Application of Ultraviolet Light-Emitting Diodes to the Removal of Cefixime Trihydrate from Aqueous Solution in the Presence of Peroxydisulfate

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Abstract

The present research involves effectual parameters on Cefixime trihydrate removal from aqueous solutions. Antibiotics are the main contributions in pharmaceutical waste; their presence causes major concern. The extensive utilization of antibiotics in aquaculture and prescriptions has led to the cultivation of various antibiotic-resistant bacteria and genes in wastewater. The UV-LED/ $S_2O_8^{2-}$ process, one of the most widely (AOPs), is an effective method for industrial wastewater treatment. Sixteen experiments were required to study the effect of parameters on UV-LED/ $S_2O_8^{2-}$ removal of the drug. Each experiment was repeated three times)n=48) to calculate the mean of average. Outcomes revealed that among different parameters, peroxydisulfate concentration was the most efficient one. Based on the mean of average, optimized condition for drug removal was temperature of 50∘C, current intensity of 1800 mA, drug concentration of 10 ppm, peroxydisulfate concentration of 120 mM and 30 min for time. Consequently, 91.79 percent of drug degradation was achieved via optimum conditions.

Keywords: *Cefixime Trihydrate, UV-LEDs, Peroxydisulfate, Photoreactor, Taguchi method, Advanced Oxidation Processes (AOPs).*

Introduction

The presence of pharmacy residuals in aquatic environment has been increasing apprehension recently [1,2]. The extensive utilization of antibiotics in aquaculture and prescriptions has led to the cultivation of various antibiotic-resistant bacteria and genes in wastewater [3]. Bacteria, once acquired antibiotic-resistant

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gene, may exist in the aquatic environment for a long time [4]. Pharmacy wastewater as mentioned above aspects of insurmountable problems which is belonging to antibiotics working, explanation and also experimental research about these medicinal materials is subtle yet intricate.

Additionally, pharmaceutical wastewater is one of the most imperative kinds of wastewater in viewpoint of environmental aspects because of their multi-dimensional impact into human life. Some of the antibiotic-resistant bacteria, even not pathogenic, have the ability to transfer their resistant gene to human pathogens [5,6] Which pose a great potential risk to human health. Deficiency of the proper management of that causes grave environmental problems. Consequently, management contiguous to treatment of pharmaceutical wastewater is the furthermost issue. Antibiotics are the main contributions in pharmaceutical waste; their presence causes major concern. A vast majority of procedure has been considered as an effective route for degradation of these kinds of pollutant such as membrane process, filtration, biological treatment, adsorption and etc [7-11].

Over the past few decades, studies have been conducted on new technologies known as Advanced Oxidation Processes (AOPs), which have been proven highly effective in the oxidation of organic and inorganic pollutants [12]. Most AOPs are based on the generation of HO• radicals in the medium which follow from traditional methods to newly scrutinize biological modus operandi [13-16]. AOPs are highly versatile, since many systems are able to generate these radicals [17]. Alternatively, it is also possible to form other types of highly oxidizing radicals, such as the sulfate radical ($SO4^{\bullet-}$), which can also react with organic compounds .The UV-LED/$S_2O_8^{2-}$ process, one of the most widely (AOPs), is an effective method for industrial wastewater treatment and also in pharmacy wastewater industry. The more attention to peroxydisulfate originates from some trait for instance, high oxidant ability, no selectivity reaction able, stability, solubility and low-cost. Additionally, producing safe byproduct and active sulfate radical causes high rate degradation of pollutant introduced peroxydisulfate as an effectual oxidant in (AOPs) [18-21].

