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Advanced oxidative degradation of pentachlorophenol from aqueous media by Taguchi analysis: comparison of dithionite/persulfate and UV/persulfate processes

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ABSTRACT

Persulfate-based processes are a sort of advanced treatment that is effective in the degradation of a variety of pollutants. The capability of persulfate (PS) activated by dithionite (DTN) and ultraviolet (UV) to remove pentachlorophenol (PCP) as an organic pollutant from aqueous media was studied. In both processes, the PCP removal efficiency was measured using a variety of factors, such as the initial PCP concentration, PS concentration, DTN concentration, solution pH, and reaction time. An experimental design based on an orthogonal array was proposed, utilizing the Taguchi method for each process to investigate the impacts of experimental parameters involved in PCP removal. With a concentration of 25 mg/L PCP, 20 mg/L PS, and 10 mg/L DTN, pH 11, and a time of 10 min, optimal conditions for PCP removal in the DTN/PS process were determined (removal efficiency = 97.28%). Additionally, optimum UV/PS conditions were determined, including a concentration of 25 mg/L PCP, 100 mg/L PS, pH 11, and a reaction time of 40 min (removal efficiency = 98.78%). An analysis of variance (ANOVA) showed that PS is the most effective agent in removing PCP in both processes (25.08% in the DTN/PS process and 57% in the UV/PS process). Additionally, the COD and TOC removal rates in the DTN/PS process were 75.2% and 41%, and 82.3% and 61% in the UV/PS process, respectively. Furthermore, using LC-MS, the PCP degradation intermediates were detected, and possible transformation pathways were suggested. Overall, this study aims to shed light on the use of AOPs-SR to remove organic pollutants in water treatment. Based on the characteristics impacting each process, the DTN/PS method may be said to be superior to the UV/PS process (less reaction time, less persulfate) and the key reactants in both reactions are sulfate radicals. The quantity of mineralization in both procedures is nearly the same. As a result, these methods, notably DTN/PS, have a higher likelihood of removing more chlorinated organic chemicals.

Keywords: Persulfate; Dithionite; Ultraviolet; Pentachlorophenol; Taguchi analysis

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1. Introduction

Water treatment and reuse have been suggested due to a scarcity of water and the presence of environmental concerns caused by the discharge of wastewater and effluents into receiving water [1,2]. Phenol and its derivatives are frequent organic pollutants found in the effluent of many chemical companies, including those producing paper and pulp, insecticides, dyes, and chemicals. Furthermore, effluent from a variety of different sectors contains diverse forms of phenols [3,4]. Chlorinated phenols (CPs) are extremely important due to the presence of benzene rings and chlorine atoms on them and their diffusion through wastewater of industries such as industries producing pesticides, pharmaceuticals, paints, and wood preservatives [5]. Pentachlorophenol (PCP) is an organic compound of phenolic derivatives that, besides its high toxicity level, is a precursor pollutant that has harmful effects on humans (liver, kidneys, skin, blood, lungs, nervous system, stomach, intestine, and digestive tract), animals, and plants [6]. The permissible level of PCP in aquatic environments and drinking water is 0.3 and 0.001 mg/L, respectively [7,8]. The Agency for Research on Cancer (IARC) has classified PCP as a class B2 carcinogen that causes disorders of the endocrine system [9]. PCP as a recalcitrant pollutant and a highly chlorinated aromatic compound threatens human health and the ecosystem because it cannot be biodegraded efficiently in nature [10]. Thus, its removal from industrial wastewater is necessary. Processes like electrochemical oxidation, photocatalytic degradation, and advanced oxidation processes (AOPs) can remove PCP from contaminated aquatic media [11–15]. These technologies have drawbacks, such as the inability to remove pollutants completely, being uneconomical, having limited adsorption capacity, requiring more chemical compounds, and producing sludge or waste products that need additional treatment [16]. AOPs are oxidation technologies that are based on the generation of hydroxyl radicals ($HO^{\bullet}$) and sulfate radicals ($SO_4^{\bullet-}$) that can degrade toxic organic components and pathogens in water and wastewater [17]. Highly reactive oxygen species such hydroxyl, sulfate, and superoxide radicals, which have a great deal of potential to facilitate the breakdown of different substances, including PCP [18,19]. Sulfate radicals (E_0 = 2.6 V) have gained a lot of interest because of their consistency, durability, high capacity to react, cheap cost, high solubility in aquatic sources, high stability at room temperature, and safe end products [20]. Advanced oxidation processes based on sulfate radical (SR-AOPs), are AOPs based on electrochemical, sonochemical, photochemical, and chemical reactions such as the combination of persulfate (PS) with ultraviolet radiation (UV) [21] and Dithionite (DTN) [22]. In the study conducted by Govindan et al. [23], a concentration of 0.115 mM was used to remove pentachlorophenol in the presence of an iron anode. Also, in the study of Xie et al. [24], 0.01 mM of persulfate was used to remove 2-Methylisoborneol in the presence of UV. The drawbacks of the most used PS activation techniques are compiled in Table 1 [25]. In order to assist examine alternative activation methods. Organic pollutants can be degraded by ultraviolet (UV) radiation, either directly or in combination with chemical oxidants (e.g., hydrogen peroxide, PS, and chlorine) [26]. DTN ($S_2O_4^{2-}$) contains a long and weak S-S bond that could serve as the precursor of $SO_4^{\bullet-}$ and be used for the degradation of organic contaminants [22].

