



ORIGINAL ARTICLE

Interaction of adsorption of reactive yellow 4 from aqueous solutions onto synthesized calcium phosphate



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Abstract The interaction of reactive yellow 4 with Apatitic Tricalcium Phosphate (PTCa) has been investigated in aqueous medium to understand the mechanism of adsorption and explore the potentiality of this phosphate toward controlling pollution resulting from textile dyes. Transmission electron microscopy (TEM) analysis demonstrates that the adsorbent is composed of needle-like nanoparticles and the SAED pattern exhibits spotted sharp and continuous rings that evidence polycrystalline grains. X-ray diffraction results showed that, the crystallinity of the dye decreased after interaction with RY4 indicating incorporation of the dye into the micropores and macropores of the adsorbent. The results of Fourier transform infrared (FTIR) spectroscopy indicate that the adsorption is due to the electrostatic interaction between the $-\text{SO}_3^-$ groups of dye and the surface of the Phosphate. The desorption efficiency was very high at about 99.4%. The presence of calcium ions favored the adsorption of the dye, while the phosphate ions inhibited it.

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1. Introduction

The problems of water resources and pollution are increasingly on the agenda. Many industries like textile or

cosmetic industry use end products of organic compounds for obtaining particular colors. In Morocco the textile industry, represents 31% of all Moroccan industries whose reactive dyes are widely used for dyeing wool and nylon. In the textile industry, about 1000 l of water is used per 1000 kg of clothes processed in 'dyeing [14]. Thus the this industry releases loaded dyes [26] which present a real danger to the environment due to the high water consumption and the important wastewater discharges are rejected without any treatment. Therefore, many technologies, such as reverse osmosis [8], nanofiltration [18], coagulation and precipitation [28],

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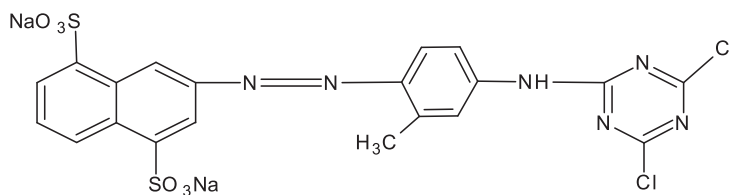
electrodialytic membrane technologies [6] and adsorption [1] are proposed for controlling the concentrations of dye in rejected wastewater discharges.

Among the above technologies, adsorption is a common technique used for dye removal from aqueous solution, mainly because it is relatively low in cost, environmental friendly and simple. Recently, calcium phosphates are very much studied in the removal of heavy metal ions [20], fluoride [21–23], dyes [10,11,5] and amino acids [12,13].

Germany) in 1300 ml of distilled water + 20 ml ammonia solution). The precipitate was filtered, washed, and dried at 80 °C for 24 h.

2.2. Adsorbate

The Reactive Yellow 4 (C.I) was obtained from a textile firm as a commercially available dye formulation and was used without further purification. It is a soluble dye in water due to the presence of two solubilizing groups (SO_3H).



Chemical structure of dye (C.I. Reactive Yellow 4).

In our laboratory, the work is in process to evaluate the possibility of the use of synthetic calcium phosphates for wastewater pollution management. Our previous study has shown that the synthesized calcium phosphates can remove the reactive dye; Reactive Yellow 4, from aqueous solutions [10]. The aim of the present study was to determine the mechanism of interaction for the removal of an azo reactive dye, Reactive Yellow 4 (CI) from aqueous solutions by synthesized Apatitic Tricalcium Phosphate (PTCa).

2. Materials and methods

2.1. Adsorbent

The PTCa was prepared at room temperature by a double decomposition method [15]. The solution A (47 g of calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Scharlau, Spain) in 550 ml of distilled water + 20 ml of ammonia solution) was added quickly at room temperature into the solution B (26 g of di-ammoniumhydrogenphosphate $(\text{NH}_4)_2 \text{HPO}_4$ (Riedel-de Haën,

The yellow color is due to the grouping diphenylparazolo-nique. The grouping dichlorotriazinique ensures reactivity of the molecule with the textile fiber. The solutions were prepared by dissolving the required amount of dye in distilled water. The concentration of the dye was determined at 385 nm, using UV spectrophotometer (“UV-2005”, Selecta, Spain).

