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Tinidazole Removal from Aqueous Solution by Sonolysis in the Presence of Hydrogen Peroxide

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Abstract Aqueous solutions of the tinidazole (TNZ) have been treated by applying the combination of ultrasound irradiation and H_2O_2. Based on the results, the maximum removal efficiency of 75 % was achieved under the optimum operating conditions (pH 3, 120 kHz frequency, 333 mM/L of H_2O_2 and 150 min of operating time) while, under the same conditions the minimum removal efficiency was found to be 8.5 by ultrasound radiation in the absence of H_2O_2. The results also revealed that the degradation of TNZ was enhanced with decreasing both TNZ initial concentrations and pH. Furthermore, TNZ removal efficiency in the case of actual wastewater was less than of synthetic wastewater (75 % and 68 % of synthetic and actual, respectively). According to the chromatographic analyses, no harmful intermediate compounds were observed. The chemical oxygen demand analysis (65 % reduction) confirmed our findings.

Keywords Tinidazole · Sonolysis process · Hydrogen peroxide

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Pharmaceuticals including antibiotics have been detected in water bodies (Kolpin et al. 2002; Anderson et al. 2004; Rabiet et al. 2006), municipal and industrial effluents (Carballa et al. 2004; Nikolaou et al. 2007; Hua et al. 2006; Fatta et al. 2007) and even in drinking water (Stackelberg et al. 2004). Pharmaceutical industry, hospital and health-care services' effluents and excretion from humans and livestock can be the major sources of these compounds (Nikolaou et al. 2007; Ikehata et al. 2006; Yang et al. 2008). Antibiotics are one of the most important pharmaceutical compounds which play essential role in the environmental pollution even at low concentration. The therapeutic use of antibiotics for human and veterinary diseases results in 90 % of them being excreted through urine and feces into wastewater and eventually in the terrestrial and aquatic environments (Seifrtová et al. 2009; Balciogglu and OOtker 2003; Yang et al.2008; Kummerer 2009; Heberer 2002; Fent et al. 2006). The presence of antibiotics in natural systems may contribute to the development of multi-resistant strains of bacteria (Elmolla and Chaudhuri 2010; Valverde et al. 2006; Balciogglu and OOtker 2003).

Nitroimidazoles, such as metronidazole and tinidazole (TNZ) are microbicidal drugs that affect anaerobic bacteria and protozoa (Chintana et al. 1986; Gordts et al. 1985). Small amounts of nitroimidazoles have been found in wastewater or the wastewater from treatment of plants effluents (Khan and Ongerth 2004). However, the concentration of these

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compounds in hospital effluent has been reported to be more than 90.2 mg/L (Lindberg et al. 2005). According to batch scale studies, nitroimidazoles seem not to be readily biodegradable, therefore, they are not expected to be effectively removed during the conventional wastewater treatment (Le-Minh et al. 2010; Rivera-Utrilla et al. 2010; Lin et al. 2009; Vieno et al. 2006; Sharma 2008). Cha et al. 2006, have also recorded the presence of different types of industrial medicine in the conventionally treated effluents.

Hence, it is necessary to use innovative technologies to treat effluents containing antibiotics adequately before discharging them into water bodies. Some chemical methods have appropriate efficiency but they end up with some undesirable by-products (Homem and Santos 2011). Thus, the methods with high removal efficiency and less environmental threats are preferred.

The advanced oxidation processes (AOPs) may be interesting methods in comparison with other techniques such as activated carbon adsorption (Elmolla and Chaudhuri 2010; Mahvi 2009; Bazrafshan et al. 2007). Pharmaceutical compounds can be removed effectively by these processes (Klavarioti et al. 2009; Wu et al. 2001; Somensi et al. 2012). AOP technologies, which are based on the intermediary of hydroxyl and other radicals, are applied to oxidize recalcitrant, toxic and non-biodegradable compounds to various by-products and eventually to inert end products (Mahvi et al. 2007; Klavarioti et al. 2009; Moussavi et al. 2012). With regard to ultrasound radiation and hydroxyl radicals, it is an eco-friendly way (Klavarioti et al. 2009; Hartmann et al. 2008; Ku et al. 2005).