The mechanism of the reaction of UV/PS and DTN/PS processes with organic pollutants is as follows [22,26]:

$$\text{UV} + \text{PS} \rightarrow SO_4^{\bullet-} \tag{1}$$

$$\text{DTN} + \text{PS} \rightarrow SO_4^{\bullet-} \tag{2}$$

$$SO_4^{\bullet-} + \text{polluants} \rightarrow \text{byproduct} \tag{3}$$

In this study, the Taguchi statistical model, which is one of the experimental optimizing design methods based on the statistical principle, was adopted [27]. The Taguchi design technique has been proposed as appropriate statistical tools for designing and optimizing the researched

Table 1
Summary of the literature on other PS activation methods and their disadvantages

Process	Disadvantages	Process	Disadvantages
UV	Expensive, needs for greater persulfate dosages and longer time (100 mg/L, 30 min)	Transition metal ions	Secondary pollution
MW	Low removal efficiency (67%)	Base activation	Need greater sodium hydroxide dosages (costly, can cause environmental complications)
Ascorbic acid	Low removal effectiveness and a long necessary time (180 min, 71.3%)	Organic substrates	Costly, environmental concerns
Heat	Costly (needs specific technology and emissions control, cumbersome to operate in the subterranean environment)	Nano-carbon materials	Costly, environmental concerns

process [28,29]. In this work, the effects of PS, DTN, and PCP concentration, pH, and reaction time during the PCP removal process were studied. The main goal of this study is to compare the efficiency of the UV/PS and DTN/PS processes in the removal of PCP from the aquatic environment. Additionally, the impacts of PS and DTN dosage, pH, PCP beginning pollutant concentration, and reaction time on the DTN/PS and UV/PS processes removal effectiveness were looked at. The primary reactive species in the pathway were also identified, as well as the consequences of PCP breakdown. The findings of this study can be used in small industrial units for the treatment of wastewater and the elimination of comparable contaminants.

2. Materials and methods

2.1. Materials and apparatus

Phosphate, ammonium hydroxide, potassium ferric cyanide, 4-aminoantiprine, PCP with a purity of 97%, sodium persulfate with a purity of 98%, and sodium DTN with a purity of 88% were purchased from Sigma-Aldrich Co. The phosphate buffer was made with potassium dihydrogen phosphate and dipotassium hydrogen phosphate. Deionized water (18.2 M) was used to make the stock solution and all working solutions. All of the reactions in the DTN/PS process were carried out at room temperature (22°C ± 2°C) in a 100 mL amber glass flask. Also, the reactions of the UV/PS process were performed in a UV reactor (Fig. 1). In the Taguchi design, Minitab17.1.0 was used. The electrode pH meter was used to determine the pH of the solution (Adwa AD8000, Romania). A DR-5000 spectrophotometer was used to detect the residual PCP in the reaction solution at a maximum absorbance wavelength of 500 nm (HACH DR-5000, USA). COD was determined using COD ampoules (HACH Chemical, USA). In addition, the rate of mineralization was assessed using a TOC analyzer (Vario TOC Cube Elementar, Germany).

2.2. Experimental design

The Taguchi approach was used in this work to obtain the optimal variables for achieving the highest PCP removal percentage utilizing the DTN/PS and UV/PS processes. The experimental design proposed by Taguchi involves using an orthogonal array of L-16 possessed four factors of control at four levels of the UV/PS process, and the five factors of control at four levels of the DTN/PS process. Table 2 lists the evaluated parameters and their levels in this study. Tables 3 and 4 illustrate the structure of Taguchi's L-16 design and the results of PCP removal efficiency via UV/PS and DTN/PS processes. For each experiment, there were two replicates. The experimental observations are converted into signal-to-noise (S/N) ratios to evaluate the outcomes. Table 5 illustrates the results of ANOM Analysis for the determination of the optimal conditions for each process. The goal of this study was to remove as much PCP as possible, hence maximizing was required. The S/N value was calculated according to Eq. (4) [29]:

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

where N is the number of experiment replications, and RE represents the removal efficiency in each run. The RE was calculated using Eq. (5) [29]:

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

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

2.3. Experimental set-up

PCP stock solutions (1,000 mg/L) and varying concentrations of PCP were made from deionized water using the standard process (dissolving 1 g of PCP powder in 0.1 M sodium hydroxide solution). DTN and PS were added to the contaminated solution depending on the type of process (UV/PS and DTN/PS). Spectrophotometry was used to assess the quantity of soluble PCP. PCP removal followed the pseudo-first-order (PFO) kinetics law and was calculated according to Eq. (6):

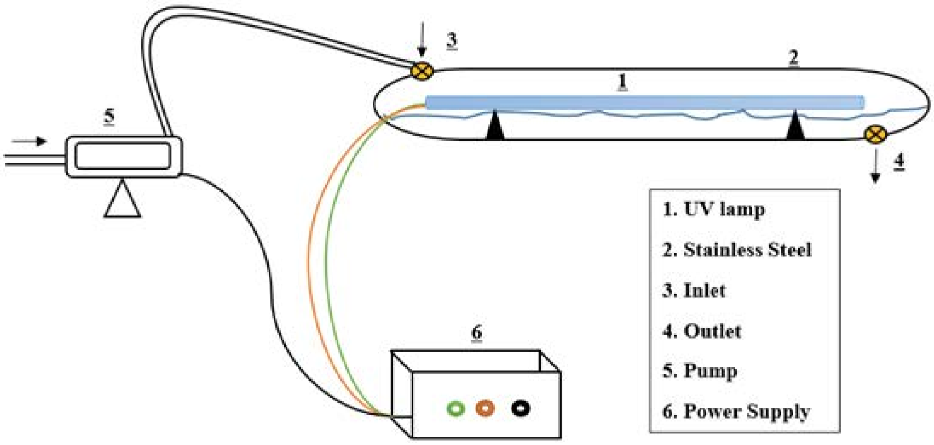


Fig. 1. Schematic of the UV reactor.

