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, H2O2 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 H2O2 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 H2O2 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 (Fe2+) react with hydrogen peroxide (H2O2) 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).

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

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^+ + \text{OH}^- \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \\
\text{OH}^+ + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \\
\text{HO}_2^- + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{Fe}^{3+} + \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{O}_2\text{H}^+ \\
\text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \\
2\text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

A neutral form of hydroxide ion (OH\(^-\)), the hydroxyl radical (OH\(^\cdot\)) is produced. As shown in Equation (1), OH\(^-\) 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\(^-\). 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\(_2\)O\(_2\)) 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\(_2\)O\(_2\) 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\(_2\)O\(_2\) 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\(_3\)OH), ethanol (C\(_2\)H\(_5\)OH), ferrous sulfate heptahydrate (FeSO\(_4\).7H\(_2\)O), copper sulfate pentahydrate (CuSO\(_4\).5H\(_2\)O), sodium borohydride (NaBH\(_4\)), hydrogen peroxide (H\(_2\)O\(_2\)), 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).

NaBH₄ was used to prepare ZVI nanoparticles through net phase reduction. 10.5 g of FeSO₄·7H₂O 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 NaBH₄ 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 CuSO₄ solution to load Cu onto it (Lai et al. 2014; Yamaguchi et al. 2018). CuSO₄ 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 be 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 H₂O₂ 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), H₂O₂ concentration, and initial TC dosage (TCi). 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
the doses of ZVI/Cu, H$_2$O$_2$ 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 $\mu$g/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 $\mu$g/L, the stirring intensity was calibrated at 150 rpm and the doses of ZVI/Cu, H$_2$O$_2$ 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

| Ranges of the influencing parameters for TC degradation |
|-------------------------------------------------------|
| Influening parameter | Values |
| TC$_i$ ($\mu$g/L) | I | II | III | IV |
| pH | 6 | 7 | 8 | 9 |
| ZVI/Cu (g/L) | 0.3 | 0.6 | 0.9 | 1.2 |
| SI (rpm) | 100 | 150 | 200 | 250 |
| H$_2$O$_2$ (g/L) | 0 | 1 | 2 | 3 |

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

**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 H2O2 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](image)

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, H2O2 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](image)

Figure 5 | Impact of stirring intensity on TC removal.
3.5. Optimization of H2O2 dose

The relationship between H2O2 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 H2O2 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 H2O2 dose is increased from 2 to 3 g/L. This shows that the optimum H2O2 dose was 2 g/L according to these conditions.

![Figure 6](Impact of H2O2 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      |
| TCi (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  |
| H2O2 (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:

\[
\text{TCremoval\%} = 6.322\text{TCi} + 3.296pH - 2.358\text{ZVI/Cu} - 0.0144\text{SI} + 3.623\text{H}_2\text{O}_2
\]  

(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, H₂O₂ 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 H₂O₂ 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.

REFERENCES

Abdel-Aziz, H. M., Farag, R. S. & Abdel-Gawad, S. A. 2019 Carbamazepine removal from aqueous solution by green synthesis zero-valent iron/Cu nanoparticles with Ficus Benjamina leaves’ extract. International Journal of Environmental Research 13(3), 843–852.

Adel, A., Alalm, M. G., El-Etriby, H. K. & Boffito, D. C. 2020 Optimization and mechanism insights into the sulfamethazine degradation by bimetallic ZVI/Cu nanoparticles coupled with H₂O₂. Journal of Environmental Chemical Engineering 8(5), 104541.

Amos, G. C., Ploumakis, S., Zhang, L., Hawkey, P. M., Gaze, W. H. & Wellington, E. M. 2018 The widespread dissemination of integrons throughout bacterial communities in a riverine system. The ISME Journal 12(3), 681–691.

Babuponnumasi, A. & Muthukumar, K. 2012 Removal of phenol by heterogeneous photo electro Fenton-like process using nano-zero valent iron. Separation and Purification Technology 98, 130–135.

Bocos, E., Iglesias, O., Pazos, M. & Sanromán, M. Á. 2016 Nickel foam a suitable alternative to increase the generation of Fenton’s reagents. Process Safety and Environmental Protection 101, 34–44.

