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Sulfamethoxazole antibiotic removal from aqueous solution and hospital wastewater using photo-Fenton process

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ABSTRACT

The presence of antibiotics in the environment can threaten the ecosystem. The current work was an aim to degrade the sulfamethoxazole (SMX) antibiotic from the aqueous solution and hospital wastewater by the photo-Fenton process. The experiments were carried out in a quartz reactor and effects of operational parameters such as pH, H_2O_2:Fe^{2+} ratio, reaction time, and SMX antibiotic concentration were evaluated. After optimizing the parameters, the efficiency of the photo-Fenton process was tested for eliminating SMX from the hospital wastewater. The optimal conditions for SMX removal by the photo-Fenton process were obtained at pH 3, H_2O_2:Fe^{2+} ratio of 11:2, the initial SMX concentration of 25 mg/L, and the reaction time of 15 min. At optimized conditions, the removal efficiency of the SMX and chemical oxygen demand was attained 98.06% and 87.65%, respectively. The efficiency of the photo-Fenton system for removing SMX antibiotics from the hospital wastewater was obtained 67.42%. The pseudo-first-order kinetic model was well fitted the data for SMX removal using the photo-Fenton process. Accordingly, the photo-Fenton process is an effective method for removing SMX antibiotics from aqueous solutions and hospital wastewaters.

Keywords: Sulfamethoxazole; Hospital wastewater; Photo-Fenton process; Antibiotic residues; Pseudo-first-order

1. Introduction

Recently, due to the population growth and increasing prescribed drugs, pharmaceutical compounds have considered a hot topic for study by environmentalists [1,2]. There is not enough information on the effects, environmental risks, and the fate of drug compounds because its concentration in the environment is very low [3]. A significant amount of drug compounds enter into wastewater through various sources like pharmaceutical industries and hospital wastewaters [4,5].

Sulfonamide is an extensively prescribed class of pharmaceutical compounds that are distributed into the aquatic environment [6]. These compounds have been found widely in the raw wastewater, wastewater treatment plants effluents, surface water, groundwater and sediments [7–9]. Sulfamethoxazole (SMX) is one of the main antibiotics of the sulfonamide group that is prescribed for control both Gram-positive and Gram-negative aerobic bacteria [10]. Also, SMX is effective against protozoa and used to treat bacterial infections in livestock, poultry, and human [10,11]. This

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antibiotic is one of the most pervasively prescribed antibiotics in Iran which is used for treating some frequent outbreak illnesses such as diarrhea, coccidiosis, and gastroenteritis [12,13]. Owing to the antibacterial feature of SMX, it shows a persistence to conventional wastewater treatment methods and is often found in effluents of the hospital wastewater plant [14]. The sulfonamides are low-biodegradable, thus, have a long half-life in the environment [15,16]. The amount of 50–370 ng/L SMX is detected in the environment [17]. It is worth noting that modern technologies should be used to eliminate antibiotics [15]. According to Carballa et al. [18]. The study, SMX has been resistant to conventional treatment; as a result, it had low removal efficiency. Bautitz et al. [19] stated that the SMX antibiotic can be sustained over a year in the environment that leads to risks like bacterial resistance and subsequently, SMX is classified in Class 1A due to the high environmental impact. The major problems of sulfonamides including SMX in aquatic environments are acute and chronic toxic effects, and the resistance of microorganisms [20,21]. However, the environmental concentrations are less than those that are likely to cause toxic effects on humans [22]. Thus, it is necessary to control the level of antibiotics in the aquatic environment by establishing treatment facilities for the removal of such compounds.