Table 2
Controllable factors and their levels

Processes	Factor	Explanation	$Level_1$	$Level_2$	$Level_3$	$Level_4$
	1	Contaminant concentration (mg/L)	25	50	100	150
UV/PS	2	PS concentration (mg/L)	25	50	75	100
	3	pH	5	7	9	11
	4	Reaction time (min)	10	20	30	40
	1	Contaminant concentration (mg/L)	25	50	100	150
	2	PS concentration (mg/L)	5	10	15	20
DTN/PS	3	DTN concentration (mg/L)	2.5	5	7.5	10
	4	pH	5	7	9	11
	5	Reaction time (min)	3	5	7	10

Table 3
Taguchi design experiments, results, and their related S/N values (UV/PS process)

Run	Factor					%RE		M_{RE}	S/N	
	[PCP] (mg/L)	[PS] (mg/L)	UV (nm)	pH	Time (min)	(1)	(2)		Actual	Predict
L_1	25	25	253.7	5	10	81	80.85	80.93	38.16	38.32
L_2	25	50	253.7	7	20	87.72	87.62	87.67	38.85	38.85
L_3	25	75	253.7	9	30	94.39	94.4	94.4	39.49	39.38
L_4	**25**	**100**	**253.7**	**11**	**40**	**98.64**	**98.93**	**98.79**	**39.89**	**39.91**
L_5	50	25	253.7	7	30	84.28	84.21	84.25	38.51	38.61
L_6	50	50	253.7	5	40	90.94	91.25	91.1	39.18	39.03
L_7	50	75	253.7	11	10	92.8	93.09	92.95	39.36	39.1
L_8	50	100	253.7	9	20	91.74	91.71	91.73	39.25	39.52
L_9	100	25	253.7	9	40	86.52	86.36	86.44	38.73	38.76
L_10	100	50	253.7	11	30	88.23	88.34	88.29	38.91	39
L_11	100	75	253.7	5	20	91.98	91.85	91.92	39.26	39.03
L_12	100	100	253.7	7	10	90.73	90.79	90.76	39.15	39.27
L_13	150	25	253.7	11	20	84.4	84.52	84.46	38.53	38.48
L_14	150	50	253.7	9	10	85.46	84.63	85.05	38.59	38.61
L_15	150	75	253.7	7	40	91.54	91.52	91.53	39.23	39.32
L_16	150	100	253.7	5	30	94.09	94.03	94.06	39.46	39.45
M	–	–	–	–	–	89.63	89.65	89.64	–	–

The maximum value of the S/N ratio is shown in boldface among the 16 tests.

$$\ln\left(\frac{C_t}{C_0}\right) = -K_{obs} \times t \tag{6}$$

where 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 [30].

Tert-butanol (TBA) and methanol (MA) were used as radical scavengers in the DTN/PS process [31,32]. The mineralization rate of PCP was determined using chemical oxygen demand (COD) and total organic carbon (TOC) measurements. In the DTN/PS and UV/PS processes, the LC-MS technique was used to identify intermediates and the PCP degradation pathway.

3. Results and discussion

3.1. Optimization of the operational parameters

3.1.1. pH of solution

pH is one of the critical parameters for removing organic pollutants by AOPs-SR because of its significant influence on pollutant solubility and the production of sulfate radicals [8]. The redox potential of $OH^{\bullet}$ was 2.9 V in alkaline conditions, and the redox potentials of $OH^{\bullet}$ and $SO_4^{\bullet-}$ both declined as the solution pH increased [25]. According to recent research [33], $SO_4^{\bullet-}$ has a much higher redox potential than $OH^{\bullet}$. Furthermore, sulfate radicals can produce $OH^{\bullet}$ by reacting with water at any pH level. Alkaline conditions

Table 4
Taguchi design experiments, results, and corresponding S/N values (DTN/PS process)

Run	Factor					%RE		M_{RE}	S/N	
	[PCP] (mg/L)	[PS] (mg/L)	[DTN] (mg/L)	pH	Time (min)	(1)	(2)		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 is shown in boldface among the 16 tests.

(pH > 8.5) can induce the mechanism of $SO_4^{\bullet-}$ interconversion to $OH^{\bullet}$ in the persulfate activation system, according to the study by Liang et al. [31]. The effect of pH on PCP removal in both processes was evaluated at four pH values of 5, 7, 9, and 11. Fig. 2a and b show the results of examining the influence of pH on the S/N ratio. As can be observed from these graphs, raising the pH to 11 increases the S/N ratio. When the pH value increases from 5 to 11, the S/N ratio in the DTN/PS process increases from 38.65 to 39.08 (the removal efficiency increases from 96.2% to 97.28%.) and in the UV/PS process from 39.02 to 39.17 (the removal efficiency increases from 98.4% to 98.78%.). According to the results, the effect of pH on the efficiency of both processes in removing PCP was the same. These observations are consistent with the findings reported by Lin et al. [34] and Gao et al. [35]. They investigated the effect of pH on the removal of organic compounds and found that the removal efficiency increased effectively in an alkaline environment (pH = 11).

3.1.2. PS and DTN concentration

As more sulfate radicals are released, the removal of PCP increases accordingly. Fig. 3a and b show the results of examining the effect of PS on the S/N ratio. In the DTN/PS process, by increasing the concentration of PS from 5 to 20 mg/L, the removal efficiency increases from 96.08% to 97.28%. Also, in the UV/PS process, when the persulfate concentration rises from 25 to 100 mg/L, the removal efficiency increases from 96.37% to 98.78%. The results of both processes indicate that the reaction rate has increased with the increasing concentration of the oxidant. This is due to the effect of UV rays and DTN reductants on persulfate molecules, which play the role of electrons and produce sulfate radicals, which play an essential role in the oxidation of organic matter [36]. Therefore, the higher the oxidizing agent, the more the production of sulfate radicals increases, which is itself a factor for further oxidation of organic matter. However, increasing the concentration of the oxidizing agent increases the reaction rate to a certain extent, and when its concentration exceeds a certain level, it has the opposite effect on the removal of organic matter. As the concentration of PS increases, sulfate radicals are trapped and quickly consumed by themselves. In addition, sulfate radicals react with excess sulfate and reduce the production of reactive sulfate species that are not economically viable [37]. The results of other studies have also shown the effect of persulfate concentration on the decomposition of organic matter. In the study on the removal of tetramethyl ammonium hydrochloride by Wang et al. [38] with increasing the concentration of persulfate from 2.38 to 11.9 mg/L, the removal efficiency of organic matter increased. Then, by increasing the concentration to 23.8 mg/L, the efficiency of the process in removing organic matter has decreased, which is due to the abduction of PS at high concentrations. Wang et al. [39] also used different concentrations of PS from 0.119 to 1.785 mg/L in the process of removing carbamazepine from different concentrations of PS. The results showed that by increasing the concentration of PS to 1.19 mg/L, process performance increased in the removal of organic matter, but more than that did not affect process efficiency. Also, the results of this study are similar to the results of studies by Song et al. and Asgari et al. [30,37]. Fig. 3c shows that the removal efficiency of PCP increased with increasing DTN concentration. By increasing the concentration of DTN from 2.5 to 10 mg/L in the DTN/PS process,