In the current study, the sonolysis process in the presence of H_2O_2 was applied to remove TNZ. Also, the effects of various influential parameters such as amounts of H_2O_2, initial pH, sonication frequencies, initial concentration of TNZ and operating time on TNZ removal were examined.

Materials and Methods

In general, this study was carried out through three major steps: 1 – starting up the batch experiments using the synthetic TNZ aqueous solution 2 – determination of the optimum conditions by changing the variables 3 – testing the feasibility of the method with actual wastewater under the optimum conditions.

The Analytical grade of TNZ was supplied by Sigma-Aldrich in order to construct HPLC analytical curves for the determination and quantification of the selected antibiotic. To prepare the TNZ aqueous solution, the commercial source was used without any further purification. The chemical structure and the characteristics of the compound are displayed in Table 1. The Stock solution of

Table 1 General characteristics of TNZ (Rivera-Utrilla et al. 2010)

Parameter	Value
Molecular formula	$C_8H_{13}N_3O_4S$
Molecular weight (g/mol)	247.27
Log Da (pH 2)	−0.74
λ_{max}	310 (nm)
Surface area (A^2)	276
Volume (A^3)	258
Solubility, S (mol/L)	0.008
pK_{a1}	2.30

Log D = distribution coefficient

Table 2 The characteristic of the selected pharmaceutical industry's effluent

Parameter	Value
Total COD	1,450
Soluble COD	1,244
pH	6.9
TSS	132
VSS	98

TNZ was prepared in methanol, of which the concentrations of 45, 80 and 100 ppm were made (hereafter, they are called "secondary standards"). Chemical oxygen demand (COD) was determined according to "Standard Methods" (APHA 2012).

Hydrogen peroxide (30 % w/w) was purchased from Merck Company. The pH was measured by a pH meter (HACH Session 4) with a pH electrode (HACH platinum series pH electrode model 51910, HACH Company, USA), adjusted with HCl (0.1 N) or NaOH (0.1 N) solutions.

Batch experiments were performed in a 400 mL Pyrex reactor filled with 100 mL of the antibiotic aqueous solution. The required amount of H_2O_2 was added to the aqueous solution. Then, the reactor was placed into the ultrasonic bath (Elmasonics 80H-Germany) generating supersonic waves at 750 W input powers.

The variables were optimized using "one factor at the time" experimental design. To determine the optimum conditions, the system was operated under varying parameters, which are as follows: time (0–160 min), pH (3, 5, 7, 9), concentration of H_2O_2 (83, 167, 250, 333 and 417 mM/L), frequency (40, 80, 120 and 160 kHz) and initial concentration of TNZ (45, 80 and 100 ppm). Depending upon the studies carried out on the actual antibiotic formulation wastewaters, initial COD values of the synthetic wastewaters were chosen in the range of 250–1,500 mg L.

The actual pharmaceutical wastewater containing TNZ underwent a number of experiments at the obtained

optimum conditions. The wastewater sample was collected from one of the pharmaceutical industries in Tehran, Iran. The corresponding effluent characterizations has been summarized in Table 2.

The samples were taken from the reactor at regular time intervals. Prior to all experiments, effluent suspensions were filtered through a 1.2 μm fiber glass filter for COD, BOD and DOC measurement. The concentration of antibiotic TNZ was measured with a HPLC (Shimadzu, LC10A HPLC, equipped with a detector UV SPD-10AV in 310 nm). Calibration standards (1, 5, 10, 20, 50 and 100 mg/L) were then prepared by adding specific quantities of the secondary standards to 30 mL of internal standard and milli-Q water in a 1 mL glass chromatography vial, whose content was filtered through a 0.20 μm PTFE syringe before the final injection.

All experiments were conducted in accordance with the standard methods for the examination of water and wastewater (APHA 2012).

