

## Removal of azithromycin from aqueous solutions using Fe<sub>2</sub>O<sub>3</sub>/Ag/Zn nanocomposites

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Received 3 November 2022; Accepted 19 March 2023

### ABSTRACT

Drugs are essential pollutants in the environment due to their resistant structure, and their high consumption in treating humans and animals. The entry of antibiotics as hospital waste into aquatic environments is considered one of the critical environmental means due to their high stability. The design and synthesis of Fe<sub>2</sub>O<sub>3</sub>/Ag/Zn as a new structure of Fe<sub>2</sub>O<sub>3</sub> were reported, because of its resistance of the structure to air and high temperature, the adsorbent of azithromycin in wastewater was studied. After characterization of Fe<sub>2</sub>O<sub>3</sub>/Ag/Zn by scanning electron microscopy, energy-dispersive X-ray spectroscopy, mapping, transmission electron microscopy, X-ray diffraction and Fourier-transform infrared spectroscopy. Then, to remove azithromycin, the effect of factors such as pH, the concentration of azithromycin solution, adsorbent dose, time and temperature was evaluated using an optimization process. The results showed that the optimal conditions for removing of 96% of azithromycin (10 mg/L) with 1.5 g/L of Fe<sub>2</sub>O<sub>3</sub>/Ag/Zn, pH = 5, and 30 min at room temperature. In other words, the nano adsorbent has a good ability to remove azithromycin from water solution, which is very important from environmental aspects.

*Keywords:* Nanoadsorbent; Antibiotic; Water purifier; Pollutants; New structure of Fe<sub>2</sub>O<sub>3</sub>

### 1. Introduction

Most drugs are highly pollutant to the environment due to their resistant structure and extensive consumption in the treatment of humans and animals [1]. Antibiotics are an important category of such drugs [2]; they have a very resistant structure and account for 15% of the total consumption of drugs worldwide [3]. Antibiotics and their resulting metabolites in aquatic environments have caused great concern in recent years [4]. Azithromycin is a very important antibiotic due to its 14-atom lactam ring which is used in the treatment of bacterial infections [5]. Due to

the lack of proper methods to remove azithromycin, this compound and its metabolite enter the municipal sewage after consumption [6]. According to the environmental standards for azithromycin content, which is about 1 mg/L, any amount more than this increases the possibility of the drug entering the human body and causing side effects and allergies [7]. A wide range of removable of azithromycin such as activated carbon, granular ferric hydroxide, natural minerals, iron oxides, oxidation processes, reverse osmosis, biological treatment and some nanoparticles have been investigated for the removal of azithromycin [8–14]. Nowadays, the use of nanoparticles in water and soil

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purification has received much attention from researchers due to their high potential, but their use is associated with problems such as their rapid oxidation and fragility [15–18].

Nowadays, the use of nanoparticles in water and soil purification has received much attention from researchers due to their high potential, but the problem of their use is associated with problems such as their rapid oxidation, fragility and high reactivity. Nowadays, the use of nanoparticles in the purification of water and soil has received much attention from researchers due to their high potential [15–18], but the problem of their use is associated with problems such as their quick oxidation and friability, due to their high reactivity, which diminishes their active regions. New structures at the nanoscale are compounds with several metals that have attracted great attention due to their unique physical and chemical properties [19–21]. Considering that each metal nanoparticle has unique physical and chemical properties [8,22], combining these metals and creating a composite with several different properties is of great interest to researchers [23].

As a result of the interaction of different metals in the structure, new properties are created [24–26]. This property of metals in a structure offers potential in physics, biotechnology, chemistry, materials science, and biology. In particular, iron and silver increase the physical and chemical properties of a nanostructure [27]. For example, the presence of silver creates antibacterial properties and promotes the biocompatibility of the compound.

In this research, a novel approach was developed for  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  that via chemical synthesis been introduced. Images by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) showed that the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  includes Fe, Zn and Ag. Also, other analyzes such as X-ray diffraction (XRD) and transmission electron microscopy (TEM) and was shown one of the applications of this compound is the removal of azithromycin antibiotics. In this research, the removal of azithromycin by  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  nanocomposite, and so important parameters such as pH, temperature, time, and amount of tetracycline, and the optimal conditions were investigated.

