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Evaluation of sulfadiazine(SDZ) removal from wastewater by persulfate activated with iron sulfate

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ABSTRACT

In this study, removal of an antibiotic (SDZ) from wastewater using an advanced oxidation process of persulfate (PS) in the presence of iron sulfate ($S_2O_8^{-2}/Fe^{+2}$) was investigated. The operational variables such as; the effect of pH, contact time, iron and PS ion concentrations and initial concentration of SDZ on the efficiency of SDZ removal was studied. High performance liquid chromatography (HPLC) was used for the analysis and monitoring of SDZ concentration. It was found that the highest rates of SDZ removal were found to be 95.83±1.342%, 87.15±0.929% and 69.09±0.848%, respectively, for initial SDZ concentration of 0.08, 0.2 and 0.4 mmol. The results showed that the $S_2O_8^{-2}/Fe^{+2}$ system would be optimized by contact time of 60 min, pH 4 and iron to PS molar ratio of 1. Therefore, these findings would help to better apply the AOPs to remove recalcitrance pollutants such as SDZ from wastewater.

Keywords: SDZ; Persulfate/iron process; Free radicals; Advanced oxidation process

1. Introduction

Antibiotics are the most important group of drugs which play a significant role to protect humans and animals against bacterial infections [1]. In other words, the use of antibiotics is the most conventional method for treating humans [2]. These drugs also are used in fish farming industries in order to improve growth [3]. Antibiotics are naturally absorbed by the human body after the use. Therefore, much of the drugs or their metabolites are removed from the body through the urine and feces into sewerage system [4,5]. In recent years, the fate of active pharmaceutical compounds in environment, especially in water sources is one of the emerging issues in environmental chemistry. This is why many scientists got interested to find the fate of a large volume and thousands release points of drugs to the environment and their impacts on the organisms [1,6]. Among the antibiotics, sulfonamides are a large group of antibiotics that are under especial attention due to a high rate of discharge into the environment and resistance to conventional treatment processes [4,7]. Sulfonamides are valuable antibiotics in order to prevent the infectious diseases spread and SDZ [4-amino-N-(2-pyrimidinyl) benzene sulfonamide] is one of the eight common sulfonamides [2,8]. Creating the problems in biological treatment processes and disrupting of treatment operation units and bioaccumulating in various micro-organisms are the problems due to the presence of sulfonamides in effluents [4,9]. The chemical structure of SDZ is shown in Fig. 1. SDZ is a strong antibacterial agent that has reported very high concentrations of 1,160 micrograms per liter in the ground water and surface water downstream from the sewage and pharmaceutical wastes disposal [4,10,11]. SDZ can cause health and environmental problems and also bacterial resistance after entering the food chain [12,13]. Different methods to remove antibiotics have been studied such as biological treatment [6], adsorption [2] size exclusion, advanced oxidation processes (AOPs) including Fenton as well as Fenton like systems based on the use of either hydrogen peroxide or persulfate

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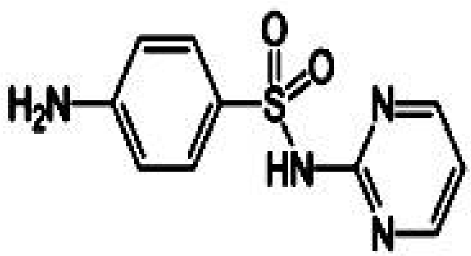

Fig. 1. Chemical structure of SDZ [19].

[14,15]. The latter can also be implemented under homogeneous as well as heterogeneous conditions [16–18].

One of the methods used to remove the pollutants from aqueous solutions is the AOPs that are based on the formation of free radicals of PS [19,20]. PS ($S_2O_8^{2-}$) is a strong oxidant with a redox potential of 2.01 V which in recent years has been attracted researchers' attention and is used in order to remove the pollutants from, wastewater including leachates and hospital effluents and soil [17,19]. PS is one of the strongest oxidants and has a higher oxidation potential than many antioxidants [7,21].

In comparison with other oxidants, PS has a better oxidation potential due to characteristics such as more stability and destructivity potential, easy maintenance and transportation, high solubility and low operational cost [19,20]. But it has low reaction rate with the pollutants is slow so to accelerate the reaction rate, catalyst is needed. The activation of PS is mainly carried out by electrolysis [17], transition metals (zero valent e.g. Fe_0) or ions [16,22], UV radiation [15,23] and heat [18,24]. Iron ion (Fe^{2+}) is an effective catalyst and is used for the activating of PS into sulfate radical (SR). Fe^{2+} stimulates the persulfate ions and produces SR which have higher oxidation potential ($SO_4^{-}, E_0 = 2.6V$) than PS alone [20,25]. It has been demonstrated that at elevated pH, SO_4^{-} can exhibited stronger oxidative ability than $\dot{O}H$ and could efficiently degrade many organic pollutants [19]. The general principles of the AOPs based on persulfate/iron can be summarizes in Eq.(1) as below [7,20].

