

Optimization of Advanced Oxidation Process Based on Persulfate (Uv/Na₂S₂O₈/Fe²⁺) for Phthalic Acid Removal from Aqueous Solutions with Response Surface Methodology

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ABSTRACT

BACKGROUND AND OBJECTIVE: Phthalic acid has high toxicity and low degradability which has put treatment of wastewater containing this compound prior to prevent its health and environmental hazards. Present study was conducted to Optimization of (UV/Na₂S₂O₈/Fe²⁺) process for phthalic acid removal from aqueous solutions with response surface methodology.

METHODS: This is an experimental study which was conducted at laboratory scale and synthetically in the cylindrical reactor containing UV-C lamp with 16 Watt power. Effects of variables including pH of solution (3-11), reaction time (0-60 min), concentration of persulfate (0.1-0.5 mmol/L), concentration of Fe²⁺ (0.1-0.2 mmol/L) and initial phthalic acid (5-50 mg/L) on efficacy of process were investigated by response surface method (box Behnken method). The residual concentration of phthalic acid was measured by HPLC at a wavelength of 254 nm

FINDINGS: The removal efficiency of phthalic acid increased by increasing pH level and reaction time. The maximum removal efficiency of phthalic acid attained as 98 percent at pH of 11, reaction time of 60 min, 0.15 mmol/L of Fe²⁺ concentration, persulfate concentration of 0.3 mmol/L and 5 mg of phthalic acid. The process of removing phthalic acid followed from first-order kinetic (R²=0.9766). The effects of all studied independent variables with p<0.05 on removal efficiency of phthalic acid were found significant.

CONCLUSION: Obtained results indicated that the UV/Na₂S₂O₈/Fe²⁺ process for removing phthalic acid from the aquatic environments has high efficiency. This issue confirms the acceptable efficiency of mentioned method for the removal of phthalic acid.

KEY WORDS: *Phthalic Acid, Ultraviolet, Fe (II).*

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Introduction

In the present century, one of the most important environmental challenges is the presence of organic and toxic compounds that are resistant to decomposition in the sewage industry (1). Due to its extensive application, these compounds enter into various environmental resources, such as surface and underground waters, soils and so on, and have adverse effects on human health, plants and aquatic organisms (2). One of these compounds is phthalic acid (PA=Phthalic Acid). Phthalic acid is the source and source of the destruction of various types of phthalate esters (3-5).

Important uses of phthalates can be considered as additives in PVC, food packaging, paint and polishes, glues, cosmetics, etc. (6-9). Phthalic acid is one of the three benzene dicarboxylic acid isomers (Table 1). The toxicity of phthalic acid has not yet been fully established, but its lethal dose (LD50) has been reported for 550 mg/kg for mice (10). Complications of this compound include infertility, abortion, mutagenicity, teratogenicity and cancer (10-12). Given the adverse effects of this compound, the US Environmental Protection Agency has placed it on the list of priority pollutants and classified as hazardous waste (11,13).

This pollutant has been found in various locations, including leachate landfill, surface water and even atmospheric aerosols and rainwater (14,15). This organic material has a bio-accumulation and decomposes slowly. Therefore, with regard to the properties of phthalic acid, including high toxicity, environmental resistance and low degradability, the treatment of wastewater containing this material has a priority in order to avoid environmental and health hazards before discharging into the environment (16,17). In recent years, various advanced oxidation techniques such as UV/H₂O₂, Fenton/UV and O₃/UV/TiO₂ have been used to decompose phthalates in water and sewage (18).

Over the past few decades, persulfate oxidation has been used with a 1.2-volt oxidation-reduction potential to remove some toxic and tough contaminants (19). Zhang et al. used the UV/persulfate process to remove and evaluate the toxicity of carbamazepine contaminants from aquatic environments (20). One of the advantages of this method is the low cost, high stability of produced radical with UV irradiation, high solubility and a lower dependence on organic matter (19,21). Bivalent iron is one of the compounds that can convert

sulfate into SO₄^{•-} as a catalyst, and its presence can significantly increase the efficiency of decomposition of pollutants. One of the effective parameters on the process is the initial concentration of pollutant, persulfate concentration, Fe²⁺ concentration, solution pH and reaction time (22). In a study Ghaneian et al., stated that the maximum photochemical oxidation efficiency of 2,4-D in 2.5 mg/l persulfate, concentration of 2 mg/l, 2,4-D, pH = 3, and contact time of 240 minutes was equal to 96 percentage (23). In another study, the optimum recovery efficiency of 4-chlorophenol by the UV/NaPS process at a concentration of sodium persulfate 8.4 mmol/L, pH=5, the initial concentration of 4-chlorophenol 1.5 mmol/L, and reaction time of 30 minutes was 89.3% (24).

