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Degradation of tetracycline using nanoparticles of zero-valent iron and copper

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ABSTRACT

Tetracycline (TC) is one of the most persistent pharmaceuticals in the ecosystem. Advanced oxidation processes (AOPs) are suitable and effective technology for treating wastewater contaminated with antibiotics such as TC. In this manner, Fenton-like reaction is effective for wastewater treatment from toxicity and non-biodegradable organic pollutants using bimetallic nanoparticles. This study aims to verify the effect of AOPs using ZVI/Cu bimetallic nanoparticles on removing the TC antibiotic via a Fenton-like reaction, and what is necessary to evaluate the factors that influence the reaction, i.e. pH, ZVI/Cu dose, stirring intensity, H_2O_2 concentration, and initial TC dosage. The obtained results indicated that the TC removal reached up to 82.3% with an initial TC dose of 8 μg/L. In addition, the TC degradation process is more effective in an acidic medium than in an alkaline medium. Furthermore, the TC removal reached up to 85.1% with a ZVI/Cu dose of 1.2 g/L. On the other hand, the optimum mixing intensity value was 200 rpm, and the optimum H_2O_2 dose was 2 g/L according to the conditions of the present study.

Key words: bimetallic, degradation, oxidation, tetracycline, wastewater treatment

HIGHLIGHTS

- The TC removal percent increases with the increase of ZVI/Cu doses. TC removal reached up to 85.1% with a ZVI/Cu dose of 1.2 g/L.
- The optimum mixing intensity value was 200 rpm, and the optimum H_2O_2 dose was 2 g/L according to the conditions of the present study.

1. INTRODUCTION

Tetracycline (TC) is one of the most widely applied antibiotics in veterinary medicine, livestock and poultry production, as well as being one of the most persistent pharmaceuticals in the ecosystem (Sarmah *et al.* 2006; Javid *et al.* 2016). In addition, TC is released into the surface and groundwater through medication manufacturing enterprises' wastewater effluent, disposal of non-consumable chemicals and expired pharmaceuticals containing TC, as well as animal and agricultural wastes (Boxall *et al.* 2003; Mompelat *et al.* 2009). TC is one of the antibiotics that are frequently found in sewage, surface and groundwater resources, drinking water, and sludge (Wang *et al.* 2011; Amos *et al.* 2018; Hassan *et al.* 2021). Hence, TC is resistant to biodegradation due to resistant compounds in the biological treatment of wastewater. Therefore, it is necessary to remove these pollutants before discharging them into conventional wastewater treatment plants (Park & Choung 2007; Abdel-Aziz *et al.* 2019; Adel *et al.* 2020; Hassan *et al.* 2021).

Advanced oxidation processes (AOPs) are suitable and effective technology for treating wastewater contaminated with antibiotics (Prousek *et al.* 2007; Adel *et al.* 2020). The idea of advanced oxidation is based on the production of highly reactive intermediates, especially hydroxyl radicals, which can oxidize almost all organic pollutants. In this manner, Fenton and Fenton-like reactions are effective AOPs for wastewater treatment from toxicity and non-biodegradable organic pollutants (Kuo 1992; Prousek 1995; Prousek *et al.* 2007; Velichkova *et al.* 2013; Saini & Kumar 2016; Adel *et al.* 2020).

Ferrous ions (Fe^{2+}) react with hydrogen peroxide (H_2O_2) to form hydroxyl radicals in the Fenton reactions. Hydroxyl radicals are highly reactive, non-selective oxidants (ROS) (Bocos *et al.* 2016; Pourzamani *et al.* 2018). However, ferrous salts' direct addition to water produces iron sludge (Lin *et al.* 2017). To overcome this limitation, sacrificial iron electrodes can be used to control ferrous ion loading (Radwan *et al.* 2018) or the ferrous ions that are extracted from iron catalysts such as zero-valent iron (He *et al.* 2018; Adel *et al.*

2020). The following equations describe the Fenton reaction mechanism (Pignatello *et al.* 2006; Adel *et al.* 2020).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\cdot 2} + H^+ \quad (2)$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (4)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2H^+ \quad (5)$$

$$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad (6)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (7)$$