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-} + Fe^{3+} + SO_4^{2-} K = 20M^{-1}S^{-1} \quad (1)$$

On the contrary of hydroxyl radicals that act as non-selective, the SRs react with certain organic compounds, especially benzene and its derivatives which involve the active groups, as a selective oxidizer [26]. In addition, SO_4^{-} is almost neutral and does not consider in terms of pollution. This is why it is known by the United State Environmental Protection Agency (USEPA) as the secondary standard of drinking water with a maximum concentration of 250 mg/L [27].

The aim of this study is to investigate Fe-activated PS system to remove recalcitrance pollutants (i.e. antibiotics) from wastewater. To evaluate the effect of the PS activated on the treatment of the wastewater containing various concentrations of antibiotics, the removal of SDZ was selected as a model recalcitrant pollutant. The effect of initial SDZ concentration, iron and PS ions concentration, pH, and contact time on the removal of SDZ were evaluated. The optimum operational parameters for obtaining maximum removal of SDZ was determined.

2. Materials and methods

2.1. Chemicals and materials

SDZ ($C_{10}H_{10}N_4O_2S$, P ≥ 98%, molecular weight 272.259 g/mol, Pk_a 6.5), sodium persulfate ($Na_2S_2O_8$, P 98%), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, P99%), methanol (CH_4O, P ≥ 99%), ammonia (NH_3), acetic acid (CH_3COOH, P ≥ 99%), and acetonitrile (CH_3CN, P ≥ 99%) were purchased from Merck company, Germany. All other chemicals were used without further purification. Solid-phase extraction (SPE)-C18-Cartridges were prepared from Chromabond Corporation. Hydrochloric acid or sodiumhydroxide were used to adjust the initial pH of the SDZ solution. All solutions in this study were prepared by deionized water.

2.2. Experimental procedure

All runs of the persulfate processes were performed in batch mode with a volume of 150 mL and at ambient room temperature (25 ± 1ºC). All synthetic samples were prepared with 0.08, 0.2 and 0.4 mmol of SDZ. The pH of the samples was adjusted at 4.0, 5.5, 7, 8.5 and 11.0 using 1 M HCL or 1 M NaOH. Suitable amounts of iron sulfate and sodium persulfate (0.08, 0.2 and 0.4 mmol) were added to the reactors and then mixed at 120 rpm for 15, 30, and 60 min. All samples were filtered through 0.45 µm membranes before analysis. All experiments were performed in triplicate and repeated twice for accuracy.

2.3. Analytical methods

SDZ concentration was examined using a high performance liquid chromatography (Agilent Technologies 1200HPLC-UV), equipped with a C18 column and a UV detector. Samples were extracted for SDZ using 3 mL SPE cartridge. The mobile phase was a mixture of sodium acetate 75% purity (0.02 mol/ L, pH 4.75) and acetonitrile 25% purity, with a flow rate of 0.8 mL/min. The detector temperature was set at 30ºC and the wavelength was set at 275 nm. The column temperature was 25ºC and the injection volume was 20 µL. The pH was measured using a digital pH meter (Metrohm Pars Azma Co Metrohm).

3. Results and discussion

3.1. Effect of pH

The effect of different pH values of 4 to 11 on removal of SDZ using persulfate/iron process is depicted in Fig. 2. As shown, the removal of SDZ in acidic condition is more than in alkaline one. The concentration of sulphate free radicals formed is a function of pH and varies strongly with pH changes. It is difficult to predict the function of various species in system versus pH changes as well. There are different mechanisms in every system contributing in removing the organic materials. The importance and priority of every mechanism involved in drug removal process, depends on the nature of the drug and pH of the environment. So, the effect of pH changes on the rate of drug removal, depends on the kinds and situations of system and antibiotic [28].