2.3. Effect of pH on the analysis of dye

We carried out by absorption UV/VIS, a study of electron delocalization in the molecules of the dye to see if the pH has an effect or not on the electronic transition of the dye molecules. The procedure is as follows: In a series of flasks containing 100 ml dye 10 mg/L, pH is varied from 1.56 to 12. The acidification or alkalization of colored solutions is made respectively by HCl or NaOH at various concentrations. The mixture is stirred at room temperature and then absorbance is measured as a function of wavelength 300–800 nm.

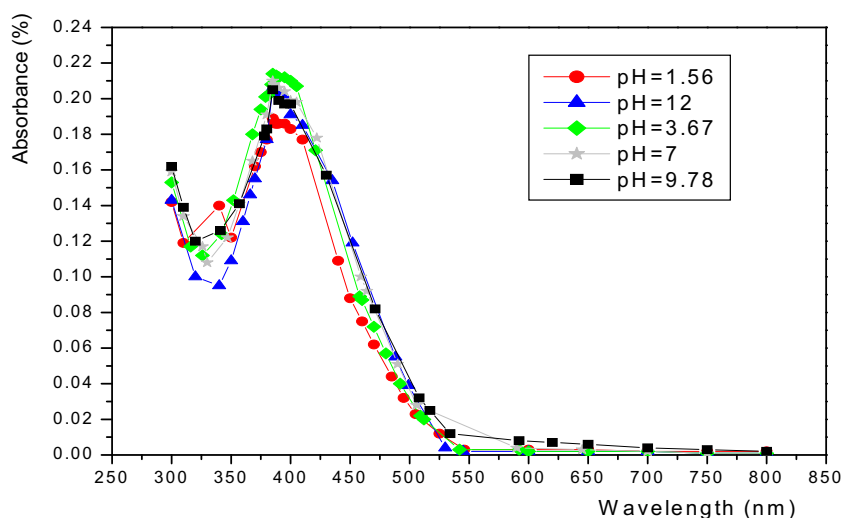


Figure 1 absorption spectrum of an aqueous solution of the dye (RY4) 10 mg/L.

2.4. Characterization of the adsorbent

The phosphate was characterized by chemical and physical analysis. The calcium content in the solid was determined by complexometry with EDTA and the phosphate ion content by spectrophotometry of phosphovanadomolybdic acid. The specific surface area was determined according to the BET method using N_2 adsorption. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis have been performed using an FEI Tecanai G2 (Philips) (120KV). An FTIR spectrum of the samples has been characterized using VERTEX 70/70v FT-IR spectrometers. An X-ray powder diffraction (XRD) pattern has been analyzed using Siemens D-500 (Germany) X-ray diffractometer with $Cu K\alpha$ radiation.

To understand the adsorption mechanism, it is necessary to determine the point of zero charge of the adsorbent.

The pH of the zero point charge (pH ZPC) has been determined by placing 0.2 g of PTCa glass stopper bottle containing 20 mL of 0.01 M NaCl solutions. The initial pH of these solutions has been adjusted to 4, 4.8, 5.1, 5.27, 5.4, 6, 6.5, 8.05, and 10.5 by either adding 0.1 M NaOH or 0.1 M HCl. The bottles have been placed in an incubator shaker at 25 °C for 48 h, and the final pH of the supernatant has been measured. The $\Delta pH = pH(\text{final}) - pH(\text{initial})$ has been plotted against the initial pH, the pH at which ΔpH was zero was taken as the pH of ZPC.

2.5. Effect of pH on the adsorption of dye

To study the influence of pH on the adsorption capacity of PTCa, experiments were performed using various initial pH varying from 1.65 to 11.85.

