

Removal of tylosin from aqueous solution by UV/nano Ag/S₂O₈²⁻ process : Influence of operational parameters and kinetic study

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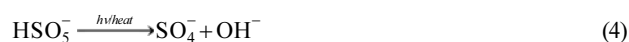
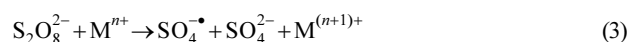
Abstract—The present work deals with the photooxidative degradation of tylosin antibiotic (TYL) in the presence of potassium peroxydisulfate (K₂S₂O₈) irradiated by UV-C in the presence of immobilized nano silver. Effects of pH, temperature, peroxydisulfate concentration and immobilized nano silver dosage on the degradation efficiency of TYL were examined. Degradation efficiency was small when the oxidation was carried out in the absence of UV irradiation. Results showed that degradation of TYL increases with temperature, nano Ag and peroxydisulfate initial concentration and decreases with pH. Due to UV/nano Ag/S₂O₈²⁻ processes, more than 90% of TYL can be degraded at room temperature in 35 min at an initial concentration of 50 mg l⁻¹. Degradation reaction order of TYL by UV/nano Ag/S₂O₈²⁻ process is 1.89. Meanwhile, the initial rates of degradation in UV/nano Ag/S₂O₈²⁻ processes can be described well by the Langmuir-Hinshelwood kinetic model.

Keywords: Advanced Oxidation Processes (AOPs), Kinetics, Tylosin, Nano Particle, Peroxydisulfate, UV Irradiation

INTRODUCTION

The major contaminants of livestock effluent are nitrogen and organic matters; however it may contain potassium, phosphorus and growth factors (hormones and heavy metals) or acute contaminants such as pharmaceuticals. Much attention has been recently devoted to the fate of pharmaceutically active compounds such as antibiotics in soil and water. Antibiotics can reach the aquatic environment through various sources such as the antibiotic industry, hospital effluent and excretion from humans and livestock [1]. Among them, tylosin antibiotic was shown to be poorly biodegradable and toxic for micro organisms [2]. Tylosin is a 16-membered ring macrolide antibiotic (Table 1) that is produced commercially from the fermentation by *Streptomyces fradiae* found in soil from Thailand and used as veterinary drug and growth promoter. It is used as vet-

erinary medicine to treat respiratory infections, leptospiroses and mycoplasmosis. It is used as a feed supplement for growth stimulation of young animals [3,4]. Thus, there is a strong need to look for physical and chemical methods as alternative and faster treatment processes for the degradation of TYL. Therefore, new technologies are being investigated for the purpose of quantitatively removing antibiotics from waters. These include photodegradation, membrane filtration, activated carbon filtration, chlorine dioxide treatment, ionic treatments, and ozonation. Membrane filtration and activated carbon adsorption are appropriate for treatment of contaminated waters with low levels of dissolved organic carbon (DOC), but also result in waste spent activated carbon and membrane retentive that also requires disposition. Advanced oxidation processes (AOPs) have received considerable attention as wastewater treatment processes due to their ability to degrade, and in many cases, mineralize various organic compounds that are otherwise resistant to conventional biological and chemical treatments. AOPs are based on strong oxidants, such as ozone, hydrogen peroxide (H₂O₂), ultrasound (US), electron beam and other methods [5-19]. The newest and least explored oxidant for organic pollutants is peroxydisulfate. Peroxydisulfate anion (S₂O₈²⁻) is a strong two-electron oxidizing agent with a redox potential of 2.01 V [20]. The sulfate radicals could be produced from peroxydisulfate (PDS) or peroxymonosulfate via thermal, photochemical, radiolytic, or redox decomposition (Eq. (1) to Eq. (4)) [20].



