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Degradation of metronidazole in aqueous solution by nano-ZnO/UV photocatalytic process

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ABSTRACT

In this study, the effects of some operational factors, such as pH value, nano-ZnO loading, UV-A irradiation time, and power of radiation on the degradation efficiency of metronidazole (MNZ) in aqueous solution were discussed through photocatalytic experiments using nano-ZnO as the photocatalyst. Results show that removal of metronidazole (MNZ) and COD has a direct correlation with power of UV-A lamp and irradiation time. MNZ solution (80 mg L^{-1}) was rapidly removed by the irradiation of UV lamp OSRAM 125 W high pressure within 180 min. In nano-ZnO/UV photocatalysis reactor, irradiation time and power of UV lamp have a great effect on metronidazole degradation. Statistical analysis (One-way ANOVA) has shown that the pH (in acedic and basic condition) and variation of nano-ZnO concentration has no significant effects on MNZ removal, COD, and BOD_5/COD ratio. But the maximum degradation of MNZ occurred at pH 10 and 1.5 g L^{-1} nano-ZnO. Maximum degradation of MNZ and COD was 96.55 and 95.42%, respectively. In addition, biodegradability improved from ~0 to 0.091 within 180 min.

Keywords: Photocatalysis; Metronidazole; Nano-ZnO/UV

1. Introduction

Pharmaceutical substances and personal care products are an emerging class of aquatic contaminants that have been increasingly detected in ground and surface water [1–7]. These compounds reach waterways mainly through the discharge of wastewaters and effluents. Additional pollution sources are the direct emissions from production sites, improper disposal of surplus drugs in households, medical care, and therapeutic treatment of livestock. Pharmaceuticals are often not completely removed in sewage treatment plants [8] and, therefore, are emitted into receiving water systems. Hence, it is necessary to treat the effluents containing pharmaceuticals adequately before

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discharge or treat drinking water using water treatment plants.

Fig. 1 shows that chemical structure of metronidazole and some physico-chemical properties. MNZ has various effects on human body. For instance, increasing levels of MNZ have been found to be potentially carcinogenic and mutagenic [9]. Aside from being widely used as antibiotics for humans, MNZ is also a used as an additive in poultry and fish feed to eliminate parasites. As a result, MNZ was accumulated in animals, fish farm water, and effluents from meat industries [10]. In order to the removal of antibiotics and other contaminant, there are different treatment techniques, such as conventional techniques (filtration, biological processes, coagulation, flocculation, and sedimentation), advanced oxidation processes, membrane processes, adsorption, and combined methods [11–15]. Study on the removal of antibiotic MNZ by using synthesized NZVI particles showed that NZVI was able to successfully eliminate antibiotic MNZ. According to the results, removal of MNZ by NZVI contain two processes that are degradation process and adsorption [16]. Certain semiconductors, notably zinc oxide (ZnO) and titanium dioxide (TiO_2), when illuminated by photons having an energy level that exceeds their band gap energy excites electrons (e^-) from the valence band to the conduction band and holes (h^+) are produced in the valence band. The photogenerated valence band holes react with either water (H_2O) or hydroxyl ions (OH^-) adsorbed on the catalyst surface to generate hydroxyl radicals (·OH) which are strong oxidants. The photogenerated electrons in the conduction band may react with oxygen to form superoxide ions ($\cdot O^{2-}$). The superoxide ions can then react with water to produce hydrogen peroxide and hydroxyl ions. Cleavage of hydrogen peroxide by conduction band electrons yields further hydroxyl radicals and hydroxyl ions. The hydroxyl ions can then react with the valence band holes to form additional hydroxyl radicals. Degradation of organic substances can be achieved by their reaction with hydroxyl radicals (·OH) or direct attack from the valence band holes. Recombination of the photogenerated electrons and holes may occur and indeed it has been suggested that the presumption of substrate (organic substance) onto the photocatalyst is a prerequisite for highly efficient degradation. Reactions (1–6) show the formation of ·OH by photocatalytic process [17,18].