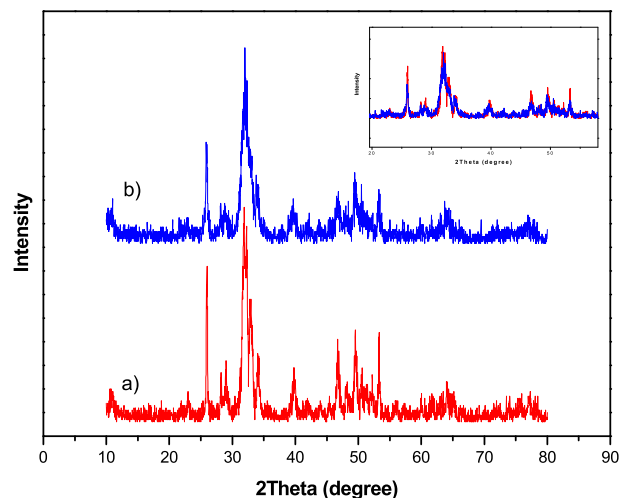


Figure 3 XRD patterns of (a) PTCa before adsorption and (b) PTCa after adsorption of RY4.

3. Results and discussion

3.1. Effect of pH on the analysis of dye

The results of dye solution studies indicated that change of the initial pH of dye solution has negligible effect on the $\lambda_{\text{max}} = 385 \text{ nm}$ (Fig. 1), but we observe a change in absorbance; this variation may be due to the dilution of the dye. This observation provided proofs that, at this range of pH, there is not any chemical structural change of dye molecules [2,3].

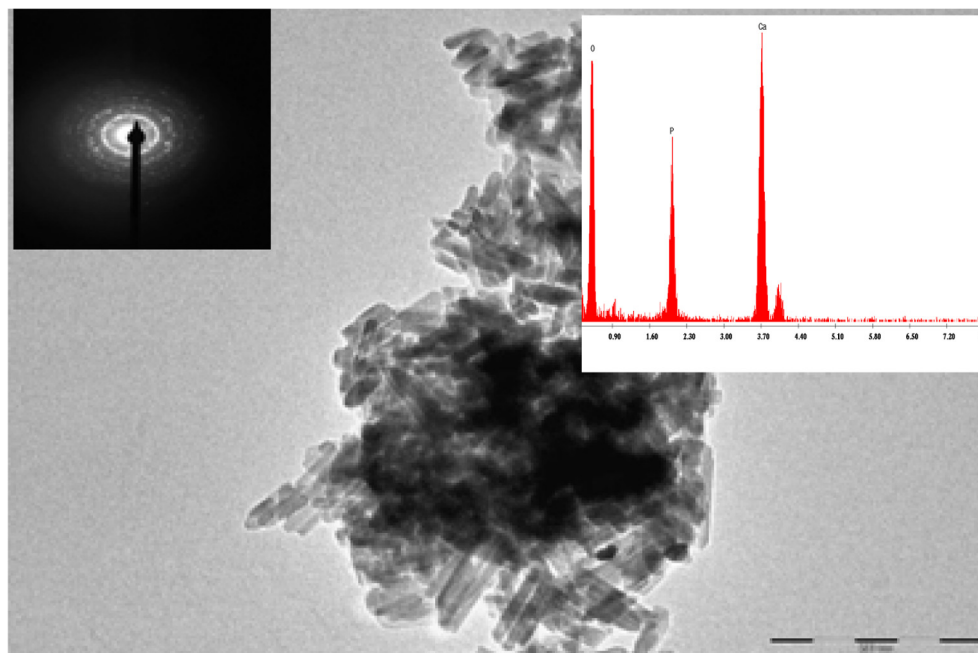


Figure 2 TEM images, SAED patterns and EDX analysis of PTCa.

3.2. Characterization of the adsorbent

Chemical analyses showed that Ca/P molar ratio was 1.5 ± 0.01 . The specific surface area of the synthetic apatite was $62 \text{ (m}^2\text{/g)}$. In Fig. 2 TEM image and SAED (selected area electron diffraction) patterns of all samples are presented. It resulted that samples are composed of needle-like nanoparticles of length 50–100 nm and width 8–20 nm. SAED pattern exhibits spotted sharp and continuous rings that evidence polycrystalline grains.

A study of the elements present in the synthesized PTCa was performed by spectroscopy of X-ray energy dispersion (EDX) coupled to a transmission electron microscope. This analysis shows that there was no foreign element present in the PTCa.

