

SOL GEL SYNTHESIS OF TITANIA XEROGELS DOPED WITH COPPER, IRON, ZINC AND HYDROXYAPATITE AND THEIR APPLICATION IN THE ELECTROPHOTOCATALYTIC DECOLORIZATION OF ACID BLACK 1

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ABSTRACT

The discharge of photostable dyes into bodies of water, such as acid black 1 dye, generates problems in aquatic life, such as a decrease in oxygen dissolved and toxicity, and in humans can generate genotoxic effects, dermatitis problems, among others. Alternatives to solve these problems are photocatalysis and photoelectrocatalysis, mediated by TiO_2 doping with copper, zinc or iron, that generates the rectification phenomenon that prevents electron-hole recombination. Specifically, photoelectrocatalysis is a way to increase the separation of charge carriers, because electrons are conducted by an external circuit and the reduction takes place in the electrode with a lower activation energy. In this work, different metal oxides were mixed to produce the ternary photoelectrocatalysts Zn-Cu-TiO_2 , Fe-Cu-TiO_2 and hydroxyapatite (HA) calcinated at 600 and 800°C, nanomaterials, synthesized through the single-step sol-gel process and used for photoelectrocatalytic discoloration of the acid black 1 dye. Solutions of Na_2SO_4 in different molarities were used as electrolyte. The Zn-Cu-TiO_2 xerogel showed the best performance, followed by the $\text{HA}_{800}\text{-Cu-TiO}_2$. However, during the photoelectrocatalytic reaction, a persistent red coloration was formed. Due to the low potential of the nanomaterials, the production of hydroxyl radicals is avoided; however, with the generation of reactive oxygen species, discoloration was possible.



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1. INTRODUCTION

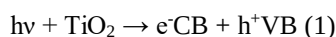
Water pollution caused by the discharge of photostable dyes from industrial activities, particularly textile manufacturing, remains an important environmental

concern. The persistence of these compounds in aquatic environments is associated with their chemical stability and resistance to conventional wastewater treatment processes, making their efficient removal a significant challenge. The presence of dyes in water bodies can

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reduce light penetration and affect aquatic ecosystems, while some dye compounds and their transformation products may exhibit toxic effects. In addition, the discharge of colored effluents can alter the aesthetic quality of water and interfere with biological processes in aquatic systems. Consequently, the development of efficient technologies capable of removing or degrading persistent dyes from wastewater continues to be an active area of research (Goodarzi et al., 2023; Houas et al., 2001; Ajmal et al., 2016; Begum et al., 2025).

Photocatalysis and photoelectrocatalysis (PEC) mediated by TiO₂ have been investigated as effective processes for the degradation of persistent organic pollutants in water. These processes involve redox reactions at the semiconductor–electrolyte interface (Gatou et al., 2024). An absorption edge around 388 nm corresponds to a band gap energy (E_g) of approximately 3.2 eV for anatase TiO₂. When TiO₂ is irradiated with photons having energy equal to or greater than its E_g, electrons are excited from the valence band (VB) to the conduction band (CB), generating electron–hole pairs, as represented by Eq. (1):



where $e^-\text{CB}$ represents an electron in the conduction band, $h^+\text{VB}$ represents a hole in the valence band, and $h\nu$ corresponds to the energy of the incident photon. The photogenerated electrons and holes can participate in reduction and oxidation reactions, respectively, at the semiconductor–electrolyte interface. The photogenerated holes may promote oxidation reactions involving water or hydroxyl species, while the electrons may participate in reduction reactions involving dissolved oxygen or other electron acceptors. The efficiency of a photocatalytic process therefore depends strongly on the generation, migration, and lifetime of these charge carriers, as well as on the extent of electron–hole recombination (Sadeghfard et al., 2021).

