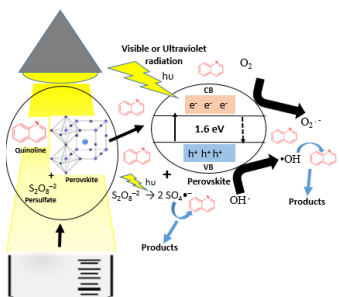


## Evaluation of quinoline degradation process using LaCuTi perovskite activated by polychromatic irradiation

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In this study, we investigated the photocatalytic degradation of the petrochemical pollutant quinoline, using persulfate as an oxidant and a perovskite  $\text{LaCu}_{0.5}\text{Ti}_{0.5}\text{O}_3$  as a photocatalyst, prepared via the sol-gel method. The crystalline structure of the perovskite was characterized by X-ray diffraction (XRD). The theoretical molar ratio of La:Cu:Ti = 2:1:1, was determined by X-ray (EDS). The obtained band-gap energy was 1.6 eV, indicating light absorption in the visible range. The photodegradation of quinoline achieved an efficiency of 90% after 120 min reaction, using a perovskite concentration of  $0.4 \text{ g L}^{-1}$  and a persulfate concentration of  $0.5 \text{ mmol L}^{-1}$ . The photocatalyst was reused for up to six cycles, with degradation efficiency ranging from 70% to 90% under artificial solar light.

### Introduction

The high demand for fossil fuels and petrochemical products leads to an increased generation of industrial effluents that require appropriate treatment [1]. Nitrogenous compounds (indole, pyridine, and quinoline) are present in refinery effluents [2]. Conventional treatments, such as biological processes, are sustainable options, but their effectiveness may be limited due to the need for adjustments in enzymatic activities and the slow adaptation of sludge, especially for recalcitrant pollutants like quinoline [3]. Advanced Oxidative Processes (AOPs) involve the generation of radical species. Hydroxyl ( $\text{OH}^\bullet$ ) and persulfate ( $\text{SO}_4^{\bullet-}$ ) radicals possess high oxidative capacity and low selectivity which are capable of mineralizing organic compounds into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  or simpler structural intermediates. Fenton, photo-Fenton, and photocatalysis are AOPs employed in the degradation of persistent pollutants [4,5]. Perovskites ( $\text{ABO}_3$ ), a class of photocatalysts, have emerged as a promising option due to their stability and the flexibility of their chemical compositions. They are also useful as catalysts in AOPs because they can generate unstable radicals such as hydroxyl and superoxides under the visible light range [6]. This study aims to use heterogeneous perovskite photocatalysts composed of lanthanum, copper, and titanium in the photodegradation of quinoline.

### Material and Methods

**Catalyst synthesis:** The  $\text{LaCu}_{0.5}\text{Ti}_{0.5}\text{O}_3$  material prepared via the sol-gel method was inspired by the works of Garcia-Muñoz *et al.* [7]. 30 mL of a solution containing  $250 \text{ mmol L}^{-1}$  of lanthanum hexahydrate nitrate  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99%, Vetec) and copper trihydrate nitrate  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (98%, Neon) in a molar ratio of La/Cu = 2 was added. Then, the titanium source, titanium isopropoxide  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$  (97%, Sigma-Aldrich), dissolved in 15 mL of isopropyl alcohol  $\text{C}_3\text{H}_8\text{O}$  (99.5%, Synth) in the nitrate solution with a molar ratio of La/Ti = 2, was slowly added. Citric acid  $\text{C}_6\text{H}_8\text{O}_7$  (99.5%, Synth) in a molar ratio Citrate/Ti = 5 was added in excess to the

system to produce metal complexes. The solution was vigorously stirred at  $\pm 80^\circ\text{C}$  for 48 h, observing the formation of a gel which was finally calcined in a muffle furnace with ramps of  $5^\circ\text{C min}^{-1}$  up to a temperature of  $600^\circ\text{C}$  for 2 h and  $5^\circ\text{C min}^{-1}$  up to a temperature of  $800^\circ\text{C}$  for 2 h.

The structural characterization of the material was conducted using X-ray diffraction (XRD) on a Rigaku Smartlab SE diffractometer. The chemical composition was assessed using an energy-dispersive X-ray spectrometer (EDS), specifically the NEX DE model from Rigaku. The light absorption and the determination of the material's band gap energy were performed using a Cary 100 spectrophotometer from Agilent Technologies, utilizing the Diffuse Reflectance Spectroscopy technique (UV-Vis/DRS).

