal of dyes from wastewater [5-8]. Among these methods, adsorption has evolved into one of the most effective processes for dye removal from aqueous solution. Many studies have been performed for removing dyes from colored effluents by adsorption. The most commonly used adsorbent is activated carbon despite its cost of production [9-14]. However, several studies using low-cost adsorbents and/or biologic, such as, coffee grounds [15-17], bone [18-20], natural phosphate [8] and synthetic calcium phosphates [21-26] have been realized. The aim of our study is to remove Remazol Brilliant Blue R dye (RBBR) from aqueous solutions using Natural Phosphate (NP). The effect of various parameters, such as, pH, contact time, dye concentration and the mass of the natural phosphate was investigated.

2. Materials and methods

2.1. Adsorbent

The adsorbent used in this study is natural phosphate (NP). The phosphate rock sample used originates from the Khouribga region (Morocco). The sample was washed with distilled water several times until a constant pH and then dried in an oven at 100°C for 48 hours. In order to obtain good homogeneity of powder, the sample obtained is ground and then sieved. Sieving was carried out with a vibrating screen "Fretsch Analysette", the mesh size of the screen is equal to 125 microns. This dimension corresponds to a common standard used [27]. The choice of this material is based on its low cost, considering its abundance in Morocco. Sample powered of NP was characterized by X-ray diffractometry (XRD), Infrared spectroscopy (IR) and chemical analyses. The calcium ion content in solid was determined by complexometry with EDTA (Ethylenediaminetetraacetic acid) and the phosphore ion content by spectrophotometry of phospho-vanado-molybdc acid. In addition, the pH of the zero point charge (pH_{ZPC}) of NP has been also determined. XRD patterns of a sample powered (Fig. 1) showed reflections characteristic of fluoroapatite. Other phases are detected, such as, dolomite, quartz and calcite. The existence of dolomite and calcite confirms the value of the Ca/P ratio of 1.97 obtained by chemical analysis which is higher than of a stoichiometric apatite ($\text{Ca/P} = 1.67$). The IR spectrum of NP (Fig. 2) shows characteristic bands of an apatite. Indeed, we note the presence of characteristic bands of PO_4^{3-} groups of the apatite in two domains located between 900-1500 cm^{-1} (especially the bands located at 1053 and 1097 cm^{-1}) and between 400-600 cm^{-1} (located at 476 and 570 cm^{-1}). In addition, absorption bands characteristic to carbonate ions appear at 1462, 1437 and 871 cm^{-1} . The bands observed at 3452 and 1641 cm^{-1} are attributed to H_2O vibration frequencies. The pH of the zero point charge (pH_{ZPC}) of the material was determined by contacting 300 mg of NP with KNO_3 solutions of concentration 0.1 M (100 mL). The initial pH ($\text{pH}_{\text{initial}}$) of these solutions has been adjusted by adding 0.1 M NaOH or 0.1 M HCl. After equilibrium of incubations solutions, the final pH (pH_{final}) of each solution has been measured. The pH_{ZPC} of the NP was found to be 9.1 (Fig. 3). When pH is higher, than 9.1, the surface of NP becomes negatively charged and the opposite for pH values lower than 9.1, the surface becomes positively charged.

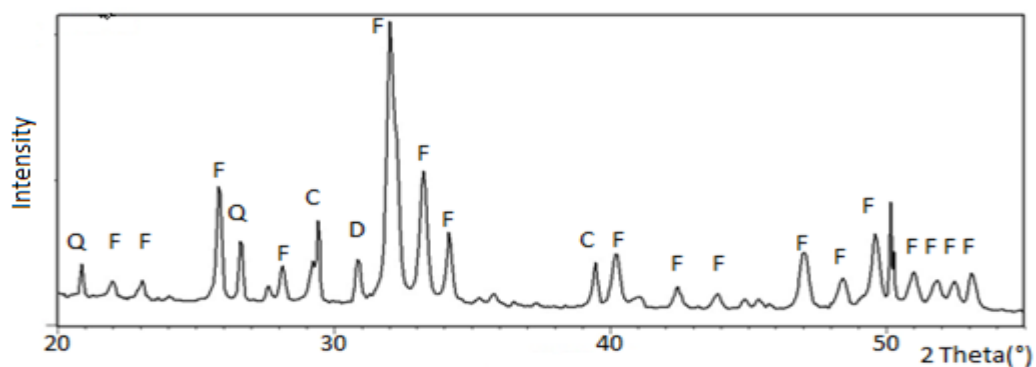


Figure 1: XRD pattern of NP (F: Fluoroapatite, Q: Quartz, C: Calcite, D: Dolomite).