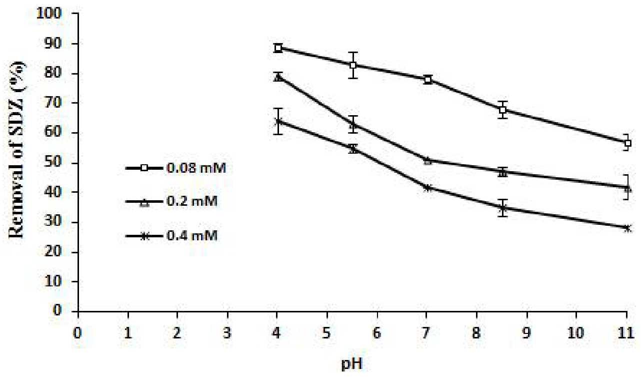

Fig. 2. Effect of pH on SDZ removal. Experimental conditions: [SDZ] = 0.08, 0.2 and 0.4 mM, contact time = 60 min, ratio Fe/PS = 1. Error bars represent standard deviation of two replicates.

The reason why the efficiency of antibiotic removal is better in acidic pH levels can be asserted as pH becomes more alkalinity, because of increasing the hydroxyl in the environment and turning Fe^{+2} to Fe^{+3} during the process, iron is deposited in the form of hydroxyl ferric $Fe(HO)_3$ and thus exit from the catalyst cycle. In process persulfate cycle, without presence of catalyst, persulfate has got a little reactivity with target pollutants [29].

Through a research to remove antibiotic penicillin with processes Fenton and photo Fenton, Arslan-Alaton et al. showed that maximum removal obtained at pH 3. According to them, pH influences directly the oxidation of organic compounds and production of free radicals and influences the efficiency of oxidation. However it is necessary for the wastewater pH in this process to be low [30]. Also in a research done by Somayeh Dehghani et al. to remove SDZ from water environments via Fenton, it was confirmed that the removal efficiency in acidic medium is more than that in basic medium [31].

3.2. Effect of contact time

Fig. 3 shows the rate of SDZ removal in persulfate/ iron system in different contact times. As observed, higher efficiency obtained in higher contact times. Although higher efficiency obtained in higher contact times, but as observed in this figure, the removal efficiency increasing does not extensively depend on the contact time. Therefore, with increasing the contact time from 11 min to 60 min (i.e. more than 5 times), the value of the removal efficiency has increased by just 6%, while the reactor volume necessary to be increased to 500 percent (i.e. 5 time) that is not cost benefit for applying is full scale.

The adequate time of reaction is one of the effective factors in operating AOPs. Passing the time increases the chance of contact between iron ion and persulfate that leads to the production of more values of free radicals and however the removal value increases with increasing in sulfate free radicals [32]. The study showed that the increase in the rate of removal is not remarkable with increasing contact time between oxidant molecules and polluted water.

Seok-Young et al. found out in an investigation on 2-4-denitrotoluene removal in persulfate/iron system

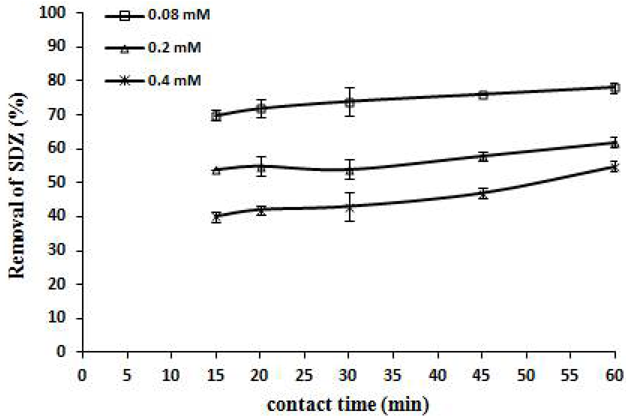

Fig. 3. Effect of contact time on SDZ removal. Experimental conditions: [SDZ] = 0.08, 0.2 and 0.4 mM, pH = 4, ratio Fe/PS = 1. Error bars represent standard deviation of two replicates.

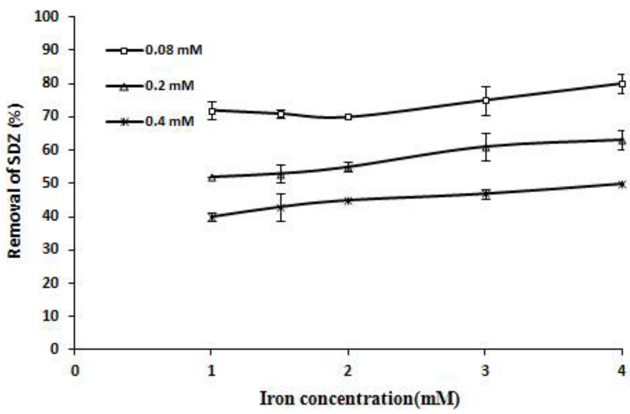

Fig. 4. Effect of Iron ion concentration on SDZ removal. Experimental conditions: [SDZ] = 0.08, 0.2 and 0.4 mM, pH = 4, contact time = 60 min. Error bars represent standard deviation of two replicates.

that as the contact time between iron ion and persulfate increases, the sulfate free radical ascends and consequently target pollutant removal increases [33].