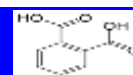
In recent decades, several approaches and models have been proposed to determine the number of experiments. In the meantime, the Response Surface Method (RSM) method has been very much considered due to a significant reduction in the number of samples, cost reduction, and a statistical model for describing the process as precisely as possible (25-27). In a study by Yeganebadi et al. on the removal of diethyl phthalate from aqueous solutions with advanced oxidation process based on persulfate (UV/Na₂S₂O₈/Fe²⁺), the effect of independent parameters on the percentage of removal of diethylphthalate by multidimensional method and response surface (Box-Behnken method) and concluded that the UV+/Na₂S₂O₈/Fe²⁺ process to remove DEP from aqueous environments yields 95% removal in optimal conditions (28). The aim of this study is to optimize the oxidation process based on persulfate (UV/Na₂S₂O₈/Fe²⁺) to remove phthalic acid from aqueous solution by the surface response method.

Table 1. Physical and chemical properties of phthalic acid in standard conditions

Molecular structure	
chemical formula	C ₈ H ₆ O ₄
Molecular weight	166.14 g/mol
Solubility in water	0.6 g/100mL
Maximum absorption wavelength	254 nm

Methods

This experimental study was carried out on a laboratory scale and closed method using deionized water and adding photocatalyst contamination to the reactor in a synthetic manner. The chemicals used



include sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), sulfuric acid, sodium hydroxide, FeCl_2 , Fe^{2+} , and phthalic acid from the German company Merck. The concentration of phthalic acid in the primary samples and the HPLC-treated wastewater was measured by the Cecil CE4100 model, made in England with a C18 column at 254 nm wavelengths. The HACH-HQ-USA pH meter was used to determine the pH of the solutions. In order to carry out this research, a steel cylindrical reactor was designed with a total volume of 1 liter (Fig. 1). In the middle of the steel tube, a quartz glass cylinder was fitted with a UV-C lamp with 16 Watts, so that UV light could be introduced into the reactor chamber. At each step, the samples were introduced into the reactor using deionized water (twice distilled water) with the chemicals used at 1 liter volume. During the reaction time, a mechanical stirrer of Heidolph Promax 2020 model was used to keep the solution homogeneous. To calculate and estimate the sample size, the surface-answer method and Box-Behnken design and the DesignExpert 7 software were used. Table 1 lists the independent variables and the range of their experimental values.

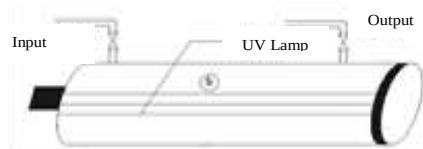


Figure 1. Pilot schematic design

Table 2. Independent variables and range and their experimental values

Variable	Symbol	-1	0	+1
Contact time(min)	A	5	32.5	60
Concentration of persulfate (Mmol/L)	B	0.1	0.3	0.5
concentration Fe^{2+} (Mmol/L)	C	0.1	0.15	0.2
pH	D	3	7	11

In order to investigate the effect of initial PA concentration on the UV/ $\text{Na}_2\text{S}_2\text{O}_8/\text{Fe}^{2+}$ process efficiency under optimal conditions, PA process of oxidation with initial concentrations of 5, 10, 20 and 50 mg/l was investigated. The phenotypic removal of phthalic acid was investigated by UV/ $\text{Na}_2\text{S}_2\text{O}_8/\text{Fe}^{2+}$ process at 0 to 60 minutes in optimal conditions. Grade-zero, degree-first and second-order models were used to investigate the reaction genotype. Correlation regression coefficient (R^2) was used to determine the best model matching with the obtained data.