In this research, a novel approach was developed for  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  introduced via chemical synthesis. SEM images and EDX showed that the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  contains Fe, Zn and Ag. Other analyses such as XRD and TEM demonstrated the applications of this compound in azithromycin removal. This study examined the removal of azithromycin by  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  nanocomposite and important parameters such as pH, temperature, time, the amount of azithromycin, and optimal conditions.

## 2. Experimental (materials and methods)

### 2.1. Materials

This study included purity azithromycin antibiotic (99%), silver nitrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , sodium hydroxide (0.1 N), acid chloride (0.1 N), sulfuric acid and nitric acid 1.0 N from Merck Company. All samples used in the volume study of 100 mL of stokes samples were prepared with a concentration of 1.0 g/L by dissolved 1.0 g of azithromycin in 100 mL of double distilled. The reagents of

analytic grade ( $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , NaOH and  $\text{AgNO}_3$ ) were used as raw materials.

### 2.2. Instruments

The  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  phase purity was investigated by XRD (Philips PW 1840,  $k = 1.54056 \text{ \AA}$ ). With a velocity of  $1.5^\circ/\text{min}$ , the peaks of the adsorbent diffraction pattern in the  $2\theta$  range between  $5.0^\circ$  and  $80.0^\circ$  were scanned, and TEM (Philips CM200-FEG apparatus) was used to measure nanoparticles size. SEM (Philips XL30) was used for surface morphology and different types of elements and the percentage of these elements. For the UV/vis spectroscopic study, Cary 100 (Varian, USA) device was used at  $23^\circ\text{C}$ – $25^\circ\text{C}$ .

### 2.3. Synthesis of $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$

To prepare  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  nanocomposite, firstly 0.1 M  $\text{AgNO}_3$  solution, 0.1 M  $\text{Zn}(\text{NO}_3)_2$  and 0.1 M  $\text{Fe}(\text{NO}_3)_3$  solutions are prepared separately. The solution is stirred for 1 h at room temperature to form a homogeneous and uniform solution, and then sodium borohydride  $\text{NaBH}_4$  (0.02 M) was added. After the complete formation of the precipitate, the solution is kept undisturbed again for 45 min and then it is centrifuged for 10 min at 4,000 rpm. To remove organic and ionic impurities, the precipitate obtained was thoroughly washed several times with DI water and then once with acetone. Then, after drying the precipitate in the oven, it was placed in an electric furnace for 12 h at a temperature of  $400^\circ\text{C}$  [27].

### 2.4. Ability to reuse of the $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ adsorbents to remove azithromycin antibiotic

To evaluate the reusability of the adsorbent under optimal conditions of temperature, pH, and contact time, 10 mg/L of azithromycin was investigated, and the sediment collected in each step using water and methanol was washed twice and reused. At each stage, the amounts of adsorption and desorption were calculated and compared with the previous steps.

## 3. Results and discussion

The  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  nanostructure was first characterized by SEM, energy-dispersive X-ray spectroscopy (EDX), mapping, TEM, XRD and Fourier-transform infrared spectroscopy (FTIR). After synthesizing the structure of the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  compound, it was used as the removable of azithromycin compounds. Important parameters such as time, pH, and the concentration of contaminants,  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  content and the effect of temperature on removal were studied.

### 3.1. Characterized of $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$

The  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  was synthesized by the well-known co-precipitation method. The materials used for this compound were  $\text{AgNO}_3$ ,  $\text{Zn}(\text{NO}_3)_2$  and  $\text{Fe}(\text{NO}_3)_3$ . A TEM was employed to study the morphology and size of the particles; the resulting structure was spherical, and the particle size was distributed almost uniformly, approximately 50

nanoparticles were seen in the image, and the particle diameter is about 20 nm (Fig. 1). Fig. 2, which is related to the surface morphology, the size of the particles, and the percentage of elements that make up the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  can also be determined that the particles are spherical, and Fig. 3 shows that there are three elements, iron, silver and zinc, in the composition, which is completely uniformly dispersed on the surface of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ . Dots on the surface indicate silver, zinc and iron as green, white and red, respectively, with silver at 50%, zinc at 27.9%, and iron at 67.1%. By using EDX/T-SEM, we attempted to correlate the elemental composition measured across a particle (line scan) to representatives of Fe, Ag, and Zn by T-SEM imaging. The results are summarized in Fig. 4.

