

Original Article**2-Chlorophenol Removal of Aqueous Solution Using Advanced Oxidation Processes Resulting from Iron/ Persulfate and Ultra Violet/ Persulfate***Shokufeh Astereki¹, Bahram Kamarehie^{*1}, Ali Jafari¹**Received: 26.12.2015**Accepted: 03.02.2016***ABSTRACT**

Background: Advanced oxidation processes are used to remove toxic aromatic compounds with low biodegradability, such as 2-chlorophenol. This study investigated the use of sulfate (SO_4^-) and persulfate ($\text{S}_2\text{O}_8^{2-}$) radicals, as one of the advanced oxidation methods, to remove 2-chlorophenol from aquatic solutions.

Methods: This experimental and pilot-scale study was carried out using two chemical batch reactors; one of the reactors equipped with UV lamps and the other was on the hot plate. In iron/ persulfate ($\text{Fe}/\text{S}_2\text{O}_8^{2-}$) and ultra violet/ persulfate ($\text{UV}/\text{S}_2\text{O}_8^{2-}$) processes different parameters were investigated.

Results: Iron, UV, the initial pH of the solution, persulfate concentration have considerable effects on the elimination of 2-chlorophenol in both processes. In both processes, the maximum elimination occurred in acidic conditions. The elimination efficiency was increased by increasing the concentration of 2-chlorophenol and UV intensity, and also by decreasing the concentration of persulfate and iron. Accordingly, in iron/ persulfate and ultra violet/ persulfate processes 2-chlorophenol was eliminated with 99.96% and 99.58% efficiencies, respectively.

Conclusion: Sulfate radicals produced from activated persulfate ions with hot-Fe ion and UV radiation have significant impact on the removal of 2-chlorophenol. Therefore, the processes of $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ and $\text{UV}/\text{S}_2\text{O}_8^{2-}$ can be regarded as good choices for industrial wastewater treatment plants operators in the future.

Keywords: 2-Chlorophenol, Iron, Persulfate, Radical Sulfate, UV Radiation.

IJT 2016 (4): 1-8**INTRODUCTION**

The increase of water pollutants is due to uncontrolled discharging of industrial effluents, treated sewage and drinking water disinfection by chlorine, leaching of farmable soils contaminated with pesticides, weed herbicides and fertilizers by rain water or accidental spills and leaked tanks containing pollutants [1].

Phenol and phenolic compounds with high toxicity in contaminated water resources are considered as the most important pollutants and therefore as vital threats to environment, humans and animals health [2].

2-chlorophenol as a phenolic organic aromatic compound is used in wastewater of many industries such as plastics, polycarbonate, resins, etc [3], and also larger industries such as oil refineries (6-500 mg/l), coal furnace (9-6800 mg/l), petrochemical plants (2-1220 mg/l), and coking (28-3900 mg/l) which have high concentrations of phenol and its derivatives such

as 2-chlorophenol [3, 4]. Due to the importance of environmental pollutants, strict standards are exerted on phenolic compounds in some countries [4]. United States Environmental Protection Agency (EPA) has listed phenol and its derivatives as the priority environmental pollutants. The standard concentration of phenol allowed by EPA in drinking water is 1 mg/l and in wastewater industries is 500 mg/l [2, 4]; moreover, the concentration of chlorophenols allowed by WHO guidelines in drinking water is 1 g/l [5]. Therefore, removing phenolic compounds from contaminated water is considered necessary and important prior to discharging wastewater into the environment [5].

Previously, many physico-chemical methods such as biological processes, wet air oxidation, wet oxidation with hydrogen peroxide and adsorption, chemical precipitation, and electro coagulation have been used for removal of chlorophenols [3, 6]. Incomplete degradation of

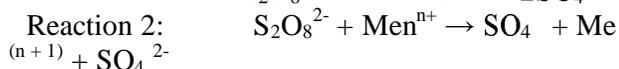
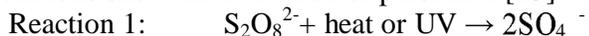
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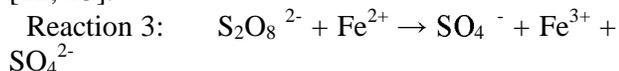
pollutant, changing the contaminants from one phase to another, and also producing complex byproduct compounds which may be more toxic than primary compounds are some of the methods problems [5, 7].