Statistical analysis: Tests were designed according to surface-response method based on the Box-Benken. The data obtained in this project was modeled using Design Expert software 7.0.0 and three-dimensional graphs (response surface curves) were designed to examine the relationship between responses and independent variables (25,29).

Results

pH Effect: The results showed that the highest and lowest phthalic acid removal by UV/ $\text{Na}_2\text{S}_2\text{O}_8/\text{Fe}^{2+}$ process was 91.88% and 80.31%, respectively, at pH = 3 and pH = 11 (Fig. 2).

The effect of persulfate concentration: was obtained at concentrations of 0.1 and 0.5 mM/l, 69/22 and 79/43 percent efficiency was achieved, respectively. The highest PA removal efficiency at initial concentration of 0.33 mM per liter was obtained 85.6% (Fig. 3).

Effect of Fe^{2+} concentration: The results showed that by increasing the concentration of Fe^{2+} from 0.1 to 0.2 mM/L, the efficiency of phthalic acid removal by the process increased from 71.75 to 79.75%, and the highest removal efficiency (85.6%) was obtained at a concentration of 0.15 molar/L iron (Fig. 4).

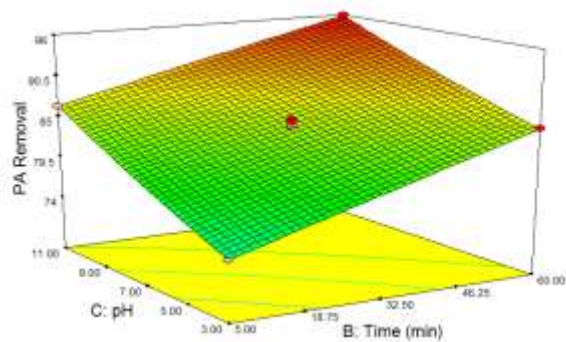


Figure 2. Effect of pH on the removal efficiency of PA in the UV/ $\text{Na}_2\text{S}_2\text{O}_8/\text{Fe}^{2+}$ process

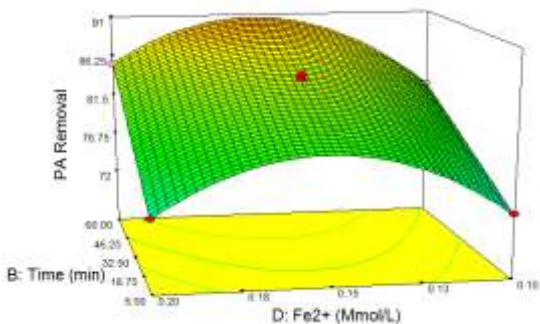


Figure 3. Effect of concentration on the removal efficiency of PA in the UV/ $\text{Na}_2\text{S}_2\text{O}_8/\text{Fe}^{2+}$ process

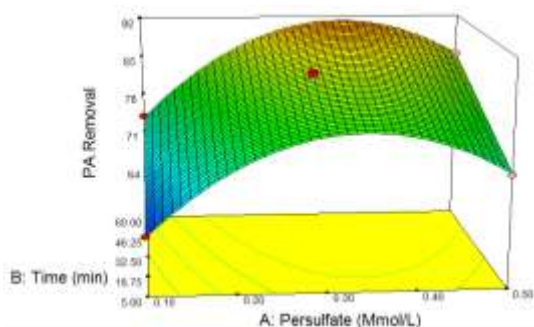


Figure 4. Effect of Fe²⁺ on PA removal efficiency in the UV/Na₂S₂O₈/Fe²⁺ process

Effect of reaction time: The results show that by increasing the time of recovery, PA removal increases, so that with increasing time from 5 to 60 minutes, the removal efficiency increased from 80.15 to 90.52 percent, respectively. (Fig. 4).

Effect of initial concentration of phthalic acid: In the study of the effect of the initial concentration of phthalic acid on the efficiency of UV/Na₂S₂O₈/Fe²⁺ process, it is observed that the PA removal efficiency after 30 minutes of reaction time at concentrations of 5, 10, 20 and 50 mg/l were about 100, 97, 90 and 83 percent.

