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Original Article

Treatment of wastewater contaminated with sulfamethoxazole drug using advanced oxidation processes

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ABSTRACT

Advanced oxidation processes constitute a promising technology for the treatment of wastewater containing non-easily removable organic compounds. In this research, Fenton oxidation process was offered as an effective method for removal of antibiotic sulfamethoxazole (SMX) from aqueous solutions. The effects of initial antibiotic concentration, the molar ratio of H_2O_2/Fe^{+2}, pH, concentration of H_2O_2, Fe^{+2}, and reaction time were studied on the oxidation of SMX in three levels. The optimal condition was determined with $H_2O_2 = 5.25 \times 10^{-3}$ M, $Fe^{+2} = 1 \times 10^{-3}$ M, pH = 3, molar ratio $(H_2O_2)/(Fe^{+2}) = 5.2$, and for SMX = 9.869×10^{-4} M (250 mg/L), 100% degradation efficiency of SMX in aqueous solution was achieved after 60 min of reaction. The concentration of SMX in aqueous solution during Fenton processes was measured using high-performance liquid chromatography studied. The experimental results showed that Fenton oxidation process was an effective process for the degradation of SMX.

Keywords: Advanced oxidation processes, antibiotic, Fenton's reagent, sulfamethoxazole

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INTRODUCTION

Pharmaceuticals (antibiotics) are a group of emerging organic compounds of environmental concern used extensively in human and veterinary medicine. The presence of antibiotics in the environment may cause potential risk for the aquatic environment and organisms. These compounds enter directly into the municipal sewage systems and wastewater treatment plants (WWTPs). A large number of important and potentially harmful organic contaminants, such as pharmaceuticals, are not regulated in drinking and other waters. Pharmaceuticals can be divided into numerous therapeutic classes such as antibiotics, analgesics, anti-inflammatory drugs, antiepileptics, beta-blocking, antidepression drugs, natural and synthetic hormones, and lipid regulators.[1] Antibiotic sulfamethoxazole (SMX) is one of the most frequent sulfonamides in municipal wastewater [Scheme 1].[2] This compound is persistent against conventional and biological treatments and its removal efficiency in WWTPs is moderately low.[3] Oxidation of organic compounds with ozone or OH radicals was more easily biodegradable process, which found to be an important to chlorination because the oxidation does not produce toxic chlorinated organic compounds.[4] Advanced oxidation technologies including oxidation process and other physiochemical conversion methods.[5] Advanced oxidation processes (AOPs) are oxidative methods based on the generation of intermediate radicals, mainly hydroxyl radicals (HO*), that have been successfully applied in wastewater treatment to degrade many organic compounds.[6] The application of either oxidation technologies using ultraviolet (UV)/O_3, O_3/H_2O_2, UV/H_2O_2, or the photo-Fenton reaction (UV/H_2O_2/Fe^{+2} or Fe^{+3}).[5] The AOPs using hydrogen peroxide are based on hydroxyl radicals attacking organic compounds in wastewater. The hydroxyl radical has an oxidation potential of 2.80 V, short-lived, and extremely strong oxidizing agent.[7] In this research, Fenton oxidation process was offered as an effective method for removal of antibiotic (SMX) from aqueous solutions.

MATERIALS AND METHODS

Reagents

All solutions were prepared using distilled water, H_2O_2 (30% w/w), and $FeSO_4.7H_2O$ (Fischer Scientific), H_2SO_4 and NaOH from BHD were used as received. The

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antibiotic SMX [4-amino-N-(5-methylisoxazol-3-yl)-benzene sulfonamide, $C_{10}H_{11}N_3O_3S$] was obtained from SDI, high-performance liquid chromatography (HPLC) mobile phase acetonitrile, and acetic acid from BHD.

Chemical Analysis

The concentration of antibiotic SMX in aqueous solution was analyzed by HPLC at a maximum absorption wavelength of 272 nm, with a YL 9100 Instrument Co. Ltd., HPLC with a UV detector and column ODS-3, 10 µm and the elution was carried out using gradient mode. Mobile phases were 50% acetonitrile and 50% acetic acid (0.5%) (v/v). Antibiotic was detected using UV absorbance at 272 nm.[8] pH was adjusted by pH m WTW, inoLab® pH 720/7200, Germany. The experiments were performed on laboratory scale in 250 ml glass reactor under complete mixing at 25 ± 2°C. The reaction solution was prepared by concentration of antibiotic SMX (250 ppm) and subjected to Fenton treatment. Degradation of antibiotic during Fenton oxidation was considered under experimental conditions include pH (3, 4, 5, 6 and 7), molar ratio of (H_2O_2)/(Fe^{+2}) (0.3–5.25), H_2O_2 ($3-10^{-4}$ M up to 5.25×10^{-3} M), Fe^{+2} (1×10^{-5} up to 1×10^{-3} M), and reaction time (1, 3, 5, 8, 10, 15, 30, and 60) min. To initiate experiments, the samples were withdrawn at the reaction times and analyzed by HPLC.[8]

