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Photocatalytic degradation of acid yellow 36 with calcined titania-hydroxyapatite-cuo xerogels

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ABSTRACT

Advanced oxidation processes (AOP), using semiconductor (SC) and hydroxyapatite (HA) composites, are promising due to the synergy of photocatalytic and adsorption properties. Still, dye removal efficiency of composites based on HA-SC remains low, because most of the research reported consider single SC materials. In this work, nanocrystalline xerogels of titanium oxide (TiO₂) with copper oxide (CuO) and HA were synthesized by the sol-gel process. HA was obtained by the precipitation method without heat treatment and calcined in the range of 200-1000 °C. TiO₂ and copper precursors were added to a sol containing HA in a 12:1 mol ratio, obtaining HA-TiO₂ and HA-CuO-TiO₂ nanomaterials. The xerogels were characterized by X-ray diffraction, scanning electron microscopy, emission field scanning electron microscopy and photoresponse. Their performance in the photocatalytic discoloration of an aqueous solution acid yellow dye 36 (AY36) was evaluated, using visible and UV light. The best discoloration was achieved with HA-CuO-TiO₂ xerogels with HA calcined at 600 °C, showing a degradation kinetic constant of 0.24 \min^{-1} . In contrast, HA-TiO₂ materials showed little or no photocatalytic activity, but strong dye adsorption/desorption. The thermal treatment of HA determines the filament-like morphology and degree of compaction of the nanomaterials, which are relevant in the crystallite size and sensitization of the SC matrix. Further studies must address the surface chemistry and rectifying properties of the best SC composite to have a more complete understanding of the mechanisms involved.

1. Introduction

The textile processing industries use a large volume of water for the dyeing, fixing, and washing processes [1]. The production of contaminated water from this industry is around 2 billion tons per year. Acid Yellow 36 (AY36) is one of the most used dyes in textile, paints, adhesives, polymers industries due to its excellent properties, but it is also one of the most harmful for human and ecosystems [2–4]. Even more, the azo functional group (N]N), responsible for its color, gives its recalcitrant character making these dyes resistant

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to high temperatures and weather conditions, and difficult to degrade or discolor [3]. Effluents from the different industries are the main source of water pollution since they contain different fractions of this dye residues. Conventional wastewater treatments rely on biological, adsorption, physical or chemical methods, which do not degrade recalcitrant pollutants [2,3]. The AY36 is only adsorbed by electro-coagulation and the problem is transferred from the water to the soil. Other technique consists in adsorbing the dye into activated carbon or other adsorbents [5–9]. Nevertheless, the combined use of adsorbents has HA and advanced oxidation process (AOP), could improve AY36 discoloration and degradation processes [10].

AOP have the characteristic that generate hydroxyl radicals ('OH), which are very powerful oxidizing agents that can break azo bonds and thereby discolor this type of dyes. Among the AOPs those using semiconductors agents such as titanium oxide (TiO₂) as a photocatalyst and dopants such as copper, iron, and zinc have been studied [11]. The process allows the generation of electron-hole pairs when illuminated with light of wavelength equal to or greater than their band gap. Electrons and holes allow the generation of hydroxyl radicals and reactive oxygen species that are responsible for the degradation of many pollutants, as they are not selective [11, 12]. The photogenerated carriers could also be used in the direct oxidation/reduction of the pollutants, but this process is highly selective and requires adsorption near the active site, a good match between the redox potentials of the pollutant and the semiconductor band positions, among other factors [11]. Furthermore, adsorption of the dye or its degradation subproducts on the hetero-doped SC surface, could cause the obstruction of active sites where hydroxyl radicals are catalytic or photocatalytic generated. So, the separation of both sites (adsorption and carrier generation sites) becomes critical.