A neutral form of hydroxide ion (OH^-), the hydroxyl radical ($OH^{\cdot}$) is produced. As shown in Equation (1), $OH^{\cdot}$ can be generated by electron transfer. On the other hand, the hydroperoxyl radical ($HO_2^{\cdot}$) can be produced as shown in Equations (2) and (3) when the Fenton reagent reduces $OH^{\cdot}$. Thus, the proportion between iron ions and hydrogen peroxide should be determined by laboratory experiments and the Fe^{3+} sludge should be removed. This makes the Fenton reaction complex and requires significant expense. Moreover, the production of hydroxyl radicals in an alkaline medium is ineffective (Pignatello *et al.* 2006; Adel *et al.* 2020).

For the reasons mentioned above, the Fenton-like reaction was developed as a promising alternative method. Specialists have given the Fenton reaction a great deal of thought in order to combat these drawbacks. Some different sorts of hetero/homogeneous catalyst (except Fe^{2+}) were utilized to supplant Fe^{2+}, including Fe^{3+}, Cu^{2+}/Cu^+, and nano zero-valent iron (ZVI). These setup frameworks are called hetero/homogeneous Fenton-like processes. The essential contrast between the homogeneous and heterogeneous Fenton-like reactions includes the various positions where the catalytic reactions occur. In the homogeneous system, the catalysis process can happen in the whole liquid phase, while in the heterogeneous system the catalysis process consistently occurs on the surface of the catalyst. The situation at which catalysis ensues in the heterogeneous framework verifies that the dissemination and adsorption processes of hydrogen peroxide (H_2O_2) and different reactants to the surface of the catalyst could be important for the catalysis process (Wang 2008, 2013, 2016; Nidheesh 2015; Jain *et al.* 2018; Adel *et al.* 2020).

It has been shown in several experiments that the rate of mineralization is faster with Fenton than with Fenton-like reagents because of the rapid arrangement of hydroxyl radicals in the Fenton reagent (Wang *et al.* 2016; Adel *et al.* 2020). In summary, Fenton-like reagent oxidation capacity was influenced by pH, H_2O_2 dose, catalyst dose, and reaction temperature (Wang 2008; Wang *et al.* 2016; Adel *et al.* 2020). Under neutral pH conditions, the Fenton-like reaction is notable among the techniques used to increase degradation efficiency and reduce economic cost. Nanoparticles of ZVI are non-toxic, inexpensive, and easy to prepare (Kobayashi *et al.* 2017; Vollprecht *et al.* 2019; Xue *et al.* 2019; Adel *et al.* 2020).

The bimetallic nanoparticles have been generally utilized in advanced wastewater treatment because of their efficiency as a catalyst as well as their high surface area (Qin *et al.* 2016; Sepúlveda *et al.* 2018; Mahmoud *et al.* 2020). Zero valent iron/copper (ZVI/Cu) as bimetallic nanoparticles have been demonstrated in the removal of non-biodegradable organics using AOPs (Thomas 2003; Wijesekara *et al.* 2014; Adel *et al.* 2020; Mahmoud *et al.* 2020).

The aim of this study is to verify the effect of AOPs using ZVI/Cu bimetallic nanoparticles on removing the TC antibiotic via a Fenton-like reaction, and what is necessary to evaluate the factors that influence the reaction; that is, pH, ZVI/Cu dose, stirring intensity, H_2O_2 concentration, and initial TC dosage.

2. MATERIALS AND METHODS

2.1. Chemicals

All the utilized chemicals were of analytical grade as well as high quality. Methanol (CH_3OH), ethanol (C_2H_5OH), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), copper sulfate pentahydrate ($CuSO_4.5H_2O$), sodium borohydride ($NaBH_4$), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), and hydrochloric acid (HCL) are available from Sigma-Aldrich Company.

