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RESEARCH PAPER

Study of New Hybrid Material of ZnO/CuO and Metal-Organic Framework as Photocatalyst for Removal of Tetracycline from Water

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ABSTRACT

Metal organic frameworks (MOFs) made of metal ions or clusters coordinated to organic ligands are classified as crystalline nano porous materials shaped in one-, two-, or three-dimensional structures. These materials have shown many applications in various aspects of technology. In this regard, applying of MOFs as promoters for semiconductor photocatalysts is one of promising applications. Thus, new photocatalyst hybrid material (CuO/ZnO/TMU-5) was synthesized from zinc-based metal-organic framework (TMU-5) and metal oxide composite (CuO/ZnO; containing ZnO and CuO oxides). Obtained materials were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), and Scanning Electron Microscopy (SEM) analyses. The efficiency of the resulting materials was evaluated in photocatalytic processes for the removal of tetracycline contaminant from water. The results showed that CuO/ZnO/TMU-5 species showed higher photocatalytic activity comparing to pristine CuO/ZnO. UV-vis spectroscopy analysis revealed that coupling of TMU-5 to CuO/ZnO changes its band gap toward lower energy resulting in increase of the photocatalytic removal of organic pollutant under visible light.

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INTRODUCTION

Iran is one of the countries that face over-prescription of antibiotics especially tetracycline. In terms of production and consumption, tetracycline is the second most common group of antibiotics in the world. Antibiotics are rarely fully metabolized in the body after ingestion, and 30-90% of them remain active after excretion [1-3]. Therefore, effective removal of these pollutants is one of the basic needs of the industry. Common methods used in pharmaceutical wastewater treatment, such as biological treatment, are generally ineffective. In fact, antibiotics, due to their antimicrobial properties, inhibit the activity of bacteria in biological treatment systems and pass through the disinfection treatment without being removed [4]. Recently, photocatalytic treatment is regarded as a very promising process for eliminating antibiotic contaminants from water [5]. Photocatalysis is a green technology, can degrade organic pollutants of wastewater into harmless substances. The only energy source of this process is light including

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sunlight. So, the manufacture and application of active photocatalysts which can efficiently converts antibiotics to harmless materials under the sunlight is doubly important. Various kind of materials are investigated as photocatalysts which Among them, semiconductors especially zinc oxide have been shown very noteworthy photocatalytic activity in removal of organic pollutants from waste water [6-7]. There are many reports about the removal of tetracyclines from water using ZnO which in all of them ZnO have been used in the composite form to increase the photocatalytic degradation efficiency of tetracycline in water [8-11].

In recent years, several reports have been presented on the performance of metal- organic frameworks as new photocatalysts in pollutant degradation and water decomposition. MOFs, depending on the type of metal, behave like a semiconductor in the presence of light. In the other hands, there is strategy for the development of optically active materials based on MOFs, and that is to make composites based on MOFs. MOF/semiconductor material composites will be useful for potential applications in chemical, photocatalytic, and other optoelectronic devices [12, 13]. In this regard, TMU-5 have been reported as a promising metal-organic framework which promotes semiconductor photocatalytic activity in organic material degradation [14].

In this work, we propose the using of CuO/ZnO nanocomposite for removal of tetracycline from water. Furthermore, to improve the CuO/ZnO photocatalytic activity, we coupled it to TMU-5 to form CuO/ZnO/TMU-5 species. Prepared materials are characterized and used in the photocatalytic removal of tetracycline contaminants from the group of antibiotics under visible light illumination.

MATERIALS AND METHODS

Materials

4,4'-oxybis-benzoic acid (OBA), zinc (II) acetate ($ZnO.2H_2O$), dimethyl formamide (DMF), copper nitrate ($Cu(NO_3)_2.3H_2O$), potassium hydroxide (KOH), and tetracycline prepared from Merck company and used without further purification. 3,6-di (pyridin-4-yl) -1,4-dihydro-1,2,4,5-tetrazine (4-bpdh) material was prepared according reported method [15].

Synthesis of TMU-5

To synthesize TMU-5 ([Zn (oba) (4-bpdh) 0.5] • $(DMF)_n$), 1 mmol of zinc (II) acetate, 1 mmol of 4-bpdh pillar, and 1 mmol of H_2OBA acid were mixed together in 30 ml of solvent containing 30 ml of DMF. The solution was placed in an ultrasonic bath for 60 minutes at room temperature. The precipitate was collected by centrifugation and washed by DMF three times. The final powder was dried at 80 ° C for two days. To activate and remove DMF molecules from the pores of these two structures before gas adsorption analysis, both frames were immersed in acetonitrile solvent for two days. They were then subjected to 125 ° C in a vacuum for 24 hours to remove solvent molecules trapped in the pores within their structure. Prepared material named as TMU-5.