Over the past decade, advanced oxidation processes (AOPs) have been considered as effective methods for the removal of organic pollutants including antibiotics from wastewater. Application of AOPs for oxidizing antibiotics like sulfonamides has been reported [19,23]. The reduction of SMX from aqueous media has been studied with different technologies such as the chemical oxidation with ferrate [24], photo-Fenton process and ozonation [25]. In the presence of ferrous or ferric ions and hydrogen peroxide, a free radical of hydroxyl is generated [26,27]. This type of homogeneous oxidation is called the Fenton process. The general mechanism of the Fenton process begins with the formation of radical hydroxyl ($OH^{\bullet}$), according to the following equation:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + {}^{-}OH \qquad k_2 = 63\ M^{-1}\ S^{-1} \tag{1}$$

Since this reaction is carried out in an acidic environment, it can be re-written as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO_2^{\bullet} + H^{+} \tag{2}$$

In addition, the higher level of hydrogen peroxide is decomposed as follows.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{3}$$

The complete cycle between Fe^{2+} and Fe^{3+} continues until hydrogen peroxide is fully used and converted to radical hydroxyl ($OH^{\bullet}$) [28]. The AOPs are based on the formation of $OH^{\bullet}$ by the combination of oxidants such as hydrogen peroxide with ultraviolet (H_2O_2/UV photolysis) and catalysts such as metal ions like Fe^{2+}. Among AOPs, the photo-Fenton process is found to be the most promising technology which is effectively used to treat pollutants like phenol [29], olive mill wastewater [30], tetracycline [31], and pulp and paper mill wastewater [32]. The major advantages of the photo-Fenton process are the simplicity and effective oxidation of pollutants. Moreover, all gradients of this process including Fe^{2+}, H_2O_2, and light sources are available, easy to handle, and eco-friendly. Based on the following equation, the dominant form Fe^{3+} is $[Fe(HO)_2]^{2+}$ which plays the main role in the photo-Fenton process.

$$Fe^{2+} + H_2O_2 \rightarrow [Fe(HO)_2]^{2+} \rightarrow Fe^{3+} + OH^{\bullet} + {}^{-}OH \tag{4}$$

During ultraviolet radiation, the trivalent iron species (the dominant form of which is $Fe(OH)^{2+}$) is reduced to 2+. Thus, according to Eq. (5), in addition to the reduction of Fe^{2+}, more hydroxyl radicals are produced. Ultraviolet radiation can also decompose some of the oxidation by-products or iron trivalent compounds and, thus Fe^{2+} is recycled [28].

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \tag{5}$$

Although various AOPs such as sonoelectrochemical, photocatalytic oxidation, and UV/chlorine processes have been reported for SMX decomposition [33–36] there is scant information about the use of the photo-Fenton process to treat this contaminant. Also, the effect of the photo-Fenton process on the treatment of SMX from hospital wastewater is not clear. Therefore, the main objective of the current study is to evaluate the photo-Fenton process in the removal of SMX from aqueous solutions and the actual environment (hospital wastewater). To accomplish this goal, the impact of important operating parameters (pH, iron to hydrogen peroxide ratio, initial SMX concentration, and contact time) was investigated, the process kinetic was studied, and a hospital wastewater sample was purified by the photo-Fenton process.

2. Experimental setup

2.1. Materials and measurement methods

The SMX antibiotic (4-amino-N-(5-methylisoxazole-3-yl)-benzenesulfonamide, $C_{10}H_{11}N_3O_3S$, the molar mass of 253.27 g/mol) and acetonitrile were supplied from Sigma-Aldrich Company (Germany). Other chemicals used in this study include iron sulfate, 30% hydrogen peroxide, sulfuric acid, sodium hydroxide, acetic acid, and oxalic acid were purchased from Merck Company (Germany).

In order to measure the input and output chemical oxygen demand (COD) of samples, the COD reactor (model DR3900) and the spectrophotometer (Shimadzu model, Japan) were used. The pH meter (AZ, Taiwan) was used to monitor the reaction pH.

To measure the concentration of SMX, an high performance liquid chromatography (Knauer model) device equipped with a reverse-phase column (with specifications: waters 5 μm ODS2 4.6 × 250 mm, C18) and an ultraviolet detector, the solvent of acetonitrile, and acetic acid 30% at 365 nm wavelengths was used. Chromatography measurements were performed on the HICHROM column with specifications of HI-5C18-4371 and given sizes (4.6 mm × 250 mm, 5 μm). After centrifugation at 12,000 rpm for 15 min, the specimens were filtered. For mobile phases A and B, "1:1 acetonitrile-methanol, 0.1% acetic acid" and "5 mM KH_2PO_4, 0.1% acetic acid" were used at the ratio of 45:55, respectively. The mobile phase B was filtered prior to use by a vacuum filtration apparatus. The mobile phase was injected at a flow rate of 1.0 mL/min.

