

Effect of dissolved oxygen/nZVI/persulfate process on the elimination of 4-chlorophenol from aqueous solution: Modeling and optimization study

Mansour Baziar*, Ramin Nabizadeh^{*,**,*†}, Amir Hossein Mahvi*, Mahmood Alimohammadi*, Kazem Naddafi*, Alireza Mesdaghinia*, and Hassan Aslani^{***}

*Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

**Center for Air Pollution Research, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran

***Department of Environmental Health Engineering, School of Public Health, Tabriz University of Medical Sciences, Tabriz, Iran

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Abstract–4-Chlorophenol (4-CP) is a hazardous and toxic chemical that enters into water bodies mainly through industrial effluents. The present study investigated the effect of under pressure dissolved oxygen on 4-CP degradation in the presence of nanoscale zero-valent iron (nZVI) and sodium persulfate. The impact of oxygen pressure, as a qualitative variable at three levels (1, 1.5 and 2 atm), along with five quantitative variables, including persulfate concentration (0-2 mM), nZVI dosage (0-1 g/L), pH (3-11), reaction time (5-90 min) and 4-CP concentration (50-500 mg/L) on the 4-CP elimination from aqueous solutions, was examined using response surface methodology. There was a direct relationship between the dissolved oxygen under pressure and the 4-CP removal efficiency. Also, the gained R^2 and adjusted R^2 for three developed models of 1, 1.5 and 2 atm oxygen pressure were 0.971 and 0.9569, 0.9689 and 0.9538, and 0.9642 and 0.9468, respectively. The best removal process conditions for pH 4.2, 1.6 mM persulfate, 64.79 min reaction time, 97.89 mg/L initial 4-CP and 1 g/L nZVI dosage. The results indicated that dissolved oxygen under pressure-nZVI-persulfate could be considered a promising process for elimination of organic compounds from aqueous solutions.

Keywords: Persulfate, nZVI, Under Pressure Dissolved Oxygen, RSM

INTRODUCTION

One of the important issues in water resources pollution, and the recycling and reusing of wastewater containing organic contaminants, is the presence of phenolic compounds, particularly chlorophenols (CPs) [1,2]. CPs are toxic [3], endocrine disruptor compounds [4]. The United States Environmental Protection Agency (US EPA) placed CPs among high priority toxic pollutants [5,6]. Moreover, strict environmental standards have been compiled, due to the increased human awareness and understanding about health and ecological risks associated with this group of environmental pollutants [7]. According to Directive 80/778/EEC of the European Union legislation, the maximum allowable concentration of CPs in drinking water is 0.5 $\mu\text{g/L}$, and 0.1 $\mu\text{g/L}$ for each of its components [8]. From the standpoint of human and environment health, one of the most important components of CPs is 4-chlorophenol (4-CP), in which the hydrogen at position 4 in the benzene ring of the phenol has been replaced with chloride. The presence of chlorine in its structure confers 4-CP as one of the most toxic and refractory substances and is responsible for decreasing the decomposition rate of 4-CP in treatment processes [9]. This pollutant enters the environment through various human activities, such as waste incineration, indiscriminate use of wood preservatives, fun-

gicides, herbicides and chlorination of drinking water and wastewater [4,10-13]. CPs and other toxic organic compounds can be removed by several processes, including chemical precipitation, ion exchange, adsorption [14-17], biological treatment and advanced oxidation processes (AOPs), for instance. The processes of chemical precipitation, ion exchange and adsorption, transfer the contaminants from one phase to another. Therefore, further treatment or disposal is necessary [18]. The decomposition of CPs is by slow and, in many cases, uncompleted biological processes. In addition, the CPs may have toxic effects on bacteria and limit their role in the treatment process [18,19]. Among others, the photo-Fenton, ozonation and photocatalytic AOPs have displayed a notable capacity to degrade dissolved organic compounds present in water [20-22]. However, they require high operating and investment costs [1]. Persulfate has attracted considerable attention as a strong oxidant in the decomposition of toxic, resistant and non-biodegradable pollutants. The popularity of persulfate usage in elimination of such compounds is related to the formation of sulfate free radicals in system [23]. Although the persulfate oxidation potential is also somewhat high, it is not sufficiently high to drastically decompose resistant organic compounds. Therefore, to increase the oxidation potential in water and sewage treatment, persulfate is activated by various methods, such as transition metal ions, to produce sulfate free radicals with a higher oxidation potential ($E_0=2.5-3.1\text{ V}$) compared to the persulfate anion [24,25]. In conventional methods, activation of persulfate using Fe^{2+} is more popular than the other ions, because it provides a non-toxic, cheap and effective means to generate sul-

[†]To whom correspondence should be addressed.

E-mail: rnabizadeh@tums.ac.ir

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fate radicals [18,26,27]. Despite these advantages, this method has a fundamental weakness. To achieve a good performance in the decomposition of pollutants, Fe^{2+} ions must constantly be injected into the system. Conversely, the extreme use of these ions may create radical scavenger reactions in the system and thereby reduce the process efficiency [28]. In recent years, nanoparticle zero-valent iron (nZVI) has received considerable attention by researchers as an alternative persulfate activator, with the capabilities of transition metal ions. Moreover, nZVI is a potential source of Fe^{2+} . It can provide ferrous ions from the surface of the nanoparticle and eliminate the need to add Fe^{2+} ions continuously [25,29]. The performance of the nZVI/persulfate system in removal of various contaminants, such as acetaminophen [23], trichloroethylene [30], dichlorophenol [31], bentazon [25] and alkylphenol polyethoxylate [32], from aqueous solutions, is well established. Another unique feature of nZVI is the activation of the O_2 molecule in aqueous solutions, to produce reactive oxygen species, which is done through nZVI surface corrosion by oxygen. Ultimately, it leads to the oxidation of organic compounds [33]. For example, Noradoun and Cheng [34] investigated the degradation of ethylenediaminetetraacetic acid (EDTA) using reactive oxygen species generated by activation of O_2 in the presence of granular ZVI. They concluded that 2.5 g granular ZVI could degrade 1 mM EDTA at 2.5 h. Also, Keenan and Sedlak [33] reviewed the reaction of nZVI with O_2 for oxidation of some organic compounds and reported that the oxidation of organic compounds could be conducted using nZVI corrosion by O_2 . Therefore, these unique characteristics of nZVI provide a proper platform for analyzing its use in aqueous solutions. Despite the extensive researches

