RESEARCH PAPER

ZnO/Co_3O_4 Nanocomposites: Novel Preparation, Characterization, and Their Performance toward Removal of Antibiotics from Wastewater

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ABSTRACT

Due to the widespread use of antibiotics in geese, water contamination by antibiotics has become a major problem. Photocatalyst semiconductors can play an important role in removing these pollutants from the aquatic environment by using sunlight. In this work, ZnO/Co_3O_4 nanocomposites as a new magnetic semiconductor is introduced to remove the antibiotics azithromycin and ciprofloxacin. First, the nanocomposite is synthesized by a simple co-precipitation method. Then, the crystalline and morphological properties of the prepared nanocomposite are identified by X-ray powder diffraction (XRD) and scanning electron microscope (SEM) methods. Also, the magnetic properties of the sample are analyzed by vibrating-sample magnetometer (VSM) technique. Because the photocatalytic properties of semiconductors directly depend on their optical properties and energy gap, the optical properties of the prepared nanocomposite are fully studied by the UV method. Photocatalytic results showed that the prepared nanocomposite could significantly remove antibiotics from the waste water. The prepared nanocomposite was able to degradation 84.5 % and 71.7% of ciprofloxacin and azithromycin in 80 minutes under visible light respectively.

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INTRODUCTION

Via the forwarding of economy and the course of society, there is a more prominent interest for a superior living climate and a developing challenges and mindfulness over water pollution. Environmental command and mitigation deterioration is one of the main problems urgent need to regulate [1-3]. Antibiotic agents saved great many lives since the disclosure of penicillin by Fleming in 1928. Almost 250 unique antibiotic agents are utilized as human and veterinary prescriptions. Nonetheless, the improper usage causes a persistent outflow of antibiotics into water climate from drug industry, families, creatures' farming, and hydroponics. Hence, antibiotics have become significant arising impurities in water because of their attributes, actually hurting human wellbeing [4-6]. Different routes have been applied for antibiotics removal from water, such as chlorination, bio-related treatments, photocatalysis, ozonation, electrochemical oxidation, and membrane filtration [7, 8]. It should be noted that mentioned process suffer from substantial limitations. For example, biological methods are not able to remove some antibiotics due to their bacterial resistance. As well as membrane process requires fluid flow, which in turn can cause further pollutions [9]. In the proposed method, photocatalysis method attracted considerable attention because uses the sunlight under ambient conditions for the degradation of antibiotics [10, 11]. Photocatalyst technology considered to be the most environmentally friendly route that offer the benefits of high efficiency, economy and environmental friendliness are new approach to solve this problem. Another important advantage of photocatalytic process is that in this process, antibiotics are converted to other organic compounds with low toxicity [12, 13].

Many researchers use semiconductor catalysts because of the unique qualities of room temperature reactions and the direct use of sunlight as a light source to activate the catalyst. The important issue in the photocatalytic process is providing sufficient semiconductor to that antibiotics can be effectively destroyed by sunlight [14, 15]. In recent years, various transition metal-based semiconductors, such as zinc oxide (ZnO) [16, 17], iron oxide (Fe_3O_4) [18, 19], titanium dioxide (TiO_2) [20, 21], cobalt oxide (Co_3O_4) [22, 23], zinc sulfide (ZnS) [24], and cadmium sulfide (CdS)[25] have been prepared and applied for photocatalytic process. Among the mentioned nanostructures, cobalt oxide-based nanomaterials have been found more attention. Part of this importance is due to their unique magnetic behavior, which can greatly help to reuse of the photocatalyst. Seyed Ali Heidari-Asil et al. prepared $ZnCo_2O_4/Co_3O_4$ nanocomposite using the Stevia extract as a green reagent that can play a fuel role in auto-combustion sol-gel route and engineering of the morphology of prepared nanocomposites. They investigated the photocatalytic performance of prepared products under visible light. They reported the excellent photocatalytic activity of $ZnCo_2O_4/Co_3O_4$ nanocomposite against Acid violet 7 (93.5% efficiency) in 70 min and 2-phenol (100%) in 18 min. The nanocomposites were recovered via magnetic field and stability of it under irradiation was revealed by removal of Acid violet 7 after 10 times recycling [26]. Chun Hui Shen et al. synthesized cobalt oxide/cerium oxide nanohybrid by a novel chemical reaction, % of followed by annealing in a muffle furnace and then applied to activate peroxymonosulfate for photodegradation of ciprofloxacin. They reported that the optimum amount as the 5 wt% cobalt oxide/cerium oxide/peroxymonosulfate nanocomposite. In this wt% the 87.8% of ciprofloxacin was removed under visible light irradiation. They claimed that the superior photocatalytic activity of prepared cobalt oxide/cerium oxide can be related to the synergistic effect between cobalt oxide and cerium oxide photocatalyst and peroxymonosulfate activation [27].