The sample injection volume was 50 μL. The detector used in this study was UV-visible (CECIL, England, CE4200). All used devices were calibrated before the tests, according to the relevant catalog, and their calibration curve was plotted.

2.2. Tests design

The present study was conducted in a batch mode. The experimental set up consists of a 1,000 mL glass reactor equipped with a low-pressure Hg lamp (11 W, GH lighting, China) emitting UV light at 365 nm which is placed in a quartz tube. The quartz tube immersed in the solution of SMX. The volume of the reactor was 500 mL. The distance of the quartz tube to the reactor body was 2 cm. To prevent the rising of the reaction temperature due to UV radiation, the outer surface of the reactor was kept cool. To do this, the reactor was designed in such a way that the tap water flowed continuously in the outer shell of the reactor and did not change the temperature of the reaction mixture. The schematic of the experimental set up is depicted in Fig. 1.

The tests were done according to "one variable at the time" procedure. To investigate the effect of the solution pH (2, 3, 4, 5, 6), the concentration of SMX antibiotics in the reactor, H_2O_2:Fe^{2+} ratio and contact time were set to 20 mg/L, 3:2, and 45 min, respectively. The pH factor of the solution was adjusted to desired value using sulfuric acid (H_2SO_4) 0.1 M and/or sodium hydroxide (NaOH) 0.1 M. The effect of the initial SMX concentration (5, 15, 25, and 35 mg/L) was assessed at the conditions of pH 3, and H_2O_2:Fe^{2+} ratio of 3:2, and contact time of 45 min. The parameter of H_2O_2:Fe^{2+} ratio (3:2, 7:2, and 11:2) was evaluated at pH 3, SMX concentration of 25 mg/L, and contact time of 45 min. The impact of reaction time (15, 30, 45, 60, and 75 min) was checked at pH 3, SMX concentration of 25 mg/L, and H_2O_2:Fe^{2+} ratio 11:2. It should be noted that the initial SMX concentration was selected based on published papers [12,13,37].

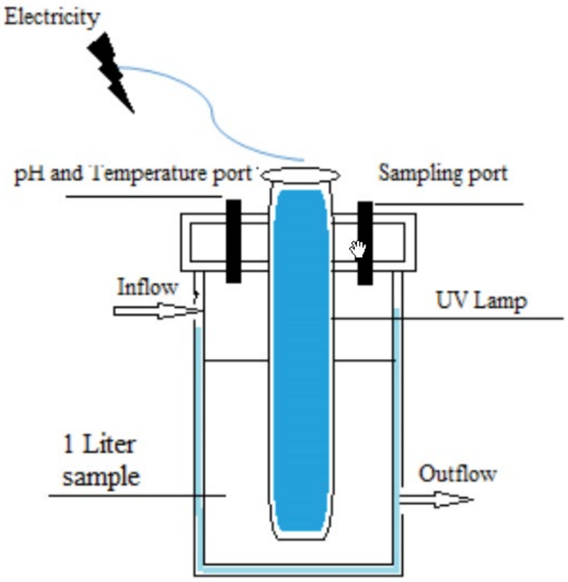

Fig. 1. Schematic of the experimental setup.

After optimizing the test conditions with the aqueous solution, the actual wastewater was refined. The actual wastewater was provided from a hospital and in the laboratory, the suspended solids were separated using fabric filter. The test on the hospital wastewater was done at the conditions of pH 3, H_2O_2:Fe^{2+} ratio of 11:2, and contact time of 45 min. For this section, the COD was measured.

All trials were repeated 3 times for more accuracy and averaged data with standard deviation was reported.

