

## Experimental investigation of ultrasound/ Fenton's reagent oxidation process on the degradation rate constant of p-nitrophenol

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### Abstract

The main objective of the present work is the investigation of the efficacy of a combination of Fenton chemistry and high-frequency sonochemistry for wastewater treatment, including p-nitrophenol (PNP) as a model pollutant. These methods have been used to degrade PNP in a batch system under different operating conditions based on ultrasound process, Fenton reaction, ultrasound/hydrogen peroxide, and ultrasound/Fenton process. The reactor consisted of six ultrasonic transducers with a frequency of 1.7 MHz. Three transducers were located in the bottom, and the other three were embedded in the wall of the reactor. The results showed that the PNP decomposition follows a pseudo-first-order reaction. The degradation rate constant was determined for various operating parameters including pH, input electric power to transducers, and concentrations and volumes of H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>. In optimum conditions, the highest PNP degradation rate constant was obtained for the combination of 1.7 MHz ultrasound and Fenton reaction (0.166 min<sup>-1</sup>) with a synergistic coefficient of 1.165. Next priorities were related to Fenton, ultrasound/hydrogen peroxide and ultrasound with degradation rate constant of 0.137, 0.0107, and 0.005 min<sup>-1</sup>, respectively. Therefore, the ultrasound/Fenton process had the highest ability to degrade PNP, because ultrasound could intensify Fenton reaction to produce more hydroxyl radicals.

**Keywords:** Ultrasound waves, Fenton reaction, P- nitrophenol degradation, Synergetic effect, Hydrogen peroxide.

### 1. Introduction

p-nitrophenol (PNP) is widely used in many industries, as a synthetic intermediate or as a raw material in the manufacturing of insecticides, pesticides, and so forth [1, 2]. Moreover, PNP is produced as a byproduct during the manufacture of pesticide parathion. Therefore, because of its harmful effects on human health, finding effective methods for its removal from

water or wastewater before discharging into water bodies is important [2, 3].

Different advanced oxidation processes (AOPs) have been used to remove phenolic derivatives from wastewater, which can intensify oxidation by producing hydroxyl radicals (OH<sup>•</sup>) and other reactive oxygen intermediates [1, 4-6]. The intensification of removing phenol derivatives from wastewater with

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higher efficiency is very valuable. Ultrasound and Fenton's reagent oxidation are two of the efficient AOPs.

Ultrasound is a longitudinal wave with frequencies above 20 kHz. Cavitation is one of the main induced effects of propagation of the ultrasonic wave in the liquid medium. The generation and collapse of the tiny bubbles during high- and low-pressure cycles is called cavitation. Production of  $OH\cdot$  or  $H\cdot$  radicals, acoustic streaming, and shock waves are as the results of cavitation [7-9]. The waves with the frequency above 600 kHz are called high-frequency waves. The frequency of the waves has a direct effect on the size of the created bubbles. In comparison to low-frequency waves, high-frequency ultrasound can generate bubbles which are smaller and more stable. They called "stable cavitation bubbles". These bubbles have more longtime effects on heat and mass transfer and reaction rate. Acoustic streams are unidirectional fluid flows, which are more important in the propagation of high-frequency waves [9, 10]. Cold vapor or fog formation is another effects of high-frequency waves. The difference between the effects of high-frequency and low-frequency waves and the study of their effects in different systems can be interesting.

In Fenton chemistry,  $Fe^{2+}$  ions are used in combination with  $H_2O_2$  to generate hydroxyl radicals and attack on the pollutants [11, 12]

It has been shown that Fenton's reagent oxidation [4, 6, 13-23], and ultrasound [2, 24-29] can affectively remove phenolic compounds, which each one has its advantages. To use the advantages of both techniques, the combination of ultrasound and Fenton's reagent oxidation has been used [1, 11, 12, 30-33]. Removal of PNP using hydrodynamic cavitation and Fenton chemistry at pilot scale operation was also investigated by Pradhan and Gogate [34].

Most of the previous works were considered the effects of low- and medium- frequencies on the degradation of phenolic derivatives. Compared to low- and medium-frequency ultrasonic waves, high-frequency ultrasound is less used in water and wastewater treatment [25, 31]. However, the kinetics of phenolic compounds

degradation in the presence of high-frequency ultrasound has not been studied systematically yet. Moreover, the combination of high-frequency ultrasound and Fenton reaction, in order to take advantage of both techniques on PNP degradation has not been done. Also, there are not any investigation on the effect of transducers location. According to the literature, no research has been addressed the investigation of the kinetics of PNP degradation based on 1.7 MHz ultrasound process, Fenton process, and their combination. Therefore, the novelty of this study is the employment of 1.7 MHz ultrasonic wave and the synergetic effects of its combination with Fenton reaction for investigating the kinetics of PNP degradation.