The SO₄^{•-} (E⁰=2.6 V) has a redox potential close to that of the hydroxyl radical (HO[•]) (E⁰=2.7 V), and is more stable in water. There-

Table 1. Properties of TYL

Name	Tylosin
Structure	
Molecular formula	C ₄₆ H ₇₇ NO ₁₇
λ _{max} (nm)	300
Molecular weight (g/mol)	916.12

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fore, it is desirable to activate the $S_2O_8^{2-}$ and produce the SO_4^{\bullet} , which leads to a higher rate of organic contaminant oxidation. Common activation approaches include heat, pH adjustment, or transition metal to produce SO_4^{\bullet} . Under thermal conditions (from 40 to 99 °C), peroxydisulfate anion can be converted into SO_4^{\bullet} . Under acidic conditions the breakdown of $S_2O_8^{2-}$ into SO_4^{\bullet} can be further acid catalyzed. Another way to activate peroxydisulfate is the use of sufficient quantities of metal cation, serving as an electron donor [20]. Additionally, some unique and important investigations consider sulfate radicals-induced degradation of organic pollutants. Also, some works concentrated on the removal of environmental contamination using peroxymonosulfate and peroxydisulfate radicals together and in the presence of diversity of metal ions [21-25]. Furthermore, there are many newly investigated routes and techniques conducted on water and wastewater treatment [26-29].

Application of nano Ag-catalyzed peroxydisulfate, as an advanced oxidation process, introduces an effective method for wastewater treatment. An accelerated reaction using $S_2O_8^{2-}$ to destroy antibiotics can be achieved via chemical activation with nano Ag to generate sulfate radicals (SO_4^{\bullet}). We studied nano Silver-catalyzed peroxydisulfate with UV irradiation for the degradation of Tylosin in an aqueous medium.

Our objectives were (1) to investigate the UV/nano Ag/ $S_2O_8^{2-}$ process, (2) calculate the optimum number of effective factors such as pH, temperature, nano Ag dosage and initial oxidant concentration; and (3) look at the kinetics of the process.

EXPERIMENTAL

1. Materials and Methods

Tyloject 20% (Tylosin) was obtained from Razak Company (Iran). An immobilized silver nanoparticle was obtained from Lotus Nanochemistry Pars Company (Iran) and potassium peroxydisulfate from Merck. The solution was immediately prepared before the measurements to avoid a change in concentration due to self-decomposition. Added to the pollutant- $S_2O_8^{2-}$ solution in a glass bottle was 100 mL of synthetic solution containing the desired initial concentration of nano Ag. The pollutant solution samples were taken at the desired time intervals and were analyzed with a UV/Vis spec-

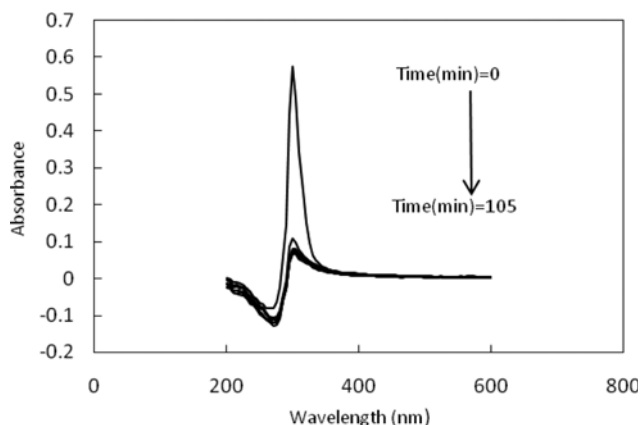


Fig. 1. UV-Vis spectra of TYL after different times of UV/nano Ag/ $S_2O_8^{2-}$ process; UV=30 W, $[TYL]_0=50 \text{ mgL}^{-1}$, $pH_0=3.1$, $[S_2O_8^{2-}]_0=2 \text{ mM}$, $[nano \text{ Ag}]_0=0.01 \text{ gL}^{-1}$, $T_0=25^\circ\text{C}$.