2.2. ZVI/Cu characteristics and preparation

ZVI/Cu is a dark powder with a particle size of under 50 nm supplied from Nano Gate Company. Figure 1 shows the shape and size of ZVI/Cu nanoparticles as determined by transmission electron microscopy (TEM) performed on a JEOL JEM-2100 high-resolution transmission electron microscope at 200 kV (Hudson *et al.* 2012).

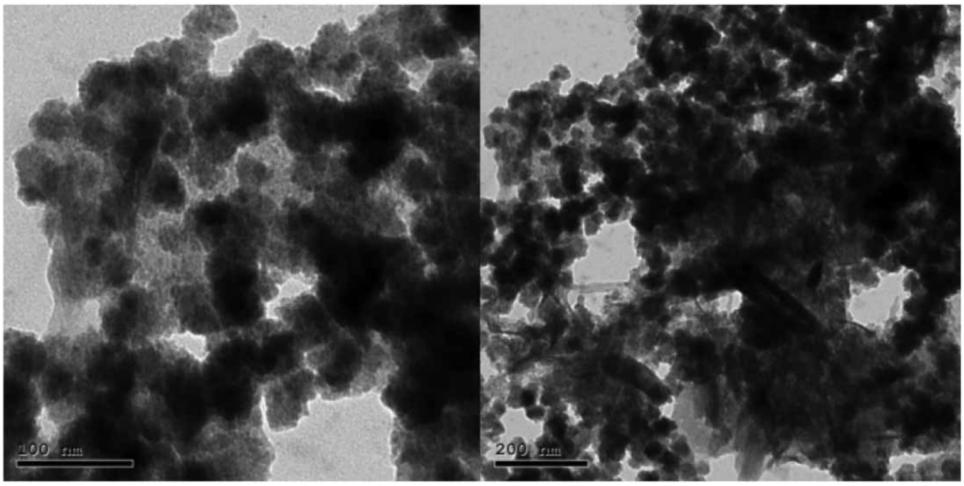

Figure 1 | ZVI/Cu characteristics (Adel *et al.* 2020).

$NaBH_4$ was used to prepare ZVI nanoparticles through net phase reduction. 10.5 g of $FeSO_4.7H_2O$ was dissolved in 100 ml of ethanol/deionized water (3:7 V/V). This was followed by a pH adjustment at 6.8. Next, 2.0 g of $NaBH_4$ was added to the solution in small amounts at a time, stirred vigorously at 250 rpm for 30 minutes and dried at 105 °C. The final product was obtained by washing the residual solids with ethanol and drying them. ZVI was dispersed in a $CuSO_4$ solution to load Cu onto it (Lai *et al.* 2014; Yamaguchi *et al.* 2018). $CuSO_4$ was added at a concentration of 3 g/L, and the pH was adjusted to 4.6 at a temperature of 40 °C at first. It was left to precipitate for about 10 minutes after 30 minutes of stirring. A magnetic separation process was used to collect the synthesized particles. They were then washed with ethanol and dried in an oven at 105 °C to obtain the final product (Babuponnusami & Muthukumar 2012; Adel *et al.* 2020).

2.3. Experimental method

The reaction was carried out in a complete mixer containing 100 mL of TC solution with different initial concentrations ranging from 2 to 8 μg/L. Before adding the reagents, the pH was neutralized with HCL or NaOH to between 6 and 9 so that it was within the limits of the treated wastewater. Then, ZVI/Cu doses between 0.3 and 1.2 g/L and H_2O_2 up to 3 g/L were added. The solution was vigorously stirred for 60 minutes, and samples were taken at predetermined intervals to monitor the change in TC concentration (Adel *et al.* 2020). The measurements were conducted using Inductively Coupled Plasma (ICP-OES); model OPTIMA™ 7000 DV, USA, HPLC apparatus (Agilent 1200). Standard Methods for Examination of Water and Wastewater, 23rd edition, prepared and published by APHA, AWWA, and WEF, was used as a guide for the analyses (Standard Methods 2017). These experiments were conducted in Central Laboratory, Tanta University, and Faculty of Science, Mansoura University, Egypt.