Experimental Procedure

All experiments were performed in an open batch glass system with a stirring bar; 250 ml of SMX sample in 500 ml conical flasks with initial SMX concentration 250 mg/l (9.869×10^{4} M) was used. The initial pH of the reaction solutions was adjusted with NaOH (0.1 M) or (0.1 M) H_2SO_4 solution for Fenton's treatment. The required amount of $FeSO_4.7H_2O$ (0.00001–0.001 M) and H_2O_2 (3×10^{-4} M–5.25×10^{-3} M) was added, mixed by stirring continuously and kept at a required temperature for different reaction time. After each reaction time, the samples were allowed to stand for 30 min. The pH of the mixture was adjusted at 8.0 to precipitate Fe^{+3} and Fe^{+2} compounds, then filtered for analysis by HPLC before and after treatment.

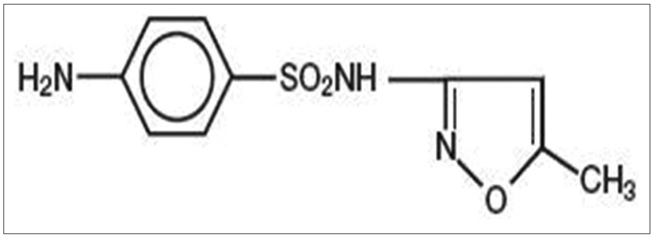
RESULTS AND DISCUSSION

The standard curve of SMX concentrations (50, 100, 250, 500, 750, and 1000 mg/L) measured by HPLC instrument response (absorbance at $\lambda_{max} = 272$ nm) was done, as shown in Figure 1.

AOPs

AOPs rely on the generation of radicals such as hydroxyl radicals, which are very reactive with many organic and inorganic compounds. These radicals are very efficient in degradation process of the contaminant. The general process for AOPs was happening in the following order: [9,10]

1. Hydroxyl radicals react with organic compounds either by hydrogen removal, double bond addition, or electron transfer, ultimately leading to the formation of organic radicals.
2. The organic radicals react with dissolved oxygen to form peroxyl radicals or peroxide radicals which undergo rapid decomposition.
3. The goal of the overall process results in the partial or total mineralization of organic pollutants.



Scheme 1: Structural formula of sulfamethoxazole

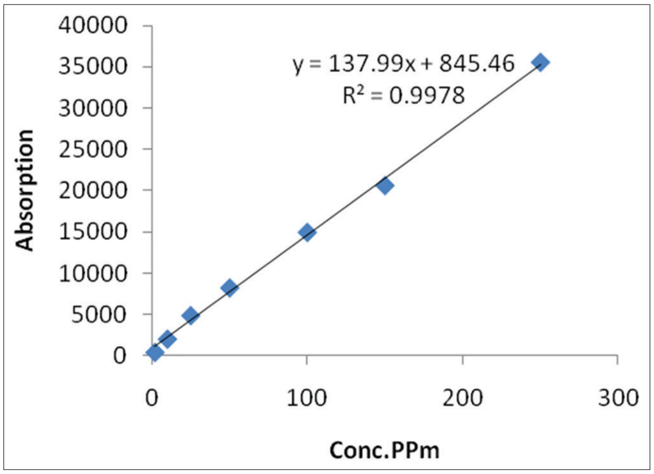


Figure 1: Standard curve for sulfamethoxazole concentration

All AOPs are designed to produce hydroxyl radicals, which act as high efficiency to destroy organic compounds.