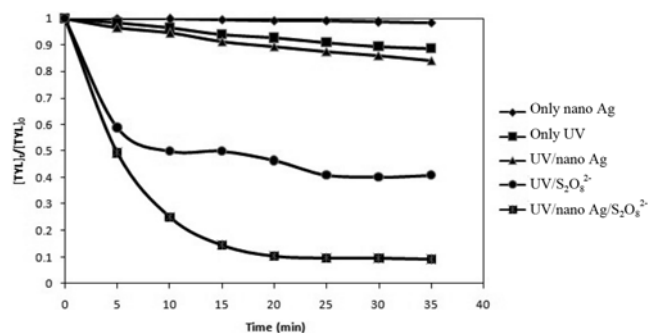


Fig. 2. Effect of UV light on different processes; UV=30 W, $[TYL]_0=50 \text{ mgL}^{-1}$, $[S_2O_8^{2-}]_0=2 \text{ mM}$, $pH_0=\text{natural}$, $T_0=25^\circ\text{C}$, $[nano \text{ Ag}]_0=0.01 \text{ gL}^{-1}$.

trophotometer (Shimadzu UV-160) at $\lambda_{max}=300 \text{ nm}$ with a calibration curve based on the Beer-Lambert law. The degradation efficiency (X) of TYL antibiotics was obtained at any time, according to [30-35]:

$$X = [TYL]/[TYL]_0 \quad (5)$$

2. Analysis Method

In a previous study the UV-Vis absorption spectra of TYL were studied using an UV-Vis spectrophotometer at different times of UV/nano Ag/ $S_2O_8^{2-}$ process, under condition of catalyst concentration 0.01 gL^{-1} , oxidant concentration 2 mM , $pH_0=3.1$, $T=25^\circ\text{C}$ and UV=30 W. As presented in Fig. 1, the absorption band relating to λ_{max} of Tylosin ($\lambda_{max}=300 \text{ nm}$) is decreased with respect to time. In this study the absorbance decrease at 300 nm was measured to follow the elimination of TYL.

RESULTS AND DISCUSSION

In general, results showed that degradation efficiency was not considerable when using peroxydisulfate alone, UV alone and nano Ag/ $S_2O_8^{2-}$ (Fig. 2). Studies revealed that increases in temperature and in the initial concentrations of peroxydisulfate and nano Ag up to 2 mM and 0.01 gL^{-1} respectively, enhanced pollutant degradation. Detailed information of the operational parameters is presented below.

1. Influence of pH

The pH value of the solution is an important factor that affects the decomposition of TYL in the UV/nano Ag/ $S_2O_8^{2-}$ system. To observe the effect of pH on the degradation of TYL, experiments were carried out at pH 3.1, 5.1, 6.1, 7.3 and 8.0 at the experiment condition of $[S_2O_8^{2-}]_0=2 \text{ mM}$, $[TYL]_0=50 \text{ mgL}^{-1}$, $[nano \text{ Ag}]_0=0.01 \text{ gL}^{-1}$, $T_0=25^\circ\text{C}$ (UV=30 W). As shown in Fig. 3, increasing the pH value would result in more TYL remaining in aqueous solutions. That is, the degradation rate of TYL decreased with the increase of pH value. The results showed that the k_{qp} of TYL degradation was significantly influenced by the pH value of solutions. As shown in Fig. 3, the degradation of TYL by peroxydisulfate could even be performed in alkaline solutions at pH of 8.0, although the reaction rate was lower than that in acidic condition. This result is much more practical in field application. Generally speaking, the pH values of soil and groundwater are between 5 and 9. Furthermore, most oxidants reported in the literature for the degradation of organic pollutants are either less effective or not effective under alkaline conditions.