Synthesis of CuO/ZnO copper

5.268 g of zinc acetate (0.024 mol) was dissolved in 200 ml of distilled water, and 1.6 g of aqueous copper nitrate (0.008 mol) was added, and the solution was stirred. The container containing the solution was then placed in an ultrasonic bath. Potassium hydroxide solution was made by dissolving 5 g of KOH in 200 ml of distilled water. The solution was then added dropwise to a solution containing copper and zinc ions under sonication. After 3 hours, the resulting light blue powder was washed several times with distilled water. Subsequently, the powder dried at 80 ° C for 24 hours. It was then calcined for 4 hours at 450 ° C. The gray powder was named CuO/ZnO.

Synthesis of CuO/ZnO /TMU-5

0.8 g of synthesized CuO/ZnO powder was dispersed in 24 mL DMF in ultrasonic bath for 5 min. Then 0.352 g of zinc acetate was added to it and the reaction vessel was stirred in an oil bath at 80° C at 500 rpm for 30 minutes. Then 24 ml of DMF solution and 0.8 g of 4-bdhp pilar were added to the reaction vessel. Then 40 ml of DMF solution and 0.4 g of OBA ligand were added to the reaction vessel. The reaction door was tightly closed and stirred at 500 rpm for 72 hours at 80 ° C. The resulting powder was then separated by centrifugation and dried several times with DMF in the oven for 24 hours at 80 ° C. Then, produced material was activated via the method mentioned in section 2.2 activated. The resulting sample was named CuO/ ZnO/TMU-5.

Photocatalytic test

A tetracycline substance with the chemical

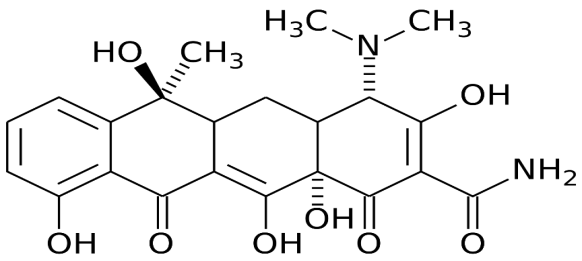

Fig. 1. The chemical structure of tetracycline.

structure shown in Fig. 1 was used as organic pollutant. Firstly, a solution with a concentration of 30 mg. L^{-1} of the contaminant was first prepared.

In each experiment, 50 ml of the freshly prepared contaminant solution and 50 mg of the prepared photocatalyst were poured into the reaction vessel. First, the solution was mixed with the photocatalyst in the dark for 30 minutes to create equilibrium adsorption and desorption conditions in the reaction medium and the contaminant was adsorbed on the surface of the photocatalyst, then the high-pressure mercury lamp W400 was turned on 4 ml of the contaminant solution was removed from the reaction medium. The samples were centrifuged at 4000 rpm for 10 minutes. Then the absorbance of the solution in the range of 200-800 nm was recorded by two-beam UV-Vis spectroscopy.

The device includes a W400 high pressure mercury lamp, a magnetic stirrer and an air pump located inside a wooden chamber. The distance from the reaction vessel to the radiation source is 15 cm. The amount of photocatalytic degradation is calculated from the following formula.

$$X = \frac{(A_0 - \mathrm{A})}{A_0} \times 100$$

In this equation, A_0 indicates the initial absorption of tetracycline, and A indicates the amount of absorption of tetracycline at λ = 380 nm at the time of sampling, and X represents the percentage of photocatalytic removal of tetracycline from water.

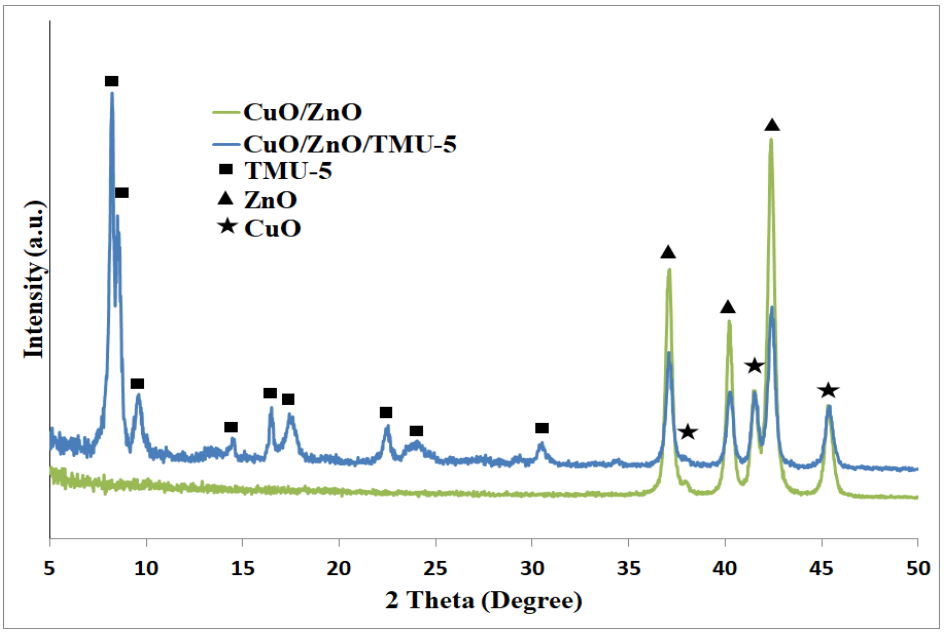

Fig. 2. X-ray diffraction pattern of CuO/ZnO and CuO/ZnO/TMU-5 samples.