Advanced oxidation processes (AOPs), such as fenton, $\text{H}_2\text{O}_2/\text{O}_3$, $\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , etc have appropriate performance on the degradation of recalcitrant pollutants [8]. The aim of AOPs is to generate OH° , O° , and SO_4° radicals with high oxidation potential for the removal of resistant substances as phenolic compounds [6, 8]. In many examples of recent studies, removal and degradation of phenolic compounds were achieved with sulfate and persulfate radicals [9-10]. Recently, because of oxidation potential of sulfate radicals, they have been used for polymerization and emulsion reactions in industry [11]. Low cost, high stability in different conditions, high solubility, solid state, and easy handling and storage are some of the advantages of persulfate radicals [9-11].

Because of slow generation rate of sulfate radical at room temperature, heat, transition metals (Me^{2+}) and UV light are used to activate operations of persulfate [12]. The final product of activation processes is sulfating radical with oxidation potentials 2/06 v. The following reactions show the activation of persulfate [13].



Among transition metals, according to reaction 3, divalent irons (Fe^{2+}) have the most applicability. The process is shown in reaction 3 [12, 13].



Therefore, the purpose of this study was to remove 2-chlorophenol from aqueous environment using $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ and $\text{UV}/\text{S}_2\text{O}_8^{2-}$. Besides, the novelty aspect of this work is [1] the comparison of the oxidation potential of $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ and $\text{UV}/\text{S}_2\text{O}_8^{2-}$ processes and using them for 2-chlorophenol degradation. The influence of important operating parameters including initial pH of solution, per sulfate concentration, initial concentration of 2-chloro phenol, UV radiation intensity, iron concentration, and reaction time are evaluated on the degradation of 2-chloro phenol in current study.

MATERIALS AND METHODS

All used chemicals were of analytical grade. Digital pH meter (model BP3001), spectrophotometer UV visible Shimadzu, HPLC (model CTO-10 A), five 6-watt Philips UV lamps (made in Netherlands) were used in this work.

In $\text{UV}/\text{S}_2\text{O}_8^{2-}$ procedure, we used a quartz batch reactor (1000 ml) equipped with five UV lamps (Fig. 1). In $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ procedure, we also used a crystal batch reactor (1000 ml) with a magnet for stirrer speed of 200 rpm on a hot plate at 65°C (Fig. 2).



Figure 1. $\text{UV}/\text{S}_2\text{O}_8^{2-}$ process reactor.

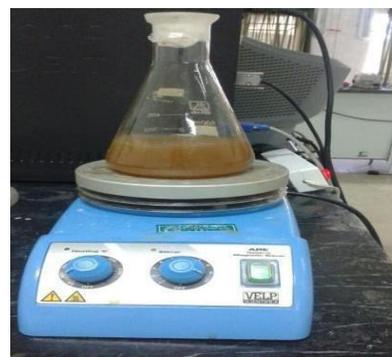


Figure 2. $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ process reactor.

Samples containing various concentrations of 2-chlorophenol (10-200 mg/l), along with a stock solution of 4000 ppm, are used in these two processes.

Before the processes start, the required concentrations of 2-chlorophenol (10-200 mg/l) and persulfate (0.01-0.05 mol/l) were measured and poured into the reactors. Caustic soda and sulfuric acid 1N were used to adjust the pH of reactors contents. In $\text{Fe}/\text{S}_2\text{O}_8^{2-}$ process, various concentrations of Fe (0.01-0.05 mol/li) were used in the reactor, and after starting to work, reactor content was being stirred and heated; reactor

content was also exposed to UV radiation after UV/S₂O₈²⁻ process started.