Fig. 5a and b depict the FTIR spectra of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  under similar experimental conditions, the adsorption bands at  $466.5$  and  $555.5\text{ cm}^{-1}$  for iron-oxygen (Fe–O) bonds which clearly shows the synthesis in both structures. However, the spectral changes that occur in  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  and are observed in the regions of  $530.35$ ,  $555.5$ , and  $466.7\text{ cm}^{-1}$  can be attributed to Ag and Zn in  $\text{Fe}_2\text{O}_3$ .

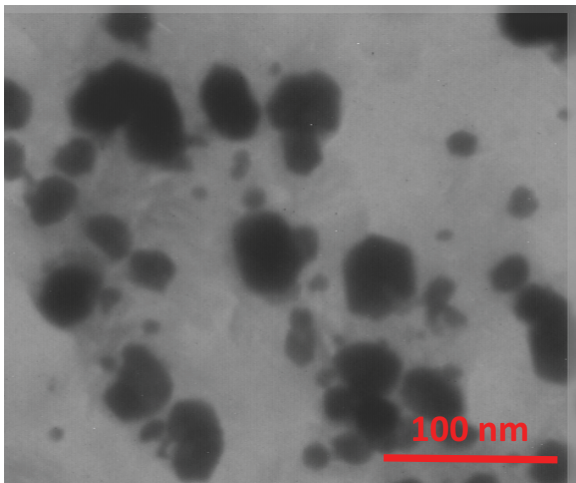


Fig. 1. Transmission electron microscopy images of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ .

Bending vibrations at  $3,386$ ;  $1,515\text{ cm}^{-1}$  (Fig. 4a),  $3,394$  and  $1,633\text{ cm}^{-1}$  in the spectrum can be attributed to the presence of hydroxyl groups, and the FTIR results strongly support the formation of the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  compound. In Fig. 6, the XRD image of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  is displayed and compared with the peaks related to the standard  $\text{Fe}_2\text{O}_3$  with JCPDS card no. (89-596). The  $\text{Fe}_2\text{O}_3$  index peaks are identified with different indices (012, 104, 110, 113, 024, 116, 018, 214, 300). The other spectra are related to silver and zinc of the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  structures. In other words, the structure of  $\text{Fe}_2\text{O}_3$  has been preserved with new peak which are related to the presence of silver and zinc.

### 3.2. Amount of $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$

In this step, the effect of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  amount on azithromycin removal was studied. At pH 4, in each experiment, different amounts of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  ( $0.5$ – $3\text{ mg/L}$ ) were exposed

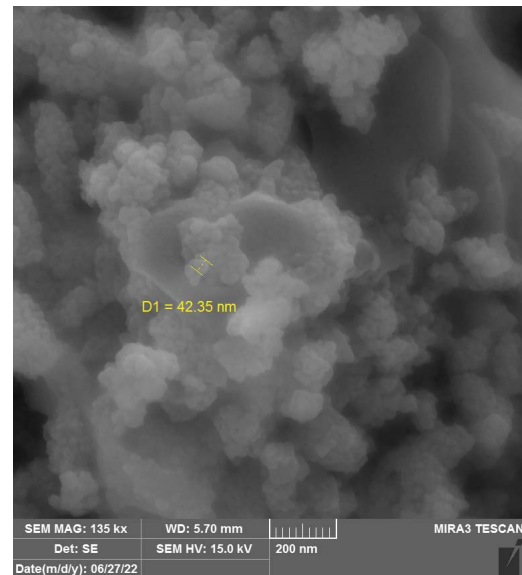


Fig. 2. Scanning electron microscopy images of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ .

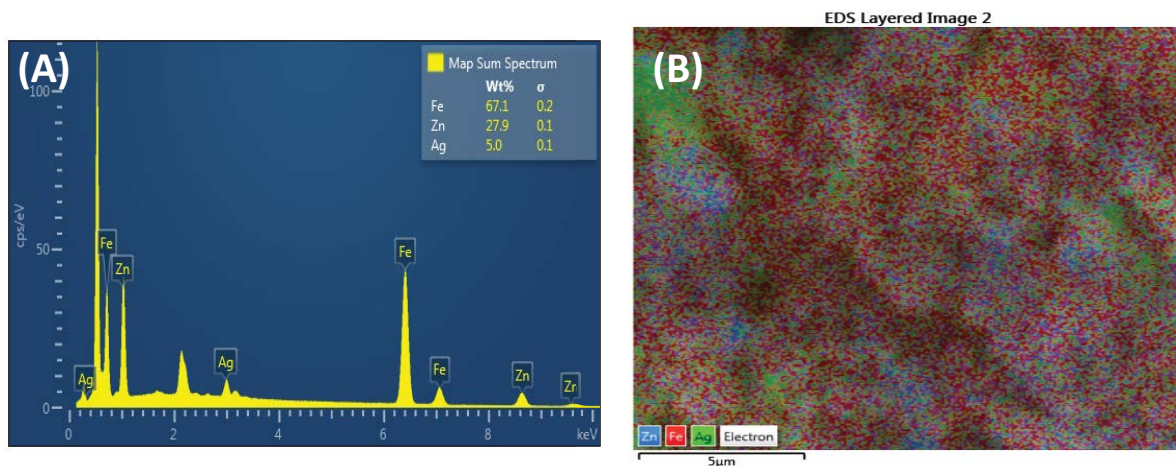


Fig. 3. (A) Energy-dispersive X-ray spectroscopy images of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  and (B) the mapping images of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ .

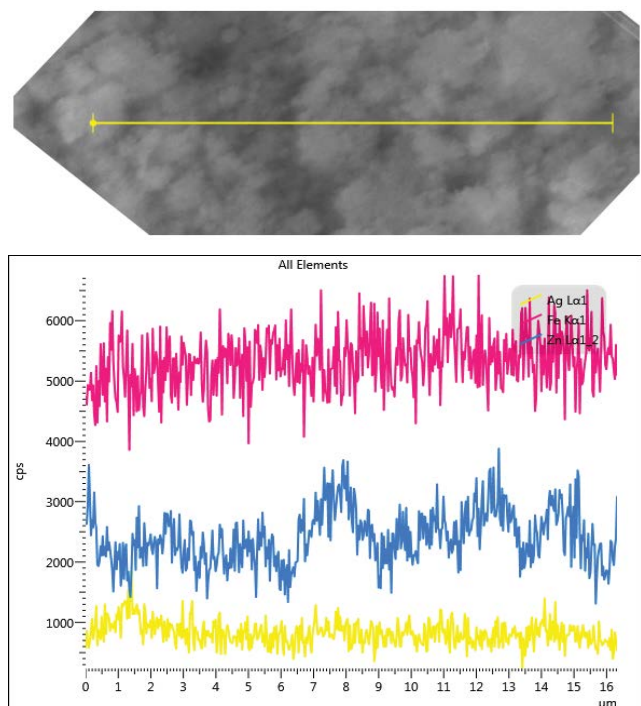


Fig. 4. Energy-dispersive X-ray spectroscopy line scan analysis for  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ .

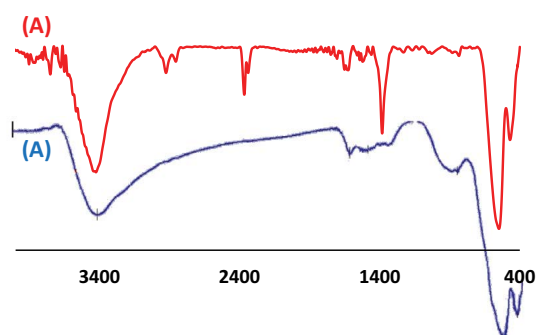


Fig. 5. (A) Fourier-transform infrared spectrum of the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ , (A) Fourier-transform infrared spectrum of the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ .

to 10 mL of azithromycin (10 mg/L) for 30 min. The results are presented in Fig. 7. The results show that increasing the amount of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  to 1.50 mg/L was accompanied with a rise in the percentage of removal of azithromycin; and with increasing the amount of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ , the percentage of removal did not change. The optimal amount of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  was 1.50 mg/L.