conducted to remove CP, the need to find an efficient and more economical treatment remains. Hence, further studies and development of more efficient methods are necessary. In this study, we used response surface methodology (RSM) for the experimental design. RSM is a specific, statistical- and graphical-based method [35-37], which can build a mathematical model for AOPs. Furthermore, it can evaluate interactions of variables in the process and find the optimum combination of the condition variables, to improve the process performance. Therefore, this study attempted to investigate the effect of under pressure dissolved oxygen on 4-CP decomposition in aquatic environments, in the presence of nZVI and sodium persulfate, using RSM.

MATERIALS AND METHODS

1. Chemicals

The chemicals used in this study, including potassium ferricyanide, sodium persulfate, 4-CP, 4-aminoantipyrine, NH_4OH , KH_2PO_4 , K_2HPO_4 , H_2SO_4 and NaOH , were purchased from Merck Company. nZVI, with a pore size of 30-45 nm, was purchased from Nanosany, Iran. Pure oxygen of 99.9% purity was prepared by Darman Gas, Tehran, Iran.

2. Experimental Procedure

For conducting the experiments, a 6-L stainless steel reactor was connected to the pure oxygen tank by using plastic pipes. Fig. 1 shows the schematic scheme of the developed system used in this study. Certain amounts of $\text{Na}_2\text{S}_2\text{O}_8$ and nZVI were added to 2-L aqueous solutions of CP with a concentration of 50-500 mg/L, at

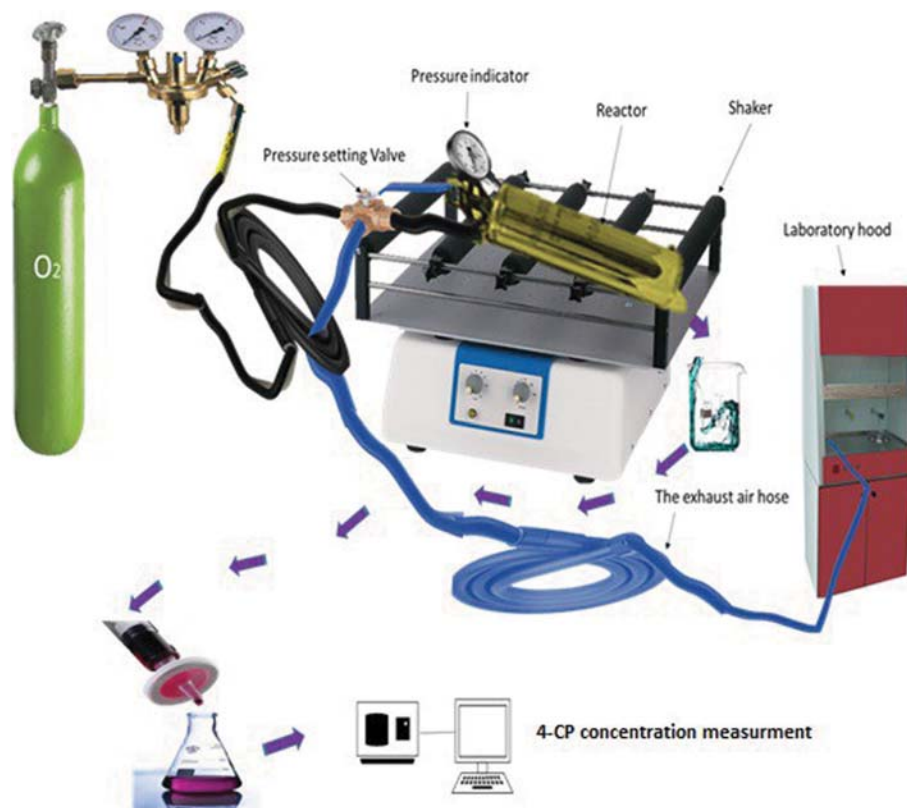


Fig. 1. Schematic scheme of the system developed for 4-chlorophenol (CP) removal.

specified pH. Then, the reactor lid was fully sealed to prevent the loss of CP through evaporation. Next, the oxygen gas inlet valve was opened, and the pressure into the reactor was regulated at the values indicated in the designed experiments. Opening and closing the oxygen gas inlet valve was performed manually to adjust the pressure. In all the experimental trials, the reactor was on a shaker for continuous mixing. At certain times, 10 mL of sample was removed from the reactor and syringe filtered (0.22 μm). The standard UV-visible spectrophotometer method 5030D (APHA-2005) was used to monitor the progress in 4-CP removal. The removal (%) of 4-CP during the process was calculated by the following equation:

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i corresponds to the initial concentration of 4-CP, and C_f corresponds to the concentration of 4-CP after the treatment process.

