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Adsorption of a textile dye on synthesized calcium deficient hydroxyapatite (CDHAp): Kinetic and thermodynamic studies

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Abstract
The adsorption of a reactive dye, Reactive Yellow 4 (RY4), from aqueous solution onto synthesized calcium deficient hydroxyapatite (CDHAp) was investigated. The adsorption kinetics was investigated using the parameters such as contact time, adsorbent quantity, initial dye concentration, initial pH, ionic strength, and solution temperature. The adsorbent has been characterized by pHzpc measurement, chemical analyses, FTIR, XRD and TEM. The kinetic study shows that equilibrium is quick. The kinetic data were best described by the pseudo second-order model (R2= 0.9999). The adsorption equilibrium was modeled by the Langmuir and Freundlich equations using linear and non-linear regression. The Langmuir model was found to be the best to describe the equilibrium isotherm data, with a maximum adsorption capacity of 51.08 $mg.g^{-1}$**.** In addition, the results showed that acid pH is favorable for the adsorption of dye, the introduction of Ca^{2+} ions in the medium favors the adsorption and the maximum of adsorption decreases with increasing temperature from 298 to 318 K. Thermodynamic studies indicated that the dye adsorption process by calcium deficient hydroxyapatite (CDHAp) was physisorption, spontaneous and exothermic in nature. The results indicate that the adsorption is due to the electrostatic interaction between the sulphonic groups–SO^{3-} of dye and the $PO_4$3- ,$Ca^{2+}$and OH- groups in the surface of the Phosphate. Finally, Compared to adsorption experiments on other adsorbents, the results show that the calcium deficient hydroxyapatite (CDHAp) is an efficient adsorbent for Reactive Yellow dye.

Keywords: Adsorption kinetics; CDHAp; Reactive dye; Equilibrium.

1. Introduction
Many industries such as textile, paper, plastics and dyestuffs consume substantial volume of water and also use chemicals during manufacturing and dyes to color their products. As a result, they generate a considerable amount of polluted wastewater [1-2]. Reactive dyes are extensively used in textile industry, fundamentally due to the ability of their reactive groups to bind to textile fibers through covalent bonds [3]. In Morocco the textile industry, representing 31% of all Moroccan industries whose the reactive dyes are widely used for dyeing wool and nylon. In the textile industry, about 1000 liters of water are used per 1,000 kg of clothes processed in dyeing [4]. The presence of these species in wastewater, ever at very low quantities, is highly visible and undesirable; their presence in aquatic systems reduces light penetration, which retard photosynthetic activity and also has a tendency to chelate metal ions producing microtoxicity to fish and other organisms [5] . Various treatment processes such as ozonation, coagulation, ultrafiltration, oxidization, electrochemical, photocatalytic degradation and adsorption have been widely investigated to remove dyes from wastewaters.
Due to the biological and chemical stability of dyestuffs in a number of conventional water treatment methods, adsorption is considered as an attractive and favorable alternate for the removal of dyes and other chemicals from wastewater streams.

In recent years, a wide variety of materials such as smectite-rich clayey rock [6], Sorel's cement [7], sepiolite [8], activated carbon [9], kaolinite [10] and cashew nut shell [11] are used to remove various types of dyes.

Calcium hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$, is an important inorganic material , their characteristic to establish bonds with organic molecules of different sizes, have conferred to this material to attract more attention . Moreover, calcium phosphate has been widely used as adsorbents for the adsorption and separation of biomolecules [12-14], for the removal of heavy metals [15-17] and for the removal of dyes [18-23]. Only the hydroxyapatite of ratio 1.67 is stoichiometric [$Ca_{10}(PO4)_6(OH)_2$], the other apatites are called calcium-deficient hydroxyapatites (CDHA). Several chemical formulas have been proposed for calcium-deficient hydroxyapatite [24]. An example of a proposed formula is:

$$Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x} \quad (0 < x < 1).$$

In the case x = 1 (the boundary condition with Ca/ P = 1.5), the chemical formula of CDHA looks as follows: $Ca_9(HPO_4)(PO_4)_5(OH)$.

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 Reactive Yellow 4 (RY4), from aqueous solutions [21] .In this work, we are interested in the possibility of using Calcium deficient hydroxyapatite (CDHAp) in order to eliminate the textile dye: Reactive Yellow 4 (RY4), from aqueous solutions. The effect of various parameters like, adsorbent amount, dye concentration, contact time, pH and temperature, kinetics, equilibrium and thermodynamic studies were investigated.

Furthermore the characterizations of CDHAp have been donned by using XRD analysis, Transmission electron microscopy (TEM) and FTIR spectroscopy.

2. Materials and methods

2.1. Materials

2.1. 1. Adsorbent

2.1. 1. a. Synthesis of the adsorbent

The adsorption tests were conducted on Hydroxyapatite (HAp). The HAp was obtained by double decomposition method. The solution A (26g of di-ammoniumhydrogenphosphate $(NH_4)_2HPO_4$ (Riedel-de Haën, Germany) dissolving in 1300ml of distilled water) of phosphate and 1500ml of ammonia solution was added quickly using a peristaltic pump in the solution B (47g of calcium nitrate Ca $(NO_3)_2$.4 H_20 (Scharlau, Spain) dissolving in 550ml of distilled water) boiled ,with a constant speed to 150tr/min.The presence of ammonia in excess is necessary for have a basic medium (PH=9). Once the addition is complete, the preparation was kept at boiling and stirring about 1/2 hour.

The precipitate was filtered hot on a Buchner, washed with a solution (1000ml of distilled water and 1000ml ammonia solution), and dried at 353 K for 24 hours.

2.1. 1. b. Characterization of the adsorbent

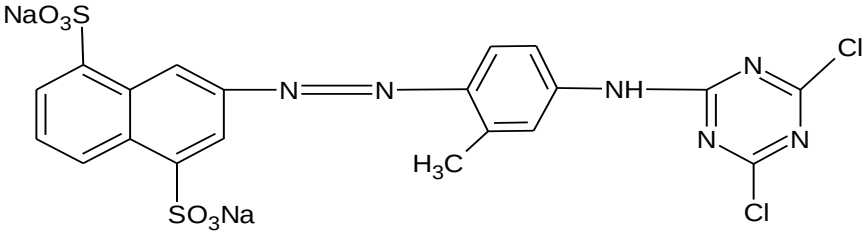
The HAP Particles were analyzed by Fourier transform infrared (FT-IR) spectroscopy (VERTEX 70/70v FT-IR spectrometers).An X-ray powder diffraction (XRD) pattern was analyzed using X'Pert PRO (Germany) X-ray diffractometer with Cu Ka radiation. The Size and morphology of the prepared HAP were investigated by Tecnai G^2 (Philips CM120, USA) Transmission electron microscope (TEM). The calcium content of the solid was determined by complexometry with EDTA (ethylene-diamine-tetraacetic acid) and the phosphate ion concentration was obtained by spectrophotometry of phospho-vanado-molybdic acid. The specific surface area was determined according to the BET (Brunauer–Emmett–Teller) method using N_2 adsorption.