Table 5
Results of ANOM analysis for determination of the optimal conditions

Processes	Factor/ Level	S/N				$M_{S/N}$
		$i = 1$	$i = 2$	$i = 3$	$i = 4$	
DTN/PS	PCP/1	38.19	38.7	39.46	39.76	**39.03**
	PCP/2	38.7	39.04	38.94	38.93	38.95
	PCP/3	38.77	38.80	39	38.88	38.86
	PCP/4	38.47	38.61	38.77	38.67	38.63
	PS/1	38.19	38.9	38.77	38.47	38.58
	PS/2	38.7	39.04	38.80	38.61	38.79
	PS/3	39.46	38.94	39	38.77	39.04
	PS/4	39.76	38.93	38.88	38.67	**39.06**
	DTN/1	38.19	39.04	39	38.67	38.72
	DTN/2	38.7	38.9	38.88	38.77	38.81
	DTN/3	39.46	38.93	38.77	38.61	38.94
	DTN/4	39.76	38.94	38.80	38.47	**38.99**
	PH/1	38.19	38.94	38.88	38.61	38.65
	PH/2	38.7	38.93	39	38.47	38.77
	PH/3	39.46	38.9	38.80	38.67	38.96
	PH/4	39.76	39.04	38.77	38.77	**39.08**
	Time/1	38.19	38.93	38.80	38.77	38.67
	Time/2	38.7	38.94	38.77	38.67	38.77
	Time/3	39.46	39.04	38.88	38.47	38.97
	Time/4	39.76	38.9	39	38.61	**39.07**
UV/PS	PCP/1	38.16	38.85	39.5	39.89	**39.1**
	PCP/2	38.51	39.18	39.36	39.25	39.08
	PCP/3	38.73	38.91	39.26	39.16	39.02
	PCP/4	38.53	38.59	39.23	39.47	38.96
	PS/1	38.16	38.51	38.73	38.53	38.48
	PS/2	38.85	39.18	38.91	38.59	38.88
	PS/3	38.5	39.36	39.26	39.23	39.09
	PS/4	39.89	39.25	39.16	39.47	**39.44**
	PH/1	38.16	38.51	38.73	38.53	38.48
	PH/2	38.85	39.18	38.91	38.59	38.88
	PH/3	38.5	39.36	39.26	39.23	39.09
	PH/4	39.89	39.25	39.16	39.47	39.44
	Time/1	38.16	39.36	39.16	38.59	38.82
	Time/2	38.85	39.25	39.26	38.53	38.97
	Time/3	39.5	38.51	38.91	39.47	39.1
	Time/4	39.89	39.18	38.73	39.23	**39.26**

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

the removal efficiency increased from 96.6% to 97.28%. The long, weak S-S bond breaks down the DTN and produces two radical anions of sulfur dioxide. This free radical anion is a powerful reductant with a standard reduction potential (–0.66) that regenerates and activates PS and converts it to persulfate radical. The results of other studies have also shown the effect of DTN concentration on the decomposition of organic matter. In a study on the removal of bisphenol A by Sung et al. [40], by increasing the concentration of DTN to 16.3 mg/L, the removal efficiency increased to over 90%. Liu et al. [41] also used different concentrations of DTN in the trichloroethane removal process, which showed that by increasing the concentration of PS to a concentration of 1.2×10^3 mg/L, the process efficiency in removing organic matter Increased from 46% to by 96%. However, when the initial dose of DTN was further increased to 1.7×10^3 mg/L, the removal efficiency decreased to 67%. This was because excess DTN could compete with the reactive species produced. According to the findings, the optimal PS concentration for effective PCP removal in the DTN/PS process (PS activated with DTN, PS: 20 mg/L) is generally lower than in the UV/PS process (PS activated with UV, PS:100 mg/L). This conclusion demonstrates the DTN/PS process' superiority in the usage of PS over the UV/PS process.

3.1.3. PCP concentration

Based on the presented results, the initial concentration of PCP is an important factor. It influences the removal rate so that with increasing the initial concentration of organic matter, the removal efficiency has decreased significantly in both processes. Increasing the initial concentration of contaminants affects the performance of the process for two reasons. First, at constant amounts of sulfate radicals produced, with increasing contaminant concentration, the amount of contact and exposure to free radicals decreases, and as a result, the oxidation rate decreases. Second, increasing the concentration of pollutants will produce more by-products of oxidation, which will consume more free radicals [42,43]. One approach to fixing the problem is to increase the contact time. Another method is to increase the concentration of oxidants. At the same time, it's probable that at high concentrations of oxidants, an increase in free sulfate radicals enhances the interaction with other sulfate radicals, lowering efficiency [43]. Fig. 4a and b show that when the concentration of PCP in the DTN/PS process is increased from 25 to 150 mg/L, the removal efficiency reduces from 97.28% to 96.28%. The removal effectiveness of the UV/PS process also decreases from 98.78% to 98.42%. The oxidizing radicals are insufficient for the oxidation of PCP as the initial concentration of the pollutant increases, and the removal efficiency decreases. The formation of oxidizing radicals rises when the initial concentration of PCP is reduced, and the removal efficiency increases. The initial concentration and the removal efficiency have an inverse relationship. The ratio of reactive radicals produced to PCP molecules is decreasing, and the radicals are insufficient to remove organic contaminants. The findings were similar to those of Asgari et al., who reported that the removal of organic pollutants is dependent on the initial concentrations of the contaminant and that the removal rate decreases as the initial concentration of the contaminant increases [30]. According to the results, the effect of pH on the efficiency of both processes in removing PCP was the same.