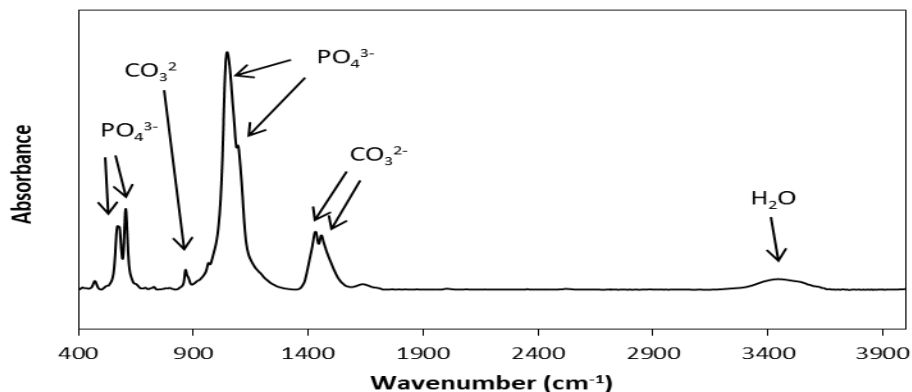


Figure 2: IR spectrum of NP.

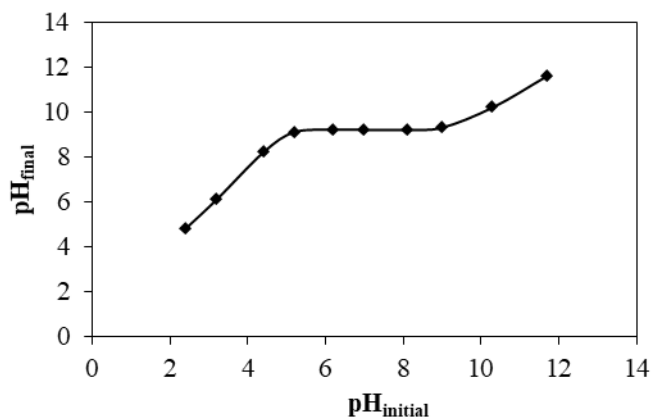


Figure 3: pH_{ZPC} of NP.

2.2. Adsorbate

The chemical structure of Remazol Brilliant Blue R dye (RBBR) is shown in figure 4. Solutions were prepared by dissolving requisite quantity of the dye in distilled water. The concentration of the dye was determined at 594 nm, using UV spectrophotometer (Jenway 6300).

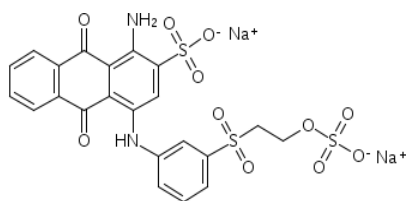


Figure 4: Chemical structure of Remazol Brilliant Blue R dye (RBBR).

2.3. Adsorption Measurements

Study of adsorption of dye (RBBR) onto NP was carried out. The samples of NP were dispersed in series of standard aqueous solutions (100 mL) of RBBR. The mixtures were gently stirred at room temperature (20°C). The suspension was centrifuged during 15 min and the supernatant was assayed for RBBR. The desired pH of the solutions was obtained by addition of sodium hydroxide (NaOH) and hydrochloric acid (HCl) solutions. The uptake of RBBR by NP was derived from the relation $Q = V(\Delta C)/m$, where Q (mol/g) is the amount adsorbed, V (L) the volume of the solution in contact with m (g) of adsorbent, and ΔC (mol/L) the difference between the initial and final equilibrium concentrations.

2.4. Analytical techniques

The XRD equipment used was a Siemens D 501 diffractometer. Samples of unoriented powder were exposed to copper K_α radiation ($\lambda = 0.15415$ nm). Measurement conditions were 2h, range 5-70°, step size: 0.08-2h, and step counting time: 4s. Data acquisition was effective on a DACO-MP microcomputer. Unit cell constants were calculated using a least squares refinement. Absorbance IR spectra were recorded on a JASCO6300 PC spectrophotometer, at a resolution of 2 cm^{-1} and averaging over 100 scans, in the range 400–4000 cm^{-1} .