Characterization

The phase characterization of samples was determined by powder X-ray diffraction (XRD) on Philips X-pert x-ray diffractometer using Cu Kα radiation (wavelength, λ = 1.5418 Å). Fourier transform infrared (FT-IR) spectra were obtained on a Shimadzu-8400S spectrometer using KBr pellets. UV-Vis absorption spectra were recorded using Shimadzu-UV-2550-8030 spectrophotometer in the range of 190-800 nm with slit width of 5.0 nm. The SEM images and energy-dispersive X-ray spectroscopy (EDS) mapping analysis were recorded by Philips XL-300 instrument

RESULT AND DISCUSSION

TMU-5 was selected as photocatalyst promoter due to the presence of amine functional groups in its structure. Studies have shown that azine groups (RR'C=N-N=CRR') of 4-bpdh pillar of TMU-5 create a new absorption band in the UV-visible range and play a significant role in absorbing visible radiation. Therefore, due to their activity in the visible light range, these materials can be used as photocatalysts or auxiliaries that improve the properties of photocatalysts.

The XRD pattern of the CuO/ZnO and CuO/ZnO/TMU-5 samples are shown in Fig. 2. XRD pattern of CuO/ZnO shows sharp peaks from 35 ° to 85 ° related to zinc oxide and copper (II) oxide phases. XRD pattern for CuO/ZnO/TMU-5 shows the same pattern of CuO/ZnO, however some new peaks are appeared between 5 and 35 which can be related to TMU- 5 species [16]. Therefore, the results show the formation of TMU-5 along with CuO/ZnO material that this also approved by FTIR analysis (Fig. 3).

Fourier transform infrared (FT-IR) spectra of CuO/ZnO and CuO/ZnO/TMU-5 are depicted in Fig. 3. The FTIR spectrum vibration modes of TMU-5 sample are assigned (as in Table 1). For CuO/ZnO, the sharp broad band below 700 cm^{-1} belongs to Cu-O and Zn-O stretching vibration modes.

For CuO/ZnO/TMU-5, all vibration bands of both CuO/ZnO and TMU-5 are detected with very slight shifts. Furthermore, a new vibration band appeared at 1650 cm^{-1} which may be attributed to new C=N vibration mode resulting from interaction between azomethine groups of TMU-5 with CuO/ZnO structure.

Fig. 4 shows the SEM image of the CuO/ZnO and CuO/ZnO/TMU-5 samples. As shown in Fig. 4 (a and b), the CuO/ZnO sample is composed of spherical particles. Such as the results of XRD and IR characterization results, SEM images can also be evidence of this claim that after adding precursors of TMU-5 to the mixture of CuO/ZnO and DMF, TMU-5 are formed along with the CuO/ZnO phase. In images c and d, the formation of TMU-5 blocks among CuO/ZnO spherical particles is clearly observable.

Energy-dispersive X-ray spectroscopy (EDS)

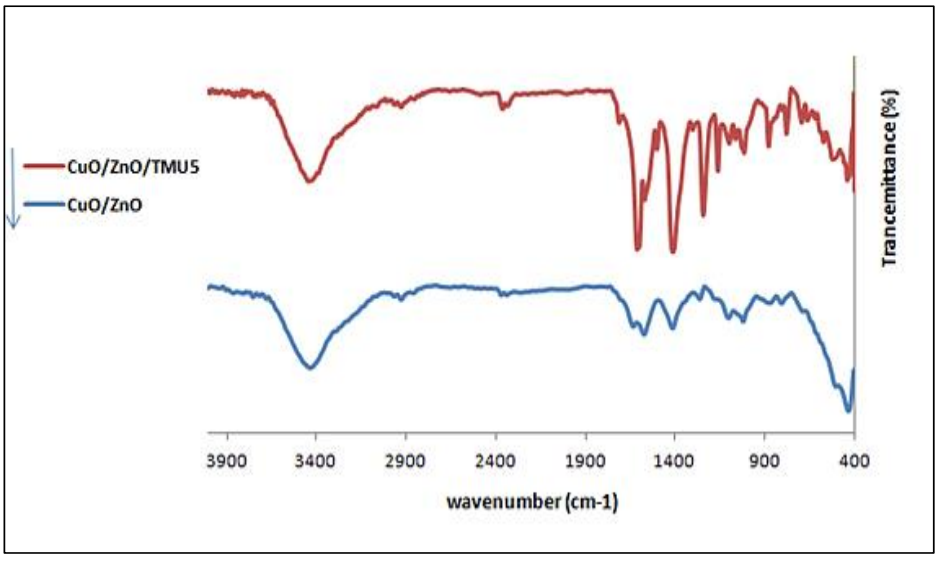

Fig. 3. IR spectra of of CuO/ZnO and CuO/ZnO/TMU-5 samples.