The objective of the present work was to investigate the degradation kinetics of PNP from the aqueous medium using different methods, including 1.7 MHz ultrasound irradiation with different input electric powers, ultrasound/hydrogen peroxide hybrid process, Fenton's reagent oxidation, and ultrasound/Fenton's reagent hybrid process. Moreover, the dependence of the reaction rate constant on various operating parameters such as pH, concentration and volume of  $H_2O_2$  and  $FeSO_4$ , etc. was investigated by different processes and synergetic effects of ultrasound/Fenton' reagent as well. Also, the effect of the ultrasonic transducers' location on reaction rate constant was investigated.

## 2. Experimental procedure

### 2.1. Materials

PNP was obtained from Merck with a purity of 99 %, and used without further purification. It was diluted to desired concentrations using distilled water for all experiments (the solubility in water: 16 g/L (25 °C) [35]). Molecular structure of PNP is depicted in Fig. 1 [20]. The pH values of solutions at required levels were made with NaOH or HCL (Merck) solutions.  $H_2O_2$  (30%, w/v) and  $FeSO_4 \cdot 7H_2O$  were prepared from Merck.

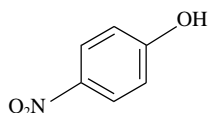


Fig. 1. Molecular structure of PNP [20].

## 2.2. Experimental setup

Schematic representation of the experimental setup and the sonoreactor used for degradation of PNP is depicted in Fig. 2. All experiments were carried out in a batch system, including a sonoreactor with an effective volume of 500 mL. The reactor consisted of two cylinders. The inner cylinder was made of stainless steel 304, with a diameter of 9 cm and a height of 15 cm, which was surrounded by another cylinder made of polyethylene with a diameter of 16 cm. The second cylinder was used as a cooling jacket containing ice and water. The cooling jacket around the reactor was used to keep the reactor temperature constant. The reactor consisted of six 1.7 MHz ultrasonic transducers with a diameter of 2.5 cm. Three of them were placed on the bottom of the reactor with a 120-degree angle to each other. The other three of them were mounted on the wall of the inner cylinder with a 120-degree angle to each other. The height of a solution in a reactor was 8 cm. The material of the reactor wall protected it against corrosion and made the heat transfer from the wall easier. The insulation material of the cooling jacket prevented the heat exchange of the fluid inside the reactor to the surrounding environment. Mean temperature of the solution in a sonoreactor was controlled and measured

using three K- type thermocouples, which were located in different locations.

## 2.3. Experimental method

Ultrasound-assisted oxidation of PNP was performed in a jacketed sonoreactor equipped with six transducers with a frequency of 1.7 MHz. The effective volume of the reactor was 500 mL. The ultrasonic transducers were actuated using actuating circuit, which was connected to a DC power supply (Dazheng, PS-305D, China). The solutions were maintained at  $10 \pm 2$  °C by cooling jacket. This cooling system was located outside of the sonoreactor to ensure that there is no disturbance in the scattering of pressure waves.

A volume of 500 mL of PNP solution with a constant concentration, 100 mg/L, was prepared for each experiment with the required pH. Then, the prepared solution was transferred to the sonoreactor.

Absorption spectra were measured with a UNICO-2100 UV-Vis spectrophotometer at  $\lambda = 406$  nm to monitor the concentration of PNP. Although ultrasonic degradation of PNP leads to various primary and secondary products [36, 2], we have restricted our analysis of measuring the concentration of PNP [2] and investigating the rate constant of PNP degradation.

The experiments of PNP degradation and investigation of the rate constant of degradation reaction were performed in four steps. First, ultrasonication was performed using six active transducers in different pH values of 5-7 and input electric powers to the transducers of 50-110 W.

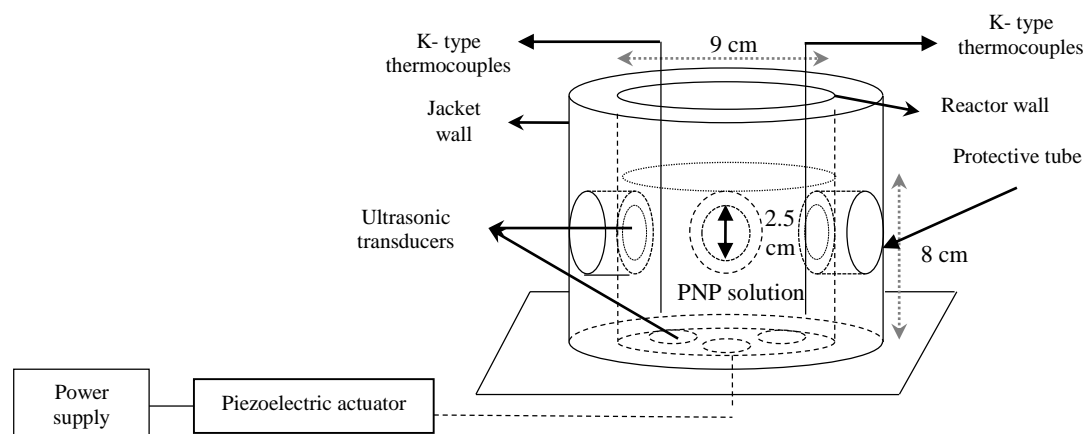


Fig. 2. Schematic representation and dimension of the experimental setup.