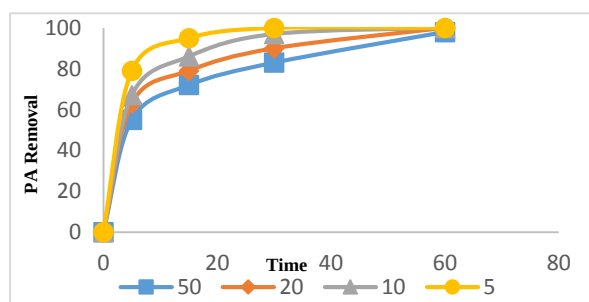


Figure 5. Effect of initial PA concentration on the efficiency of UV/Na₂S₂O₈/Fe²⁺ process under optimal operating conditions (pH=11, 0.3 Mmol/L sulfate concentration, 0.15 Mmol/L Fe²⁺ concentration)

Using the statistical method of the response surface, the following equation shows the experimental relationship between the test variables and the percentage of efficiency as encoded:

$$\text{PA Removal} = +85.40 + 5.10 * A + 5.19 * B + 5.48 * C + 1.12 * D + 0.49 * A * B + 0.52 * A * C + 0.52 * A * D - 0.50 * B * C + 0.57 * B * D - 0.25 * C * D - 11.07 * A^2 - 0.06 * B^2 + 0.40 * C^2 - 6.76 * D^2$$

As shown in the above equation, it is clear that a number of factors have a positive sign and some have a negative sign. The negative sign in the resulting

equation means increasing the efficiency with decreasing of that parameter and the positive sign in the equation shows a direct relationship between the efficiency and the parameter studied. In the present study, all four main parameters (A, B, C and D) have a positive sign, which indicates the positive effect of these parameters in the process of phthalic acid removal. The statistical parameters obtained by Box-Benken design, such as LACK OF FIT, as well as the high statistical coefficient of regression analysis ($R^2=0.9508$), confirm that the removal of phthalic acid by the UV/Na₂S₂O₈/Fe²⁺ process is well described by the model. Also, the effect of all parameters studied on the removal of phthalic acid was significant ($p<0.05$).

Confirmation of the Surface-Response Model: To ensure the validity of the proposed model, assumptions such as residuals with a normal distribution with mean zero, static variance and residues are independent of each other, can be used. Figure 6a shows the normalization of the residues, and, given that the deviation is not seen in the remaining normal, it assumes the presumption of the normalization of the residuals.

Diagram (6b) is used to check the assumption that the variance of the variables is constant. If there is no particular trend in this chart, the assumption of the variance of the variance is also accepted. In the diagram, a trend which is indicative of the increase or decrease of variance, the assumption that the variance is constant is also accepted.

Diagram (6-c) to check the independence between the remainders. In the absence of any process such as being sine in this chart, the assumption is also accepted. It is not seen in the diagram of a particular trend that can be ruled out by assuming the independence of the remainders.

Therefore, considering the analysis of the above diagrams and accepting the hypotheses, the selected model is suitable for data analysis.

The kinetics of the UV/Na₂S₂O₈/Fe²⁺ process: Curves for zero, first, and second degree kinetic models of PA removal by the UV/Na₂S₂O₈/Fe²⁺ process under optimal conditions for a concentration of 50 mg/L PA were shown in Fig 7. Regarding the above figures, it can be seen that regression coefficient is higher in the first-order kinetic model ($R^2=0.6697$) compared to the second-order model ($R^2=0.842$) and zero-grade kinetics ($R^2=0.926$). Therefore, the kinetics of the reaction follows a first-order model.