Table 1. Assignment of FTIR spectrum vibration modes of TMU-5 sample.

Wavenumber (cm^{-1})	Vibration mode	bond
1241 and 1161	$\nu_{sym.}$	C-O-C
1299	$\nu_{asym.}$	C–O
1320 - 1420	$\nu_{asym.}$	C–O
1500	$\nu_{sym.}$	C=N pyridine
1553 and 1573	$\nu_{sym.}$	C=C
1596 and 1615	$\nu_{sym.}$	C=N−N=C and C=N (azomethine)

mapping analysis of CuO/ZnO/TMU-5 was carried out. Fig. 5 shows the presence of elements C, O, N, and Zn which confirms the presence of TMU-5 species. Furthermore, the presence of elements O, Cu and Zn is related to the CuO and ZnO materials. So, EDS mapping analysis confirms the successful synthesis of the CuO/ZnO/TMU-5 material.

The optical properties of the synthesized samples were investigated using UV-Vis spectroscopy (Fig. 6). Optical absorption spectra of samples can be used to calculate of optical band gap which is related to electron excitation from the valence band to conduction band. The relation between the absorbance (A), the photon energy (hν), and band gap energy (Eg) can be written as following equation:

$$A = \frac{k(h\nu - E_g)^{\frac{n}{2}}}{h\nu}$$

where, h is the Planck's constant, v is the

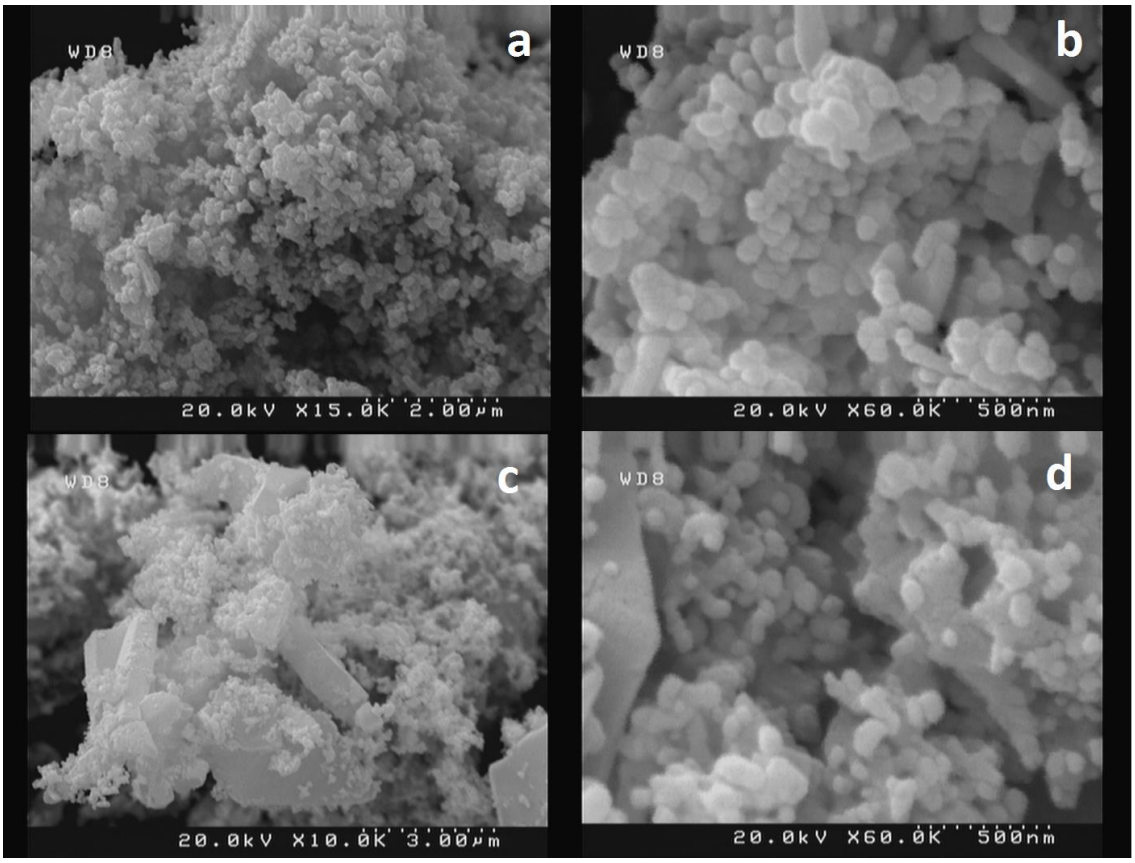

Fig. 4. SEM image of CuO/ZnO (a, b): CuO/ZnO/TMU-5 (c, d).

