Low-cost composites based on porous titania–apatite surfaces for the removal of patent blue V from water: Effect of chemical structure of dye

C. El Bekkali, H. Bouyarmane, S. Saoiabi, M. El Karbane, A. Rami, A. Saoiabi, M. Boujtita, A. Laghzizil

a Laboratoire de Chimie Physique Générale, Faculté des Sciences, Université Mohammed V, Av. Ibn Batouta, B.P. 1014 Rabat, Morocco
b Laboratoire National du Contrôle des Médicaments, Rue Lamfaddal Cherkaoui, B.P. 6206 Rabat, Morocco
c Chimie Interdisciplinarité: Synthèse, Analyse, Modélisation CNRS (CEISAM), Faculté des Sciences et Techniques, Université de Nantes – UBL, B.P. 92208, 44322 Nantes Cedex 03, France

GRAPHICAL ABSTRACT

* Corresponding author. Fax: +212 537 77 54 40.
E-mail address: laghzizil@fsr.ac.ma (A. Laghzizil).
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Hydroxyapatite/titania nanocomposites (TiHAp) were synthesized from a mixture of a titanium alkoxide solution and dissolution products of a Moroccan natural phosphate. The simultaneous gelation and precipitation processes occurring at room temperature led to the formation of TiHAp nanocomposites. X-ray diffraction results indicated that hydroxyapatite and anatase (TiO2) were the major crystalline phases. The specific surface area of the nanocomposites increased with the TiO2 content. Resulting TiHAp powders were assessed for the removal of the patent blue V dye from water. Kinetic experiments suggested that a sequence of adsorption and photodegradation is responsible for discoloration of dye solutions. These results suggest that such hydroxyapatite/titania nanocomposites constitute attractive low-cost materials for the removal of dyes from industrial textile effluent.

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Photodegradation experiments

The photocatalytic degradation of patent blue under a 125W UV A-B-C (200–600 nm) irradiation in the presence of wTiHAp powders heated at 500 °C was carried out using a home-made Pyrex helical photoreactor of 250 mL (Fig. 1). The source of irradiation was placed in the center of the reactor to insure the maximum energy exchange between the source of the irradiation and the reaction mixture that flows out continuously. Two tubular compartments surrounding the lamp were used for cooling system. Based on the previous kinetics sorption studies, the wTiHAp suspensions (200 mg) were constantly stirred for 30 min in the dark before irradiation to reach adsorption equilibrium. During the irradiation, the photoreactor was maintained under magnetic stirring to keep a homogeneous suspension, and promotes diffusion of the dyes to the solid surface. At each selected time, the suspensions were centrifuged at 4000 rpm for 20 min, and the supernatants were stored in the dark. The Langmuir–Hinshelwood (L–H) model was used to analyze the heterogeneous reactions occurring on the surface of catalysts. The rate law derived from the model was approximated by a simpler “pseudo-first order” model [21,22] represented by \( \frac{C}{q_t} = \frac{C_0}{k_{app} t} \), where \( C_0 \) is the initial concentration and \( k_{app} \) the apparent reaction constant.

Results and discussion

Characterization

Fig. 2 shows the typical XRD patterns of wTiHAp powders recorded on a Philips PW131 diffractometer, analytical Device using Cu Kα radiation. Dried powders exhibit broad diffraction peaks characteristic of a poorly crystalline hydroxyapatite structure. However, no clear diffraction peak corresponding to TiO₂ could be obtained, even for the 40TiHAp composite.
40TiHAp material exhibits a larger specific surface area compared to other wTiHAp and TiO₂ powders. A significant increase of the dried powders increases with TiO₂ content. The analysis of TiO₂ with an anatase structure could be identified in well-crystallized HAp structure were evidenced and the presence of TiO₂ lead to a little reduction of S BET value (225 m² g⁻¹) compared to other wTiHAp and TiO₂ powders. A significant increase in oxide content is obtained when the sample is previously heated. This result can be explained on the basis of the dramatic decrease in specific surface area, which their values do not reach 40 m² g⁻¹. Elemental analyses are conducted using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with ICP-7500 Shimadzu-France as the analytical device. Using unvarying Ca and P contents dissolved from phosphate rock as calcium and phosphorus precursors, the added Ti alkoxide could be distributed based on Ca/P molar ratio of the precipitates. It is confirmed that the Ti content in the final powder increases linearly with the amount of introduced Ti alkoxide (Table 1). It is worth noticing that in the case of 40TiHAp, a corresponding theoretical Ti/Ca molar ratio equal to 0.3 has been found.