The pH of the zero point charge (pH ZPC) has been determined by placing 0.2 g of adsorbent in glass stopper bottle containing 20 mL of 0.01 M NaCl solutions. The initial pH of these solutions has been adjusted by either adding 0.1 M NaOH or 0.1 M HCl. The bottles have been emplaced incubator shaker at 298K for 24 h, and the final pH of supernatant has been measured. The ΔpH=pH (final) −pH (initial) have been plotted against the initial pH, the pH at which ΔpH was zero was taken as a pH ZPC.

2.1. 2. Adsorbate

The Reactive Yellow 4 (RY4) 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 (SO3H). The structure and characteristics of this dye are illustrated in Table1.

Table 1 Structure and characteristics of RY4.

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
Molecularweight(g/mol)	613.36

The yellow color is due to the grouping diphenylparaazolonique. The grouping dichlorotriazinique ensures reactivity of the molecule with the textile fiber.

The solutions ware prepared by dissolving the required amount of dye in distilled water .The concentration of the dye was determined at 385nm, using UV spectrophotometer ("UV-2005", Selecta, Spain).

2.2. Experimental Protocol

To study the kinetics of adsorption of the dye at 298 K, a volume of 10 ml of the dye at concentration 100 mg/L was placed in contact with 200 mg of 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 quantity of dye per which was fixed gram of adsorbent was given by the following equation:

$$Q_t = (C_0\text{-}C_t)\ V/m \qquad (1)$$

Where:

-Q_t: the quantity of dye in mg per gram of adsorbent (mg/g).

-Co and Ct: are respectively the initial and equilibrium concentrations at time t of dye (mg/L).

-V: volume of solution (L).

-m: mass of adsorbent used (g).

The percentage of dye removal was calculated from the relation-ship:

$$\%\ of\ dye\ removal = ((C_0\text{-}C_t)\ /C_0\ )) \times 100 \qquad (2)$$

C_0 and C_t : are respectively the initial concentrations and in the time t of the dye (mg/L).

The classical models of Langmuir and Freundlich characterizing the formation of a monolayer are used for their simplicity of implementation.

Thus the Langmuir equation [25] allowed us to determine the characteristic parameters of adsorption, namely the amount adsorbed at saturation Q∞ and the constant interaction adsorbate-adsorbent b.

$$Q_{ads} = Q_\infty b\ C_{eq}/\ (1+bC_{eq}) \qquad (3)$$

and linearized equation:

$$C_{eq}\ /Q_{ads} = 1/\ (bQ\infty) + C_{eq}\ /\ Q_\infty \qquad (4)$$

Freundlich's law is a purely empirical relationship [26] :

$$Qads = K_F\, Ce^{1/n} \qquad (5)$$

Qads: the quantity of substance adsorbed per unit area (or mass) of adsorbent.
Ce: concentration of adsorbate in solution at equilibrium.

The parameters K_F and 1/n characterize the adsorbent-adsorbate pair.

The linear transform of this equation is:

$$\ln(Qads) = Ln\,(K_F) + 1/n\ \ln(Ce) \qquad (6)$$

The variation of ln (Qads) versus ln (Ce) allows to determines K_F and 1/n. It should be noted that when the amount adsorbed is very low, it is generally the Freundlich's law that describes mode of adsorption. For a high recovery rate, it is the law of Langmuir which allows describing this process.

3. Results and discussion

3.1. Characterization of the adsorbent

In Fig.1 TEM image and SAED (selected area electron diffraction) patterns of a sample are presented. It resulted that sample are composed of needle-like nanoparticles of length 30–100 nm and width 10–20 nm. SAED pattern exhibit spotted sharp and continuous rings that evidence polycrystalline grains. A study of the elements present in the CDHAp synthesized was carried out by using energy-dispersive X-ray spectroscopy (EDX) coupled to a transmission electron microscopy. This analysis shows that there was no foreign element present in the CDHAp.

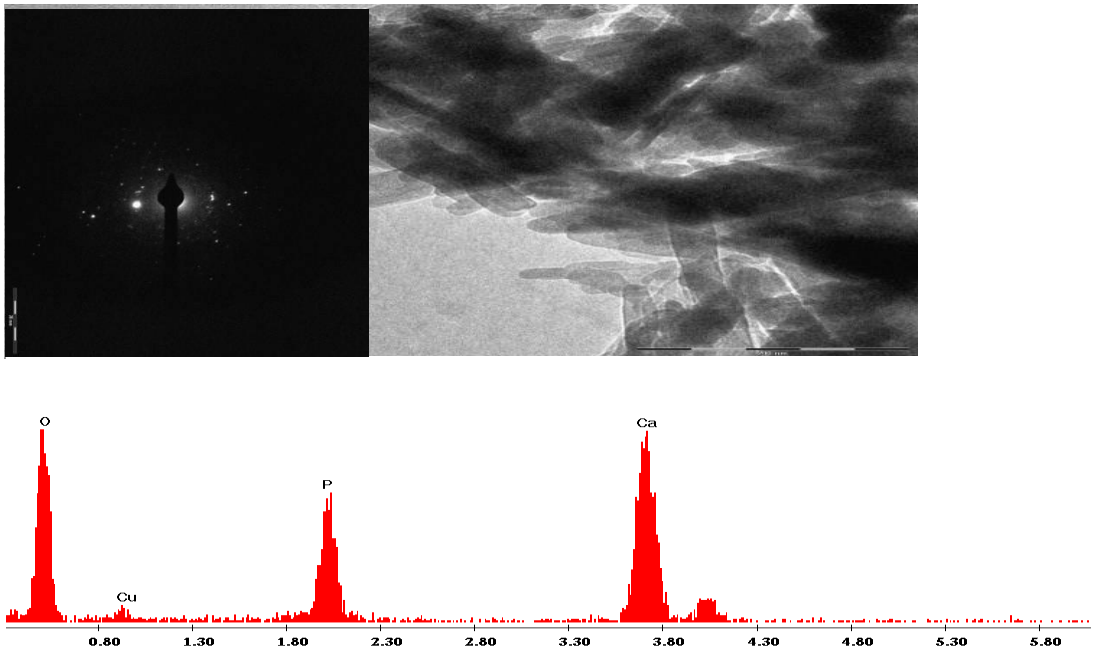


Figure 1: TEM image SAED and EDX analysis of CDHAp.