The process duration was 50 min in two reactors, and samples were taken at intervals of 10 min. All experiments were performed in a duplicated manner in accordance with standard deviation of >5% at room temperature. The constant amount of sodium sulfate (0.1 g/l) was increased in all experiments to increase the ionic potential in reactors. Tert-butanol (0.04 mol/l) was used to determine the effect of interfering organic matter to 2-chlorophenol degradation.

2-chlorophenol degradation efficiency was calculated as:

$$\text{Degradation efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100$$

Where, C₀ and C_t are 2-chlorophenol concentrations before and after the reaction, respectively.

The remaining concentrations of 2-chlorophenol in the samples were measured by a spectrophotometer and HPLC at 240 nm wavelength. Of course, in two processes the final optimization concentrations were measured by HPLC.

RESULTS

The influence of solution initial pH (3-11) on the performance of Fe/S₂O₈²⁻ and UV/S₂O₈²⁻ processes in the degradation of 2-chlorophenol was examined by using 2-chlorophenol (200 mg/l), iron (0.01 mol/l) and persulfate (0.01 mol/l) constant concentrations at 50 minutes and UV 30W (Figs. 3 and 4).

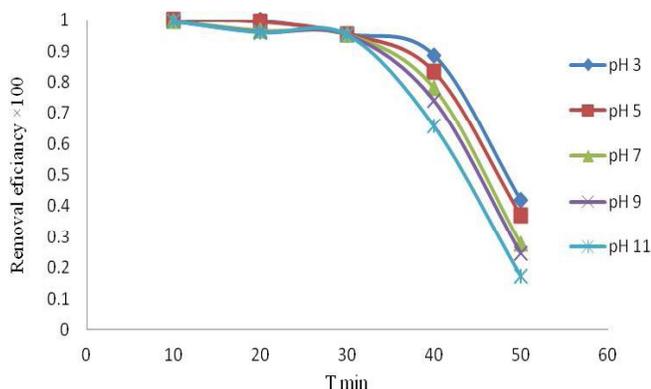


Figure 3. The influence of solution initial pH on Fe/S₂O₈²⁻ process (2-chlorophenol =200 mg/l, iron =0.01 mol/l and persulfate=0.01 mol/l).

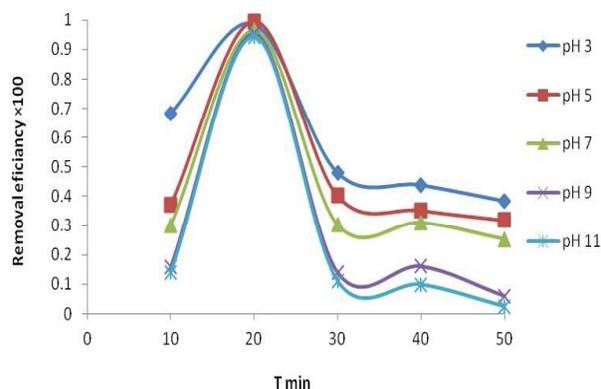


Figure 4. The influence of solution initial pH on UV/S₂O₈²⁻ process (2-chlorophenol =200 mg/l, and persulfate=0.01 mol/l, UV= 30W).

The highest efficiency of 2-chlorophenol removal in Fe/S₂O₈²⁻ process was seen at pH =3. At this pH, after 20 min of reaction time, the removal efficiency was 96.99%. Nevertheless, the highest efficiency of 2-chlorophenol removal in UV/S₂O₈²⁻ process was at pH = 5. In this pH after 10 min, the removal efficiency was 96.58%. In both processes, increasing samples initial pH decreased the removal efficiency of 2-chlorophenol dramatically.

The influence of 2-chlorophenol initial concentration (10-200) on degradation efficiency of Fe/S₂O₈²⁻ and UV/S₂O₈²⁻ processes was also examined by using pH (5 and 3), iron (0.01 mol/l), UV 30W and persulfate (0.01 mol/l) constant concentrations at 50 min (Figs. 5 and 6).