3.3. Effect of iron ion concentration

Iron concentration is one of the essential factors in persulfate/iron system. Different iron ion concentrations (i.e. 1, 1.5, 2, 3, 4 mmol) were examined in the present study. As depicted in Fig. 4, there is a nominal difference in removal percentage between concentration 1 mmol and 2 mmol while in concentration 4 mmol of iron the removal percentage increases remarkably.

The efficiency of sulphadiazine removal increases when iron concentration increased. The main reason for this phenomena is that iron plays an important role in the production of sulfate free radicals. Increasing of iron ions in persulfate/iron system leads to increase of persulfate reaction rates and produces SO_4^- in which rises the sulphadiazine removal efficiency [34].

Chen et al. obtained in an investigation on MTBE removal via persulfate/iron that the removal efficiency increases as the concentration of iron increase [35]. Also the study conducted by Liang et al. for tetrachloroethylene removal, using iron/persulfate, that the removal efficiency increased with increase in concentration of iron [36]. Similar results were reported by Ghauch and Naim [16].

3.4. Effect of persulfate ion concentration

Fig. 5 shows the changes of SDZ removal versus different concentrations of persulfate (2, 3, 4, 6, and 8 mmol). Sulphadiazine removal with different concentrations of persulfate and sulphadiazine shows different functions so that it is not possible to grant a monotonous trend for this process regarding the increase or decrease in persulfate concentration of medium.

According to Fig. 5, there is a direct relation between oxidizing agent concentration and the rate of drug removal. Thus with the increase of sulfate ion concentration from 2 to 4 mmol, the removal efficiency increases as well, but when increasing the persulfate concentration is being continued (i.e. more than 4 mmol) this consolidation became reversed. So that when the concentration is 8 mmol, removal efficiency decreases again and reaches the value of approximately equal with obtained efficiency for persulfate concentration of 2 mmol. Therefore, persulfate concentration of 4 mmol was chosen research in this study.

However, the highest removal rate (80%) of SDZ in different concentrations was obtained in persulfate/iron ratio equal 1:1. This results corroborates whit the results obtained on Ranitidine removal as well [16]. The experiments showed that the removal efficiency of SDZ decreased with increase in the contamination concentrations. Optimal removal efficiency for SDZ concentrations of 0.08, 0.2, and 0.4 mmol obtained 95.83%, 87.15%, and 69.09%, respectively.

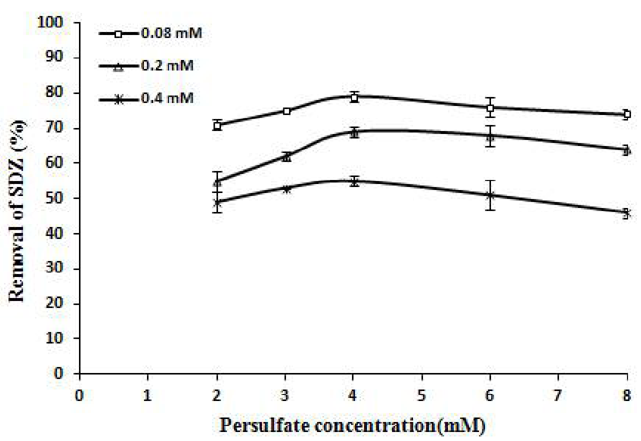

Fig. 5. Effect of persulfate concentration on SDZ removal. Experimental conditions: [SDZ] = 0.08, 0.2 and 0.4 mM, pH = 4, contact time = 60 min. Error bars represent standard deviation of two replicates.

4. Conclusion

In the present research the optimum experimental conditions of persulfate/iron reaction were calculated to achieve better efficiency for SDZ removal and economical advantage using cheap chemicals. According to the obtained results, using the PS based on AOP system, the rate of SDZ can be decreased remarkably by providing the optimum situations in experiments and this method can be used to treat completely the wastewater containing antibiotic SDZ. The study demonstrated that the removal of SDZ from industrial wastewaters will be obtainable between 69–95% by applying this process.

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