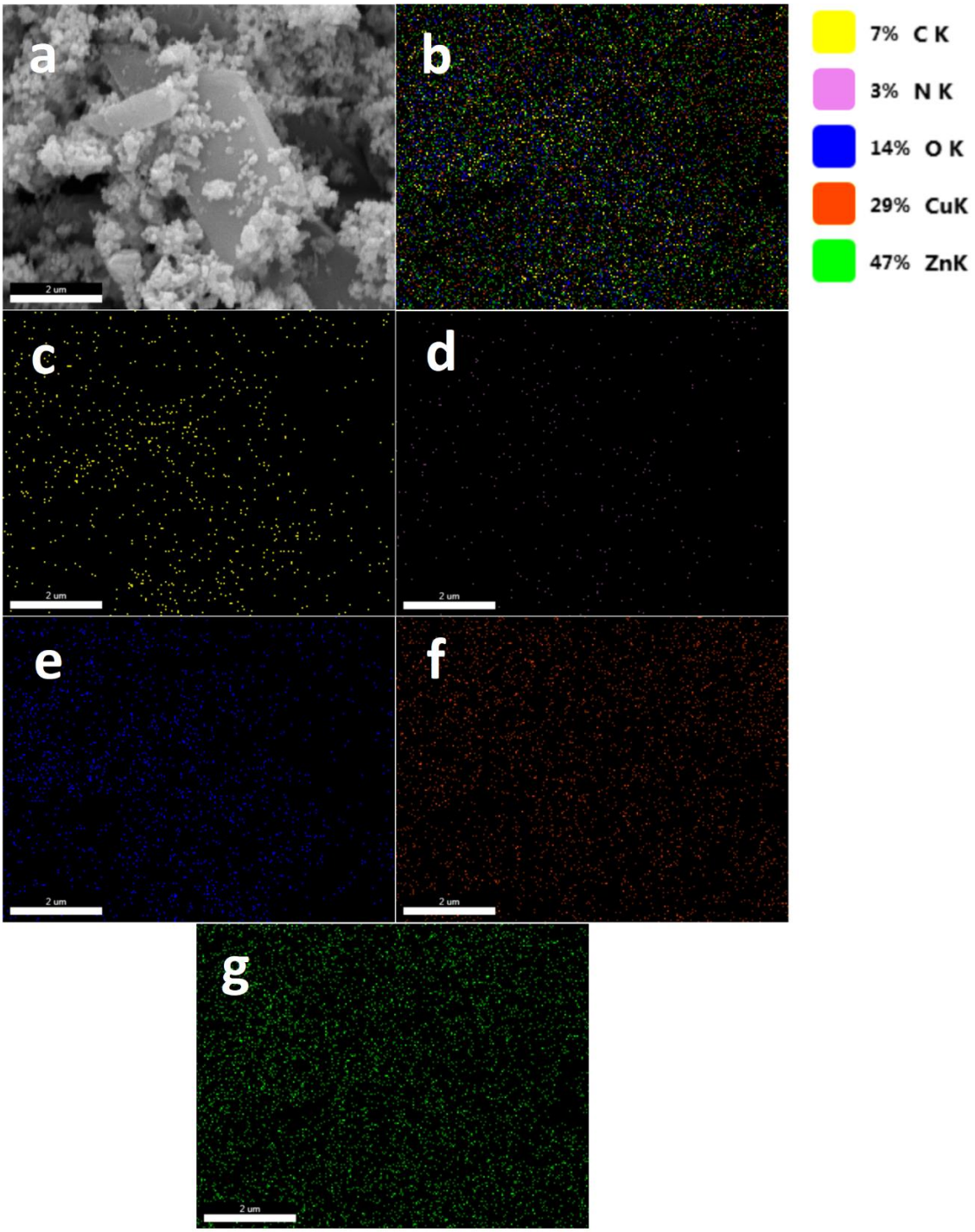

Fig. 5. Energy-dispersive X-ray spectroscopy (EDS) mapping of CuO/ZnO/TMU-5, including SEM image (a), all elements (b), C element (c), N element (d), O element (e), Cu element (f) and Zn element (g).

frequency, k is a constant, and n is a value of either 1 or 4 (for the direct transition n = 1 and for indirect transition n = 4) [16]. For Zinc oxide, a semiconductor with a direct wide band gap**,** the $(\alpha hv)^2$ versus hv graph is predicted to be a straight line with a photon energy axis intercept giving the