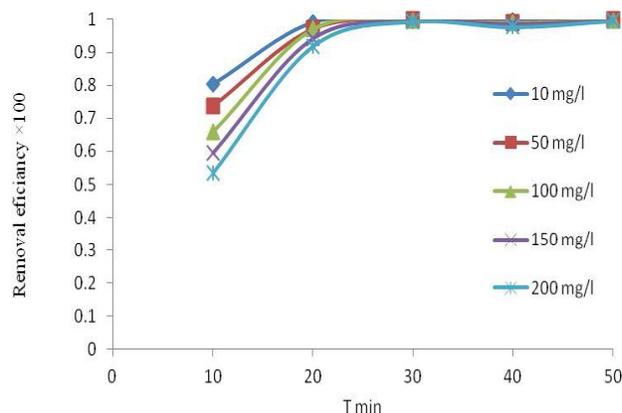


Figure 5. The influence of 2-chlorophenol initial concentration on removal efficiency in Fe/S₂O₈²⁻ (pH =3, iron =0.01 mol/l and persulfate=0.01 mol/l).

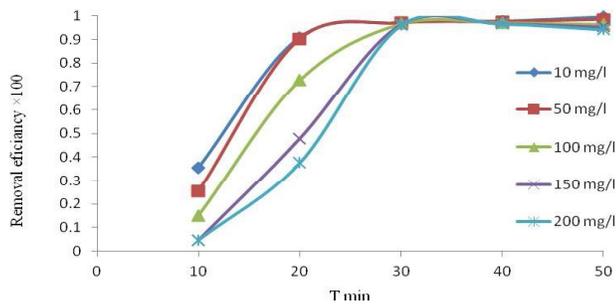


Figure 6. The influence of 2-chlorophenol initial concentration on removal efficiency in UV/S₂O₈²⁻ (pH=5, UV 30W and persulfate=0.01 mol/l).

Removal efficiency of Fe/S₂O₈²⁻ process rose with increasing concentration of 2-chlorophenol, so that, raising 2-chlorophenol from 10 to 200 mg/l increased removal efficiency from 53.33% to 99.65%. Furthermore, in UV/S₂O₈²⁻ process, adding 10 to 200 mg/l of 2-chlorophenol increased removal efficiency from 47.42% to 94.37%.

In Fig. 7, the influence of iron quantity on removal efficiency of 2-chlorophenol is shown in Fe/S₂O₈²⁻ process. Increasing the initial concentration of iron from 0.01 to 0.05 decreased the removal efficiency from 99.98% to 99.21%, at 20 min, and decreased removal efficiency from 99.6% to 99.4% at the 50 min.

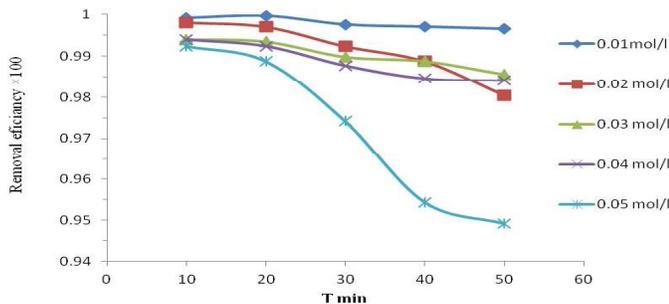


Figure 7. The influence of iron amount on removal efficiency in Fe/S₂O₈²⁻ process (pH=3, 2-chlorophenol =200mg/l and persulfate=0.01 mol/l).

The influence of UV radiation on the removal efficiency of 2-chlorophenol in UV/S₂O₈²⁻ process is shown in Fig. 8. By increasing UV radiation from 6 to 30 w, the removal efficiency increased from 95% to 97.7% at 20 min. After 20 min, the increasing of UV radiation almost did not influence the removal efficiency.