3. Design of Experiments

Our experiment plan was based on the central composite design

(CCD) technique, which is the most commonly used approach in RSM. Overall, RSM helps to formularize the relationship between the response (% removal) and parameters affecting the process (independent variables) [38]. A random order design matrix, which contained coded factors with five levels, was created by the R software,

Table 1. Experimental parameters and coded levels of the variables for removal of 4-chlorophenol (4-CP)

Factor	Coded variable	Variable level				
		-1	-0.42	0	0.42	1
pH	x1	3	5.3	7	8.7	11
Persulfate (mM)	x2	0	0.58	1	1.42	2
Reaction time (min)	x3	5	30	47.5	65	90
4-CP (mg/L)	x4	50	180	275	369	500
nZVI dosage (g/L)	x5	0	0.3	0.5	0.7	1

nZVI is nanoparticle zero-valent iron

Table 2. Central composite design of experiments and responses for 4-chlorophenol removal

Run	Variable					Response			Run	Variable					Response		
	x1	x2	x3	x4	x5	1-atm	1.5-atm	2-atm		x1	x2	x3	x4	x5	1-atm	1.5-atm	2-atm
1	8.7	0.58	30	180	0.29	36.49	39.6	46.59	32	7	1	47.5	275	0.5	44.25	54.5	54.35
2	5.3	1.42	30	180	0.29	52.56	62.39	62.66	33	7	1	47.5	275	0.5	46.9	52.8	53.25
3	8.7	0.58	30	369	0.29	37.95	36.23	48.05	34	5.3	0.58	65	180	0.71	58.21	68.65	68.31
4	8.7	1.42	65	180	0.29	51.6	54	61.7	35	8.7	1.42	65	369	0.29	47.94	46.44	58.04
5	5.3	0.58	30	180	0.71	48	62.3	58.1	36	7	1	47.5	275	0.5	47.13	56.32	57.23
6	5.3	1.42	30	180	0.71	71.73	70.78	81.83	37	5.3	1.42	65	180	0.29	57.34	66.62	67.44
7	5.3	1.42	30	369	0.71	63.26	69.31	73.36	38	8.7	0.58	65	369	0.29	50.1	37.84	60.2
8	8.7	0.58	65	180	0.29	48.08	45.16	58.18	39	5.3	1.42	65	180	0.71	69.23	77.23	79.33
9	8.7	1.42	30	180	0.71	55.93	52.85	66.03	40	8.7	0.58	30	369	0.71	42.45	44.21	52.55
10	7	1	47.5	275	0.5	45.12	54.8	55.22	41	8.7	1.42	65	369	0.71	44.46	55.05	54.56
11	5.3	0.58	30	180	0.29	35.8	46.31	45.9	42	7	1	47.5	275	0.5	47.9	54.6	58
12	5.3	1.42	65	369	0.29	50.4	57	60.5	43	11	1	47.5	275	0.5	54.22	45.11	64.32
13	8.7	1.42	30	369	0.71	51.12	52.32	61.22	44	7	1	47.5	500	0.5	45.28	51.37	55.38
14	8.7	1.42	65	180	0.71	52.42	51.32	62.52	45	3	1	47.5	275	0.5	69.54	73.85	79.64
15	8.7	0.58	30	180	0.71	42	46.69	52.1	46	7	1	47.5	275	0.5	44.68	52.11	54.78
16	5.3	1.42	30	369	0.29	52.33	57.07	62.43	47	7	1	47.5	275	0	28.7	28.12	34.42
17	7	1	47.5	275	0.5	46.52	53.3	56.62	48	7	1	47.5	275	1	47.87	52.37	57.97
18	8.7	1.42	30	180	0.29	48.29	48.5	58.39	49	7	1	47.5	275	0.5	47.32	54.47	57.42
19	7	1	47.5	275	0.5	49	49.35	59.1	50	7	0	47.5	275	0.5	33.53	37.71	43.63
20	7	1	47.5	275	0.5	46.35	54.2	56.45	51	7	1	47.5	275	0.5	47.1	55.65	57.2
21	7	1	47.5	275	0.5	46.31	53.9	56.41	52	7	1	47.5	275	0.5	46.3	54.84	56.4
22	8.7	0.58	65	180	0.71	42.36	53.12	52.46	53	7	1	47.5	50	0.5	52.95	59.62	63.05
23	7	1	47.5	275	0.5	47.23	50.34	57.33	54	7	1	47.5	275	0.5	45.59	53.34	55.69
24	8.7	1.42	30	369	0.29	40	43.67	50.1	55	7	1	47.5	275	0.5	44.9	52.92	54
25	5.3	0.58	65	369	0.71	53	64.24	63.1	56	7	2	47.5	275	0.5	53.9	64.54	64
26	5.3	0.58	30	369	0.71	49.64	57.64	59.74	57	7	1	47.5	275	0.5	47.34	54.74	57.44
27	5.3	0.58	30	369	0.29	37	40.84	47.1	58	7	1	5	275	0.5	54	46.25	64.1
28	8.7	0.58	65	369	0.71	44.3	49.32	54.4	59	7	1	47.5	275	0.5	47.28	55.13	57.38
29	5.3	0.58	65	369	0.29	47.6	47.52	57.7	60	7	1	47.5	275	0.5	44.5	52.94	54.6
30	5.3	1.42	65	369	0.71	58.26	74.5	68.36	61	7	1	90	275	0.5	61.8	62	71.9
31	5.3	0.58	65	180	0.29	48.82	58.31	58.92	62	7	1	47.5	275	0.5	49.21	54.72	59.31

version 3.3.2. The coded values (x_i) of the variables were determined, using the equation below:

$$x_i = \frac{X_i - X_j}{\Delta X} \quad (2)$$

where ΔX represents the step change, and X_i and X_j belong to the actual values of the process variables and actual values of process variables in the center point, respectively [39]. Table 1 presents the levels and domain of the variables considered in this study.