Modification of TiO₂ with transition-metal species such as Cu, Zn, or Fe can alter its electronic structure and charge-transfer characteristics, potentially influencing charge separation and electron–hole recombination (Lopez-Ayala et al., 2015). In PEC, the photocatalytic process is additionally assisted by an externally applied electric field, which can facilitate the separation and transport of photogenerated charge carriers. Under appropriate conditions, electrons can be transferred through the external circuit, while holes remain available at the photoanode surface for oxidation reactions. This charge-transfer process can enhance the availability of reactive species and increase the photo-oxidation rate (Gatou et al., 2024; Zheng et al., 2025). Photoelectrocatalysis, also referred to as potential-assisted photocatalysis, has therefore been investigated for the degradation of different organic pollutants in

aqueous systems (Goodarzi et al., 2023; Mohlala et al., 2023).

In recent years, a variety of physical, chemical, electrochemical, and biological technologies have been investigated for the treatment of dye-containing wastewater. These approaches include membrane filtration, adsorption, electrolysis, advanced oxidation processes (AOPs), and biological treatments, among others (Chuang et al., 2025; Esmaelzadeh et al., 2024; Quiroz et al., 2017; Agarwala & Mulky, 2023; Qulatein & Yilmaz, 2023; Ismail & Sakai, 2022; Pan et al., 2024). Each technology has particular advantages, but its effectiveness may depend on the chemical structure and concentration of the dye, the composition of the wastewater, and the operating conditions. For example, adsorption can efficiently remove dyes from aqueous solutions, but it primarily transfers the contaminant from the liquid phase to a solid adsorbent rather than necessarily destroying it. Membrane processes can provide high removal efficiencies, although membrane fouling and the management of concentrated waste streams may limit their application. Biological treatments are generally attractive because of their relatively low energy requirements; however, the biodegradability and chemical stability of many synthetic dyes can restrict their efficiency. In contrast, electrochemical and advanced oxidation processes can promote the transformation or degradation of persistent organic compounds through highly reactive species.

Among these technologies, PEC is particularly attractive because it combines semiconductor photocatalysis with an externally applied electrical bias, providing an additional means of controlling the separation and transport of photogenerated charge carriers. The efficiency of a PEC system depends on several factors, including the semiconductor band gap and band positions, charge-carrier separation, surface area, morphology, and stability of the photocatalyst, as well as the electrolyte composition and applied potential. Several semiconductor materials, including TiO₂, SnO₂, CeO₂, ZrO₂, and ZnO, have been investigated for photocatalytic and photoelectrocatalytic applications. Among them, TiO₂ remains one of the most widely studied materials because of its chemical stability, relatively low cost, availability, and suitable photocatalytic properties (Goodarzi et al., 2023; Gatou et al., 2024).

Noble metals, such as platinum, have been widely investigated as catalysts because of their favorable electronic properties and high catalytic activity; however, their high cost and limited availability can restrict their use in large-scale environmental applications. Transition-metal species such as copper (Cu), zinc (Zn), and iron (Fe) provide potentially accessible alternatives for modifying TiO₂ because of their relatively low cost and their ability to alter the electronic and surface properties

of semiconductor materials. When incorporated into TiO_2 , these metals can influence charge transfer, surface reactions, and the recombination behavior of photogenerated electron-hole pairs, depending on their chemical state, concentration, and interaction with the TiO_2 matrix. Therefore, the incorporation of transition-metal species represents a potentially useful strategy for tailoring the photocatalytic and photoelectrocatalytic properties of TiO_2 while maintaining the economic advantages required for wastewater-treatment applications (Kumaravel et al., 2019; Nyamai et al., 2024).

In this work, TiO_2 -based nanomaterials modified with zinc and copper (Zn-Cu-TiO_2), iron and copper (Fe-Cu-TiO_2), and copper and hydroxyapatite (HA-Cu-TiO_2) were synthesized by a single-step sol-gel process and evaluated for the photoelectrocatalytic degradation of Acid Black 1 (AB1) in aqueous solution. For the HA-containing materials, two xerogels were prepared and thermally treated at 600 and 800 °C, designated as $\text{HA}_{600}\text{-Cu-TiO}_2$ and $\text{HA}_{800}\text{-Cu-TiO}_2$, respectively. Acid Black 1 was selected as a model pollutant because of its high chemical stability and persistence, which can make its removal by conventional wastewater-treatment processes difficult. The synthesized materials were incorporated into working electrodes and evaluated under photoelectrocatalytic conditions. The effects of the operating conditions on dye discoloration were investigated, with particular attention to the electrolyte concentration, applied current density, and reaction temperature. The photoelectrocatalytic performance of the different TiO_2 -based xerogels was subsequently compared to identify the material and operating conditions that provided the most favorable discoloration of AB1.

