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Photochemical Degradation of 2,4-dichlorophenol in Aqueous Solutions by Fe^{2+}/ Peroxydisulfate/ UV Process

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A B S T R A C T

Phenol and its derivatives are one of the most common contaminants in the aquatic ecosystem. Because of high toxicity of 2,4-DCP for aquatic life, resistance to biodegradation and potential for biological accumulation it is known as a priority contaminant in the aquatic environment. Advanced Oxidation Processes were successfully used for degradation of non-biodegradable contaminants that are resistant to conventional treatment processes. So, it would be interesting that advance oxidation technologies was used which apply such effective radicals as radicals (SO_4). In present study, effects of concentrations of 2,4-DCP, Fe^{2+}, peroxydisulfate (PDS) and pH value were investigated on the 2,4-DCP photochemical degradation efficiency. The increase of pH value negatively influenced the removal efficiency and reaction rate constant while an increase in the Fe^{2+} and (PDS) concentrations increased both the removal efficiency and reaction rate constant. In addition, the reaction rate constant increased linearly with increasing (PDS) concentration. In this study, in general, PDS was found as the most effective factor on the degradation of 2,4-DCP by Fe^{2+}/PDS/UV.

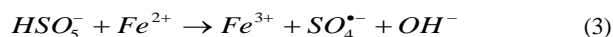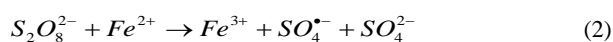*doi: 10.5829/idosi.ije.2017.30.01a.03*

1. INTRODUCTION

The increasing need for reliable and safe water resources resulted in a significant development in water and wastewater treatment technologies. Research and development in the field of water and wastewater treatment have developed rapidly during the recent decade, mainly due to increasing public health concerns and more stringent regulations on the treatment and disposal [1]. Recently, Advanced Oxidation Processes (AOPs) were successfully used for degradation of non-biodegradable contaminants that are resistant to conventional treatment processes [2, 3]. In the AOP processes, the objective is the production of reactive hydroxyl radicals ($^\bullet OH$) which are suitable for rapid and non-discrimination reactions with organic compounds [4]. In recent years, processes based on Fenton (Fenton (F), electro-Fenton (EF), UV/Fe^{2+}/

H_2O_2, US/Fe^{2+}/ H_2O_2, UV/US/ Fe^{2+}/H_2O_2, etc.), have been successfully used for wastewater treatment [5].

According to the recent studies, reactive sulfate radicals ($SO_4^{\bullet-}$) can be considered as a suitable alternative for $HO^\bullet$ radicals because of their high reaction power. Reduction power of the $SO_4^{\bullet-}$ radical (2.5 to 3.1 V) considerably is higher than reduction power of $HO^\bullet$ radical (1.8 to 2.7 V), that is more appropriate for the oxidation of organic contaminants in a wide pH range. Moreover, $SO_4^{\bullet-}$ radical has a longer half-life than the $HO^\bullet$ radical, hence $SO_4^{\bullet-}$ radical has a higher ability than $HO^\bullet$ radical to transfer electron in reaction with the organic material [6]. In general, $SO_4^{\bullet-}$ radical can be generated through the activation of peroxymonosulfate (PMS) or peroxydisulfate (PDS) ions with transition metals, heat, UV or ultrasonic waves [7]. Activation of PDS or PMS is like the classic Fenton reactions in that both can be activated by ferrous ion and other transition metal, via Equations (1)-(3) [8, 9].

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

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet -} + SO_4^{2-} \qquad (2)$$

$$HSO_5^- + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet -} + OH^- \qquad (3)$$

In these reactions, in general, metallic catalysts are used as homogeneous and heterogeneous catalysts. Homogeneous catalysts are usually more efficient than heterogeneous catalysts because in the homogeneous catalysts every catalytic entity can be as a reaction site. Thereby, this characteristic makes the homogeneous catalysts more active and effective than heterogeneous catalysts [10]. In past studies, $SO_4^{\bullet -}$ radical has been used to degrade of bisphenol in the process of electro/Fe^{3+}/PDS [11], degradation of acid orang 7 by the TiO_2/PMS [6], degradation of volatile organic compounds with thermally activated persulfate oxidation [12] and decomposition of perfluorocarboxylic acids using microwave-induced persulfate [13].