3. Results and discussion

3.1. Effect of pH

The study of effect of pH was carried out by adding 30 mg of NP in 100 mL of solution concentration of RBBR equal to 200 mg/L. The pH of each dye solution was adjusted, before adding adsorbent. The tests were performed in the initial pH range of 4 to 11. The mixtures were stirred for 90 min. The evolution of the amount of RBBR retained by NP, according to the pH, is represented on figure 5. It appears that the process of adsorption is favorable for pH basic. Indeed, a maximum adsorption is obtained at pH 11. Similar results were observed in studies of the adsorption of the methyl blue onto the activated carbon [9].

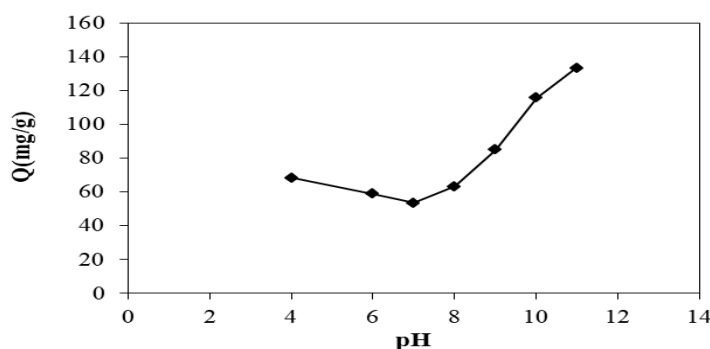


Figure 5: Effect of pH on adsorption of RBBR onto NP

($C_{\text{RBBR}} = 200$ mg/L ; $m_{\text{NP}} = 30$ mg ; contact time = 90 min ; $T = 20$ °C).

3.2. Adsorption kinetic models

For kinetic study, 30 mg of NP was mixed with 100 mL of RBBR solution (200 mg/L). The contact adsorbate-adsorbent was carried out in solutions at room temperature (20 °C) and pH 11. The mixtures were stirred for various time intervals (10-150 min). For each time, the suspension was filtered and the supernatant was assayed for dye.

The evolution of amount adsorbed of RBBR as a function of time is shown in figure 6. It was observed that the adsorption process is relatively fast. The equilibrium is reached within 60 minutes, by establishing an equilibrium plateau.

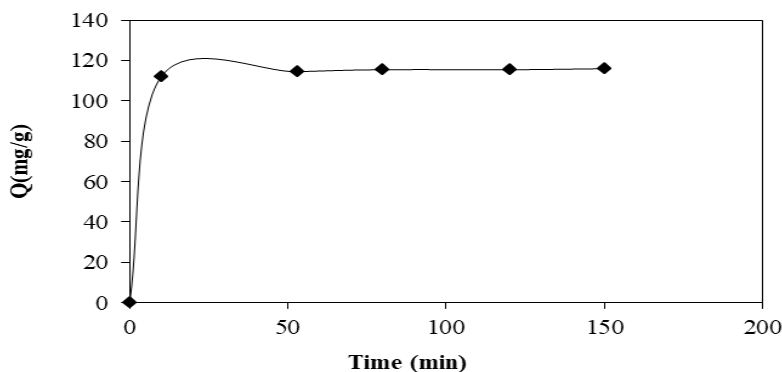


Figure 6: Kinetic of adsorption of RBBR onto NP

($C_{\text{RBBR}} = 200 \text{ mg/L}$; $m_{\text{NP}} = 30 \text{ mg}$; $\text{pH} = 11$; $T = 20^\circ \text{C}$).

In order to examine the mechanism of adsorption process, kinetic adsorption data were analyzed by using suitable models: the Lagergren pseudo-first order, the pseudo-second order and the intra-particle diffusion models.