Sorption of patent blue by wTiHAp nanocomposites

In order to investigate in detail the surface properties of wTiHAp nanocomposites, patent blue is selected not only due to its environmental relevance but also to study the effect of charge, size, structure, and relative affinities towardapatite and titania. Firstly, the effect of contact time on the adsorption of PB by wTiHAp nanocomposites is investigated to determine the adsorption saturation time (Fig. 3). A two-step mechanism occurs. The first step indicates that a rapid adsorption occurs during the first 30 min, after which the equilibrium is slowly reached. Therefore, 3 h period is taken as aging time for studying adsorption isotherms. The pseudo-first order and the pseudo-second order models have been applied to support the experimental data and to evaluate the kinetic parameters (Table 2). The R² values and the illustrated fits in Fig. 3 demonstrate that the pseudo-second-order model agrees with the experimental data, similar to the case of methylene blue (MB) [14], while the pseudo first order model does not depict a reliable agreement with the experimental data.

In order to describe the interaction between adsorbate and adsorbent, the adsorption isotherm has been investigated. The effect of initial concentration of patent blue is shown in Fig. 4 and indicates that the maximum adsorption capacity depends.

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**Fig. 2** X-ray diffractograms of the wTiHAp composite powders heated at 100 °C, 500 °C and 800 °C.

| Samples  | Ca/P  | Ti/Ca | S BET (m² g⁻¹) | Pore diameter Dp (nm) |
|----------|-------|-------|----------------|----------------------|
|          |       |       |                | 100 °C   | 500 °C   | 100 °C | 500 °C |
| HAp      | 1.89  | –     | 165            | 105      | 12       | 3.5 and 11.5 | 4 and 9 |
| 5TiHAp   | 1.81  | 0.04  | 205            | 145      | 3.5 and 11.5 | 4 and 9 |
| 10TiHAp  | 1.80  | 0.38  | 225            | 150      | 3.5 and 9  | 4 and 9 |
| 25TiHAp  | 1.67  | 0.21  | 260            | 185      | 3.5 and 9  | 4 and 9 |
| 40TiHAp  | 1.63  | 0.34  | 250            | 225      | 3.5 and 9  | 4 and 9 |
| TiO₂     | –     | –     | 280            | 155      | 3.5       | 5.5    |
on both Ti content and the thermal treatment of wTiHAp powders. The highest capacity is obtained in the case 40TiHAp500, whereas the powder calcination at 500 °C is also very interesting in the regeneration adsorbent to decompose the adsorbed PB dye. It is noteworthy that certain attempts have also been made to fit the experimental data with the Langmuir and Freundlich models. Nevertheless, the Langmuir model is not adoptable ($R^2 = 0.832$), while a good fit is obtained with the Freundlich model. Parameters obtained from selected simulations are pasted in Table 3 and the corresponding fits are shown in Fig. 4. These results can be understood by taking into account the well-known complexation of PB dye at wTiHAp surface involving both sulfate and/or azo groups, but a limited affinity for charged negative surface such as titania or a large part of apatite surface is observed. Therefore, the sorption of PB does not follow the same trend as MB in terms of maximum capacity with increasing Ti content in samples. A higher PB sorption capacity of dried titania than that of received by 40TiHAp100 adsorbent is observed due to the large specific surface area of TiO$_2$ sample prepared with the ultrasonic assisted sol–gel method. However, their calcination at 500 °C affects the sorption process which 40TiHAp exhibits a good affinity with the coloring PB agent. The electrical nature of the 40TiHAp surface is still somewhat obscure but evidence suggests that probably a positive charge may be able to react with the negative charge of PB dye containing SO$_4$ groups. In addition, titania and apatite structures are also known to possess additional positive surface charges, which become significant with the acid pH. Feng et al. [17] have demonstrated a strong correlation between the acidity/alkalinity of TiO$_2$ and its adsorption capacity. Furthermore, the surface charge on the apatite layer is also contributed by the contamination with small amounts of Ti [24,25], which can affect the surface charge. It therefore explains the observed lower sorption of anionic patent blue as compared to the cationic methylene blue sorption. It must be noted that the sorption capacity does not seem to be directly dependent on the specific surface area but related to the chemical structure of dye including the ionic charge and the nature of chemical functions. Contrary to the cationic MB dye over all the pH range, the PB exhibits two negative sulfate groups and that should be interacted by the apatite surface and presumed to be positively charged. Therefore, our data reflect both the low affinity of calcined titania for PB sorption due to electrostatic repulsion with the oxygen-Ti and -SO$_4$ groups of PB dye, so the calcined TiO$_2$ at 500 °C attained a lower sorption capacity of PB than of pure HAp apatite.