2.4. Design of experiments

As a statistical tool, the multiple linear regression (MLR) model has been used to find a relationship between the efficiency of TC removal (TC %) given the influencing parameters, namely pH, ZVI/Cu dose, stirring intensity (SI), H_2O_2 concentration, and initial TC dosage (TC_i). The experiments of TC degradation were conducted according to the following ranges of the influencing parameters as shown in Table 1.

3. RESULTS AND DISCUSSION

3.1. Impact of initial TC range on TC removal

The relationship between the initial TC dose and the percentage of its removal after the degradation process was found, as shown in Figure 2. The pH was adjusted to 7.0, the stirring intensity (SI) was calibrated at 150 rpm, and

Table 1 | Ranges of the influencing parameters for TC degradation

	Values			
Influencing parameter	**I**	**II**	**III**	**IV**
TC_i (μg/L)	2	4	6	8
pH	6	7	8	9
ZVI/Cu (g/L)	0.3	0.6	0.9	1.2
SI (rpm)	100	150	200	250
H_2O_2 (g/L)	0	1	2	3

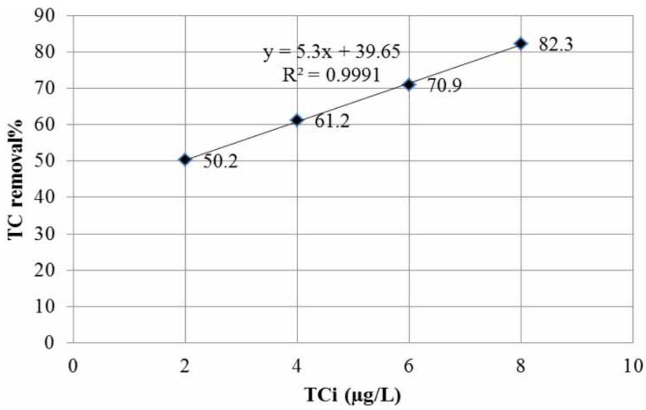

Figure 2 | Relationship between the initial TC dose and the percentage of its removal.

the doses of ZVI/Cu, H_2O_2 were 0.6, 1.0 g/L respectively. It can be noticed that the TC removal percent increases with the increase of initial TC doses. TC removal reached up to 82.3% with an initial TC dose of 8 μg/L. These results are well matched with those obtained by Abdel-Aziz *et al.* (2019) and Adel *et al.* (2020).

3.2. Determination of optimum pH value

The percent of TC removal was observed at a sequence of pH values from 6.0 to 9.0 to get the optimum pH value for TC removal as represented in Figure 3. The initial TC dose was 6 μg/L, the stirring intensity was calibrated at 150 rpm and the doses of ZVI/Cu, H_2O_2 were 0.6, 2.0 g/L respectively. An increase in the percentage of TC removal can be observed from 71.6 to 80.4% when the pH value is increased from 6 to 7. On the contrary, it is noticed that the removal percentage of TC decreases from 80.4% to 50.1% when the pH is increased from 7 to 9. This shows that the TC degradation process is more effective in an acidic medium than in an alkaline

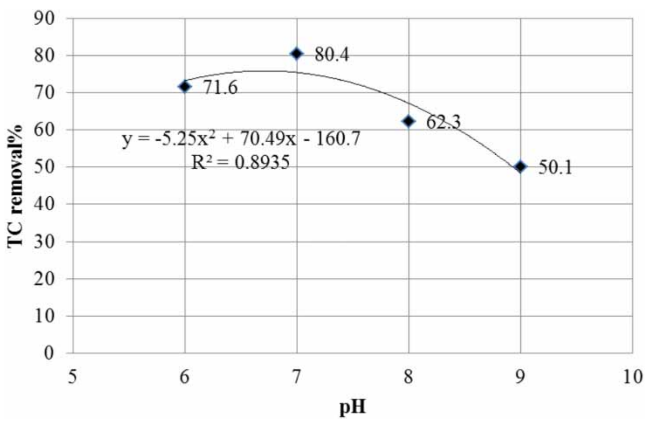

Figure 3 | Impact of pH on TC removal.

medium, and the optimum pH value became 7 according to these conditions. The relationship between the pH values and TC removal in this study is similar to the pH relationship with the carbamazepine removal in Abdel-Aziz *et al.* (2019).