Every year we are facing with an increase in the environmental pollutants. The problem is caused due to excessive arrival of wastes from the oil industries, refineries, wood and paper plants and other industries. Phenol and its derivatives are one of the most common contaminants in the aquatic ecosystem. chlorophenols (Mono, di and tri-chlorophenols) are created from combination of chlorine and phenol. Disinfection of water, including natural organic compounds, using chlorine is reason for the formation of chlorophenols [14-16].

2,4-diclirophenol (2,4-DCP) is one of these compounds. In the industries it was used as intermediate compound for the production of many products such as pesticides (i.e., 2,4-dichlorophenoxyacetic acid) and wood preservative. Presence of 2,4-DCP in the aquatic ecosystem may be as a result of disinfection of water and wastewater industrial, and discharge of municipal, agricultural and industrial wastes in the environment [16]. Because of high toxicity of 2,4-DCP for aquatic life, resistance to biodegradation and potential for biological accumulation it is known as a priority contaminant in the aquatic environment, with a health guideline of $0.5 \mu g / l$ in the drinking water. It has been observed when human and animal be exposed to the 2,4-DCP, it could be led to permanent disorder of vision or blindness, severe damage to eye and upper respiratory tract. Therefore, the harmful effects of 2,4-DCP in the water resources, rivers and coastal ecosystems are a significant concern [17, 18].

The chlorophenolic compounds can be treated by biological processes and adsorption onto solids [19, 20]. However, biological treatments can be affected by the toxicity of some substances and an adsorption process

requires a post-treatment to remove the pollutants from the newly contaminated environment. So, it can be favorable to use advanced oxidation processes which have effective radicals such as $SO_4^{\bullet -}$ radicals as a suitable method to provide an almost total degradation. Such an advantage has been reported by Shiying et al. [21] and Liang et al. [22] in the decomposition of organic contaminants. However, in this study degradation of 2,4-DCP by Fe^{2+}/PDS process was investigated in presence UV radiation. The effects of different variables including concentrations of 2,4-DCP, Fe^{2+}, peroxydisulfate (PDS) and pH value were investigated on the 2,4-DCP photochemical degradation efficiency. Also, the synergetic effect of different systems on the degradation of 2,4-DCP were investigated.

2. MATERIAL AND METHODS

2. 1. Chemicals   The 2,4-DCP, Sodium peroxydisulfate ($Na_2S_2O_8$, 99%), ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and ethyl acetate were purchased from Merck Company (Germany). A low pressure UV lamp (254 nm) with nominal power of 9W was purchased from Philips Company. The other equipment was from Merck Company. 2,4-DCP stock solution was made by dissolving 1 g 2,4-DCP crystal in one liter of distilled water, also $Na_2S_2O_8$ and $FeSO_4 \cdot 7H_2O$ solutions were made using distilled water, then all the solutions were stored at 4 ° C.

2. 2. Experimental Set Up   All experiments were carried out in a 400 ml jacketed thermostatic photo reactor (diameter 5 cm and height 20 cm,) equipped with a low pressure UV lamp inside a quartz jacket (diameter 3 cm) placed in its center (Figure 1).The lamp emits radiation basically at 254 nm. The reactor was equipped with a magnetic stirrer to provide suitable mixing for solution.
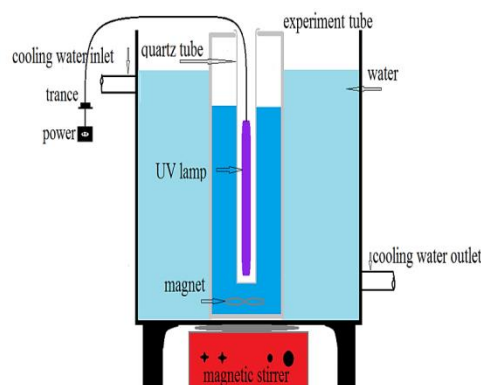

Figure 1. Schematic diagram of the experimental set-up

All the reactions were conducted at atmospheric pressure. The temperature was fixed at 25 ± 0.5 °C by circulating water from a thermostatic bath. All the experiments were carried out in batch mode.