$$ZnO + hv \rightarrow ZnO(e^- + h^+) \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + \cdot OH \quad (2)$$

$$h^+ + \cdot OH^- \rightarrow OH \quad (3)$$

$$e^- + O_2 \rightarrow \cdot O_2^- \quad (4)$$

$$\cdot O_2^- + H_2O + H^+ \rightarrow H_2O + OH^- \quad (5)$$

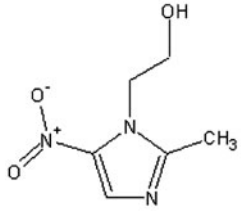
$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \quad (6)$$

The ·OH produced from this photocatalytic process attacks to the metronidazol:

$$\cdot OH + \text{Metronidazol} \rightarrow \text{degradation}$$

Recently, nano catalyst particle has become a promising approach for treating antibiotic from water and wastewater, because of its small particle size, large specific surface area, high density, and greater intrinsic reactivity of reactive surface sites [19].

To date, the removal of MNZ by nano-ZnO has not been explored. This paper aims to: (1) investigate the use of nano-ZnO/UV for MNZ removal and (2) study the influence factors, such as power of radiation of UV lamp, pH, irradiation time, and nano-ZnO dosage, on the MNZ removal; The findings of this study can provide the basis for further engineering applications and could be useful for treating antibiotic in water and wastewater.



Chemical compound	= $C_6H_9N_3O_3$
Molecular Weight	= 171.154
Composition	= C(42.11%) H(5.30%) N(24.55%) O(28.04%)
Molar Refractivity	= 40.98 ± 0.5 cm^3
Molar Volume	= 117.8 ± 7.0 cm^3
Parachor	= 328.6 ± 8.0 cm^3
Index of refraction	= 1.612 ± 0.05
Surface tension	= 60.4 ± 7.0 dyne/cm
Density	= 1.45 ± 0.1 g/cm^3
Dielectric Constant	= Not available
Polarizability	= 16.24 ± 0.5 $10^{-24} cm^3$

Fig. 1. The structure of metronidazole and some properties.

2. Material and methods

2.1. Chemicals

Analytical grade of metronidazole was purchased from Merck company (Germany) to construct high performance liquid chromatography (HPLC) analytical curves for the determination and quantification of the antibiotic (Fig. 2). MNZ (99%, Chemical Reagent) was purchased from commercial sources. The commercial product was purchased from Guangzhou Chemical Factory (Guangdong, China). Potassium dihydrogen phosphate (KH_2PO_4) and acetonitrile (HPLC grade) were purchased from Merck company, Germany. Sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from HACH Company, USA. Nano-ZnO was purchased from Amornano Company, USA. Physical characteristics of nano-ZnO were determined by X-ray diffraction (XRD) instrument (Fig. 3). The antibiotic aqueous solution was prepared by dissolving 80 mg of metronidazole in 1 L distilled water. The aqueous solution characteristics were: MNZ concentration 80 mg L^{-1}, initial COD 126 mg L^{-1}, BOD_5/COD ratio~0. The antibiotic aqueous solution was prepared weekly and stored at 4 °C.

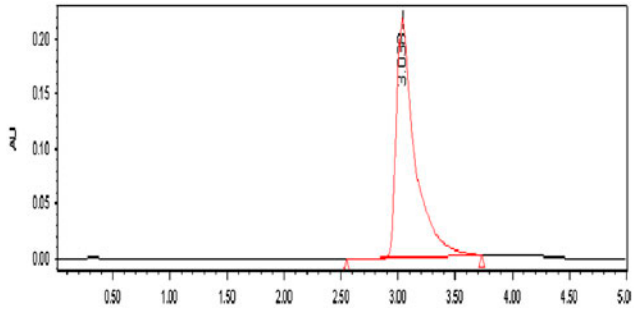


Fig. 2. HPLC of metronidazole.

