

Mineralization and degradation of 4-Nitrophenol using homogeneous Fenton oxidation process

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ABSTRACT

The mineralization analysis of wastewater is important for the growth of flora and fauna. The mineralization along with the degradation of 4-NP has been studied using homogeneous Fenton oxidation process. The mineralization of 4-NP has been reported in terms of chemical oxygen demand (COD) removal % and total organic carbon (TOC) removal %. The main parameters that affect the mineralization and degradation of 4-NP i.e. initial pH (1 - 5), reaction time (0 - 60 min), the concentration of hydrogen peroxide (1 - 5 mM) and concentration of ferrous ions (0.05 - 0.5 mM) have been optimized. In the present study, optimum reaction conditions for mineralization and degradation of 4-NP are observed at pH 3, 4 mM of H₂O₂ concentration, 0.2 mM of Fe²⁺ concentration and in 40 min of reaction time. At the optimum condition, COD removal and TOC removal were 50% and 60.3%, respectively along with 93.6% of 4-NP degradation. At optimized conditions, intermediate products obtained after homogeneous degradation of 4-NP were identified based on LC-MS spectra analysis. The degradation of 4-NP followed, second order reaction rate. The present study showed the higher degradation and mineralization of 4-NP as compared to available studies on 4-NP.

Keywords: Chemical oxygen demand, Degradation, 4-Nitrophenol, Mineralization, Total organic carbon

1. Introduction

4-Nitrophenol (4-NP) is a hazardous, bio-refractory organic compound and is widely used for the production of pesticides, herbicides, insecticides and synthetic dyes [1]. It is highly stable and soluble in water and persists in soil and ground water for a longer period of time [2]. The discharge of 4-NP from various industries to water streams is of main concern due to its toxicity and suspected carcinogenicity. The development of efficient methods for removal of 4-NP, is becoming an important field of study for researchers.

Several treatment methods such as chemical, physical and biological have been employed for the treatment of 4-NP from wastewater [3]. Physical and biological treatment techniques are not very satisfactory as they transfer the pollutants from one phase to another, and the equipment required for these processes is also very costly [4]. Recently advanced oxidation processes (AOPs) showed considerable potential for the removal of 4-NP from industrial effluents [5-9]. In AOPs, the hydroxyl radicals (OH) are generated in solution and are responsible for the oxidation and mineralization of the organic pollutants to water and carbon dioxide [10-13]. Among various AOPs, the Fenton oxidation process has been used extensively, as reagents (ferrous sulphate heptahydrate and hydrogen peroxide) used are easy to handle and environmental friendly [14]. The main advantage of this method is that the reaction takes place at ambient temperature, atmospheric pressure and short reaction period, which makes the process less expensive [15].

Various studies available on degradation of organic pollutants using a homogeneous Fenton oxidation process are presented in Table 1.

It is observed from Table 1, that the homogeneous Fenton oxidation process is still very active for the degradation of various organic pollutants. Further, it is observed that most of the studies are available on the degradation/ decolourization of organic pollutants, however, very few studies are reported on mineralization (TOC and COD removal) of the organic pollutants. The studies of Fathi and Keshmirizadeh [4], Ertugay and Acar [16], Giri and Golder [17] and Barbusinski [18] have analyzed COD removal % for various organic pollutants. Giri and Golder [17] has reported TOC removal (37.9%) for ciprofloxacin. The degradation studies alone do not reveal the conversion of toxic organic pollutants in simpler organic compounds. Thus mineralization of organic pollutants