The sol-gel process provides a versatile approach for synthesizing TiO_2 -based nanomaterials with controlled composition and structural properties. Previous studies have shown that the incorporation of Cu, Zn, and Fe species into TiO_2 can modify its electronic structure and promote interactions between different semiconductor components, which may favor charge transfer and influence the separation of photogenerated carriers (Lopez-Ayala et al., 2015, 2025). In addition, the application of an external electrical bias during photocatalysis can provide an additional driving force for charge separation and transport, thereby influencing the photoelectrocatalytic oxidation of organic pollutants. The photoelectrocatalytic performance of semiconductor materials is therefore related not only to their band-gap energy but also to their surface properties, morphology, and interactions with the electrolyte. These characteristics can influence the formation and availability of reactive species involved in pollutant discoloration.

2. METHODS

2.1 Synthesis of photoelectrocatalysts

The Fe-Cu- TiO_2 xerogel was synthesized using a single-step sol-gel process. First, 100 mL of ethanol was placed in a 150 mL beaker under constant magnetic stirring. Subsequently, 0.2 mL of 37% hydrochloric acid was added, followed by 0.435 g of copper(II) chloride dihydrate. The mixture was continuously stirred until complete dissolution of the copper salt, resulting in a green solution. Then, 0.126 g of iron(II) chloride tetrahydrate was added and stirred until complete dissolution. Once the copper and iron salts had dissolved, 10 mL of titanium isopropoxide was added dropwise under continuous stirring. Finally, 4 mL of distilled water was added dropwise. The liquid reagents were added slowly and gradually to control the hydrolysis and condensation reactions and to minimize the formation of undesired precipitates. After addition of all reagents, the mixture was maintained under stirring until gelation occurred, which took approximately 0.5-1 h. The resulting gel was subsequently calcined in a muffle furnace using a heating rate of 1.5 °C/min until reaching 450 °C, where it was maintained for 1 h.

The Zn-Cu-TiO_2 , $\text{HA}_{600}\text{-Cu-TiO}_2$, and $\text{HA}_{800}\text{-Cu-TiO}_2$ xerogels were synthesized following the same general sol-gel procedure, with the corresponding precursor salt or hydroxyapatite-containing precursor being varied according to the material composition. For the hydroxyapatite-containing materials, the xerogels were thermally treated at 600 and 800 °C to obtain the samples designated $\text{HA}_{600}\text{-Cu-TiO}_2$ and $\text{HA}_{800}\text{-Cu-TiO}_2$, respectively. Table 1 summarizes the reagents used for the synthesis of the different photoelectrocatalysts, including their amounts and molar ratios relative to titanium.

Table 1. Reagents for the photoelectrocatalysts synthesis.

Reagent	Amount for each reaction	Molar ratio
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	0.126 g	$\text{Fe/Ti} = 0.04$
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.4356 g	$\text{Cu/Ti} = 0.08$
ZnCl_2	0.1743 g	$\text{Zn/Ti} = 0.04$
HA_{600} or HA_{800}	0.1 g	$\text{HA/Ti} = 0.08$
Ti-isopropoxide	5 mL	---
EtOH	100 mL	$\text{EtOH/Ti} = 45$
HCl	0.2 mL	$\text{H}^+/\text{Ti} = 0.23$
H_2O	4 mL	$\text{H}_2\text{O/Ti} = 4.8$