In this work, the ZnO/Co_3O_4 nanocomposites were prepared via facile co-precipitation method. The structural and morphological features of prepared nanocomposites were determined via XRD and SEM analysis. The magnetic behavior of prepared nanocomposites was studied via VSM analysis. Also, the optical properties of samples were characterized via DRS-UV analysis. Finally, the prepared nanocomposites was applied for photodegradation of azithromycin and ciprofloxacin under visible light.

MATERIALS AND METHODS

Materials and instruments

All reagents were purchased in synthesis grade from Scharlu without extra purification. Structural data of the pure nanostructure was investigated by the XRD technique (Philips diffractometer of X'pert

Company with monochromatized Cu Kα radiation, λ = 1.5406 Å). The study of functional groups of obtained nanostructure was performed using FT-IR spectroscopy (Nicolet Magna 550, KBr pellets). FE-SEM (LEO-1455VP) approach was carried out for morphological investigation. TG analysis was measured by V5.1A DUPONT 2000.

Preparation of ZnO/Co_3O_4 nanocompsoites (ZnO/Co_3O_4 NCs)

For the preparation of ZnO/Co_3O_4 NCs, $Zn(OAc)_2.2H_2O$ and $CoCl_3$ were dissolved separately in 50 ml DI water. Under continuous conditions, $Co^{3+}_{(aq)}$ solution was added dropwise into $Zn^{2+}_{(aq)}$ solution and mixed for 10 min. After that, alkaline solution (KOH 10 M) was added to the above solution by dropping. The as-prepared mixture was put into the autoclave at 170 °C for 15 h. At completion, the dark solid was separated and washed with DI water and acetone several times. The solid was first dried at 60 °C for overnight and then, calcined at 600 °C.

Photodegradation of azithromycin and ciprofloxacin

For each test, a solution with certain dosage (60, 80,100, and 120 ppm) of ciprofloxacin and azithromycin was prepared. Then 0.1 $g.L^{-1}$ concentration of prepared ZnO/Co_3O_4 nano photocatalyst was added to the antibiotics solution and the resulting mixture was placed in a dark environment under stirrer for 40 minutes to equilibrate adsorption. To maintain the solution oxygen-saturated throughout the reaction, air was blown into the vessel via a pump. Then ZnO/Co_3O_4 nano photocatalyst was separated from the mixture, taken from the degraded solution at various time intervals, using 5 min centrifuging at 12,000 rpm. The antibiotics concentration was measured with aid of a UV-Vis spectrophotometer. To calculate the antibiotics degradation efficiency, Eq. 1 was utilized:

$$\%\,\text{Efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

The crystallite structure of ZnO/Co_3O_4 NCs was studied by the XRD approach. The XRD graph of ZnO/Co_3O_4 is illustrated in Fig. 1. The pure nanocomposites show a well-defined cubic structure of ZnO/Co_3O_4 and also, and the intensity and position ratio of these peaks have acceptable to the reference pattern Co_3O_4 (JCPDS= 43-1003) and ZnO (80-0075), respectively [28]. Besides,