$$S_2O_8^{2-} + h\upsilon \rightarrow 2SO_4^{\bullet-} \tag{1}$$

$$SO_4^{\bullet-} + RH_2 \rightarrow SO_4^{2-} + H^+ + RH^{\bullet} \tag{2}$$

$$RH^{\bullet} + S_2O_8^{2-} \rightarrow R + SO_4^{2-} + H^+ + SO_4^{\bullet-} \tag{3}$$

$$SO_4^{\bullet-} + RH \rightarrow R^{\bullet} + SO_4^{2-} + H^+ \tag{4}$$

$$2R^\bullet \rightarrow RR(\text{dimer}) \tag{5}$$

$$SO_4^{\bullet-} + H_2O \rightarrow HSO_4^- + OH^\bullet \tag{6}$$

$$HSO_4^- \rightarrow H^+ + SO_4^{2-} \tag{7}$$

$$OH^\bullet + S_2O_8^{2-} \rightarrow HSO_4^- + SO_4^{\bullet-} + \frac{1}{2}O_2 \tag{8}$$

An efficient photo oxidation reactor demands an effective illumination source [22]. Desirable factor for a light source for photo oxidation applications includes high irradiance; high energy efficiency, appropriate wavelength, and ruggedness coupled with a long useful lifetime. However, especially the utilization of UV-lamps, which are typically based on continuous mercury vapor, has shown to be disadvantageous. They are unstable due to overheating, have low mechanical stability, low photonic efficiency and relatively short lifetime, need high voltages to operate, and contain toxic mercury [23-25].

Considering new light-emitting diodes (LEDs), laser light was assumptive as viable light sources for photo mineralization and photo oxidation goals [26]. By using a semiconductor p-n junction device which emits light in narrow spectrum, produced by a form of electro luminescence. It needs no special circuit like conventional UV lamps and can be programmed to automatically switch on and off at definite time intervals [27-29]. Consequently, LED is a diode to make ultraviolet radiation combining electron and block on two surfaces of semi conductive materials. In conventional system of light radiation, most of energy changed to thermal but in LEDs, most of received energy is converted to light. As other pros of LEDs, they are programmable for alternative radiation, small structure, stability, longevity and increase of photon yield. In at hand work, LEDs were chosen as an ultraviolet source due to the above mentioned points [30-33].

Herein we represent a step forward comparing homogeneous photooxidative degradation of Cefixime trihydrate under LED light and the main objective of this study is to analyze the feasibility mineralization of Cefixime trihydrate by LED/$S_2O_8^{2-}$ processes. The influence of different operational parameters (drug concentration, current intensity, persulfate concentration, time and temperature) that affect the efficiency of homogeneous photooxidation processes were studied by Taguchi method. On the whole, the combination of homogeneous process and LED technology is hypothesized to decrease

the operational costs and increase the energy efficiency of wastewater treatment processes.

Experimental

Materials and methods

The antibiotic used in this study was Cefixime trihydrate (Tehran Chemie Company) and its structure is shown in Figure 1.
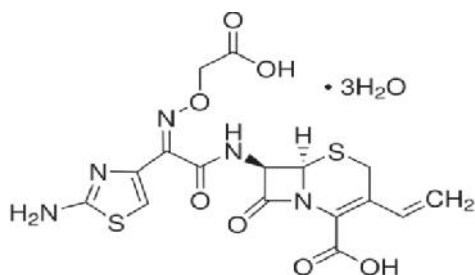

Figure 1. Structure of Cefixime trihydrate.

The absorbance was measured by a double beam spectrophotometer (Shimadzu UV-160, Japan) at maximum absorption wavelength number of 288(λ max =288 nm). The effectiveness of drug removal was expressed as the percentage ratio of degradation drug concentration to that of initial one [34]. Potassium peroxydisulfate applied in this process as an oxidant (Merck, 98%). TO-18 LEDs were manufactured by Seoul Optodevice Co., Ltd., and the power of each LED was 1 W. After electrical connection, the LEDs were put into plastic covers. In order to increase the longevity of LEDs, a novel cooling system was designed using an aluminum radiator and an appropriate connection to transfer the heat from LEDs to the radiator (Figure 2). UV-LEDs and cooling system were attached with a 5-cm clamp above the beaker. Current and voltage was adjusted by a DC power supply with galvanostatic operational options (Figure 3).
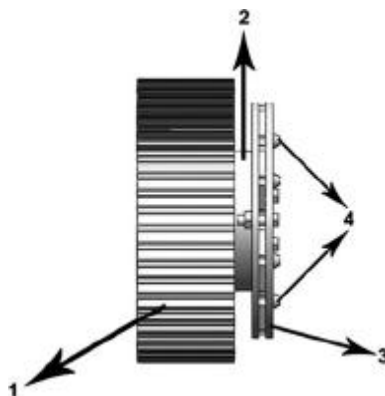