The IR spectrum (**Figure 2)** shows all characteristic absorption peaks of hydroxyapatite**.** The first indication of the formation of hydroxyapatite is in the form of a broad band centered at approximately 1000-1100 cm -1 **[27].** The bands at 962.3 ,604.6 and 566.5 cm^{-1} correspond to symmetric stretching vibration v1 and v4 P-O of PO43- **ions,** respectively **[28] .**The band at 422.1 cm -1 corresponds to P-O symmetric vibration **[29]** ions PO43- **.** The band characteristic of ion **$HPO4^{2-}$** (**875.5** cm^{-1}**)** is also present in the spectrum. Bands allocated to the stretching vibration of hydroxyl (OH) groups in the hydroxyapatite (**3571.2**, 632.5 and 471.9 cm -1) **[27, 28]** are clearly observed in the spectrum. The band at 1545.2 is due to CO_3^{2-} **.**The bands at 1633.9 and 3431cm^{-1} are assigned to the vibration of the hydroxyl group in water **[30]**. Observed in the spectrum at 1384.2 cm^{-1} band could possibly be attributed to residual NH4+ ions **[31].**

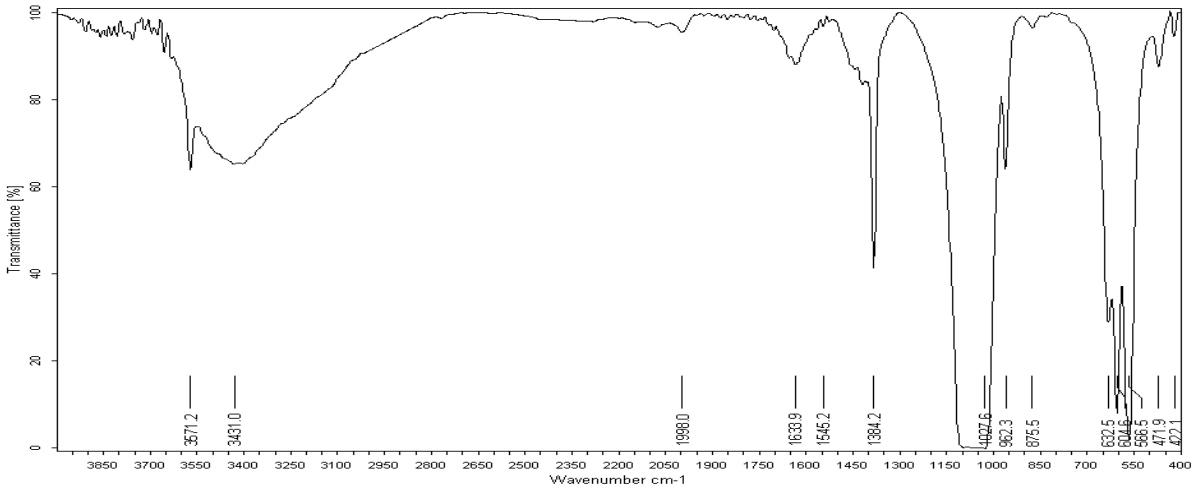


Figure 2: Infrared transmission spectrum of CDHAp.

The spectrum of X-ray diffraction of the prepared powder is shown in Figure 3. The spectrum of the synthetic sample is in good agreement with the reference model of pure hydroxyapatite (JCPDS no. 09-0432), and no characteristic peaks of impurities, such as calcium hydroxide and calcium phosphate, were observed, which means that the samples of phase-pure HAP. The precipitate yielded broad and overlapping reflections, indicating its low crystallinity.