The following parameters were investigated as factors influencing the removal efficiency of 2,4-DCP in Fe^{2+}/PDS/UV process; pH (3, 4, 5, 6, 7 and 8), Fe^{2+} (0.25, 0.5, 1 and 2 mM), PDS (2, 4, 8, 12 mM) and 2,4-DCP (50, 100, 150, 250 and 300 mg/l). In each experiment a 2,4-DCP solution 50 mg/l was prepared. To prepare reaction solution, $Na_2S_2O_8$ and $FeSO_4.7H_2O$ solution were added into 2,4-DCP solution 50 mg/l to reach volume of 200 ml and pH_0 was set with adding NaOH (0.1 M) or H_2SO_4 (0.1 M) solutions and was monitored using a portable device (Aqualytic AL15).

2. 3. Analysis   The 2,4-DCP was extracted by adding ethyl acetate as an extraction solvent to determine the 2,4-DCP concentration at 286 nm using an UV–visible spectrophotometer (DR 5000) [23].

2,4-DCP removal efficiency was calculated according to the following equations:

2,4-DCP removal efficiency $(\%): \dfrac{A_0 - A}{A_0} \times 100$, where

the A_0 and A were the absorbance of the sample at time 0 and t, respectively.

3. RESULTS AND DISCUSSION

3. 1. Kinetic Studies   Pseudo-first order kinetic:

$$\ln C_t = -k_1 t + \ln C_0 \qquad (4)$$

Pseudo-second order kinetic:

$$1/C_t = -k_2 t + 1/C_0 \qquad (5)$$

where (k_1, k_2) are pseudo-first order rate constant and pseudo-second order rate constant, C_t is the concentration of 2,4-DCP during reaction, C_0 is the initial concentration, and t is the reaction time [24]. Kinetics of degradation for the Fe^{2+}/PDS/UV process in different concentrations of PDS was shown in Figure 2 a, b where (a) and (b) are pseudo-first order and pseudo-second order kinetics, respectively. The results of rate constants (k_1, k_2) and correlation coefficient (R^2) for 2,4-DCP degradation kinetics were presented in Table 1. Pseudo-second order rate constant was used to calculate rate destruction of 2,4-DCP, because it has the highest correlation coefficient (R^2).

3. 2. Degradation of 2,4-DCP under Different Systems   To study the degradation of 2,4-DCP in different systems, different experiments were conducted using the optimal conditions obtained from this study: PDS alone, Fe^{2+} alone, UV alone, PDS/UV, Fe^{2+}/PDS, evaporation of 2,4-DCP and Fe^{2+}/PDS/UV process in the 2,4-DCP concentration 50 mg/l (Figure 3).
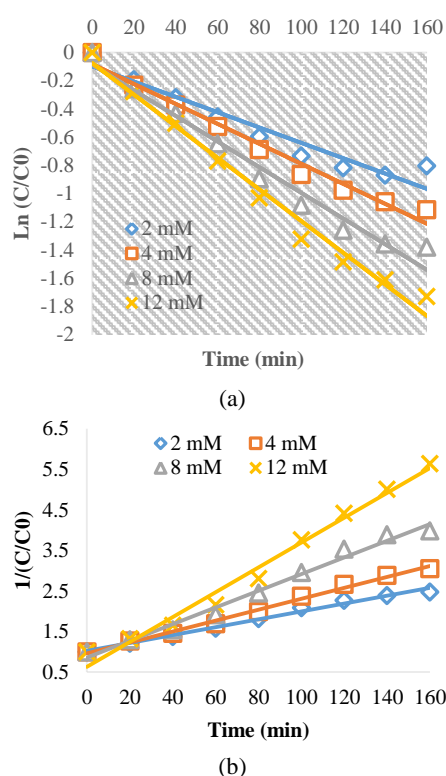

