Green Synthesis of Zero Iron Nanoparticles and its Application in the Degradation of Metronidazole

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Abstract

Background: The production and consumption of pharmaceutical compounds, including antibiotics, and their entry into the environment have raised concerns for experts. It is important to find appropriate methods for treatment of these pollutants from aquatic environments. In this study, nano-persulfate process using green synthesis of zero iron nanoparticles was used in decomposition of the antibiotic Metronidazole (MNZ).

Methods: In this study, first, zero iron nanoparticles were synthesized using oak leaves. Then, the characteristics of these nanoparticles were determined using electronic images such as SEM, and TEM. In the experimental part of the study, the effect of operating conditions such as nZVI dosage, persulfate concentration and pH of the PS/nZVI process on degradation of MNZ in aqueous solution Was examined.

Results: The results of this study showed that the PS/nZVI process had an acidic nature for removal of MNZ. The optimal conditions for this process were: the dosage of nZVI was 1.8 g/l, the concentration of persulfate was 1.5 mg/l, and pH was 3 for the degradation of 50 mg/l MNZ at contact time of 90 min. The maximum MNZ removal efficiency using PS / NZVI process was about 98.4 % in these conditions.

Conclusion: It can be concluded that the synthesis of green zero iron nanoparticles is an economical and environmentally friendly method that can be used to remove MNZ from aqueous solutions.

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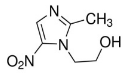
Introduction

Metronidazole is a drug from the group of nitroimidazole antibiotics that has antibacterial and anti-inflammatory properties (Table 1). It is widely used in the treatment of infections caused by anaerobic bacteria and protozoa such as Giardia lamblia and Trichomonas vaginalis. In addition to human use, metronidazole is used as an additive in poultry and fish feed to remove the parasites, so it accumulates in the meat of these organisms.[1, 2] Therefore, a large amount of this antibiotic is excreted unchanged from the human and animals body and enters the environment, especially water environments, and it is necessary to treat it from water and wastewater.

Various physical, chemical and biological methods such as enzymatic biotechnology, adsorption, chemical coagulation, etc. have been used for elimination of antibiotics and other drugs from aqueous solution.[3-5] The use of nanoparticles in the environmental field has recently attracted much attention. One of the most important applications of these particles is to remove the organic and inorganic pollutants from aquatic environments. Zero iron nanoparticles are one of the most widely used of these nanoparticles. The characteristics of these particles are having a high surface area and high

Table 1: General characteristics of the antibiotic metronidazole

Molecular structure	
Chemical structure	$C_6H_9N_3O_3$
Molecular weight	171.2 g/mol
Solubility in water	9.5 g/L
pk_a	2.55
Melting point	159-163 c̊

reactivity. The common method of preparing zero iron nanoparticles is the use of reducing agents such as sodium borohydride or potassium borohydride.[6] The use of this method has disadvantages; for example, borohydride is a toxic substance; therefore, the synthesis of zero iron nanoparticles with this method can cause environmental pollution.[7] Also, another group of environmental pollutants that may enter the environment with this method are chemical dispersants that are often used to prevent agglomeration of nZVI. In addition, the use of chemicals on a large scale is not economically viable. Therefore, it is essential to find a suitable economic and environmental method. Green synthesis, as an environmentally friendly method, is a suitable alternative in nanoparticle synthesis. The use of plant extracts, as an alternative method, has been widely studied. Organic compounds such as amines, carboxylic acids as well as phenol can reduce Fe^{3+} and Fe^{2+} in aqueous media. Various studies have been performed on the green synthesis of nanoparticles using plants, including leaf extract of *Jatropha curcas* L, Carica papaya, Ficus carica, and walnut green skin.[8-11]

In the present study, oak leaves were used to green synthesize the zero iron nanoparticles, and then the effectiveness of this type of nanoparticles in the degradation of MNZ antibiotic in aqueous solution was investigated.

Methods

Reagents and Materials

The antibiotic MNZ was purchased from Sigma Aldrich. The oak leaves were obtained from the Oak forests in the Zagros Mountains, Noorabad Mamasani region, Fars province, Iran. Acetonitrile (HPLC grade), Ferrous chloride, sulfuric acid, sodium hydroxide, methanol and potassium persulfate were procured from German Merk Company. All of these chemicals were of analytical grade.