In the next step, Fenton's reagent oxidation of PNP was used on 500 mL of the PNP solution in the absence of waves. A magnetic stirrer constantly mixed the solution in a glass reactor. The reactions were performed with different concentrations of  $\text{H}_2\text{O}_2$  (0.2-0.8 M) and  $\text{Fe}^{2+}$  (0.01- 0.05 M).

At the third step, a combination of ultrasound and hydrogen peroxide was investigated. The reactions were performed with different volumes and concentrations of  $\text{H}_2\text{O}_2$  (4- 12 mL and 0.2- 0.8 M). Finally, Sono-assisted Fenton's reagent oxidation of PNP was investigated in the sonoreactor. Effects of volume and concentration of  $\text{FeSO}_4$  (0.7-2.8 mL and 0.01-0.05 M) and numbers and location of transducers were investigated on rate constant of PNP degradation. All experiments were repeated three times, and the reported values were the average of three runs. The experimental error was about 2%. Typical reaction runs lasted below 150 min.

### 3. Results and discussion

#### 3.1. PNP degradation using ultrasound

##### 3.1.1. Effect of input electric power

A solution with an initial PNP concentration ( $C_{\text{PNP},0}$ ) of 100 mg/L at a constant pH value of 5 was exposed to the radiation of six active transducers. Three different levels of the input electric powers ( $P$ ) (50, 80, and 110 W) were investigated.

The obtained results of the effects of electric powers on PNP degradation are shown in Fig. 3. The  $\ln(C_{\text{PNP},t}/C_{\text{PNP},0})$  and time had a good linear relationship [1, 2]. This figure shows pseudo-first-order degradation of PNP using 1.7 MHz ultrasound according the following equations [1]:

$$-r_A = -\frac{dC_{\text{PNP}}}{dt} = kC_{\text{PNP}} \quad (1)$$

$$C_{\text{PNP},t} = C_{\text{PNP},0}e^{-kt} \quad (2)$$

$$\ln(C_{\text{PNP},t}/C_{\text{PNP},0}) = -kt \quad (3)$$

In these equations,  $C_{\text{PNP},0}$  and  $C_{\text{PNP},t}$  are PNP concentrations (mg/L) in the time of 0 and  $t$  (min) and  $k$  is the PNP degradation rate constant.

The rate constant of 0.0017, 0.0035, and 0.0055  $\text{min}^{-1}$  were obtained for 50, 80, and 110 W, respectively. The extent of PNP decomposition increased with increasing electric power. When power increases, the transfer of ultrasonic energy to the sonoreactor increases, and because of this energy transfer, the bubble explosion occurs more quickly. Moreover, the concentration of hydroxyl radical increases in the solution.

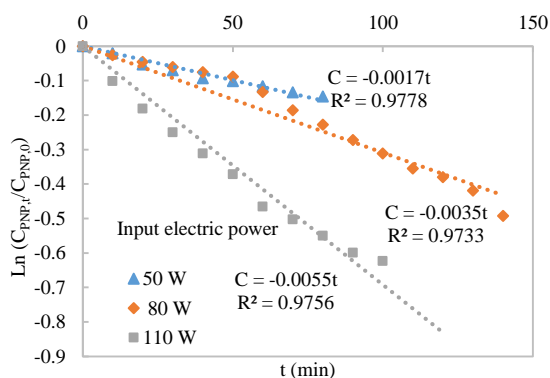


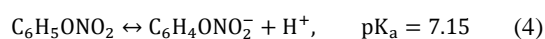
Fig. 3. Effect of input electric power to ultrasonic transducers on  $\ln(C_{\text{PNP},t}/C_{\text{PNP},0})$  vs. time, pH:5,  $C_{\text{PNP},0}$ : 100 mg/L.

Therefore, increasing the ultrasound power leads to an increase in cavitation, which is more desirable for a severe bubble explosion and the production of OH· radicals. Also, acoustic streams and micro-streams create in the liquid medium, which increases better mixing in the liquid. Therefore, increasing the power of the ultrasound leads to PNP degradation at a higher rate [24, 25].

### 3.1.2. Effect of pH

A solution with  $C_{\text{PNP},0}$  of 100 mg/L was exposed to the radiation of six active transducers at a constant input electric powers of 110 W. Three different levels of the pH values (5, 6 and 7) were investigated. The obtained results are shown in Fig. 4.