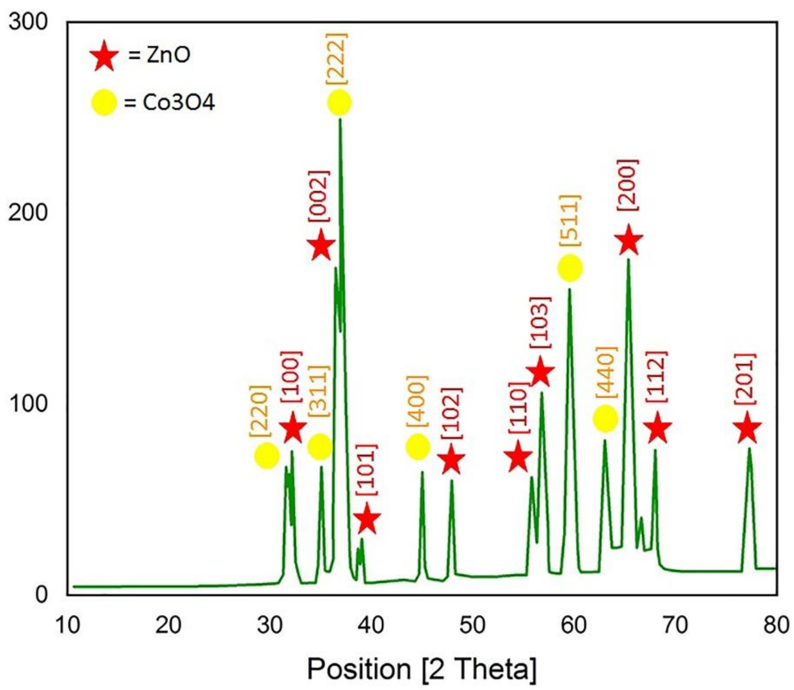


Fig. 1. XRD graph of ZnO/Co_3O_4 NCs.

ZnO/Co_3O_4 NCs Miller's index is seen. Based on the Debye-Scherrer equation (D= kλ/βcosθ), the crystallite size was calculated at approximately 21 nm.

FT-IR spectra of pure Co_3O_4, pure ZnO, and ZnO/Co_3O_4 NCs are displayed in Fig. 2. In the first graph (Fig. 2a), the main peaks at 662 cm^{-1} and 586 cm^{-1} are related to the Co^{2+}-O and Co^{3+}-O, respectively [29]. Also, the strong absorption peak at 430 cm^{-1} corresponded to Zn-O (Fig. 2b) [30]. According to Fig. 2c, all metal-oxygen bonds are seen in the final graph. In addition, two bonds at 3434 cm^{-1} and 1625 cm^{-1} related to the stretching and bending absorption of water, respectively.

EDS test was measured to determine the elemental composition of ZnO/Co_3O_4 NCs (Fig. 3).