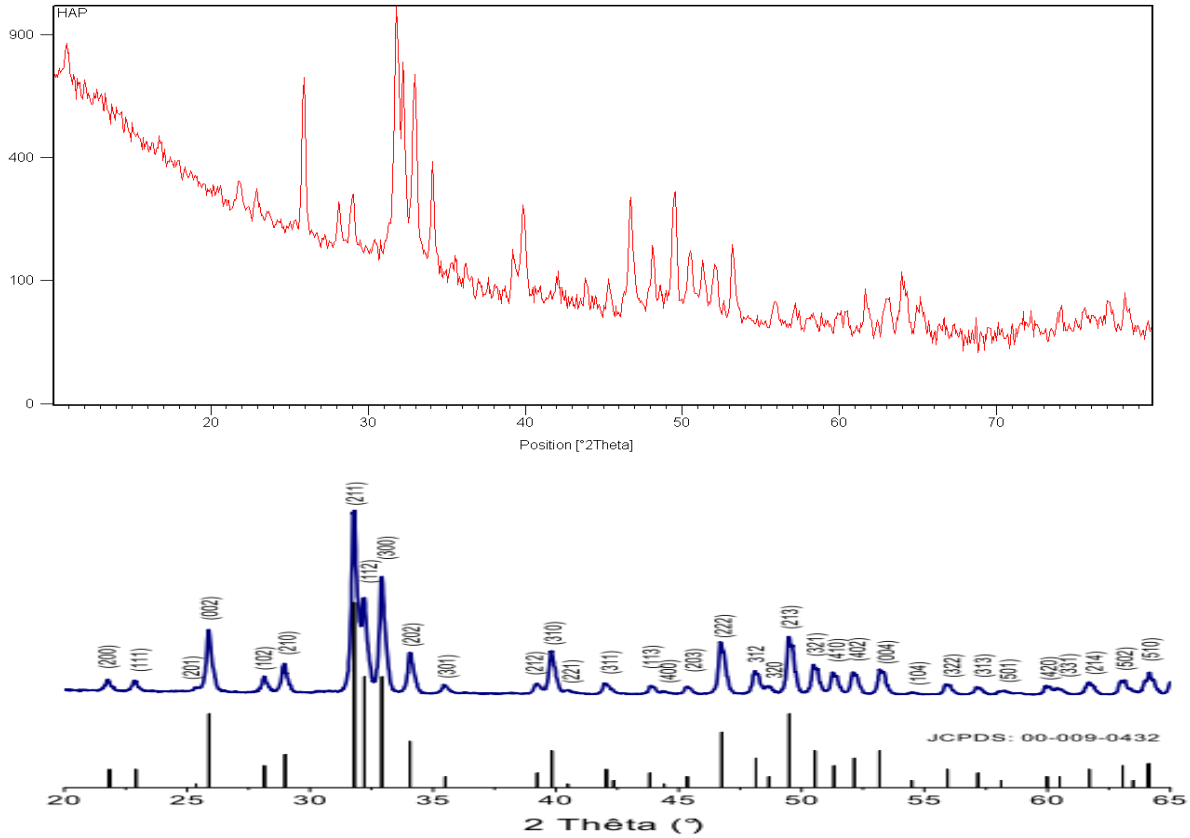


Figure 3: XRD pattern of CDHAp and of pure hydroxyapatite (JCPDS no. 09-0432).

The Chemical analyses showed that Ca/P ratio was 1.60 ± 0.01, which is lower than that of stoichiometric hydroxyapatite (1.67). This finding is in agreement with the presence of hydrogenophosphate groups as observed in the IR spectra. This calcium deficient hydroxyapatite (CDHAp) can have the chemical formula:

$Ca_{9.6}(PO_4)_{5.6}(HPO_4)_{0.4}(OH)_{1.6}$ (x = 0.4 for Ca/P = 1.60).

The specific surface area of the precipitate was determined according to the Brunauer, Emett and Teller (BET) method using nitrogen adsorption. It is about 137 m^2/g.

We traced the evolution of the ΔpH (= pH (final) - pH (initial)) according to the initial pH adjusted. The pH ZPC of the CDHAp was found to be 6.2 (Fig.4). When pH is lower than 6.2, the surface of CDHAp becomes positively charged and the opposite for pH values higher than 6.2, the surface becomes negatively charged.

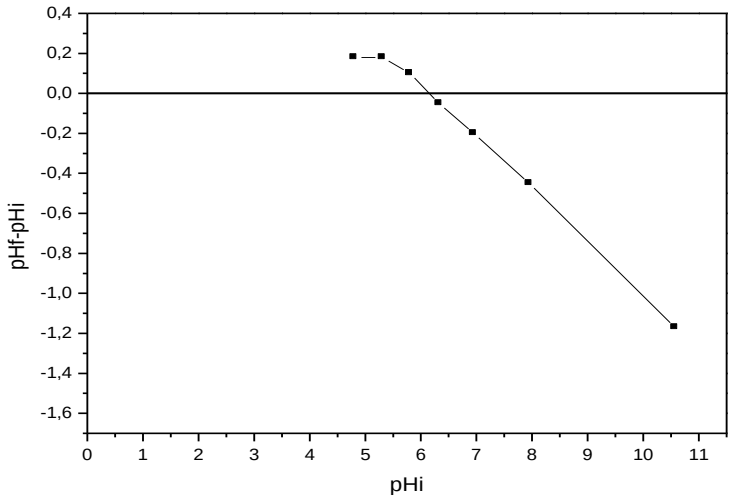


Figure 4: evolution of pHf- pHi versus pHi of CDHAp.

3.2. Effect of solid quantity

The effect of solid quantity on the removal of Reactive Yellow 4 (RY4) was investigated in batch experiments by adding various amount of adsorbent in the range of 0.05–0.4g powder into a test tube containing 10mL of dye solution. The initial dye concentrations of the solutions were fixed at 100mg/L, for all batch experiments. The suspension was then stirred for 1 min and then placed in water batch 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. Results are shown in Fig.5.

As indicated, 33.7 % of RY4 were removed at the initial quantity of 0.05 g of CDHAp. The removal of dye increased with increasing solid quantity up to 0.2 g and reached to 91%, at this quantity. So, 0.2 g was considered as the optimum dose and was used for further study.

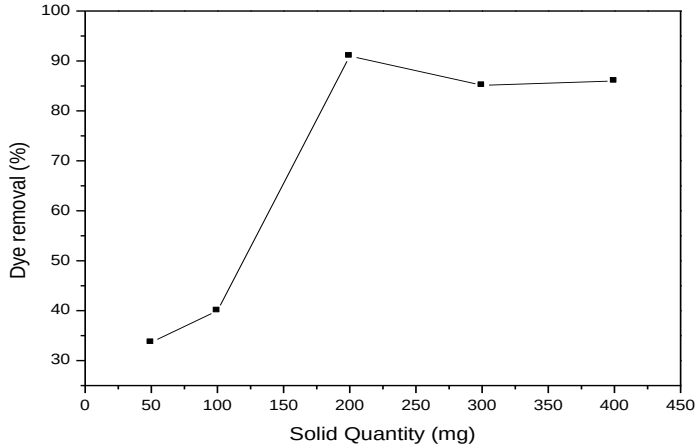


Figure 5: Effect of adsorbent dosage on the removal of RY4 on CDHAp (initial dye concentration: 100mg/L, stirring time: 1min , at 298 K).

3.3. Effect of pH on Dye adsorption

The pH of de medium is the most critical parameter affecting the adsorption processes in the removal of dyes .The adsorption of RY4 on CDHAp powders was studied at different initial pH between 4 and 12.4 (The initial pH of solutions has been adjusted by either adding 0.1 M NaOH or 0.1 M HC). Fig.6 shows the effect of the initial solution pH on the RY4 adsorption onto CDHAp powders .It is clear to see that the adsorption capacity decreases with increasing pH. The maximal adsorption capacity of dye was at pH 4. At low pH values, the CDHAp would be protonated and become positive, which enhance the interactions between $R\text{-}SO_3^-$ groups of dye and CDHAp through attractive force. However, at high pH values, the decrease of the amount of adsorbed dye molecules is prevented by the repulsive electrostatic forces existing between the negative charged surface of Calcium deficient hydroxyapatite (CDHAp) and $R\text{-}SO_3^-$ groups of dye. However, the details for the dye adsorption mechanism need to be further investigated.