X-ray diffraction patterns of PTCa (Fig. 3a) showed reflections characteristic of poorly crystalline apatite, no other phase was detected. The overlapping reflections indicate its low crystallinity. No structural changes of PTCa were detected by the powder X-ray diffraction analysis of the solid obtained after

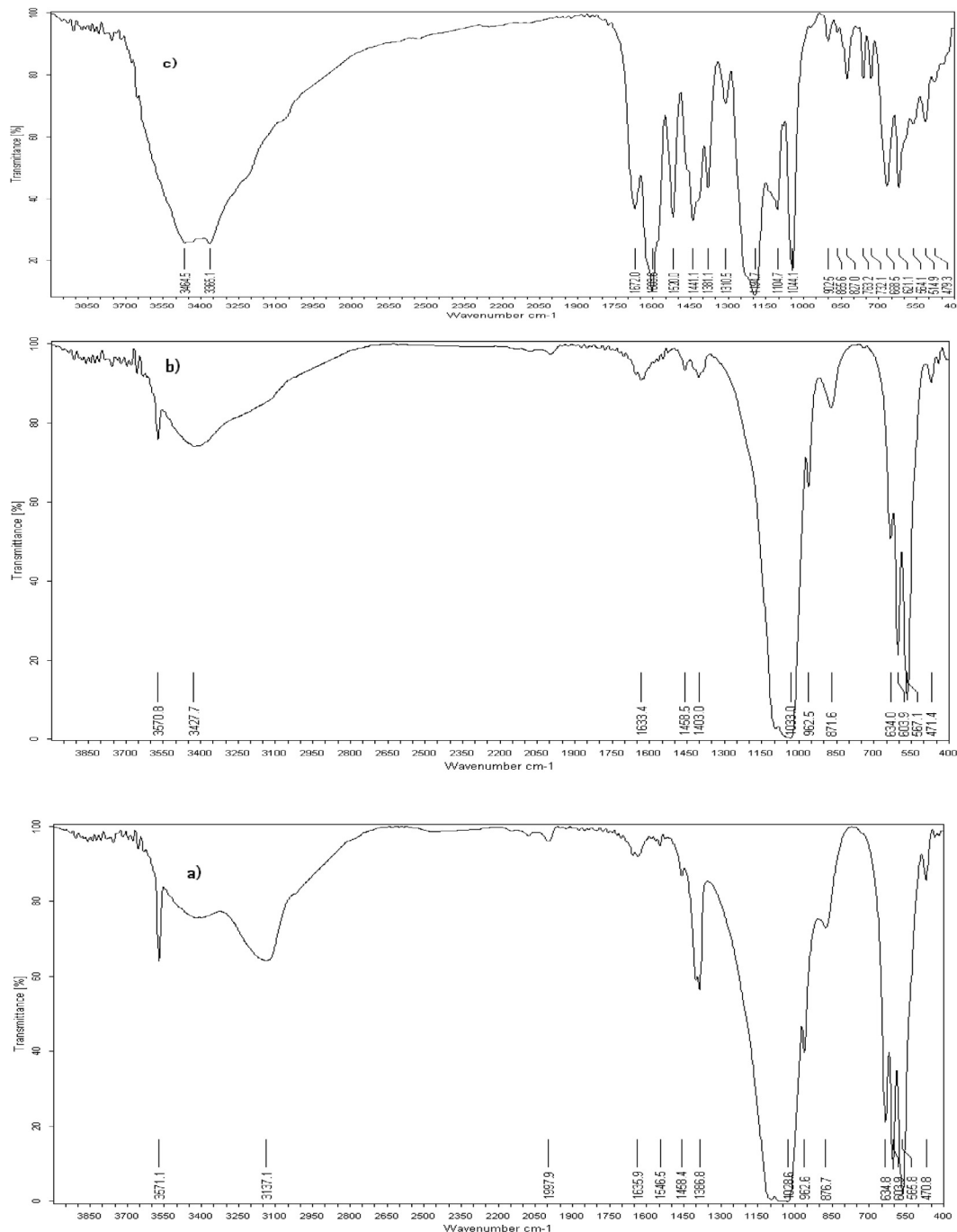


Figure 4 FTIR spectra: (a) PTCa before adsorption, (b) PTCa after adsorption of RY4 and (c) RY4.

interaction of PTCa with dye solution (Fig. 3b). In addition, the intensity of XRD pattern was apparently lower than that of the original PTCa, which showed the degree of crystallinity decreased after adsorption of the dye. These decreases may be due to the incorporation of dye into the micropores and macropores of the adsorbent [17], the dye molecules entered in the crystalline region and interrupted its continuity and also may be ascribed to the inherent disorder introduced by the adsorption process [16].