2.2 Preparation of the working electrode

A 5 cm length of insulated copper wire was used to prepare the working electrode. The insulation was removed by sanding the ends of the wire to expose a small section of the copper conductor, allowing electrical contact to be established. The copper wire was then attached to the conductive indium tin oxide (ITO) glass substrate using conductive carbon tape. Subsequently,

0.4 g of the TiO₂-based xerogel was mixed with a polymeric binder consisting of colorless nail polish diluted with acetone, using 10 drops of nail polish and 2 mL of acetone. The resulting suspension was deposited onto the conductive glass, ensuring that the exposed surface of the ITO was uniformly covered with the photocatalytic material. Finally, electrical continuity between the ITO substrate and the opposite end of the copper wire was verified to ensure adequate electrical connection of the working electrode.

2.3 Characterization

The synthesized materials were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and UV-Vis spectroscopy. X-ray diffraction patterns were obtained using a Bruker D2 Phaser diffractometer operated at 35 kV and 20 mA with Cu K α radiation ($\lambda = 1.548 \text{ \AA}$). The crystallite size was calculated from the full width at half maximum (FWHM) of the (101) reflection of the anatase phase using the Debye-Scherrer equation. The morphology and elemental composition of the synthesized materials were examined using a Hitachi S-5500 field-emission scanning electron microscope (FE-SEM). The optical properties of the materials were evaluated using a Shimadzu UV-3100PC spectrophotometer. The absorbance spectrums were obtained from the measured transmittance data, and the optical band-gap energy was subsequently estimated using the Tauc method.

2.4 Experiments

The photoelectrocatalytic experiments were conducted in an electrochemical cell containing 100 mL of an Acid Black 1 (AB1) aqueous solution. Na₂SO₄ was used as the supporting electrolyte at different molar concentrations. The electrochemical cell consisted of the TiO₂-based photoelectrocatalyst film deposited on ITO as the working electrode, a silver/silver chloride (Ag/AgCl) reference electrode, and a graphite counter electrode. The electrochemical response was monitored using a GillAC ACM potentiostat. The working electrode was irradiated with a black-light lamp emitting at 380 nm.

The discoloration of AB1 was monitored by UV-Vis spectroscopy using a Genesys 10S UV-Vis spectrophotometer. The absorption spectrum of AB1 exhibited a characteristic main absorption band at 618 nm. This wavelength was selected for quantitative monitoring of the dye concentration during the photoelectrocatalytic experiments. A calibration curve was prepared from AB1 standard solutions, and the concentration of AB1 in the reaction samples was determined in mg/L from the measured absorbance at 618 nm. The decrease in the characteristic absorption band at 618 nm was used as an indicator of the discoloration of the dye during the photoelectrocatalytic treatment.

3. RESULTS

The structural and morphological characterization of the synthesized TiO₂-based nanomaterials by X-ray diffraction (XRD) and scanning electron microscopy (SEM) is presented in Figure 1. Figure 1a shows the XRD patterns of TiO₂, Cu-TiO₂, Fe-TiO₂, Zn-TiO₂, Fe-Cu-TiO₂, Zn-Cu-TiO₂, HA₆₀₀-TiO₂, and HA₈₀₀-TiO₂; the diffractograms of HA₆₀₀-Cu-TiO₂ and HA₈₀₀-Cu-TiO₂ show patterns similar to those of the samples not containing copper. The diffraction patterns predominantly show the characteristic reflections of the TiO₂ crystalline phase. In most of the modified materials, no intense additional reflections attributable to the incorporated species are observed, which may be associated with their relatively low concentration, high dispersion, or crystallite dimensions below the detection limit of the XRD technique. The nominal molar ratios used for the metal modifications were Cu/Ti = 0.08, Zn/Ti = 0.04, and Fe/Ti = 0.04. An exception is observed for Cu-TiO₂, where additional diffraction features can be distinguished, suggesting the presence of a crystalline copper-containing phase.

For the materials containing Fe and Zn oxides, the absence or low intensity of additional reflections indicates that no crystalline secondary phases were detected under the conditions used for XRD analysis. The HA-containing materials were also evaluated after thermal treatment at 600 and 800 °C, respectively, allowing the effect of calcination temperature on their structural characteristics to be examined.