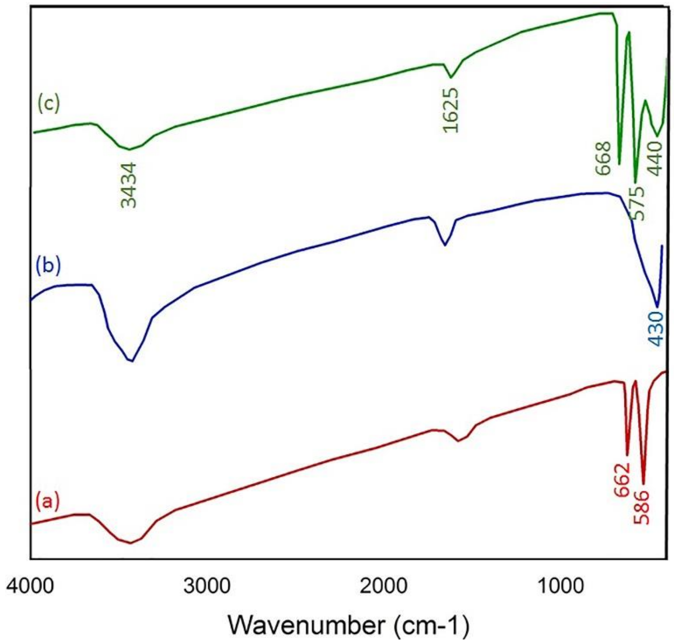
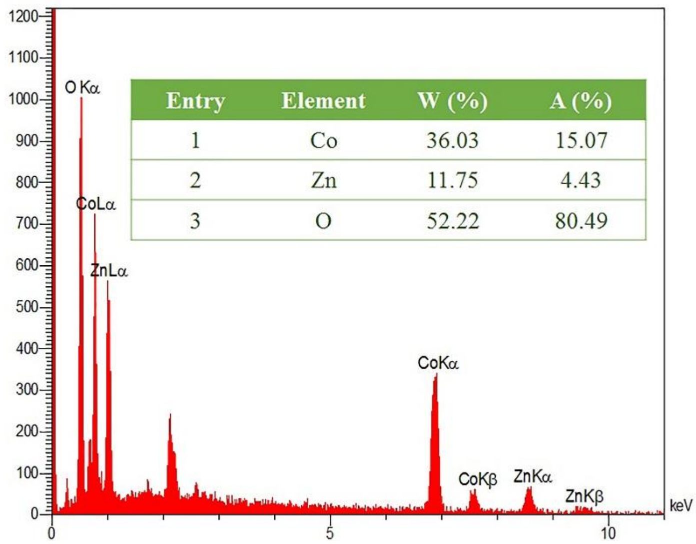


Fig.2. FT-IR graph of a) pure Co_3O_4, b) pure ZnO, and c) ZnO/Co_3O_4 NCs.



Entry	Element	W (%)	A (%)
1	Co	36.03	15.07
2	Zn	11.75	4.43
3	O	52.22	80.49

Fig.3. EDS pattern of ZnO/Co_3O_4 NCs

EDS information displays the percentage of cobalt, zinc, and oxygen in the structural composition. So, data approved the formation of ZnO/Co_3O_4 NCs without any impurities.

Microstructural characteristics of pure ZnO/Co_3O_4 NCs are studied using the FE-SEM method with various magnifications and the results are revealed in Fig. 4. It can be seen that the obtained average particle sizes (68.52 nm) are clearly in the nanostructure range with agglomeration.

The Thermogravimetric technique was carried out to investigate the thermal stability of the ZnO/Co_3O_4 NCs (Fig. 5). This nanostructure shows suitable thermal stability. The weight loss at temperatures below 215 ˚C is due to the removal of physically adsorbed solvent and surface hydroxyl groups. The second break-in curve is attributed to the decomposition of ZnO/Co_3O_4 NCs.

UV-vis analysis was applied for investigation of optical properties of prepared ZnO/Co_3O_4 NCs (Fig. 6). It was observed a sharp absorption peak in the ultraviolet range with a broad absorption range in the visible range that relates to the Co_3O_4 in the ZnO matrix (Fig. 6a). The optical energy gap (Eg) of the ZnO/Co_3O_4 NCs was calculated by using Tauc equation (Eq. 2):