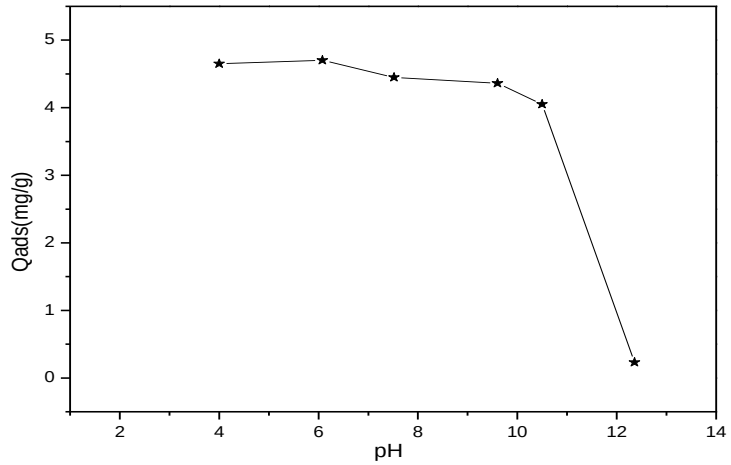


Figure 6: Effect of pH on the adsorption of RY4 onto calcium deficient hydroxyapatite (solid quantity: 200 mg, C_0:100 mg/L, contact time: 6 h).

3.4. Effect of some ions on the adsorption of the dye

Few studies have shown that the addition of ions can cause an increase or decrease of adsorption of dyes [32,33]. The adsorption of dyes can also be insensitive to the addition of ions [34].

To clarify the role of phosphate ions and calcium ions on the adsorption phenomena, we added to mixtures of phosphate-dye varying masses going from 2 to 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 Calcium deficient hydroxyapatite (CDHAp) is 200 mg at initial pH.

The results of the study of the adsorption in the presence of calcium ions are shown in fig.7.The addition of calcium ions to a solution of Reactive Yellow 4 causes an increase in the adsorption capacity. This increase is explained whereas calcium ions in solution may form bridges between apatite and anionic dye molecules. This promotes interaction between the dye molecules and the surface apatite.

The results of the study of the adsorption of the dye in the presence of phosphate ions are shown in Fig.8. We note that the ability to remove the dye by the calcium deficient hydroxyapatite (CDHAp) used decreases in the presence of PO_4^{3-}. This decrease is even more important than the mass of KH_2PO_4 is high. This is interpreted by the fact that the ions PO_4^{3-} enter in competition with the group $\Phi\text{-}SO_3^-$ of dye molecules to interact with Ca^{2+} ions on the surface of CDHAp, a similar result was observed by Mahmoodi et al [35] and Bihi et al [36] .

3.5. Kinetics of adsorption

Figure 9 presents the kinetic results of the adsorption process. The equilibrium was within a few minutes, by establishing a well-formed plateau, indicating also that the CDHAp is very effective adsorbent in a very short time for this textile dye. The maximum adsorption of the dye was observed in the first half hour of contact. This fast kinetics can be explained by the high number of active sites available at the beginning of relative adsorption sites remaining after some time.

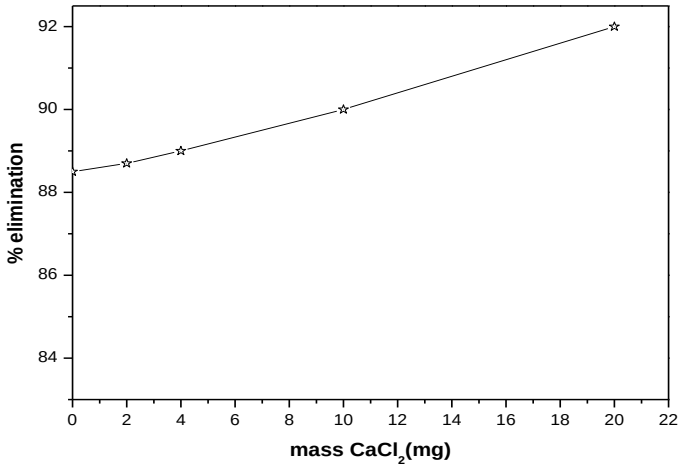


Figure 7: Effect of $CaCl_2$ on the adsorption of RY4 (C_0=100mg /L).

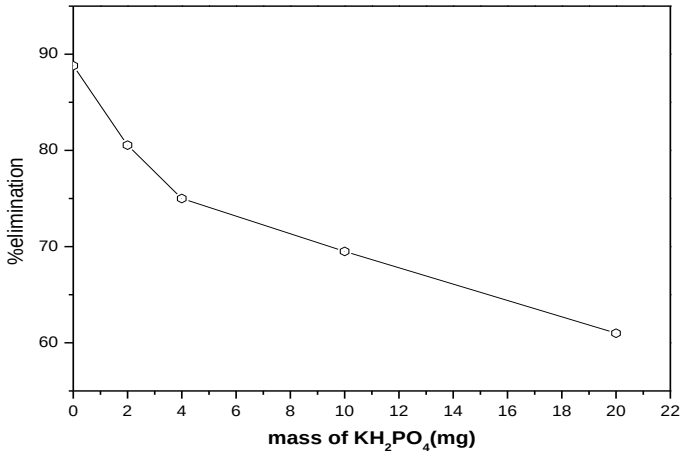


Figure 8: Effect of KH_2PO_4 on the adsorption of RY4 (C_0=100mg/L).

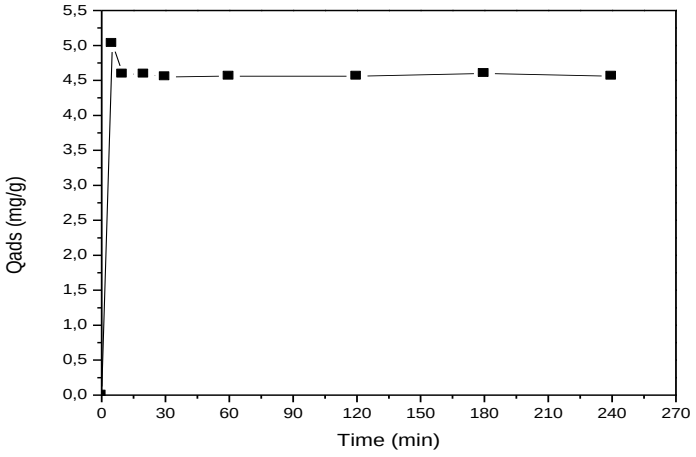


Figure 9: Kinetics of adsorption of Reactive Yellow 4 (RY4) on CDHAp (solid quantity: 200 mg, initial dye concentration: 100 mg/L, initial pH, stirring time: 1 min, at 298 K).