Boxall, A. B., Kolpin, D. W., Halling-Sørensen, B. & Tolls, J. 2003 Peer reviewed: are veterinary medicines causing environmental risks? Environmental Science & Technology 37(15), 286A–294A.

Hassan, M., Zhu, G., Lu, Y. Z., AL-Falahi, A. H., Lu, Y., Huang, S. & Wan, Z. 2021 Removal of antibiotics from wastewater and its problematic effects on microbial communities by bioelectrochemical technology: current knowledge and future perspectives. Environmental Engineering Research 26(1), 190405.

He, F., Li, Z., Shi, S., Xu, W., Sheng, H., Gu, Y. & Xi, B. 2018 Dechlorination of excess trichloroethene by bimetallic and sulfided nanoscale zero-valent iron. Environmental Science & Technology 52(15), 8627–8637.

Hudson, R., Li, C. J. & Moores, A. 2012 Magnetic copper–iron nanoparticles as simple heterogeneous catalysts for the azide–alkyne click reaction in water. Green Chemistry 14(3), 622–624.

Jain, B., Singh, A. K., Kim, H., Lichtfouse, E. & Sharma, V. K. 2018 Treatment of organic pollutants by homogeneous and heterogeneous Fenton reaction processes. Environmental Chemistry Letters 16(3), 947–967.

Javid, A., Mesdaghinia, A., Nasseri, S., Mahvi, A. H., Ali Mohammad, M. & Gharibi, H. 2016 Assessment of tetracycline contamination in surface and groundwater resources proximal to animal farming houses in Tehran, Iran. Journal of Environmental Health Science and Engineering 14(1), 1–5.

Kobayashi, M., Kurosu, S., Yamaguchi, R. & Kawase, Y. 2017 Removal of antibiotic sulfamethoxazole by zero-valent iron under oxid and anoxic conditions: removal mechanisms in acidic, neutral and alkaline solutions. Journal of Environmental Management 200, 88–96.

Kuo, W. G. 1992 Decolorizing dye wastewater with Fenton’s reagent. Water Research 26(7), 881–886.

Lai, B., Zhang, Y. H., Yuan, Y., Chen, Z. Y. & Yang, P. 2014 Influence of preparation conditions on characteristics, reactivity, and operational life of microsized Fe/Cu bimetallic particles. Industrial & Engineering Chemistry Research 53(31), 12295–12304.
Lin, J., Sun, M., Liu, X. & Chen, Z. 2017 Functional kaolin supported nanoscale zero-valent iron as a Fenton-like catalyst for the degradation of Direct Black G. *Chemosphere* 184, 664–672.

Mahmoud, A. S., Ismail, A., Mostafa, M. K., Mahmoud, M. S., Ali, W. & Shawky, A. M. 2020 Isotherm and kinetic studies for heptachlor removal from aqueous solution using Fe3O4 nanoparticles, artificial intelligence, and regression analysis. *Separation Science and Technology* 55(4), 684–696.

Mompelat, S., Le Bot, B. & Thomas, O. 2009 Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. *Environment International* 35(5), 803–814.

Nidheesh, P. V. 2015 Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: a review. *RSC Advances* 5(51), 40552–40577.

Park, H. & Choung, Y. K. 2007 Degradation of antibiotics (tetracycline, sulfathiazole, ampicillin) using enzymes of glutathion S-transferase. *Human and Ecological Risk Assessment: An International Journal* 13(5), 1147–1155.

Pignatello, J. J., Oliveros, E. & MacKay, A. 2006 Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Critical Reviews in Environmental Science and Technology* 36(1), 1–84.

Pourzamani, H., Haji zadeh, Y. & Mengelizadeh, N. 2018 Application of three-dimensional electro-Fenton process using MWCNTs-Fe3O4 nanocomposite for removal of diclofenac. *Process Safety and Environmental Protection* 119, 271–284.

Prousek, J. 1995 Fenton reaction after a century. *Chemické Listy* 89(1), 11–21.

Prousek, J., Palacková, E., Priesolová, S., Marková, L. & Alevová, A. 2007 Fenton-and Fenton-like AOPs for wastewater treatment: from laboratory-to-plant-scale application. *Separation Science and Technology* 42(7), 1505–1520.

