Evaluate the effectiveness of the UV/ persulfate process to remove catechol from solution aqueous

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GRAPHICAL ABSTRACT



Abstract

Catechol is used as an antioxidant, fungicide, and polymerization inhibitors in a variety of industries such as petrochemical. Catechol must be removed from effluents before it enters to environment. This study aimed to investigate combined UV radiation and persulfate process in removal of catechol from aqueous solutions. All experiments were performed in a batch reactor. Data analysis were done with Design of Experiment (DoE) software. The effects of various variables such as pH, initial persulfate concentration, and initial Catechol concentration were investigated. The findings indicated with increases in persulfate concentration and decrease in catechol concentrations, the removal efficiency increased. Acidic pH and UV radiation were the leading factors in removal of catechol. The optimum pH, persulfate concentration, and catechol concentration were obtained 7, 0.04 M, and 100 mg l⁻¹, respectively. More removes of catechol was achieved in optimum conditions within contact time of 60 min. The synergic effects of UV and persulfate radical were about 88%. Approximately 60% of catechol was mineralized within contact time of 60 min. Persulfate radicals resulting from $UV/S_2O_8^{2-}$ were the main effective oxidants in removal and mineralization of catechol. Owing to high removal efficiency of persulfate compounds which are, also, abundant and inexpensive, these can be applied in removal of persistent organic pollutants from aqueous solutions.

Keywords: Persulfate radical, catechol, UV radiation, advanced oxidation

1. Introduction

Catechol, one of the derivation of phenol, is colorless and has a phenol-like smell (Moussavi et al., 2014). Catechol has a phenolic ring which bonds to two Hydroxyl (OH°) functional groups (Bayram et al., 2009; Liu et al., 2014). Catechol can enter into our environment from various sources such as photographic developer, paper and pulp, textile, pharmacy, insecticides, paint, engine lubricants, oil refinery, petrochemical lubricating oils, polymerization inhibitors and pharmaceutical (Lofrano et al., 2009). It is applied as an antioxidant, fungicide, and polymerization inhibitors in various industries. The catechol concentration in the effluents of different industries is range less than one to 1000 mg 1^{-1} (Bayram et al., 2009; Liu et al., 2014). The catechol concentration is typically low in environment but the effluents of industrials processes may contain

catechol concentrations ranging from one to 1000 mg/l. It is synthetically produced by hydroxylation of phenol using Hydrogen peroxide (H₂O₂) or created by Hydrolysis of 2chlorophenol with alkali metals hydroxides (Shakir et al., 2008; Moussavi et al., 2014). Catechol similar to other phenol derivations has toxicity and can cause environmental and health concerns such as irritation of eye, skin, pulmonary, liver dysfunction, DNA destruction, and neurological diseases. Catechol easily adsorbed to digestive tract, and it can result in hemolysis and acute tubular necrosis (!!! INVALID CITATION !!! (Zhao et al., 2010; Gunawardana et al., 2011; Hamad et al., 2011)). Catechol is more toxic and hazardous to human, environment, and microorganisms compared to phenol (Sun et al., 2010). To date, a variety of physicochemical methods have been investigated for the removal of catechol compounds from the aqueous solutions, including biological process, air oxidation, wet oxidation by H₂O₂, and adsorption (Kamali and Ghaziaskar, 2010; Haidari et al., 2016). The important drawbacks of these technologies include failure to complete degradation of contaminants, contaminant transmission from a phase to another, and production by-products as well (Sun et al., 2010; Zhao et al., 2010; Azarpira et al., 2019; Hasanpour and Hatami, 2020a). In recent decades, advanced oxidation processes (AOPs) such as Fenton, H₂O₂/O₃, H₂O₂/UV, and O₃/UV have been widely using as highefficiency processes for removal of resistant (persistent) pollutants from soil, water, and wastewater (Kamali and Ghaziaskar, 2010; Shukla et al., 2010c; Ghaderpoori and Dehghani, 2016; Haidari et al., 2016; Hasanpour and Hatami, 2020b). The major purposes of these techniques are producing high-oxidation radical, including OH°, O°, and the sulfate radical, which rapidly oxidize and remove resistant substances to biodegradation (Antoniou et al., 2010). For these reasons, a great number of studies have been done to remove phenol derivations with different radicals (Kamali and Ghaziaskar, 2010; Rokhina et al., 2010; Sun et al., 2010; Kamarehie et al., 2018; Kamarehie et al., 2020). These radicals provide situations to react with persistent substances and increase pollutants degradation (Boukari et al., 2011). Persulfate has an oxidizing potential equal to 2.01 V (Gayathri et al., 2010). An effective mechanism of persulfate is generating the sulfate radical and OH° radicals and using them for degradation of organic matters. However, more studies have concluded that degradation rate of organic matter, in room temperature, is very low by persulfate radicals. Therefore, accelerating process for activation (increases in concentration of radicals) is needed(Shukla et al., 2010a). Persulfate can be activated by various method such as increasing temperature, adding intermediate metals (Me²⁺) and UV radiation (Liang et al., 2006; Astereki et al., 2016). Physical and chemical activations of persulfate are shown as follows(Shukla et al., 2010b; Karimi et al., 2013):