value of band gap. As shown in Fig. 6, the band gap of 3.06 eV was calculated for CuO/ZnO composite, which is about 0.14 eV less than the reported values for pristine zinc oxide (3.2 eV), which can be attributed to the presence of copper oxide species. After coupling of TMU-5 to CuO/ZnO the band gap value decreased to 2.84 eV. Deep studies shown that of chemical bonding within linker molecules has an important role in creation semiconductor characters of MOF compounds for engineering applications as previous reported [17]. Indeed, the production of new energy levels between valence band (VB) and conductive band (CB) leads to reduction of recombination of charge carriers that is desirable occurrence in photocatalytic reaction. N_2 adsorption- desorption analysis of samples is shown in Fig. 7. An isotherm of type III is detected for sample which is related to nonporous or macroporous solids. After coupling of TMU-5 with CuO/ZnO, an isotherm of type I corresponding to microporous materials is observed. The BET surface areas, calculated from nitrogen adsorption–desorption isotherms, are about 6.6 and 128 m^2g^{-1} for CuO/ZnO and CuO/ZnO/TMU-5 samples, respectively. By considering the relatively large BET surface area of TMU-5 (580 m^2g^{-1}) which is the structural feature of MOF materials, It seems that the coupling of TMU-5 to CuO/ZnO increased the surface area of the CuO/ZnO/TMU-5 material [18].

CuO/ZnO and CuO/ZnO/TMU-5 samples were used in the photocatalytic process of tetracycline removal from aqueous medium. The test results shown in Fig. 8 reveal that CuO/ZnO/TMU-5

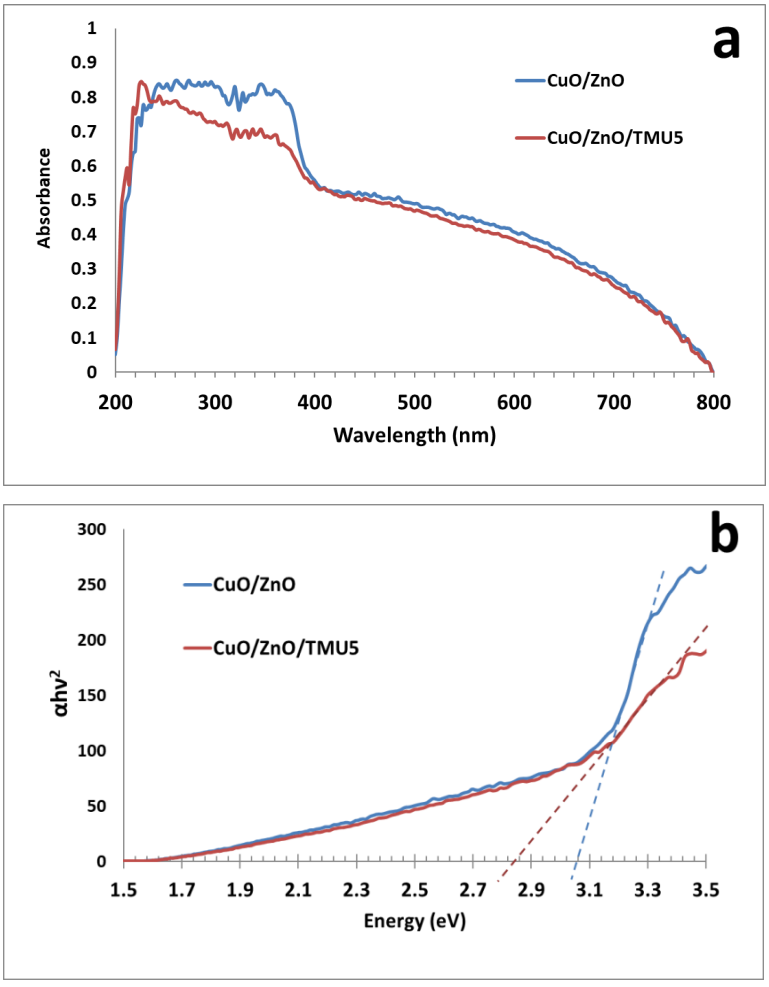

Fig. 6. (a) UV-Vis absorption spectrum and (b) plots of $(\alpha hv)^2$ versus the energy of exciting light of (hv) for CuO/ZnO and CuO/ZnO/TMU-5 samples.