Figure 2. Kinetics of 2,4-DCP degradation; (a) pseudo-first order plot and (b) pseudo-second order plot, in various PDS concentration and Fe^{2+} 1 mM and 2,4-DCP concentration 5 mg/l in presence of UV radiation

TABLE 1. Kinetic constants of degradation of 2,4-DCP

|		Pseudo-first order		Pseudo-second order	
		R^2	k (min^{-1})	R^2	k (M^{-1} min^{-1})
pH	3	0.9831	0.0054	0.9975	0.0097
	4	0.9764	0.0046	0.9941	0.0073
	5	0.9456	0.0038	0.9915	0.0061
	6	0.9581	0.0035	0.9834	0.0048
	7	0.9664	0.0033	0.9821	0.0046
	8	0.9739	0.0032	0.9967	0.0052
Fe^{2+} (mM)	0.25	0.951	0.0047	0.99	0.0075
	0.5	0.9664	0.0054	0.9975	0.0097
	1	0.9784	0.0074	0.9977	0.0133
	2	0.9782	0.0071	0.9967	0.0132
PDS (mM)	2	0.9272	0.0054	0.9878	0.006
	4	0.9784	0.0074	0.9977	0.0133
	8	0.9729	0.0091	0.9914	0.0212
	12	0.9722	0.0112	0.9977	0.0295
2,4-DCP (mg/l)	50	0.9732	0.0112	0.9977	0.0295
	70	0.9799	0.0096	0.9903	0.0222
	100	0.9626	0.0072	0.9953	0.0139
	150	0.9038	0.0013	0.9786	0.0054
	200	0.9287	0.0012	0.9397	0.0051
	300	0.8945	0.0009	0.9389	0.004
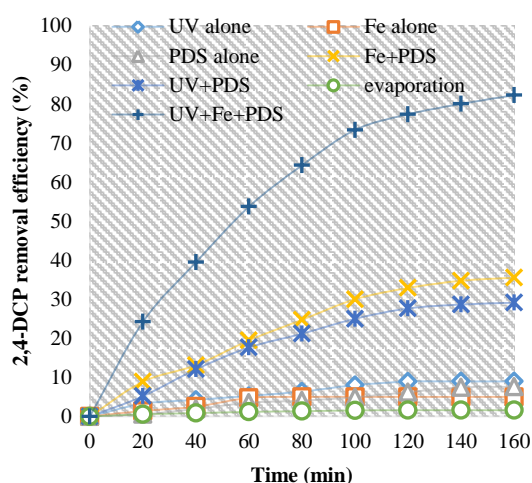
Figure 3. Degradation of 2,4-DCP in different systems at pH 3: UV alone (254 nm), Fe^{2+} alone (1 mM), PDS alone (12 mM), Fe^{2+}/PDS (Fe^{2+} and PDS; 1 and 12 mM, respectively), UV/PDS (UV (254 nm) and PDS; 12 mM), evaporation (25 ± 0.5 ^{0}C), Fe^{2+}/PDS/UV (Fe^{2+}, PDS and UV; 1 and 12 mM and (254 nm) respectively)

2,4-DCP surface evaporation was evaluated by mixing 2,4-DCP aqueous solution for 160 minutes at the same mixing conditions with other experiments. As can be seen in Figure 3, negligible removal efficiency was observed for the system. The maximum removal efficiency was obtained approximately 1.6% after 100 minutes.