$$S_2O_8^{-2}$$
 + heat or UV $\rightarrow 2SO_4^{\circ}$ 1

$$Me^{n+} \rightarrow SO_4^{\circ-} + Me^{(n+1)} + SO_4^{-2} + S_2O_8^{-2}$$
 2

$$S_2O_8^{-2} + Fe^{+2} \rightarrow SO_4^{\circ} + Fe^{+3} + SO_4^{-2}$$
 3

The studies have shown that $UV/S_2O_8^{-2}$ is an effective process to remove persistent organic pollutants (Salari et al., 2008; Lin et al., 2011). A number of researchers have applied this method to remove POPs and obtained similar results. Delavaran Shiraz et al study showed that persulfate activated by UV and ferrous ions was an effective process in removing catechol (Lin et al., 2011;

Fang and Shang, 2012; Lin et al., 2013). Yoon et al study showed that $UV/S_2O_8^{-2}$ was very effective in removing bisphenol compared to $UV-H_2O_2$ was an effective process in removing catechol (Yoon et al., 2012). The advantages of the process include low cost, high stability and solubility, storage and easy transfer (Fang and Shang, 2012; Gao et al., 2012). The response surface methodology is good procedure to study the relationship between independent and dependent variables (Massoudinejad et al., 2018; Yazdanbakhsh et al., 2018). In response surface methodology category, central composite design that is appropriate for fitting second order polynomial equations has been frequently discussed for optimizing several research problems. To design experiments, Design of Experiments Software (DOE) and Central Composite Design (CCD) was applied. In the study, five coded levels ($+\alpha$, +1, 0, -1, and $-\alpha$) factorial experimental design was used to optimize the reaction conditions. The aim of present study was to evaluate the effectiveness of the UV/S₂O₈⁻² process to remove Catechol from solution aqueous.

2. Methods

2.1. Chemicals and instruments

Catechol (C_6H_6O , white to brown feathery crystal, phenolic odor), NaOH, H₂SO₄, were purchased from Merck Company, Germany. Digital pH meter model BP300 and spectrometer UV/VIS (DR-5000) were used to measure pH and contaminant concentrations, respectively. Samples pH were adjusted by adding a few drops of NaOH and H₂SO₄ (1N).

Design of Experiments (DoE)

To determine removal efficiency of catechol by $UV/S_2O_8^{2-}$, initial catechol concentrations (100-500 mg l⁻¹), pH (3-11), and persulfate radicals (0.01-0.05 M) were considered as dependent variables. Removal efficiency of catechol was dependent variables. The constant UV radiation throughout study was 30W. The number of experiment were determined 20 run (central point=20 run and not center point=14 run. Optimum time for experiment was determined 60 min after pretest. The samples were exposed to UV for 60 min, and then the samples were detected. After experiments, the coefficient of the polynomial model were calculated to equation 1 (Eq. 1) (Massoudinejad et al., 2016)

$$Y(\%) = a_0 + \sum_{i=1}^{n} a_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} a_{ij} X_i X_j + e$$