3.1.4. Reaction time

One of the parameters considered in the removal of PCP by DTN/PS and UV/PS processes is the reaction time. By examining different reaction times on removing PCP by

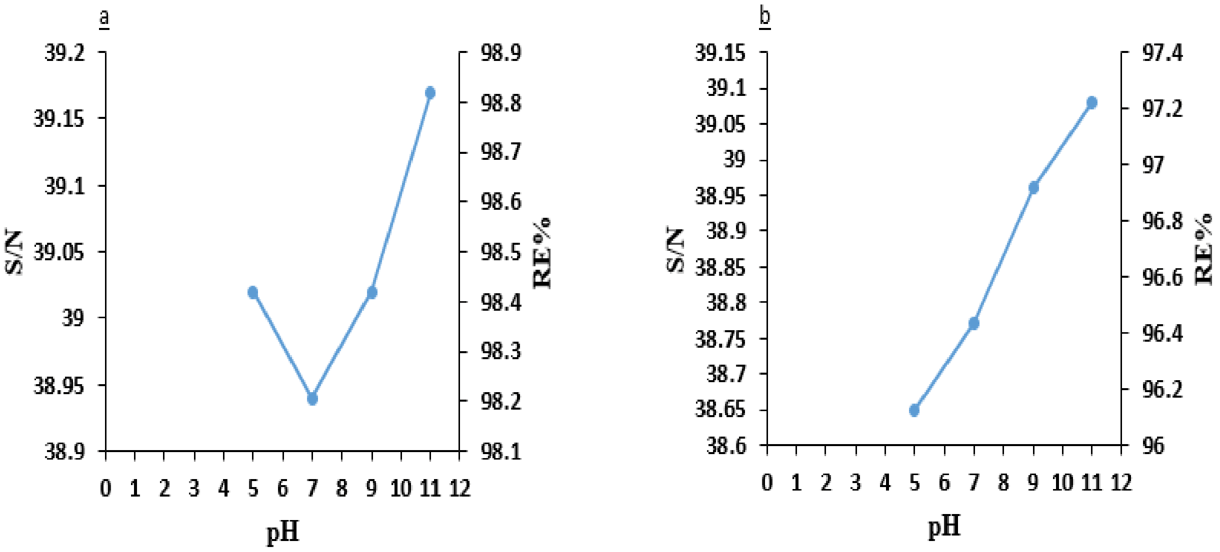


Fig. 2. Signal-to-noise main effect plots for the pH effect under different processes (a) UV/PS and (b) DTN/PS.

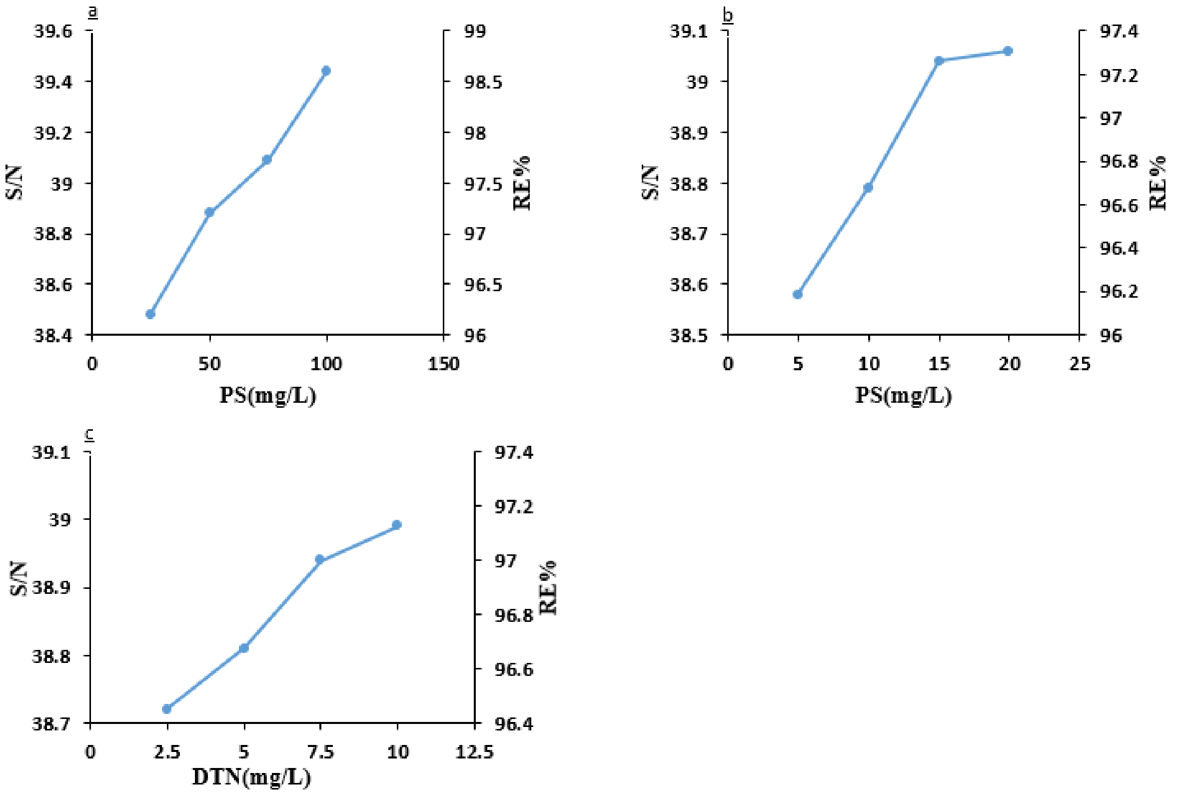


Fig. 3. Signal-to-noise main effect plots for the PS and DTN effect under different processes (a) UV/PS and (b,c) DTN/PS.