3. Results and discussion

3.1. Effect of solution pH

The effect of solution pH on the SMX removal efficiency from aqueous media by photo-Fenton was tested (see Fig. 2). As shown in this figure, at pH 2, the SMX removal efficiency was attained as 90.32%. With rising pH to 3, the removal efficiency was increased and reached a maximum value of 97.08%. For other tested pHs (4, 5, and 6), the removal efficiency of SMX was reduced and reached to about 82% at pH 6. Based on the results, it can be proposed that a low pH of 2 and pH > 3 have a negative effect on the process efficiency. At the pH value lower than 3, the $OH^{\bullet}$ level is significantly reduced owing to the inhibitory effect of the radicals by H^+ ions and the formation of $[Fe(H_2O)]^{2+}$ ion, which reacts with H_2O_2 at a low rate. Another plausible reason is the stability of H_2O_2 at pH below 3 by the formation of $H_3O_2^+$, which inhibits the production of $OH^{\bullet}$. The decreasing of the process performance at pH above 3 could be justified by:

- Prevention of H_2O_2 decomposition for the production of hydroxyl radicals due to insufficient ion H^+;
- Rapid decomposition of H_2O_2 to water and oxygen; and
- More production of other ferric species to produce $OH^{\bullet}$ at high solution pH. The development of ferric oxide hydroxide (FeOOH) at pH 4 can reduce the decomposition rate of the target pollutant. In addition, at pH values higher than 4, iron is settled as a ferric hydroxide, which leads to a decrease in light transmission in the photo-Fenton process [38]. These results are confirmed by other researchers [39,40].

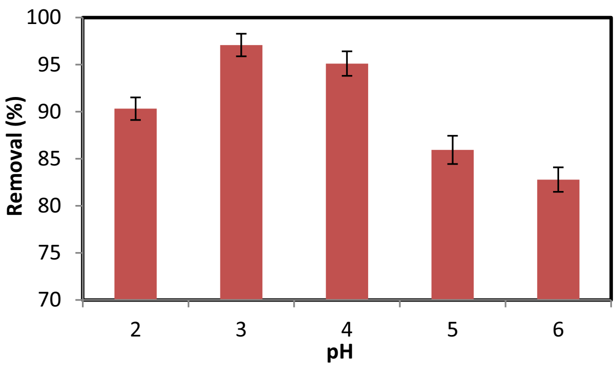

Fig. 2. Effect of solution pH on SMX removal from aqueous solution by photo-Fenton (SMX concentration: 20 mg/L, H_2O_2:Fe^{2+} ratio: 3:2, and contact time: 45 min).

3.2. Effect of initial SMX concentration

The initial concentration of the contaminant is important in the photo-Fenton process because it affects the amount of Fenton reagent used in the process. Fig. 3 shows the effect of different initial concentrations of SMX (5–35 mg/L) on its removal from the aqueous solution by the photo-Fenton process. As can be seen in the figure, by increasing the initial SMX concentration from 5 to 25 mg/L, the removal efficiency was increased from 87% to 93%, respectively. Thereafter, with increasing concentrations up to 35 mg/L, the removal efficiency dropped to about 82%.

Based on Fig. 3, the initial increase in efficiency can be related to greater access to the reactive species to oxidize pollutants. Ahmed [40] and Pourzamani et al. [41] have been stated the higher efficiency at low pollutant concentration can be owing to greater access to $OH^{\bullet}$. In contrast, the lower degradation efficiency at SMX > 25 mg/L can correspond to an increase of the UV light trapping and lack of proper contact with hydrogen peroxide molecules and ferric ions for the production of $OH^{\bullet}$. When all parameters including pH, reaction time, hydrogen peroxide concentration, and divalent iron content are constant, a certain amount of $OH^{\bullet}$ is produced. This amount of generated radical has the ability to remove and degrade certain amounts of organic compounds. Therefore, if the initial concentration of organic compounds increases, the amount of $OH^{\bullet}$ present in the environment is not enough to remove the additional molecule of organic compounds [42]. Such interpretation was reported by Elmolla and Chaudhuri [43] which demonstrated that by increasing the initial concentration of amoxicillin, ampicillin, and cloxacillin antibiotics the photo-Fenton efficiency is reduced.