Rate constants of 0.0020, 0.0045, and 0.0055  $\text{min}^{-1}$  were obtained for pH values of 7, 6, and 5, respectively. The obtained values of rate constants show that  $k$  increases by decreasing pH. There is an equilibrium in the aqueous solutions between the molecular and ionic form of PNP. Also, PNP is relatively acidic in aqueous solutions. In an acidic solution, according to Eq. (4), the equilibrium proceeds to neutralize the acidity of the solution, thus reacts to create the molecular form.



Compounds that have ionic deformation are affected by pH changes because the molecular shape does not exhibit similar hydrophobicity compared to the ionic form. Depending on the pH, the ionic form decomposes at a lower rate than the molecular form, because it is more soluble than the non-charged

structure and therefore has less accumulation at the interface. PNP, with  $\text{pK}_a = 7.15$ , decomposes three times faster at acidic pH (molecular form) than at pH above eight (ionic form) [37]. The molecular form of PNP has a more hydrophobic effect than its ionic form, which leads to the decomposition larger amount of PNP molecules. Unlike, the ionic form of PNP has very high hydrophilic effects and achieve themselves to the mass of the bubbles, which leads to reducing reaction efficiency [2, 26, 38, 39].

In these experiments, the optimum operating parameters for PNP degradation using ultrasound were found to be pH 5 and input electric power of 110 W.

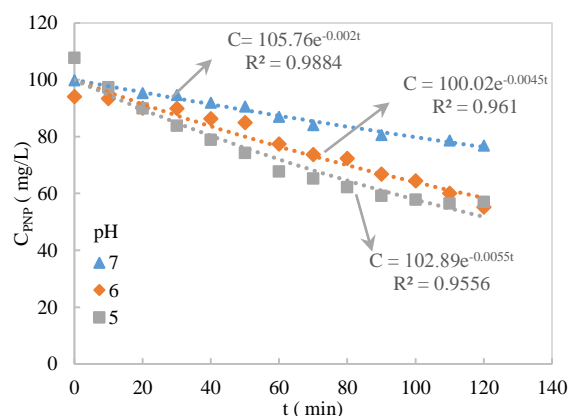
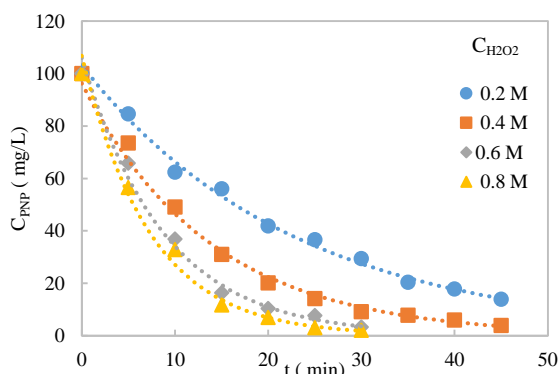


Fig. 4. Effect of pH on PNP concentration using ultrasound,  $C_{\text{PNP},0}$ : 100 mg/L, P: 110 W.

## 3.2. PNP degradation using Fenton's reagent oxidation process

### 3.2.1. effect of $\text{H}_2\text{O}_2$ concentration

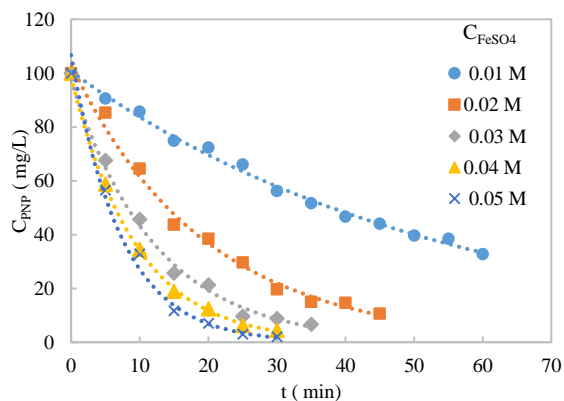
The effect of  $\text{H}_2\text{O}_2$  concentration ( $C_{\text{H}_2\text{O}_2}$ ) on the rate constant of PNP degradation by Fenton's reagent oxidation process is shown in Fig. 5 and Table 1. The values of pH, the volume of  $\text{H}_2\text{O}_2$  ( $V_{\text{H}_2\text{O}_2}$ ), the concentration and volume of  $\text{FeSO}_4$  ( $C_{\text{FeSO}_4}$  and  $V_{\text{FeSO}_4}$ ) were set at 5, 8 mL, 0.05 M and 2.8 mL, respectively. The rate constant values of 0.044, 0.0073, 0.0114 and 0.0137  $\text{min}^{-1}$  were obtained for 0.2, 0.4, 0.6 and 0.8 M concentrations of  $\text{H}_2\text{O}_2$ , respectively. It was found that by increasing the concentration of  $\text{H}_2\text{O}_2$ , the rate of degradation of PNP increases by Fenton's reagent oxidation process [13, 14]. Increasing the concentration of  $\text{H}_2\text{O}_2$  causes more OH· radicals to form, which accelerates the PNP degradation.