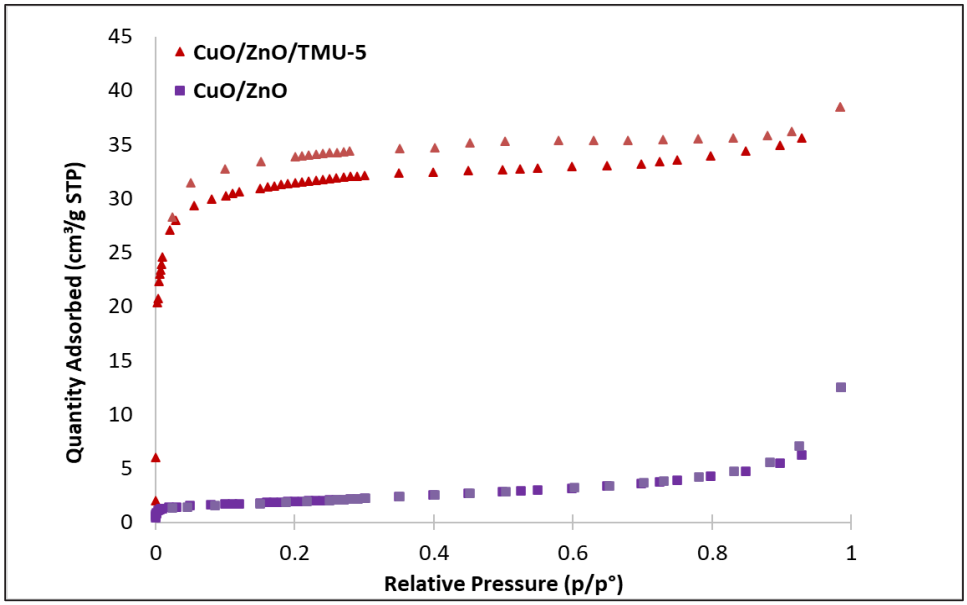

Fig. 7. N_2 adsorption-desorption isotherms of CuO/ZnO and CuO/ZnO/TMU-5 samples.

hybrid material have better efficiency than CuO/ZnO. In 3 hours photocatalyst material consisting of TMU-5 (with 62% removal percentage) has better performance than CuO/ZnO composite (removal percentage of 43%). This difference can be related to two reasons: The first is the less band gap of CuO/ZnO/TMU-5 composite which increase its photocatalytic capability under visible light irradiation. Second, the surface area of CuO/ZnO/TMU-5 is larger than that of CuO/ZnO, which allows tetracycline molecules to adsorb more easily on the photocatalyst surface. As shown in the diagram, the adsorption of tetracycline in the dark on the surface of photocatalyst after 30 minutes is 18% for CuO/ZnO/TMU-5 and only 9% for CuO/ZnO. Comparison of CuO/ZnO/TMU-5 with other composite material composed of MOFs and metal oxides reported for photocatalytic removal of tetracycline is shown in Table 2. The exact comparison of these material is not possible because of different applied condition of photocatalytic tests. Coupling of MOFs to ZnO metal oxide for removal of tetracycline had been reported previously. Liu et al. [25] synthesized ZnO/ZIF-9 photocatalyst which removed 87% of tetracycline from water under UV light. however, the photocatalytic efficiency ZnO/ZIF-9 is remarkable, but its operation under UV irradiation

Table 2. Comparison of various composite material composed of MOFs and metal oxides in photocatalytic degradation of tetracycline.

Composite material	Antibiotic dosage (mg/L)	Catalyst dosage (mg/L)	Dark reaction time (min)	Illumination time (min)	Light source	Degradation efficiency (%)	Ref.
GO/ WO_3/UiO-66	20	1.67	30	70	Visible	84	[12]
TiO_2/UiO-66-NH_2	20	0.167	60	60	Visible	80	[19]
TiO_2/MIL-100(Fe)	100	-	30	60	Solar	90	[20]
TiO_2/MIL-101(Fe)	20	1	-	20	Visible	94	[21]
TiO_2/MIL-101(Fe)	20	1	-	80	Solar	98	[22]
TiO_2/ZIF-8	100	0.6	30	120	Solar	92	[23]
$CuBi_2O_4$/ZIF-8	20	0.5	60	60	Visible	75	[25]
ZnO/NH_2-UiO-66	20	0.25	60	90	Solar	61	[8]
ZnO/ZIF-9	10	0.2	60	60	UV	87	[25]
CuO/ZnO/TMU-5	30	1	30	180	Visible	62	This work

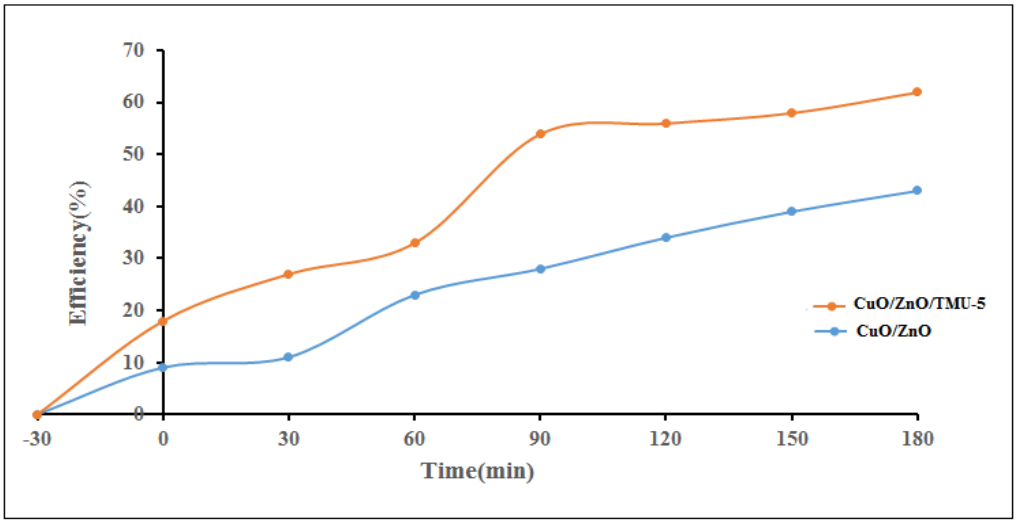

Fig. 8. Diagram of the photocatalytic removal of tetracycline in the presence of various synthesized materials.