The pseudo-first order model was described by equation [28]:

$$\log(Q_e - Q_t) = \log Q_e - (k_1/2.303).t$$

A pseudo-second order model was represented by equation [29]:

$$(t/Q_t) = (1/k_2 Q_e^2) + (1/Q_e).t$$

Where Q_e and Q_t are the amounts of dye adsorbed at equilibrium and at contact time t (mg/g) respectively, k_1 and k_2 are rate constants of adsorption, respectively, for the pseudo-first order (min^{-1}), and the pseudo-second order (g/mg.min), t is the contact time. The intra-particle diffusion model was used to determine the rate-limiting step of the adsorption process. It was described by the following equation [30]:

$$Q_t = k_i.t^{1/2} + C$$

Where, Q_t is amount of adsorbent on the surface of the sorbent at time t (mg/g), k_i is the intra-particle diffusion constant ($\text{mg/g.min}^{0.5}$), and t is the contact time (min) and C is the constant that gives an idea about the thickness of boundary layer. The kinetic data obtained using the pseudo-first and pseudo-second order equations is given in figures 7 and 8. Table 1 gathers parameters for pseudo-first and pseudo-second order models from linear regression, which also presents the coefficients of correlation. Examination of result given in table 1 showed that the theoretically calculated value of $Q_{e(\text{th})}$ (106.38 mg/g) from pseudo-second order kinetic model corresponds to the experimentally determined value $Q_{e(\text{exp})}$ (114.7 mg/g). Furthermore, pseudo-second order kinetic model shows the best correlation with R^2 equal to 1. These facts suggest that the process of sorption of RBBR onto NP follow the pseudo-second order kinetic. Similarly, it was reported for adsorption of Direct Yellow 28 onto apatitic phosphate [8] and adsorption of Acid Green 25 onto organo-bentonite [31].

According to intra-particle diffusion model proposed by Weber and Morris [30], the plot of Q_t vs $t^{1/2}$ is depicted in figure 9. Examination of the graph indicates a linear plot. This result shows that the adsorption process is not governed by intra-particle diffusion mechanism and may be described by one step corresponding to the adsorption equilibrium state. The adsorption process is relatively fast according with the kinetic results.

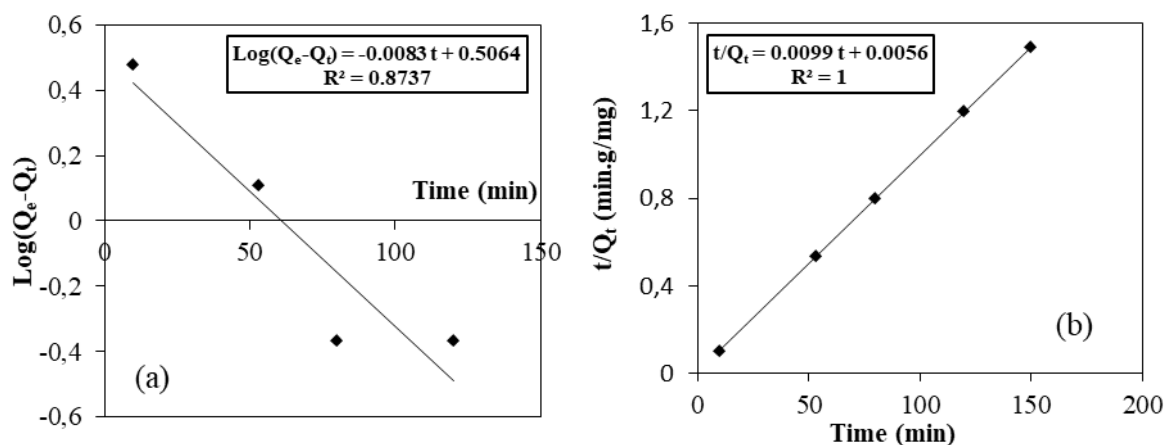


Figure 7: The kinetic models of pseudo-first order (a) and pseudo-second order (b)

($C_{\text{RBBR}} = 200 \text{ mg/L}$; $m_{\text{NP}} = 30 \text{ mg}$; $\text{pH} = 11$; $T = 20^\circ\text{C}$).

Table 1: Kinetic parameters for adsorption of RBBR onto NP.

Pseudo-first order				Pseudo-second order			
$Q_{e \text{ th}}$	$Q_{e \text{ exp}}$	k_1	R^2	$Q_{e \text{ th}}$	$Q_{e \text{ exp}}$	k_2	R^2
(mg/g)	(mg/g)	(min^{-1})		(mg/g)	(mg/g)	(g/mg.min)	
3.209	114.7	0.019	0.874	106.38	114.7	0.009	0.999