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Reference	Organic pollutants	Operating parameters/conditions	Observations
Barbeni et al., 1987 [19]	2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 3,4-dichlorophenol and 2,4,5-trichlorophenol.	$C_0 = 3x10^4 \text{ M},$ $T = 25^{\circ}\text{C}$	- Increase in concentration of Fe^{2+} ions enhanced decomposition rate of chlorophenols Chlorinated aliphatic species were formed as intermediates.
Kwon et al., 1999 [20]	p-chlorophenol	$C_0 = 2.0 \text{ mM},$ $[H_2O_2] = 3 - 12 \text{ mM},$ $[Fe^{2+}] = 0.1 - 1.0 \text{ mM},$ $pH = 1 - 5$	 The optimum reaction conditions were: 6 mM H₂O₂, 0.3 mM Fe²⁺ and pH 3. The decomposition of p-chlorophenol was high in pH range 2 - 4. The initial reaction rate was high and followed first order reaction rate with initial concentration of Fe²⁺ and H₂O₂.
Ma et al., 2000 [21]	4-Nitrophenol	$C_0 = 1 \text{ mM},$ $[H_2O_2] = 1 - 10 \text{ mM},$ $[Fe^{2+}] = 1 - 10 \text{ mg/L},$ $pH = 3$	 99% decomposition of 4-NP was achieved at 5 mM H₂O₂ and 5 mg/L Fe²⁺ in 2 h. The dissolved organic carbon removal efficiency was 30.6%. 4-NP degradation obeyed pseudo first order reaction rate.
Meriç et al., 2004 [22]	Reactive Black 5	$C_0 = 100$ and 200 mg/L, $[FeSO_4]/H_2O_2 = 0.5$ to 0.2, pH = 2.5 - 4, $T = 30 - 60^{\circ}C$	and COD removal were 99% and 71% with 100 mg/L of FeSO ₄ , 400 mg/L of H ₂ O ₂ , pH 3 and 40°C. For 200 mg/L of reactive black 5, the color removal and COD removal were 99% and 84% with 200 mg/L of FeSO ₄ , 1000 mg/L of H ₂ O ₂ , pH 3 and 40°C.
Barbusinski, 2005 [18]	Industrial wastewater having maleic acid anhydride (MAA), 2-ethylhexyl alcohol (2-EHA) n-butanal, urea-formaldehyde resin adhesive (UFRA), pesticide-containing wastewater (PCRA)	$[H_2O_2] = 2 - 10 \text{ g/dm}^3,$ $[Fe^{2+}/H_2O_2] = 0.2 - 0.75,$ $pH = 2 - 5,$ $t = 2 - 24 \text{ h}$	- At optimized conditions of 5 g/dm³ H ₂ O ₂ , molar ratio of Fe²+/H ₂ O ₂ : 0.33 and pH 3, the toxicity removal% for MAA, 2-EHA, UFRA and PCW were 47%, 51%, 12% and 100%, respectively COD removal for MAA, 2-EHA, UFRA and PCW were 87.8%, 86.3%, 88.6% and 71.7%, respectively Only for MAA, 2-EHA and UFRA, the toxicity was reduced to non-toxic level.
Kavitha and Palanivelu, 2005 [23]	2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP)	C_0 for [2-NP/4-NP] = 1.43, [DNP] = 1.08 mM and [TNP] = 0.87 mM, pH 3	 For mono-NP, at the optimum conditions of 17.3 mM H₂O₂ and 0.45 mM Fe²⁺, the mineralization efficiency was 32%. For DNP, at the optimum conditions of 12.9 mM H₂O₂ and 0.36 mM Fe²⁺, the mineralization efficiency was 25%. Whereas for TNP at 10.4 mM of H₂O₂ and 0.36 mM of Fe²⁺, it was 21%. Degradation of NPs followed pseudo-first-order reaction.
Chang et al., 2008 [10]	p-nitrophenol (PNP)	$C_0 = 0.1 - 0.4 \text{ mM},$ $[H_2O_2] = 2 - 20 \text{ mM},$ $[Fe^{2+}] = 0.1 - 0.8 \text{ mM},$ PH = 3	- The optimum conditions obtained for the degradation of PNP were 0.1 mM Fe ²⁺ , 4 mM H ₂ O ₂ and pH 3 For low concentration of PNP, the reaction rate was first order whereas at higher concentrations of PNP, it was zeroth order.
La Nafie, 2010 [24]	Spiked soil having polycyclic aromatic hydrocarbons	$C_0 = 200$ each PAHs, pH = 3, $H_2O_2/Fe^{2+} = 10.1$	- Polycyclic aromatic hydrocarbons containing naphthalene, anthracene, fluoranthene, pyrene and benzo(a)pyrene in spiked soil were degraded to 96%.

