Removal of a Pharmaceutical Pollutant by Heterogeneous Photocatalysis Using Mixed Oxides Derived from Hydrotalcite-type Materials

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Abstract—This study develops a CuZnAl-MO photocatalyst (CuO/ZnO) for the heterogeneous photodegradation of Ramipril in water. The photocatalyst, prepared by calcining CuZnAl-HT hydrotalcite-type material at 450°C, showed 79% photocatalytic efficiency and excellent stability. Its enhanced performance is due to efficient charge separation in the S-scheme heterostructure, a large surface area, and improved sunlight harvesting. Scavenger experiments identified HO^{\bullet} and h^+ radicals as key contributors to the degradation. The CuZnAl-MO photocatalyst outperforms individual ZnO and CuO, offering a promising solution for solar-driven photocatalysis.

Keywords— CuO/ZnO solid solutions; Calcination; Layered double hydroxide; Heterogeneous photocatalysis; Ramipril.

I. INTRODUCTION

Algeria has been identified as the fourth largest consumer of medicines in the Middle East. This high consumption has been linked to the release of micropollutants into sewage systems, representing a significant concern for the relevant authorities. A study undertaken in 2022 revealed that the emergence of the novel Coronavirus (SARS-CoV-2) has led to an increase in the presence of organic micropollutants in wastewater treatment facilities [1]. These micropollutants originate from a variety of everyday products, including medicines, cosmetics, and insecticides, and they enter aquatic ecosystems, thereby posing significant health and ecological risks. Of particular concern is the detection of Ramipril, a pharmaceutical agent used to treat hypertension, in elevated concentrations within water bodies, thereby posing a significant threat to aquatic fauna [2]. While several treatment methods exist, they all have their limitations. Photocatalysis, a process with great potential, uses oxidizing radicals to break down contaminants without the need for additional chemicals, thereby enabling the degradation of organic pollutants in a more efficient and environmentally friendly way [3]. Semiconducting mixed oxides, derived from hydrotalcite-type materials (HT), have been shown to be particularly effective in this field [4][5]. This research focuses on the use of HT-derived CuO/ZnO solid solutions to effectively remove Ramipril, by improving visible light absorption and interaction with pollutants.

II. MATERIALS AND METHODS

A. Preparation of Photocatalysts

CuZnAl-HT hydrotalcite-type photocatalyst was produced using a co-precipitation technique [6][7], with an $R=M^{II}/M^{III}$ molar ratio equal to 2.0 and a Cu^{2+}/Zn^{2+} molar ratio equal to 1.0. A mixed salt solution and an alkaline solution containing Na_2CO_3 were prepared. These two solutions were added dropwise and simultaneously under vigorous stirring for 3 h at room temperature, while the pH was maintained around 10 ± 0.2 by varying the rate of addition. This pH value, which was determined after a series of studies with several pH values, provides the highest

crystallinity. The suspension was stirred for 0.5 hours before being aged at 70°C for 18 h. The product was then filtered, rinsed with deionized water, and dried at 80°C for 20 h, then ground to a homogeneous powder.

CuZnAl-MO mixed oxides photocatalyst was synthesized by calcining CuZnAl-HT material at 723 K in a muffle furnace. The heating rate observed was 1°C min⁻¹. Following the achievement of the target temperature, the heating process was prolonged for an additional 6 h.