DTN/PS and UV/PS, it was found that there was a direct relationship between the reaction time and the efficiency of the studied processes, and the efficiency increased with increasing the reaction time. Increased efficiency with increasing reaction time is because at higher times, there is an opportunity for an advanced oxidation reaction with the active radical, thereby increasing the removal efficiency of PCP [25]. The selected reaction times for the DTN/PS process are between 3 and 10 min, and for the UV/PS process, between 10 and 40 min. In the UV/PS process, when the reaction time is increased from 10 to 40 min, the removal efficiency increases from 97.67% to 98.78% (Fig. 5a). Also, in the DTN/PS process, by increasing the reaction time from 3 min to 10 min, the removal efficiency increases from 96.28%

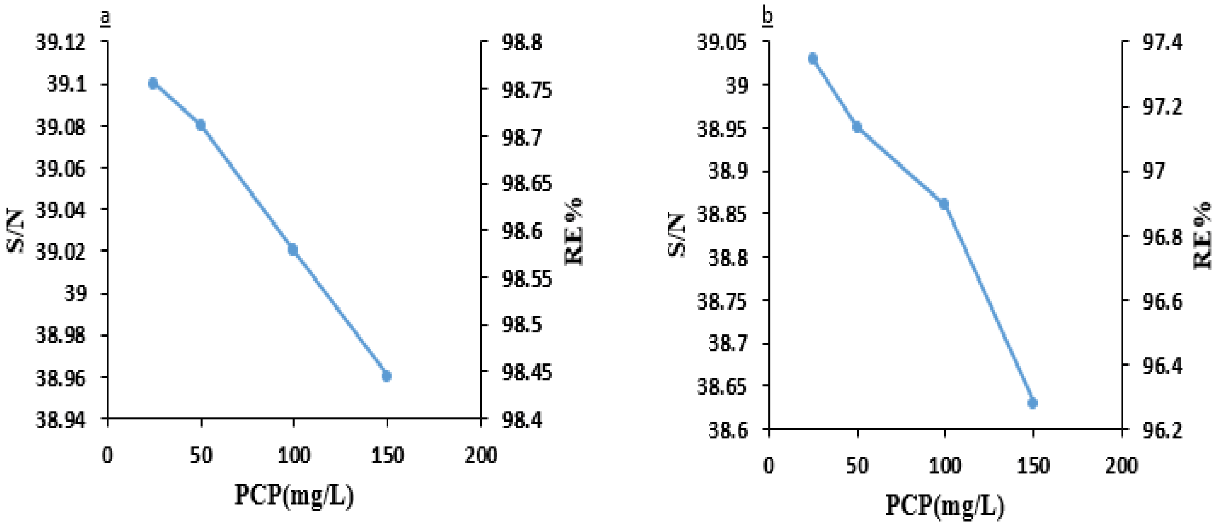


Fig. 4. Signal-to-noise main effect plots for the PCP concentration effect under different processes (a) UV/PS and (b) DTN/PS.

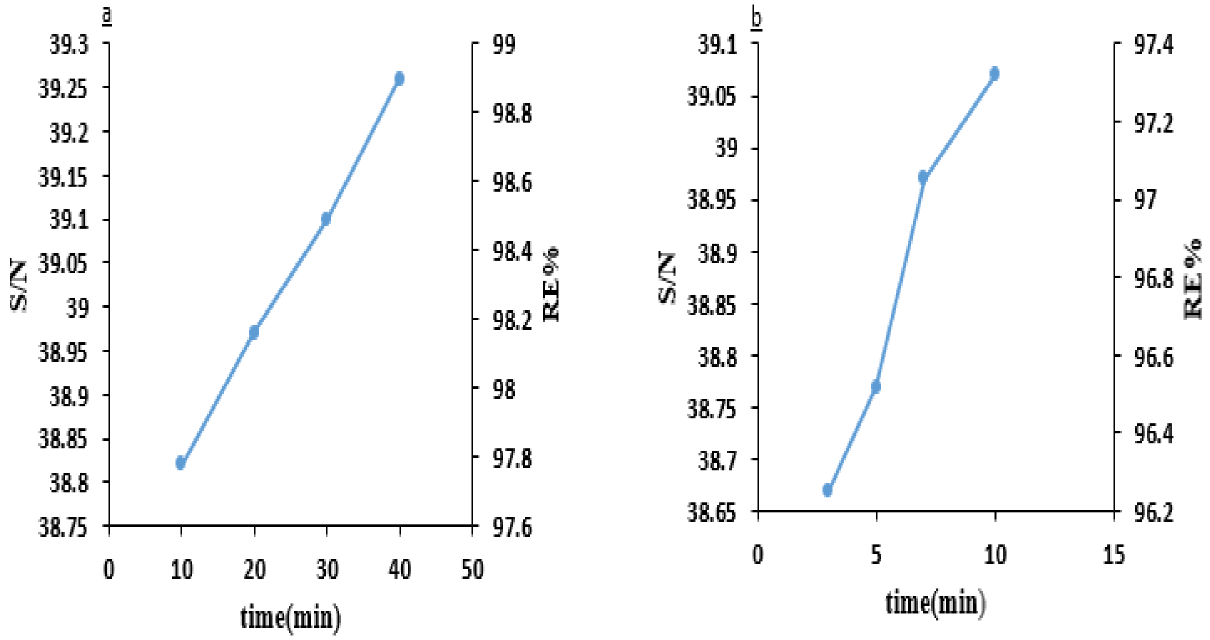


Fig. 5. Signal-to-noise main effect plots for the reaction time effect under different processes (a) UV/PS and (b) DTN/PS.