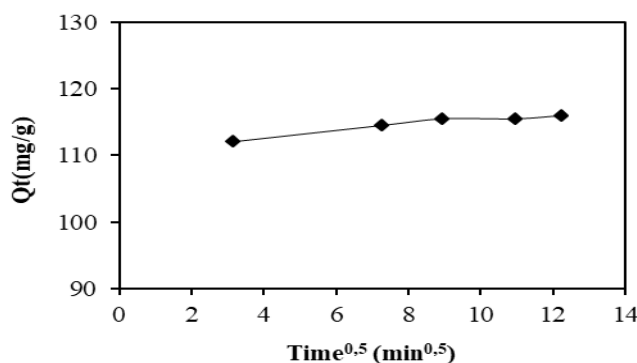


Figure 9: Intra-particle diffusion model ($C_{\text{RBBR}} = 200 \text{ mg/L}$; $m_{\text{NP}} = 30 \text{ mg}$; $\text{pH} = 11$; $T = 20^\circ\text{C}$).

3.3. Adsorption isotherms

The study of the variation of the adsorbed amount of RBBR onto NP in the range of its initial concentration: 100-1000 mg/L, was performed for three masses of apatite: 30, 50 and 70 mg at pH 11. The adsorption isotherms obtained are plotted in figure 10. This results show weak amount adsorbed of dye for low concentration, in particular. As the concentration increases, the amount adsorbed increases. This evolution is very fast for 30 mg of NP. According to classification given in literature [32], the shape of isotherms obtained is of type S, indicating that the retention process is governed by « co-operative adsorption » between adsorbed molecules of RBBR. This "S" form of the isotherms obtained has a point of inflection revealing the existence of several adsorption layers.

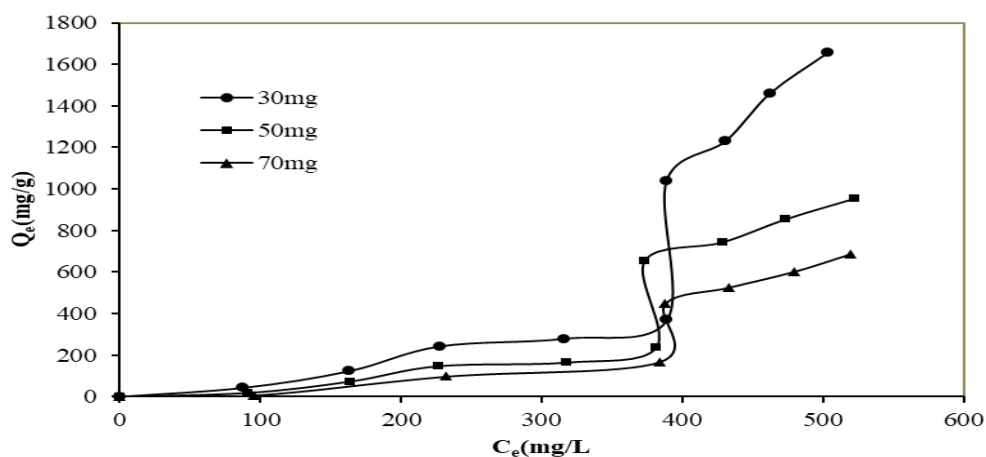


Figure 10: Adsorption isotherms of RBBR onto different masses of NP (30, 50 and 70 mg).

In order to describe the adsorption process, the Freundlich model [33] was investigated. The uptake data were analyzed by linearizing the isotherm equation, providing a way to determine the adsorption parameters. The adsorption isotherm model of Freundlich is given by the following equation:

$$\log Q = \log K_f + m \log C$$

The constants K_f (mg/g) and m reflect respectively the adsorption affinity and capacity. Q_e is the amount adsorbed (mg/g), and C is the equilibrium concentration (mg/L). Table 2 gives the parameters characterizing the model of Freundlich adsorption isotherms obtained for the various masses of apatite. According to values correlation coefficients (R^2), one can say that the Freundlich model appears appropriate for modeling the adsorption isotherms of RBBR on NP. This result is in agreement with the shape of the adsorption isotherms (S-form) which suggests that the adsorption process can be described by the formation onto NP of multilayered of RBBR molecules with the possibility of interactions between these adsorbed molecules.