Table 2 Kinetic rate constants ($k_i$) and adsorption capacities ($q_{e,i}$) as obtained for different models for the patent blue removal by wTiHAp powders.

| Temperature | Model       | $k_1$ (min$^{-1}$) | $q_{e,1}$ (mg g$^{-1}$) | $R^2$  | $q_{e,2}$ (g mg$^{-1}$ min$^{-1}$) | $R^2$  | $q_{e,1}$ (mg g$^{-1}$) | $R^2$  | $q_{e,2}$ (g mg$^{-1}$ min$^{-1}$) | $R^2$  |
|-------------|-------------|--------------------|----------------------|-------|----------------------|-------|----------------------|-------|----------------------|-------|
| 100 °C      | Pseudo 1st order | $k_1$ (min$^{-1}$) | 0.037                | 1.40  | 0.94553              | 0.9286 | 0.043                | 0.93  | 4.89                 | 0.9998 |
|             | $q_{e,1}$ (mg g$^{-1}$) | 0.076                | 1.21           | 0.8819 | 0.8232              |       | 1.401                |       | 3.35                 | 4.40   |
|             | $R^2$       | 0.94553            | 0.9286            |       | 0.8819              |       | 0.8232              |       | 4.40                 |       |
|             | Pseudo 2nd order | $k_2$ (mg g$^{-1}$) | 0.112                | 4.89  | 0.9998              | 0.9998 | 0.028                | 0.9998 | 3.67                 | 3.35   |
|             | $q_{e,2}$ (g mg$^{-1}$ min$^{-1}$) | 0.123               | 0.203            | 0.236  | 0.236               |       | 0.991                |       | 3.5                 | 4.0    |
|             | $R^2$       | 0.9998             | 0.9998            |       | 0.9998              |       | 0.9998              |       | 0.9998               |       |
| 500 °C      | Pseudo 1st order | $k_1$ (min$^{-1}$) | 0.031                | 1.230  | 0.9242              | 0.85651 | 0.030                | 1.245  | 4.59                 | 0.9998 |
|             | $q_{e,1}$ (mg g$^{-1}$) | 0.028                | 1.439           | 0.8756 | 0.8192              |       | 0.30                  |       | 3.19                 | 2.76   |
|             | $R^2$       | 0.8756             | 0.8192            |       | 0.8192              |       | 0.30                  |       | 3.19                 | 2.76   |
|             | Pseudo 2nd order | $k_2$ (min$^{-1}$) | 0.260                | 4.59  | 0.9998              | 0.9998 | 0.0185               | 0.9998 | 3.49                 | 3.19   |
|             | $q_{e,2}$ (g mg$^{-1}$ min$^{-1}$) | 0.185               | 1.143           | 0.8756 | 0.8192              |       | 0.185                |       | 3.49                 | 3.19   |
|             | $R^2$       | 0.8756             | 0.8192            |       | 0.8192              |       | 0.185                |       | 3.49                 | 3.19   |
Photodegradation process

The present section involves the photocatalytic degradation of the patent blue (PB) compared to the methyl blue (MB), employing heterogeneous photocatalytic process. Photocatalytic activity of 25TiHAp and 40TiHAp compared to titanium dioxide (TiO$_2$) and hydroxyapatite (HAp) as references has been investigated. An attempt has been made to study the effect of initial time, nature of catalyst, and concentration of dye on the photocatalytic degradation of patent blue. Fig. 5 shows that in the presence of wTiHAp catalysts, PB is less efficiently degraded compared to methylene blue. In fact, PB dye was fully degraded after 24 h, whereas 1 h was crucial to degrade the methylene blue under the same conditions, taking into consideration their chemical structures. The kinetics of the

\[ q_e = \frac{q_L}{1 + \frac{C_e}{K_L}} \]

\[ q_e = K_f C_e^{1/n} \]

**Table 3** Adsorption constants related to Langmuir and Freundlich models.

| Adsorbents | Exp. $q_{max}$ (mg g$^{-1}$) | Langmuir | Freundlich |
|------------|-------------------------------|-----------|------------|
|            | $q_L$ | $\beta$ | $R^2$ | $1/n$ | $K_f$ | $R^2$ |
| 100 °C     |       |       |      |     |       |      |
| HAp        | 5.8   | 11.2  | 0.04 | 0.8763 | 0.98 | 9.46 | 0.9802 |
| 25TiHAp    | 7.7   | 12.5  | 0.07 | 0.9254 | 0.90 | 9.51 | 0.9872 |
| 40TiHAp    | 9.8   | 13.8  | 0.08 | 0.9305 | 0.92 | 9.93 | 0.9862 |
| TiO$_2$    | 12.0  | 13.7  | 0.08 | 0.9622 | 0.84 | 9.96 | 0.9918 |
| 500 °C     |       |       |      |     |       |      |
| HAp        | 8.33  | 8.33  | 0.03 | 0.9345 | 0.89 | 9.48 | 0.9886 |
| 25TiHAp    | 10.98 | 10.98 | 0.06 | 0.9207 | 0.90 | 9.44 | 0.9886 |
| 40TiHAp    | 12.28 | 12.28 | 0.07 | 0.9401 | 0.88 | 9.97 | 0.9687 |
| TiO$_2$    | 3.30  | 5.26  | 0.05 | 0.9575 | 0.89 | 9.35 | 0.9939 |

Fig. 4 Effect of the initial concentration of patent blue on its adsorption on the dried (a) and calcined (500 °C) (b) wTiHAp powders. Plain lines correspond to the theoretical fits obtained by using a Freundlich-derived equation.

Fig. 5 Comparison of degradation kinetics between (a) patent blue and (b) methylene blue on wTiHAp catalysts.
degradation reaction vary between PB and MB dyes. Both the dyes follow a Langmuir–Hinshelwood model based on the linear relation of the log($C/C_0$) versus time. For PB photodegradation data, the $k_{app}$ constant and the full degradation time are given in Table 4. It can be predicted that the significant difference in reaction rates might be due to the different structural features and Ti content in catalyst.

The photocatalytic oxidation kinetics of PB compounds is often simulated by Langmuir–Hinshelwood equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. As shown in Table 4, the apparent first-order rate constant increases with TiO$_2$ content. The dependence of the patent blue disappearance on its initial concentration in its kinetics is shown in Fig. 6. It is noticeable that the residual concentration of PB into solution decreases as the irradiation time increases and the decomposition rate depends on the initial PB concentration. On the other hand, the presence of the catalyst under irradiation may induce different reactions such as photo-ionization, hemolytic breaking of chemical bonds with formation of different radical moieties, beyond hydroxyl radicals (HO$_\cdot$) themselves, which are the principal agents responsible for the oxidation of numerous aqueous organic contaminants [26,27]. Detailed reaction pathways have already been described in relatively more detail in most of the works on photodegradation reactions by using TiO$_2$ catalyst or titania derivate [29,30]. In our case, the kinetics of degraded products are documented, whereas their chromatographic peaks are plotted against the irradiation time (Fig. 7). Patent blue is absorbed in 8 min as retaining time and less detectable after 13 h of irradiation, while a few peaks are appeared contrary to MB degradation. Barka et al. [28] have detected a great number of intermediate compounds during the photocatalytic degradation of patent blue by supported TiO$_2$ and suggested the existence of various degradation routes, resulting in multi-step and interconnected pathways. However, the porous apatite structure can fix numerous by-products, knowing that the MB can discolor without degrading in accordance with R or S structures, but its HPLC-time of retention is always maintained well at 5 min with both the R or S configurations. The disappearance of their peaks in HPLC spectra with the absence of intermediate photoproducts proves that there is (i) a possible degradation instead of discoloration or (ii) a sorption of the blanched methylene dye onto apatite surface. From these hypotheses, it was recognized that major parts of degraded products were fixed by porous apatite. This fact sheds light on the reason that why no intermediate photoproducts have been detected in aqueous solution by photocatalytic decomposition of methylene blue compared to a few traces of degraded products within patent blue. Nishikawa [29] has demonstrated that hydroxyapatite is a photoactive catalyst and is a good support of fixing the intermediate products after methyl mercaptan photodegradation. Various studies consider that the hydroxyapatite is a good photoactive catalyst.

Table 4 Rate constant and full degradation time of patent blue V degradation. Conditions: 20 mg/L of PB; pH 5.6 and ambient temperature.

|       | HAp   | 25TiHAp | 40TiHAp | TiO$_2$ |
|-------|-------|---------|---------|---------|
| $k_{app}$ (h$^{-1}$) | 0.03  | 0.09    | 0.21    | 2.71    |
| Full degradation time (h) | >48   | 36      | 24      | 2       |

Fig. 6 Effect of initial concentration of PB dye on its degradation on 40TiHAp500 catalyst.

Fig. 7 HPLC curves of PB and MB degradation kinetics on 40TiHAp500 catalyst and their intermediate products.
for a few organic pollutants [30–32]. In our case, the porous hydroxyapatite is considered as adsorbent instead photocatalyst linked to its low photocatalytic activity.

Regeneration

The results of the regeneration of the adsorbent are shown in Fig. 8. The 40TiHAp adsorbent/catalyst is separated from solution after dye sorption and degradation reactions, calcined at 500 °C, and then utilized as new adsorbent or catalyst to test that whether the catalyst undergoes any change in its original adsorbing and photocatalytic activities. This process has been carried out several times to achieve the effect of regeneration on the adsorption capacity of the resulting material. Thus, no apparent change in the adsorption capacity has been observed after several regenerations up to 5 cycles while the average loss in photodegradation activity during regeneration is found to about of 3% per cycle due to the change of the particles size.

Conclusions

Herein, wTiHAp nanocomposites prepared from natural phosphate and Ti-alkoxide were evaluated for the removal of the patent blue dye from aqueous solutions. The adsorption of PB was strongly related to the specific surface area of dried powders whereas the mineral surface charge appears a key parameter for the calcined powders. The extent of sorption and degradation of PB was significantly affected by the illumination time, the Ti content in the composites and the initial concentration of PB pollutant. Kinetic studies demonstrated that these two steps occur with different regimes, involving PB dimer adsorption but PB monomer photodegradation. Comparison with previous data on the removal of methylene blue suggests that the high negative charge of PB is detrimental to its interaction with the TiO₂ phase, resulting in a slower degradation rate. These results indicate that wTiHAp are promising nanocomposites for the removal of cationic dyes from contaminated waters.

Conflict of Interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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