Anatase is the crystalline phase of TiO₂ is a SC that is considered photocatalytically active (band gap of 3.2 eV). It can be decorated with metal oxides such as CuO, that is a SC with band gap of ~1.5–2.2 eV [11,13], and materials with an abundance of oxygen such as hydroxyapatite (HA), to increase its catalytic and/or photocatalytic activity and, at the same time, promote the interaction and adsorption of the aqueous pollutant onto HA. Additionally, the combination of various SC can avoid electron-hole recombination if coupled properly [4,13]. CuO has been shown to be a very active photocatalytic when supported in anatase [11,13], as well as economic and abundant in nature. On the other hand, HA [Ca₁₀(PO₄)₆(OH)₂] is a n environmentally friendly phosphate material widely used in biomedicine, especially for the manufacture of bone implants, due to its biocompatibility. It is a very promising candidate for the treatment of air, water, and soil pollution due to its ability to adsorb many contaminants on its surface, its ion exchange capacity, and its good thermal stability [14]. HA composites are known for combining good photocatalytic, however, HA is an insulating material



Fig. 1. XRD patterns of xerogels as a function of the HA annealing temperature: (a) TiO₂ and CuO–TiO₂, (b) HA, (c) HA-TiO₂, (d) HA-CuO-TiO₂. HA calcined in the range of 200–1000 °C. WHT refers to HA without thermal treatment.

that has a band gap of \sim 5.4 eV [10], and adsorbent properties that make them suitable for application in the treatment of contaminated water and the elimination of microorganisms [14,15]. Conversely, for dye removal, the efficiency remains low as it depends on the photocatalytic characteristics of the SC matrix [10,14–17].

In this work, calcined HA-CuO-TiO₂ xerogels were used for the degradation of AY36 dye in water solution. The proper morphology that leads to the synergy among dye adsorption, catalytic and photocatalytic properties is pursue. The results showed that the composite with Cu and HA calcined at 600 °C (HA₆₀₀-CuO-TiO₂) has the best performance due to its morphological and photo response properties. These results are promising since regardless the recalcitrance of AY36, the color disappears in 24 min while its elimination by conventional treatment processes is almost null. Similarly, studies on the degradation of dyes by other SC matrix, electro, and electro Fenton [1–3,17,18], indicate that discoloration occurs within several hours for recalcitrant dyes such as AY36 and others. It has also been reported that doping HA with Ti has given good results in the degradation of dyes [19].

2. Results and discussion

2.1. Characterization

XRD patterns of the various xerogels are shown in Fig. 1. For the TiO₂ xerogel, peaks related to the anatase phase (JCPDS 21-1272) are evident, while for the CuO–TiO₂ xerogel, an additional peak related to CuO (JCPDS 01-089-2529) (Fig. 1a) is observed. For HA, the samples without heat treatment (HA_{WHT}), or thermally treated below 1000 °C as indicates in the sub index (HA₂₀₀, HA₄₀₀, HA₆₀₀, HA₈₀₀ and HA₁₀₀₀), appears disordered and only that calcined at 1000 °C shows typical peaks (Fig. 1b) (JCPDS 09-0432). Consequently, the patterns of HA-CuO-TiO₂ xerogels based on HA (HA_{WHT}-CuO-TiO₂, HA₂₀₀-CuO-TiO₂, HA₄₀₀-CuO-TiO₂, HA₆₀₀-CuO-TiO₂, and HA₈₀₀-CuO-TiO₂), only show the anatase phase, suggesting a good dispersion of HA and CuO in the TiO₂ matrix up to 800 °C. Segregation and sintering of HA becomes evident in samples calcined at 1000 °C (Fig. 1b and c).

The crystal size of anatase in the various xerogels, TiO₂, CuO–TiO₂, HA-TiO₂ and HA-CuO-TiO₂ materials, are shown in Table 1. The largest crystal sizes were those in TiO₂ (19 nm) and CuO–TiO₂ (22 nm) xerogels, while the smallest ones corresponded to HA₄₀₀-TiO₂ (9 nm), HA₆₀₀-TiO₂ (10 nm). HA₄₀₀-CuO-TiO₂ and HA₆₀₀-CuO-TiO₂ xerogels maintained values between 14 and 13 nm, respectively.