Figure 1b presents the SEM micrographs of the synthesized materials. The images show nanometric particles and agglomerates with different morphologies among the TiO₂-based materials. The crystallite sizes, calculated from the (101) reflection of the anatase phase using the Debye-Scherrer equation and the corresponding full width at half maximum (FWHM), ranged from approximately 10 to 21 nm, as summarized in Table 2. These values confirm the nanocrystalline nature of the synthesized materials. The nanoscale crystallite dimensions and the degree of particle aggregation may influence the accessible surface area and the interaction between the semiconductor surface and the aqueous electrolyte. The observed structural and morphological differences among the TiO₂-based materials provide relevant information for interpreting their PEC behavior.

Figure 2 presents the determination of the optical band-gap energy (E_g) of the synthesized materials. The E_g values were estimated, assuming direct electronic transitions using the Tauc approach (Bharad et al., 2018). For pristine TiO₂, extrapolation of the linear region of the corresponding plot gives an E_g value of approximately 3.24 eV, which is consistent with the expected optical band gap of anatase. In the Cu-TiO₂ material, two linear regions were observed, yielding E_g values of 2.68 and approximately 2.00 eV, value that represent a significant

decrease in the apparent optical band gap relative to pristine TiO_2 and is consistent with the introduction of electronic states within the TiO_2 band structure associated with Cu incorporation. The second contribution, at approximately 2.00 eV, is consistent with the optical response associated with CuO, whose band-gap energy has been reported within a range of approximately 1.0–2.1 eV (Zhao et al., 2024). It should be noted that CuO was not identified as a distinct crystalline phase by XRD; therefore, the assignment of its optical contribution is based on the optical analysis rather than on the detection of a separate CuO crystalline phase.

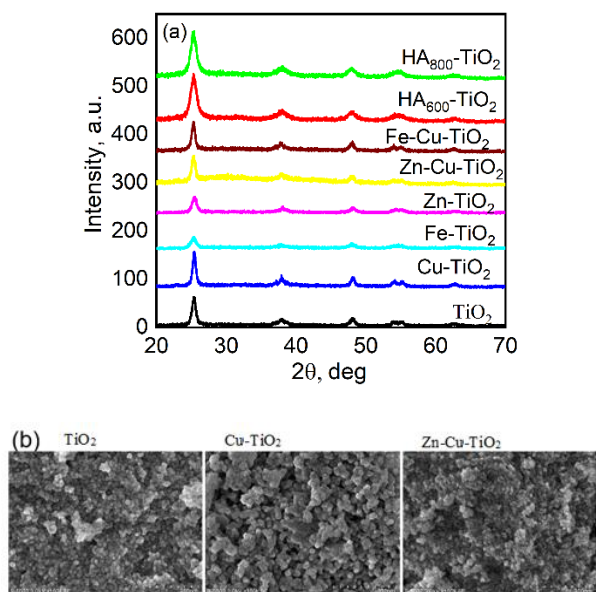


Figure 1. (a) XRD of doped TiO_2 , (b) SEM of TiO_2 , Cu-TiO_2 and Zn-Cu-TiO_2 materials.

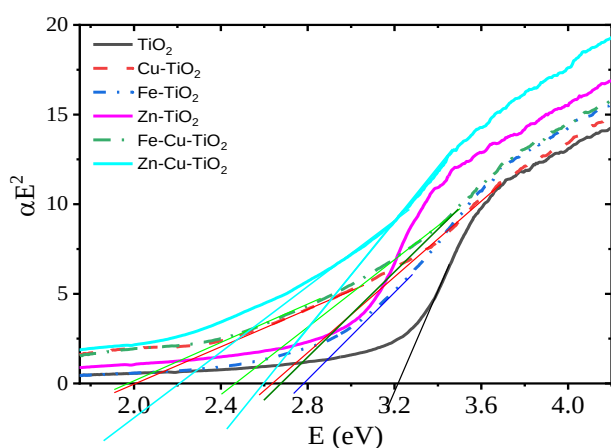


Figure 2. Band gap energy of nanomaterials, obtained from transmittance data assuming direct optical transitions