to 97.28% (Fig. 5b). Increasing the reaction time plays an important role in the removal process, and the removal efficiency is directly dependent on the concentration of persulfate produced, which increases with an increased retention time of the concentration of these radicals, and as a result, the removal efficiency also increases. The results of a study conducted by Asgari et al. [44] regarding the removal of PCP by UV/sodium hydrosulfide process are consistent with the above results in this regard. Also, in a study in which Sung et al. [37] examined the removal of atrazine, atrazine was entirely eliminated by increasing the reaction time to 90 min. According to the data, the optimum reaction time for effective PCP removal in the DTN/PS process (10 min) is often lower than in the UV/PS process (40 min). This conclusion illustrates the superiority of the DTN/PS process over the UV/PS process.

3.2. Detection of effective radicals

AOPs-SR typically produce reactive radicals (sulfate radicals, hydroxyl radicals, etc.) [32]. To assess the contribution of sulfate and hydroxyl radicals to the removal of PCP in DTN/PS and UV/PS processes, radical scavengers such as tert-butanol ether (TBA) and methanol (MA) are utilized. MA was selected as an efficient sulfate and hydroxyl radical scavenger, whereas TBA was chosen as an effective hydroxyl radical scavenger [5]. According to the findings, the DTN/PS process removed 97.28% of PCP under optimal conditions without MA or TBA. They decreased the removal efficiency to 78.4% and 24%, respectively, by adding 0.2 mol/L TBA and 0.2 mol/L MA. The addition of TBA and MA to the UV/PS process lowered the removal efficiency of PCP to 73.5% and 19.7%, respectively. However, without MA or TBA, 98.78% of PCP was removed in this process under optimal conditions. Although both sulfate and hydroxyl radicals were involved in PCP removal processes, sulfate radicals played a rather more prominent role under some conditions. Similar results were also obtained by Sung et al. [37] and Liu et al. [41].

3.3. Reaction kinetics

Chemical kinetics studies the speed of chemical reactions. The velocity of a reaction can be expressed by decreasing the concentration of a reactive substance per unit time by increasing the concentration of a product per unit time [42]. The kinetic studies showed that the removal of PCP under optimal conditions of DTN/PS and UV/PS processes follows the pseudo-first-order kinetics (PFO), and the regression coefficient (R^2) in these processes for the pseudo-first-order equation is 0.9915 and 0.9848, respectively. Also, the reaction rate constants (K_{obs}) in these processes are equal to 0.299 and 0.152 min^{-1}, respectively. In a study performed by Qi et al. [45] to remove PCP using the microwave/PS process, they concluded that the removal process followed pseudo-first-order kinetics, and at 130°C, the reaction rate constant was 0.0265 min^{-1}. Also, in a study conducted by Cao et al. [46] to remove PCP using the ascorbic-acid/PS process, they concluded that the removal process followed pseudo-first-order kinetics and had a reaction rate constant of 0.00959 min^{-1}. According to the kinetics of DTN/PS and UV/PS processes (0.299 and 0.152 min^{-1}), the superiority of these processes over previous studies can be expressed. In addition, the DTN/PS process outperforms the UV/PS process.

3.4. Contribution percentage of parameters

An ANOVA analysis of variance was performed to determine the share of participation and the effectiveness of each parameter (RF) [25]. The results are presented in Table 6. Based on these results, the most influential parameter in the DTN/PS process is related to PS concentration, and the least effective parameter is related to DTN concentration. Also, the most effective parameter in the UV/PS process is associated with PS concentration, and the least effective parameters are related to pH and PCP concentration.

3.5. Mineralization of PCP

The results of studying the DTN/PS process showed that the levels of TOC and COD in the removal of PCP in 10 min of reaction time under optimal conditions were 41% and 75.2%, respectively. This is while the removal efficiency of PCP in the same conditions is 97.28%. However, with increasing reaction time to 90 min, TOC and COD mineralization efficiencies increased by 78% and 95%, respectively. Also, the amount of TOC and COD in removing PCP by the UV/PS process in 40 min of reaction time under optimal conditions was 61% and 82.3%, respectively. However, with increasing the reaction time to 90 min, the mineralization efficiencies of TOC and COD increased by 81.5% and 98.9%, respectively. This study showed that sufficient reaction time is required for almost complete mineralization of PCP. However, Q et al. [47] have reported that heat-activated sulfate has a low degree of mineralization, which may be due to the production of intermediates such as coupled products. The rate of PCP mineralization in both processes is almost identical after 90 min, according to the data, but at the optimal time for each process, the DTN/PS process is superior.

3.6. Degradation pathways and intermediates

The LC-MS technique was used in this study to identify the possible intermediates generated during PCP degradation in the DTN/PS and UV/PS processes under optimal conditions. Sulfate radicals degrade PCP in three ways: hydrogen abstraction, electron transfer, and replacement and addition reactions with aromatic compounds [32]. The intermediate compounds produced in the DTN/PS process (published by Asgari et al. [25]) contain eight intermediates

Table 6
ANOVA results for S/N

Process	DOF	Factor	Sum of squares	Mean square	F-value	p-value	RF (%)
DTN/PS	PCP (mg/L)	3	0.323391	0.323391	31.87477	0.0002	18.84
	PS (mg/L)		0.572666	0.572666	56.44429	<0.0001	25.08
	DTN (mg/L)		0.178407	0.178407	17.58488	0.0018	13.99
	pH	3	0.428388	0.428388	42.22365	<0.0001	21.68
	Time (min)		0.372525	0.372525	36.71753	0.0001	20.41
	Error	0	0.010146	0.010146	–	–	–
	Total	15	1.976833	–	–	–	100
UV/PS	PCP (mg/L)	3	0.049183	0.049183	1.775088	0.2097	9
	PS (mg/L)	3	2.21227	2.21227	79.84223	<0.0001	57
	pH	3	0.0428388	0.061191	2.208478	0.1653	9
	Time (min)	3	0.0372525	0.0416858	15.04488	0.0026	25
	Error	3	0.304782	0.027707	–	–	–
	Total	15	3.044	–	–	–	100