Where, i and j are linear and quadratic coefficients, respectively. a_0 , a_i , a_{ii} , and a_{ij} are constant, linear, interaction, and quadratic coefficients, respectively. The removal efficiency of Catechol was calculated according to Eq. 2 (Massoudinejad et al., 2016):

$$R,\% = \frac{(C_0 - C_t)}{C_0}$$
2

Where, C_o and C_t represent the initial and final concentration of catechol (mg L⁻¹), respectively. To measure Chemical Oxygen Demand (COD), volumetric method (titration) was applied. All experiments were performed based on standard method for examination of water and wastewater (Eaton AD et al., 2005). First, A 100 mg L⁻¹ of stock solution was prepared with catechol (purity 98%). Then, the calibration curve were drawn in different catechol concentrations (2, 10, 50, 100, 150, and 200 mg L⁻¹). After that, residual concentration of catechol were determined by High-Performance Liquid Chromatography (HPLC) (UV detector, wavelength=275nm, the column=100-5C18; 4.6mm×250mm, 5µm, temperature=23°C, Mobile phase= a mixture of methanol and water 44:55) (Yoon et al., 2012). The experimental runs of CCD show at Table 1. In this work, a 1000 mL Plexiglas reactor was applied to experiments. Five ultraviolet (UV) tubes 6W, low pressure (PHILIPS), also were used as UV radiation sources. The experiments were performed in a batch reactor, as shown in Figure 1.

Run	Catechol Conc.	pН	Persulfate	Removal Efficiency	Predicted Value
	(mg L ⁻¹)	_	(mg L ⁻¹)	(%)	(%)
1	300	7	0.03	94.97	94.55
2	300	3	0.03	92.88	94.55
3	420	5	0.02	68.28	69.64
4	180	9	0.04	100	99.88
5	500	7	0.03	75.44	71.82
6	300	7	0.01	71.22	73.05
7	300	7	0.03	90.54	94.55
8	180	5	0.4	100	99.98
9	180	5	0.02	100	97.68
10	180	9	0.02	95	97.68
11	300	7	0.03	69.86	94.55
12	420	9	0.02	94.5	69.64
13	300	7	0.03	94.19	94.55
14	420	5	0.04	87.19	90.72
15	420	-9	0.04	89	90.72
16	300	7	0.03	95.2	94.55
17	300	7	0.05	98.6	96.32
18	100	7	0.03	99.85	102.82
19	300	7	0.03	95	94.55
20	300	11	0.03	99	94.55

Table 1. The runs for removal process of catechol by $UV/S_2O_8^{-2}$



Figure 1. A view of the pilot used for UV/S₂O₈⁻² [1- Wooden removable cap, 2- UV lamps, 3- Hinge, 4-Glass reactor with aluminum cover, 5-Switching keys, 6-Power source, 7-Current cables]

3. Results and discussion 3.1. Statistical analysis and model fitting

The results of present study showed that the catechol removal by UV/S₂O₈⁻² was fitted to polynomial models. Also, Analysis of variance (ANOVA) indicated that the selected model has a capability to estimate (predict) process (P-value <0.05). The model F-value of 61.13 implied the model was significant. There was only a 0.01% chance that a model F-value this large could occur due to noise. Values of prob>F less than 0.05 indicated model terms were significant. In this case C, BC, B², C² were significant model terms. Values greater than 0.1 indicated the model terms were not significant. If there were many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The lack of fit (LoF) of F-value of 2.74 implied the lack of fit was not significant relative to the pure error. There was a 13.98% chance that a LoF of F-value this large could occur due to noise. Non-significant LoF was good. The correlation coefficient, modified correlation, and predicted correlation were in order 0.99, 0.97, and 0.81, respectively. The predicted R-squared, R², of 0.86 was in reasonable agreement with the adjustment R-squared of 0.94. Adequate precision measures the signal to noise (S/N) ratio. A ratio greater than four is desirable. In this study, S/N ratio of 23.015 indicated an adequate signal. This model can be used to navigate the design space. It show the selected model was of high accuracy. The removal efficiency of this study were found to have range 68% to 100%. The DoE software works based on multivariable linear regression model, the outputs are discussed as following Eq. 3:

$$R,\% = 89.81 + (4.82*B) - (21.35*C) + (11.13*B*C) - (2.56*B^{2}) - (13.95*C^{2})$$

Where, B and C are catechol concentration and the sulfate radical concentration, respectively. The optimum pH, persulfate concentration, and catechol concentration were obtained 7, 0.04 M, and 100 mg L⁻¹, respectively. Finally, data validation was performed with the tests: I. normal probability plot of the studentized residuals to check for normality of residuals, II. studentized residuals versus predicted values to check for constant error, III. externally studentized residuals to look for outliers, i.e., influential values. And IV. Box-Cox plot for power transformations.