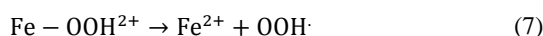
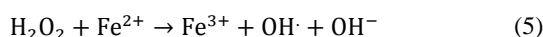
**Fig. 5.** Effect of  $C_{H_2O_2}$  on PNP concentration using Fenton reaction, pH:5,  $C_{PNP}$ : 100 mg/L,  $V_{H_2O_2}$ : 8 mL,  $C_{FeSO_4}$ : 0.05 M,  $V_{FeSO_4}$ : 2.8 mL.

### 3.2.2. Effect of $FeSO_4$ concentration

The effect of the concentration of  $FeSO_4$  on the rate constant of PNP degradation is shown in Fig. 6 and Table 2. The obtained results indicate that with increasing the concentration of  $FeSO_4$ , the rate constant of PNP degradation for Fenton's reagent process increases. Increasing the concentration of  $H_2O_2$  and  $FeSO_4$  results in the release of  $OH^\cdot$  radicals (in accordance with Eq. (5)) which lead to increase the reaction efficiency. Moreover, the reaction between hydrogen peroxide and produced ferric ion leads to the production of  $OOH^\cdot$  radical (Eqs. (6) and (7)), which is one of the oxidizing agents of organic pollutants [13, 40, 41].



**Fig. 6.** Effect of  $C_{FeSO_4}$  on PNP concentration, pH:5,  $C_{PNP,0}$ : 100 mg/L,  $V_{FeSO_4}$ : 2.8 mL,  $C_{H_2O_2}$ : 0.8 M,  $V_{H_2O_2}$ : 8 mL



### 3.3. PNP degradation using a combination of ultrasound and hydrogen peroxide

Effect of volume and concentration of  $H_2O_2$  on the rate constant of PNP degradation under ultrasound field was investigated. As shown in Fig. 7 and Table 3, increasing the volume of  $H_2O_2$  in a solution up to 8 mL increases the PNP degradation rate. As the concentrations of  $OH^\cdot$  and  $OOH^\cdot$  radicals increase in the solution (according to Eqs. (5), (6), and (7)) the reaction efficiency enhances.

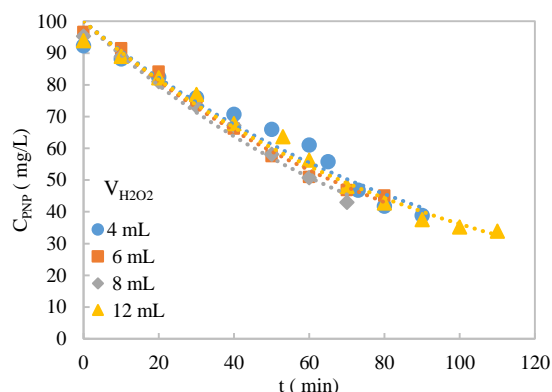
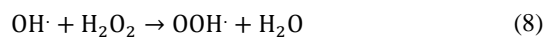
However, the rate constant decreases by adding more  $H_2O_2$  volume from 8 to 12 mL. Due to the excessive increase in  $H_2O_2$ , this substance acts like a hydroxyl radical robber (see Eqs. (8) and (9)), which reduces the reaction rate constant [13].

**Table 1.** Effect of  $H_2O_2$  concentration on PNP degradation rate constant in Fenton's reagent process.

$H_2O_2$ concentration (M)	0.2	0.4	0.6	0.8
Rate constant ( $\text{min}^{-1}$ )	0.044	0.073	0.114	0.137
$R^2$	0.984	0.9918	0.9889	0.9922

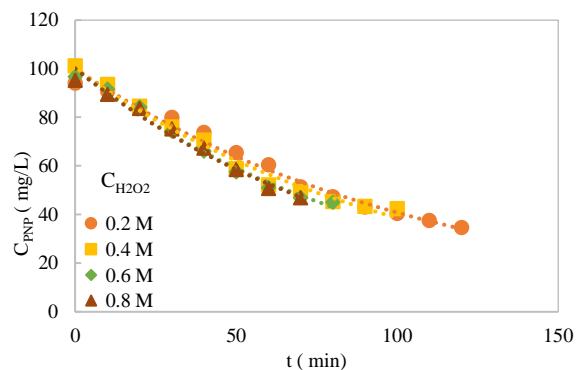
**Table 2.** Effect of  $FeSO_4$  concentration on PNP degradation rate constant in Fenton's reagent process.