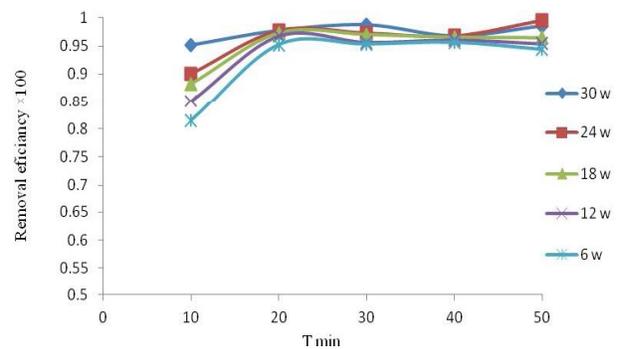


Figure 8. The influence of UV radiation on removal efficiency of 2- chlorophenol in UV/S₂O₈²⁻ process (pH=5, 2-chlorophenol =200mg/l and persulfate=0.01 mol/l).

The influence of persulfate concentration on removal efficiency of 2- chlorophenol in UV/S₂O₈²⁻ and Fe/S₂O₈²⁻ processes is illustrated in Fig. 9. Increasing persulfate concentration from 0.01 to 0.05 mol/l had no significant effect on the removal efficiency of 2- chlorophenol in Fe/S₂O₈²⁻ process after 20 min. In Fe/S₂O₈²⁻ process, by increasing concentrations of persulfate from 0.01 to 0.05 mol/l, the removal efficiency dramatically reduced, so that, after 10 min, the removal efficiency reduced from 99.58% to 74.90%. Comparing two processes with convenient variables showed that convenient persulfate concentration is 0.01 mol/l.

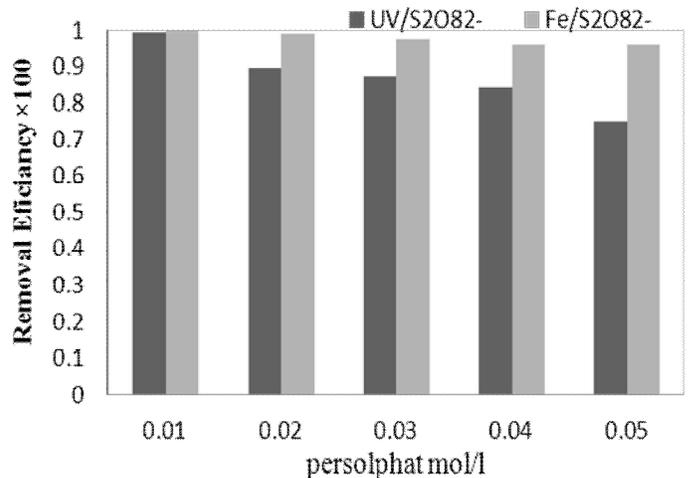


Figure 9. The influence of persulfate concentration on removal efficiency of 2- chlorophenol in UV/S₂O₈²⁻ (pH = 5, 2- chlorophenol =200mg/l, UV=30 w, time =10min) and Fe/S₂O₈²⁻ (pH =3 and 3, 2-chlorophenol =200mg/l, iron=0.01 mol/l, time =20min) processes.

The degradation rate of 2- chlorophenol was fitted with first-order kinetic model in 15 min early from Fe/S₂O₈²⁻ process (Fig. 10). Besides, the degradation rate of 2- chlorophenol was fitted with first-order kinetic model in 10 min early from UV/S₂O₈²⁻ process (Fig. 11). The degradation rate of 2- chlorophenol the UV/S₂O₈²⁻ process was 5 times larger than the Fe/S₂O₈²⁻ process.