### 3.3. Effect of pH

The pH of the solution plays a key role in removal by the adsorbent. To study the effect of pH on removal percentage, 10 mL of azithromycin solution with a concentration of 10 mg/L was added to 1.50 mg/L of iron and its pH was

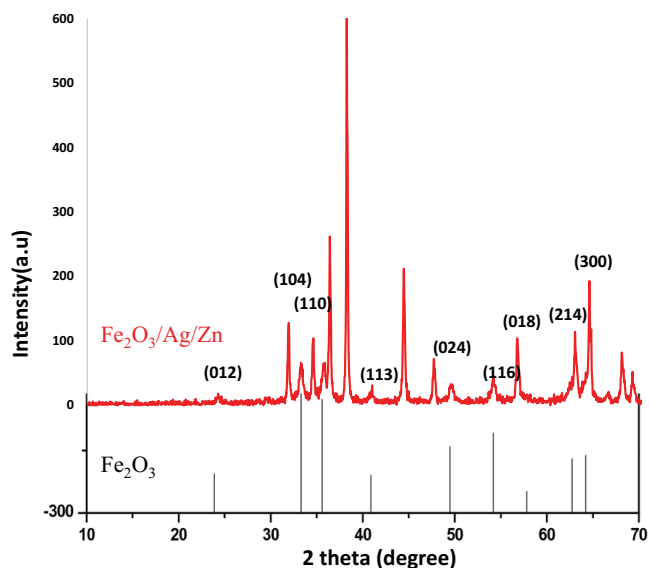


Fig. 6. X-ray diffraction patterns of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ .

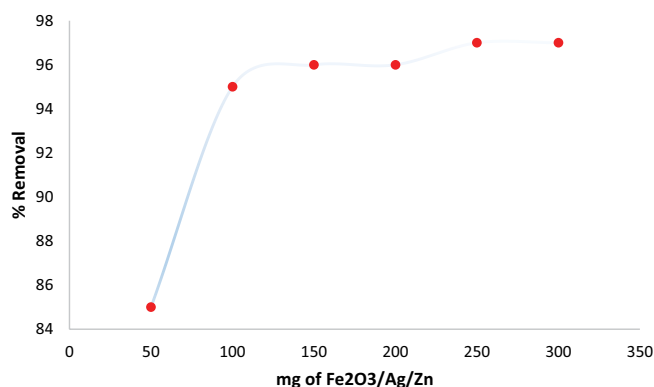


Fig. 7. Effect of the amount of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  (time = 30 min, pH = 4).

adjusted from 3 to 11. NaOH and HCl were used to adjust the pH to acidic or alkaline. The solution placed on a shaker at room temperature at 200 rpm for 30 min. It was centrifuged at 4,000 rpm and the azithromycin removal percentages were measured by a spectrophotometer at 547 nm. The results of Fig. 8 show that by increasing the pH from 3 to 5, the removal efficiency increased from about 45% to 96%, and then by increasing the pH, efficiency declined. The highest removal efficiency was obtained at pH 5; so the pH of 5 was chosen as the optimal pH. The  $\text{pH}_{\text{zpc}}$  value for the adsorbent was 4; at a pH lower than the  $\text{pH}_{\text{zpc}}$  the surface charge of the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  was positive and above that, the surface charge was negative. Since azithromycin has different functional groups, at pH 5, the surface of azithromycin has a negative charge and an electrostatic attraction between the surface of the catalyst and azithromycin occurs. With increase in electrostatic attraction percentage removal of azithromycin was increased, although the pH increases, the amount of removal does not differ much, so the best condition for removal is pH 5.

### 3.4. Effect of time

The results of the effect of time on the removal of azithromycin (10 mg/L), at the pH of 5 and the amount of 1.50 mg/L of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ , are shown in Fig. 9. The highest removable efficiencies of azithromycin had the highest and the lowest removal rate in 30 and 50 min; but since we did not see a significant increase in efficiency after 30 min, the time of 30 min is the optimal removal time. Considering that the removal mechanism is physical and chemical, within 30 min, the interaction between the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  and azithromycin is complete and leads to the maximum removal in this period, in longer time, because the active sites are saturated. The removal is not more than 96% and this interaction is not complete in less time [28,29].