$FeSO_4$ concentration (M)	0.01	0.02	0.03	0.04	0.05
Rate constant ( $\text{min}^{-1}$ )	0.018	0.051	0.081	0.106	0.137
$R^2$	0.9939	0.9892	0.9809	0.9969	0.9922



**Fig. 7.** Effect of  $V_{\text{H}_2\text{O}_2}$  on PNP concentration using a combination of ultrasound and hydrogen peroxide, pH:5,  $C_{\text{PNP},0}$ : 100 mg/L, P: 110 W,  $C_{\text{H}_2\text{O}_2}$ : 0.8 M.

Fig. 8 and Table 4 show the results of changes in  $\text{H}_2\text{O}_2$  concentration on the reaction rate constant. As observed in this figure, increasing the  $\text{H}_2\text{O}_2$  concentration increases the reaction rate constant of PNP degradation [11]. According to the experiments, the optimum concentration and volume of  $\text{H}_2\text{O}_2$  were found to be 0.8 M and 8 mL, respectively.



**Fig. 8.** Effect of  $C_{\text{H}_2\text{O}_2}$  on PNP concentration using a combination of ultrasound and hydrogen peroxide, pH:5,  $C_{\text{PNP},0}$ : 100 mg/L, P: 110 W,  $V_{\text{H}_2\text{O}_2}$ : 8 mL.

### 3.4. PNP degradation using a combination of ultrasound and Fenton's reagent oxidation process

#### 3.4.1. Effects of concentration and volume of $\text{FeSO}_4$

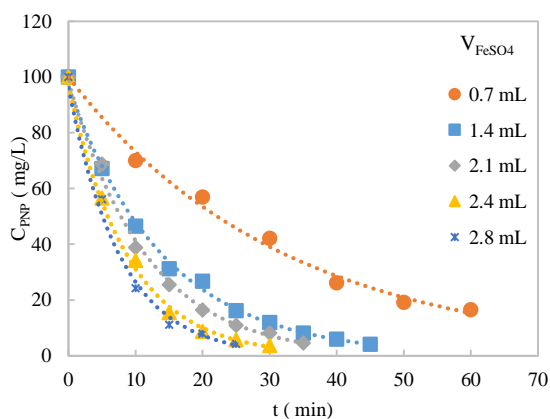
Effects of volume and concentration of  $\text{FeSO}_4$  solution on the rate constant of PNP degradation using a combination of ultrasound and Fenton's reagent oxidation process are depicted in Figs. 9 and 10, and Tables 5 and 6. According to these figures, with increasing the concentration and volume of  $\text{FeSO}_4$  solution, the reaction rate constant of PNP degradation in the Ultrasound/Fenton's reagent oxidation process increases [42, 31].

**Table 3.** Effect of  $\text{H}_2\text{O}_2$  volume on PNP degradation rate constant using a combination of ultrasound and hydrogen peroxide.

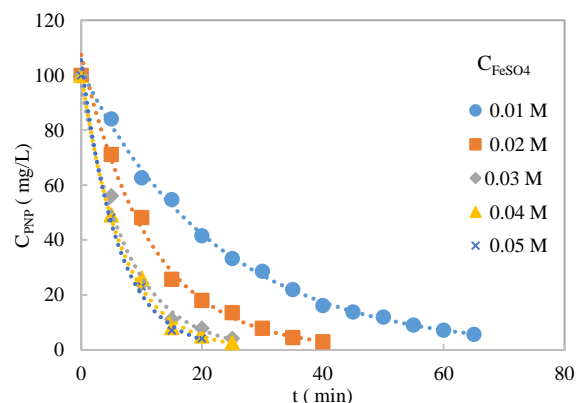
$\text{H}_2\text{O}_2$ volume (mL)	4	6	8	12
Rate constant ( $\text{min}^{-1}$ )	0.0098	0.0105	0.0107	0.0102
$R^2$	0.9539	0.9875	0.9864	0.9845

**Table 4.** Effect of  $\text{H}_2\text{O}_2$  concentration on PNP degradation rate constant using a combination of ultrasound and hydrogen peroxide.

$\text{H}_2\text{O}_2$ concentration (M)	0.2	0.4	0.6	0.8
Rate constant ( $\text{min}^{-1}$ )	0.009	0.0095	0.0105	0.0107
$R^2$	0.99	0.9767	0.9875	0.9864



**Fig. 9.** Effect of  $V_{FeSO_4}$  on PNP concentration using combination of ultrasound and Fenton reaction, pH:5,  $C_{PNP,0}$ : 100 mg/L, P: 110 W,  $V_{H_2O_2}$ : 8 mL,  $C_{H_2O_2}$ : 0.8 M,  $C_{FeSO_4}$ : 0.03 M