3.2. Optimization and model validation

In DoE software, the optimization of variables is performed in three methods: numerical, graphical, and point prediction. This study was to optimize with the use of numerical methods. To obtain the optimal condition for catechol removal and for maximum desirability. catechol concentration, persulfate concentration, initial pH, and contact time were set minimum, minimum,

in the range and, in the range, respectively. The best local maximum was found to be at the pH 7, catechol concentration of 181.08 mg L^{-1} , persulfate concentration of 0.04 M, contact time of 60 min. Removal efficiency of catechol in the optimal conditions obtained 90 percent, and desirability of one.

3.3 The effects of SO4° concentration on the removal efficiency of UV-S2O8⁻²

The study findings showed that an increase in the sulfate radical concentration can effect on removal efficiency of catechol. Increasing in concentration of oxidant leads to increases in the sulfate radical concentration, which result in promotion of reaction and catechol degradation. Types and concentrations of oxidants are important factors in AOP_S. Persulfate $(S_2O_8^{2-})$, a twoelectron oxidant, produces SO₄° with higher redox potential compared to O₃ and OH°. This radicals can break down organic pollutants (Karimi et al., 2013). In degradation of organic matter, first, the sulfate radical is activated through physical and chemical reaction with UV radiation. Then, the intermediate products such as the sulfate radical are produced (Azbar et al., 2004). The sulfate radicals can mineralize organic matters and produce CO₂, H₂O, and acidic organics. It not only can attack directly to organic matters and degrade them, but also is capable of indirectly reacting to H₂O and OH°, which are two main factors in degradation of organic matters. The polynomial model showed that there as significant relationship between the sulfate radical and removal efficiency of catechol (P-value<0.02). Removal efficiency of catechol in different concentrations of SO4° are illustrated in Figure 2. As can be seen, increases in the sulfate radical concentrations can significantly effect on removal efficiency, so that increases in the sulfate radical concentration from 0.04 to 0.08 M has removal efficiency approximately 18%. The increasing in the removal efficiency of catechol along with increase in concentration of OH° and the sulfate radicals is justifiable (Azbar et al., 2004; Rasoulifard et al., 2012). Yegane et al achieved the highest removal efficiency in concentration 0.04 mM L⁻¹ of the sulfate radical (Khataee, 2009; Olmez-Hanci and Arslan-Alaton, 2013; Wang and Liang, 2014; Esrafili et al., 2016). Persulfate concentrations can increase the sulfate radical to a specified range, which subsequently result in increases of degradation rate and removal efficiency. The results agreement to Shaing et al called dye degradation using microwave process and persulfate (Astereki et al., 2016).



Figure 2. The effects of SO₄° on removal efficiency [pH= (3-11), UV radiation= 30 W, persulfate concentration (0.0- 2.1 M), Catechol concentrations (100- 500 mg L⁻¹), and contact time: 60 min].

3.4. The effects of initial catechol concentrations on the removal efficiency

In most studies related to organic matters oxidation, increasing in pollutant concentration have been along with reduction in removal efficiency (Massoudinejad et al., 2020). The study results showed that initial concentrations can significantly effect on removal efficiency. Other similar studies, removal efficiency decreased by increasing catechol concentrations. When the concentrations of persulfate radical and the sulfate radical were constant, but the catechol concentrations are increasing, removal efficiency decreased. Therefore, there were not sufficient available the sulfate radical for degradation. As well, high concentrations of catechol avoid UV radiation to permeate to depth of solution and decreased the persulfate radicals. As a result, the rate of catechol degradation decreased (Lee et al., 2009; Shiying et al., 2009; Olmez-Hanci and Arslan-Alaton, 2013). The results obtained the polynomial model showed that there was significant correlation between initial catechol concentration and the removal efficiency (P-value <0.001). The results of the effects of initial catechol concentrations on removal efficiency are shown in Figure 3. By increasing the initial catechol concentration from 181.08 to 418.92, the removal rate decreased by approximately 45%. The results showed that adsorption is not appropriate for the removal of higher concentrations of 110 mg L^{-1} (Lofrano et al., 2009). The results of this study were consistent with other studies (Rasoulifard et al., 2012; Zarrabi et al., 2013).



Figure 3. The effects of initial catechol concentrations on efficiency [pH= (3-11), UV radiation= 30 W, Persulfate concentrations (0.0-2.1 M), catechol concentrations (100- 500 mg L⁻¹), and Time: 60 min].

3.5. The effects of pH on the removal efficiency

pH is very effective factor in generation of the sulfate radical and OH° radicals However, most studies emphasize that pH has important effects on removal efficiency (Olmez-Hanci and Arslan-Alaton, 2013; Moussavi et al., 2014; Alinejad et al., 2019; Kamarehie et al., 2019). For this reason, solution pH was considered as an important factor in the present study. The results showed pH can impact on the removal efficiency. The polynomial model indicated that the effect of initial pH of solutions was not significant (P-value <0.46). Figure 4 shows the effects of pH on the removal efficiency of catechol. The best pH to remove the catechol was neutral conditions. The removal efficiency of catechol was reduced by almost 20% at acidic and alkaline pH. In a neutral pH, the highest persulfate radicals may be produced, which the increase in radical concentration could have a positive impact on removal efficiency. The study results of Yegane et.al on removal of diethyl phthalate with UV/S₂O₈⁻² showed that the optimum pH for high removal efficiency was 11 (Esrafili et al., 2016). Solution pH in alkaline range were more appropriate than acidic (Lin et al., 2011; Rasoulifard et al., 2012; Guo et al., 2014).



Figure 4. The effects of initial pH on removal efficiency of catechol pH= (3-11), UV radiation= 30 W, Persulfate concentrations (0.0-2.1 M), catechol concentrations (100- 500 mg L⁻¹), and Time: 60 min].

3.6. The interaction effects of pH and SO4° on the removal efficiency

As can be seen in Figure 5, the findings showed that there were significant relationship between the interaction effects of pH and the sulfate radical on the removal efficiency of catechol. The most removal efficiency of catechol was observed at neutral. At a constant pH with increasing concentrations of sulfate radicals, the removal efficiency of Catechol increased. persulfate radical is an oxidizing agent and by increasing the concentration the rate of decomposition increased(Esrafili et al., 2016). The stability of persulfate in aqueous solutions are more than OH°(Shokouhi et al., 2010). Another reaction which occurred in in alkaline pH is reaction between persulfate and OH° radicals (Eq. 4) (Xu et al., 2012). This reaction significantly decreases the removal efficiency, because of the lack of radicals under this conditions.

$$SO_4^{\circ} + OH^{\circ} \rightarrow H^+ + SO_4^{-2}$$
4

The results were agreement with the results of Piternal et.al (Chu et al., 2015). Also, Seymohamaddi et.al obtained the similar results in removal of 2,4-dichlorophenol by ultrasound - activated persulfate in aqueous solutions (Shukla et al., 2010c). Cho et.al concluded removal efficiency in acidic pH was much better than alkaline (Peternel et al., 2010).



Figure 5. The simultaneous effects of pH and initial catechol concentrations on removal efficiency [pH= (3-11), UV radiation= 30 W, Persulfate concentrations (0.0-2.1 M), Catechol (100- 500 mg L⁻¹), and Time: 60 min].

3.7. The interaction effects of SO4° and catechol concentrations on removal efficiency

As can be seen in Figure 6, the results showed that there was a significant relationship between the sulfate radical and catechol concentrations on removal efficiency of catechol ($P_{valve} < 0.05$). At constant concentration of persulfate radical, catechol removal efficiency decreases with increasing of catechol concentration.