The PTCa prepared (Fig. 4a) shows characteristic bands of Apatitic Tricalcium Phosphate. On see bands PO_4^{3-} vibration groups in surrounding apatite located at 470.8, 565.8, 603.9, 962.6 and 1028.6 cm^{-1} . We also note the presence of characteristic bands of hydroxide ions OH^- at 3571.1 cm^{-1} . The band located at 876.7 cm^{-1} associated with HPO_4^{2-} ions due to the stretching vibration of the link PO (H), confirms that it is a deficient apatite. The bands located at 1635.9 and 3137.1 cm^{-1} [4] are assigned to the vibration of the hydroxyl group in water. The band located to 1386.8 cm^{-1} is assigned to nitrate groups resulting from synthesis residuals [9].

The FTIR spectrum of PTCa-RY4 (Fig. 4b) described a number of alterations in the band position compared with the PTCa before adsorption. Transmittance at wave number 3571.1 cm^{-1} is found to be shifted to 3570.8 cm^{-1} on adsorption and this may be responsible for the chemical interaction of the dye with O-H groups on the PTCa. The disappearance of the band at 1546.5 cm^{-1} observed in the dye adsorbed PTCa indicates chemical interactions involving the dye on the PTCa. Transmittance at wave number 1028.6, 962.6, 565.8 and 470.8 cm^{-1} is found to be shifted to 1033.0, 962.5, 567.1 and 471.4 cm^{-1} respectively on adsorption and this may be responsible for the chemical interaction of the dye with PO_4^{3-} groups on the PTCa. Transmittance at wave number 876.7 cm^{-1} is found to be shifted to 871.6 cm^{-1} on adsorption and this may be responsible for the chemical interaction of the dye with HPO_4^{2-} groups on the PTCa. Moreover, there is a decrease in intensity of bands characteristic of PTCa (at 470.8, 565.8, 603.9 and 962.6 cm^{-1} characteristic of PO_4^{3-} groups, at 3571.1 cm^{-1} characteristic of OH^- , at 876.7 cm^{-1} associated

with HPO_4^{2-} ions) after adsorption of RY4. Generally, the intensity of these bands decreases. These facts clearly supported the suggestion that the introduction of dye decreased the degree of crystallinity of PTCa and was consistent with the XRD results.

3.3. Effect of pH on the adsorption of dye

The pH is the most important factor affecting the adsorption process. The adsorbate and adsorbent may have functional groups, which are affected by the concentration of hydrogen ions (H^+) in the solution which are involved in molecular adsorption process at the active sites of the adsorbent. To study the influence of pH on the adsorption capacity of PTCa, experiments were performed using various initial pH varying from 1.65 to 11.85 Fig. 5. shows the effect of pH on the adsorption of reactive yellow 4 by PTCa, with initial concentration of 100 mg/L and a mass of PTCa of 200 mg/L. It was observed that the adsorption is highly dependent on the pH of the solution, the adsorption of RY4 decreased with increasing pH these results can be interpreted by; the point of zero charge pHPZC of the PTCa is found to be 5.6. Hence, for pH values higher than 5.6, the surface of the PTCa becomes negatively charged and the opposite for pH values lower than 5.6. Moreover, the dye is an anionic molecule; the high adsorption capacity is due to the strong electrostatic interaction between the positively charged surface of PTCa and $-\text{SO}_3^-$ groups of dye. A lower adsorption at higher pH may be due to the ionic repulsion between the negatively charged surface of adsorbent and $-\text{SO}_3^-$ groups of the dye. Similar behavior has been observed by Mourabet et al. [22].