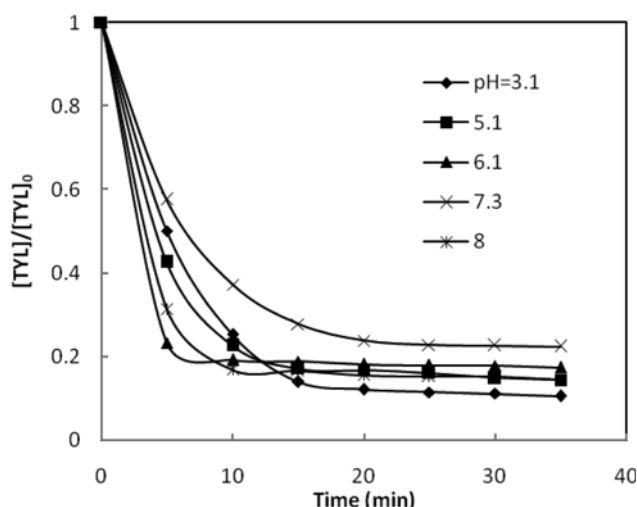


Fig. 3. Plot of $[TYL]/[TYL]_0$ at different initial pH values; UV=30 W, $[S_2O_8^{2-}]_0=2$ mM, $[TYL]_0=50$ mgL⁻¹, $T_0=25$ °C, $[nano Ag]_0=0.01$ gL⁻¹.

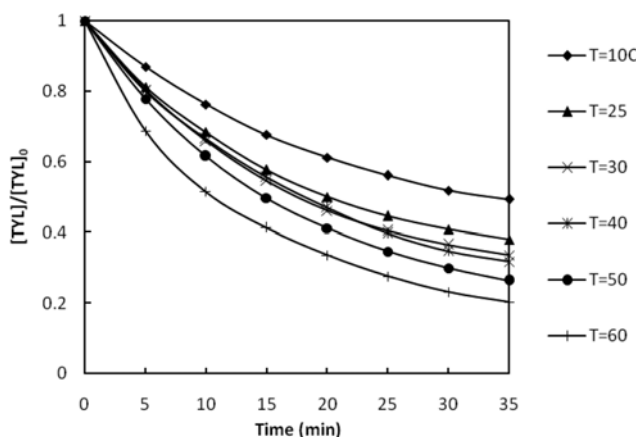


Fig. 4. Plot of $[TYL]/[TYL]_0$ at different temperatures; UV=30 W, $[S_2O_8^{2-}]_0=2$ mM, $[TYL]_0=50$ mgL⁻¹, pH_0 =natural, $[nano Ag]_0=0.01$ gL⁻¹.

Therefore, peroxydisulfate could be used in remediation of soil and groundwater contaminated with TYL in a wider range of pH values [36].

2. Influence of Temperature

Temperature is a key parameter impacting the reaction rate. To define the influence of reaction temperature on the degradation of TYL a series of experiments were put into practice by varying temperature. The results are in Fig. 4. It is shown that the rate of degradation of TYL increased with rise of reaction temperature from 10 °C to 60 °C. Eventually, it is worth mentioning, increasing the temperature based on Eq. (1) to Eq. (3) amounts of sulfate radical will be increased. Consequently, this multiplication in sulfate radicals results in more TYL removal performance.

3. Influence of Peroxydisulfate Concentration and Nano Silver Dosage

Effect of peroxydisulfate concentrations (1.0-10.0 mM) on the degradation of TYL was studied at the initial peroxydisulfate concentrations of 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mM, with initial TYL

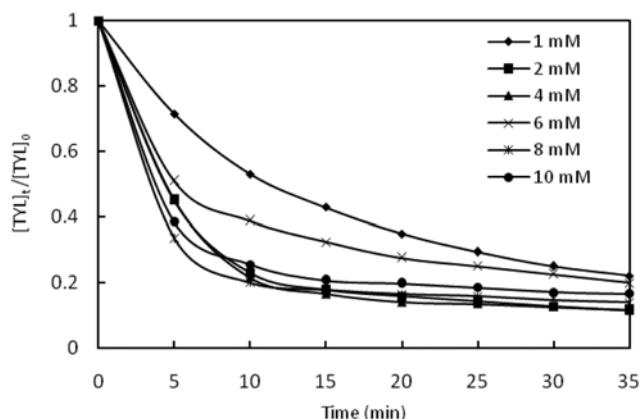
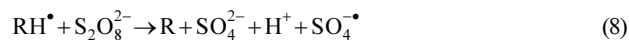
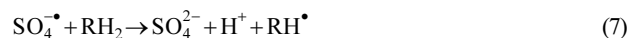