3.3. Impact of ZVI/Cu dose on TC removal

The relationship between ZVI/Cu dose and the percentage of TC removal after the degradation process was found, as shown in Figure 4. The initial TC dose was 4 μg/L, the pH was adjusted at 7.0, the stirring intensity (SI) was calibrated at 150 rpm, and the H_2O_2 was 2.0 g/L respectively. It can be noticed that the TC removal percent increases with the increase of ZVI/Cu doses. TC removal reached up to 85.1% with a ZVI/Cu dose of 1.2 g/L. These results are well-matched with those obtained by Adel *et al.* (2020).

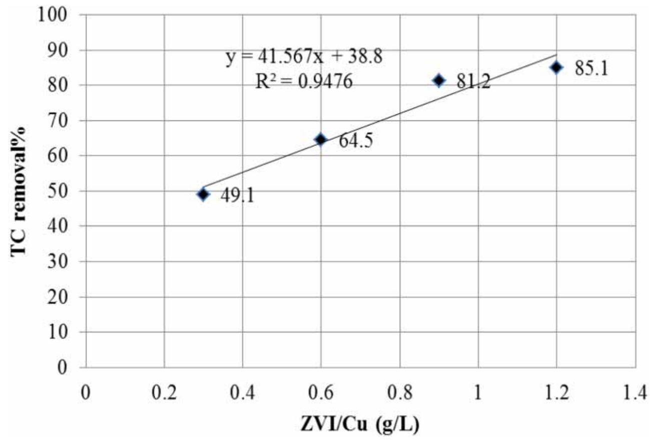

Figure 4 | Impact of ZVI/Cu dose on TC removal.

3.4. Optimization of stirring intensity conditions

The percent of TC removal was observed at a sequence of stirring intensity (SI) or mixing rotational speed values from 100 to 250 rpm to get the optimum SI value for TC removal as shown in Figure 5. The initial TC dose was 6 μg/L, the pH value was 7, and the doses of ZVI/Cu, H_2O_2 were 0.6, 2.0 g/L respectively. An increase in the percentage of TC removal can be observed from 51.1 to 73.8% when the SI is increased from 100 to 200 rpm. On the contrary, it is noticed that the removal percentage of TC decreases from 73.8% to 69.1% when the SI is increased from 200 to 250 rpm. This shows that the optimum SI value was 200 rpm according to these conditions. The relationship between the SI values and TC removal in this study is similar to Adel *et al.* (2020).

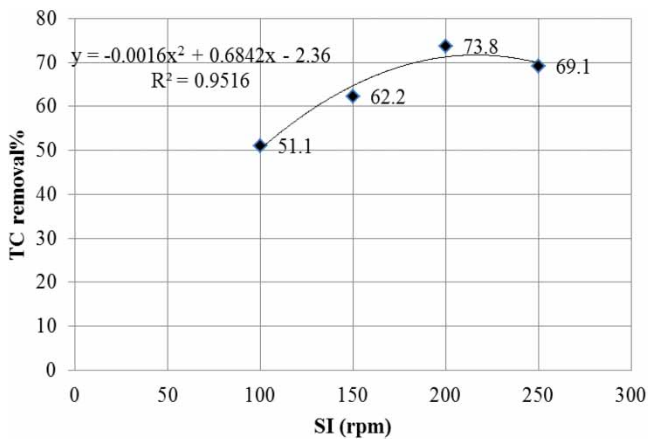

Figure 5 | Impact of stirring intensity on TC removal.