B. Characterization of Photocatalysts

The prepared photocatalysts were characterized using various analytical techniques. X-ray diffraction (XRD) investigations were conducted utilizing a BENCHTOP powder diffractometer (para, theta - Bragg-Brentano configuration with two focusing theta angles). Fourier transform infrared (FTIR) spectra were obtained to detect chemical bonds and functional groups in the catalysts, making structural analysis more practical. Using a Perkin-Elmer FT1730 spectrometer in the 4000-400 cm⁻¹ range with a resolution of 2 cm⁻¹. thermogravimetric analysis (TGA) was performed using a TGA 51 (Shimadzu) in the presence of 30 sccm of flowing Ar. Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted using Spectro Arcos 160 CCD spectrometer. UV-Vis diffuse reflectance (DRS) were recorded on a Shimadzu UV-2550 spectrophotometer. Electrochemical properties of materials were analyzed by cyclic voltammetry (CV), and electrochemical impedance spectrum (EIS) on an electrochemical workstation (Gamry 1010E) using three-electrode configuration with a platinum electrode as the counter, a saturated calomel electrode (SCE) as the reference electrode, and the platinum working electrode. Textural properties were determined using nitrogen sorption tests. The surface area was determined using the BET technique from the N₂ adsorption isotherm, and the pore size was calculated using the BJH method using the QuandraSorb SI Models 4.0 with the QuandraWin Software (quantachrome Instruments v. 5.0+ newer) instrument at 77 K. Field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FESEM-EDS) was used to provide morphological and compositional information on materials using Scios 2 from FEI® (Waltham, Massachusetts, USA) with various integrated detectors. Zero-charge point (pH_{PZC}) was determined using the room temperature salt addition method as shown by [8].

C. Heterogeneous Photocatalysis Procedure

1) Adsorption Tests

The adsorption tests were conducted to study the adsorption isotherm of Ramipril on the surface of prepared photocatalysts. An amount of photocatalyst was added to 50 mL flasks, while simultaneously mixing 30 mL of Ramipril solution. The initial concentrations of the solution ranged from 0 to 200 mg L⁻¹. The pH of the solutions was not initially modified. The vials were placed in a water bath that was thermostated at a temperature of 25°C. After 3 h of adsorption, the suspended solutions were subjected to centrifugation. The HPLC chromatograph was used to measure the amounts of Ramipril. The quantity of Ramipril adsorbed at equilibrium Q_e (mg g⁻¹) was determined using Eq. (01):

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \tag{01}$$

where, C_0 and C_e (mg L⁻¹) are the concentrations of Ramipril in solution before and after adsorption, respectively, V (mL) is the volume of the suspension and m (mg) is the amount of photocatalyst added.

Langmuir and Freundlich models (Eqs. 02 and 03) [9] [10] were applied to model adsorption isotherms.

$$Q_e = \frac{Q_{\max} k_L C_e}{1 + k_L C_e} \tag{02}$$

$$Q_{e} = k_{F}C_{e}^{n} \tag{03}$$

where, $C_e (\text{mg L}^{-1})$ is the concentration of Ramipril at equilibrium, Q_e and $Q_{max} (\text{mg g}^{-1})$ are the quantity of Ramipril adsorbed at equilibrium and maximum adsorbed, respectively, k_L is the equilibrium constant, k_F and n are the adsorption constants indicating adsorption capacity and adsorption intensity, respectively.

2) Heterogeneous Photocatalysis Tests

For comparison purposes, heterogeneous photocatalysis of Ramipril using CuZnAl-HT and CuZnAl-MO materials was carried out under sunlight irradiation. In these tests, the vials containing the Ramipril solution were placed outdoors, allowing direct exposure to sunlight with a UV irradiance of 293 W m⁻² recorded using a digital luxmeter (AS803, Chanfong, CN).

Prior to light exposure, the Ramipril solution (50 m L^{-1}) was stirred in the dark for 30 min to ensure adsorption equilibrium with the photocatalyst, which was used at a amount of 1.0 g L^{-1} . The photocatalytic reaction was then initiated by irradiating the system under continuous magnetic stirring for a duration of 3 h.

This study investigated the influence of several operational parameters on the heterogeneous photocatalytic degradation of Ramipril, including the contact time, the amount of photocatalyst, the initial Ramipril concentration, and the initial pH of the solution. Each parameter was varied independently, while all others were held constant, to evaluate its specific effect on the degradation process.

At predetermined time intervals during the reaction, samples were collected and centrifuged to separate the solid catalyst. The resulting supernatant was subjected to high-performance liquid chromatography (HPLC) analysis. All experiments were performed in duplicate to ensure reproducibility.

Additionally, radical scavenging tests were conducted to identify the reactive species responsible for Ramipril degradation. Specific scavengers were employed to quench hydroxyl radicals ('OH), superoxide radicals (O_2^{-}) , photogenerated holes (h⁺), and electrons (e⁻), thereby elucidating the dominant species involved in the degradation mechanism.

3) Samples analysis

The solution aliquots were examined using High Performance Liquid Chromatography (HPLC), and Total Organic Carbon (TOC), yielding both qualitative and quantitative outcomes. An Agilent 1220 Infinity LC gradient equipment with a UV detector was used to perform high performance liquid chromatography (HPLC). The analytes were separated at ambient temperature using a Mediterranea type C18 column with dimensions of 5 μ m, 4.6 mm, and 150 mm, manufactured by Teknokrom in the United States. The wavelength was configured to a value of 210 nm. The mobile phase comprised two solutions: solution A (0.1% phosphoric acid) and solution B (Acetonitrile). The photocatalysis efficiency of Ramipril was determined using equation (04).

Photodegradation efficiency (%) =
$$\frac{C_0 - C_f}{C_0} \times 100$$
 (04)

where, C_0 and C_f are the initial and the final concentrations of Ramipril (mg L⁻¹).

The degree of mineralization during the tests was determined using a Shimadzu TOC-L analyzer to measure the total organic carbon (TOC). Equation (05) was utilized to ascertain the percentage of Total Organic Carbon (TOC) that was eliminated:

TOC removal (%) =
$$\frac{\text{TOC}_0 - \text{TOC}_f}{\text{TOC}_0} \times 100$$
 (05)

where, TOC_0 and TOC_f are the initial and the final total organic carbon (mg L⁻¹).

III. RESULTS AND DISCUSSIONS

A. Characterization of Photocatalysts

Figure 1 shows the XRD patterns of CuZnAl-HT and CuZnAl-MO photocatalysts. As shown in CuZnAl-HT XRD patterns, the diffraction peaks at $^{\circ}2\theta$ =11.8°, 23.6°, 35.1°, 39. 6°, 47.0°, 53.2°, 60.9° and 62.2° can be attributed to reflections (0 0 3), (0 0 6), (0 1 2), (0 1 5), (0 1 8), (1 0 10), (1 1 0) and (1 1 3) of indexed hydrotalcite (PDF No. 00-054-1030), characteristic of a layered structure [11]. In addition, reflections at $^{\circ}2\theta$ =34.4°, 37.0°, 56.5° and 62.8° can be indexed to Zn(OH)₂ (PDF No. 00-048-1066). In other words, Zn(OH)₂ and HT coexist and no diffraction peaks corresponding to copper compounds in the CuZnAl-HT photocatalyst are observed, suggesting that Cu²⁺ ions

are well dispersed in the ZnAl-HT lattice. The same result was found by Zhang et al. [4] when synthesizing the ZnAl-LDH and ZnNiAl-LDH phases.





Crystalline phases: H: Hydrotalcite (00-054-1030), ■ : Zn(OH)₂ (00-048-1066), ▼ : ZnO (01-089-0510), ● : CuO (00-045-0937)

XRD diagram of CuZnAl-MO photocatalyst calcined at 450° C shows that reflections corresponding to HT material disappear completely and new reflections appear after calcination. Reflections at $^{\circ}2\theta=31.7^{\circ}$, 34.4° , 36.2° , 48.0° , 56.9° , and 63.1° can be indexed to the hexagonal Wurtzite structure of ZnO (PDF No. 01-089-0510), while those at $^{\circ}2\theta=35.2^{\circ}$, 38.7° , 48.7° and 61.6° can be indexed to the Monoclinic Tenorite CuO structure (PDF No. 00-045-0937). These results can be attributed to the homogeneous distribution of metal ions within HT-type material, which facilitates the formation of well-dispersed, crystalline mixed metal oxides by a topotactic process during calcinations. No signal corresponding to the Al₂O₃ phase is detected, implying that Al₂O₃ is amorphous. Indeed, the collapse of the CuZnAl-HT layered structure during calcination generates 55% CuO and 45% ZnO, calculated using the Rietveld method (% by weight) [12], indicating the high purity of the CuO/ZnO hybrid.

Figure 2 presents the FTIR spectra of the CuZnAl-HT and CuZnAl-MO photocatalysts. The broad absorption band observed around 3400 cm⁻¹ is attributed to the O–H stretching vibrations, which arise from hydroxyl groups within the metal hydroxide layers as well as interlayer water molecules [13]. A weak band appearing near 1620 cm⁻¹ corresponds to the bending vibrations of water molecules [14]. A distinct peak at approximately 1355 cm⁻¹ is associated with the asymmetric stretching vibrations of C–O bonds in carbonate ions located in the interlayer region of the CuZnAl-HT structure [15]. Additionally, the band detected at 1079 cm⁻¹ is linked to the bending vibration of carbonate ions. Although this mode is IR inactive in free carbonate ions, it becomes active due to the reduced symmetry of carbonate anions confined in the interlayer space [16]. Absorption bands below 1000 cm⁻¹ correspond to various vibrational modes of carbonate species and the stretching vibrations of metal–oxygen (M–O) and metal–oxygen–metal (M–O–M) bonds within the brucite-like layers of the material [17]. Peaks around 800 cm⁻¹ and 550 cm⁻¹ are attributed to the vibrational modes of the AlO₆ octahedral coordination and Al–OH bonds, respectively. The Zn–OH stretching vibration is observed at 617 cm⁻¹, while the band at 430 cm⁻¹ is characteristic of M–O stretching vibrations [15] [18].



Fig. 2 FTIR spectra of prepared photocatalysts.

The absorption bands around 3400 and 1620 cm⁻¹ are significantly reduced in the CuZnAl-MO photocatalyst, indicating the removal of water molecules and confirming the dehydration of the CuZnAl-HT structure following calcination at 450 °C. The bands observed at 2930 cm⁻¹ and 2850 cm⁻¹ in the CuZnAl-MO photocatalyst are attributed to the stretching vibrations of free and hydrogen-bonded –OH groups, as well as water molecules. These bands also correspond to CO₃–H₂O bridging modes formed between adsorbed water and atmospheric CO₂ on the surface of the calcined material [19]. Additionally, a peak observed at 2350 cm⁻¹ in the CuZnAl-MO spectrum is assigned to the asymmetric stretching vibration of CO₂, which may originate from atmospheric adsorption or residual CO₂ trapped within the grains of the calcined material. Calcination of CuZnAl-HT at elevated temperatures, such as 450 °C, induces notable changes in the carbonate region. The carbonate ion coordination due to the loss of interlayer water molecules [20]. In the higher-frequency region, bands at 1100 and 790 cm⁻¹ are attributed to the deformation and translational vibrational modes of hydroxyl groups, influenced by the presence of Al³⁺ ions [21]. Furthermore, the peaks at 520 cm⁻¹ and 490 cm⁻¹ correspond to the formation of Zn–O and Cu–O bonds, respectively, confirming the structural incorporation of these metal oxides following calcination [22].

Thermogravimetric analysis is very useful for tracking the decomposition of prepared CuZnAl-HT photocatalyst, or how the mass of a material varies with temperature. By examining the thermograms in **Figure 3**, the multi-step mass loss of type 4 according to the shape-based classification of TGA curve was observed [23].

The first loss occurs between room temperature and 250° C and is attributed to the loss of physisorbed water at the material surface, the second loss occurs between 250 and 350°C and is attributed to the first dehydroxylation step (departure of structural hydroxyl groups, hence the formation of H₂O, the decarbonation (departure of carbonate anions from the inter-lamellar space, hence the formation of CO₂); to give rise to decomposition of the lamellar structures and formation of the derived mixed oxides, above 600°C, HT material undergoes a series of total decarbonation reactions to produce the metal oxides, resulting in the destruction of the lamellar phase. The ZnCuAl-LDH photocatalyst underwent a 13% weight loss when subjected to temperatures ranging from room temperature to 250°C.



Fig. 3 TGA curve of CuZnAl-HT prepared photocatalyst.

The physicochemical properties of the CuZnAl-HT photocatalyst, including the elemental composition, empirical formula, and actual molar ratios of $M_{(II)}/Al^{3+}$ and Cu^{2+}/Ni^{2+} , were determined based on ICP-OES analysis. The results indicate that the experimental M(II)/M(III) molar ratio is very close to the theoretical value of 2.0, confirming the successful synthesis of the HT structure. Furthermore, the CuZnAl-HT photocatalyst was found to have the following empirical formula:

Cu_{0.210} Zn_{0.241}Al_{0.236}(OH)₂(CO₃)_{0.118}.0.325H₂O

As shown in **Figure 4**, UV-Vis analysis was performed to verify the optical properties of the prepared photocatalysts using a wavelength range of 200 nm to 900 nm. The absorption spectra of the CuZnAl-HT showed that they responded to sunlight due to the presence of absorption bands in the visible region at about 780 nm. However, calcination of the CuZnAl-HT photocatalyst resulted in a ZnO/CuO nanocomposite with increased absorption in the visible range and absorption of UV light in the 200–400 nm range. This material combines the optical properties of the two oxides CuO and ZnO. Thus, UV-Vis activation of the CuO/ZnO n-p heterojunction in sunlight will help increase its photocatalytic efficiency. In addition, the light absorption of CuZnAl-MO photocatalyst is higher than that of CuZnAl-HT throughout the visible region of the spectrum. The optical bandgap energy was explored using the Tauc diagram expression (Figure 5), which is revealed in Eq. (06) [24].

$$(Ah\upsilon)^{n} = k(h\upsilon - E_{g}) \tag{06}$$

where *A* is the absorption coefficient, *hv* is the photon energy, *k* is a specific constant, and E_g is the bandgap energy. *n* is given by the nature of transition: for a direct gap, n = 2, and for an indirect gap, n = 0.5 [25]. In this study, n = 2 is due to the presence of a direct transition.



Fig. 4 UV-Vis absorbance from diffuse reflectance measurements of prepared photocatalysts.

The E_g values are 4.19 eV, and 1.86 - 2.98 eV for CuZnAl-HT and CuZnAl-MO, respectively. For the CuZnAl-MO photocatalyst, Figure 5-(b) shows two E_g at 1.86 eV for CuO oxide and at 2.98 eV for ZnO oxide. The CuZnAl-MO photocatalyst, which is composed of CuO and ZnO, absorbs irradiations in the visible range and should therefore exhibit better photocatalytic activity than CuO and ZnO under visible light.



Fig. 5 Tauc plots of prepared photocatalysts: (a) CuZnAl-HT and (b) CuZnAl-MO.

The electrochemical performance of CuZnAl-HT and CuZnAl-MO electrodes was evaluated using cyclic voltammetry (**Figure 6**). The CuZnAl-HT electrode demonstrated a larger CV area, indicating a higher electron transfer rate. This enhancement is attributed to its higher surface area, layered structure, and better ionic conductivity, which together facilitate faster and more reversible redox reactions compared to the more rigid CuZnAl-MO material [26].



Fig. 6 CV curves of prepared photocatalysts.

Electrochemical impedance spectroscopy (EIS) analysis, as shown in **Figure 7**, reveals that the CuZnAl-MO photocatalyst exhibits a smaller semicircle in the Nyquist plot, indicating lower charge transfer resistance and enhanced electron mobility [27]. This improved charge transport suggests better separation and mobility of photogenerated charge carriers, contributing to its superior photocatalytic performance [28]. Additionally, the steeper slope observed in the low-frequency region reflects more efficient ion diffusion. The two-phase impedance response also confirms the presence of distinct interfacial charge transfer processes within the material, further supporting the effective separation of photogenerated electron–hole pairs.



Fig. 7 EIS Nysquist plots of prepared photocatalysts.

Figure 8 show the N₂ adsorption-desorption isotherm of prepared photocatalysts. The H3-type hysteresis loops are located in the region $P/P_0 > 0.8$, indicating the presence of mesoporous materials comprising plate-shaped particle aggregates. These loops do not exhibit a plateau at high P/P_0 values and must be classified as type II isotherms. This pseudo-type II behavior is associated with the metastability of the adsorbed multilayer and the non-rigidity of the aggregate structure [29]. The specific surface values were determined using the Brunauer-Emmett-Teller (BET) method [30] and were found to be 46.79 m² g⁻¹ and 55.53 m² g⁻¹ for CuZnAl-HT and CuZnAl-MO, respectively. This increase in specific surface area is attributed to the formation of new mesopores in the MO structures through the elimination of carbonates and water molecules at high temperatures [31].



Fig. 8 N₂ adsorption-desorption isotherm of prepared photocatalysts.

The particle morphology of the prepared photocatalytic powders was investigated using FESEM, as shown in **Figure 9**. The CuZnAl-HT material (**Figure 9**-(**a**)) exhibited a high degree of platelet-like morphology and irregular agglomerates with particle sizes between 120 nm. In contrast, the HT structure collapsed and the platelets became irregular aggregates in the MO calcined material (**Figure 9**-(**b**)). The CuZnAl-MO structure shows a rough lamellar structure. It should be noted that the MO material retained the characteristic morphology of mixed oxides, with interconnected pores with wrinkled edges, which influenced its surface adsorption and photocatalytic properties.



Fig. 9 FESEM images of prepared photocatalysts: (a) CuZAl-HT and (b) CuZnAl-MO.

B. Heterogeneous Photocatalysis Procedure

4) Photolysis tests

Prior to the heterogeneous photocatalysis tests to removal Ramipril, the photolysis was measured. The results in **Figure 10** showed that 11.1% of Ramipril was removed by photolysis under sunlight irradiation, this indicates that radiation is not sufficient for the removal of Ramipril.

5) Adsorption tests

. The adsorption tests using the prepared photocatalysts was carried out in the dark for 30 min, and the removal of Ramipril was 12.9% and 22.3% for the CuZnAl-HT and CuZnAl-MO photocatalysts, respectively. The results show that the higher the BET-specific surface area of the photocatalyst, the higher the adsorption percentage. In this adsorption tests, the results were low on the photocatalyst surface, so this pollutant could not be removed by this process.

Photocatalyst	Langmuir constants			Freundlich constants		
	Q _{max} (mg g ⁻¹)	kL	$\mathbf{R}_{\mathbf{L}^2}$	kF	n	$\mathbf{R}_{\mathbf{F}^2}$
CuZnAl-HT	05.38	0.090	0.9872	0.582	0.904	0.9267
CuZnAl-MO	11.21	0.012	0.9778	0.373	0.604	0.9542

 TABLE I

 Adsorption isotherm models applied prepared photocatalysts by using Ramipril as model pollutant.

 R_{L^2} and R_{F^2} : correlation coefficients of Langmuir and Freundlich, respectively.

6) Heterogeneous Photocatalysis Tests

Time 0 of the reaction began when the system was exposed to irradiation under sunlight. According to **Figure 10**, the calcined CuZnAl-MO photocatalyst showed the highest efficiency (79%) under sunlight irradiation in just 180 min, comparing it with the CuZnAl-HT photocatalyst exhibited very low photocatalytic activity (32%). Two-stage degradation are showed: a fast initial phase where Ramipril degrades rapidly according to pseudo-first-order kinetics, and a slower second phase, likely due to the accumulation of intermediates that compete with Ramipril for active sites. This result can be correlated with the XRD observation that only a small amount of $Zn(OH)_2$ is present at this stage, and the rest of the Cu²⁺ and Zn²⁺ ions are incorporated into the brucite-like sheets. Furthermore, given the low activity of the CuO and ZnO oxides, it is evident that a synergistic interaction between CuO and ZnO in the

CuZnAl-MO photocatalyst considerably enriched the catalytic active sites and improved the efficiency of ramipril degradation.



Fig. 10 Heterogeneous photolysis activity tests of prepared photocatalysts under sunlight irradiation.

Several parameters, such as photocatalyst amount, Ramipril concentration, and initial solution pH, can affect the removal of Ramipril by heterogeneous photocatalysis processus. To optimize the catalytic process, it is necessary to identify the parameters that have the greatest impact.

The study explored the influence of photocatalyst quantity on Ramipril degradation by adjusting the photocatalyst dose between 0.05 g L⁻¹ and 1.4 g L⁻¹ at room temperature and pH 4.7, while keeping the Ramipril concentration constant (Figure 10). Adsorption tests showed that the amount of Ramipril adsorbed decreased as the photocatalyst dose increased, reaching a maximum of 09% and 15% at 1.0 g L⁻¹ of CuZnAl-HT and CuZnAl-MO, respectively. On the other hand, the rate of photodegradation increased with higher doses of photocatalyst. However, above the optimum dose of 1.4 g L⁻¹, the conversion rate dropped due to factors such as radical self-quenching, reduced contact between radicals and Ramipril, increased turbidity and aggregation of catalyst particles, all of which hindered the degradation process [32] [33].



Fig. 10 Heterogeneous photolysis activity tests of prepared photocatalysts under sunlight irradiation.

Figure 11 shows that Ramipril photodegradation is highest at low concentrations (around 25%) with the CuZnAl-MO photocatalyst, while CuZnAl-HT remains significantly less efficient. As Ramipril concentration increases, degradation efficiency gradually decreases. This can be explained by the absorption of UV light by excess Ramipril molecules, blocking of the catalyst's active sites or saturation of its surface, thus limiting its photocatalytic activity [34] [35].



Fig. 11 Heterogeneous photolysis activity tests of prepared photocatalysts under sunlight irradiation.

Figure 12 shows that Ramipril degradation efficiency is highest under acidic (pH 3) and basic (pH 11) conditions, particularly with the CuZnAl-MO photocatalyst, while it is lowest at neutral pH (7). This variation can be explained by the effect of pH on the surface charge of the catalyst and on the ionization state of Ramipril, which influences their interaction and the generation of reactive radicals responsible for photodegradation [36].



Fig. 12 Heterogeneous photolysis activity tests of prepared photocatalysts under sunlight irradiation.

In this study, the photodegradation activity of CuO and ZnO photocatalysts was enhanced by the cooperative effects of CuO and ZnO metal oxides in the CuZuAl-MO photocatalyst, the formation of a p-n heterojunction between p-type CuO and n-type ZnO in the CuZnAl-MO photocatalyst can prolong charge recombination between electrons and holes, where the electric field created at the heterojunction limits electron/hole transfer between CuO and ZnO in the ZnCuAl-LDO photocatalyst. The photoresponse range of semiconductors extends from UV to visible light, enabling mixed oxides to make greater use of solar energy.

IV. CONCLUSIONS

This study proposes an efficient method for degrading Ramipril, a pharmaceutical pollutant, in water under sunlight, using an S-CuO/ZnO heterojunction. This photocatalyst offers higher degradation efficiency, reaching 79% in 180 minutes, compared with only 26% and 30% for CuO and ZnO alone. It offers high stability, better light absorption and improved charge carrier separation. The study paves the way for applications such as hospital water decontamination and other Fenton-like reactions.

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