From the model established by Lagergreen [37] , the rate constant of adsorption of the pseudo first order is derived. However, as Ho and Mc Kay [38, 39] , we opted for a kinetic model of order 2 to interpret the best possible reaction mechanism.
For the pseudo first order rate constant k_1 is given by the following equation:
$Log(Q_e-Q_t)=Log(Q_e)-K_1/2.3t$ (7)
For the pseudo second order rate constant k_2 is given by the following equation:
$t/Q_t=1/K_2Q_e^2+t/Q_e$ (8)
For the second order rate constant k_3 is given by the following equation:
$1/(Q_e-Q_t)= 1/Q_e+K_3t$ (9)

With:
Q_e: Amount of adsorbate at equilibrium per gram of adsorbent (mg/g)
t: contact time (min)
K_1, K_2 and K_3 rate constant of adsorption, respectively, for the pseudo first order (min^{-1}), the pseudo second order (g.min / mg) and the second order (min^{-1}.g / mg).

The kinetic data obtained from batch studies have been analysed by means of pseudo-first order model. It was established that it was not suitable for describing the kinetic behaviour of the systems. However, the straight-line plot of t/Q_t vs t for the pseudo second-order reaction for CDHAp (Fig.10) has been tested to obtain rate parameters k, **Q**∞, and the correlation coefficient R^2 of dye are given in table 2.

Table 2 : The kinetic parameters obtained for Dye adsorption on CDHAp.

$Q_e$exp ($mg.g^{-1}$)	second order			Pseudo-second order			Pseudo-first order		
parameters	$Q_e$cal ($mg.g^{-1}$)	k_3 (g/mg .min^{-1})	R^2	$Q_e$cal (mg. g^{-1})	k_2 (g/mg .min^{-1})	R^2	$Q_e$cal (mg. g^{-1})	k_1 (min^{-1})	R^2
4.56	0.128	-0.1299	0.168	4.57	- 2.0202	0.9999	0.0141	0.0016	0.1889

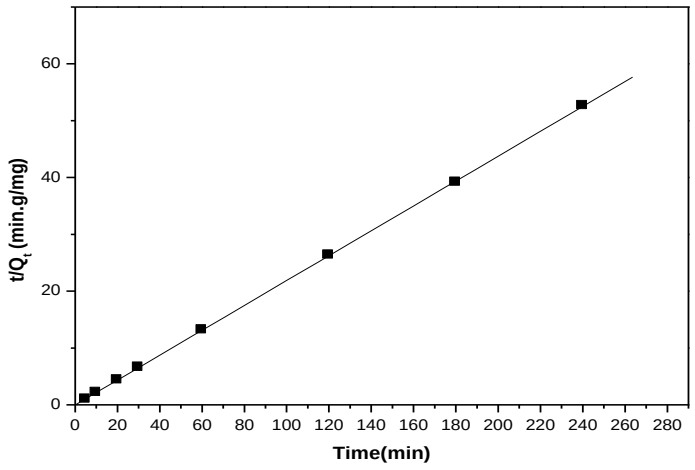


Figure 10: t/Qt versus time for the pseudo second order adsorption of Reactive Yellow 4 (RY4) by CDHAp.

3.6. Equilibrium of adsorption

The adsorption isotherms of Reactive Yellow 4 (RY4) on CDHAp was determined by using 200mg of adsorbent in contact for 6 hours with 10ml of solution concentration of variable color ranging from (100 to 900 mg/L).

The evolution of the amount adsorbed as a function of its equilibrium concentration in the medium has been shown in Figure 11.

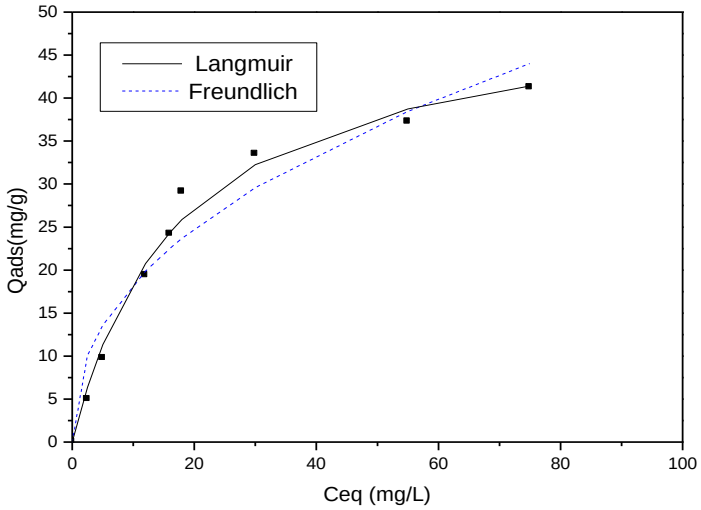


Figure 11: isotherms obtained using the non-linear method of Reactive Yellow 4 (RY4) by CDHAp (Solid quantity: 200 mg, stirring time: 1 min, T: 298 K).

It was observed that the amount of absorbed dye increases more quickly for low concentrations in solution, indicating that plenty of readily accessible sites are available at the start of adsorption. After equilibration, when the adsorbent becomes saturated, a plateau is reached indicating that no more sites are available for further adsorption.

The adsorption equilibrium dada were analyzed using Freundlich and Langmuir models .the isotherm parameters were estimated by linear and non-linear regression using origin 6.0 software. The results of modeling of adsorption isotherms by linear and non-linear regression using the Langmuir and Freundlich models are shown in Figures 11, 12 and 13. According to the values of correlation coefficients (Table 3), the highest R^2 was obtained by Langmuir model. Finally, it can be concluded that the Langmuir model appears appropriate for modeling the adsorption isotherms of dye on CDHAp.

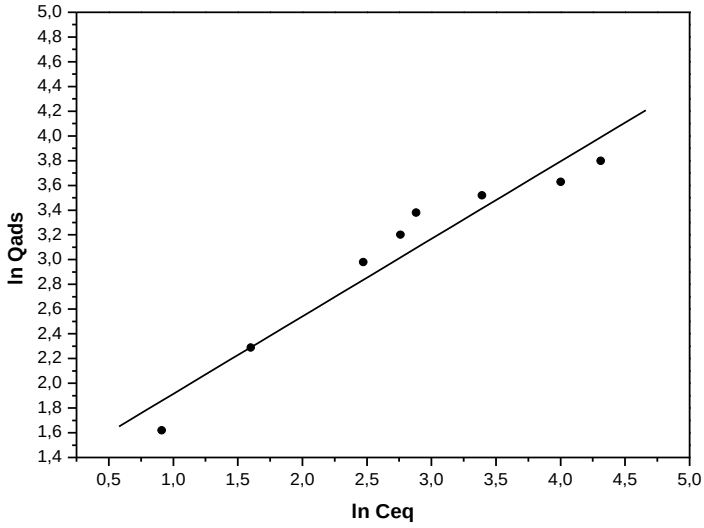


Figure 12 : Ln(Qads) versus Ln(Ce) for the adsorption isotherms Reactive Yellow 4 (RY4) from calcium deficient hydroxyapatite by Freundlich model using linear regression.