The TNZ removal efficiency was calculated by Eq. (1) (Godini et al. 2012; Rahmani et al. 2013).

$$\text{Removal efficiency } (\%) = ((C_o - C_t)/ C_i) \times 100 \qquad (1)$$

where C_o and C_t are the concentrations of the TNZ in feed and in the sonochemical treated solution at a given time t, respectively.

Results and Discussion

The effect of H_2O_2 initial concentrations on the TNZ removal has been shown in Fig. 1. Two mechanisms play the major role in these results: (1) pyrolysis of TNZ in cavitation bubbles, (2) TNZ decomposition through hydroxyl radical (Ku et al. 2005; Naddeo et al. 2007; Hartmann et al. 2008). Without adding H_2O_2, the efficiency was low and just 8.5 % of TNZ was removed in 150 min. However, by sonolysis at the presence of different concentrations of H_2O_2 at the following condition (pH 3, 120 kHz of frequency, and 80 ppm of TNZ), decomposition rate was increased so that the maximum decomposition of TNZ (75 %) and COD (65 %) were obtained at 333 mM/L of H_2O_2 and the operating time of 150 min, which could be due to the formation of hydroxyl radicals in aqueous solution. However, higher concentration of H_2O_2 (over 333 mM/L) could lead to a decrease in TNZ removal, as confirmed by the other studies (Ku et al. 2005; Zhou et al. 2012).

It should be noted that the ultrasound waves improve agitation and also play a significant role in increasing the reaction rate, which could be due to the enhancement of the contact area between the hydroxyl radicals and the pollutants.

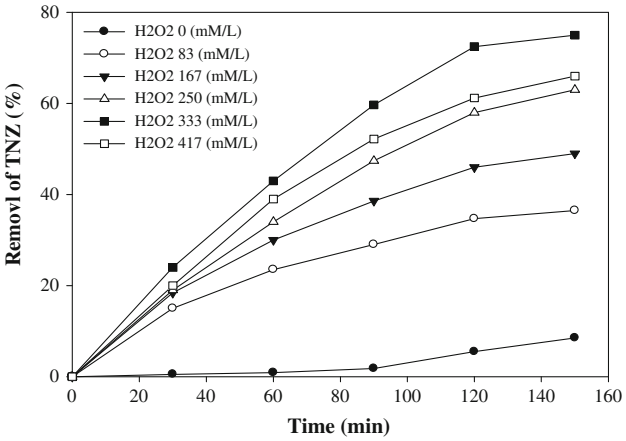

Fig. 1 Influence of H_2O_2 concentration on the decomposition of TNZ (pH 3; frequency = 120 kHz, TNZ concentration = 80 ppm and T = 25°C)

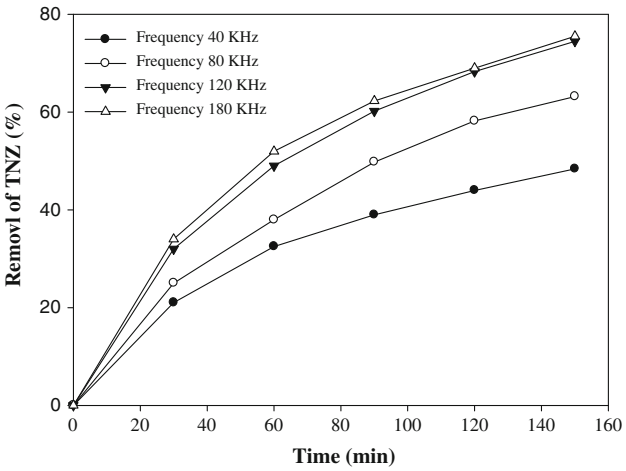

Fig. 2 Influence of the frequency on decomposition of TNZ (pH 3; H_2O_2 concentration = 333 mM/L, TNZ concentration = 80 ppm and T = 25°C)

The effect of frequency on TNZ removal efficiency was demonstrated in Fig. 2. Obviously, the application of the frequencies over than 120 kHz does not have a noticeable effect on TNZ removal and it only increases the applied energy of the system. By increasing the frequency, the number of acoustic cycles and bubble collapses increase (Mason et al. 2011). The resulting bubbles release less energy than the low-frequency ones for one single pulsation. Thus, applying higher frequency may compensate for the lower energy released in the single bubble explosion. Petrier et al. (1998) demonstrated that the hydroxyl free radical formation increased when the high sanction frequency was applied; while, the low frequencies associated with strong shock waves, favor the mechanic effects. The most effective frequency was found to be 120 kHz at the presence of the 333 mM/L of H_2O_2.