The experimental studies to evaluate the effects of process parameters on 4-CP removal were implemented according to CCD. A set of 62 experiment runs, containing 10 axial points, 32 factorial points, and 20 center points, at two blocks, was used for the study. Also, to determine the effect of oxygen pressure, the experiments were performed at three pressure levels of 1, 1.5 and 2 atm. After

conducting the suggested experiment runs, a quadratic model was used to optimize the results of the response as follows:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2 + \varepsilon \quad (3)$$

where y corresponds to the response, the coefficients of β_0 , β_i and β_{ij} belong to the terms of linear, quadratic and cross product, respectively; x_i and x_j belong to the process parameters, and k represents the number of process parameters.

RESULTS AND DISCUSSION

1. Process Modeling

In this study, the impact of independent parameters, such as initial concentration of 4-CP, oxygen pressure, reaction time, nZVI

Table 3. Results of analysis of variance and estimated coefficients of model terms for 4-chlorophenol removal

Oxygen pressure levels															
	1 atm				1.5 atm				2 atm						
Source	Coefficient	Std. error	t-Value	p-Value	Coefficient	Std. error	t-Value	p-Value	Coefficient	Std. error	t-Value	p-Value			
Intercept	46.54	0.37	126.70	<2.2e-16	53.85	0.45	119.45	<2.2e-16	56.43	0.42	134.28	<2.2e-16			
x1	-8.46	0.60	-14.21	<2.2e-16	-16.08	0.73	-21.99	<2.2e-16	-8.46	0.68	-12.42	1.75E-15			
x2	10.63	0.60	17.84	<2.2e-16	11.25	0.73	15.39	<2.2e-16	10.63	0.68	15.60	<2.2e-16			
x3	4.29	0.60	7.20	8.52E-09	6.21	0.73	8.49	1.4E-10	4.29	0.68	6.30	1.64E-07			
x4	-3.70	0.60	-6.20	2.21E-07	-4.96	0.73	-6.78	3.37E-08	-3.70	0.68	-5.42	2.84E-06			
x5	8.22	0.60	13.80	<2.2e-16	12.06	0.73	16.51	<2.2e-16	8.79	0.68	12.90	5.03E-16			
x1 : x2	-8.66	1.65	-5.26	4.88E-06	-6.56	2.02	-3.24	0.00235	-8.66	1.89	-4.60	4.07E-05			
x : x3	-0.97	1.65	-0.59	0.557546	-3.40	2.02	-1.68	0.100055	-0.97	1.89	-0.52	0.608			
x1 : x4	2.01	1.65	1.22	0.230245	3.24	2.02	1.60	0.117181	2.01	1.89	1.06	0.2933			
x1 : x5	-13.24	1.65	-8.03	5.96E-10	-9.75	2.02	-4.82	1.99E-05	-13.24	1.89	-7.02	1.53E-08			
x2 : x3	-11.79	1.65	-7.16	9.91E-09	-4.43	2.02	-2.19	0.034167	-11.79	1.89	-6.26	1.87E-07			
x2 : x4	-9.48	1.65	-5.75	9.77E-07	2.47	2.02	1.22	0.22903	-9.48	1.89	-5.03	1.03E-05			
x2 : x5	4.92	1.65	2.99	0.004754	-4.72	2.02	-2.33	0.02464	4.92	1.89	2.61	0.01258			
x3 : x4	-2.64	1.65	-1.60	0.116378	-2.54	2.02	-1.26	0.21621	-2.64	1.89	-1.40	0.16839			
x3 : x5	-11.20	1.65	-6.80	3.2E-08	-0.17	2.02	-0.08	0.934226	-11.20	1.89	-5.94	5.25E-07			
x4 : x5	-3.13	1.65	-1.90	0.06423	6.71	2.02	3.32	0.001922	-3.13	1.89	-1.66	0.10404			
x1^2	15.25	1.15	13.25	<2.2e-16	7.23	1.41	5.12	7.7E-06	15.80	1.32	12.00	5.41E-15			
x2^2	-2.92	1.15	-2.53	0.015245	-1.13	1.41	-0.80	0.430218	-2.37	1.32	-1.80	0.07967			
x3^2	11.27	1.15	9.79	2.73E-12	1.87	1.41	1.33	0.191964	11.82	1.32	8.97	3.18E-11			
x4^2	2.48	1.15	2.16	0.036803	3.24	1.41	2.30	0.026841	3.03	1.32	2.30	0.0264			
x5^2	-8.35	1.15	-7.25	7.34E-09	-12.01	1.41	-8.50	1.39E-10	-9.99	1.32	-7.58	2.5E-09			
Model formula	Df	Sum Sq	Mean Sq	F value	Pr (>F)	Df	Sum Sq	Mean Sq	F value	Pr (>F)	Df	Sum Sq	Mean Sq	F value	Pr (>F)
FO	5	2175.6	435.1	160.2	<2.2e-16	5	4545.4	909	222	<2.2e-16	5	2250.1	450.03	126.6	<2.2e-16
TWI	10	650.6	65	23.96	4.78e-14	10	259.6	25.9	6.3	8.42e-06	10	650.6	65.06	18.3	4.07e-12
PQ	5	904.8	180.9	66.6	<2.2e-16	5	423.4	84.6	20.7	<2.8e-10	5	1025.8	205.16	57.7	<2.2e-16
Residuals	41	111.3	2.7			41	167.7	4.0			41	145.6	3.55		
Lack of fit	22	74.6	3.3	1.75	0.1098	22	113	5.1	1.7	0.1028	22	94.3	4.29	1.5	0.1557
Pure error	19	36.7	1.9			19	54.7	2.8			19	51.3	2.7		

1 atm: R^2 , 0.971; R^2_{adj} , 0.9569. 1.5 atm: R^2 , 0.9689; R^2_{adj} , 0.9538. 2 atm: R^2 , 0.9642; R^2_{adj} , 0.9468 FO: First order, TWI: Two way interaction, PQ: Pure quadratic

dose, initial sodium persulfate concentration and pH on 4-CP removal efficiency, were investigated. Table 2 shows the results of the experiments suggested by the software.