### 3.5. Effect of temperature

Fig. 10 shows the effect of temperature on the adsorption of azithromycin. The temperature analysis showed the removal of azithromycin by  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  at pH = 5 and with 1.50 mg/L of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  and 10 mg/L of azithromycin in 30 min. The highest removal was related to 25°C. Because there is a chemical removal mechanism, as the temperature of the interaction between the adsorbent surface and tetracycline increases through the formation of hydrogen bonds, the percentage of removal increases, so it takes less time for removal percentage to reach 96%.

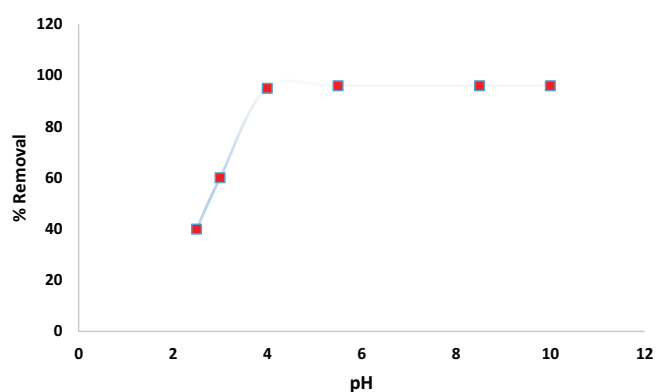


Fig. 8. Effect of initial pH on the removable of azithromycin,  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  = 1.50 mg/L and time = 30 min).

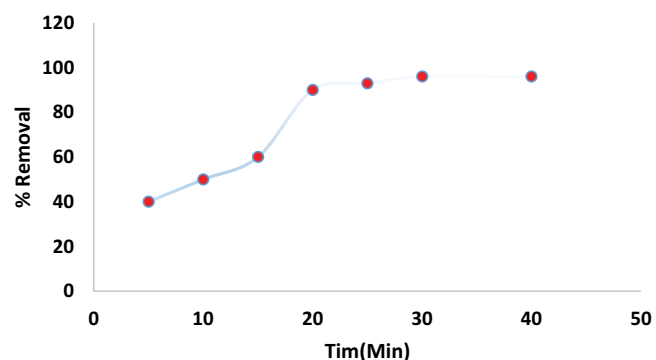


Fig. 9. Effect of time on the removable of azithromycin (azithromycin = 10.0 mg/L,  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  = 1.50 mg/L and pH = 5.0).

### 3.6. Effect of azithromycin concentrations

Fig. 11 displays the effect of the initial concentrations of azithromycin on its removal by  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ . To perform this experiment, the time,  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  amount and pH were set to their optimal values (i.e., time of 30 min, 1.50 g/L of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ , and pH = 5). Based on Fig. 11, by increasing the initial concentration of azithromycin, the percentage of azithromycin removed decreased; therefore, the removal of azithromycin was under the influence of the initial concentration. This is because the active sites where the absorption take place decrease with an increase in azithromycin.

### 3.7. Reuse of $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ nano-adsorbent to remove azithromycin from aqueous solution

The recovery of the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  is depicted in Fig. 12. It was performed 4 times and in each step, the ability to remove azithromycin decreased. In step 4 the removal rate reached 85%, which is due to the reduction of active points in each step; this shows that adsorption and desorption takes place in the surface layers [8].