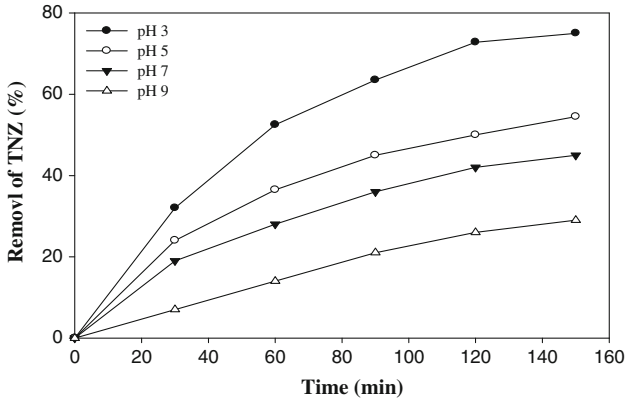

Fig. 3 Effect of pH on decomposition of TNZ (Frequency = 130 kHz, H_2O_2 concentration = 333 mM/L, TNZ concentration = 80 ppm and T = 25°C)

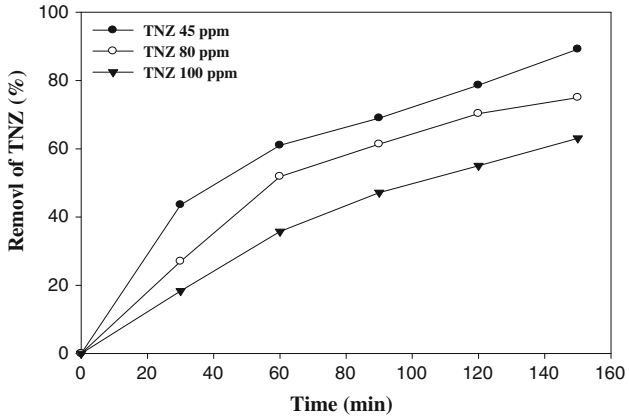

Fig. 4 The impact of initial concentration of TNZ on the decomposition rate (Frequency = 120 kHz, H_2O_2 concentration = 333 mM/L, pH 3 and T = 25°C)

Ultrasound waves, as a method of mechanical degradation of complex compounds, enhance the efficiency and reduce the reaction time. Studies have shown that organic compound degradation happens continually due to the establishment of numerous microscopic bubbles called cavities made by ultrasonic waves. The destruction of these cavities leads to the creation of potent free radicals (Ku et al. 2005; Hartmann et al. 2008; Naddeo et al. 2007). Thus, organic materials are degraded first by the paralysis mechanism followed by the powerful free radicals. These radicals are more effective than paralysis (Ku et al. 2005).

Chemical oxidation of compounds, particularly in the ultrasonic process heavily depends on the pH of the solution. (Maleki et al. 2005).

The effect of pH on TNZ removal efficiency has been shown in Fig. 3. A notable pH effect was observed in the sonochemical process (74.4 % removal efficiency at pH 3). By Contrast, low TNZ removal efficiencies were observed at pH 5, 7 and 9. Depending on pH, the stream of the bubbles stemmed from the cavitation might be in forms of OH· and/or H· (Naddeo et al. 2007). For instance; at pH $\geq$ 3, the oxidation potential of hydroxyl radical and subsequently, the decomposition rate decrease; While, at alkaline pH (high pH values), H_2O_2 tends to react with hydroxyl radicals leading to the formation of hydroperoxyl radicals (HO_2·) having the weak oxidizing ability (Molina et al. 2006). These radicals react with extra hydroxyl radicals and decrease the TNZ removal efficiency. And finally, at pH 1–2, due to H ions scavenging, the inhibition of the hydroxyl radical formation is most likely to happen (Lucas and Peres 2006).