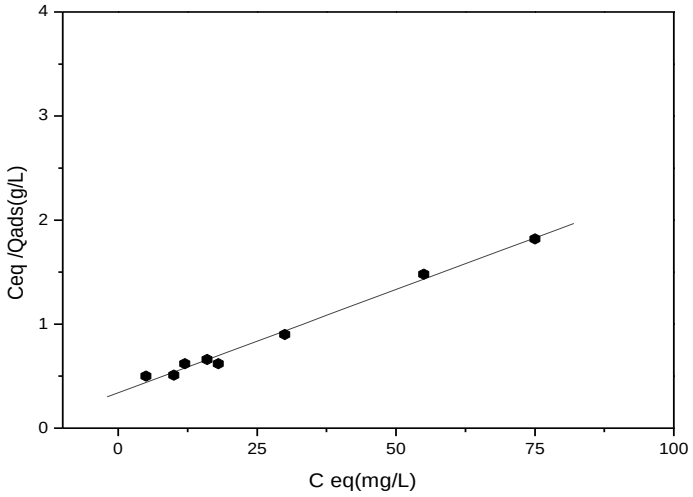


Figure 13: Ce/Qads versus Ce for the adsorption isotherms Reactive Yellow 4 (RY4) from calcium deficient hydroxyapatite by Langmuir model using linear regression.

Table 3: Values of the constants obtained by linear and non-linear regression of Freundlich and Langmuir models.

Isotherm	Langmuir				Freundlich		
Parameters	Q_∞ (mg/g)	b (l/g)	R_L	R^2	1/n	K_F (l/g)	R^2
Linear equation	50.38	0.058	0.147-0.017	0 .995	0.63	3.624	0.965
Non-linear equation	51.08	0.057	0.149- 0.019	0.988	0.43	6.765	0.943

The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L, which is defined by Hall et al., 1966 [40], as

$$R_L = 1/(1+bC_0) \quad (10)$$

where C_0 is the highest initial dye concentration (mg/L) and R_L values indicate the shape of the isotherm. The value of the coefficient (R_L) indicates the type of isotherm either to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). In our case, the R_L values were between 0 and 1 indicate applicability of the Langmuir isotherm and suggests the monolayer coverage of the Reactive Yellow 4 dye on the surfaces of calcium deficient Hydroxyapatite (CDHAp) .

The maximum adsorption capacity (q max) for the removal of RY4 by CDHAp obtained from the adsorption isotherms was 50.38 mg/g. When compared with previously reported adsorbents (table 4), the above results confirmed that CDHAp was favorable for Reactive dye removal.

Table 4: Comparison of maximum monolayer adsorption capacity of adsorbents for Reactive Yellow removal.

Adsorbents	**Dyes**	**Q_∞ (mg/g)**	**Ref**
CDHAp	Reactive Yellow 4	50.38	this work
PTCa	Reactive Yellow 4	40.85	[21]
Hydroxyapatite	Reactive Yellow 84	50.25	[20]
Natural untreated clay	Reactive Red 120	29.94	[41]
Bentonite MX80	Reactive Red 120	2.8	[32]
Sepiolite	Reactive blue 221	3.0–17.05	[42]

3.7. Effect of temperature on adsorption equilibrium

On Fig.14, we represented the evolution of the amount adsorbed as a function of temperature. There is an increase in temperature which causes a decrease in the adsorption capacity of dye at equilibrium. The decrease in the temperature range 298–318 K, can be explained by the fact that adsorption is an exothermic process.

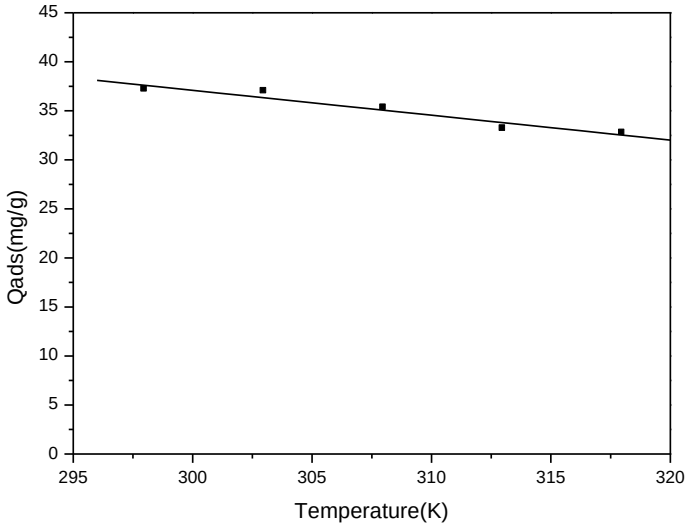


Figure 14: Effect of temperature on the equilibrium adsorption of Reactive Yellow 4 (RY4) on CDHAp.

Thus, generally, the phenomenon of adsorption is accompanied by a heat exchange [43, 44] which can be either exothermic or endothermic. The main criterion which leads to a chemisorption or physisorption is the determination of the enthalpy ΔH.

The thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS) were determined using the equations [45]:

$$\Delta G = -RTLnKc \quad (11)$$

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

$$LnKc = \Delta S/R - \Delta H/RT \quad (13)$$

$$Kc = (C_0 - C_{eq})/C_{eq} \quad (14)$$

With:

Kc: Equilibrium constant.

ΔG: Gibbs free energy (Joule / mole).

ΔH: Enthalpy (Joule / mole).

ΔS: Entropy (Joule / mol K).

T: Absolute temperature (K).

C_0: Initial concentration of the adsorbate.

C_{eq}: Equilibrium concentration.

R: Gas constant.

The curve Ln Kc as a function of the inverse of temperature (1 / T) (Fig.15) allowed us to determine ΔH and ΔS for the CDHAp. The straight line obtained shows good correlation coefficient.