3.5. Optimization of H_2O_2 dose

The relationship between H_2O_2 dose and the percentage of TC removal after the degradation process was found, as shown in Figure 6. The initial TC dose was 6 μg/L, the pH was adjusted at 7.0, the stirring intensity (SI) was calibrated at 200 rpm, and the dose of ZVI/Cu was 0.6 g/L respectively. An increase in the percentage of TC removal can be observed from 50.9 to 73.2% when the H_2O_2 dose is increased from 0 to 2 g/L. On the contrary, it is noticed that the removal percentage of TC decreases from 73.2% to 67.9% when the H_2O_2 dose is increased from 2 to 3 g/L. This shows that the optimum H_2O_2 dose was 2 g/L according to these conditions.

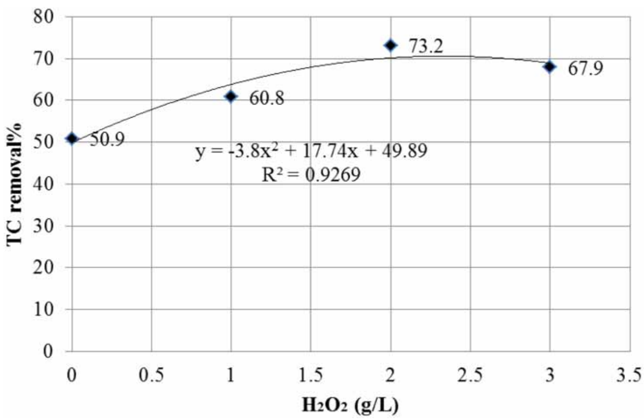

Figure 6 | Impact of H_2O_2 dose on TC removal.

3.6. Model development for predicting TC removal

The multiple linear regression (MLR) model was applied for predicting TC removal depending on the recorded influencing parameters. Table 2 shows the output data from the ANOVA model, while Table 3 shows the coefficients and statistical results from the MLR model (3).

Table 2 | Output data from analysis of variance (ANOVA) model

Source	df	SS	MS	F	Significance F
Regression	5	116,985.4021	23,397.08	493.1214	2.05E-19
Residual	20	948.9378929	47.44689		
Total	25	117,934.34			

Table 3 | Coefficients and statistical results of multiple linear regression model

	Coefficients	Standard error	t Stat	*P*-value	Lower 95%	Upper 95%
Intercept	0.000	#N/A	#N/A	#N/A	#N/A	#N/A
TC_i (μg/L)	6.322090938	0.640972409	9.863281	3.99E-09	4.985046	7.659136
pH	3.296046347	1.08668104	3.033131	0.006567	1.029269	5.562823
ZVI/Cu (g/L)	−2.357980559	8.453612279	−0.27893	0.783161	−19.9919	15.27595
SI (rpm)	−0.014378872	0.052397564	−0.27442	0.786577	−0.12368	0.094921
H_2O_2 (g/L)	3.623346769	1.782438151	2.032804	0.055562	−0.09475	7.341448

The following equation can be used to calculate the predicted TC removal percent from the MLR model:

$$TCremoval\% = 6.322TC_i + 3.296pH - 2.358ZVI/Cu - 0.0144SI + 3.623H_2O_2 \quad (8)$$

An R-squared value of 0.996 confirmed that TC removal percent was a dependent variable, while the other parameters were independent variables. Degradation of TC can be assessed using MLR because it is simple, direct, and highly accurate.

4. CONCLUSIONS

The scope of this study is evaluating the effect of AOPs using ZVI/Cu bimetallic nanoparticles on removing the TC antibiotic via a Fenton-like reaction, and what is necessary to evaluate the factors that influence the reaction; that is, pH, ZVI/Cu dose, stirring intensity, H_2O_2 concentration, and initial TC dosage. A number of important conclusions were drawn as follows:

1. The TC removal percent increases with the increase of initial TC doses. TC removal reached up to 82.3% with an initial TC dose of 8 μg/L.
2. The TC degradation process is more effective in an acidic medium than in an alkaline medium, and the optimum pH value became 7 according to the conditions of the present study.
3. The TC removal percent increases with the increase of ZVI/Cu doses. TC removal reached up to 85.1% with a ZVI/Cu dose of 1.2 g/L.
4. The optimum SI value was 200 rpm according to the conditions of the present study.
5. The optimum H_2O_2 dose was 2 g/L according to the conditions of the present study.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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