Figure 2. Schematic drawing of LEDs and cooling system: (1) aluminum radiator; (2) transfers the heat from LEDs to the radiator; (3) LEDs; (4) plastic cover.
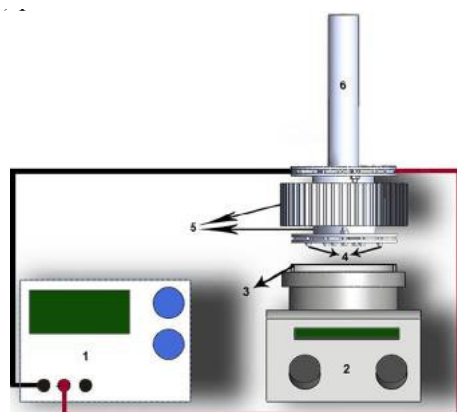
Figure 3. Schematic drawing of a batch reactor: (1) DC power supplier; (2) magnetic stirring; (3) beaker; (4) UV light-emitting diodes; (5) cooling system; (6) clamp.

Batch degradation process

The experiment was conducted in 100ml beaker containing a Cefixime Trihydrate concentration (10-40 ppm), oxidant concentration (0-120 mM (, in the presence of UV intensity (0-1800 mA) during (10-40 min) in various temperatures (10-50° C).

Orthogonal array and operational factors

Taguchi method has been found helpful by means of improved productivity, which brings along obtaining high quality items at low costs. In addition, this method was found appropriate for a wide range of industrial fields all over of the world [35-37]. Taguchi is the preferable technique among statistical experimental design methods [38] since it uses a special design of an orthogonal array (OA) to study the entire parameter space with few numbers of experiments. To analyze the significance of five factors at four different levels, a full factorial experimentation would require 4^5 (=1024) experiments to find the influencing parameters, while the Taguchi design involves only sixteen experiments using OA L_{16} (4^5) [39]. In present study, Cefixime trihydrate destruction from wastewater has been investigated. The effect of operational parameters such as drug concentration, peroxydisulfate concentration, intensity current, temperature and time of reaction in photo reactor were surveyed using an L_{16} (OA). The conventional approach of experimenting with one variable (or one factor) at a time is labor-intensive and time consuming. Based on our previous work from drug degradation of system the main operating parameters and their levels were selected and showed in Table 1.[40] The orthogonal array of L_{16} type was used, and is represented in Table 2. L and 16 means Latin square and the replication number of the experiment, respectively. Five–four level factors can be positioned in an L_{16} orthogonal array table. The number in table indicates the levels of a factor [41].

Table.1. Parameters and their values corresponding to their levels to be studied in experiments**.**

Parameter	Levels of desige of experiment			
	1	2	3	4
A: Drug concentration (mg.L^{-1})	10	20	30	40
B: current intensity (mA)	0	450	725	1800
C: Persulfate concentration(mM)	0	30	80	120
D: Time (min)	10	20	30	40
E: Temperature (°C)	25	10	30	50

Table 2. Experimental layout using the L$_{16}$ orthogonal array.