### 3.8. Removal mechanism

In the optimal conditions used to remove azithromycin in an aqueous solution, two other compounds of  $\text{Fe}_2\text{O}_3/$

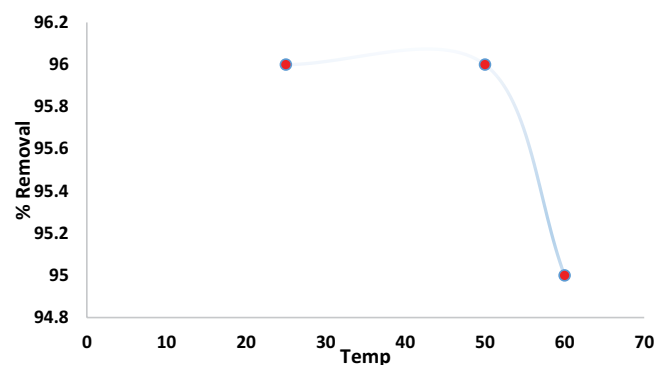


Fig. 10. Effect of temperature on the removable of azithromycin (azithromycin = 10.0 mg/L,  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  = 1.50 mg/L and pH = 5.0).

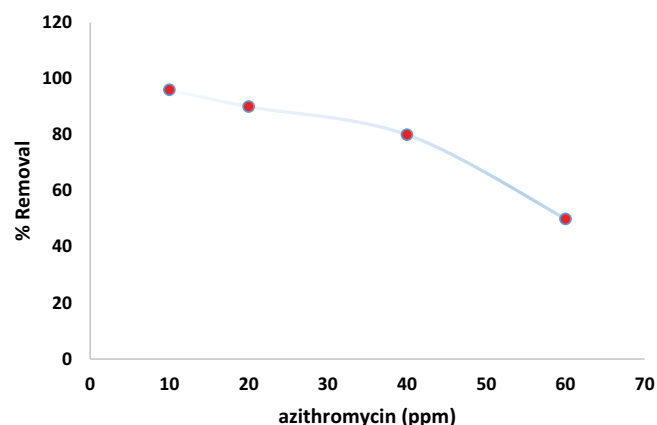


Fig. 11. Effect of azithromycin concentrations (time = 30 min,  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  = 1.50 mg/L and pH = 5.0, temp. = 25°C).

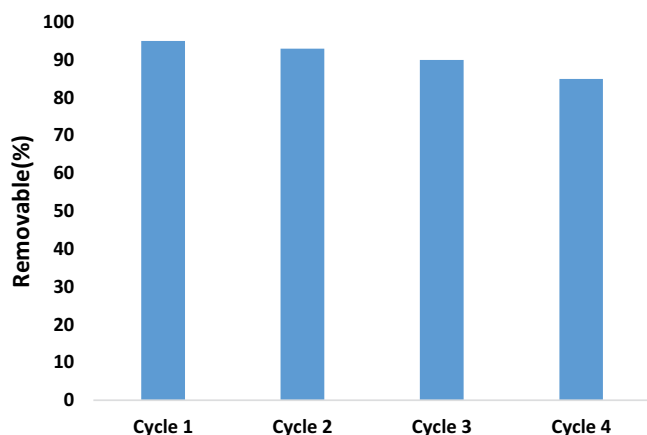


Fig. 12. Reusability of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  for adsorption removal of azithromycin antibiotic after 4 cycle adsorption/desorption.

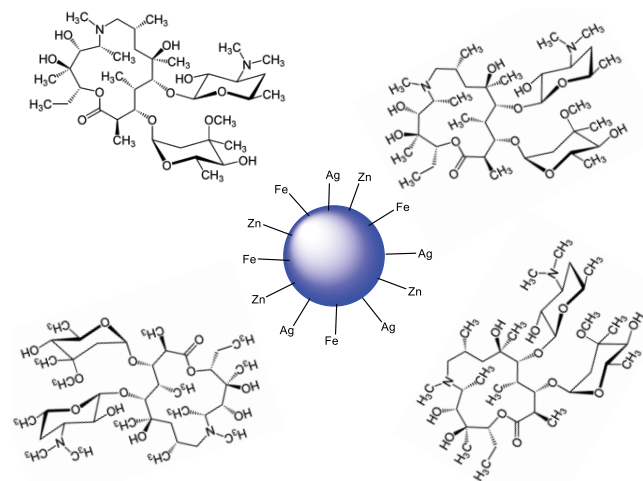


Fig. 13. Illustration of interaction between  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  and azithromycin antibiotic.