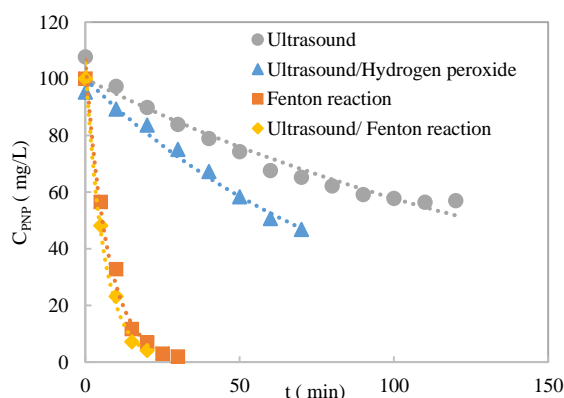


**Fig. 10.** Effect of  $C_{FeSO_4}$  on PNP concentration by a combination of ultrasound and Fenton reaction, pH: 5,  $C_{PNP,0}$ : 100 mg/L, P: 110 W,  $V_{H_2O_2}$ : 8 mL,  $C_{H_2O_2}$ : 0.8 M,  $V_{FeSO_4}$ : 2.8 mL.

### 3.4.2. synergistic effect

According to the obtained results of the experiments, ultrasound technique and Fenton's reagent oxidation process can intensify each other. A comparison of

different treatment techniques; ultrasonic irradiation, Fenton's reagent oxidation, ultrasound/hydrogen peroxide, and ultrasound/Fenton's reagent oxidation for  $C_{PNP,0}$ : 100 mg/L is shown in Fig. 11 and Table 7. Degradation of PNP using only ultrasound (P: 110 W and pH:5) leads to  $k = 0.0055$ . While, using only Fenton process ( $V_{H_2O_2}$ : 8 mL,  $C_{H_2O_2}$ : 0.8 M and  $V_{FeSO_4}$ : 2.8 mL and  $C_{FeSO_4}$ : 0.05 M) results in  $k=0.137$ . In the combined Ultrasound/ Fenton's reagent oxidation process at the same experimental conditions  $k = 0.166$ .



**Fig 11.** Comparison of the performance of different treatment techniques on PNP concentration.

Therefore, the PNP degradation rate in ultrasound/Fenton's reagent oxidation process was higher than the sum of PNP degradation rates in individual ultrasound irradiation and Fenton's reagent process.

**Table 5.** Effect of  $FeSO_4$  volume on rate constant of PNP degradation by a combination of ultrasound and Fenton reaction.

$FeSO_4$ volume (mL)	0.7	1.4	2.1	2.4	2.8
Rate constant ( $\text{min}^{-1}$ )	0.031	0.070	0.087	0.114	0.129
$R^2$	0.988	0.9976	0.9962	0.9931	0.9888

**Table 6.** Effect of  $FeSO_4$  concentration on rate constant of PNP degradation by a combination of ultrasound and Fenton reaction.

$FeSO_4$ concentration (M)	0.01	0.02	0.03	0.04	0.05
Rate constant ( $\text{min}^{-1}$ )	0.044	0.088	0.129	0.150	0.166
$R^2$	0.9983	0.9953	0.9888	0.9896	0.9893



Table 7. Comparison of the rate constant of PNP in different processes.

PNP degradation Process	Ultrasound	Ultrasound/Hydrogen peroxide	Fenton's reagent oxidation	Ultrasound/Fenton's reagent oxidation
Rate constant (min <sup>-1</sup> )	0.0055	0.0107	0.137	0.166

It is obvious that there was a synergistic effect in the combined ultrasound/Fenton's reagent process [1]. In order to calculate the synergistic effect of the combined treatment process, the synergistic coefficient, S, is defined from the following equation [43, 44, 1]:

$$s = \frac{k_{\text{Ultrasound/Fenton}}}{k_{\text{Ultrasound}} + k_{\text{Fenton}}} = \frac{0.166}{0.0055 + 0.137} = 1.165 \quad (10)$$

Since pseudo-first-order kinetic constants were 0.0055 min<sup>-1</sup> for ultrasound, 0.137 min<sup>-1</sup> for Fenton, and 0.166 min<sup>-1</sup> for ultrasound/Fenton, the synergistic coefficient was calculated to be 1.165. This calculation shows that the effect of ultrasound/Fenton process is greater than the sum of its parts, ultrasound process, and Fenton process. Therefore, ultrasound/Fenton's reagent treatment process would be a good alternative for wastewater treatment.

In ultrasound/ Fenton's reagent oxidation process, an increase in the rate constant is due to the acceleration of the decomposition of Fe-OOH<sup>2+</sup> into Fe<sup>2+</sup> and OOH<sup>-</sup> under ultrasound field. Because the ultrasonic process produces more Fe<sup>2+</sup> ions for more reaction with H<sub>2</sub>O<sub>2</sub> and produces more OOH<sup>-</sup> radicals to attack organic pollutants in the solution medium (see Eq. (7)) [15, 11, 31].