Degradation of organic compounds depend on the factors such as maximum absorption of radiation by compound, wavelength, exposure time, and reaction conditions [25]. To evaluate UV effect alone on the 2,4-DCP degradation, the experiment was conducted in the presence of UV radiation (254 nm) in 160 minutes. 2,4-DCP removal efficiency (about 9%) was obtained by UV radiation (Figure 3) [26]. Poor removal efficiency (7.5%) was observed for PDS alone system as a result of limited oxidation power PDS (E_0 = 2.01 V), (Figure 3). Removal efficiency reached to 29.117% when PDS was stimulated by UV radiation (Figure 3). It indicates that UV radiation (254 nm) has a great influence on the UV/PDS system. 2,4-DCP degradation under UV/PDS system occurs due to the generation of $SO_4^{\bullet-}$ radical from PDS. In the presence of UV irradiation (254 nm), $S_2O_8^{2-}$ generates $SO_4^{\bullet-}$ radical during a direct photodissociation [27]. Removal efficiency (5%) by Fe^{2+} could be explained by adsorption of 2,4-DCP onto iron hydroxides (Fe $(OH)_2$, Fe $(OH)_3$), Fe^{2+} ion easily is oxidized and then is led to flocculation [23]. Removal efficiency enhanced when the 2,4-DCP was treated by Fe^{2+}/PDS process (Figure 3). Removal efficiency (35.52%) was obtained by the process. In addition, it showed that Fe^{2+} could react with $S_2O_8^{2-}$ to generate $SO_4^{\bullet-}$ radical via Equation (2).

The results were improved in the presence of all the components of the system (Fe^{2+}/PDS/UV) (Figure 3). Removal efficiency (82.26%) was obtained using the system (Fe^{2+}/PDS/UV) although it was conducted in a similar situation with other systems. It shows the effect of UV radiation on the improvement of 2,4-DCP degradation through an increase in the production of $SO_4^{\bullet-}$ radicals.

3. 3. Effect of the Operational Parameters
3. 3. 1. Effect of the Initial pH   It was well known that pH is one of the factors affecting on the performance of the Fe^{2+}/PDS/UV process and production of $SO_4^{\bullet-}$ radical. This effect could be included its role in controlling the catalytic activity, PDS stability and activity of iron species [28]. The effect of initial pH on degradation of 2,4-DCP by the Fe^{2+}/PDS/UV process was studied at different pH values (3, 4, 5, 6, 7 and 8), when PDS, Fe^{2+} and 2,4-DCP concentrations were 4 mM, 0.5 mM and 50 mg/l, respectively. The results were presented in Figure 4.

The highest 2,4-DCP removal efficiency (57.14%) occurred at pH 3 in 160 minutes (Figure 6). Removal efficiency decreased with the increase of pH value, so that the removal efficiency of 39% was obtained at pH 8. A similar result was reported by Zhang et al. [7]. As can be seen in Table 1, with increasing pH from 3 to 8 reaction rate constant decreased from 0.0097 M^{-1} min^{-1} to 0.0052 M^{-1} min^{-1}. It indicates that the acidic pH is more favorable for the degradation of 2,4- DCP although pH variation has not been very sufficient on the 2,4-DCP degradation.

The decreased 2,4-DCP removal efficiency in neutral and alkaline pH may be related to iron deposition (Fe^{2+}, Fe^{3+}).
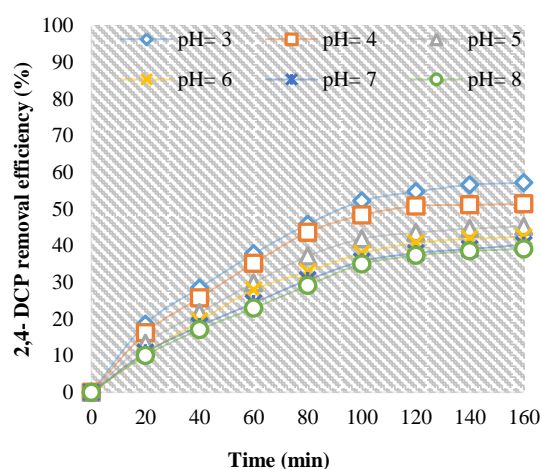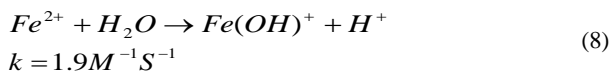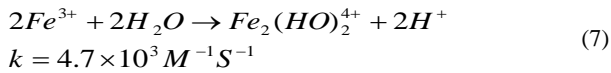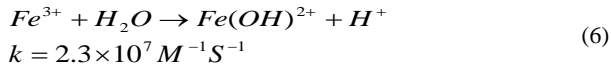