The negative value of the enthalpy ΔH confirm that the adsorption of the dye molecule with calcium deficient hydroxyapatite (CDHAp) is an exothermic process (Table 5).

The negative value of entropy ΔS confirms the decrease in random molecules of the dye in the solid-liquid interface. The Negative values (Table 6) of free energy (ΔG) at each temperature indicated the feasibility and spontaneity of ongoing adsorption. The change in free energy for physisorption and chemisorption are between −20 and 0 kJ/mol and−80 to −400 kJ/mol, respectively [35]. Moreover, the values of ΔG in Table 5 are within the ranges of −20 and 0 kJ/mol indicating that the physisorption is the dominating mechanism [35].

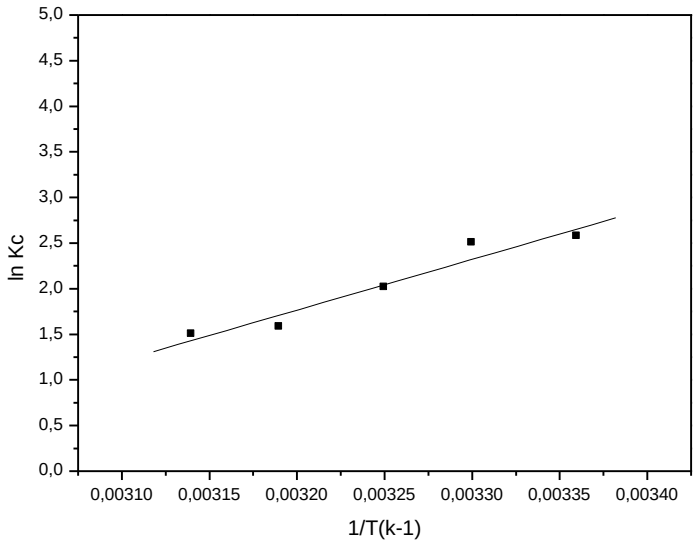


Figure 15: Ln(Kc) versus 1/T for the adsorption of Reactive Yellow 4 (RY4) on CDHAp.

Table 5 :Thermodynamic parameters of adsorption of the dye from CDHAp.

ΔH (K Joule/mole)	**ΔS (Joule/mole K)**	**R^2**
-46,22	**-132,22**	**0,9685**

Table 6: Values of Gibbs free energy of adsorption of the dye from CDHAp.

T (K)	**ΔG (K Joule/ mole)**	**Kc**
298	**-6.52**	**2.57**
303	**-5.86**	**2.50**
308	**-5.19**	**2.01**
313	**-4.52**	**1.58**
318	**-3.86**	**1.50**

The possible processes involved in the dye adsorption can be resumed as follows:

Process 1: The sulphonic group of the dye molecules attracted to and binds to a calcium surface site on the structure of the calcium deficient hydroxyapatite (CDHAp).

Process 2: The calcium ions Ca^{2+} in solution may form bridges between the calcium deficient hydroxyapatite (CDHAp) particles and the anionic dye molecules. Also, the presence of Ca^{2+} ions acting as bridges between the anionic dye molecules.

Process 3: In acid condition, the hydroxyl groups on surface of the calcium deficient hydroxyapatite (CDHAp) became positively charged by protonation (OH+) and attract anionic dye groups.

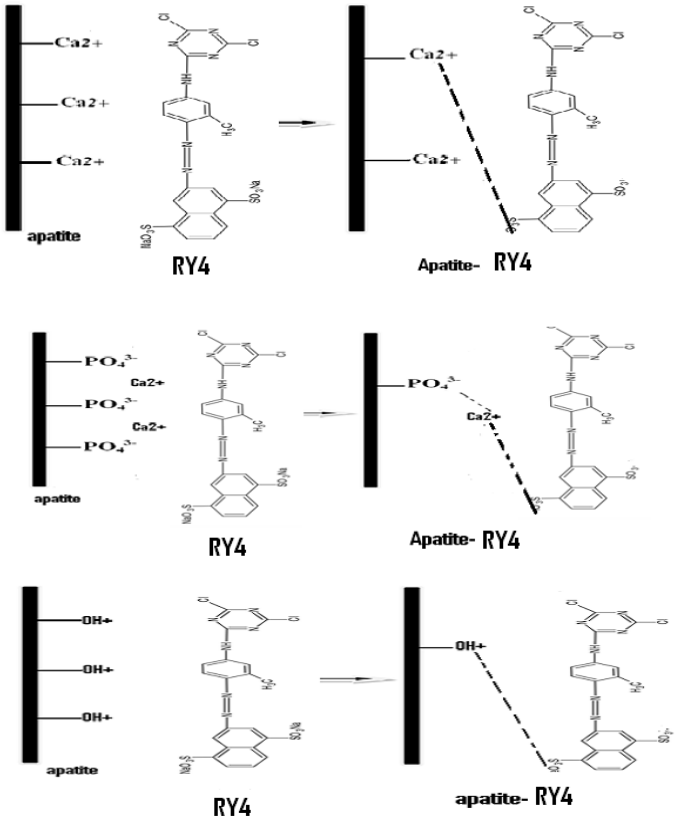


Figure 16: Possible interactions between the molecules of Reactive Yellow 4 and the surface apatite.

Conclusion

In this study, the results of characterization techniques (IR, XRD, and TEM) and chemical analysis showed that the hydroxyapatite is calcium deficient and poorly crystalline. Its Ca/P ratio was 1.60. The chemical formula of this calcium deficient hydroxyapatite (CDHAp) is: $Ca_{9.6}(PO_4)_{5.6}(HPO_4)_{0.4}(OH)_{1.6}$
The use of calcium deficient Hydroxyaptite (CDHAp) reduces the pollution discharge textiles in an important amount, the dye is adsorbed quickly. An increase in the initial dye concentration and calcium ions enhanced the interaction between dye and Calcium deficient hydroxyapatite, resulting in greater adsorption capacity. On the contrary, the dye adsorption capacity decreased with increase in pH, temperature or orthophosphate ions. The kinetic of adsorption are the pseudo second order. The lungmuir model better represents the equilibrium isotherm data on calcium deficient Hydroxyapatite (CDHAp). Thermodynamic studies indicated that the dye adsorption process onto CDHAp was physisorption, spontaneous and exothermic in nature. Based on the data of present study, the calcium deficient hydroxyapatite (CDHAp) may be a promising adsorbent for Reactive dyes removal from colored textile wastewater.

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