3.4. Desorption experiments

Desorption is a phenomenon where by a substance is released from or through a surface. This study was performed to assess the regeneration capacity of the adsorbent for reuse in a more economic manner. The recycling of an adsorbent is most

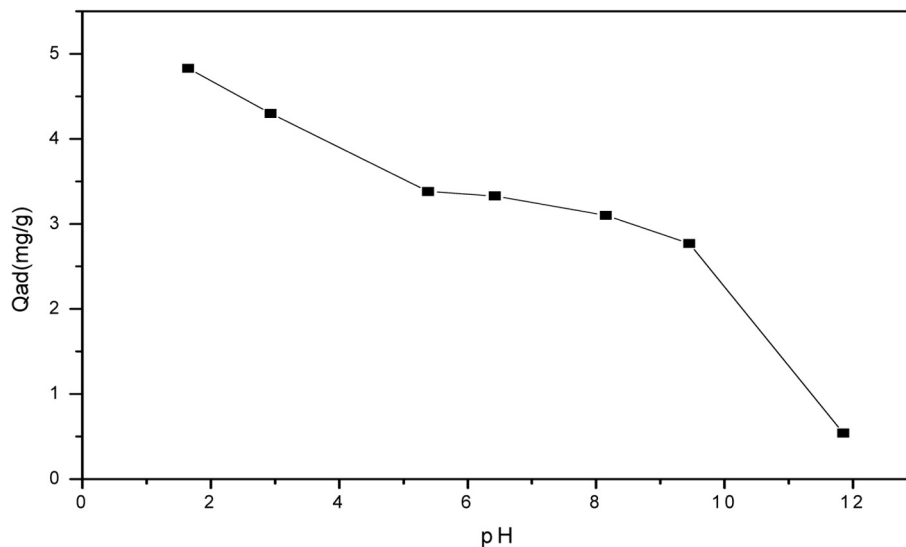


Figure 5 Effect of pH on the adsorption of Reactive Yellow 4 on PTCa. (Solid quantity: 200 mg, initial dye concentration: 100 mg/l, stirring time: 1 min, contact time: 6 h).

important aspect for an economical technology. For this purpose, first, the dye-adsorbed PTCa is generated by adsorbing 100 mg/L dye solution on 0.2 g PTCa at 25 °C. After the equilibration, the residue was filtered and the filtrate was measured for dye content. Then the solution was filtered and the adsorbent was transferred to 10 mL of distilled water with varying pH (2.5, 5.63, 8.9 and 12). The solutions were then shaken for about 60 min after which the dye amount desorbed into the solution was determined to calculate the removal extent (percent). The ratio of desorption was calculated using the relation:

$$\text{Desorption (\%)} = (C_{\text{des}}/C_{\text{ads}}) \times 100$$

where: C_{des} and C_{ads} are respectively the desorbed and adsorbed concentrations of the dye (mol/l).

It was observed (Fig. 6) that at pH 2.5, 5.63, 8.9 and 12 around 6%, 10%, 12.9% and 99.4% desorption efficiency was found respectively. The desorbed amount of dye increased continuously with the increasing initial pH values. The reason for this behavior can be explained, as follows: under strong basic (high pH) conditions, the number of negatively charged sites increases. These negatively charged sites on the adsorbent surface may favor the desorption of the dye due to electrostatic repulsion [24,27]. The desorption efficiency of PTCa is very high,

more than 99% at pH = 12. However, it is noted that the PTCa can be regenerated easily by shifting the solution pH. Considering the commercial adsorbents, such as activated carbons which are not very easy to be regenerated [25], apatitic tricalcium phosphate has great potential as a reusable dye adsorbent.

3.5. Effect of ions on adsorption

We studied the effect of Ca^{2+} and HPO_4^{2-} ions on the adsorption process of Reactive yellow 4. The experiments were examined by the addition of varying mass (2, 4, 10 and 20 mg) of calcium chloride CaCl_2 or potassium phosphate KH_2PO_4 . The initial dye concentration is 100 mg/L and the mass of Apatitic Tricalcium Phosphate is 200 mg at initial pH.

Fig. 7 shows that the adsorption of Reactive yellow 4 was influenced by the addition of these ions. Indeed, the addition of Ca^{2+} ions increases the adsorption (Fig. 7a), while the addition of orthophosphate ions decreases it (Fig. 7b), this decrease is more important as the content of PO_4^{3-} ions is higher. This is interpreted by the fact that the ions PO_4^{3-} enter in competition with the group -SO_3^- of dye molecules to interact with Ca^{2+} ions on the surface of phosphate, a similar result was observed by Mahmoodi et al. [19,7].

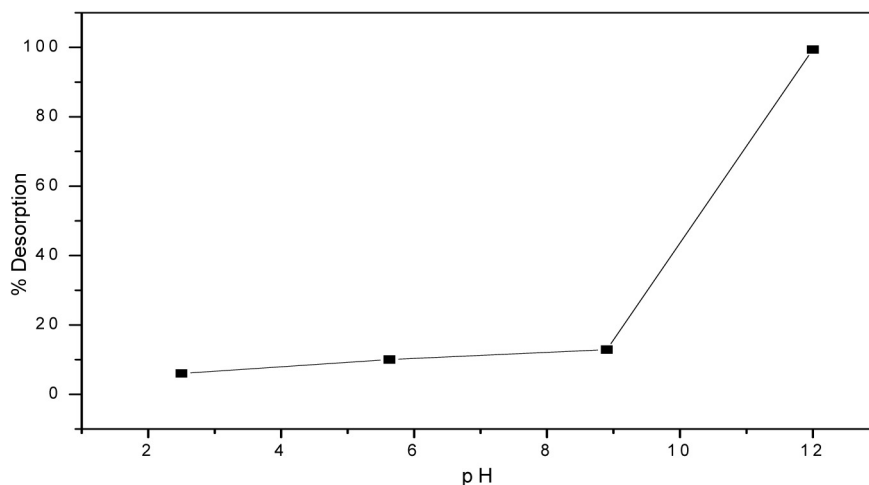


Figure 6 Effect of pH on the desorption of RY4 at 25 °C.

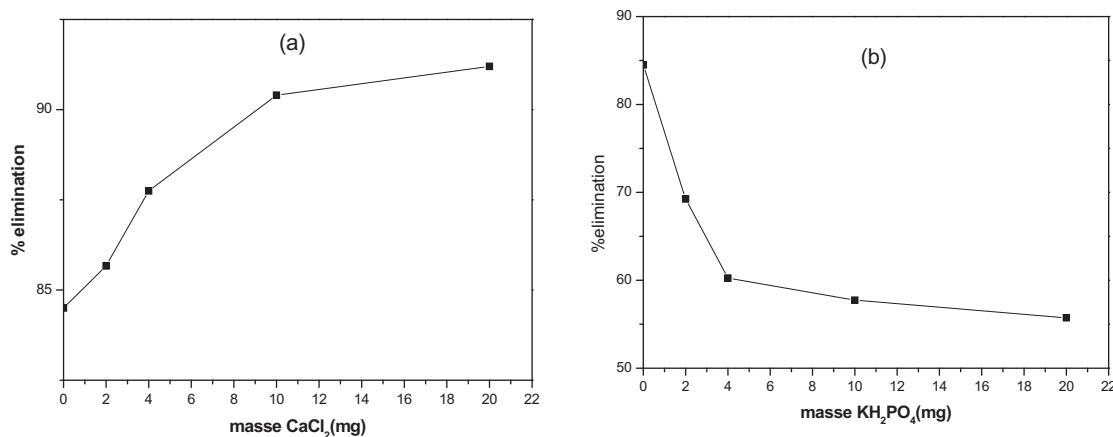


Figure 7 Effect of (a) CaCl_2 and (b) KH_2PO_4 on the adsorption of reactive yellow 4 ($C = 100$ mg/L).

4. Conclusion

The present study shows that reactive yellow 4 can be removed from dye bearing effluent in an eco-friendly way using Apatitic Tricalcium Phosphate (PTCa), an agro waste as adsorbent. The adsorption is greatly pH dependent, with a high uptake of dye at low pH and low uptake at high pH. The adsorption of the dye molecule on the PTCa may be attributed to physical forces e.g. hydrogen bonding, van der Waals interactions etc. operating between the dye molecule and the surface of PTCa. The desorption efficiency is 99%, 4% at pH 12. The interaction of Reactive yellow 4 with apatitic phosphate was influenced by the addition of Ca^{2+} and orthophosphate ions. Finally, the use of the PTCa shows a greater potential for the removal of reactive textile dyes, the main advantages; easy to prepare in large scale and low-cost due to easy regeneration of the adsorbent.

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