Leaf Preparation

Oak leaves were collected from oak forest trees in the Zagros Mountains in the Nurabad Mamasani region of Fars province, Iran, in September 2020. After separating the leaves from the tree, they were washed three times with distilled water and then dried in the sun. The dried leaves were crushed by a mill, sieved and then stored in the refrigerator for testing.

Synthesis of nZVI

In this study, oak leaf extract was prepared by heating 100 g / 1 of oak leaf powder in a container to boil. After settling the leaf extract for 2 hours, its supernatant was filtered with the help of a vacuum pump. Elsewhere, a solution of 0.2 M $FeCl_2{\cdot}4H_2O$ was prepared by dissolving about 40 g of powder $FeCl_2{\cdot}4H_2O$ in 1 L of deionized water. Then, 0.2 M $FeCl_2{\cdot}4H_2O$ solution ferric was added to the stirring leaf solution in a ratio of 2:3. Sodium hydroxide and sulfuric acid were used to adjust the pH of the solution. The formation of iron nanoparticles was accompanied by the appearance of a black precipitate. The nanoparticles were then separated by evaporation of water and drying in an oven.

Experimental Procedures

Batch experiments were performed on a rotary shaker in a 100 ml Erlenmeyer containing 50 mL reaction solution at room temperature. Samples containing MNZ were synthetically prepared using diluted stock solution of 1 g/L. The number of required samples was determined using the one-time factor statistical method. In this study, factors such as contact time, pH, persulfate concentration and nanoparticle dose were investigated and accordingly, the optimal process conditions were obtained. All experiments were repeated three times.

Analysis of MNZ

The concentration MNZ was determined by high performance liquid chromatography (HPLC) equipped with a UV detector at 320 nm. A Diamonsil (R) C18 column (5 µm, 250 mm long×4.6 mm ID) was used, and the mobile phase was composed of a mixture of acetonitrile and water (20/80, v/v). The flow speed was set at 1.0 mL min^{-1}, and 20 µL injections were used.

Results

Size Determination of the Nanoparticles

The morphology and size of the iron nanoparticles synthesized by green method were determined by Scanning Electron Microscope (SEM). After preparing the image and using the software, the average particle size was estimated in the range of 50-100 nm. The SEM image of zero iron nanoparticles is shown in Figure 1. Also, Figure 2 shows a TEM image from synthesized nZVI.

Effect of pH

The effect of pH on STZ removal by nano-persulfate process was studied at different pH values. The results