The morphology of HA thermally treated in the range of 200–1000 °C is shown in Fig. 2. Filament-like structures were formed at 200 and 400 °C (Fig. 2b–c), while at 600 °C there is a reduction in particle size and sphere-like structures begin to form and coexist with the elongated structures (Fig. 2d). At the calcination temperature of 800 °C, the transition from the elongated to sphere-type structures is clearly seen as well as the reduction in surface area (Fig. 2e). At the calcination temperature of 1000 °C, pentahedron and tetrahedron type structures are observed (Fig. 2f), characteristic of the hexagonal structure of HA [20]. The HA morphological changes impact the degree of compaction and growth of TiO₂, determining its crystal size. The morphology of TiO₂, HA and HA-TiO₂ xerogels are shown in Fig. 3. It is evident the presence of smaller particle sizes for HA-TiO₂ relative to TiO₂, this coincides with what was obtained from XRD data and the Debye-Scherrer formula (Table 1), details of the procedure used are given in the supplementary information. Moreover, FE-STEM images of HA₆₀₀-TiO₂ show the filament-like shape. HA subjected to calcination in the range of 200–800 °C could serve as an instantaneous nucleation center for TiO₂ which grows in multiple crystallites, explaining the smaller particle size and greater surface area relative to pristine TiO₂. Fig. 4 shows FE-STEM images of HA₄₀₀-CuO-TiO₂ and HA₁₀₀₀-CuO-TiO₂. The loss of surface area and segregation of the components is notable when HA is highly crystalline (i.e. calcined at 1000 °C).

Changes in crystallinity and morphology impact the optoelectronic properties of the composites, the last give information on the ability to photogenerate charge carriers, as well as the amount of structural disorder promoting charge recombination. The results of the photoresponse tests, carried out with a tungsten-halogen lamp with 100 mW/cm² irradiance, are shown in Fig. 5 for HA, HA-TiO₂ and HA-CuO-TiO₂ xerogels. HA₄₀₀-CuO-TiO₂ and HA₆₀₀-CuO-TiO₂ nanomaterials showed the largest photo-response, although the slow rise and decay when illumination is on and off are characteristic of highly disordered materials, with long excitation and relaxation times. Fig. 6 shows a close-up of the photoresponse of HA (Fig. 6a) and HA-TiO₂ (Fig. 6b) xerogels. These materials show incipient photoresponse, orders of magnitude lower than the HA-CuO-TiO₂ composites. The fact that a broad band gap SC such as TiO₂

Xerogel	Crystal size, nm	
TiO ₂	19	
CuO-TiO ₂	22	
HA _{WHT} -TiO ₂	11	
HA200-TiO2	10	
HA ₄₀₀ -TiO ₂	9	
HA ₆₀₀ -TiO ₂	10	
HA ₈₀₀ -TiO ₂	10	
HA1000-TiO2	17	
HA _{WHT} -Cu-TiO ₂	17	
HA200-Cu-TiO2	15	
HA400-Cu-TiO2	14	
HA ₆₀₀ -Cu-TiO ₂	13	
HA800-Cu-TiO2	17	
HA1000-Cu-TiO2	14	

 Table 1

 Crystal size of TiO2 in the produced xerogels



Fig. 2. STEM of hydroxyapatite with and without calcination: (a) HA_{WHT}, (b) HA₂₀₀, (c) HA₄₀₀, (d) HA₆₀₀, (e) HA₈₀₀, (f) HA₁₀₀₀.

is photosensitive in the presence of HA would indicate that HA promotes intraband states in TiO_2 ; this sensitization is not observed if HA is not subjected to thermal treatment or if it is calcined at 1000 °C.