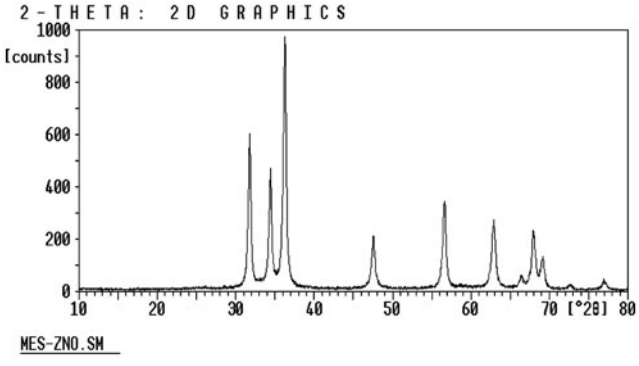


Fig. 3. XRD of nano-ZnO.

2.2. Analytical method

MNZ concentration was determined by high performance liquid chromatography (HPLC, Waters, USA) equipped with a UV detector at 348 nm. A Diamonsil (R) C18 column (5 μm, 250 mm long × 4.6 mm ID) was used. The data were recorded by a chemistation software. The mobile phase was composed of a mixture of acetonitrile and distilled water (30/70, v/v). The flow speed was set at 1.0 mL min^{-1}, and 20 μL injections were used. COD was determined by COD reactor model AR851 (HACH, USA) and biodegradability was measured by five-day biochemical oxygen demand (BOD_5) according to the Standard Methods [20]. A pH meter (Metrohm 827, Swiss) with glass electrode was used for pH measurement.

2.3. Photocatalytic reactor

Photocatalytic processes were preformed in a 3 l steel reactor. The sources of UV light were two UV lamps, one of them Philips 8 W low-pressure and another was Osram 125 W high-pressure mercury lamp (Fig. 4), which were placed in the photocatalytic reactor (Fig. 5).

2.4. Experimental procedure

The synthetic sample with 80 mg L^{-1} simulated wastewater was placed in the reactor with required amount of nano-ZnO and mixed by a mixer. The pH was adjusted to the required value by 1 N H_2SO_4 or 1 N NaOH, and the mixture was kept in the dark for 30 min for adsorption. Thereafter, the mixture was subjected to UV irradiation. Samples were taken at pre-selected time intervals using a syringe and filtered

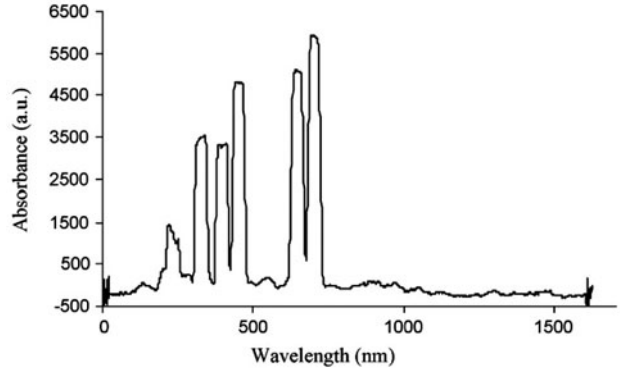


Fig. 4. The spectrum of the UV source that provided by 125 W lamp.