Table 2: Freundlich parameters of RBBR adsorption onto different masses of NP (30, 50 and 70 mg)

m_{NP} (mg)	30	50	70
$K_f \cdot 10^3$ (mg/g)	4.2	0.9	0.02
m	1.978	2.138	2.669
R^2	0.928	0.946	0.973

3.4. Infrared spectroscopic analysis of the adsorption of RBBR by NP

Figure 11 illustrates the IR spectra (domain 400-1600 cm^{-1}) of NP before adsorption and NP after adsorption of RBBR. A comparison of these spectra shows that absorptions bands of NP are affected by the adsorption of the dye. Indeed, the bands located at 1053 cm^{-1} (associated to PO_4^{3-} ions) and at 871 cm^{-1} (associated to CO_3^{2-} ions) are found, respectively, to be shifted to 1010.7 cm^{-1} and 875 cm^{-1} after adsorption. In addition, there is a decrease in the intensity of band attributed to the phosphate group at 570 cm^{-1} . Therefore, it can be concluded that PO_4^{3-} and CO_3^{2-} groups are involved in the interaction between RBBR molecules and NP surface.

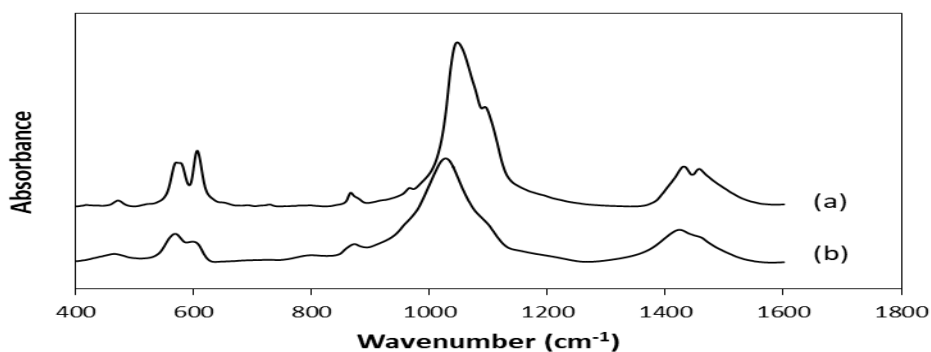


Figure 11: IR spectra of NP before (a) and after (b) adsorption.

3.5 Influence of the mass ratio (NP/RBBR) on adsorption capacity of NP

The influence of the mass ratio (adsorbent/adsorbate) on the adsorption capacity was performed in the RBBR concentration range of 100 to 1000 mg/L. The adsorption capacity also called the removal efficiency (% RE) is given by the following expression:

$$\% \text{ RE} = ((C_i - C_e)/C_i) \times 100$$

Where C_i and C_e are initial and equilibrium concentrations of adsorbate respectively. The evolution of the dye removal efficiency (%RE) as a function of the mass ratio of NP/RBBR is shown in Figure 12. Examination of these results shows that the removal rate of dye by NP reaches 50% for mass ratio NP/RBBR of 0.3.

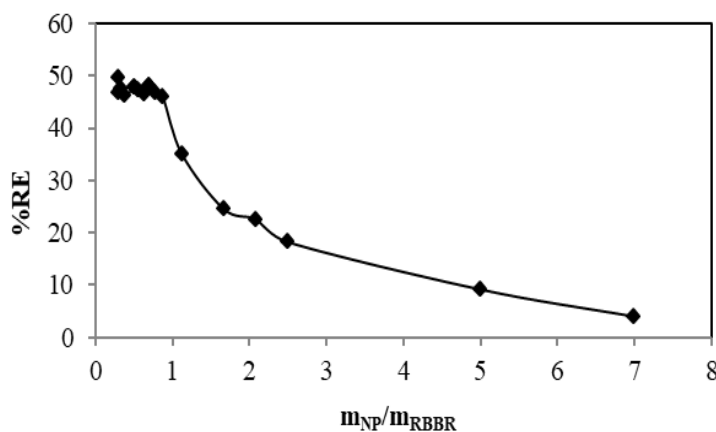


Figure 12: The variation of the removal efficiency (%RE) versus the mass ratio of NP/RBBR.

4. Conclusion

The present study investigated the removal of Remazol Brilliant Blue R dye (RBBR) from aqueous solution by natural phosphate (NP). The results obtained showed that the adsorption is greatly pH dependent. Indeed, we have observed a high uptake of dye onto NP at basic pH and low uptake at relatively acidic pH. The kinetic study shows that the equilibrium is relatively fast. The kinetic of adsorption is a pseudo-second order. It was also shown that the amount of dye adsorbed was high for low mass of adsorbent, and the adsorption process may be governed by « co-operative adsorption » between adsorbed molecules of RBBR. The dye removal rate reaches 50% for a mass ratio (NP/RBBR) of 0.3.

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