3.3. Effect of H_2O_2:Fe^{2+} ratio

Estimation of the optimal of H_2O_2:Fe^{2+} ratio is one of the most important steps in the degradation efficiency and operational cost of the photo-Fenton process. Moreover, the selection of suitable concentration Fenton reagent (H_2O_2 and Fe^{2+}) is essential because their content affects the designation and kinetics of the process [38]. In order to investigate the effect of Fenton reagent on the removal efficiency of SMX from the aqueous solution, different ratios of H_2O_2:Fe^{2+} (3:2, 7:2, 11:2) were tested and results are shown in Fig. 4. As shown in this figure, the SMX removal efficiency gradually increased from 87% to 99%, with increasing the H_2O_2:Fe^{2+} ratio from 3:2 to 11:2, respectively. The findings are similar to those reported by Sun et al. [44], which show that the increasing of Fenton reagents in the photo-Fenton process up to a suitable value the ciprofloxacin decomposition increased. Similar findings were reported by other researchers on the sulfamonomethoxine oxidation using the photo-Fenton process [45]. In the review conducted by Xu and Wang [46] on 2,4-dichlorophenol oxidation by the Fenton-coupled process found that by increasing Fenton reagent concentration, in the first step, the removal efficiency of pollutant increased and then decreased. Reducing the efficiency of the photo-Fenton process in high concentrations of H_2O_2:Fe^{2} is due to the inhibitory effect of this oxidant on $OH^{\bullet}$ and production of radicals with lower oxidation potential such as $HOO^{\bullet}$ and $O_2^{\bullet}$.

3.4. Effect of contact time

The effect of contact time on the removal efficiency of SMX from the aqueous solution using the photo- Fenton process was evaluated (Fig. 5). The photo-Fenton process had the maximum SMX removal (≈98%) at the first tested contact time (15 min). By increasing contact time from 15 to 60 min, the SMX removal efficiency was almost constant. After 60 min of contact time, the removal efficiency was reduced to the lowest

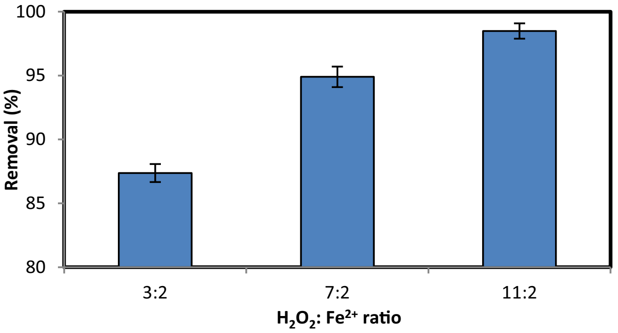

Fig. 4. Effect of H_2O_2:Fe^{2+} ratio on SMX removal from aqueous solution by photo-Fenton (pH: 3, SMX concentration: 25 mg/L, and contact time: 45 min).

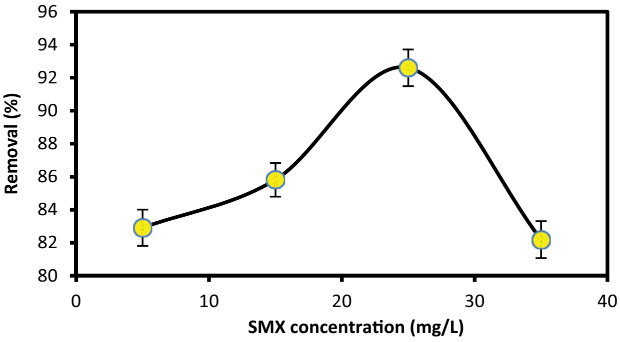

Fig. 3. Effect of the initial SMX concentration on its removal from aqueous solution by photo-Fenton (pH: 3, H_2O_2:Fe^{2+} ratio: 3:2, and contact time: 45 min)