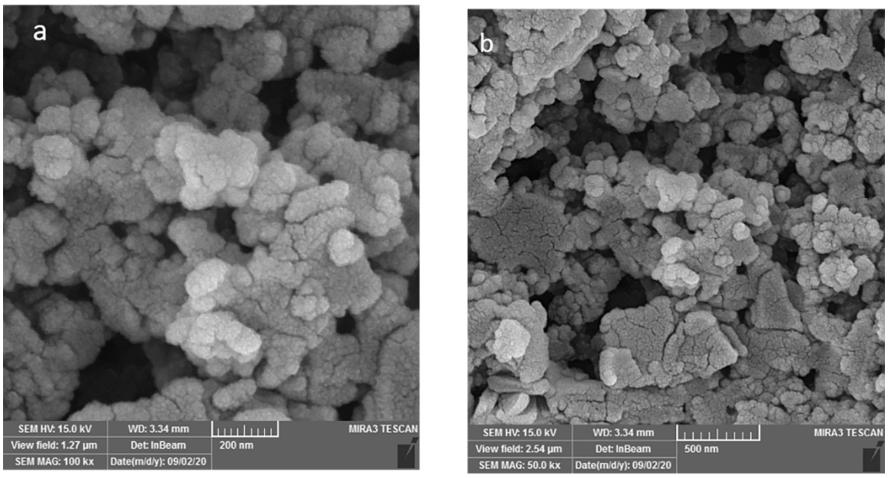


Figure 1: SEM images of nZVI: a) 200 nm and b)500 nm

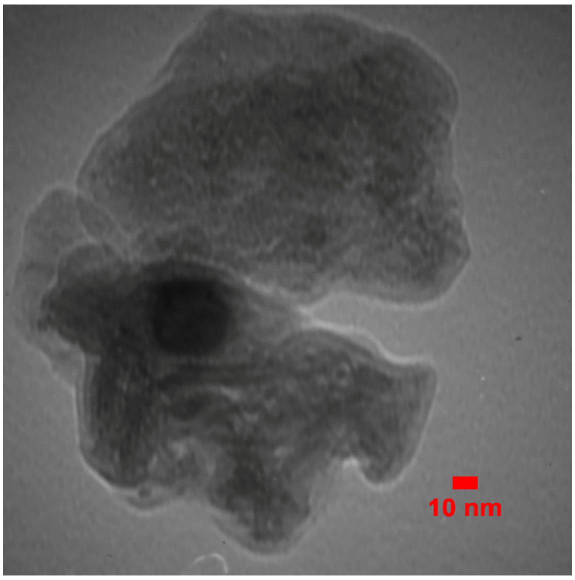


Figure 2: TEM images of synthesized nZVI

are illustrated in Figure 3. The effect of pH on STZ degradation is examined in the pH range 3–10. All the variables such as, nZVI dosage, PS concentration, STZ concentration and contact time were kept constant. The obtained data indicated that as the pH increases, the removal efficiency of MNZ decreases.

Effect of Initial PS Concentration

To investigate the effect of persulfate concentration on the efficiency of PS/nZVI process, 6 concentrations of 0.05, 0.1, 0.3, 0.5, 1, 1.5 and 2 mg/l of persulfate were selected. The results are shown in Figure 4. The results showed that persulfate had a great effect on the PS / nZVI process, so that at a concentration of 0.05 mg/l persulfate, the process could decompose 9.5% of MNZ in 90 minutes, and this efficiency at a concentration of 1.5 dincrease by 98%.

Effect of nZVI Dosage

The effects of nZVI dosage wee studied over the concentration range of 0.05-3 g/L. As shown in Figure 5, with increasing nanoparticle concentration, an increasing trend in removal efficiency was observed, so that at concentrations of 0.05, 0.1, 0.5, 1, 1.5, 1.8, 2, 2.5 and 3 g/L, the removal efficiencies were 4.5, 24.5, 54.1, 73.57, 93.7, 98.4, 99.23, 98.81 and 98.39, respectively. As the dose of NZVI increased, the surface area of the particles and the active sites in the adsorption increased.

Effects of Variations in Initial MNZ Concentration

Eight concentrations of 1, 5, 10, 25, 50, 100, 150 and 200 ppm were used to evaluate the efficiency of the PS/nZVI process at different concentrations of MNZ. As shown in Figure 6, the results showed that with increasing MNZ concentration, its removal efficiency decreased by PS / nZVI process, so that in a period