Experimental	A	B	C	D	E	Drug degradation=$\frac{A_0-A_t}{A_0}\times100$ **(%)**			
						1	2	3	Average (M$_i$)
1	1	1	1	1	1	0.01	0.01	0.01	0.010
2	1	2	2	2	2	35.73	35.46	34.28	33.490
3	1	3	3	3	3	92.94	85.49	84.53	78.653
4	1	4	4	4	4	89.24	100.00	86.15	91.796
5	2	1	2	3	4	78.45	60.96	71.51	70.306
6	2	2	1	4	3	10.80	10.00	10.06	10.286
7	2	3	4	1	2	30.14	32.65	26.65	29.813
8	2	4	3	2	1	53.42	54.22	51.50	53.046
9	3	1	3	4	2	3.44	1.09	2.26	2.263
10	3	2	4	3	1	61.48	50.40	52.08	54.653
11	3	3	1	2	4	0.01	1.73	1.45	1.063
12	3	4	2	1	3	15.16	14.53	12.15	13.946
13	4	1	4	2	3	27.37	28.03	26.71	27.370
14	4	2	3	1	4	21.62	25.00	27.44	24.686
15	4	3	2	4	1	18.14	18.22	18.06	18.146
16	4	4	1	3	2	1.91	1.42	0.88	1.403

Results and discussion

Determination of optimal conditions using Taguchi Method

A Taguchi method was used to identify the optimal conditions and to select the parameters having the most effective influence on the drug removal. The structure of Taguchi's L_{16} design and the results of measurement are shown in Table 2 and Table 3. In these Tables analyses of the mean of impacts factors and variance were discussed. The optimum condition of

levels of factors calculated in order to compare experiments results. The mean of each result is defined as:

$$I_i = \frac{1}{3}\sum_{i=1}^{3} T_i \qquad (9)$$

Where Ti is the characteristic property and n is the replication number of the experiment. The mean of average for each level of the parameters was summarized as average response, which was shown in Table 3.

Table 3. Analysis of variance.

parameter	degree of freedom	sum of squs	variance	F-ratio	pure sum	percent
A	3	11086.587	3695.529	268.864	11045.352	26.091
B	3	1429.947	476.649	34.678	1388.712	3.28
C	3	15463.886	5154.628	375.019	15422.651	34.431
D	3	8346.473	2782.157	202.413	8305.238	19.618
E	3	5566.979	1855.659	135.006	5525.744	13.052

To calculate the mean of average of factor A in level 2 on removal of drug:

$$M_{A_2} = \frac{1}{4}\left\{\left(I_4 + I_5 + I_6 + I_7\right)\right\} \qquad (10)$$

According to Eq. 9 and Eq. 10, the mean of each level and factor in removal percentage was computed and shown in Table 4. Fig. 4 shows the average response graph for degradation

of Cefixime trihydrate solution. Therefore the optimum condition is A1, B4, C4, D3 and E4. In other words, based on the mean of Average, the optimal parameters for drug removal are A (Cefixime trihydrate concentration), B (current intensity), C (peroxydisulfate concentration), D (time) and E (temperature) which presented in Table 5.

Table 4. Response for the Taguchi analysis of drug removal data.

Parameters	Mean of Average			
	Level 1	Level 2	Level 3	Level 4
A:Drugconcentration (mg.L^{-1})	53.237	40.836	17.981	17.901
B:Intensity current (mA)	24.981	30.779	34.169	40.048
C:Persulfateconcentration(mM)	3.19	33.972	41.912	50.908
D:Time (min)	17.114	28.742	53.504	30.623
E:Temperature (°C)	16.742	31.464	34.814	46.963

Table 5. The optimum condition for removal of drug.

parameters		
A	Level 1	10 (mg.L^{-1})
B	Level 4	1800 (mA)
C	Level 4	120 (mM)
D	Level 3	30 (min)
E	Level 4	50 (°C)

UV– Vis spectrum

Figure 4 shows a typical time-dependent UV–Vis spectrum of Cefixime Trihydrate solution during UV/S2O82- degradation. The absorbance peaks, corresponding to drug, diminished, which indicated that the drug had been removed. The spectrum of Cefixime trihydrate solution in the ultraviolet region exhibits a main peak with a maximum at 285nm. The decrease of the absorbance peak of Cefixime trihydrate at λ max = 288 nm in this figure indicated a rapid degradation of drug in optimum condition. Meanwhile, to measure the electric energy consumption in optimal conditions using equation (1) was calculated and obtained 140 KWh.m3-:

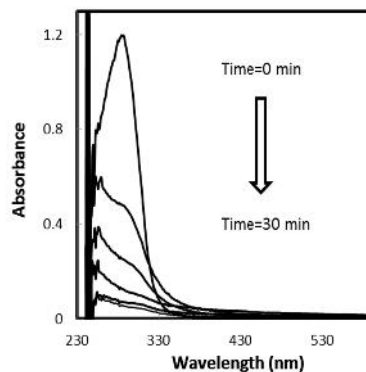$$E_E = \frac{1000 \times P \times t}{60 \times V \times \log(C_i / C_f)} \quad (1)$$

Figure 4. Spectral changes of [*Cefixime Trihydrate*] =10 ppm, [S$_2$O$_8^{2-}$] = 120mM, temperature= 50°C, intensity=1800 mA.

Effect of efficient parameters

As it can be seen in Figure 5, the higher the drug concentration is, the lower the degradation rate will be achieved. One possible

reason may be that as the drug concentration increases, the hydroxyl radical to drug ratio decreases and the process efficiency reduce. Furthermore, since the rate of photolysis of $S_2O_8^{2-}$ is strongly dependent on the UV light, it appears that by increasing the current intensity the removal rate increases. This increase is due to the enhanced production of hydroxyl and sulfate radicals. By low UV power, the rate of photolysis of $S_2O_8^{2-}$ is limited, and at high UV power, more hydroxyl and sulfate radicals are formed upon the photo dissociation of $S_2O_8^{2-}$, hence, removal rate increases. As well as heat is known as significant factors to catalyst of Advanced Oxidation reactions.