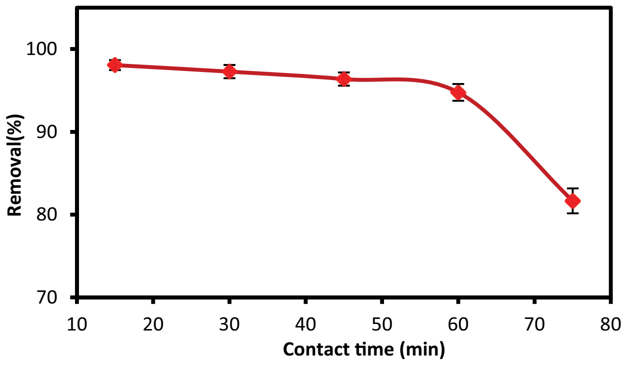

Fig. 5. Effect of contact time on the SMX removal from aqueous solution by photo-Fenton (pH: 3, SMX concentration: 25 mg/L, and H_2O_2:Fe^{2+} ratio: 11:2).

level. According to Possetto et al. [47] study, with increasing reaction time, the removal efficiency of the photo-Fenton was first increased and then remained constant.

3.5. Kinetic of SMX removal by photo-Fenton process

The kinetic of SMX removal from the aqueous solution by the photo-Fenton process was evaluated. The pseudo-first-order model was used for fitting the experimental data:

$$\ln\frac{\left[\mathrm{SMX}\right]_t}{\left[\mathrm{SMX}\right]_0} = -k_{\mathrm{obs}}t \tag{6}$$

where $[\mathrm{SMX}]_0$ and $[\mathrm{SMX}]_t$ are the initial and final concentration of SMX, k_{obs} denotes the observed reaction rate constant for the SMX removal.

Kinetic of SMX removal in the photo-Fenton process was evaluated under optimal conditions given in Fig. 6. The data for SMX removal using the photo-Fenton process was in good agreement with the pseudo-first-order kinetic model ($R^2 > 0.9$). The k_{obs} value for the process (0.034 min^{-1}) was much higher than those obtain for antibiotic removal in an AOP method using S-MgO/PMS process (k_{obs} = 0.023 min^{-1}) [48] and nanocrystalline MgO nanoparticle ($k_{\mathrm{obs}} = 0.008\ \mathrm{min}^{-1}$) [49].

3.6. Feasibility of the photo-Fenton process for COD and SMX removal from the hospital wastewater

In order to investigate the efficacy of the photo-Fenton process for removing the residual drug from the real wastewater sample, a test was done under obtained optimum conditions. The findings are illustrated in Fig. 7. Based on Fig. 7a, the highest removal percentage of the residual drug was related to metronidazole (85.27%) and the lowest one has belonged to clindamycin (41.35%). On the other hand, the percentage of removal of SMX in the real sample was obtained 67.42%. As it is observable in Fig. 7b, by comparing the efficiency of the photo-Fenton process for the SMX removal from the hospital wastewater and aqueous solution, it was observed that the removal percentage of SMX from aqueous solution (89.61%) is much higher than that of hospital wastewater (67.41%). This difference in the removal rate can be due to the presence of other drugs or oxidizable compounds in the hospital wastewater. The presence of other drugs and compounds can prevent the oxidation of the target pollutant. Zhang et al. [50] in the study on 2,4-dichlorophenol removal using the electro-Fenton reported that the presence of total organic carbon in the working solution reduces contaminant removal. Lee et al. [51] obtained a similar finding in the study on the use of AOP for treating anaerobically digested livestock wastewater.

On the other hand, according to Fig. 7c, the COD value of the raw real wastewater (542 mg/L) is less than the treated one (1,927 mg/L). In contrast to this, it is observed that for the aqueous solution the concentration of COD in influent of the reactor (1,783 mg/L) is expectedly greater than that of in the effluent (238 mg/L). The reason for the increase of the COD parameter of the hospital wastewater after treatment by photo-Fenton is to break down complex compounds and produce oxidizing by-products.