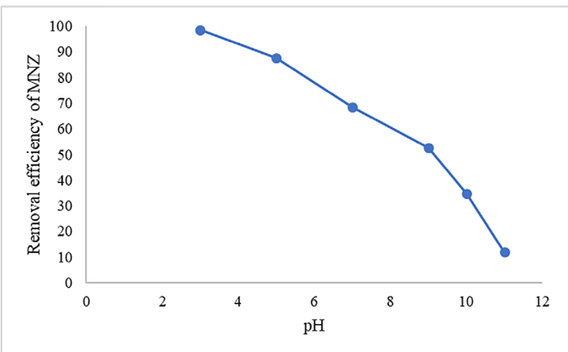


Figure 3: Effect of the pH on the removal of MTZ

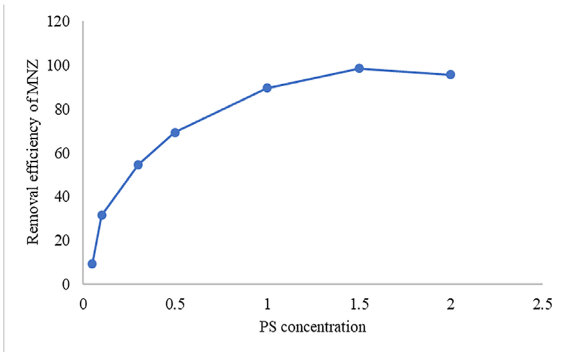


Figure 4: Effects of PS concentration on the removal of MTZ

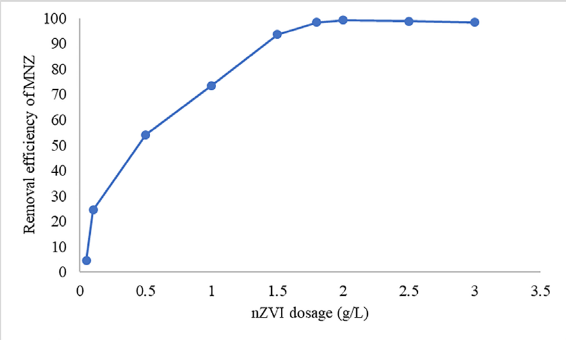


Figure 5: Effect of nZVI concentration on the removal of MTZ

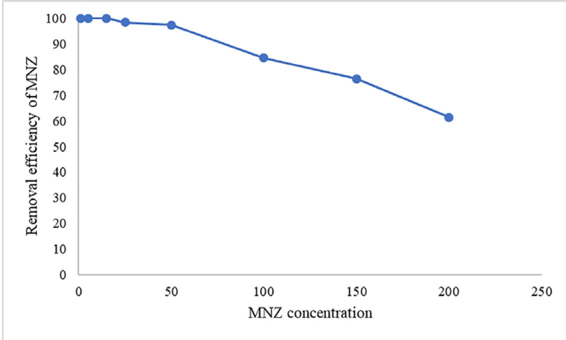


Figure 6: Effect of initial concentration of MTZ on the process

of 30 minutes at PH 3, the dose of 1.5 g/l nZVI and the concentration of persulfate 2 mg/l, up to 25 ppm, complete elimination of MNZ was observed and at a concentration of 200 ppm efficiency reduced 61%.

Discussion

The solution pH is considered as one of the most important factors that affect the removal of contaminants using Fe^0 from water. At low and acidic pH, the amount of iron corrosion accelerates and the amount of hydrogen atoms increases, which is suitable for hydrogenation reaction.[12, 13] At pH 11, the removal efficiency drastically reduced to 11.8%, which is attributed to the discharge of $SO_4^{\bullet -}$ and $^{\bullet}OH$ in reaction with OH^-. Similar results can be seen in other studies.[14] In a study by Huang et al .(2019) for investigating the efficiency of the PS / nZVI process for trichloroethylene degradation in groundwater, low pH had a higher efficiency, so that at pH 4, the removal efficiency was 98% and at pH 10, it was about 77%.[15]

Because persulfate is a radical donor, increasing it in the PS / nZVI process increases the degradation of MNZ. In this study, due to the fact that the removal efficiency at concentrations of 1.5 and 2 mg/l was not observed much, the concentration of 1.5 mg/l was selected as optimal. In the study of Zhang et al. (2020) on the removal of chloramphenicol using PS / NZVI process, the concentration of persulfate in the range of 0.3 to 1.5 mM was selected, which showed that with increasing the concentration of persulfate, the removal efficiency of chloramphenicol increased.[16]

One of the most common methods of activating $S_2O_8^{2-}$ is the use of metal ions, including iron ions due to their cheapness and lack of adverse health effects. The most common metal for activating $S_2O_8^{2-}$ and producing radicals is ferrous sulfate ($FeSO_4$) used in most studies as a source of Fe^{2+} ions and good results have been obtained. A study by Zhang et al. (2020) in the analysis of chloramphenicol using nZVI / PS used a dose range of 0.2-2 g / L. The results of this study showed that after 90 minutes the decomposition rate increased from 71.6 with 0.2 g / l to 98.1% with higher doses of nZVI (PS concentration was kept constant at 1 mM and the initial pH was 7 without PH adjustment during the reaction).[16]

Reaction time, as the time required to achieve the desired goals in a treatment process, is one of the important variables in order to design and manage an oxidation process. High reaction time means high reactor volume and higher construction costs, which is very important. Regarding the PS / nZVI process, it should be noted that this process requires less reaction time. This reduction in the required reaction time is probably due to the production of sulfate radicals due to the presence of zero-valent iron nanoparticles, which increases the strength and rate of decomposition.

Conclusion

The use of oak leaf extract in the synthesis of zero iron nanoparticles is an environmentally friendly and cost-effective method. This method of synthesis of zero iron nanoparticles was investigated in this study and then the properties of nanoparticles were evaluated using electronic images. Also, it examined the ability of these nanoparticles in combination with hydrogen peroxide and ultrasonic waves to degrade the MNZ. The influence of factors such as pH, nanoparticle dosage, persulfate concentration, and antibiotic concentration on this process was studied. This simple, effective and environmentally friendly method can be considered in the decomposition of other environmental pollutants. It is hoped that with this approach we can biosynthesize other suitable catalysts with a higher ability to degrade environmental pollutants.

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Conflict of Interest: No declared.

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