Removal efficiency was found to be dependent on the initial concentration of TNZ (Fig. 4). At constant H_2O_2 concentration level, an increase in the amounts of pollution leads to more consumption of the existed radicals, subsequently, it gives rise to the removal efficiency (Fan et al. 2009; Zhang et al. 2005, Shu and Chang 2005).

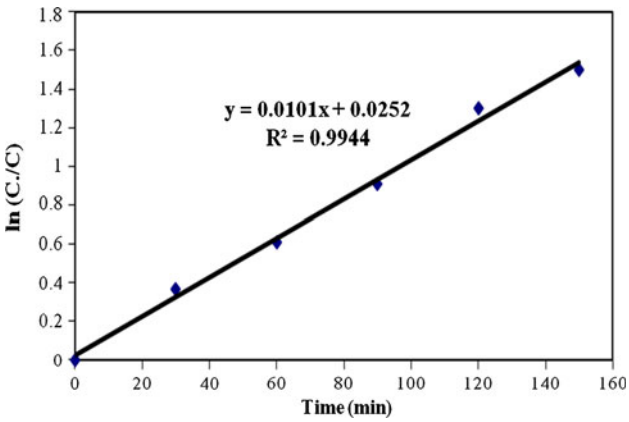

Fig. 5 First order kinetic studies of TNZ removal (frequency = 120 kHz, H_2O_2 concentration = 333 mM/L, TNZ concentration = 100 ppm, pH 3 and T = 25°C)

The kinetic study of TNZ removal by H_2O_2-US process, could be fitted to the first order kinetic equation with the correlation coefficient of 0.99 (Fig. 5).

To evaluate the effect of ultrasonic/H_2O_2 treatment on the real wastewater containing TNZ, a series of experiments were performed under the optimum conditions (concentration of TNZ, 80 ppm; pH, 3; the concentration of hydrogen peroxide, 333 mM/L; frequency 120 kHz at 25°C). The preliminary experiments indicated that better degradation was achieved in the case of the synthetic wastewater (75 % in synthetic and 68 % in actual) (Fig. 6).

In the pharmaceutical industry, the production of different drugs in a short time interval causes variations in the pollutant loading and in the composition of wastewater. Therefore, the produced hydroxyl radicals are consumed by these impurities.

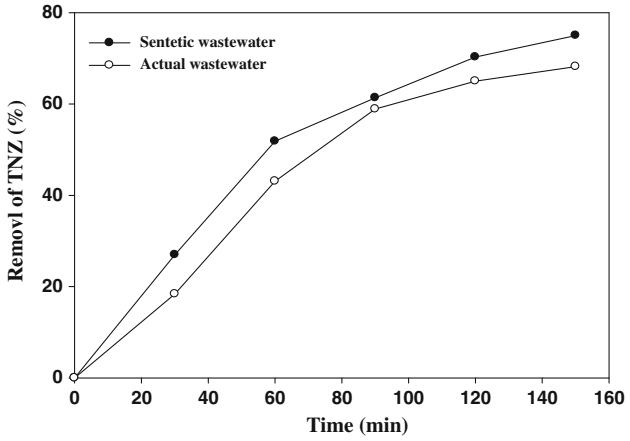

Fig. 6 The actual wastewater versus the synthetic wastewater, regarding TNZ removal by US-H_2O_2

Finally, The GC–MS study was employed to evaluate the residual products formed after the tinidazole degradation by ultrasonic/H_2O_2 process. According to the obtained results, there was a significant reduction of the selected antibiotic – almost free of hazardous intermediate(s). On the other hand, the COD analysis (70 % COD removal efficiency) can also confirm the above-mentioned finding.

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