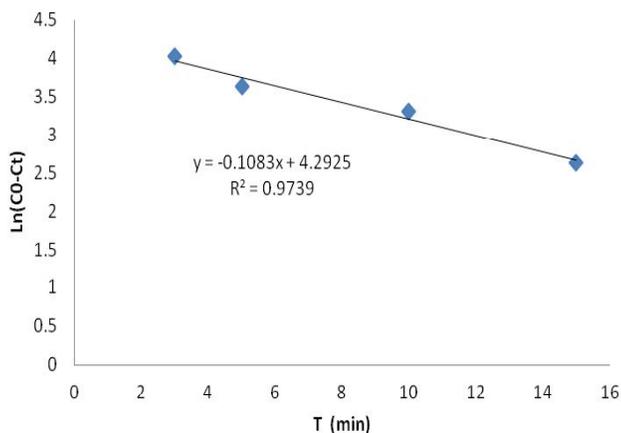


Figure 10. The diagram of Fe/S₂O₈²⁻ process kinetic (pH =3 , persulfate=0.01mol/l, 2-chlorophenol =200mg/l, iron=0.01 mol/l).

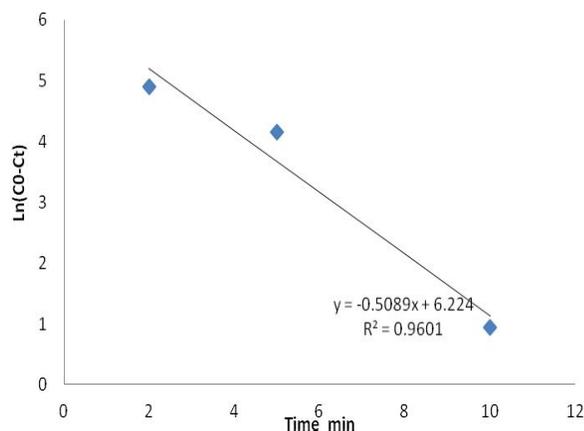


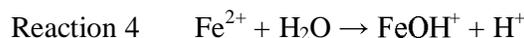
Figure 11. The diagram of UV/S₂O₈²⁻ process kinetic (pH =5, persulfate=0.01mol/l, 2-chlorophenol =200mg/l, UV=30w).

DISCUSSION

In many studies on advanced oxidation processes, pH has had a very important role on pollutants removal [14]. The most influential variable affecting processes efficiency has been reported to be the solution pH [14]. Sulfate radical

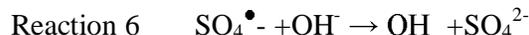
is produced in advanced oxidation process of iron by peroxodisulfate and divalent iron. Type, pH, and state of iron in the solution have affected factors in reaction of persulfate with pollutants [14, 15].

Increasing pH from acidic conditions to alkaline changed Fe²⁺ to Fe³⁺, and accordingly the process efficiency considerably reduced. In the event that divalent iron is able to activate persulfate with a ratio of divalent iron to ferric iron. Iron solubility decreases at pH above 9, because divalent iron becomes insoluble and colloidal state and therefore reduces removal efficiency (reaction 4) [14-16].



With further increase of pH to above 9, ferric hydroxides species (FeOH₃⁺, Fe(OH)₄⁺, Fe₂(OH)₃⁴⁺) are being produced, which have very low ability to activate persulfate [17].

By increasing pH, part of produced persulfate radical can be changed to hydroxyl radical. This reaction often occurs in alkaline conditions (reactions 5 and 6) [18].



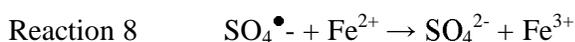
Rao et al. studied degradation of carbamazepine with persulfate / divalent process. Accordingly, reaction rate increased in acidic conditions, and optimized pH during the process was 3 [19]. UV radiation with acidic pH increased removal of pollutants and changed their structure into simple and safe combination [18-20].

The convenient pH of the process, in the presence of UV and proxy bisulfate, was 5; this result is in accord with the results of azo dyes degradation by UV/S₂O₈²⁻ process [20]. Therefore, sulfate radical production is completely dependent on pH in both processes. At pH below 7, particularly between 3 to 5, sulfate radical is dominant, and with pH between 7 to 9 both radicals are existed (sulfate and hydroxyl). In intensive alkaline conditions (pH above 11) hydroxyl radical is dominant. On the one hand, hydroxyl radical oxidation potential decreases the alkaline conditions even in the presence of most of the radicals. On the other hand, removal efficiency of 2-chlorophenol reduced; the stability of persulfate radicals is also far more than hydroxyl radicals in aqueous [21].