$$\alpha hv = [A(hv - E\,g)]^{(1/2)} \quad (2)$$

The results showed the two optical band gaps

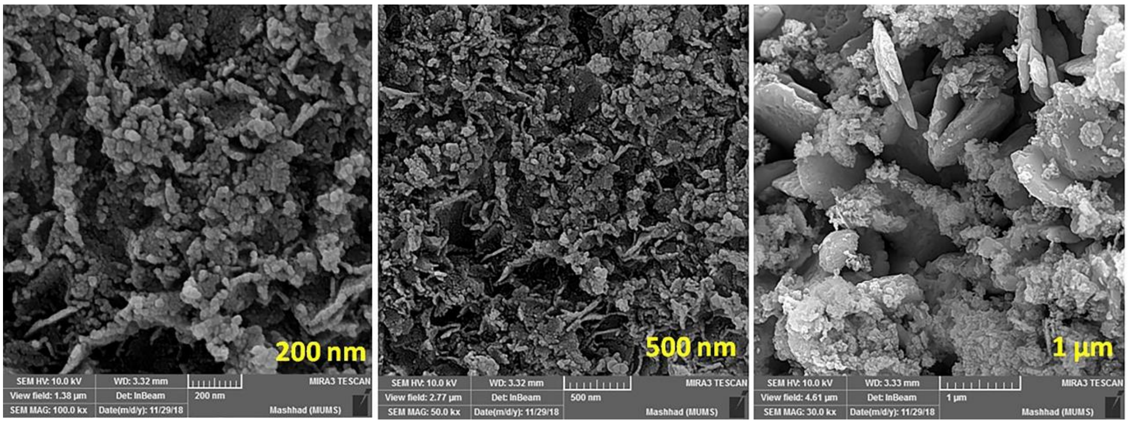


Fig. 4. FE-SEM images of ZnO/Co_3O_4 NCs with various magnifications.