**Degradation of the contaminant:** The degradation of 250 mL of quinoline (98% purity, Dinâmica) at a concentration of  $10 \text{ mg L}^{-1}$  occurred at pH 6.5. An initial adsorption study of quinoline on the  $\text{LaCu}_{0.5}\text{Ti}_{0.5}\text{O}_3$  catalyst was performed for 30 min at a temperature of  $25^\circ\text{C}$ , using a catalyst concentration of  $0.4 \text{ g L}^{-1}$ , followed by artificial sunlight irradiation provided by an ULTRAVITALUX 300 W E27 OSRAM lamp. Compressed air was bubbled through the solution to ensure the presence of dissolved oxygen in the aqueous medium during the photocatalytic process. In the experiment combining the photocatalyst and persulfate, the initial persulfate concentration was maintained at  $0.5 \text{ mmol L}^{-1}$  at a temperature of  $35^\circ\text{C}$ . All experiments were conducted in an open reactor under stirring. The decay in quinoline concentration was measured by spectrophotometric analysis at 317 nm. For quantification, aliquots of 4 mL were collected at regular time intervals (0, 5, 15, 30, 60, 90, and 120 min) and analyzed using a Cary 100 spectrophotometer from Agilent Technologies. Recycling tests were conducted on the photocatalyst exhibiting the best performance to evaluate the material's stability. After each test, the catalyst was recovered by centrifugation at 3000 rpm and washed with water. Finally, it was dried in

an oven at 100°C for 24 h before being reused in the subsequent test.

## Results and Discussion

The diffraction patterns of the perovskite  $\text{LaTiO}_3$  (ICSD 32537) and the spinel  $\text{La}_2\text{CuO}_4$  (ICSD 56528) were not observed in the diffractogram obtained in this work (Figure 1). These structures were previously observed as  $\text{LaTi}_{1-x}\text{Cu}_x\text{O}_3$  perovskites ( $0.4 < x_{\text{Cu}} < 0.6$ ) for the  $\text{LaTiO}_3$  perovskite (JCPD 75-0267) [8].

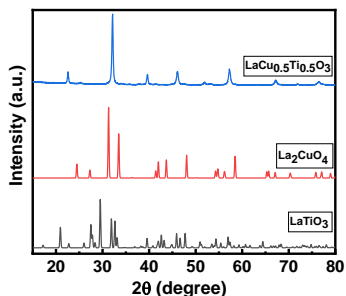


Figure 1. Diffractogram of the catalyst.

The EDS results indicated a 1.7:1:1 molar ratio for La:Cu:Ti, thus obtaining metallic values close to the expected composition in the  $\text{LaCu}_{0.5}\text{Ti}_{0.5}\text{O}_3$  formula. The light absorption of the catalyst included the visible region, with a band gap energy of 1.62 eV, calculated by the Kubelka-Munk method. This value is lower than several perovskites reported in the literature, making it a semiconductor susceptible to photocatalytic activities [9]. The investigations of quinoline photodegradation under artificial solar, with visible light and 4% of UV-A+UV-B, included adsorption, photolysis, photocatalysis, photocatalyst-persulfate, and persulfate (Figure 2a). Results show that photolysis had no influence on contaminant degradation, confirming its stability under natural conditions. phenomena occurring during this period. In the adsorption study, a removal of 45% of the pollutant was observed in the first 30 minutes, followed by a 10% decrease in removal in the subsequent 120 minutes. This indicates that the material has an adsorption limit of 35% for the contaminant, with adsorption and desorption phenomena occurring during this period.

## Conclusions

The  $\text{LaCu}_{0.5}\text{Ti}_{0.5}\text{O}_3$  perovskite was successfully synthesized and showed improved photocatalytic activity with persulfate, likely due to persulfate radicals. It remained effective over multiple cycles and can aid in degrading petroleum-derived contaminants.

## Acknowledgments

Thanks to PRH30.1 ANP/FINEP for financial support.

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Photocatalysis and persulfate systems showed similar performances after 60 min of reaction, reaching 49% and 56.5% degradation, respectively, in 120 min. The photocatalyst shows 45% of adsorption in the dark. However, the best result was obtained using the photocatalyst-persulfate system achieving 90% quinoline degradation in 120 min. This result may be associated with the conversion of persulfate into persulfate radicals ( $\text{SO}_4\cdot^-$ ) by the catalytic sites, increasing the efficiency of the process.

The reuse results, presented in Figure 2b, demonstrated that five reuses of the material were achieved with degradation percentages ranging from 70% to 80% after 120 min, totaling six reaction cycles. However, a 10% decrease in efficiency was observed, a minor reduction that may have been caused by material losses during the recovery procedures. This issue is a characteristic of dispersed catalysts and can be addressed through additional recovery processes, such as vacuum membrane filtration or using the catalyst immobilized in a photoreaction structure.

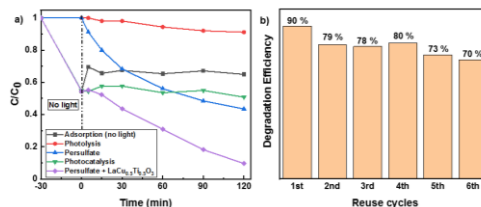


Figure 2. (a) Photodegradation of quinoline at  $10 \text{ mg L}^{-1}$  and (b) catalyst cycle under the best condition.