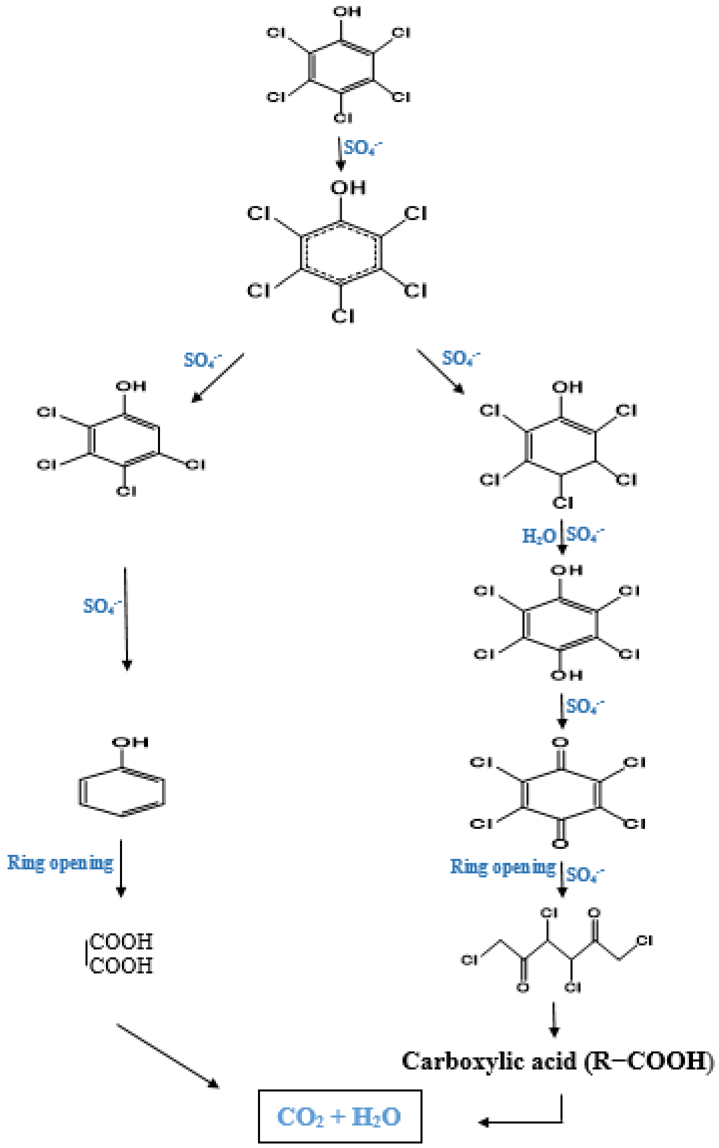


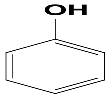
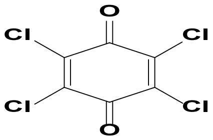
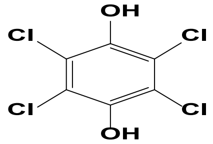
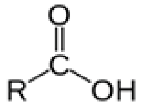
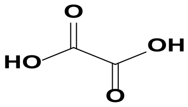
Fig. 6. A possible degradation pathway of pentachlorophenol.

(phenol, 3,4-dichlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, oxalic acid, propionic acid, tetrachloro-o-benzoquinone, and butanedioic acid). Based on the identified intermediates in the UV/PS process, two possible degradation pathways are proposed, shown in Fig. 6. Considering the obtained mass/charge (m/z) ratio, five intermediates were detected, named as phenol, tetrachloro-o-benzoquinone, tetrachlorocatechol, carboxylic acid, and oxalic acid (reported in Table 7). Intermediate degradation converts them to minor molecule compounds, which are then mineralized to CO_2 and H_2O.

4. Conclusions

The performance of the DTN/PS and UV/PS processes for PCP removal was investigated using the Taguchi statistical model. The UV/PS process removed PCP with a removal efficiency of 98.78%, which is similar to the DTN/PS process (97.28%). However, according to the parameters affecting each process, the superiority of the DTN/PS process over the UV/PS process can be inferred. In the DTN/PS process, the time required to reach the maximum efficiency is 10 min, which is four times longer than in the UV/PS process (40 min). The amount of PS consumed in the DTN/PS process (20 mg/L) is one-fifth of the UV/PS process (100 mg/L), which is better than the UV/PS process, both economically and in terms of the production of by-products. The optimum pH for both processes is 11 (alkaline). Sulfate radicals are the main reactants in both processes. The amount of mineralization in both processes is almost the same. As a result, these methods, especially DTN/PSS, have a greater chance of removing more chlorinated organic chemicals. One of the advantages of these two methods is high efficiency. Also, the production of safe side compounds and the ability to

Table 7
PCP degradation intermediate and products identified with LC-MS

Number	Name	Chemical formula	Structure	Molecular mass
1	Phenol	C_6H_6O		94.11
2	Tetrachloro-o-benzoquinone	$C_6Cl_4O_2$		245.88
3	Tetrachlorocatechol	$C_3H_6O_2$		110
4	Carboxylic acid	R-COOH		90
5	Oxalic acid	$C_2H_2O_4$		90.03

remove similar organic compounds are other advantages of these two methods. But the toxicity of persulfate may be known as the limitation of these processes.

Competing interests declaration

The authors state that they have no known competing financial interests or personal relationships that might have influenced the research presented in this study.

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Supplementary information: