



ORIGINAL ARTICLE

Mineralization, kinetics, and degradation pathway of pentachlorophenol degradation from aqueous media via persulfate/dithionite process



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Abstract The applicability of the dithionite/persulfate (DTN/PS) process for the degradation of pentachlorophenol (PCP) as an organic contaminant from aqueous solutions was investigated. Effective operational parameters, including the initial PCP concentration (25, 50, 100, and 150 mg/L), PS concentration (5, 10, 15, and 20 mg/L), DTN concentration (2.5, 5, 7, and 10 mg/L), solution pH (5, 7, 9, and 11), and reaction time (3, 5, 7, and 10 min) were investigated. To identify the influences of experimental factors involved in PCP degradation, an experimental design based on an orthogonal array was proposed using the Taguchi method. Based on the results, 97.28% of the PCP was removed at the optimal conditions (initial concentration of 25 mg/L, Na-PS (sodium persulfate) concentration of 20 mg/L, Na-DTN (sodium dithionite) concentration of 10 mg/L, pH of 11, and reaction time of 10 min) in the DTN/PS process. Moreover, COD and TOC removal rates were 75.2% and 41% in the DTN/PS process, respectively. An analysis of variance (ANOVA) indicated that PS is the most effective agent in removing PCP in the DTN/PS process. The compounds of phenol, 3,4-dichlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, oxalic acid, propionic acid, tetrachloro-o-benzoquinone, and butanedioic acid were identified as intermediates.

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1. Introduction

The recalcitrant and toxic organic compounds in industrial wastewaters have caused serious public health and environmental problems when released into the environment. Phenol and its derivatives are organic pollutants in industrial wastewaters (Busca et al., 2008). Pentachlorophenol (PCP) with the chemical formula of C_6Cl_5OH is a derivative of the phenol family. Due to the high number of chlorine on its benzene ring, it has received more attention than other derivatives (Willis et al., 1995). PCP is utilized for various purposes such as the manufacture of wood preservatives, reinforcement of wooden stairs, fences, pesticides, and herbicides (Zheng et al., 2011). The World Health Organization (WHO) reported PCP concentrations as high as 25–150 mg/L in industrial effluents, 10.5 mg/L in a river, and 0.01 mg/L in water samples (WHO, 1996). According to the guidelines of the National Toxicology Program (NTP), the permissible level of PCP is 0.3 mg/L in aquatic environments (NTP, 1999) and 0.001 mg/L in drinking water (Choi et al., 2020). This organic matter adversely affects the blood, immune system, kidneys, liver, lungs, central nervous system, gastrointestinal tract, skin, and eyes (Willis et al., 1995, Wilhelm et al., 2008, Rahman and Anuar, 2009). The Environmental Protection Agency (EPA) has classified PCP into group B2 (possibly carcinogenic to humans) in its classification of organic substances as carcinogenic (EPA, 1984). Since PCP is a toxic substance with high mutagenicity and carcinogenicity, its removal from industrial wastewater has been considered by researchers (Seyedi et al., 2019). There are several ways for PCP removal from contaminated aquatic media, such as electrochemical oxidation, photocatalytic degradation, and advanced oxidation processes (AOPs) (Seyedi et al., 2019, Edgehill and Finn, 1983, Tolardo et al., 2019, Liu et al., 2004, Pan et al., 2011). These methods offer disadvantages, including the impossibility of incomplete removal of pollutants, being uneconomical, low adsorption capacity, increased need for chemical compounds, and the production of sludge or waste materials that require further treatment (Song et al., 2019, Jung et al., 2017, Turi and Rossky, 2012). Hydroxyl radicals (OH^\bullet), sulfate radicals ($SO_4^{\bullet-}$), and superoxide radicals ($O_2^{\bullet-}$) are produced in AOPs for removing organic pollutants from aquatic sources (Song et al., 2019). Of the most common approaches to persulfate activation for producing sulfate radical ($SO_4^{\bullet-}$) (with a high redox potential, 2.5–3.1 V), one can refer to ascorbic acid (Cao et al., 2019), UV irradiation (Qian et al., 2016), heat (Fang et al., 2017), and carbon (Chen et al., 2016). Table 1 summarizes the disadvantages of the most common approaches to PS activation methods. Hence, it is useful to help investigate other activation methods. $SO_4^{\bullet-}$ derived from persulfate (PS) has attracted considerable attention due to its constancy, durability, and high ability to react. The advantages of $SO_4^{\bullet-}$ include relatively low cost, high solubility in the aquatic source, high stability at room temperature, and safe end products. Therefore, $SO_4^{\bullet-}$ is considered an effective oxidant among AOPs (Romero et al., 2010). Dithionite (DTN) as a reducing agent activates PS and converts it to $SO_4^{\bullet-}$. Weak S-S bond of DTN breaks to produce two radical anions of sulfur

dioxide ($SO_2^{\bullet-}$) with a standard reduction potential (-0.66) (Song et al., 2019, Rinker et al., 1959, Song et al., 2020). When persulfate is combined with DTN, it is important to investigate whether it can form some highly active radicals. As an environmentally friendly reductant, dithionite and its reaction products (thiosulfate, sulfite, and sulfate) can activate persulfate to produce reactive species. DTN can act as a free radical initiator in the AOPs with the normal reduction potential ($E_0 = 1.12$ V) (Song et al., 2020). As a redox system, the PS/DTN process may produce sulfate radicals and other oxysulfur radicals. It is possible to improve the degradation of organic pollutants by combining PS and DTN (Liu et al., 2019). The RSE% (reaction stoichiometric efficiency) values were calculated to evaluate the utilization efficiency of PS under different operating conditions (Qi et al., 2021). Sulfate ion (SO_4^{2-}) is a common product of the DTN/PS process that is not usually considered a contaminant at low concentrations.

In this study, the Taguchi statistical model (an OA (4^5) L16) was adopted as the experiment design. Taguchi is an efficient method for optimizing the factors affecting the test, reducing the number of tests required to determine the optimal conditions, decreasing time and costs, and achieving the best response in the elimination conditions (Maazinejad et al., 2020). The principle goal of this study was to apply the Taguchi approach to compare the efficiency of the DTN process, the PS process, and the DTN/PS combination process in removing PCP from an aquatic environment, and identify the synergistic effect of PS and DTN. In addition, the effects of PS and DTN dose, pH, initial concentration of PCP as a pollutant, and reaction time on the removal efficiency of the DTN/PS process were investigated. The by-products after the PCP degradation process and predominant reactive species in the DTN/PS process were also identified. The results of this study can be used in wastewater treatment and the removal of similar pollutants in small industrial units.

2. Materials and methods

2.1. Chemicals and reagents

PCP with a purity of 97%, sodium persulfate with a purity of 98%, sodium dithionite with a purity of 88%, phosphate, ammonium hydroxide, potassium ferric cyanide, and 4-aminoantiprine reagent were purchased from Sigma-Aldrich Co. Potassium dihydrogen phosphate and dipotassium hydrogen phosphate were used to prepare the phosphate buffer. The stock solution and all the working solutions were prepared using deionized water (18.2 M Ω).

2.2. Experimental setup and method

The stock solution of PCP (1000 mg/L) was prepared according to the standard method (dissolving 1 gr of PCP powder in

Table 1 The summary of the literature on other PS activation methods and their disadvantages.

Process	Disadvantages	Reference
UV	Costly, requires higher doses of the persulfate and more time (100 mg/L, 30 min)	
MW	Low removal efficiency (67%).	
Ascorbic acid	High required time and low removal efficiency (180 min, 71.3%)	
Heat	Costly (requires specific equipment and emissions control, inconvenient to operate in the subsurface environment)	
Transition metal ions	Secondary pollution	
Base activation	Requires higher doses of the sodium hydroxide (costly, and can cause environmental complications)	
Organic substrates	Costly, environmental concerns	
Nano-carbon materials	Costly, environmental concerns	

Table 2 Controllable factors and their levels.

Factor	Explanation	Level ₁	Level ₂	Level ₃	Level ₄
A	Contaminant concentration (mg/L)	25	50	100	150
B	PS concentration (mg/L)	5	10	15	20
C	DTN concentration (mg/L)	2.5	5	7.5	10
D	pH	5	7	9	11
E	Reaction time (min)	3	5	7	10

0.1 M sodium hydroxide solution), and different concentrations of PCP (25, 50, 100, and 150 mg/L) were prepared from deionized water. This study considered five influential factors on removal in the DTN/PS process, and each factor had four levels (Table 2). Depending on the type of process (DTN/PS, DTN alone, and PS alone), DTN and PS were added to the contaminant solution. Mixing was performed with a magnetic stirrer during specific reaction times. All the reactions were conducted at room temperature (22 ± 2 °C) in an amber glass flask with a volume of 100 mL. Then, the amount of soluble PCP was determined by spectrophotometry.

PCP removal followed the pseudo-first-order (PFO) kinetics law and was calculated according to Eq. (1):

$$\ln\left(\frac{C_t}{C_0}\right) = -K_{\text{obs}} \times t \quad (1)$$

C_t is the PCP concentration at t time, C_0 is the PCP concentrations at 0 time, and K_{obs} (min^{-1}) is the removal rate constant (Asgari et al., 2020).

To determine the synergistic effect of DTN and PS on PCP degradation, the DTN/PS, PS alone, and DTN alone processes were investigated under the defined optimal conditions. Tert-butanol (TBA) and methanol (MA) were used as radical scavengers in the DTN/PS process (Liang and Su, 2009, Ghorbanian et al., 2019). Chemical oxygen demand (COD) and total organic carbon (TOC) tests were performed to determine the mineralization rate of PCP. The average oxidation state (AOS) was calculated according to Eq. (2):

$$\text{AOS} = \frac{\text{TOC}_t - \text{COD}_t}{\text{TOC}_t} \times 4 \quad (2)$$

The carbon oxidation state (COS) was obtained from Eq. (3):

$$\text{COS} = \frac{\text{TOC}_0 - \text{COD}_t}{\text{TOC}_0} \times 4 \quad (3)$$

TOC_0 is the TOC concentration at 0 time, and TOC_t and COD_t are the TOC and COD concentrations at t time, respectively (Orts et al., 2020). The LC-MS technique was used to detect the intermediates and degradation pathway of PCP in the DTN/PS process.

2.3. Experimental design and data analysis

The experiments were designed with the Taguchi OA L16 (4^5), as given in Table 3. To evaluate the experimental outcomes, the signal-to-noise ratio (S/N) was utilized. How to calculate this ratio varies concerning the type of optimization, and three types of S/N ratio analysis are performed: higher is better (HB), nominal is better (NB), and lower is better (LB) (Ramavandi et al., 2014). ‘‘Noise’’ refers to the effect of each factor on each operation, and ‘‘signal’’ refers to the response

to the change in each operational variable (Mohan et al., 2005). The aim of this study was the maximum removal of PCP, and maximization was thus necessary. The S/N value was calculated according to Eq. (4) (Zolfaghari et al., 2011):

$$S/N = -10 \log_{10} \left[\frac{1}{n} \sum \left(\frac{1}{RE_i} \right)^2 \right] \quad (4)$$

n is the number of experiment replications, and RE represents the removal efficiency in each run. The RE was calculated using Eq. (5): $C_0 - C_e$

$$\% \text{Removal Efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (5)$$

C_0 is the initial concentration, and C_e is the balance concentrations of PCP (mg/L).

Mean analysis (ANOM) was performed to achieve the optimal conditions for each parameter involved in the DTN/PS process in PCP removal. First, the mean of the signal-to-noise ratio ($M_{S/N}$) for each parameter was determined at specific levels. The maximum value of $M_{S/N}$ was selected as the best condition for each parameter (Zolfaghari et al., 2011). $M_{S/N}$ is given in Eq. (6):

$$M_{S/N} = M_{\text{Factor}=I}^{\text{Level}=i} = \frac{1}{n_i} \sum_{j=1}^{n_i} \left[\left(\frac{S}{N} \right)_{\text{Factor}=I}^{\text{Level}=i} \right]_j \quad (6)$$

The $M_{S/N}$ for each factor is presented in Table 4. The highest mean of the S/N is determined as the best condition of each factor. Moreover, the effect of each factor on PCP removal was determined by variance analysis (ANOVA). The percentage contribution of each factor (R_F) on PCP removal in the DTN/PS process was calculated by the following Eq.

$$R_F = \frac{SS_F - (DOF \times V_{ER})}{SS_T} \times 100 \quad (7)$$

By subtracting 1 from the number of levels of each factor ($L-1$), the degree of freedom for each factor (DOF_R) is obtained. The total sum of squares (SS_T) is given by Eq. (8):

$$SS_T = \sum_{j=1}^m \left(\sum_{i=1}^n RE_i^2 \right) - mn(\overline{HDE}_T)^2 \quad (8)$$

\overline{RE}_T , is given by Eq. (9)

$$\overline{RE}_T = \sum_{j=1}^m \left(\sum_{i=1}^n RE_i \right) / (mn) \quad (9)$$

m characterizes the number of tests, and n indicates the number of replications. The factorial sum of squares, SS_F , is given by Eq. (10):

$$SS_F = \frac{mn}{L} \sum_{k=1}^m \left(\overline{RE}_k^F - \overline{RE}_T \right)^2 \quad (10)$$

Table 3 Taguchi design experiments, results, and their corresponding S/N values.

Run	Factor					%RE ^a			S/N	
	[PCP] (mg/L)	[PS] (mg/L)	[DTN] (mg/L)	pH	Time (min)			M _{RE}	Actual	Predict
1	25	5	2.5	5	3	81.05	81.31	81.18	38.19	38.25
2	25	10	5	7	5	86.05	86.05	86.05	38.7	38.78
3	25	15	7.5	9	7	93.92	94.07	93.99	39.46	39.31
4	25	20	10	11	10	97.5	97.07	97.28	39.76	39.9
5	50	5	5	9	10	88.03	88.10	88.06	38.9	38.93
6	50	10	2.5	11	7	89.62	89.45	89.53	39.04	38.97
7	50	15	10	5	5	88.58	88.41	88.49	38.94	38.87
8	50	20	7.5	7	3	88.44	88.37	88.40	38.93	38.97
9	100	5	7.5	11	5	86.83	86.70	86.76	38.77	38.74
10	100	10	10	9	3	87.17	87.06	87.11	38.8	38.74
11	100	15	2.5	7	10	89.22	88.91	89.06	39	38.9
12	100	20	5	5	7	88.02	87.92	87.97	38.88	38.84
13	150	5	10	7	7	83.81	84.00	83.90	38.47	38.54
14	150	10	7.5	5	10	85.34	85.19	85.26	38.61	38.64
15	150	15	5	11	3	86.73	86.86	86.79	38.77	38.74
16	150	20	2.5	9	5	85.86	85.73	85.79	38.67	38.79
M	–	–	–	–	–	87.82	87.88	85.87	–	–

The maximum value of the S/N ratio Shown boldface among the 16 tests.

^aRemoval efficiency.

A variance of error, V_{ER} , is given by Eq. (11):

$$V_{ER} = \frac{SS_T - \sum_{F=A}^E SS_F}{m(n-1)} \quad (11)$$

2.4. Analytical methods

Minitab®17.1.0 was employed in the Taguchi design. The pH of the solution was measured using the electrode pH meter

(Adwa AD8000, Romania). The residual PCP in the reaction was measured by a DR-5000 spectrophotometer at the maximum absorbance wavelength of 500 nm (HACH DR-5000, USA). COD ampoules (HACH Chemical, USA) were used to determine COD. Moreover, a TOC analyzer (Vario TOC Cube Elementar, Germany) was employed to evaluate the rate of mineralization. A liquid chromatograph-mass spectrometer (LC-MS) (Shimadzu LC-MS 2010 A, Japan) system was utilized for intermediates' analysis. This sys-

Table 4 ANOM results for determining the optimum conditions.

Factor/Level	S/N				M _{S/N}
	i = 4	i = 3	i = 2	i = 1	
PCP/1	39.76	39.46	38.7	38.19	39.03
PCP/2	38.93	38.94	39.04	38.7	38.95
PCP/3	38.88	39	38.80	38.77	38.86
PCP/4	38.67	38.77	38.61	38.47	38.63
PS/1	38.47	38.77	38.9	38.19	38.58
PS/2	38.61	38.80	39.04	38.7	38.79
PS/3	38.77	39	38.94	39.46	39.04
PS/4	38.67	38.88	38.93	39.76	39.06
DTN/1	38.67	39	39.04	38.19	38.72
DTN/2	38.77	38.88	38.9	38.7	38.81
DTN/3	38.61	38.77	38.93	39.46	38.94
DTN/4	38.47	38.80	38.94	39.76	38.99
pH/1	38.61	38.88	38.94	38.19	38.65
pH/2	38.47	39	38.93	38.7	38.77
pH/3	38.67	38.80	38.9	39.46	38.96
pH/4	38.77	38.77	39.04	39.76	39.08
Time/1	38.77	38.80	38.93	38.19	38.67
Time/2	38.67	38.77	38.94	38.7	38.77
Time/3	38.47	38.88	39.04	39.46	38.97
Time/4	38.61	39	38.9	39.76	39.07

The maximum value of the mean of the S/N ratio Shown boldface for a specific factor among the four levels.

tem has a C18 column (100 mm × 2.1 mm) and an electron spray ionization source. The mobile phase consisted of 60/40% acetonitrile/ultra-pure water + 0.1% formic acid employed for the analysis. Mass spectra (MS) was conducted under the following conditions: mode, ESI⁺; detection gain, 1.8 kV; prob volt, 4 kV; CDL volt, 25 V; gas nebulizer, N2 (grade 5); flow gas, 1.2 L min⁻¹; CDL temperature, 250 °C; block temperature, 250 °C.

3. Results and discussion

3.1. Optimization of the operational parameters

Fig. 1a depicts the PCP removal efficiency as a function of reaction time in various processes, including PS, DTN, and DTN/PS. As shown in Fig. 1a, PCP cannot be efficiently removed by a single PS and DTN process. The results exhibited that PCP removal obeys the PFO kinetic, calculated according to Eq. (1). To compare the potential of the DTN/PS, PS, and DTN processes for the PCP removal efficiency, the rate constants (K_{obs}) were calculated by plotting $-\ln\left(\frac{PCP_t}{PCP_0}\right)$ versus reaction time (t), as shown in Fig. 1a. For this purpose, the kinetics of the PCP removal were evaluated under optimum conditions. The K_{obs} obtained for PCP removal from the DTN/PS process (0.299 min⁻¹) was approximately 4.3 times higher than the sole PS process (0.07 min⁻¹) and 9.96 times higher than the sole DTN process (0.03 min⁻¹), and a sole PS process was approximately 2.33 times higher than the sole DTN process. PS is activated by DTN and produces more sulfate radicals, thereby enhancing the efficiency of PCP removal. The kinetic information indicated the superiority of the DTN/PS process over PS alone and DTN alone processes. Due to the decline of the production rate of reactive radicals in the absence of DTN or PS, as well as the reduction of the synergistic effect of DTN coupled with PS, the efficiency of the processes of PS alone and DTN alone decreased. This finding indicates a synergistic effect between DTN and PS. A similar result was reported in the analysis by Song et al. (Song et al., 2020). Therefore, using the DTN/

PS process is an efficient option for PCP removal. Hence, it is beneficial to explore the optimal reaction parameters of the DTN/PS system.

To acquire the optimal conditions of the DTN/PS process, 16 experiments were designed and performed (Table 3). The maximum value of the S/N ratio is shown in boldface. In Table 4, the maximum value of the $M_{S/N}$ is shown in boldface for a specific factor among the four levels, indicating the optimum condition for PCP removal. According to Table 4, the optimal PCP concentration is 25 mg/L, and the optimal conditions for the parameters of PS, DTN, pH, and reaction time are 20 mg/L, 10 mg/L, 11, and 10 min, respectively. The optimal conditions of Run 4 and the optimal condition proposed by the Taguchi model are the same. The results demonstrated that, at the optimal condition of effective parameters in PCP removal, an average removal efficiency of 97.28% was obtained.

Fig. 2 shows that when the PCP concentration increases from 25 to 150 mg/L, the S/N for PCP removal drops from 39.03 to 38.63. The results of the PCP degradation at different initial PCP concentrations (in the 25–150 mg/L range) are depicted in Fig. 3. According to Fig. 3, at a concentration of 25, 50, 100, and 150 mg/L PCP, approximately 97.28%, 88.4%, 79.06%, and 67.31% of PCP degradation in 10 min contact time were achieved. In addition, the K_{obs} value of PCP degradation at 25 mg/L initial concentration of PCP was 0.299 min⁻¹ that is approximately 3.15 times higher than the value of 150 mg/L initial concentration (0.095 min⁻¹). As the initial concentration of the contaminant increases, the oxidizing radicals are insufficient to oxidize pentachlorophenol, and the removal efficiency decreases. By decreasing the initial concentration of pentachlorophenol, the production rate of oxidizing radicals exceeds the rate of consumption, and the removal efficiency increases. There is a reverse correlation between the initial concentration and removal efficiency. In fact, the ratio between reactive generated radicals and the content of PCP molecules decreased, and the radicals are not sufficient for degrading organic pollutants. The outcome was similar to the study by Seidmohammadi et al. (Seidmohammadi et al., 2020) who confirmed that the organic removal rate is dependent on the pollutant's initial concentrations, such that removal rates gradually decreased with increasing the initial organic concentrations.

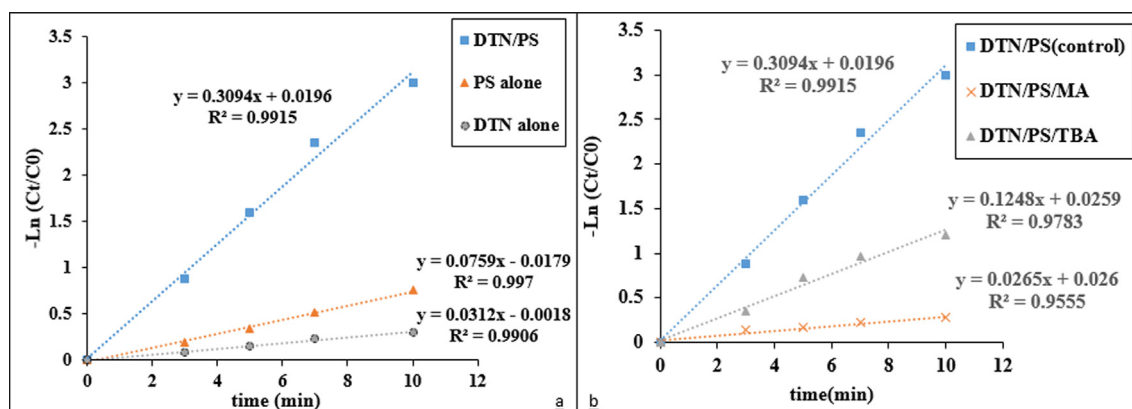


Fig. 1 Kinetic of PCP Removal under different process. Experimental conditions: PS = 20 mg/L, DTN = 10 mg/L, pH = 11, initial Concentration of PCP = 25 mg/L.

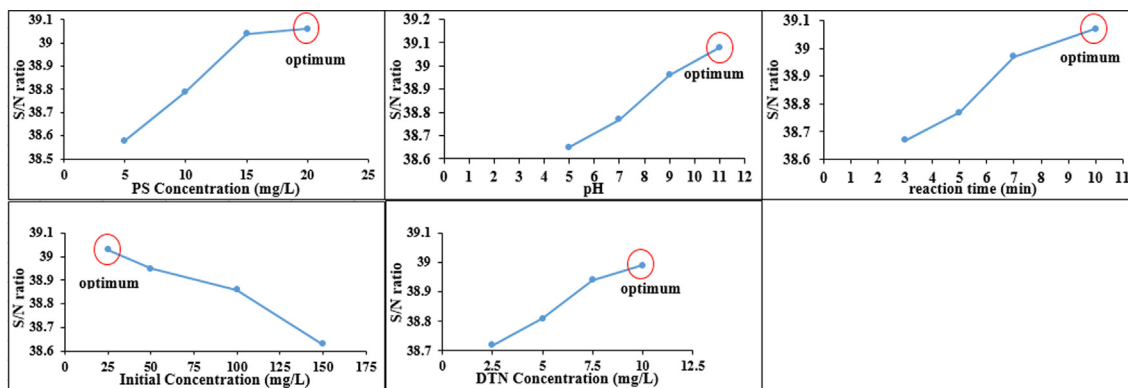
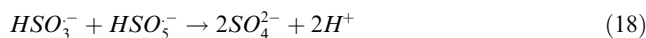
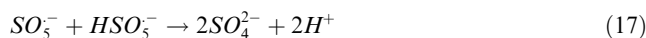
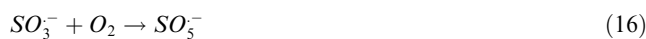
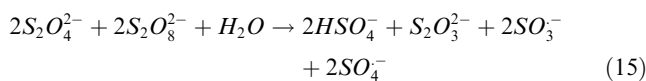
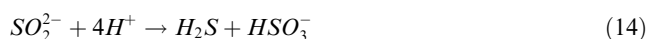


Fig. 2 Signal-to-noise main effect plots: Persulfate dosage, pH, time, initial concentration, and Dithionite dosage.

The most important reactive species in AOPs processes are sulfate radicals, and PS and DTN are their sources. DTN as a reducing agent activates PS and converts it to $SO_4^{\cdot-}$, according to Eqs. (12)-(19) (Song et al., 2019, Liu et al., 2019).



When more sulfate radicals are released, PCP degradation will increase accordingly. Fig. 2 shows that the efficiency of PCP removal was increased with the elevated concentration of PS and DTN. When the PS concentration rises from 5 to 20 mg/L, the S/N ratio increases from 38.58 to 39.06, and

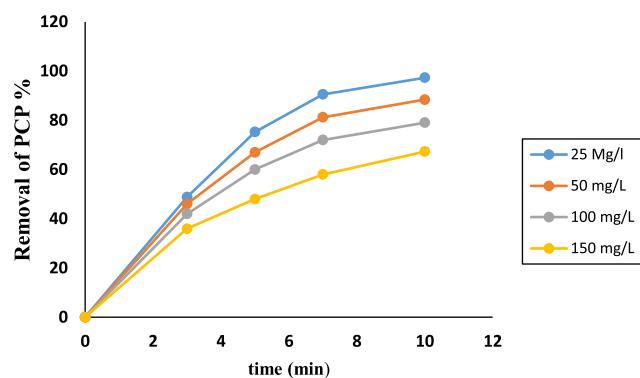
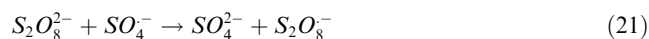


Fig. 3 Effect of initial concentration of PCP on PCP removal. Experimental conditions: PS = 20 mg/L, DTN = 10 mg/L, and pH = 11.

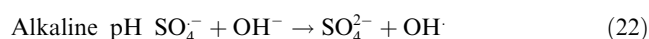
when the DTN concentration increases from 2.5 to 10 mg/L, the S/N ratio increases from 38.72 to 38.99. Based on Eqs. (20) and (21), by raising the concentration of PS, sulfate radicals are trapped and quickly consumed by themselves. Moreover, sulfate radicals react by surplus PS and decrease the generation of PS reactive species, which is not economically viable. Furthermore, the excess concentration of DTN leads to scavenging of the generated reactive species (Song et al., 2019). Song et al. (Song et al., 2020) have reported that DTN potentially reduces PS, which leads to the release of more sulfate radicals, which subsequently promotes the removal efficiency.



The RSE values were 3.7% and 18.1% in the presence of 20 mg/L PS after 10 min of reaction in the DTN/PS and PS alone systems, respectively. It was found that the oxidative species in the DTN/PS system are more efficient.

In AOPs technologies, the type and concentration of active radicals depend on the pH of the solution (Ghorbanian et al., 2019). In alkaline conditions, the redox potential of OH^{\cdot} was < 2.9 V and, with increasing the solution pH, the redox potentials of OH^{\cdot} and $SO_4^{\cdot-}$ both decreased. According to a previous study (Pan et al., 2021), the redox potential of $SO_4^{\cdot-}$ was much higher than OH^{\cdot} . In addition, sulfate radicals can react with water at all pH values to produce OH^{\cdot} . According to the study by Liang et al., alkaline conditions (i.e., $pH > 8.5$) can induce the mechanism of $SO_4^{\cdot-}$ interconversion to OH^{\cdot} (Eq. (22)) in the persulfate activation system (Liang and Su, 2009).

Fig. 2 shows that when the pH value increases from 5 to 11, the S/N ratio is enhanced.



These observations are consistent with the findings reported by Lin et al. (Lin et al., 2011) and Gao et al. (Gao et al., 2015). They investigated the influence of pH on the removal of organic compounds, and found that the removal efficiency effectively increases in the alkaline environment ($pH = 11$).

Fig. 2 indicates that the S/N for PCP removal increases from 38.67 to 39.07 as the reaction time rises from 3 to 10 min. Consequently, raising the reaction time has a direct effect on degradation efficiency because the production of

Table 5 ANOVA results for S/N.

Factor	DOF	Sum of Squares	Mean Square	F Value	p-value	R _F (%)
PCP(mg/L)	3	0.323391	0.323391	31.87477	0.0002	18.84
PS(mg/L)	3	0.572666	0.572666	56.44429	< 0.0001	25.08
DTN(mg/L)	3	0.178407	0.178407	17.58448	0.0018	13.99
PH	3	0.428388	0.428388	42.22365	< 0.0001	21.68
Time(min)	3	0.372525	0.372525	36.71758	0.0001	20.41
Error	0	0.101457	0.010146	—	—	—
Total	15	1.976833	—	—	—	100

the radical sulfate is increased by raising the reaction time, thereby promoting the efficiency of PCP degradation using the DTN/PS process.

3.2. Contribution percentage of parameters

An analysis of variance (ANOVA) was performed on M_{S/N} to determine each factor's participation in the DTN/PS process. The factorial sum of squares (SS_F), the total sum of squares (SS_T), the variance of the error (V_{Er}), and the percentage contribution of each factor (R_F) were obtained from Eqs. (7)–(11), and these values are presented in Table 5. The contribution percentage and rank order of each factor for PCP removal are in the following order: PS concentration (25.08%); solution pH (21.68%); reaction time (20.41%); initial concentration (18.84%); DTN concentration (13.99%). The most influential factor among the five factors affecting the removal process was the initial PS concentration. For example, as the PS concentration is 20 mg/L, the average of PCP removal efficiencies in Runs 4, 8, 12, and 16 were 97.28%, 88.40%, 87.97%, 85.79%, respectively, and the average of all of them was 89.86%. Moreover, as the PS concentration was 5 mg/L, the average of PCP removal efficiencies in Runs 1, 5, 9, and 13 was 81.18%, 88.06%, 86.76%, and 83.90%, respectively, and the average of all of them was 84.97%. In other words, the effi-

ciency of PCP removal at a PS concentration of 20 mg/L was 4.89 times the efficiency of PCP removal at a PS concentration of 5 mg/L. In comparison, the efficiency of PCP removal at a DTN concentration of 10 mg/L was about 2.8 times the efficiency of PCP removal at a DTN concentration of 2.5 mg/L.

3.3. Mineralization of PCP

In PCP removal, an acceptable amount of PCP converts to CO₂, H₂O, and other mineral ions (mineralization). TOC and COD removal efficiencies in the optimal conditions were 41% and 75.2%, respectively. The variation of carbon oxidation state (COS) and the variation of the AOS determine the performance of the oxidation process, and mineralization is calculated according to Eqs. (2) and (3) (COS = 2.24, and AOS = 1.020). Although the process can continue to oxidize and mineralize the sample, oxidation processes were approximately 2 times higher than the mineralization magnitude. The results of this study are similar to other studies (Tolardo et al., 2019, Song et al., 2020, Song et al., 2019).

Based on the mineralization rates, if the reaction time is increased to 90 min, the TOC and COD values will reach 78% and 95%, respectively. It was demonstrated that enough reaction time was required for the almost complete mineralization of PCP, meaning that the breakdown of refractory

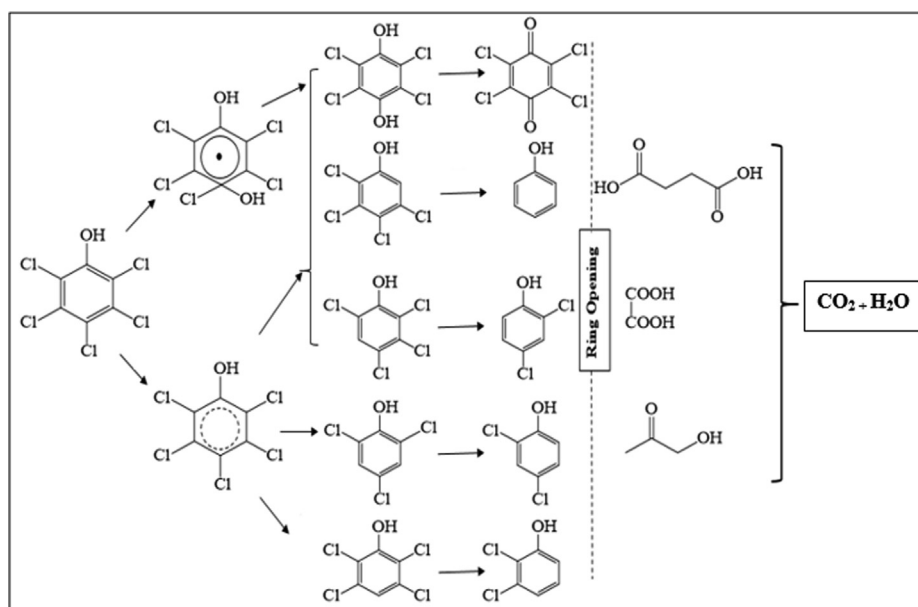
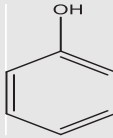
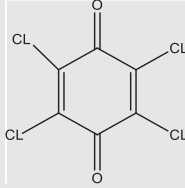
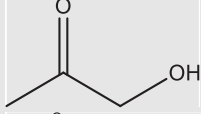
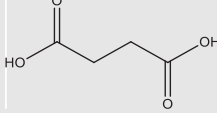
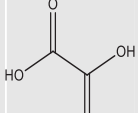
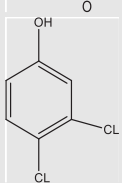
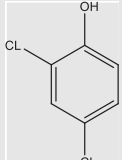
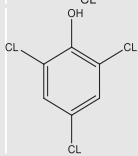


Fig. 4 A possible degradation pathway of pentachlorophenol.

Table 6 PCP degradation intermediate and products identified with LC-MS.

Number	Name	Chemical formula	Structure	Molecular mass
1	Phenol	C ₆ H ₆ O		94.11
2	Tetrachloro-o-benzoquinone	C ₆ Cl ₄ O ₂		245.88
3	Propionic acid	C ₃ H ₆ O ₂		74.08
4	Butanedioic acid	C ₄ H ₆ O ₄		118.08
5	Oxalic acid	C ₂ H ₂ O ₄		90.03
6	3,4-Dichlorophenol	Cl ₂ C ₆ H ₃ OH		163
7	2,4-Dichlorophenol	Cl ₂ C ₆ H ₃ OH		163
8	2,4,6-Trichlorophenol	Cl ₃ C ₆ H ₂ OH		197.45

organic compounds such as PCP can achieve proper response mineralization under the optimal operating parameters. However, Qi et al. reported that thermally activated persulfate has a low mineralization degree, which might be due to the production of refractory intermediates such as coupling products (Qi et al., 2021).

3.4. Detection of effective radicals

Reactive radicals (sulfate radicals, hydroxyl radicals, etc.) are often produced in PS-based AOPs (Song et al., 2019, Liu et al., 2019). TBA and MA are used as radical scavengers to assess the contribution of SO₄⁻ and OH[•] to PCP removal in the DTN/PS process. MA was selected for SO₄⁻ and OH[•] as an effective scavenger, and TBA was selected for OH[•] as an effective scavenger. Fig. 1b demonstrates that 97.28% of

PCP can be removed in 10 min without scavengers (Control). The addition of TBA (0.2 mol/L) and MA (0.2 mol/L) in the optimum condition decreased PCP degradation rate to 78.4% and 24%, respectively, compared with the free radical scavenger process within 10 min of reaction time. This finding indicated that both SO₄⁻ and OH[•] radicals are produced in the DTN/PS process, but SO₄⁻ played a more important role. The contributions of SO₄⁻ and OH[•] were 54.4% and 18.88%, respectively, suggesting that SO₄⁻ was the primary reactive species in the DTN/PS process, and OH[•] was also involved in this process. Fig. 1b displays that the K_{obs} obtained for PCP removal from the DTN/PS process (0.299 min⁻¹) was approximately 2.3 times higher than the DTN/PS/TBA process (K_{TBA, OH•} = 0.13 min⁻¹, K_{TBA, SO4•-} = 0.074), and 9.96 times higher than the DTN/PS/MA process (K_{MA, OH•} = 0.053, K_{MA, SO4•-} = 0.03). These K_{obs} indicate that in the presence

of methanol, removal efficiency is further reduced than in the presence of *tert*-butanol. Although both SO_4^- and OH^\cdot were produced and involved in the PCP removal reactions, SO_4^- played a prominent role in the PCP removal under the selected conditions. Note that PS or other radicals (SO_3^- , SO_5^- , etc.) produced in the series reactions were responsible for approximately 26.72 % of PCP degradation with alcohol-containing systems. Song et al. (Song et al., 2019), (Zou et al., 2021) and Liu et al. (Liu et al., 2019) reported similar results.

3.5. Pathways and intermediates

The LC-MS technique was adopted in the DTN/PS process to identify the intermediates generated and the degradation pathway of PCP. Molecular structure (MS) spectra were compared with PCP degradation intermediates in another AOP study to determine the intermediates. The results showed that PCP is degraded by sulfate radicals through three fundamental mechanisms: hydrogen abstraction; electron transfer; replacement and addition reaction with aromatic compounds (Ghorbanian et al., 2019). Based on the available results and previous studies (Qi et al., 2015, Asgari et al., 2020), a reasonable degradation pathway is depicted in Fig. 4. As shown in Table 6, several compounds such as phenol, 3,4-dichlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, oxalic acid, propionic acid, tetrachloro-o-benzoquinone, and butanedioic acid were defined as the main degradation intermediate products. More degradation on the intermediates converts them to more minor molecule compounds and finally mineralizes them to CO_2 and H_2O .

4. Conclusion

This study examined the optimum conditions for PCP removal from aquatic media using the DTN/PS process and the Taguchi method. The findings revealed that the optimum condition for PCP degradation occurs at the PS concentration of 20 mg/L, pH of 11, reaction time of 10 min, initial concentration of 25 mg/L, and DTN concentration of 10 mg/L. Experimental results showed that the DTN/PS process is highly effective in removing the PCP with a high RE (97.28% under optimum conditions). PS concentration is the most efficient factor in the performance of the DTN/PS process. After 10 min of reaction time using the DTN/PS process, COD and TOC removal rates of 75.2% and 41% were obtained in optimum conditions, respectively. The removal process of PCP followed the PFO kinetic, and sulfate radical was the predominant reactive radical produced in the oxidation process. During the PCP removal process, various products were identified and their degradation pathways in the DTN/PS process involved dechlorination and mineralization. The DTN/PS process as an advanced, capable, and environmentally friendly oxidation process can be utilized in most industries' wastewater treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.arabjc.2021.103357>.

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