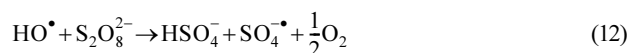
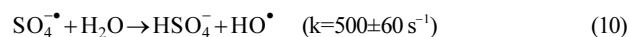
Fig. 5. Effect of peroxydisulfate concentration on the degradation of TYL; UV=30 W, $[TYL]_0=50$ mgL⁻¹, pH_0 =natural, $T_0=25$ °C, $[nano Ag]_0=0.01$ gL⁻¹.

and nano Ag concentrations of 50 mgL⁻¹ and 0.01 gL⁻¹, respectively, at room temperature (25 °C). The degradation rate of TYL increased with increase in the peroxydisulfate concentration from 1.0 to 2.0 mM at natural pH (Fig. 5) and a slight decrease was observed at higher than 2.0 mM concentrations. The increased rate of degradation of TYL with addition of peroxydisulfate may be explained as follows: the peroxydisulfate can trap the photogenerated conduction band electrons, and generate strong oxidizing SO₄²⁻ according to the following reaction (Eq. (2)) [37].

Sulfate radical anion (SO₄^{•-}) is a very strong oxidant that engages in at least three reaction modes with organic compounds: by abstracting a hydrogen atom from saturated hydrocarbon, by adding to unsaturated or aromatic hydrocarbon and by removing one electron from carboxylate anions and from certain neutral molecules. Sulfate radical anion is also generated thermally or photolytically and can participate in reactions with the solvent, according to the following scheme [37-39]:



Also, the available oxidants in the solution and its related intermediates were indicated in the following reactions [37-39]:



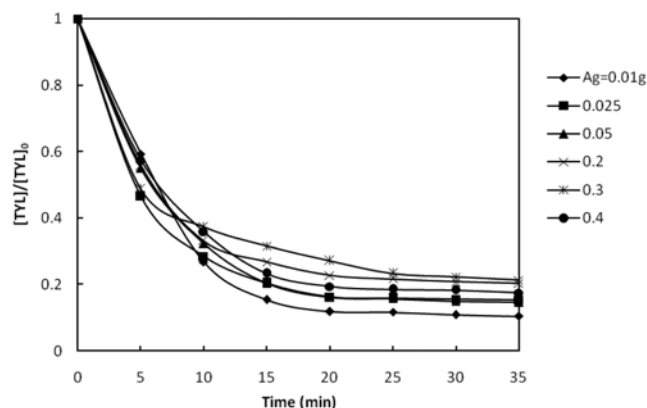
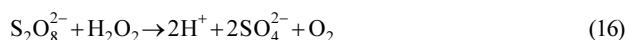


Fig. 6. Effect of nano Ag dosage on the degradation of TYL; UV=30 W, $[S_2O_8^{2-}]_0=2$ mM, $[TYL]_0=50$ mgL $^{-1}$, pH $_0$ =natural, T $_0$ =25 °C.



In addition, other aspects related to the mechanism of $HO_2^{\bullet}/O_2^{\bullet-}$ species could be found in recent papers [39,40]. To further confirm the role of immobilized nano silver in the UV/nano Ag/ $S_2O_8^{2-}$ system, we investigated the concentration of nano silver in aqueous solution at neutral pH. Fig. 6 shows the trend of nano silver in the different loadings in the UV/nano Ag/ $S_2O_8^{2-}$ system. The loading of nano silver was in the range of 0.01-0.40 gL $^{-1}$. As it can be observed from Fig. 6, by addition in amount of loading nano silver dosage, the remaining TYL in aqueous solution was increased, except for the 0.4 gL $^{-1}$ of nano silver dosage. When the amount of nano silver was 0.40 gL $^{-1}$, the degradation of TYL decreased.