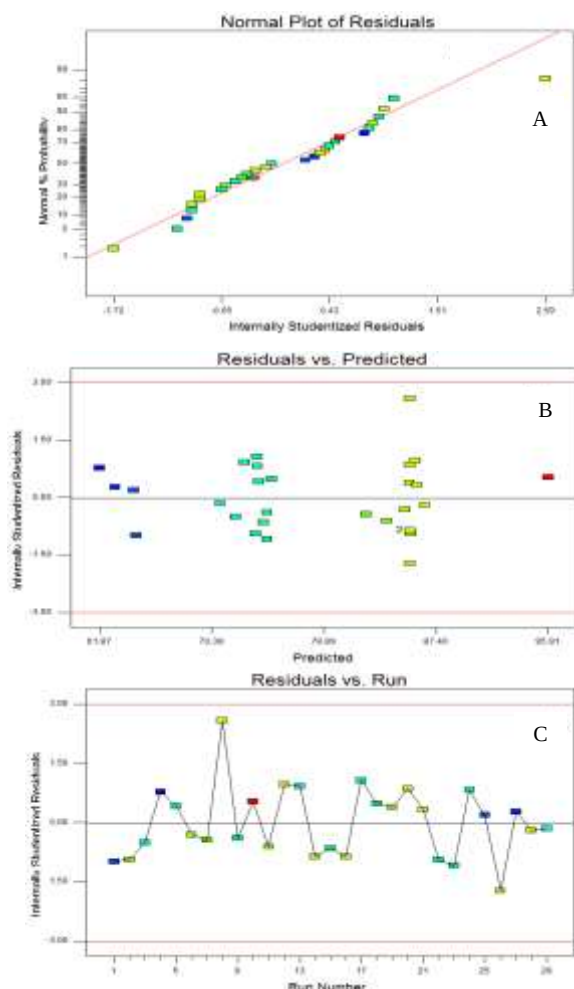


Figure 6. Distribution of test data against the predicted values of the model

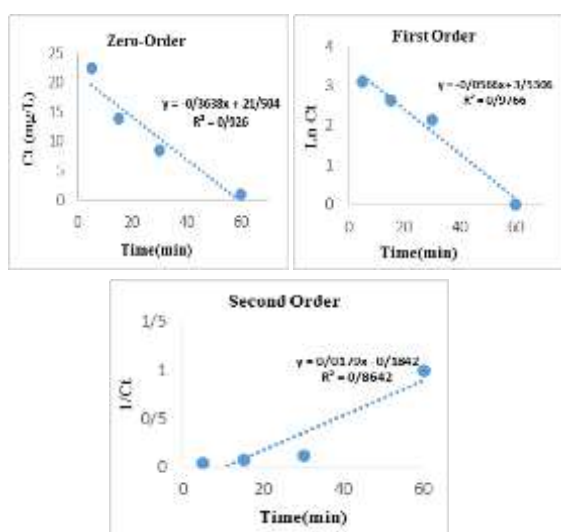


Figure 7. The rate of reaction of PA concentration by using the UV/Na₂S₂O₈/Fe²⁺ process under optimal conditions (PA concentration= 50 mg/L, pH=11, concentration of persulfate 0.3 Mmol/L, Fe²⁺+concentration of 0.15 Mmol/L)

Discussion

In this study, PA removal has increased with increasing pH, and the highest removal efficiency in alkaline pH was 11. In advanced oxidation processes, pH changes through the production of various radicals affect the amount of organic matter oxidation; the type and number of radicals produced in these processes is the most important cause of the effect of the pH changes of the environment on the decomposition of organic compounds in the oxidation processes. (19, 30). The concentration of OH increases in alkaline pH, which causes formation of SO₄ and OH (O⁻) (31).

In the study of Asgari et al., the obtained results in the presence of 0.01 mol/L of persulfate and the concentration of contamination of 100 mg/L and energy of 600 watts after 30 minutes of reaction, 47, 50 and 63% of the pollutant were removed, respectively at pH 3, 7 and 11, indicating that the removal efficiency is higher in alkaline pH (30). In addition, study of Yang et al. on the treatment of AO7-colored sewage sludge using microwave activated persulfate showed that the highest removal efficiency occurs in alkaline pH (32).

In this study, the PA removal rate increased with increasing concentrations of oxidizing matter. Increasing the concentration of the oxidizing agent increases a certain amount of reaction speed. As by increasing the concentration of persulfate more than 0.3 mmol/L, a reverse trend was observed in PA removal. By increasing the dose of sulfate, excess radical sulfate is produced, which can act as a radical agent and, by converting the radicals of sulfate to persulfate and eventually anion sulfate, prevents them from attacking the PA molecules, therefore, pollutant removal efficiency will also decrease (33-35).