According to the results of experiments, three quadratic models were developed to predict the values of the responses as follows:

Oxygen pressure level of 1 atm:

$$y = 46.54103 - 8.46323X_1 + 10.62646X_2 + 4.28965X_3 - 3.69501X_4 + 8.21837X_5 - 8.66347X_1X_2 - 0.97439X_1X_3 + 2.006X_1X_4 - 13.23845X_1X_5 - 11.7931X_2X_3 - 9.47665X_2X_4 + 4.9200X_2X_5 - 2.64317X_3X_4 - 11.1991X_3X_5 - 3.1339X_4X_5 + 15.2496X_1^2 - 2.91539X_2^2 + 11.2696X_3^2 + 2.4846X_4^2 - 8.34539X_5^2 \quad (4)$$

Oxygen pressure level of 1.5 atm:

$$y = 53.85381 - 16.07506X_1 + 11.25039X_2 + 6.20883X_3 - 4.955861X_4 + 12.06438X_5 - 6.56018X_1X_2 - 3.4029X_1X_3 + 3.23678X_1X_4 - 9.74923X_1X_5 - 4.43179X_2X_3 + 2.46957X_2X_4 - 4.71817X_2X_5 - 2.54028X_3X_4 - 0.16794X_3X_5 + 6.70514X_4X_5 + 7.22938X_1^2 - 1.12562X_2^2 + 1.87438X_3^2 + 3.24438X_4^2 - 12.0056X_5^2 \quad (5)$$

Oxygen pressure level of 2 atm:

$$y = 56.42541 - 8.46323X_1 + 10.62646X_2 + 4.28965X_3 - 3.69501X_4 + 8.79041X_5 - 8.66347X_1X_2 - 0.97439X_1X_3 + 2.00677X_1X_4 - 13.23845X_1X_5 - 11.79313X_2X_3 - 9.47665X_2X_4 + 4.92005X_2X_5 - 2.64317X_3X_4 - 11.19916X_3X_5 - 3.13390X_4X_5 + 15.79832X_1^2 - 2.36668X_2^2 + 11.81832X_3^2 + 3.03332X_4^2 - 9.98668X_5^2 \quad (6)$$

Table 3 illustrates the results of analysis of variance (ANOVA) for the experimental design described in Table 2. A multiple regression analysis of the coded data in R software was applied to generate a quadratic regression equation. The significance of the developed models and each term was assessed by ANOVA. Usually, for establishing a statistically valid model, the adjusted determination coefficient (R_{adj}^2) must be in the domain of the determination coefficient (R^2) ± 0.2 [39]. Furthermore, the model lack of fit (model toward the pure error) must not be significant.

Based on the ANOVA results for 1 atm oxygen pressure, the linear effects of X_1 to X_5 variables and the interaction effects of X_1X_2 , X_1X_5 , X_2X_3 , X_2X_4 , X_2X_5 and X_3X_5 variables were significant ($p < 0.05$). The same results were obtained at 2 atm oxygen pressure. However, the quadratic effect of X_1 , X_2 , X_3 , X_4 and X_5 , along with X_1 , X_3 , X_4 and X_5 variables, was significant for oxygen pressures of 1 and 2 atm, respectively. At 1.5 atm oxygen pressure, the linear effect of all coded variables, the interaction effect of X_1X_2 , X_1X_5 , X_2X_3 , X_2X_5 and X_4X_5 variables, as well as the quadratic effect of X_1 , X_4 and X_5 variables were significant. The p-value, R^2 and lack of fit were used to judge the accuracy of the model, so that the higher values of R^2 , lower p-value ($p < 0.05$) and insignificance of lack of

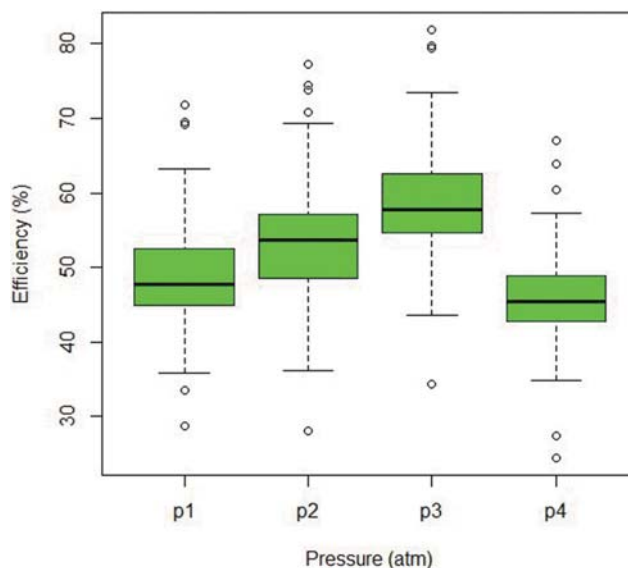


Fig. 2. Effect of oxygen pressure on 4-chlorophenol degradation. p1= 1 atm, p2=1.5 atm, p3=2 atm, p4=0 atm (no pressurized).

fit demonstrated that the model had a high ability to correlate the experimental and predicted response values.