Figure 6. The simultaneous effects of SO_4° and catechol concentrations on removal efficiency [pH= (3-11), UV radiation= 30 W, persulfate concentration (0.0-2.1) M, catechol concentrations (100- 500 mg L⁻¹), and contact time= 60 min].

3.8. The effect of contact time on removal efficiency

Kinetic studies are used to predict the rate of degradation and its mechanisms (Golmohammadi et al., 2016). Figure 7 shows the results of kinetic studies of catechol degradation with $UV/S_2O_8^{-2}$ processes in optimum coditions. The results showed that the rate of pollutant removal was fitted to pseudo- the pseudo- first order model (R²=0.98%).



Figure 7. The effects of contact time on removal efficiency in optimum conditions [pH= 7, UV radiation= 30 W, persulfate concentrations (0.04 M), catechol concentration (100 mg L⁻¹).

3.9. The simultaneous effects of variables

The removal efficiency obtained in optimum conditions by each variable are illustrated in Figure 8. The results showed removal efficiency of UV radiation and the sulfate radical radicals alone were 8.5% and 45%, respectively. The results indicated that UV radiation was caused low degradation of catechol. Ghaderpoori et al study (2016) showed that UV radiation alone was not useful to degrade the linear alkylbenzene sulfonate (LAS) (Ghaderpoori and Dehghani, 2016). Like UV radiation, the sulfate radical had little effect on catechol degradation (actually a little more of UV radiation alone). However, combination of UV radiation and the sulfate radical had removal efficiency of catechol about 88%. In this stage, the sulfate radical produced, which was an effective factor in promotion of removal efficiency. In fact, the synergic effects were result from the presence of UV radiation (Safari et al., 2015). It enhances UV/S₂O₈²⁻ and produces the sulfate radical which can be effective in degradation of organic matters. The previous studies in agreement to this study that the UV radiation was an activation important factor for persulfate radicals and the sulfate radical (Liu and Li, 2006; Sun et al., 2011; Wang and Liang, 2014; Astereki et al., 2016).



Figure 8. Removal efficiency of various processes in optimum conditions [pH= 7, UV radiation= 30 W, persulfate concentrations (0.04 M), catechol concentration (100 mg L⁻¹), and contact time= 60 min].

3.10. Mineralization of Catechol

COD is an important indicator for complete degradation of organic matters. Figure 9 shows the removal efficiency of COD and catechol in optimum conditions. As can be seen in figure 9, the removal efficiency trends of COD and catechol are the same. On the other hand, after 80 min the removals efficiency of catechol and COD were 99.6 and 85%, respectively, which are agreement to Mousavi et al(2014) obtained removals efficiency 98 and 74.4% for catechol and COD, respectively(Moussavi et al., 2014). The results showed UV/S₂O₈²⁻ completely degraded catechol instead of slight degradation of target pollutant. The differences between two charts in figure 9 demonstrate the production of by-products, which are created by degradation of catechol. Lin et.al concluded which this process can completely (100%) remove phenol from aqueous solutions within 20 min (Fang and Shang, 2012). In another study conducted by Fang et.al, this process could remove 2-bromoacetamide completely from aquatic environments (He et al., 2013). Finally, the use of these processes before biological systems can decrease COD less than discharge standards for wastewater into environment



Figure 9. The removals efficiency of COD and catechol in optimum conditions [pH= 7, UV radiation= 30 W, persulfate concentrations (0.04 M), catechol concentration (100 mg L⁻¹].

4. Conclusion

In this study, we investigated the optimization of fluoride removal with $UV/S_2O_8^2$. To design experiments, Design of Experiments Software and CCD was applied. In order to determine removal efficiency of catechol, initial catechol concentrations, pH, and persulfate radicals were considered. The results showed that the catechol removal by $UV/S_2O_8^{-2}$ was fitted to polynomial models. Removal efficiency of catechol in the optimal conditions obtained 90%. The best pH to remove the catechol was neutral conditions. The removal efficiency of catechol was reduced by almost 20% at acidic and alkaline pH.

5. Acknowledgement

The study authors are grateful for financial support from Khorramabad University of Medical Sciences

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