Fenton Oxidation

Fenton's reagent, demonstrated that a mixture of H_2O_2 and Fe^{+2} in acidic medium, has been proposed as a very effective oxidizing agent for organic compounds.[11] Mechanism of Fenton process proposes that HO* is formed according to the reaction (1), then the catalyst Fe^{2+} was regenerated through reaction (2).[12]

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^* + HO- \qquad (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2^* \qquad (2)$$

Hydroxyl free radical can oxidize organic compounds (RH or R) by hydrogen abstraction (R*) or by hydroxyl addition (*ROH). The highly reactive molecules (R* and *ROH) can be oxidized, then the highly reactive molecules (R* and *ROH) oxidized, as shown in reactions (3) and (4).

$$RH+HO^* \rightarrow H_2O+R^* \rightarrow \text{Further oxidation} \quad (3)$$

$$R+HO^* \rightarrow {}^*ROH \rightarrow \text{Further oxidation} \quad (4)$$

Effect of H_2O_2 Concentration

Hydrogen peroxide is a determining factor in Fenton oxidation of wastewater. Excessive H_2O_2 consumes hydroxyl radicals without the degradation of the target organic matter. As a result, the oxidation efficiency of pollutant by the Fenton process would be reduced.[13] Result of wastewater degradation was 5.2, which calculated by the molar ratio of H_2O_2/Fe^{2+} through constant Fe^{2+} at 1×10^{-3} M and variable value of H_2O_2.

Degradation of wastewater was increased after Fenton oxidation with raising the concentration of H_2O_2 (3×10^{-4} M) up to 5.25×10^{-3} M for 60 min due to the higher yield of hydroxyl radical. Therefore, H_2O_2 (5.25×10^{-3} M) was chosen as the optimal concentration to use in the next experiments and evaluate the effects of Fe^{2+} concentration on the SMX wastewater degradation [Figure 2].

Effect of Fe^{2+} Concentration

Fe^{2+} concentration is an important parameter in Fenton's reactions because it directly influences the yield of hydroxyl radical ($^\bullet$OH) by catalytic decomposing of H_2O_2 as shown in reaction (1), also acts as scavengers of ($^\bullet$OH) radicals if it was overdosed.[14] Therefore, the influence of Fe^{2+} concentration on the SMX wastewater degradation was evaluated by fixing the initial H_2O_2 concentration at 5.25×10^{-3} M and pH 3. Results showed that wastewater was not degraded with the absence of Fe^{2+} and the presence of H_2O_2 (5.25×10^{-3} M), which demonstrated the important role of the Fe^{2+} in the Fenton process. However, when concentration of H_2O_2 was constant at 5.25×10^{-3} M, the wastewater degradation was increasing with the raising of Fe^{2+} concentration from 1×10^{-6} to 1×10^{-3} M. Reducing of degradation with concentration than (5×10^{-5} M) may be attributed to low concentration of Fe^{2+} and produced low amount of hydroxyl radical in solution. Therefore, (1×10^{-3} M) was chosen as the optimum concentration of Fe^{2+} as shown in [Figure 3].

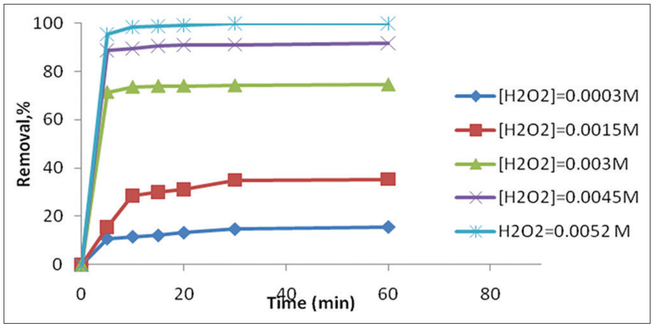


Figure 2: Effect of variable value of H_2O_2 dosages, experimental condition (pH=3, sulfamethoxazole=250 mg/L [0.986×10^{-3} M], and $FeSO_4.7H_2O$=0.001 M) to removal by Fenton's process

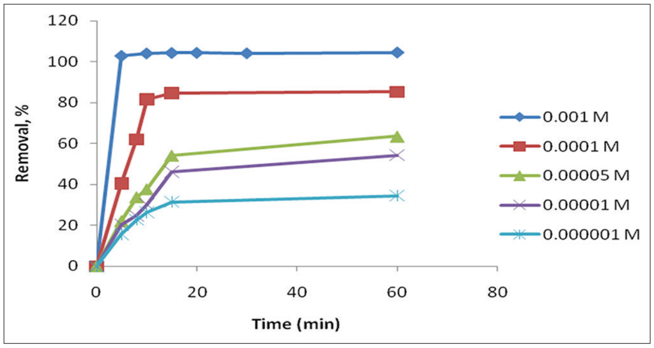


Figure 3: Effect of varying $FeSO_4$ dosages, experimental condition (pH=3, sulfamethoxazole=250 mg/L [0.986×10^{-3} M], and H_2O_2=5.25×10^{-3} M) to removal by Fenton's process