Recent researches have shown that peroxydisulfate activated by thermal is effective in oxidation of 59 unstable organic compounds, including Ethyl benzene, Xylene, Toluene, chlorinated solvents. Increasing temperature according to Arrhenius equation leads more efficient drug degradation with a lower activation energy and conversion of peroxydisulfate ions to stranger oxidant sulfate radicals [42]. Studies revealed that increase in the amount of $S_2O_8^{2-}$ leads to enhanced removal percentage around 80-100% in optimal condition, which is in accordance with previous studies that used conventional UV lamps [43]. The observation may be explained by the fact that by increasing the peroxydisulfate concentration, more hydroxyl and sulfate radicals are generated.
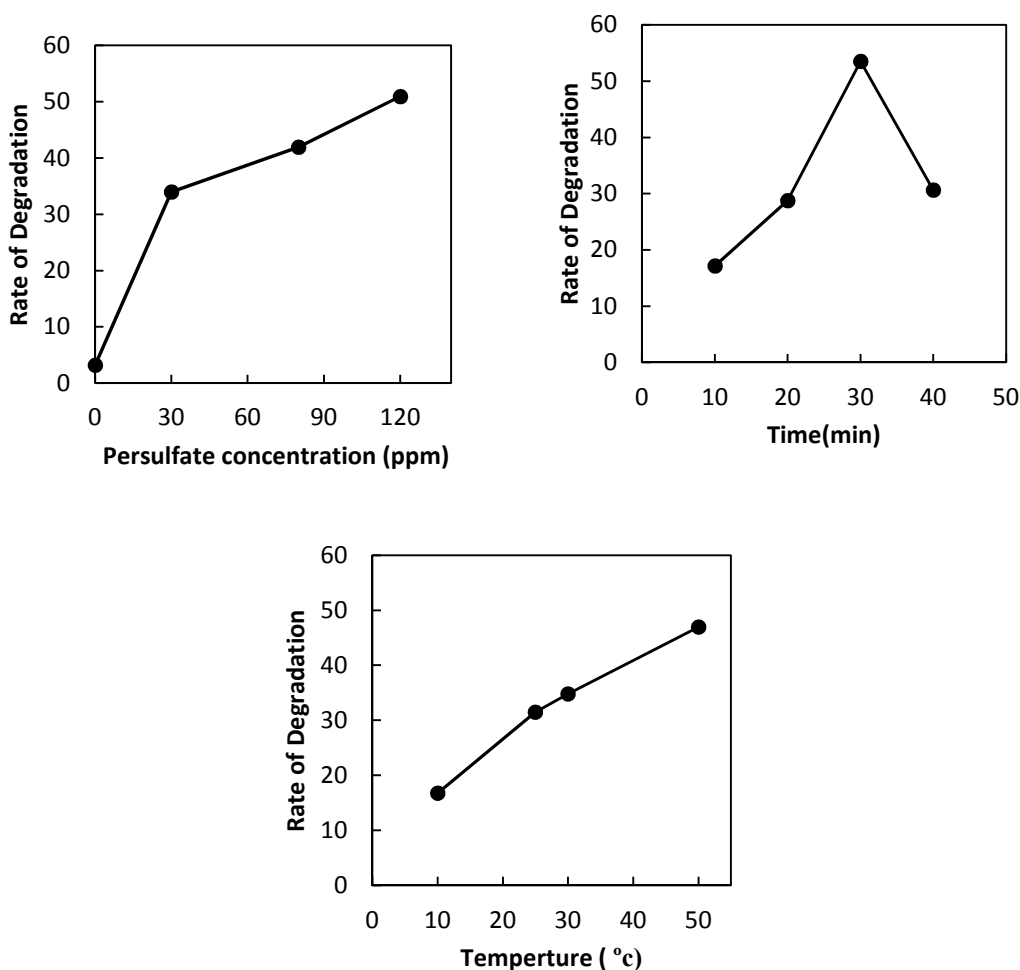
$$S_2O_8^{2-} \xrightarrow{h\upsilon/heat} 2SO_4^{\bullet-} \quad (11)$$
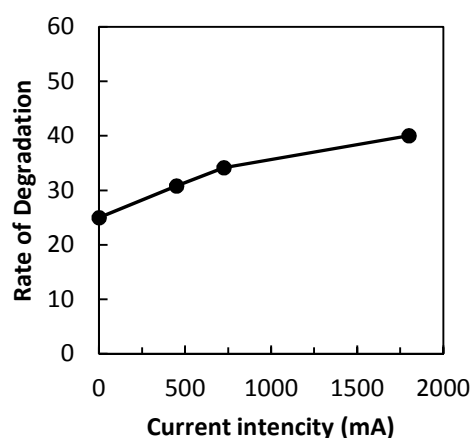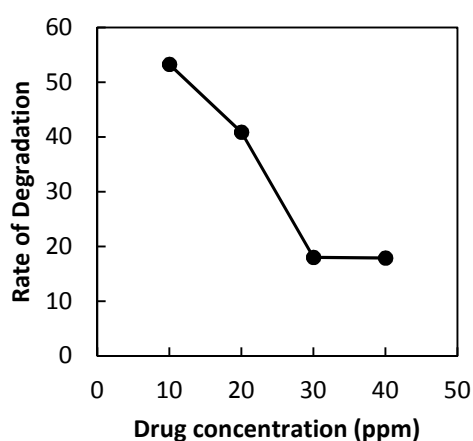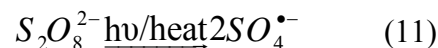
Figure 5. Effect of each parameter on drug removal.

Conclusion

The results in this study indicated that the utilization of Taguchi method was suitable for optimization of UV/S$_2$O$_8^{2-}$ degradation. The destruction was dependent on the drug concentration, current intensity, peroxydisulfate concentration, time and temperature. The most effective parameter for drug removal in comparison with other operational factors was C (peroxydisulfate concentration) at level 4. As a result, 100 percent of drug degradation was accessed in optimum conditions.

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