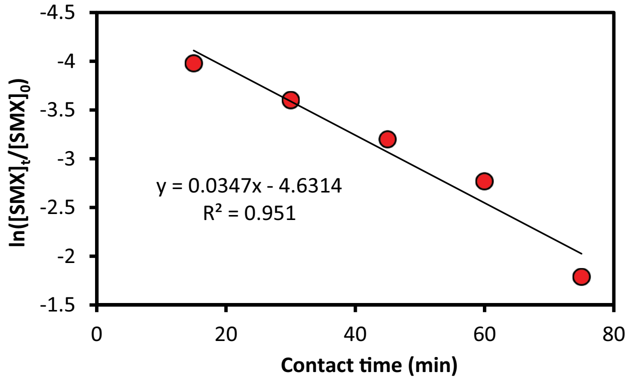

Fig. 6. Pseudo-first-order kinetic model for SMX removal by the photo-Fenton process.

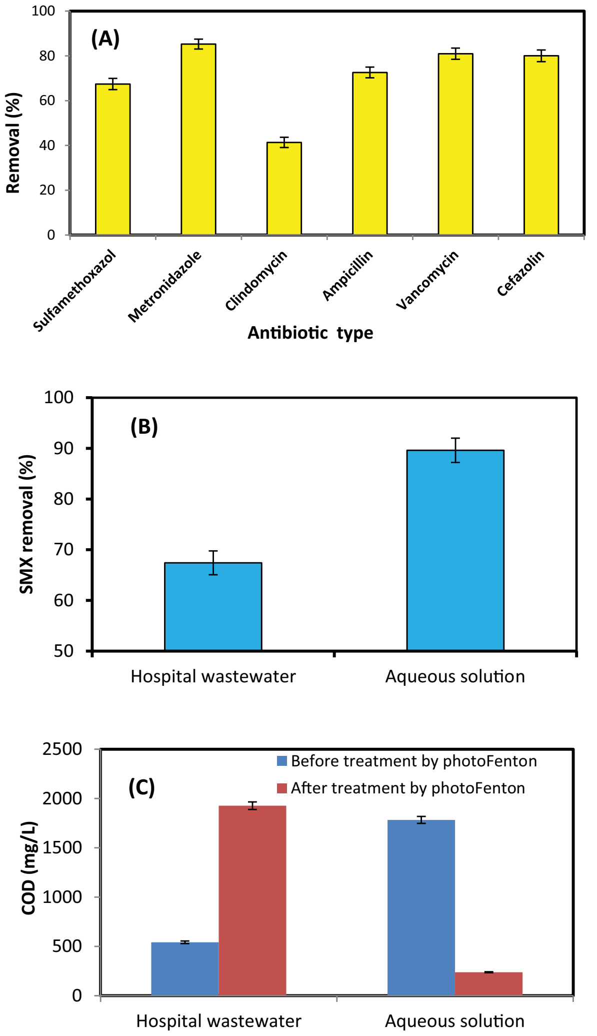

Fig. 7. (a) Antibiotics removal from hospital wastewater by the photo-Fenton process, (b) comparing the SMX removal efficiency from hospital wastewater and aqueous solution by photo-Fenton, and (c) comparing the COD removal from hospital wastewater and aqueous solution by photo-Fenton.

4. Conclusions

In this research, the removal of SMX antibiotic by the photo-Fenton process was assessed and the following findings are recorded:

- Maximum SMX removal was obtained at pH 3.
- Among the initial SMX concentrations (5 to 35 mg/L), the concentration of 25 mg/L had the highest removal efficiency.
- The H_2O_2:Fe^{2+} ratio of 11:2 had the highest removal efficiency among other studied ones (3:2, 7:2, 11:2).
- The SMX removal at 15th min of contact time was attained 98%.
- For the real sample of hospital wastewater, the highest removal percentage of the residual antibiotic was recorded for metronidazole (85.27%).
- The SMX removal was in good agreement with the pseudo-first-order model.

According to this study, the photo-Fenton process can be a promising method for treating hospital wastewater.

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