Effect of pH

The pH was strongly affected the degradation efficiency in Fenton process since a change in pH solution involves a variation of Fe^{2+} concentration, and consequently, the production rate of $^\bullet$OH radicals.[15] Parallel experiments were conducted at four initial pH values (3, 4, 5, and 7). Results showed that the antibiotic SMX was completely degraded (100%) in pH of 3. The Fenton process can operate well under acidic condition,[16] but its function reduces in low pH because of slower $FeOOH^{+2}$ formation and decreases production rate of Fe^{+2} and $^\bullet$OH.[17] The Fenton reactions have a maximum catalytic activity and greater degradation at pH 3 with higher generation of $^\bullet$OH radicals. The reasons for hydroxyl radical ($^\bullet$OH) as a reduction factor belong to the formation of ferric hydroxo complexes, which subsequently form $Fe(OH)_3$ at higher pH [Figure 4].

The optimal conditions for 100% degradation of SMX in aqueous solution were achieved after 60 min of reaction were determined and found to be $H_2O_2 = 5.25 \times 10^{-3}$ M, $Fe^{+2} = 1 \times 10^{-3}$ M, pH = 3, molar ratio $(H_2O_2)/(Fe^{+2}) = 5.2$, and for SMX = 9.869×10^{-4} M [Figure 5] show the chromatogram of SMX by HPLC instrument before and after treatment by Fenton's process at the optimum conditions.

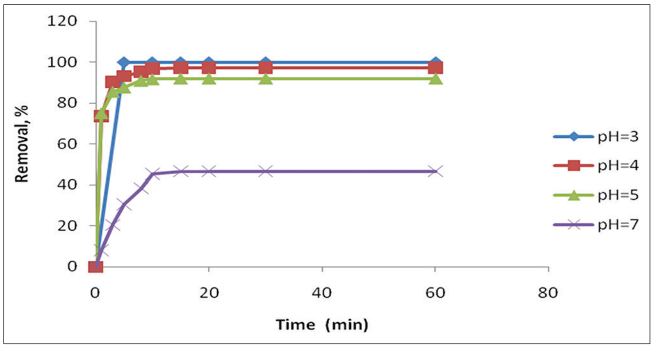


Figure 4: Effect of pH, experimental condition H_2O_2=5.25×10^{-3} M and FeSO4=1×10^{-3} M to removal sulfamethoxazole=250 mg/L (0.986×10^{-3} M) by Fenton's process

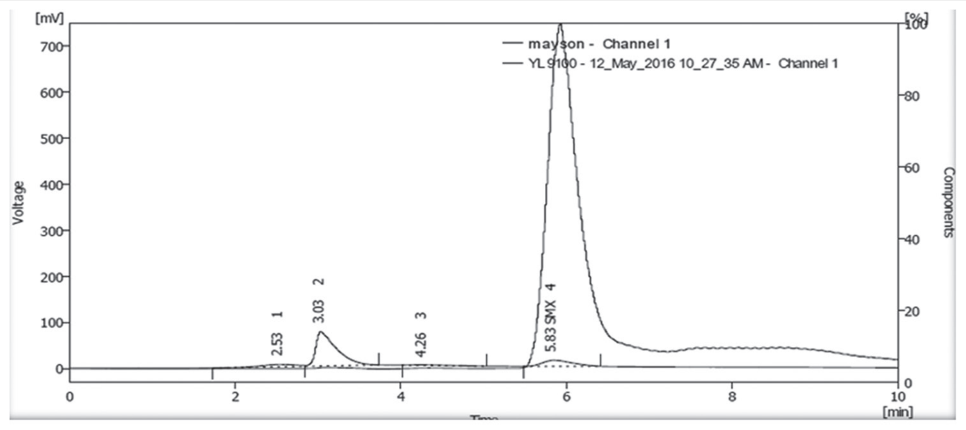


Figure 5: Measured concentration of sulfamethoxazole before and after treatment by Fenton's process at the optimum conditions

CONCLUSION AND RECOMMENDATIONS

The following conclusions might be drawn as a result of application of Fenton oxidation which indicates that:

1. The optimum reaction time was 60 min at pH 3, the dose of $H_2O_2 = 5.25 \times 10^{-3}$ M, $Fe^{2+} = 1 \times 10^{-3}$ M.
2. Finally, it is highly recommended to apply the used technique (Fenton's oxidation process) as treatment of SMX wastewater containing organic compound.

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