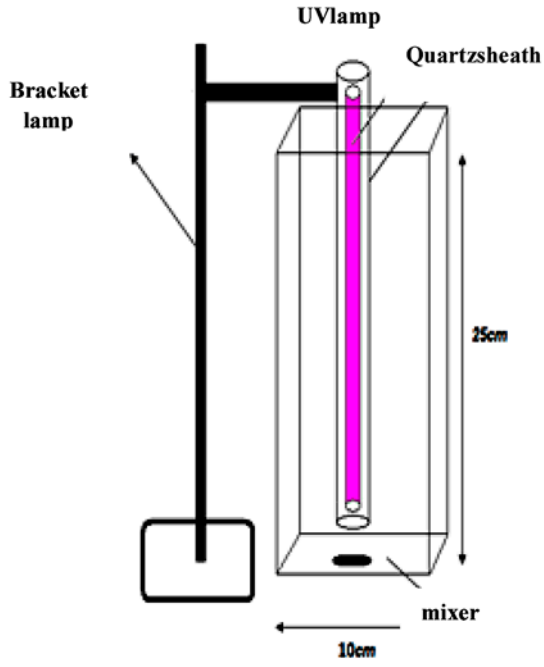


Fig. 5. Schematic of photocatalytic reactor.

through 0.45 μm membrane filter for COD, BOD_5 determination, and through 0.20 μm membrane filteration for the determination of antibiotic concentration by HPLC. All the experiments were carried out in room temperature.

2.5. Statistical desgin

In this study, we have 72 samples and 12 witnesses. All experiments were duplicated. After determining residual metronidazole, COD, and BOD_5, regression analysis is performed. Regression analysis is a statistical technique used to investigate and model the relationship between a variable response and one or more independent variables. Each explanatory variable (factor) consists of two or more categories (levels). Study type in this study was factorial and initial design was full factorial, the objectives of this method are:

(1) Identify the important statistical analysis variables.
(2) Statistically analyze a data-set.
(3) Explain the proper steps in developing a full factorial design of experiment.
(4) Design a full factorial experiment.
(5) Evaluate the results of experimental data.
(6) Organize technical information into a clear and concise formal laboratory report.

3. Results and discussion

3.1. The effect of radiation power of UV lamps and irradiation time

The experimental conditions were, initial metronidazole concentration 80 mg L^{-1}, and initial COD 126 mg L^{-1}, BOD_5/COD ~0. By 3-h UV irradiation, results has shown that the removal efficiency of MNZ and COD with radiation UV lamp 125 W were 96.55, 95.42% and with 8 W were 27.83, 27.7%, respectively (Figs. 6 and 7), optimum condition occurred with UV lamp 125 W at 180 min. Photodegradation efficiency (50%) of ciprofloxacin by UV/ZnO nanoparticles was observed at pH 10 after 60 min [18] that compared with this is very low. Based on (Table 1), time and power of UV lamp have a significant effect on MNZ removal. These results include the effect of antibiotics hydrolysis. The hydrolysis reaction would proceed through the attack of the nucleophile H_2O to the ring, followed by ring opening [21]. These results also include the effect of antibiotics hydrolysis. These results agree well with previous studies on degradation of basic dye decomposition [21], degradation amoxicillin, and cloxacilin Antibiotics [22].

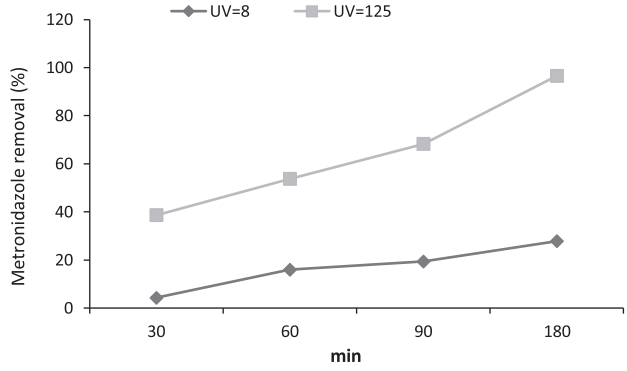


Fig. 6. Removal efficiency of MNZ with radiation intencity 8, 125 W in nano-ZnO/UV process.