Figure 4. Effect of the initial pH on the 2,4-DCP degradation efficiency: 2,4-DCP (50 mg/l), PDS (4 mM) and Fe^{2+} (0.5 mM), under UV irradiation (254 nm)

When the pH is higher from 4 some ferric ion hydroxide (Fe^{3+}) such as Fe $(OH)^{2+}$ and $Fe_2(OH)_2^{4+}$ is formed via Equations (6) and (7) that finally is converted to ferric iron hydroxide Fe $(OH)^{3+}$. In addition, the amount of iron species (Fe^{2+}) can also be reduced at a pH higher than 4, via Equation (8), which may delay the next reaction between Fe^{2+} and $S_2O_8^{2-}$ [8].

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$$
$$k = 2.3 \times 10^7 M^{-1}S^{-1} \tag{6}$$

$$2Fe^{3+} + 2H_2O \rightarrow Fe_2(HO)_2^{4+} + 2H^+$$
$$k = 4.7 \times 10^3 M^{-1}S^{-1} \tag{7}$$

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$$
$$k = 1.9 M^{-1}S^{-1} \tag{8}$$

3. 3. 2. Effect of Fe²⁺ Concentration

Fe^{2+} stimulates PDS for the production of $SO_4^{\bullet-}$ radicals. Effect of Fe^{2+} concentration on the 2,4-DCP degradation was evaluated in various Fe^{2+} concentrations (0.25, 0.5, 1 and 2 mM). The initial concentrations of 2,4-DCP, PDS and initial pH value were 50 mg/l, 4 mM and 3, respectively. According to Figure 5, the removal efficiency increased from 51.9% to 67.3% with increasing concentration of Fe^{2+} from 0.25 to 2. The results of reaction rate constant showed that with increasing Fe^{2+} concentration the rate constant increased from 0.0075 M^{-1} min^{-1} to 0.0132 M^{-1} min^{-1} (Table 1). Nevertheless, with the increase of Fe^{2+} concentration from 1 to 2 mM the removal efficiency increased from 67.2% to 67.3% ($k = 6.1 \times 10^5 M^{-1}S^{-1}$) while the rate constant decreased from 0.0133 M^{-1} min^{-1} to 0.0132 M^{-1} min^{-1} (Table 1). This agrees with study of Wu et al. [26]. It mainly occurs because of excessive and undesirable reactions between Fe^{2+} and $SO_4^{\bullet-}$ radical which
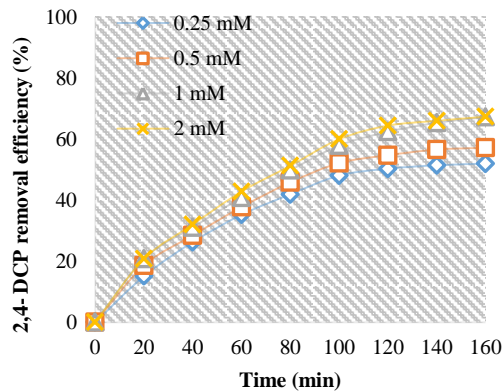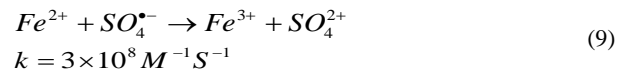
reduces the amount of $SO_4^{\bullet-}$ radical, via Equation (9) [7].

$$Fe^{2+} + SO_4^{\bullet-} \rightarrow Fe^{3+} + SO_4^{2+}$$
$$k = 3 \times 10^8 M^{-1}S^{-1} \tag{9}$$

3. 3. 3. Effect of PDS Concentration

Effect of PDS concentration was studied on the 2,4-DCP degradation in the concentrations of 2, 4, 8 and 12 mM, when the initial 2,4-DCP concentration was 50 mg/l, the concentration of Fe^{2+} was 1 mM and the pH value was 3.