In high pH, persulfate radicals combine with hydroxyl radicals and produce sulfate ions (reaction 7). This reaction is undesirable and significantly reduces process efficiency because the oxidation reactions were being carried out in the absence of radicals [22].



In high pH, even with increasing more than specified values, the concentration of divalent iron will not improve the performance of the process, and it is possible to increase sludge volume and reduce process efficiency because persulfate radicals combine with divalent iron (reaction 8) [23].



The UV/S₂O₈²⁻ process, UV radiation breaks C-Cl, C-OH and -SO₂- bands and degrade aromatic organic compounds, such as 2-chlorophenol. Moreover, the UV radiation increases the oxidation power of S₂O₈²⁻ by formation of SO₄[•] radicals [24]. Our results in this study confirm Karimi et al. results which showed using UV/H₂O process for naphthalene removal from water [25].

In the two processes, increasing the concentration of persulfate of specified value reduces the process efficiency because it gets an agent for capturing and consuming persulfate radicals in aqueous solution that is shown in reaction 9 [26,27].



In this study, in order to minimize radical capturing, the maximum amount of persulfate was 0.01 mol/l after pretests [26-28]. In previous studies increasing the concentration of organic compounds caused the process efficiency to increase [29, 30]. High concentration of organic compounds in the solution increases oxidant demand and decreases process efficiency, because the amount of oxidant in solution has a negative effect on them. Low concentration of organic compounds also reduces process efficiency [31].

In an environment where the concentration of iron ions increases, in comparison with organic material concentration, stable complexes of iron ions and hydroxyl radicals form and reduce the amount of free radicals (reactions 9 and 10) [32].

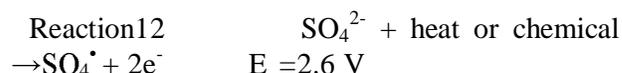


Persulfate salts and water form persulfate anion (reaction 11).



$$E = 2.01 \text{ V}$$

Persulfate anions have low oxidizing power at room temperature, so in order to increase oxidizing power, persulfate anions active by chemical processes or thermal methods and produce sulfate radical as one of intermediate products and a strong oxidizing compound (reaction 12) [33, 34].



In previous studies, the influence and power of sulfate radicals have been analyzed in removal processes. Organic substances have the role of scavenger radical and properly scavenge hydroxyl radicals; while, persulfate radicals are more resistant than organic substances [35, 36]. Therefore, in this study, in order to determine the effect of radical type and to determine the optimized operation condition, tert-butanol used as a scavenger radical [37].

The UV/S₂O₈²⁻ and Fe/S₂O₈²⁻ processes, sulfate radical was dominant and impact factor on the decomposition of 2-chlorophenol while hydroxyl radical has very little effect on 2-chlorophenol decomposition [38]. This result is consistent with results of Asgari which used persulfate to remove pentachlorophenol from synthetic wastewater [39].

CONCLUSION

UV/S₂O₈²⁻ and Fe/S₂O₈²⁻ processes have high efficiency in decomposition of 2-chlorophenol. Moreover, the removal efficiency decreases with increasing pH. Persulfate concentration has critical effect on processes efficiency, so it must be controlled during the processes. Finally, the removal efficiency of 2-chlorophenol increased by reducing the concentration of iron in Fe/S₂O₈²⁻ and increased the intensity of UV radiation in UV/S₂O₈²⁻.

ACKNOWLEDGMENTS

This article is the result of an adapted research project by Lorestan University of

Medical Sciences. The authors wish to express their sincere thanks to all respected authorities in Lorestan Medical Sciences University during the implementation of the study. The authors declare that there is no conflict of interests.

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