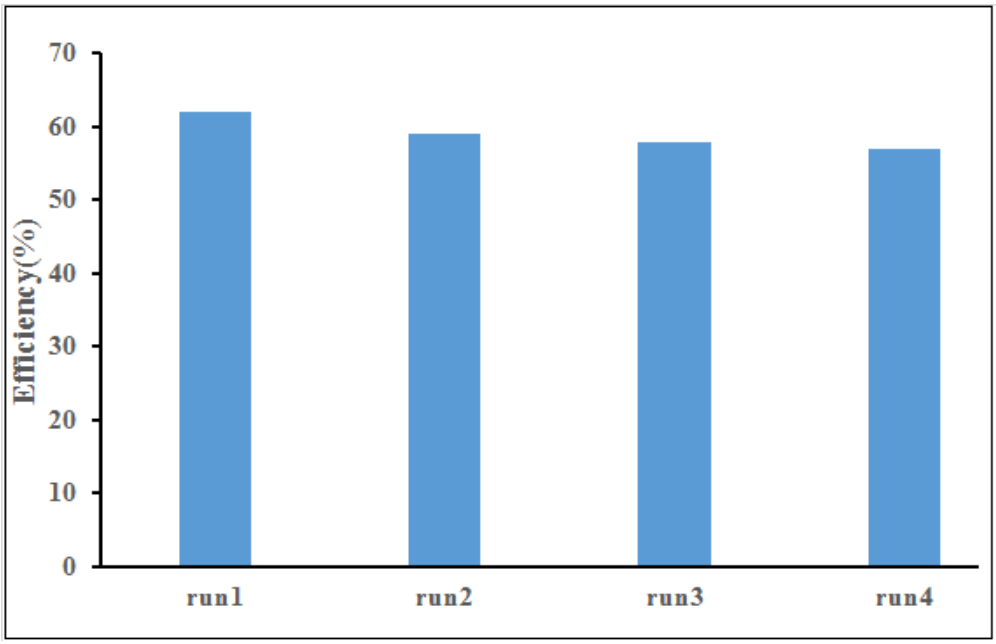

Fig. 9. Recyclability test of CuO/ZnO/TMU-5

limits its applications under solar light. For address this issue, Du et al. [8] synthesized ZnO/NH_2-UiO-66 composite which degraded 61% of tetracycline under solar light. The reported photocatalyst in this work (CuO/ZnO/TMU-5) sightly increased the removal efficiency of tetracycline from water under visible light (62%) compared to similar composite made of UiO-66 MOF and ZnO metal oxide.

A photocatalytic mechanism propose for degradation of tetracycline pollutant by CuO/ZnO/TMU-5 composite; after visible light

illumination, electron transitions lead to produce free electrons and holes, and in following free radical reagents such as dissolved oxygen and hydroxyl ions are produced. These active reagents degrade the adsorbed pollutants on the surface of photocatalyst as indicated in below:

$CuO/ZnO \rightarrow e^-_{CB} + h^+_{VB}$

$CuO/ZnO/TMU\text{-}5 \rightarrow e^-_{CB} + h^+_{VB}$

$h^+_{VB} + OH^- \rightarrow OH^\cdot$

$e^-_{CB} + O_2 \rightarrow O_2^{-\cdot}$

$O_2^{-\cdot} + H^+ \rightarrow HO_2^{-\cdot}$

$OH^\cdot + Pollutant \rightarrow CO_2 + H_2O$

$O_2^{-\cdot} + Pollutant \rightarrow CO_2 + H_2O$

$HO_2^{-\cdot} + Pollutant \rightarrow CO_2 + H_2O$

One of the important parameters in the photocatalytic process is the recovery of the catalyst. In order to check this parameter, after performing the photocatalytic process, the catalyst was washed several times with water and ethanol, and it was dried in oven. Then the photocatalyst (CuO/ZnO/TMU-5) was reused in the photocatalytic process. The results showed that after four periods of using the catalyst, only 5% of the ability of the photocatalyst has decreased (Fig. 9), which promises the use of the photocatalyst in industrial processes.

CONCLUSION

In this study, CuO/ZnO and new hybrid material of metal-organic frame work of TMU-5 with CuO/ZnO were prepared. Obtained materials were characterized and used in the photocatalytic removal of tetracycline contaminants from water under visible light extinction. The results confirmed that the presence of metal-organic framework attached to CuO/ZnO, lowers the optical band gap and increase the surface area which leads to more photocatalytic removal efficiency of antibiotic pollutant from water compared to pristine metal oxide material.

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CONFLICTS OF INTEREST

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

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