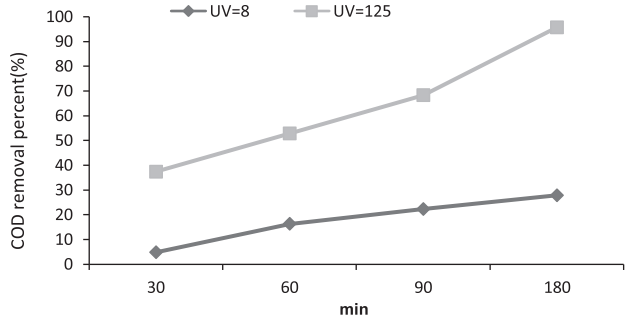


Fig. 7. Removal efficiency of COD with radiation power 8, 125 W in nano-ZnO/UV process.

Table 1
One-way MNZ degradation at different pH, time ZnO concentration, and radiation intensity

Parameter	Antibiotics	No. of groups	*P*-value	*F*
Nano-ZnO	MNZ	3	0.1873	1.76
pH	MNZ	3	0.1315	2.3
Time	MNZ	4	<0.0001	256.84
Power of UV	MNZ	2	<0.0001	475.26

Significant improvement in biodegradability was observed and maximum BOD_5/COD ratio in optimum condition was 0.091.

3.2. Effect of nano-ZnO concentration

To observe the effect of nano-ZnO concentration, initial nano-ZnO concentration was varied in the range 0.5–3 g L^{-1}. The experimental conditions were metronidazole concentration 80 mg L^{-1}, with initial COD 126 mg L^{-1}, pH 10, by 3-h UV irradiation. Figs. 8 and 9 show the degradation of MNZ and COD. Results show that degradation of MNZ was 95.90, 96.55, and 85.62% and COD was 95.63, 96.42%, and 86.9% in 0.5, 1.5, and 3 g L^{-1} nano-ZnO, respectively. It has been due to the increase of OH production. A statistical analysis (one-way ANOVA) performed on the results at a 5% level of significance indicated that MNZ degradation was not significantly affected by nano-ZnO concentration (Table 1). No significant improvement in biodegradability was observed and BOD_5/COD ratios were 0.089, 0.091, and 0.09, respectively in 0.5, 1.5, and 3 g L^{-1} nano-ZnO. Low biodegradability may be due to the toxicity of antibiotic degradation products.

3.3. Effect of pH

To study the effect of pH on the degradation of Metronidazole, experiments were conducted by varying the pH in the range 3–10. The experimental conditions were metronidazole concentration 80 mg L^{-1}, with initial COD 126 mg L^{-1}, by 3-h UV irradiation. The results show (Figs. 10 and 11) degradation in 300-min irradiation with UV lamp 125 W in pH 3, 7, and 10. The degradation of MNZ in pH 3, 7, and 10 was 95.21, 65.78, and 96.55%, respectively. And the maximum BOD_5/COD ratio was 0.083, 0.091 at pH 3 and 10. Statistical analysis has shown that pH has no significant effect between acidic and basic condition on MNZ and COD removal and the BOD_5/COD ratio. In the study of the effect of pH on

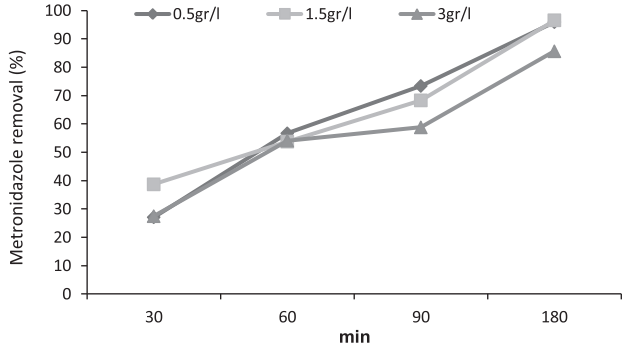


Fig. 8. Effects of variations in nano-ZnO concentration on the removal of MNZ.