A similar behavior was observed for Fe-Cu-TiO_2 , for which two linear regions were obtained, corresponding to E_g values of 2.79 eV and 2.02 eV. The first value can be associated with the modified TiO_2 phase, whereas the lower-energy contribution is consistent with the optical response attributed to CuO. As observed for Cu-TiO_2 , the

lower apparent band-gap energies relative to pristine TiO_2 suggest changes in the electronic structure of the modified materials. These changes may influence the energy required for photoexcitation and the generation and transport of photogenerated charge carriers. However, a lower E_g alone does not necessarily imply higher photoelectrocatalytic activity, since charge-carrier separation and recombination, surface properties, and interfacial electron-transfer processes also contribute to the overall performance of the materials.

Table 2. Crystal size and band gap energy of TiO_2 nanomaterials

Nanomaterial	Crystal Size, nm	Band Gap energy, TiO_2 , eV	Band Gap energy, CuO, eV
TiO_2	19	3.24	---
Cu-TiO_2	21	2.68	2.0
Zn-Cu-TiO_2	20	2.77	---
Fe-Cu-TiO_2	17	2.79	2.02
$\text{HA}_{600}\text{-Cu-TiO}_2$	13	---	---
$\text{HA}_{800}\text{-Cu-TiO}_2$	17	---	---

Photoelectrocatalytic discoloration experiments using Zn-Cu-TiO_2 working electrodes were performed under galvanostatic conditions using an initial AB1 concentration of 25 mg/L. The main operating parameters investigated were the applied current density, Na_2SO_4 electrolyte concentration, and temperature, as shown in Figure 3. Current densities of 0.10, 0.125, and 0.25 mA/cm^2 were evaluated, together with Na_2SO_4 concentrations of 0.075, 0.10, and 0.20 M and temperatures of 40, 50, and 60 $^\circ\text{C}$.

As shown in Figure 3a, the highest discoloration of AB1 was obtained at a current density of 0.25 mA/cm^2 . The increase in current density can enhance the electrochemical contribution to the photoelectrocatalytic process by promoting charge transfer at the electrode–electrolyte interface and influencing the transport of photogenerated charge carriers. However, the effect of the applied current cannot be considered independently of the other operating parameters, since excessive current densities may also promote competing electrochemical reactions. Under the conditions evaluated in this study, 0.25 mA/cm^2 provided the most favorable response.

The effect of Na_2SO_4 concentration is presented in Figure 3b. Among the concentrations evaluated, the lowest electrolyte concentration, 0.075 M, resulted in the highest AB1 discoloration. This result indicates that increasing the ionic strength of the solution did not improve the discoloration efficiency under the experimental conditions used. The electrolyte provides ionic conductivity and supports the electrochemical current, but its concentration may also influence the interfacial environment and the relative contribution of competing electrochemical reactions. Therefore, the highest Na_2SO_4

concentration was not necessarily associated with the highest photoelectrocatalytic performance.

Figure 3c shows the effect of temperature on AB1 discoloration. The best overall response was obtained at 50 °C. Although the discoloration process was initially slower at this temperature, it continued progressively and resulted in the highest discoloration at the end of the evaluated reaction period. The improved response at 50 °C may be associated with enhanced mass transfer and reaction kinetics at the semiconductor–electrolyte interface. Nevertheless, increasing the temperature beyond the optimum did not result in a further improvement in discoloration, indicating that 50 °C provided the most favorable conditions among those evaluated. Based on these experiments, the selected operating conditions for subsequent experiments PEC were a current density of 0.25 mA/cm², 0.075 M Na₂SO₄, and a temperature of 50 °C.