As can be seen from the Figure 6a, with increasing concentration of PDS from 2 to 12 mM removal efficiency increased from 59.524% to 82.26%, and reaction rate constant increased from 0.006 M^{-1} min^{-1} to 0.0295 M^{-1} min^{-1} (Table 1). Figure 6 b shows reaction rate constants for 2,4-DCP degradation at various initial PDS concentrations (2–12 mM). Rate of degradation increased linearly (R^2=0.9865) with the increase of PDS concentration.
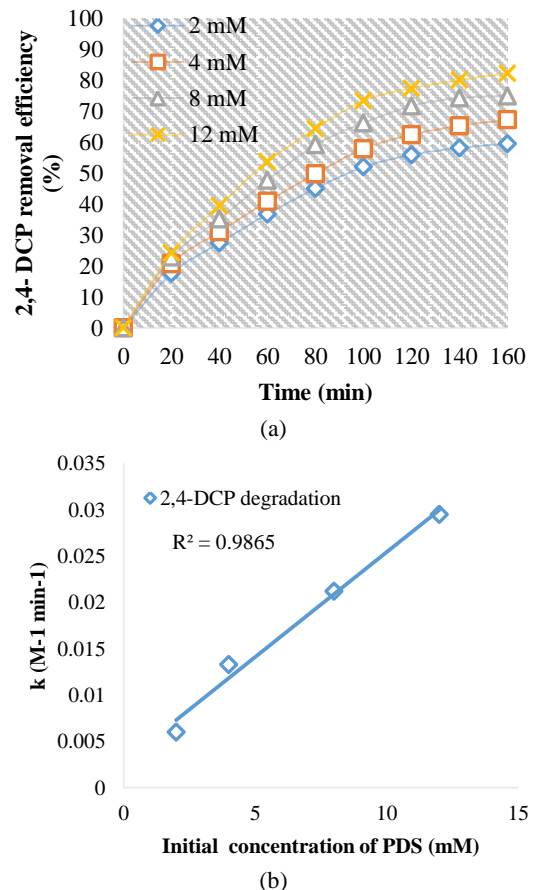

(a)

(b)

Figure 6. Effect of the initial PDS concentration on the 2,4-DCP degradation efficiency (a) and relationship between the initial PDS concentration and degradation rates (b): 2,4-DCP (50 mg/l), pH 3 and Fe^{2+} (1 mM), under UV irradiation (254 nm)

Figure 5. Effect of the initial Fe^{2+} concentration on the 2,4-DCP degradation efficiency: 2,4-DCP (50 mg/l), pH 3 and PDS (4 mM), under UV irradiation (254 nm)

This analysis was carried out because it would be found coefficient of determination (R^2) between increase of PDS concentrations and reaction rate constant. This phenomenon agrees with reported result by Lee et al. [13]. It occurs because the PDS is a source of $SO_4^{\bullet-}$ radical in the system, hence $SO_4^{\bullet-}$ radical could be generated to degrade 2,4-DCP in higher concentrations of PDS. On the other hand, the side reaction between $S_2O_8^{2-}$ and $SO_4^{\bullet-}$ radical became more significant with the increase of $S_2O_8^{2-}$ concentration, which would consume more PDS via Equation (10) [26].

$$S_2O_8^{2-} + SO_4^{\bullet-} \rightarrow S_2O_8^{\bullet-} + SO_4^{2-}$$
$$k = 6.1 \times 10^5 M^{-1} S^{-1} \tag{10}$$
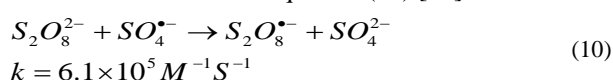
3. 3. 4. Effect of Time and the Initial Concentration of 2,4-DCP
To evaluate the effect of initial 2,4-DCP concentration and reaction time on performance of the Fe^{2+}/PDS/UV process, experiments were studied with different initial concentrations of 2,4-DCP (50, 70, 100, 150, 200 and 300 mg/l) while the concentration of Fe^{2+} and PDS were 1 and 2 mM, respectively, and pH value was 3, the results are presented in Figure 7.