Ag and  $\text{Fe}_2\text{O}_3/\text{Zn}$  were used and compared with  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  (Table 1). Evidently, the removal rate for each one is around 85% for  $\text{Fe}_2\text{O}_3/\text{Ag}$  and 87% for  $\text{Fe}_2\text{O}_3/\text{Zn}$ , while for  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ , the removal rate is 96%. By comparing  $\text{Fe}_2\text{O}_3/\text{Ag}$  and  $\text{Fe}_2\text{O}_3/\text{Zn}$  with the  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$ , we can suggest the removal mechanism through chemical bonding (Fig. 13), azithromycin has OH, C=O and  $\text{NH}_2$  groups, which are adsorbed by  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  due to the presence of metals such as iron, zinc, and silver. These electron donor-acceptor interactions including the  $\pi$ - $\pi$  conjugation and  $\sigma$ - $\pi$  hyper-conjugation between the OH and N groups and metal surfaces in  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  nanocomposite may also promote the adsorption of the selected azithromycin on this composite. Bonding between functional groups such as OH, C=O and  $\text{NH}_2$  increases with the increase of M; however,  $\text{Fe}_2\text{O}_3/\text{Ag}$  and  $\text{Fe}_2\text{O}_3/\text{Zn}$ , have iron and silver or iron and zinc, and bond formation is less, so the amount of removal is less.

### 3.9. Limitations of a study

There are several challenges to nanocatalyst development in terms of fabrication and synthesis. The most

significant limitation is being controlled by particle size and distribution; other limitations of this catalyst are its saturation with antibiotics, which dramatically reduces the efficiency of the catalyst after recovery.

## 4. Conclusion

In this study,  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  was successfully synthesized by the co-precipitation method and used as an adsorbent for the removal of azithromycin from aqueous solutions. The structure was characterized by SEM, mapping, EDX, TEM, and FTIR. The particles had 20 nm diameter and spherical shape based on TEM analysis. The percentage elements of iron, silver and zinc in the composition was shown by EDX; FTIR also proved the formation of the structure. The optimal conditions for  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  for the removal of azithromycin (10 mg/L) were as follows: the amount of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  = 1.50 mg/L, time = 30 min, pH = 5, and at room temperature. Due to the favorable performance of  $\text{Fe}_2\text{O}_3/\text{Ag}/\text{Zn}$  in the removal of azithromycin, its feasible separation from aqueous solutions, and the high activity stability after several cycles (four cycles), it can be used as an efficient adsorbent in water and wastewater treatment without further need for filtering and centrifugation. It can also be used as an alternative to activated carbon.

## Data availability

All data generated or analyzed during this study are included in this published article.

## Conflicts of interest

The authors declare that they have no conflicts of interest.

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## Supporting information

### S1. Batch adsorption experiments

After preparing azithromycin samples with known concentration, specific amounts of adsorbents were added to them and then the samples were shaken at 200 rpm at 25°C. After 2, 5, 10, 20, 30 and 60 min, the samples were centrifuged at 4,000 rpm for 10 min to separate the azithromycin from the Fe<sub>2</sub>O<sub>3</sub>/Ag/Zn. The adsorption experiments were done on different dosages of the Fe<sub>2</sub>O<sub>3</sub>/Ag/Zn (0.5–2.5 mg/L) at pHs 2–11. Adjustment of pH was performed by adding HCl or NaOH 0.1 M to azithromycin solution until the desirable pH was reached. The concentration of azithromycin in the solution was measured with the purpose of computing the amount of removed azithromycin by the adsorbents. All of the experiments were done at least three times and with less than 5% error. The concentration of azithromycin was measured using a spectrophotometric method by the spectrophotometer at wavelength of 547 nm. The adsorption capacity of the adsorbents and their azithromycin removal percentage were calculated using Eqs. (1) and (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$\%R = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where  $q_e$  is the adsorption capacity of the adsorbent (mg/g),  $V$  is the sample volume (L),  $C_i$  is the initial concentration of azithromycin in the solution (mg/L),  $C_f$  is the residual concentration of azithromycin in the solution (mg/L) after the adsorption process, where, parameters  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of azithromycin and  $R$  is the azithromycin removal percentage, and  $m$  is the mass of the adsorbent in the adsorption process (g).