Table 8. Effect of numbers and location of ultrasound transducers on rate constant of PNP degradation by a combination of ultrasound and Fenton's reagent oxidation process.

Numbers/ location of transducers	Three/ wall of the sonoreactor	Three/ bottom of the sonoreactor	Six/bottom and wall of the sonoreactor
Rate constant (min <sup>-1</sup> )	0.102	0.133	0.166
R <sup>2</sup>	0.993	0.9798	0.9893

### 3.4.3. The effect of numbers and location of 1.7 MHz transducers

Effect of numbers and location of ultrasound transducers on PNP degradation using ultrasonic/Fenton's reagent oxidation process are depicted in Fig. 12 and Table 8.

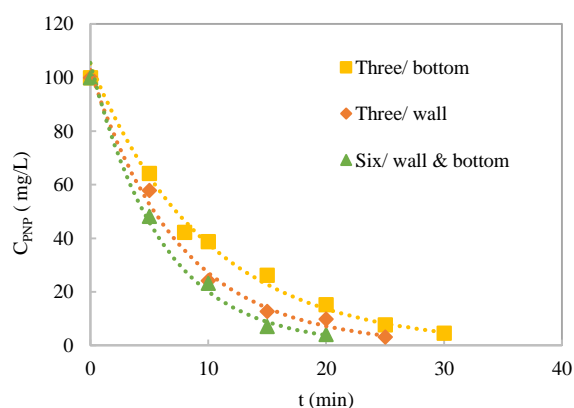


Fig. 12. Effect numbers and location of ultrasound transducers on PNP concentration using a combination of ultrasound and Fenton reaction, pH:5, C<sub>PNP,0</sub>: 100 mg/L, P: 110 W, V<sub>H<sub>2</sub>O<sub>2</sub></sub>: 8 mL, C<sub>H<sub>2</sub>O<sub>2</sub></sub>: 0.8 M, V<sub>FeSO<sub>4</sub></sub>: 2.8 mL and C<sub>FeSO<sub>4</sub></sub>: 0.05 M.

As it is shown in this figure, with increasing the number of transducers, from three to six, the rate of degradation of PNP increases.

This increase can be due to an increase in cavitation activities, more hydroxyl radicals, and higher mixing due to the acoustic streams. As it is known, ultrasonic waves can intensify or destroy each other while propagating in the liquid medium. As can be seen in Table 8, the rate constants were obtained to be 0.102, 0.133, and 0.166  $\text{min}^{-1}$  for the wall, bottom, and all transducers, respectively. It shows that the transducers which located in the bottom of the reactor are more effective than they mounted on the wall. The rate constant of all active transducers is less than the summation of the rate constants by the bottom or wall transducers. Therefore, the ultrasound waves of the bottom and wall transducers likely have a destructive effect on each other.

#### 4. Conclusion

In this study, different processes, including ultrasound, Fenton's reagent oxidation, a combination of ultrasound and hydrogen peroxide, and the combination of ultrasound/ Fenton's reagent oxidation processes have been compared in order to degrade PNP from water. In these experiments, 1.7 MHz ultrasound waves were employed for the first time. A sonoreactor equipped with six ultrasonic transducers were used, which three transducers were located on the wall and three of them were located in the bottom. The initial concentration of PNP was 100 mg/L for all experiments. As PNP degradation followed the pseudo-first-order reaction, the rate constant,  $k$ , was compared in all experiments. Following conclusions were obtained from the experiments:

- For only ultrasound, electric power of 110 W and pH value of 5 were obtained as the best conditions, which resulted in  $k= 0.0055 \text{ min}^{-1}$ .
- In Fenton reaction, the best concentration of  $\text{H}_2\text{O}_2$  and  $\text{FeSO}_4$  solutions were 0.8 M and 0.05 M, which resulted in  $k= 0.137 \text{ min}^{-1}$
- In the ultrasound/hydrogen peroxide process, the best condition was related to  $\text{H}_2\text{O}_2$  concentration and volume of 0.8 M and 8 mL ( $k= 0.0107 \text{ min}^{-1}$ ).
- In ultrasound/Fenton reaction, the best conditions were: pH: 5, electric power: 110 W,  $\text{FeSO}_4$

concentration: 0.05 M and volume of  $\text{FeSO}_4$  solution: 2.8 mL. Moreover, the synergistic coefficient was 1.165, with  $k= 0.166 \text{ min}^{-1}$ . Therefore, the ultrasound/Fenton process had the highest ability to degrade PNP, because ultrasound could intensify Fenton reaction to produce more hydroxyl radicals.

Moreover, it was found that the effect of three transducers on the wall is greater than the effect of three transducers located in the bottom. Also, the wall and bottom transducers have a destructive effect on each other.

- Ultrasound/Fenton's reagent oxidation, using 1.7 MHz ultrasonic waves, is a proper treatment process for PNP removal from polluted water.

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