As is shown in Figure 7, removal efficiency of 2,4-DCP increased at concentrations of 50, 70 and 100 mg/l with time. In addition, 2,4-DCP removal efficiency stopped after time of 20 minutes at concentrations of 150, 200 and 300 mg/l, (Figure 7). Also, removal efficiency of 2,4-DCP decreased from 82.24% to 18.45% when the initial concentration of 2,4-DCP increased from 50 mg/l to 300 mg/l (Figure 7). Li et al. [23] has reported a similar behavior for Fenton-like process on the removal of 2,4-DCP. Also, reaction rate constant decreased from 0.0295 M^{-1} min^{-1} to 0.004 M^{-1} min^{-1} with the increase of 2,4-DCP concentration (Table 1).
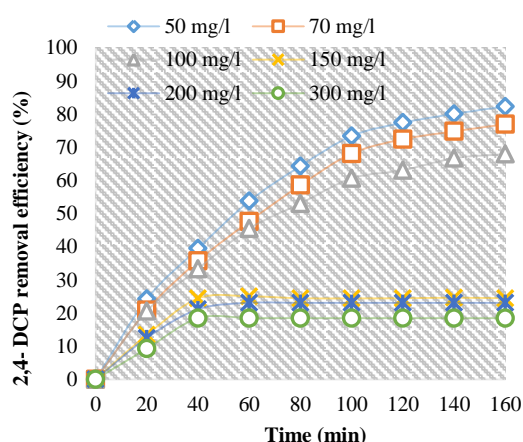

Figure 7. Effect of time and the initial 2,4-DCP concentration on the 2,4-DCP degradation efficiency: pH 3, Fe^{2+} (1 mM) and PDS (12 mM), under UV irradiation (254 nm)

4. CONCLUSIONS

In summary, our results show that 2,4-DCP is sufficiently removed by Fe^{2+}/PDS/UV process. Although the optimum pH was 3, significant removal efficiency was observed in natural pH. In past studies that was investigated removal of 2,4-DCP by $HO^{\bullet}$ radical in the natural pH, the reported removal efficiency was lower than this study. A linear relationship between the concentration of PDS and reaction rate constants indicates the effectiveness of the PDS on the 2,4-DCP degradation rate at all the PDS concentrations. Also, PDS species was found as effective parameter in the removal of 2,4-DCP by Fe^{2+}/PDS/UV process. Furthermore, it was observed that an increase in the 2,4-DCP concentration influenced negatively the 2,4-DCP removal efficiency. It is concluded that this process can be sued for water solution containing medium concentration of 2,4-DCP in acidic and nearby natural pH.

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Photochemical Degradation of 2,4-dichlorophenol in Aqueous Solutions by Fe^{2+}/ Peroxydisulfate/ UV Process

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چکیده

فنل و مشتقات آن یکی از رایجترین آلایندهها در اکوسیستمهای آبی هستند. به دلیل سمیت بالای۲،۴-دیکلروفنل برای زیست آبی، مقاومت به تجزیه بیولوژیکی و توانایی تجمع بیولوژیکی به عنوان یک آلاینده دارای تقدم در محیط آبی شناخته میشود. فرآیندهای اکسیداسیون پیشرفته بطور موفقیت آمیزی برای تجزیه آلایندههای غیرقابل تجزیه بیولوژیکی که به فرآیندهای متداول تصفیه مقاوم هستند استفاده شده اند. بنابراین استفاده از تکنولوژیهای پیشرفته اکسیداسیون که از رادیکال سولفات استفاده میکنند میتواند مورد توجه باشد. در این مطالعه اثرات غلظت ۲،۴-دیکلروفنل، آهن دو ظرفیتی، پرسولفات و pH و زمان بر کارایی حذف فتوشیمیایی ۲،۴-دیکلروفنل بررسی شد. افزایش pH اثر منفی بر کارایی حذف و ثابت سرعت واکنش داشت در حالی که افزایش در غلظت پرسولفات و آهن دو ظرفیتی راندمان حذف و ثابت سرعت واکنش را افزایش داد. بعلاوه، ثابت سرعت واکنش بطور خطی با افزایش غلظت پرسولفات افزایش یافت. بطور کلی در این مطالعه پرسولفات به عنوان مؤثرترین فاکتور در تجزیه ۲،۴-دیکلروفنل به وسیله فرآیند Fe^{2+}/PDS/UV مشخص شد.

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