Qin, N., Zhang, Y., Zhou, H., Geng, Z., Liu, G., Zhang, Y. & Wang, G. 2016 Enhanced removal of trace Cr (VI) from neutral and alkaline aqueous solution by FeCo bimetallic nanoparticles. *Journal of Colloid and Interface Science* 472, 8–15.

Radwan, M., Alalm, M. G. & Eletriby, H. 2018 Optimization and modeling of electro-Fenton process for treatment of phenolic wastewater using nickel and sacrificial stainless steel anodes. *Journal of Water Process Engineering* 22, 155–162.

Saini, R. & Kumar, P. 2016 Optimization of chlorpyrifos degradation by Fenton oxidation using CCD and ANFIS computing technique. *Journal of Environmental Chemical Engineering* 4(3), 2952–2963.

Sarmah, A. K., Meyer, M. T. & Boxall, A. B. 2006 A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment. *Chemosphere* 65(5), 725–759.

Sepúlveda, P., Rubio, M. A., Baltazar, S. E., Rojas-Nunez, J., Llamazares, J. S., García, A. G. & Arancibia-Miranda, N. 2018 As (V) removal capacity of FeCu bimetallic nanoparticles in aqueous solutions: the influence of Cu content and morphologic changes in bimetallic nanoparticles. *Journal of Colloid and Interface Science* 524, 177–187.

Standard Methods 2017 *Standard Methods for the Examination of Water and Wastewater*, 23rd edn. American Public Health Association, Washington, DC, USA.

Thomas, H. 2003 *Groundwater Quality and Groundwater Pollution*. University of California, Davis & Kearney Agricultural Center Parlier, CA, USA.

Velichkova, F., Julcour-Lebigue, C., Koumanova, B. & Delmas, H. 2013 Heterogeneous Fenton oxidation of paracetamol using iron oxide (nano) particles. *Journal of Environmental Chemical Engineering* 1(4), 1214–1222.

Vollprecht, D., Krois, L. M., Sseladzeck, K. P., Müller, P., Mischitz, R., Olbrich, T. & Pomerberger, R. 2019 Removal of critical metals from waste water by zero-valent iron. *Journal of Cleaner Production* 208, 1409–1420.

Wang, S. 2008 A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater. *Dyes and Pigments* 76(5), 714–720.

Wang, P., Yap, P. S. & Lim, T. T. 2011 C–N–S tridoped TiO2 for photocatalytic degradation of tetracycline under visible-light irradiation. *Applied Catalysis A: General* 399(1–2), 252–261.

Wang, Z., Liu, Z., Yu, F., Zhu, J., Chen, Y. & Tao, T. 2013 Siderophore-modified Fenton-like system for the degradation of propanolol in aqueous solutions at near neutral pH values. *Chemical Engineering Journal* 229, 177–182.

Wang, N., Zheng, T., Zhang, G. & Wang, P. 2016 A review on Fenton-like processes for organic wastewater treatment. *Journal of Environmental Chemical Engineering* 4(1), 762–787.

Wijesekara, S. S. R. M. D. H. R., Harischandra, I. G. J. C., Kumarathilaka, S. M. P. R. & Vithanage, M. 2014 Fate and transport of selection nutrients and heavy metals in nanoscale zero valent iron amended sand columns. University of Peradeniya, Sri Lanka.

Xue, G., Wang, Q., Qian, Y., Gao, P., Su, Y., Liu, Z. & Chen, J. 2019 Simultaneous removal of aniline, antimony and chromium by ZVI coupled with H2O2: implication for textile wastewater treatment. *Journal of Hazardous Materials* 368, 840–848.

Yamaguchi, R., Kurosu, S., Suzuki, M. & Kawase, Y. 2018 Hydroxyl radical generation by zero-valent iron/Cu (ZVI/Cu) bimetallic catalyst in wastewater treatment: heterogeneous Fenton/Fenton-like reactions by Fenton reagents formed in-situ underoxic conditions. *Chemical Engineering Journal* 334, 1537–1549.

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