According to Table 3, the model was significant for the three levels of oxygen pressure, with a p-value of 2.2×10^{-16} , and R^2 of 0.971, 0.968 and 0.964 for 1, 1.5 and 2 atm, respectively. The insignificant lack of fit values (0.1098, 0.1028 and 0.1557) also confirmed the accuracy of the developed models. The most influential model terms in 4-CP degradation at oxygen pressure levels of 1, 1.5 and 2 atm were persulfate (X_2), pH (X_1) and persulfate (X_2) with R^2 of 10.63, -16.08 and 10.63, respectively.

2. Process Optimization

The optimum conditions of 4-CP degradation were obtained by a Solver program in Excel 2013 Microsoft Office. The optimum conditions were set as follows: maximum 4-CP removal (100%) and the independent variables in a defined range. According to the program, the obtained optimum conditions for removal of 4-CP at the three oxygen pressure levels are presented in Table 4.

3. Effect of Independent Variables on 4-CP Degradation

Fig. 2 displays the box plot of 4-CP degradation during the treatment by the nZVI-persulfate system, at the three levels of designed oxygen pressures. The 4-CP degradation increased with increasing oxygen pressure. The degradation ranged from 36 to 63%, with a median of 48% in an oxygen pressure of 1 atm. Conversely, for oxygen pressures of 1.5 and 2 atm, the rates of 4-CP decomposition

Table 4. Optimum conditions for removal of 4-chlorophenol (4-CP) at three oxygen pressure levels

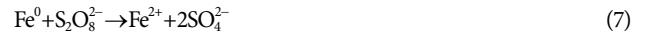
Pressure (atm)	pH	Persulfate (mM)	Time (min)	4-CP (mg/L)	nZVI (g/L)	Removal %	
						Predicted	Experimental
1	3.38	2	64.19	187.63	0.89	100	89.34
1.5	4.12	1.96	87.14	65.77	0.71	100	92.22
2	4.24	1.60	64.79	97.89	1	100	93.8

nZVI=nanoparticle zero-valent iron

ranged from 37-70%, and 44-75%, with medians of 53% and 58%, respectively.

A plausible justification for the observed results of Fig. 2 may be primarily attributed to the formation of the reactive oxygen species, the sulfate radicals and ferryl ion (Fe [IV]). In aqueous solutions, nZVI is rapidly oxidized to ferrous and ferric ions, respectively, in the presence of oxygen. Although, the reaction of nZVI with oxygen in the processes that are aimed at identifying the reductive capacity of ZVI, is undesirable. It generates reactive oxygen species (like the hydroxyl free radical) that can eliminate contaminants that cannot be removed by ZVI alone [33]. Two mechanisms have been proposed to describe the formation of oxidants and kinetics of the reaction. One, iron is reacted with oxygen through the transfer of two electrons and produces hydrogen peroxide. Second, ferrous iron, produced by iron oxidation, is reacted with oxygen through a series of single electron transfer reactions and generates hydrogen peroxide [40,41]. Furthermore, Keenan and Damlock [33] reported the presence of ferryl ion as one of the oxidants produced in the reaction between ZVI and oxygen. Given that these authors declared that the ferrile iron is generated at near neutral pH levels and the highest removal efficiency in the present investigation was obtained at $\text{pHs} \leq 5.3$, the role of ferryl iron cannot be considerable in this field. Besides, the presence of persulfate as an oxidant in the system can lead to additional release of Fe^{2+} as a result of ease of oxidation nZVI using persulfate [42].

Generally under persulfate-nZVI system, persulfate tends to attract electron and form sulfate free radicals. Therefore, presence of persulfate increases the dissolution of nZVI and formation of Fe^{2+} as well as production of sulfate free radical (Reactions 7 and 8) [42].



Considering that the effect of the oxygen pressure increase on 4-CP degradation was increased up to 2 atm, two separate experi-

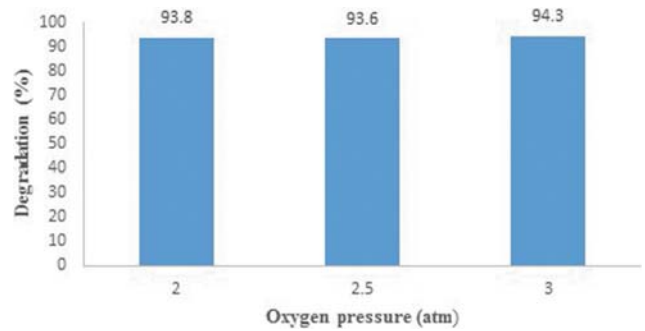


Fig. 3. Effect of oxygen pressure level on 4-chlorophenol degradation at and above the optimum conditions of 2 atm oxygen pressure.