4. Kinetic Study

The kinetic degradation of TYL was investigated under UV/nano Ag/ $S_2O_8^{2-}$ process under conditions of $S_2O_8^{2-}$ 2 mM, 0.01 gL $^{-1}$ nano silver, initial natural pH, up to 35 min of the degradation process for the temperature range of 10-60 °C. Here, a preliminary power law kinetic model was chosen for modeling the experimental data, as [31-35]

$$r = -\frac{dC}{dt} = kC^n \quad (16)$$

and was employed for correlating data, where r , t , k and n are the rate of degradation, time, rate constant and order of the reaction, respectively. As it is well known, the rate constant is related to temperature by Arrhenius equation:

$$k = k_0 e^{-E_a/RT} \quad (17)$$

where k_0 , E_a and R are frequency factor, activation energy and the universal constant of gases, respectively. Combining Eqs. (16) and (17) and applying logarithmic function leads to:

$$\ln r = \ln k_0 - \frac{E_a}{R} \frac{1}{T} + n \ln [C] \quad (18)$$

The differential method of analysis, based on the data of concentration versus time, was used to find the rates. Seven temperatures of 10, 20, 25, 30, 40, 50 and 60 °C (around ambient temperature) were considered. The goodness of fit in agreement with Eq. (18) is

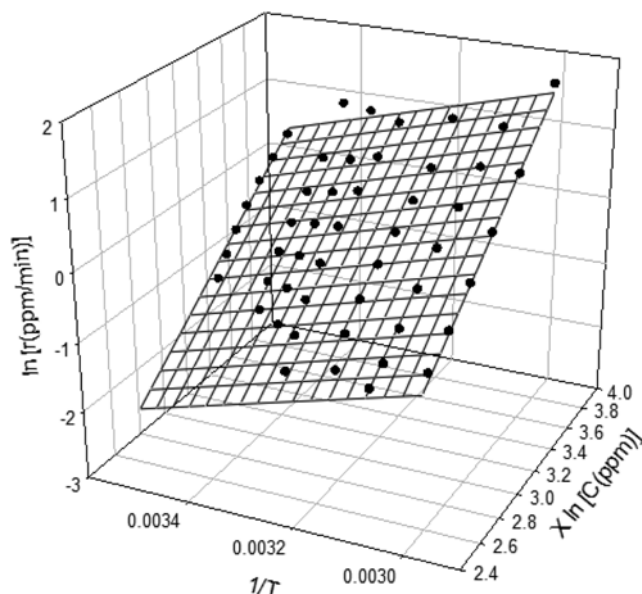


Fig. 7. Correlation diagram for experimental kinetic data; z , x and y are $\ln r$, $\ln C$ and $1/T$ respectively; $[TYL]_0=50$ ppm, $[S_2O_8^{2-}]_0=2$ mM, pH=3.1, $[nano Ag]_0=0.01$ gL $^{-1}$.

shown in Fig. 7. In this figure experimental data are marked with bold dots and the fitted 3D equation with a meshed plane. Variables z , x and y are attributed to the $\ln r$, $\ln C$ and $1/T$, respectively, and from the coefficients of a , b and c , kinetic parameters can be obtained. The estimated coefficient of determination (R^2) for this fitting is 0.9554. The kinetic parameters appropriate to UV/nano Ag/ $S_2O_8^{2-}$ process, i.e., activation energy and reaction order, are 17.222 kJ/mol and 1.8897, respectively.

CONCLUSION

The following conclusions could be obtained based on the above investigations:

- (i) Using heterogeneous UV/nano Ag/ $S_2O_8^{2-}$ process, a 90.9% degradation of TYL under the optimum condition (UV=30 W, 50 mgL $^{-1}$ of TYL, peroxydisulfate 2 mM, 0.01 gL $^{-1}$ nano silver, natural pH and temperature of 25 °C) can be achieved during about 35 min.
- (ii) The use of very low energy consumption UV light source can lead to efficiency improvement of the oxidation process in degradation of TYL.
- (iii) A power law kinetic model can describe the degradation rate of the used processes adequately well.
- (iv) Hybridizing UV/ $S_2O_8^{2-}$ and nano silver processes under the natural initial pH will lead to an effective new process of UV/nano Ag/ $S_2O_8^{2-}$ with promising results in degradation (more than 90% in 35 min) of TYL.

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