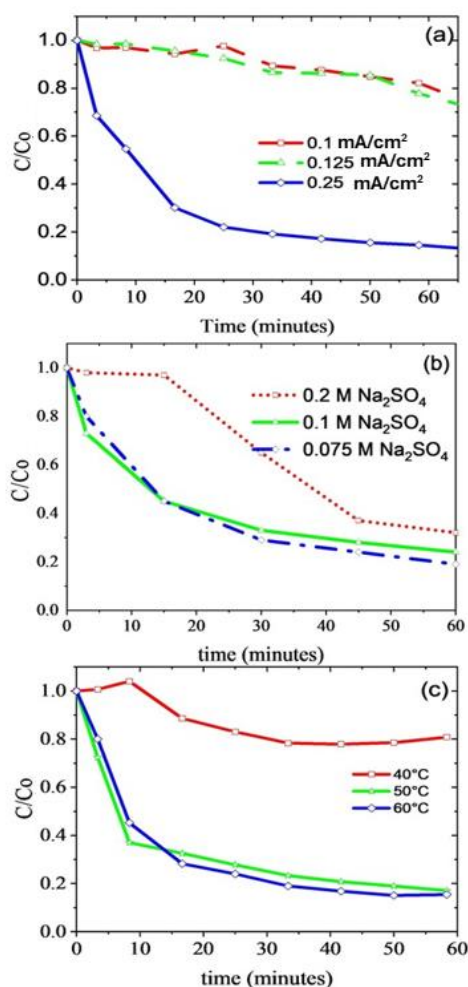


Figure 3. Obtaining of operating parameters (a) Current intensity, (b) electrolyte concentration, (c) Temperature, on AB1 discoloration, [AB1] = 25 mg/L, Zn-Cu-TiO₂. (a) T = 60 °C, [Na₂SO₄] = 0.2 M; (b) current density = 0.25 mA/cm², T = 60 °C, (c) [Na₂SO₄] = 0.075, I = 0.25 mA. Test galvanostatic.

Figure 4 shows the AB1 discoloration obtained using the binary and TiO₂ pristine (a) and, ternary (b), photoelectrocatalysts under the selected operating conditions. In binary materials, the fastest initial discoloration was observed for Cu-TiO₂. However, HA₆₀₀-TiO₂ achieved the greatest discoloration, whereas the nanomaterials of HA₈₀₀-TiO₂ and Zn-TiO₂ showed less discoloration. In ternary nanomaterials a clear difference in the discoloration behavior of the four materials can be observed. Zn-Cu-TiO₂ produced the highest overall AB1 discoloration at the end of the treatment period, indicating that this material provided the most favorable overall photoelectrocatalytic response under the experimental conditions used. In contrast, HA₈₀₀-Cu-TiO₂ exhibited a higher initial discoloration rate, indicating a faster initial removal of the dye. However, its performance did not result in the highest final discoloration. This difference suggests that the initial reaction rate and the overall extent of discoloration are not necessarily governed by the same factors. The faster initial response observed for HA₈₀₀-Cu-TiO₂ may be associated with its surface characteristics and the effect of the 800 °C hydroxyapatite treatment on the properties of the resulting composite. In contrast, the superior final performance of Zn-Cu-TiO₂ may be related to the combined influence of its optical and structural properties, including its reduced apparent band-gap energy (2.77 eV) compared with pristine TiO₂ (3.24 eV). However, the lower apparent band-gap energy alone cannot explain the higher final discoloration observed for Zn-Cu-TiO₂.