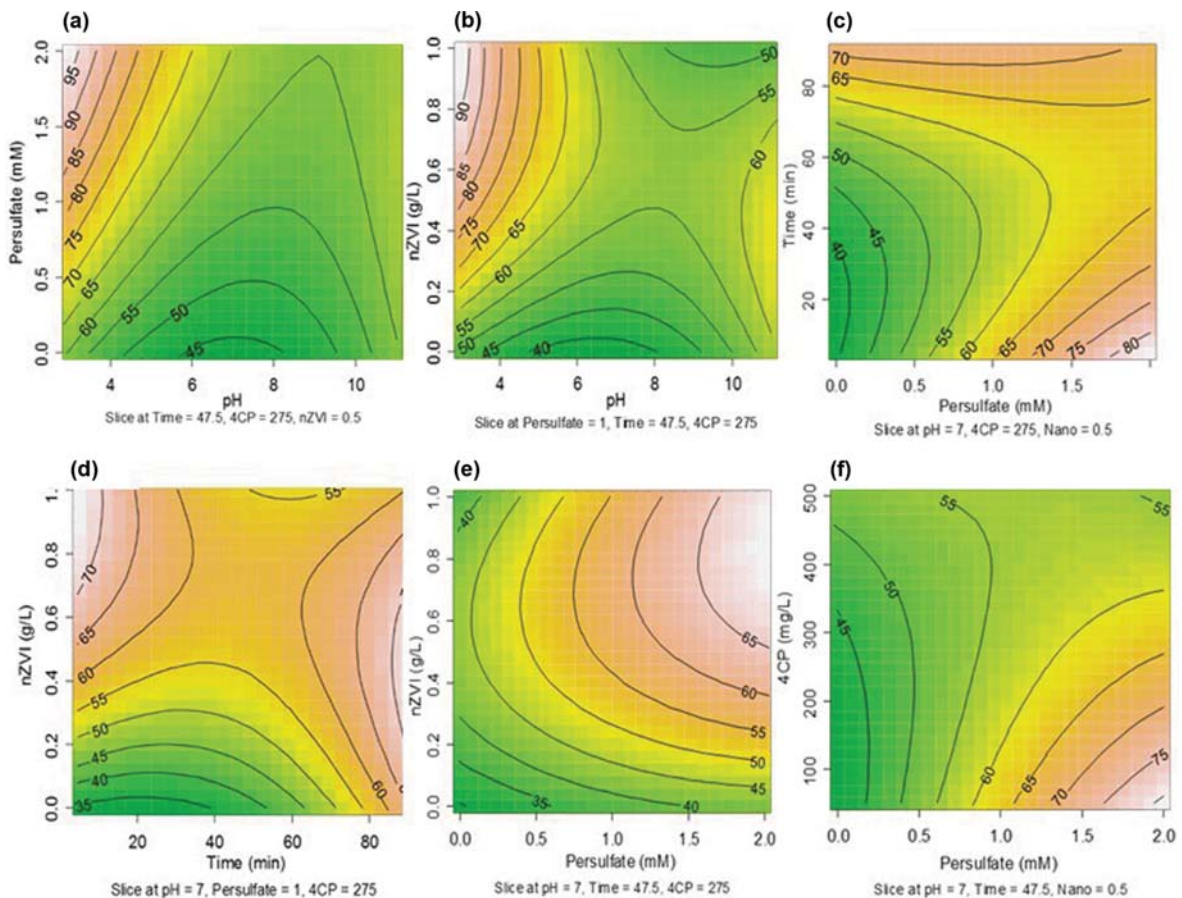


Fig. 4. The contour plots of the response surface methodology study.

ments were conducted, in which the oxygen pressure was further increased to 2.5 and 3 atm, to identify the increased oxygen pressure effects (Fig. 3). Accordingly, further increasing the oxygen pressure did not have a significant impact on the 4-CP degradation.

Fig. 4 illustrates the contour plots of the RSM study, which reveals the interactions between the process independent variables and response (4-CP removal). Fig. 4(a) demonstrates the interactive relationship between pH and persulfate. It was evident that increasing the persulfate concentration and decreasing the pH of the solution would lead to a dramatic increase in the 4-CP removal efficiency. A similar pattern was also observed between pH and nZVI dosage (Fig. 4(b)). The solution pH is an important factor that plays a vital role in an iron nanoparticle/persulfate system, by affecting the release of Fe^{2+} from the iron surface. In acidic conditions, the decomposition of organic compounds increases, due to the rapid destruction of iron nanoparticles and the enrichment of the solution with ferrous ions, which would, subsequently, lead to the generation of sulfate free radicals. Previous studies showed that the performance of the persulfate/ZVI (or Fe^{+2}) system, regarding the degradation of organic compounds, improves in acidic conditions. Xu and Li [43] found that the maximum degradation of Azo dye occurred at pH 3.5 in a persulfate/ Fe^{+2} system. In addition, Hussein and co-workers [44] noticed that the highest degradation of *p*-chloroaniline took place at pH 4 in a persulfate/ZVI system. The results of the current work agree with those documented in the studies mentioned above. The degradation fraction was less in the neutral and alkaline conditions than the acidic medium. This behavior might be as a result of the Fe^{3+} oxyhydroxides formed in the system, which hinder the activation of persulfate (Eqs. (9)-(11)) [42,44].



Fig. 4(c) shows the mutual relationship between persulfate and reaction time. Increasing the initial persulfate concentration and reaction time had a positive effect on 4-CP elimination. The same trend was also observed between the nZVI dosage and reaction time (Fig. 4(d)). A higher addition of persulfate in the nZVI/persulfate system could generate more sulfate free radicals. Hence, a higher degradation of 4-CP could be observed in the system. Additionally, increasing the nZVI loading would lead to an enhanced generation of ferrous iron, as well as the rapid deterioration of persulfate and production of sulfate free radicals. The results of this study concurred with Wei and his colleagues [25], who noted that the generation rate of ferrous iron constantly increased as a function of the reaction time at different ZVI loadings. This behavior is because ZVI is a potential source of Fe^{+2} ions and maintains its ability to generate Fe^{+2} ions with increasing reaction time.

Fig. 4(e) displays the interaction between persulfate and nZVI on the 4CP degradation. 4-CP degradation gradually increased as the persulfate concentration and nZVI dosage increased. In the persulfate/nZVI system, with decomposition (or activation) of persulfate, many H^+ ions are generated, which can facilitate the corrosion of the nanoparticle surface, as the solution pH is decreased. As a result of this process, corrosion products are yielded, which

can accelerate activation of persulfate in the system.