2.2. Discoloration of AY36

Discoloration tests of AY36 (50 mL of a dye solution with an initial concentration of 50 mg/L), using HA-TiO₂ xerogels (2.5 mg catalyst/mL dye sol), are shown in Fig. 7. Fig. 7a shows the discoloration under the diffuse visible light of the laboratory. It corresponds mainly to the removal of AY36 by adsorption since the dominant semiconductor has a poor response to visible light. An asymptotic behavior reaches ~10-20% of discoloration (50–46-38 mg/L), except for the composite based on HA_{WHT}-TiO₂ or HA₆₀₀-TiO₂, where discoloration reaches ~30–40% in 25 min (~50–29 mg/L). Fig. 7b shows discoloration under UV illumination for the HA-TiO₂ xerogels. The behavior is like the one obtained in Fig. 7a, confirming the dominance of the illumination independent adsorption phenomena. Discoloration reaches values between 10 and 30% after 3 min (50–45–33.5 mg/L). There was no discoloration with TiO₂ xerogels under both types of illumination sources, but at the end of the reaction there was a notable change in TiO₂ color, from white to yellow. Further adsorption tests under dark were carried out for 20 min for TiO₂ or CuO–TiO₂ xerogels, using 5 mL of an ethanolic solution with 50 mg/L of AY36 and 0.5 g of catalyst. Both showed 15 % of adsorption approximately, equivalent to 0.08 mg of AY36



Fig. 3. STEM of TiO₂, and HA-TiO₂ xerogels subjected to annealing: (a) TiO₂, (b) HA₄₀₀-TiO₂, (c) HA₆₀₀-TiO₂, (d) HA₈₀₀-TiO₂.



Fig. 4. SEM of HA-CuO-TiO₂ xerogels based on calcined HA: (a) HA₄₀₀-CuO-TiO₂, (b) HA₈₀₀-CuO-TiO₂.

per g of catalyst, substantially lower than the lower limit observed in HA-TiO₂ xerogels, corresponding to 1.6 mg of AY36 per g of catalyst.

As it is well known, the direct degradation route of the dye through the interaction with the photogenerated hole in the catalyst is much slower and more selective than the degradation by highly oxidizing species [11,21]. On the other hand, the lifetime of highly







Fig. 6. Photo-response of HA (a) and HA-TiO₂ (b) nanomaterials, as a function of HA annealing temperature, under 100 V, 20 s darkness - 20 s illumination - 20 s darkness. Illumination: 100 W tungsten-halogen lamp with 100 mW/cm² irradiance.

oxidizing species is relatively short, so the degradation of the dye must be carried out at relatively close distances to the photocatalyst. The combination of HA-SC aims to immobilize the dye in the vicinity of the SC, so that the use of the photogenerated holes favors the formation of the oxidants. Even so, the direct route remains a possibility, given the low HA content.



Fig. 7. Discoloration with HA-TiO₂, under: (a) diffuse visible light and, (b) UV light of AY36. HA calcined in the range of 200–1000 °C and without calcine. Reactions at 60 °C, 2500 mg/L of H₂O₂, 2.5 mg/mL of calcined xerogels (catalysts Cu/Ti molar ratio = 0.08 and HA/Ti = 0.08), volume of dye solution = 50 mL, UV photocatalytic tests: UV lamp (λ = 365-460 nm, intensity of 40 mW/cm²).

All HA-CuO-TiO₂ samples showed discoloration of AY36. However, all xerogels were affected by adsorption-desorption phenomena and do not present typical contaminant degradation curves. This is more accentuated in HA_{WHT} -CuO-TiO₂ and HA_{1000} -CuO-TiO₂, most likely due to segregation of HA_{1000} and excess of functional groups in HA_{WHT} . Fig. 8a and b makes evident that the HA-CuO-TiO₂ catalyst has the best performance when HA is calcined in the range of 200–800 °C.

As stated in the introduction, HA-SC composites are known for combining good photocatalytic and adsorbent properties for the elimination of microorganisms [22], but for dye elimination its efficiency remains low [16,17]. This contribution shows the successful preparation of HA-CuO-TiO₂ xerogels, where the proper annealing of HA was critical to promote the fiber-like morphology that serves as nucleation sites to decrease the crystallite size of TiO₂, increasing its active surface area, and also the introduction of intraband states for visible light sensitization of TiO₂, in addition to the doping caused by Cu. We have proved that HA-CuO-TiO₂ xerogels are efficient in the discoloration of AY36 in min under the conditions shown here, whereas other SC matrix and no doped require several hours for discoloration of recalcitrant contaminants, such as dye AY36 [10,18,19], The degradation kinetic constants and linear regression factor R^2 of experiments performed by duplicate are reported in Table 2; they were calculated assuming pseudo-first order reactions. HA₆₀₀-CuO-TiO₂ and HA₈₀₀-CuO-TiO₂ show the highest values and R^2 of 0.99 under UV and visible light. The best discoloration was achieved with HA₆₀₀-CuO-TiO₂ xerogels under UV illumination, showing a degradation kinetic constant of 0.24 min⁻¹.

3. Conclusions

This contribution describes the study involving SC-hydroxyapatite composites for dye removal, highlighting synthesis methods, characterization techniques, and photocatalytic efficiency. The goal was the proper photocatalyst morphology that leads to the synergy among dye adsorption, catalytic and photocatalytic properties in HA-CuO-TiO₂, to degrade the recalcitrant AY36 dye. Our findings indicate that the dispersion of the active semiconductors TiO_2 and CuO into HA depends on its functionality and morphology, which is controlled by its thermal treatment. No thermal treatment of HA leads to a poor regeneration of electron and hole carriers (lack of photoresponse) in the composite, whereas treatment at temperatures superior to 1000 °C causes segregation of its various



Fig. 8. Discoloration of AY36 by HA-CuO-TiO₂ xerogels, with HA subjected to various thermal treatment as indicated. Discoloration under visible light (a) and UV-light (b). Reaction at 60 °C, 50 mL dye solution containing 2500 mg/L H₂O₂, 2.5 mg/mL calcined xerogels with 0.08 Cu/Ti and 0.08 HA/Ti molar ratio. UV lamp ($\lambda = 365$ -460 nm, with 40 mW/cm² irradiance.

Table 2

First-order kinetic constant of AY36 discoloration by HA-CuO-TiO2 xerogels under visible and UV illumination.

	Diffuse light		UV light	
Xerogel	k (min ⁻¹)	R ²	k (min ⁻¹)	R ²
CuO-TiO ₂	0.11	0.99	0.12	0.99
HA _{SST} -TiO ₂	0.02	0.99	a	a
HA _{SST} -CuO-TiO ₂	0.08	0.99	0.1	0.99
HA200-CuO-TiO2	0.16	0.98	0.16	0.98
HA400-CuO-TiO2	0.15	0.98	0.14	0.98
HA600-CuO-TiO2	0.17	0.96	0.24	0.99
HA800-CuO-TiO2	0.16	0.97	0.23	0.99
HA1000-CuO-TiO2	0.153	0.98	0.16	0.98

^a Did not show discoloration activity.

components. Response to visible light is not observed for TiO₂ doped with Cu, unless it is combined with HA calcined in the range of 400–600 °C, suggesting an active role of HA in the promotion of photoactive sites. Under UV-light, generation of charge carriers is enhanced and so does the degradation of AY36. The ability of Cu-doped titania to generate hydroxyl radicals near adsorbed AY36 is best for the HA-CuO-TiO₂ xerogel based on HA calcined at 600 °C, showing a degradation kinetic constant of 0.24 min⁻¹. Further studies must address the surface chemistry and rectifying properties of the SC matrix to have a more complete understanding of the mechanisms involved.

4. Methods

4.1. Materials synthesis

4.1.1. Synthesis of HA

HA was synthesized by the precipitation method using a 800 mL mixture of 0.3 M H_3PO_4 (phosphoric acid) and 0.5 M Ca(OH)₂ (calcium hydroxide), in distilled water and agitation at 50 RPM. The solution of 0.3 M H_3PO_4 (400 mL) was added drop by drop (11 drops/min, to keep the pH between 11 and 12) to the 0.5 M Ca(OH)₂ solution (400 mL), at room temperature (25.8 °C), followed by the aging process, keeping the solution at rest for 5 days. After this time, the solution was washed and centrifuged several times with distilled water, and the precipitate dried at 65 °C for 2 h. 20.5 g of HA was obtained.

4.1.2. Sol gel synthesis of TiO₂, HA-TiO₂, CuO-TiO₂ and HA-CuO-TiO₂

Titanium xerogels containing copper, and/or HA were obtained following a modified procedure [23]. 0.1 g of HA samples calcined at 200, 400, 600, 800, 1000 °C, and without heat treatment, were dissolved in a mixture of anhydrous ethanol (50 mL) and hydrochloric acid (0.1 mL) stirring vigorously, then 0.22 g of Cu II chloride (Fermont) was added in the mixture of anhydrous ethyl alcohol (Fermont) until homogenization is achieved. 5 mL of titanium isopropoxide (Aldrich) was subsequently added and stirred until homogenization is achieved (15 min). Finally, 2 mL of water was added to initiate a controlled hydrolysis, stirred for 5 min, and then left standing until gelation. The molar ratios of the components of the sol-gel synthesis were $H_2O/Ti = 7$, EtOH/Ti = 45, $H^+/Ti = 0.3$ and the molar ratios for copper-doped titania and HA were Cu/Ti = 0.08 and HA/Ti = 0.08. In summary, gelation of TiO₂, CuO–TiO₂, HA-TiO₂, HA-CuO-TiO₂ with HA calcined in the range of 200–1000 °C, was obtained after 20 min to 1 h. The gels obtained were calcined at a rate of 1.5 °C/min until reaching 450 °C for 1 h; the calcined gel formed millimetric aggregates.

4.2. Characterization

XRD characterization was carried out using a Bruker D2 Phaser diffractometer (35 kV, 20 mA), with CuK α radiation ($\lambda = 1.548$ Å). The average crystal size of anatase (101) was determined using the Debye-Scherrer equation [5]. Chemical composition and morphology of the xerogels were obtained using a high-resolution scanning electron microscope (HRSEM) MAIA 3 (TESCAN, Czech Republic) equipped with a Bruker Quantax 200 energy dispersive spectroscopy (EDS) detector. Samples were mounted on top of an aluminum pin with a double conductive graphite tape and analyzed using a 15 keV electron beam. Images at higher magnification were obtained with an emission field scanning electron microscopy (FE-STEM), SEM Hitachi S-5500, also equipped with EDS.

Photo-response tests were carried out applying 100 V with a programmable Keithley 230 device and with a tungsten-halogen lamp with 100 mW/cm² irradiance. The generated current intensity was measured every second during 20 s under dark, 20 s under illumination and again 20 s under dark, with a programmable Keithley 619 electrometer/multimeter device.

4.3. Discoloration of acid yellow 36 (AY36)

For degradation of AY36, a 50 mL aqueous solution with concentration of 50 mg/L of AY36 was prepared. The discoloration of AY36 was determined by following the changes in the absorption spectra using a Genesys 10S UV–Vis spectrophotometer. The main peak at 436 nm was used to generate the calibration curve dye concentration in mg/L. The experiments were carried out at 60 °C, with 2500 mg/L of hydrogen peroxide (H₂O₂), 2.5 mg of calcined xerogeles/mL of dye solution. The molar ratio of Cu/Ti and HA/Ti in the xerogels was 0.08. A 125 mL Erlenmeyer flask was used as a reactor for the tests carried out in the diffuse visible light of the laboratory. For the UV photocatalytic tests, a 300 mL beaker with an adapted lid to fix the UV lamp ($\lambda = 365-460$ nm, irradiation intensity of 40 mW/cm²), a thermometer and the sampling port, was used.

Ethics declarations

Review and/or approval by an ethics committee was not needed for this study because it does not involve animals or people.

Data availability statement

No data associated with this study has been deposited into a publicly available repository. Data included in article/supp. material/referenced in article.

CRediT authorship contribution statement

S.López Ayala: Writing – original draft, Validation, Supervision, Methodology, Investigation, Conceptualization. **C. Menchaca Campos:** Writing – review & editing, Supervision, Funding acquisition. **M.E. Rincón:** Writing – review & editing, Funding acquisition, Conceptualization. **C.A. García Pérez:** Writing – review & editing, Investigation. **J. Uruchurtu:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e27269.

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