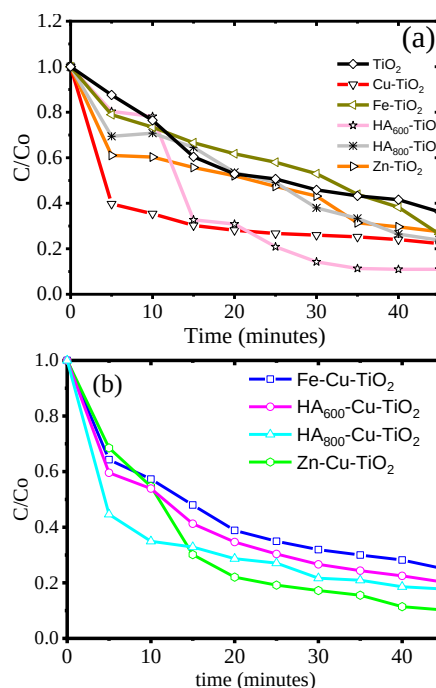


Figure 4. AB1 discoloration photoelectrocatalytic with (a) binary and, (b) ternary semiconductors. [AB1] = 25 mg/L, T = 50 °C, [Na₂SO₄] = 0.075, current density = 0.25 mA/cm². Test galvanostatic.

Both HA₆₀₀-TiO₂ and Zn-Cu-TiO₂ were nanomaterials that achieved greater decolorization, although the process was slightly faster with Zn-Cu-TiO₂. In HA₆₀₀-TiO₂, Adsorption properties (of HA) play a significant role in achieving superior decolorization; in the case of Zn-Cu-TiO₂, the potential CuO-TiO₂ heterojunction likely plays a key role in electron-hole separation. The results suggest that overall discoloration behavior is influenced by the combined effects of semiconductor composition, surface properties, charge-carrier processes, and interactions with the electrolyte and AB1 molecules.

Despite the good AB1 discoloration obtained with the photoelectrocatalytic materials, an important observation was made during the treatment. A red coloration developed in the solution and remained difficult to eliminate as the reaction proceeded. Under the experimental conditions used, the relatively low potential of the work electrodes may have favored the anodic oxidation of water and the generation of molecular oxygen at the working electrode, this was notable, as indicated by the intense bubbling at the working electrode under anodic conditions. Consequently, the formation of hydroxyl radicals (•OH), which is generally associated with sufficiently positive anodic potentials for water oxidation, may have been limited. Instead, oxygen generated at the electrode may have participated in subsequent reactions leading to the formation of reactive oxygen species (ROS), which could contribute to the oxidation of AB1 and its transformation products. However, ROS such as superoxide and peroxide-derived species generally have lower oxidation potential than hydroxyl radicals and may therefore exhibit lower oxidation capacity toward certain organic intermediates.

This behavior may help explain why the main AB1 absorption peak decreased substantially while the residual red coloration remained in the solution. Thus, the results suggest that substantial discoloration was achieved, but complete mineralization or elimination of colored transformation products was not necessarily attained under the applied photoelectrocatalytic conditions.

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4. CONCLUSION

The most suitable operating conditions for the photoelectrocatalytic discoloration of Acid Black 1 (AB1) were a temperature of 50 °C, a Na₂SO₄ concentration of 0.075 M, and a current density of 0.25 mA/cm². Among the ternary photoelectrocatalysts evaluated, the Zn-Cu-TiO₂ xerogel exhibited the highest overall AB1 discoloration at the end of the treatment period, whereas the HA₈₀₀-Cu-TiO₂ xerogel showed a faster initial discoloration rate. Among binary nanomaterials, HA₆₀₀-TiO₂ exhibited the best decolorization. These results indicate that the overall photoelectrocatalytic performance depends on the combined effects of the material composition, optical properties, charge-carrier behavior, surface characteristics, and operating conditions, rather than on the band-gap energy alone.

Under the applied electrochemical conditions, the generation of molecular oxygen at the working electrode may have limited the contribution of hydroxyl radicals and favored reaction pathways involving other reactive oxygen species (ROS). The lower oxidation capacity of some ROS compared with hydroxyl radicals may have contributed to the persistence of colored transformation products. This behavior was evidenced by the substantial decrease in the characteristic AB1 absorption peak, while a residual red coloration remained in the solution. Therefore, although significant AB1 discoloration was achieved, the results do not demonstrate complete mineralization of the dye. Further studies using complementary analytical techniques would be necessary to identify the transformation of products and determine the extent of mineralization. Furthermore, additional treatment must be carried out to remove the by-products generated that were not eliminated.

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