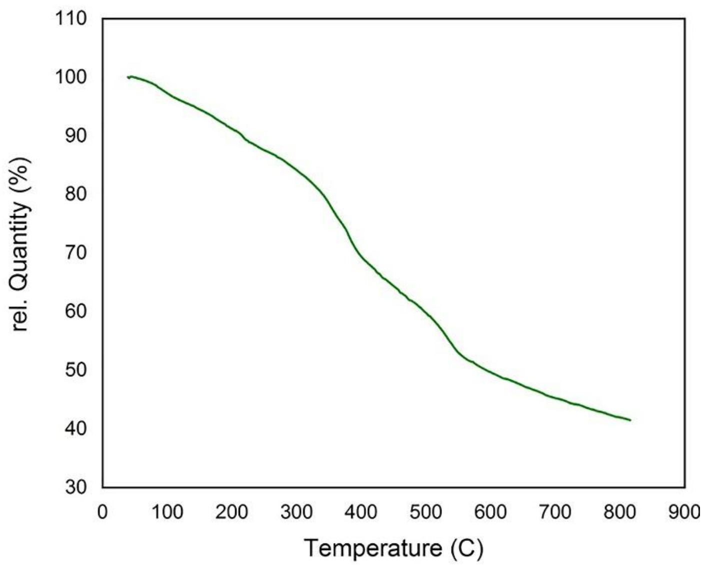


Fig. 5. TGA curve of ZnO/Co_3O_4 NCs

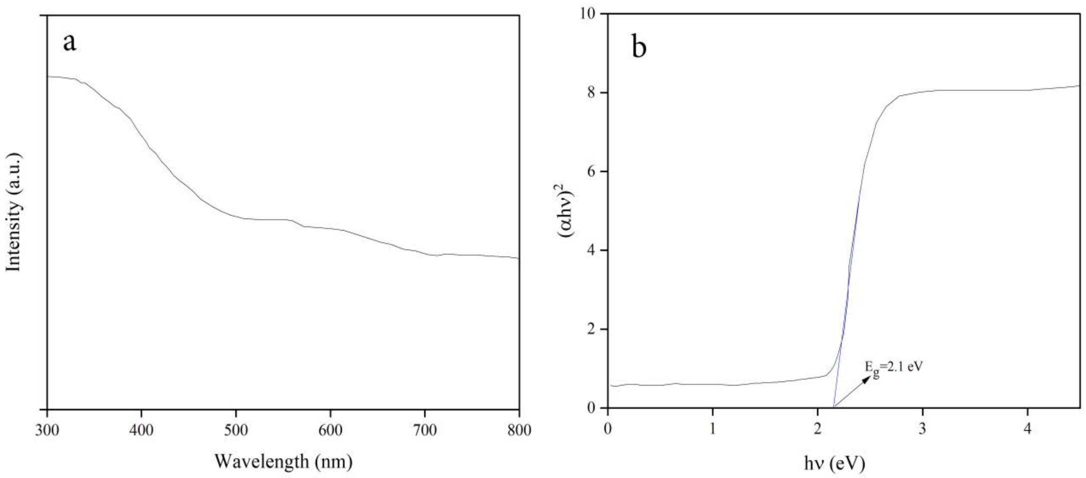


Fig. 6. a) UV-visible absorption spectrum b) band gap energy of prepared ZnO/Co_3O_4 NCs

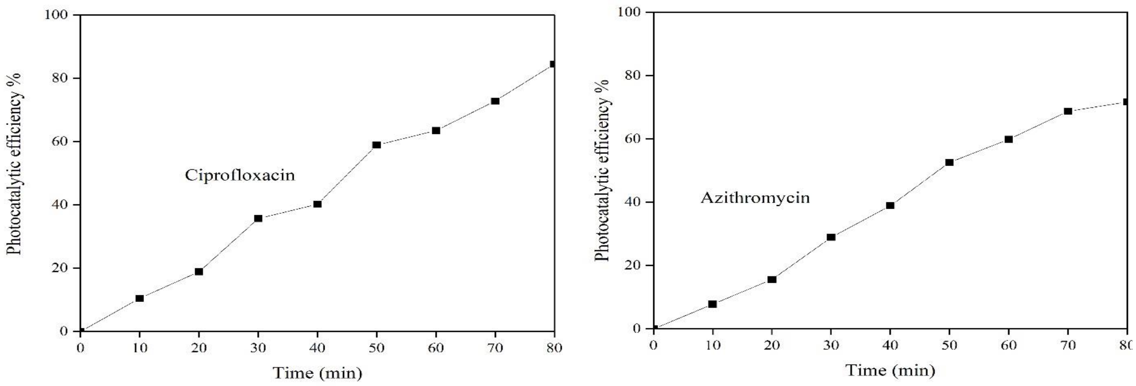


Fig. 7. Photocatalytic activity of prepared ZnO/Co_3O_4 NCs against ciprofloxacin and azithromycin

that related to the ZnO (3.3 eV) and Co_3O_4 (2.1eV). The results is in good agreement with previously reported papers. These optical band gaps lead to good photocatalytic activity of prepared nanocomposites.

Photocatalytic performance of prepared nanocomposites was studied against ciprofloxacin and azithromycin. Fig. 7 shows the photocatalytic efficiencies of ZnO/Co_3O_4 NCs against ciprofloxacin and azithromycin after 80 min under visible light. The results revealed that p-n heterojunction of ZnO/Co_3O_4 NCs removed both of antibiotics effectively. It can be found from Fig. 7 that the photodegradation of ciprofloxacin (84.5%) is clearly better than azithromycin (71.7%).

CONCLUSION

In conclusion, the ZnO/Co_3O_4 nanocomposites was introduced as a new magnetic semiconductor to degradation of the azithromycin and ciprofloxacin. For this aim, the ZnO/Co_3O_4 nanocomposites was prepared via simple chemical route. Then, the physical and chemical properties of prepared nanocomposites were characterized via X-ray powder diffraction (XRD), scanning electron microscope (SEM), vibrating-sample magnetometer (VSM) technique. The optical properties of the ZnO/Co_3O_4 nanocomposites were recorded by the DRS-UV spectroscopy. Photocatalytic tests showed that the prepared ZnO/Co_3O_4 nanocomposites could effectively remove azithromycin and ciprofloxacin from the waste water. The ZnO/Co_3O_4 nanocomposites degraded 84.5 % and 71.7% of ciprofloxacin and azithromycin in 80 minutes under visible light respectively.

CONFLICT OF INTEREST

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

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