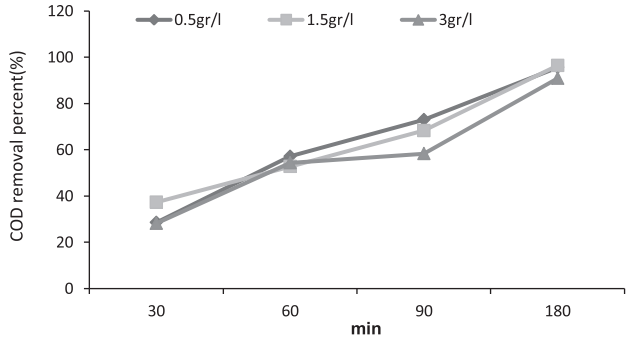


Fig. 9. Effects of variations in nano-ZnO concentration on the removal of MNZ in term of COD.

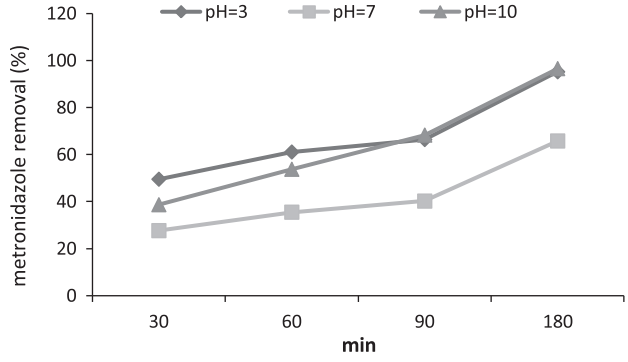


Fig. 10. Effect of pH variation on MNZ removal.

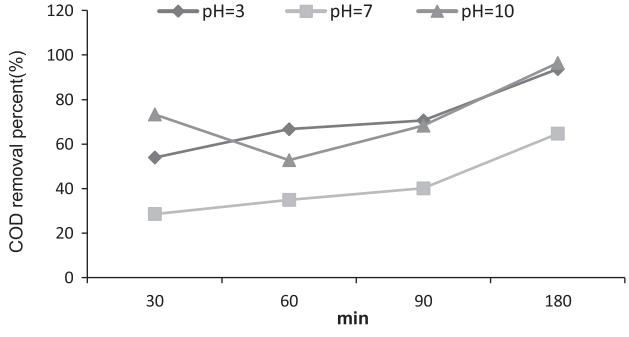


Fig. 11. Effect of pH variation COD removal.

photodegradation of nitroimidazoles showed no significant effect of removal as a function of the solution pH [23]. But in another study of photocatalytic degradation of ciprofloxacin by ZnO nanoparticles, the results showed that the photocatalytic degradation process is effective at pH 7 and 10, but it is rather slow at pH 4 [18].

4. Mathematical model

A mathematical model for predicting the elimination of metronidazole according to selected factors and levels was studied, so that if y is the removal of metronidazole and X, variables to be studied (pH, time, concentration of nano-ZnO, power of UV lamp) and b are constant (17.5975). So, between the values of variable scan be set at any level.

$$Y = a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + b \quad (7)$$

a_1 = for radiation intensity (+0.281); a_2 = for nano ZnO concentration (+1.428); a_3 = for pH (−1.4009); a_4: for irradiation time (+0.1174).

5. Conclusions

In nano-ZnO/UV photocatalysis, irradiation time and power of UV lamp have a great effect on metronidazole degradation. Removal of metronidazole has a direct correlation with UV-A power irradiation time. Removal efficiency of metronidazol in this process increases linearly with increasing the UV light intensity. The maximum degradation of MNZ occurred at pH 10 and 1.5 g L^{-1} nano-ZnO. Maximum degradation of MNZ and COD was 96.55 and 95.42%, respectively. In addition, biodegradability improved from ∼0 to 0.091 within 180 min. High oxidation efficiency, low cost in comparison with other advanced oxidation processes, easy handling, and application in full scale are some advantages of the photocatalytic process.

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