The results at this stage are consistent with the results of Lin et al., that used the UV/persulfate process to remove phenol. The results of this study showed that phenol was completely decomposed in the dose ratio of molar sodium persulfate/phenol to 0.5: 84 and 0.5: 4.4 after 20 and 60 minutes of filtration, respectively (36). Furthermore, Yegane et al. stated that using the UV/Na₂S₂O₈/Fe²⁺ process during the study of ethyl phthalate removal, the highest DEP removal efficiency was obtained at a concentration of 0.4% Mmol/L of persulfate (84%) (28).

In this study, it was found that the increase of Fe²⁺ concentration to a certain degree increases the removal rate, and then, with increasing Fe²⁺, the rate of removal does not change and is constant. Bivalent

capacity iron is one of the compounds that can convert sulfate into SO₄²⁻ as a catalyst and its presence can significantly increase the efficiency of decomposition of pollutants (37,38). The results of the study by Liu et al. on the oxidation of Propachlor using persulfate activated with ions of iron and copper (II) at a concentration of 10 mg/L Propachlor, 5 mM/L of persulfate and pH=4, showed that both intermediate metals were effective in activation of persulfates in aqueous medium (39). In the study of Xu et al., which worked on the decomposition of azo-orange G-color in aqueous solutions using persulfate and iron ions, the persulfate/Fe + 2 molar ratios were 8: 1, 4: 1, 2: 1, and 1: 1. When the concentration of Fe + 2 rises from 0.5 to 4 mM, the orange G decomposition efficiency at the reaction time of 30 minutes is 54, 80, 94 and 99 percent, respectively (40).

Time remaining is one of the most effective variables in increasing the performance of advanced oxidation systems. In this study, with increasing contact time, the efficiency of PA removal increased. Increasing the amount of time in many of the purification methods can lead to more contact between the pollutant and the purifying agent and increase the final efficiency. In this study, the highest removal efficiency occurred at 60 minutes. In a study by Silveira et al., which optimized the removal of tetrachlorophenol using the activated peroxide process with Fe/Ag nanoparticles, they optimized the surface response method and concluded that the complete elimination and the highest degree of mineralization (83%) of tetrachlorophenol were obtained after reaction time of 60 minutes (41).

Investigating the changes in the initial concentration of PA showed that reducing the concentration of pollutants increases the removal efficiency. In a fixed UV radiation, a certain amount of radical is produced in the environment. This radical amount of production can absorb and remove a certain amount of organic matter molecules (42-44). Therefore, if the initial concentration of organic matter increases, the amount of radicals in the environment is

not sufficient to remove excess molecules. Metheniti et al. (1999) stated that propyl paraben degradation by persulfate activated with the use of carbon-containing magnetic iron indicated that a 4-fold increase in the initial concentration of propyl paraben (from 420 to 1690 µg/L) resulted in a 4-fold constant decrease in the rate and equal to 73% (45). The results of kinetic studies in optimal operating conditions for PA decomposition in the UV/Na₂S₂O₈/Fe²⁺ + process show that the rate of reduction of PA concentration follows a first-order reaction.

The study by Asgari et al. regarding the removal of pentachlorophenol by the microwave/persulfate system also indicated that the degree of reaction was first-reaction reactions with a reaction constant of 0.093 min⁻¹ (30). During the study of Orange G color analysis, using the persulfate/Fe²⁺ + process, it was reported that the kinetics of this process followed the first-order model and the constant rate of OG decomposition under test conditions (Persulfate 4 mM, Fe²⁺ 0/1 mM and pH=3) was equal to 0.040 min (40). The results showed that the removal efficiency of phthalic acid with direct increase of pH and contact time was inversely related to the initial concentration of pollutant.

Also, increasing the concentration of persulfate and iron to a certain extent increases the efficiency, but does not increase more than this efficiency. The UV/Na₂S₂O₈/Fe²⁺ + process for purifying the effluent containing phthalic acid in optimal conditions (pH=11, 0.3 Mmol/L sulfate concentration, 0.15 Mmol/L iron concentration, and 60 minutes) can reduce the phthalic acid by 98 removal percentage. According to the results, the UV/Na₂S₂O₈/Fe²⁺ + process can be considered as a suitable method for the removal of phthalic acid in aqueous media.

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