Fig. 4(f) shows the interactive relationship between nZVI and initial 4-CP concentration. From the figure, it can be concluded that by enhancing the nZVI dose and decreasing the concentration of 4-CP, the removal efficiency is increased. At higher 4-CP concentration, the removal efficiency was reduced. This pattern can be attributed to the adsorption of 4-CP molecules on the surface of iron nanoparticles, which decrease the active sites on the nZVI surface [26]. Therefore, the sulfate free radicals are not generated sufficiently in the nZVI/persulfate system for degradation of 4-CP.

4. Identification of Main Radicals in under Pressure Dissolved Oxygen/nZVI/Persulfate Process

Alcohols were used to quench the hydroxyl and sulfate radicals in order to recognize the main radical species in the process of under pressure dissolved oxygen/nZVI/persulfate. Accordingly, we used ethanol (with alpha hydrogen) as sulfate and hydroxyl radical scavenger. Moreover, tert-butyl alcohol (TBA) with no alpha hydrogen was detected to be operative quenching mediators for hydroxyl radicals. An alcohol (ethanol, TBA) concentration of 1 M was used in this study. It is evident from the findings that the addition of alcohols significantly reduced degradation of 4-CP. The percentages of 4-CP fractionation were 89.34%, 92.22% and 93.8% at oxygen pressures of 1, 1.5 and 2 atm, respectively, (Table 4) with no radical scavenger.

The presence of ethanol (EtOH), however, reduced the 4-CP degradation to below 18% in the whole radical scavenger tests. On the other hand, 4-CP degradation percentages in the presence of TBA were 42%, 47% and 49% at oxygen pressures of 1, 1.5 and 2 atm, respectively. According to the results, addition of EtOH as OH radical and SO_4 radical scavengers completely quenched the reaction. By contrast, the inclusion of TBA mildly affected the fractionation rate of 4-CP. Therefore, a conclusion can be drawn that the 4-CP degradation in TBA system was caused by the production of sulfate radicals because only hydroxyl radicals were quenched by TBA. The use of EtOH, however, markedly lowered (18%) 4-CP degradation efficiency owing to scavenging of both radicals. It is known that electron transfer reaction selectively favors sulfate radicals, whereas hydrogen addition or abstraction quickly influences hydroxyl radicals [42]. Consequently, sulfate radicals were observed to be the prevailing active species for the 4-CP degradation.

5. Intermediate Products of 4-CP Degradation

Mineralization and intermediate products were evaluated at the obtained optimal conditions of the experiments. This set of experimental tests was the solution pH of 4.24, the nZVI dosage of 1 g/L, the reaction time of 64.79 min, the initial 4-CP concentration of 97.89 mg/L, the persulfate concentration of 1.6 mM and the pressurized oxygen level of 2 atm. At this condition 93.8% 4-CP degradation was observed. GC-MS analysis was employed to detect the 4-CP degradation by-products in pressurized oxygen-nZVI-persulfate system. The main products during 4-CP degradation were the aromatic compounds of Hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$) and 1, 4-Benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$) along with aliphatic acids such as oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$), maleic acid and formic acid. The main reason for the decomposition of organic pollutants in the nZVI-persulfate system is generation of sulfate free radicals. When the system is com-

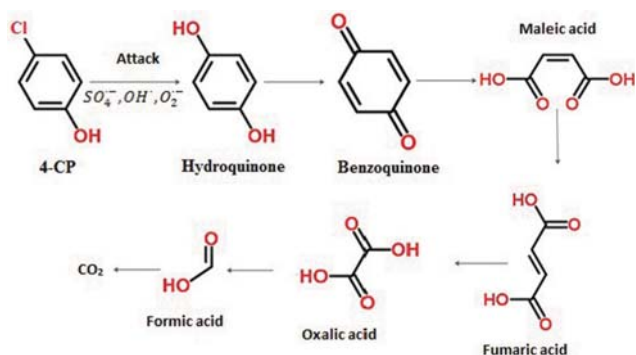


Fig. 5. Intermediate products and the possible mechanism of 4-CP degradation in under pressure dissolved oxygen/nZVI/persulfate process.

combined with pressurized oxygen the expected free radicals would be superoxide, hydroxyl and sulfate free radicals. The pressurized oxygen can also accelerate the generation of the free radicals by affecting on the nZVI corrosion and Fe^{+2} production.

Fig. 5 displays the proposed pathway of 4-CP degradation. As can be seen, first, free radicals (superoxide, hydroxyl and sulfate radicals) attack to 4-CP and remove chlorine (Cl) atom from the structure of compound and produce hydroquinone. Then molecules of this compound in the process of dehydrogenation convert to the 1, 4-Benzoquinone. The presence of excess free radicals in the system leads to the breakdown of 1, 4-Benzoquinone ring and generation of the aliphatic acids. Finally, CO_2 molecules generate from aliphatic acids in some successive stages of oxidation.

CONCLUSION

The main objective of the present study was to survey the effect of under pressure dissolved oxygen on the 4-CP decomposition in the presence of nZVI and sodium persulfate. The effects of various operating parameters, including nZVI dosage, reaction time, persulfate concentration, pH and 4-CP concentration, as well as the oxygen pressure, on the percentage degradation of 4-CP were evaluated, by applying the RSM technique, regarding the main, interaction and quadratic effects. Also, the forecasted degradation fraction attained from RSM was compared with the actual value of degradation, in terms of R^2 value. Optimization of the 4-CP degradation condition was conducted using the quadratic model generated from RSM. The developed oxidation process was effective in degrading 4-CP via generation of the highly reactive sulfate free radicals. The current study indicates that the combination of nZVI, sodium persulfate and dissolved oxygen under pressure could be a promising approach to degrade organic compounds in aqueous solutions.

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