RESEARCH PAPER

CuO/ZrO_2 Nanocomposites: Facile Synthesis, Characterization and Photocatalytic Degradation of Tetracycline Antibiotic

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ABSTRACT

Different antibiotic drugs are widely present in the environment for the treatment of bacterial infections. Overuse of antibiotics leads to the accumulation of these drugs in water systems. Removing antibiotics-based pollutants from water is essential. Nanoscience and nanotechnology can be very helpful in this field. In this work, CuO/ZrO_2 nanocomposites was prepared via the simple and facile method. The prepared samples were analyzed X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FTIR) analysis, and UV-Vis analysis. The results indicate the high potential of synthesized nanocomposites made in photocatalytic degradation. The prepared CuO/ZrO_2 Nanocomposites degrades 96.4% of Tetracycline antibiotic under ultraviolet light irradiation after 120 min. The effect of CuO/ZrO_2 nanocomposites dosage and solution pH was studied. It was found that the photocatalytic performance of CuO/ZrO_2 nanocomposites can be improved via increasing concentration until optimal dosage (0.8 g/L) and in a higher dosage than 0.8 g/L no significant improvement was observed. Also, the results confirmed that the photodegradation of tetracycline can be elevated via increasing pH.

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INTRODUCTION

In recent years, metal oxide nanoparticles have been widely used in photocatalyst [1-4]. Metal oxide nanoparticles have unique physical and chemical properties such as chemical stability, large surface areas, proper redox potential, attractive optical properties, biocompatibility, and shape-dependent properties [5-7]. These nanoparticles also have different limitations such as expensive synthesis methods, absorption wavelength range, and recovery capability. Therefore, various researches have been conducted to overcome

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these limitations [8, 9]. Copper oxide (CuO), a p-type semiconductor with a constrained band gap (1.2-2.0 eV) and a foundation for many high-temperature superconductors and giant magnetoresistance materials, has attracted a lot of attention in recent years [10, 11]. One of the attractive features of copper oxide is that by controlling its shape and size, optical properties can be controlled. This feature is very important because it directly affects photocatalyst features. This gives importance to copper oxide synthesis methods because applied synthesis methods can be lead to different shapes and sizes [12-14]. Optical properties play an important role in the photocatalyst process, so here the optical properties of copper oxide are investigated in more detail. CuO nanostructures have the unique ability to regulate the possible energy levels of CBs and VBs, as well as the bandgap, by adjusting the size and shape of CuO. The band gap in CuO nanostructures is blue-shifted than bulk CuO. As a result, for wider bandgap nanostructured CuO samples exhibiting absorption in the UV field, CuO photocatalyst exhibits strong absorption in the visible spectrum with a little transparency [15-19]. Various techniques have been used to improve the photocatalytic properties of CuO such as nanocomposites formation, binary and ternary heterojunction formation, Z-scheme based photocatalytic system, introducing of different metal ions as dopants, and coupling with carbonaceous materials [20-25]. CuO/ZrO_2 nanocomposites is one of the most prominent member of CuO-based nanostructures which have been widely prepared and applied in the photocatalytic process. The physical and chemical properties of ZrO_2 nanoparticles lead to excellent photodegradation via CuO/ZrO_2 nanocomposites [26-28].

Binita Nanda et al. prepared CuO/ZrO_2–MCM-41 nanocomposites via integrating ZrO_2 into the MCM-41 (M-41) framework, then loading copper oxide using the wetness impregnation process while maintaining a Si/Zr ratio of 10. For the photo-reduction of Cr^{6+}, CuO/ZrO_2–MCM-41 was found to be an effective photocatalyst. Within 30 minutes, CuO/ZrO_2–MCM-41 nanocomposites achieved a nearly 100 percent reduction in Cr^{6+} [29].

In another work, CuO/ZrO_2 nanocomposites were prepared via modified sol-gel and solid-state process. The structural and morphological properties of as-prepared samples were compared. Then, The photocatalytic H_2 evolution from oxalic acid solution under solar irradiation was used to examine the photocatalytic activity of CuO/ZrO_2 nanocomposites. It was reported that when CuO/ZrO_2 nanocomposite photocatalyst is made by sol-gel process and the mole ratio of CuO to ZrO_2 is 40%, the optimum activity of photocatalytic H_2 evolution (2.41 $mmol.h^{-1}\mu^{-1}$) is achieved [30].

In this work, the CuO nanoparticles, ZrO_2 nanoparticles, and CuO/ZrO_2 nanocomposites were prepared via a simple hydrothermal and sonochemical route. The shape and size features of prepared samples were investigated via SEM and TEM analysis. Tho optical characteristics of prepared products were evaluated via UV-Vis absorption spectra. Finally, the CuO/ZrO_2 nanocomposites was applied for photocatalytic degradation of tetracycline in aqueous solution under different conditions.

MATERIALS AND METHODS

Materials

The entire reagents and solvents applied in this study were of analytical grade: $ZrOCl_2.8H_2O$ (99.9%), Potassium hydroxide (KOH), $CuSO_4.5H_2O$, ammonia (NH_3).

Synthesis of ZrO_2 nanoparticles

In a conventional synthesis, in 100 ml of distilled water 0.1 M of $ZrOCl_2.8H_2O$ was dissolved with effective stirring. After a few minutes, 0.2 M of KOH is added to the above solution. Afterward, the solution formed is transferred into a stainless steel Teflon lined sterilized capacity of 100 ml and kept in an oven at 180 ˚C for 16 h. To remove the soluble impurities and depress agglomeration, the resulting precipitates are cleaned with distilled water and absolute ethanol. The final product was dried for 3 h in a vacuum at 80 ˚C.

Preparation of CuO nanoparticles

CuO nanoparticles were prepared as the following: First, copper sulfate and NH_3 were applied as reactants. The stock solution of copper sulfate (0.1 M) was prepared in 100 ml deionized water. To this stock solution, aqueous ammonia was added under continuous stirring to get the pH value of reactants at 9. The solution is next transferred into Teflon lined sealed stainless steel autoclaves and maintained at a constant temperature of 200 °C for 6 hours. It was then let to cool to 35 °C. The precipitate so obtained

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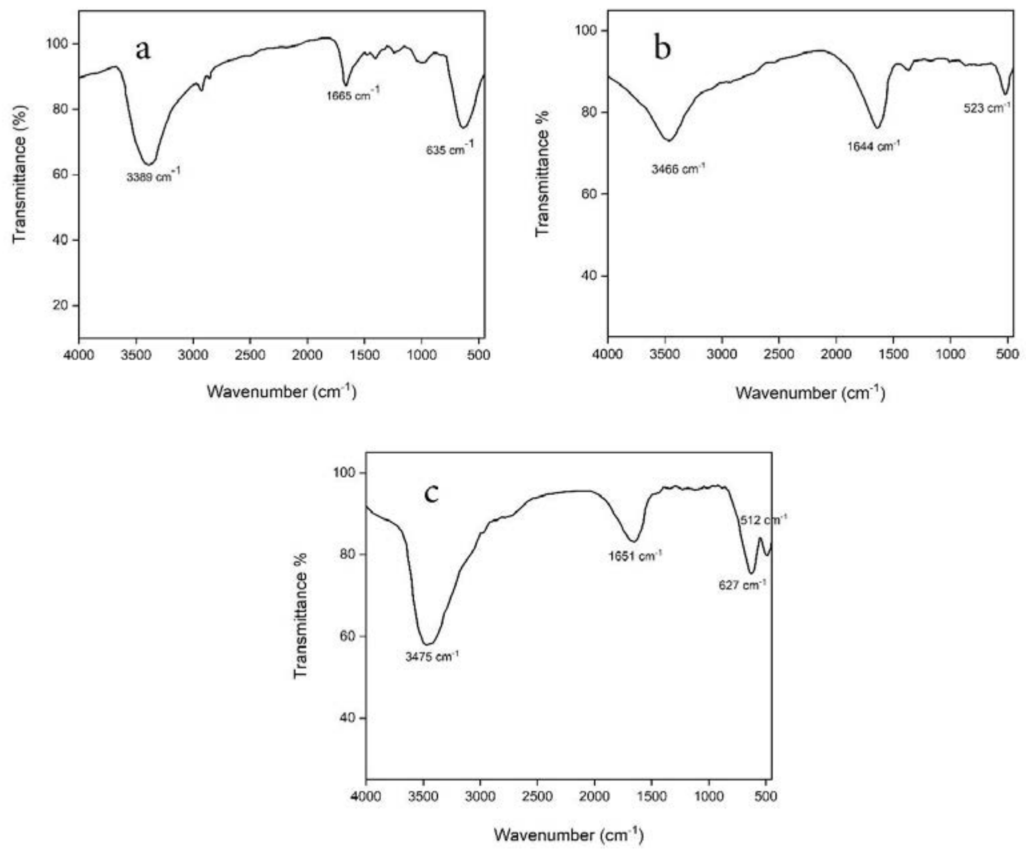

Fig. 1. FTIR spectrum of prepared a) ZrO_2 nanoparticles, b) CuO nanoparticles, and c) ZrO_2/CuO nanocomposites

is placed in a furnace and calcined for 2 hours at 500 °C.

Preparation of CuO/ZrO_2 nanocomposites

The as-prepared CuO and ZrO_2 nanostructures were dispersed in deionized water under vigorous stirring separately. After that, the CuO dispersion was added to ZrO_2 dispersion under ultrasonic for 60 min at room temperature. The final *CuO/ZrO_2* was filtered and dried at 60 ˚C for 10 hours.

Photocatalytic degradation experiments

The photocatalytic activity of CuO/ZrO_2 nanocomposites was studied against the photodegradation of tetracycline and ofloxacin antibiotics under ultraviolet and visible irradiation. To attain the adsorption–desorption equilibrium, 0.03 of CuO/ZrO_2 nanocomposites powder was dispersed into a 50 mL solution of tetracycline with the concentration of 0.001 g/L, then stirred in the dark for 30 min. After then, the as-obtained suspension was exposed to the light of various wavelengths. For providing UV-Vis test, 5 mL suspensions were taken at various periods and filtered to remove the CuO/ZrO_2 nanocomposites.

Characterization

A D8 DaVinci X-ray diffractometer was used to analyze X-ray diffraction (XRD) patterns using Ni-filtered Cu K radiation. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet Magna-550 spectrometer in KBr pellets. SEM LEO-1455VP and Philips EM208S transmission electron microscope were used for studying the shape and size of samples. UV-Vis (Shimadzu, Japan) analysis was applied for the investigation of optical properties of samples.

RESULTS AND DISCUSSION

The FTIR analysis was applied for further investigation of prepared nanostructures. The presence of a significant peak at 530 cm^{-1} is confirmed zirconium -oxygen bond in ZrO_2 nanoparticles (Fig. 1a). For the copper oxide case,

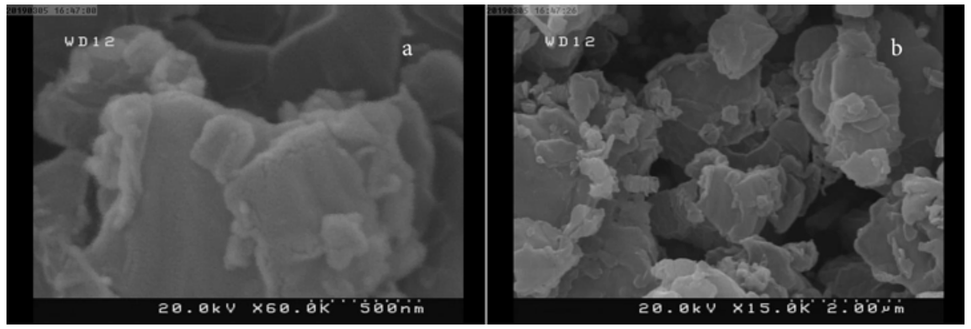

Fig. 2. SEM images of Prepared ZrO_2 nanoparticles

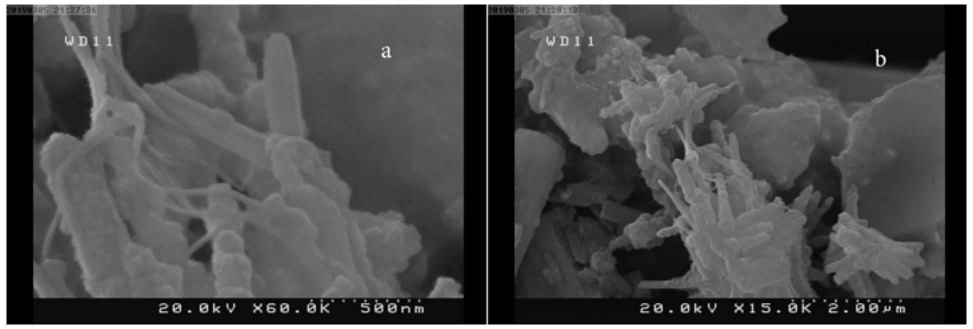

Fig. 3. SEM images of Prepared CuO nanoparticles

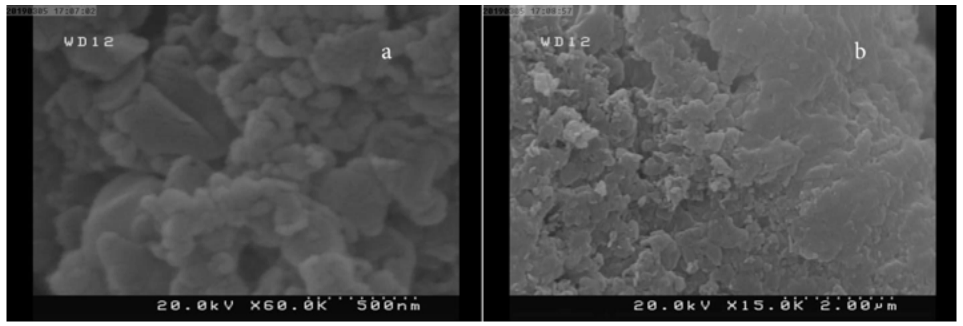

Fig. 4. SEM images of Prepared ZrO_2/CuO nanocomposites

the peaks at 500-650 cm^{-1} were attributed to the Cu-O bond (Fig. 1b). In CuO/ZrO_2 nanocomposites Zr-O and Cu-O-related stretching modes were observed in 450-700 cm^{-1} (Fig. 1c). The peaks at 3000-3500 and 1600-1700 cm-1 in all samples were related to the H_2O.

Scanning electron microscope (SEM) analysis was applied for studying the shape and size of prepared samples. As well as shown in Fig. 2, the irregular shape of ZrO_2 was formed. The agglomerated particles were observed in Fig. 2, which was be expected since the applied synthesis method was the surfactant-free route. For the CuO case, the 1D morphology of copper oxide was formed along with the other irregular morphology (Fig. 3). Fig. 4 shows the SEM images of as-prepared CuO/ZrO_2 nanocomposites. The applied synthesis method for the preparation of CuO/ZrO_2 nanocomposites leads to the keep morphology of CuO and ZrO_2 nanoparticles. The SEM images of CuO/ZrO_2 nanocomposites confirmed no change in morphology in comparison with the shape and size of CuO and ZrO_2 nanoparticles. For further investigation of shape and size, TEM analysis was applied for CuO/ZrO_2 nanocomposites. It is accepted that the TEM analysis gives accurate information about the morphology of nanostructures. It is observable that irregular

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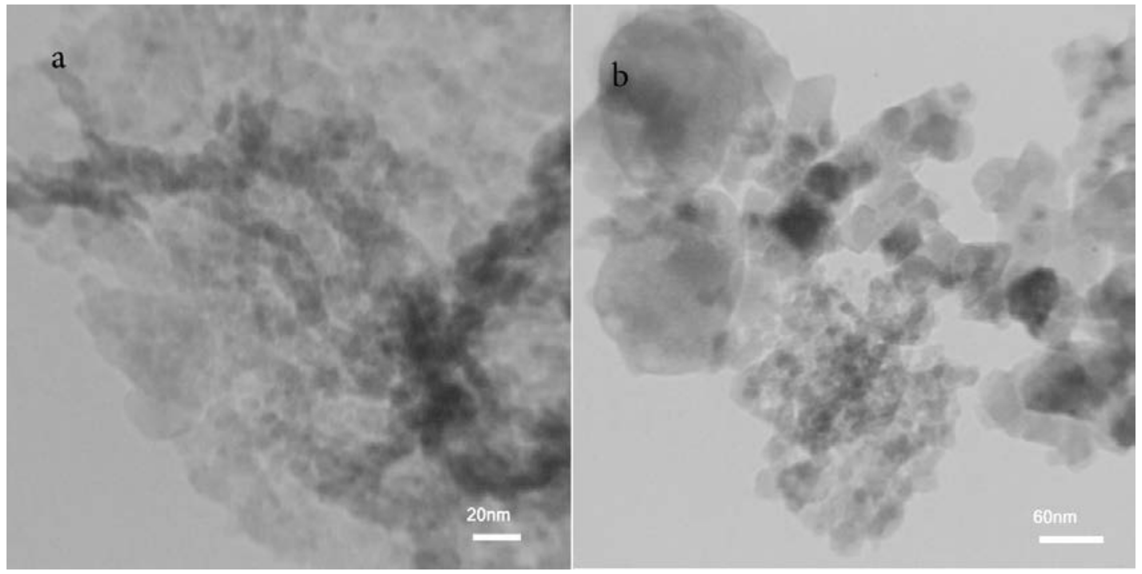

Fig. 5. TEM images of prepared ZrO_2/CuO nanocomposites

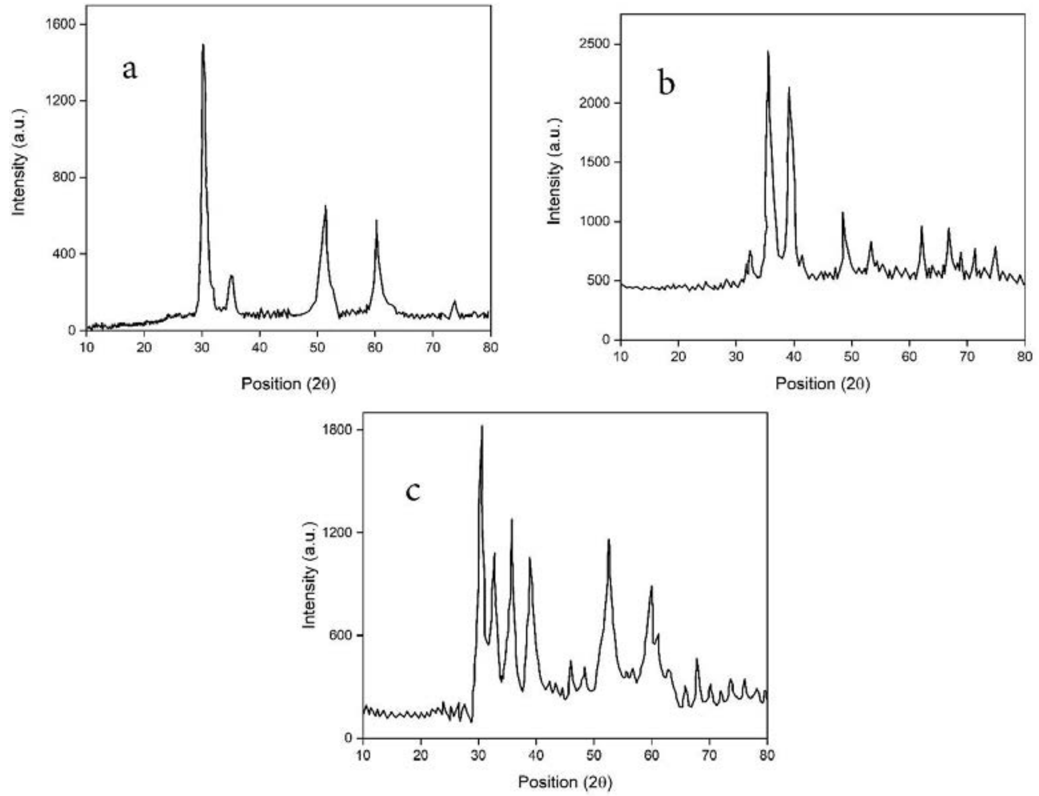

Fig. 6. XRD pattern of prepared a) ZrO_2 nanoparticles, b) CuO nanoparticles, and c) ZrO_2/CuO nanocomposites

shape CuO nanoparticles were formed beside ZrO_2 nanoparticles (Fig. 5).

Fig. 6 displays the XRD pattern of prepared CuO nanoparticles, ZrO_2 nanoparticles, and CuO/ZrO_2 nanocomposites. For zirconia, It was revealed that a tetragonal phase with JCPDS No. 050-1089 with a P42/nmc space group was formed. It is expected that via decreasing grain size, the diffraction peak at its half-maximum intensity (FWHM) be increased. The Scherrer equation was

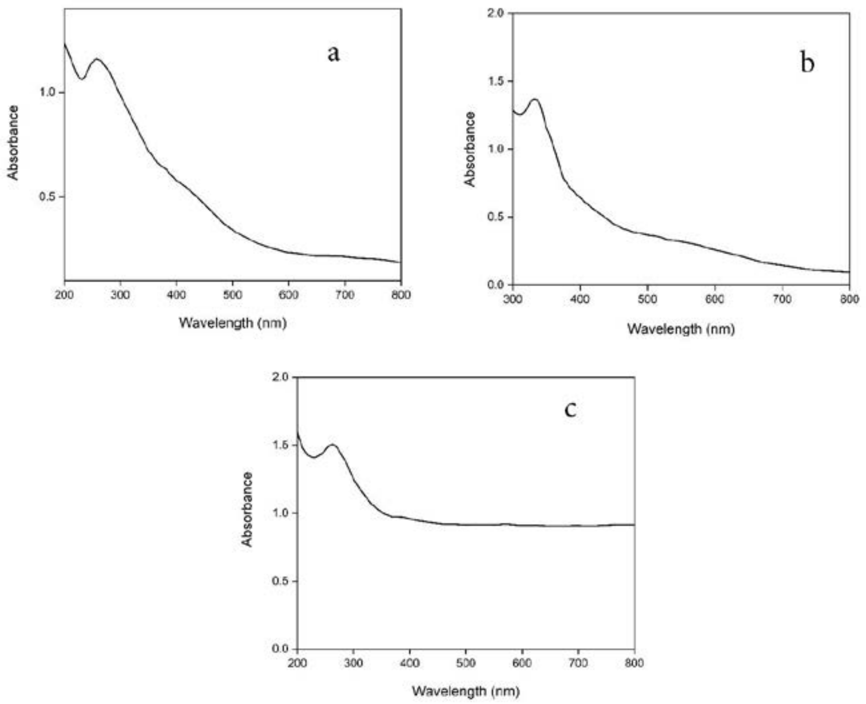

Fig. 7. UV-Vis absorption spectrum of a) ZrO_2 nanoparticles, b) CuO nanoparticles, and c) ZrO_2/CuO nanocomposites

used to compute the crystalline size:

$$D = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

where β is the width of the observed diffraction peak at its half maximum intensity, K is the shape factor, which takes a value of about 0.9, and λ is the X-ray wavelength (CuKα radiation, equals 0.154 nm). According to the Scherrer equation, grain sizes of as-prepared zirconia nanoparticles was calculated 27 nm. For copper oxide nanoparticles, the monoclinic phase with JCPDS No. 89-5895 was formed. It is formed of pure CuO nanoparticles with no impurity. The grain size of CuO nanoparticles was measured 31 nm. The XRD pattern of CuO/ZrO_2 nanocomposites confirms the formation of sample with any impurity.

UV-Vis analysis was utilized for the investigation of optical properties of as-obtained ZrO_2 nanoparticles, CuO nanoparticles, and CuO/ZrO_2 nanocomposites. Fig. 7 shows UV-Vis absorption spectrum of prepared ZrO_2 nanoparticles, CuO nanoparticles, and CuO/ZrO_2 nanocomposites. For ZrO_2 spectra, it is seen that the presence of absorbance peak at 257 nm is attributed to the formation of ZrO_2 nanoparticles (Fig. 7a). The broad absorbance spectra were observed at 331 nm for CuO nanoparticles which were attributed to the preparation of CuO nanoparticles (Fig. 7b). Continuous light absorption in the 360–800 nm region is observed in the CuO/ZrO_2 nanocomposites. This might be due to the CuO-based effective collection of visible light in CuO/ZrO_2 nanocomposites in comparison with ZrO_2 nanoparticles (Fig. 7c).

The photocatalytic degradation of tetracycline
Effect of CuO/ZrO_2 concentration

Without CuO/ZrO_2 nanocomposites, there was no substantial tetracycline degradation under ultraviolet irradiation. Different amounts of CuO/ZrO_2 nanocomposites (0.1, 0.2, 0.4, 0.8, and 1.6 g/L) were applied in this work to investigate the effect of CuO/ZrO_2 nanocomposites dosage on photocatalytic performance under ultraviolet. The results showed that the photodegradation of tetracycline was increased via the increasing amount of CuO/ZrO_2 nanocomposites until 0.8 g/L after 120 min at pH=4. After that, the photocatalytic activity did not significantly improve via increasing the dosage of CuO/ZrO_2 nanocomposites (Fig. 8). Therefore, the optimal concentration was determined 0.8 g/L. The

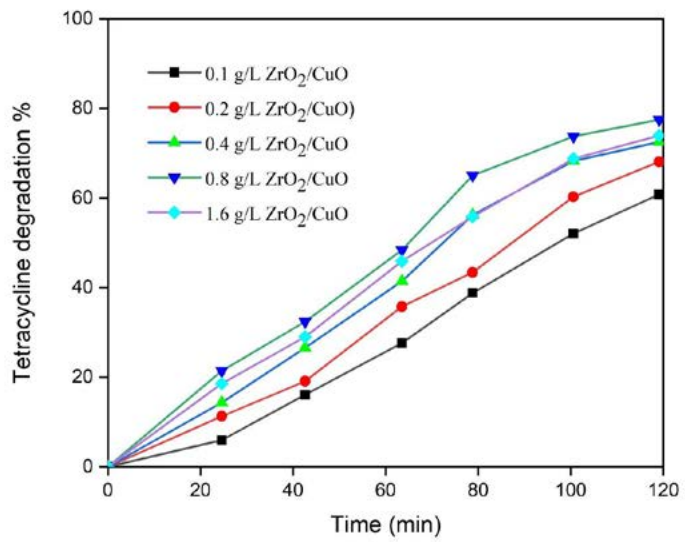

Fig. 8. The effect of ZrO_2/CuO nanocomposites concentration on the photocatalytic activity

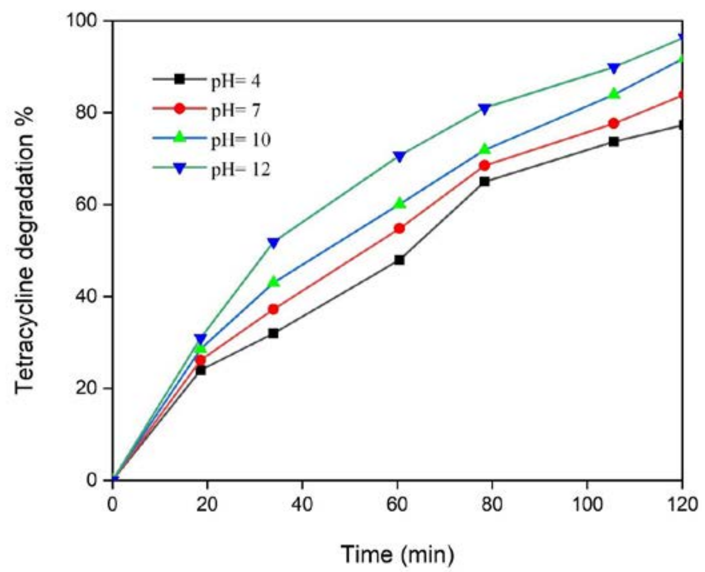

Fig. 9. The effect of solution pH on the photocatalytic activity

photocatalytic efficiency was measured 77.4 after 120 min under UV irradiation. The proposed mechanism for photodegradation of tetracycline is provided:

CuO/ZrO_2 nanocomposites + hυ → CuO/ZrO_2 nanocomposites, e^- + h^+
h^+ + H_2O → OH●
e^- + O_2 → O_2^-●
OH● + O_2^-● + Tetracycline → Degradation products

Effect of pH

KOH and H_2SO_4 were used to modify the pH of the solutions to 4.0, 7.0, 10.0, and 12.0 in order to test the effects of pH. It should be noted that the concentration of CuO/ZrO_2 nanocomposites was kept 0.8 g/L. The results revealed that the photocatalytic efficiency was improved via increasing pH (Fig. 9). At pH=12, the efficiency was measured 96.4%. CuO/ZrO_2 nanocomposite surface is positively charged at pH 10.0 and negatively charged at pH > 10. Similarly, tetracycline displayed distinct species at various pH levels. When the pH was increased from 5.0 to 9.0, more negative tetracycline species lead to more attraction between positively charge CuO/

ZrO_2 nanocomposites and tetracycline. This more attraction leads to higher photocatalytic activity.

CONCLUSION

In this work, ZrO_2, CuO, and CuO/ZrO_2 nanostructures were synthesized via simple hydrothermal and ultrasonic-assisted routes. The shape and size feature f as-prepared samples were characterized via SEM and TEM analysis. The crystalline structure of prepared products was investigated via XRD pattern. The optical properties of prepared nanostructures were studied via UV-Vis analysis. It is found that CuO/ZrO_2 nanocomposites can be applied as an attractive photocatalyst for the degradation of tetracycline from an aqueous solution. It is found that the optimal concentration of CuO/ZrO_2 nanocomposites was 0.8 g/L for degradation of tetracycline and after that, the photocatalytic performance did not significantly improve via increasing dosage of CuO/ZrO_2 nanocomposites. In addition, the effect of solution pH on the photocatalytic performance of CuO/ZrO_2 nanocomposites was investigated. The findings proved that the photodegradation of tetracycline was improved via increasing pH. At pH=12 the photocatalytic performance was measured 96.4%.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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