Table 1. Continuation	ation		
Reference	Organic pollutants	Operating parameters/conditions	Observations
Khamaruddin et al., 2011 [25]	Diisopropanolamine	$C_0 = 3 g/L,$ $T = 30^{\circ}C - 60^{\circ}C,$ pH = 2 - 4, $[H_2O_2/Fe^{2^+}] = 95$	 Degradation efficiency of diisopropanolamine increased with increase in temperature and at 60°C, it was 85%. The optimum pH for diisopropanolamine degradation was 2.5. The degradation of diisopropanolamine followed pseudo first-order reaction rate.
Ghosh et al., 2012 [26]	p-Chlorophenol (pCP) and Nitrobenzene (NB)	$\begin{split} C_{\text{PpGP}} &= [3.889 - 7.778] \times 10^3 \text{ gmol/l}, \\ &[\text{H}_2\text{O}_2] \ / \ [\text{pCP}] = 5.65 - 7.55, \\ &[\text{H}_2\text{O}_2] \ / [\text{Fe}^{2+}] = 8.2 \\ &C_{\text{O-NB}} = [3.25 - 4.87] \times 10^3 \text{ gmol/l}, \\ &[\text{H}_2\text{O}_2] \ / [\text{NB}] = 3.6 - 10.8, \\ &[\text{H}_2\text{O}_2] \ / [\text{Fe}^{2+}] = 8.2 \end{split}$	- The degradation of p-chlorophenol was 99.29% at $[H_2O_2]/[pCP]$ of 7.55 whereas for nitrobenzene, it was 96.32% at $[H_2O_2]/[pCP]$ of 3.60 The degradation of p-chlorophenol and nitrobenzene followed second order reaction rate with constants 2.144 \times 10 6 /M-s and 1.102 \times 10 6 /M-s, respectively.
El Haddad et al., 2014 [27]	Reactive Yellow 84 dye	$C_0 = 60 \text{ mg/L},$ $H_2O_2 = 50 - 500 \text{ mg/L},$ $Fe^{2+} = 10 - 100 \text{ mg/L},$ $pH = 2 - 10, T = 20^{\circ}C - 50^{\circ}C$	- 85% decolorization efficiency for reactive yellow 84 was obtained at the optimum conditions of 25 mg/L $\rm Fe^{2^+}$, 250 mg/L $\rm H_2O_2$, pH 3, $\rm 20^\circ C$ in 20 min. - Decolorization of reactive yellow 84 followed pseudo second order reaction rate. - The activation energy for the Fenton reaction was 16.78 kJ/mol.
Giri and Golder, 2014 [17]	Giprofloxacin	$C_0 = 15 \text{ mg/L},$ $[Fe^{2+}/H_2O_2] = 0.125,$ time = 45 min, $T = 25^{\circ}C$ and pH 3.5	- The degradation, COD and TOC removal for ciprofloxacin were 74%, 47.1% and 37.9%, respectively Thirteen intermediate products have been reported by mass spectra analysis The degradation of ciprofloxacin followed $2^{\rm nd}$ order reaction rate with rate constant of 3.13 x $10^3~{\rm M}^1~{\rm s}^1$.
Fathi and Keshmirizadeh , 2015 [4]	Acid Red 52 dye, Basic Red 18 dye	$C_{\text{O-MR2}}$ and $C_{\text{O-BR18}} = 100 - 500 \text{ mg/L}$, $[\text{H}_2\text{O}_2] = 1 - 3.5 \text{ g/L}$, $[\text{Fe}^{2+}] = 4 - 8 \text{ mg/L}$, $\text{pH} = 3 - 9$.	- The optimum conditions were: pH 3, 8 mg/L of $\mathrm{Fe^{2^+}}$, 1.5 g/L of $\mathrm{H_2O_2}$, 25°C and 18 min reaction time. - The color and COD removal for acid red 52 dye were 99.5% and 92%, whereas for basic red 18 dye, it were 98.5% and 85%, respectively.
Ertugay and Acar, 2017 [16]	Direct Blue 71 azo dye	$C_0 = 25 - 150 \text{ mg/L},$ pH = 2.0 - 6.0, $[Fe^{2+}] = 0 - 5 \text{ mg/L},$ $[H_2O_2] = 25 - 150 \text{ mg/L},$ $T = 20^{\circ}\text{C} - 60^{\circ}\text{C}$	- At optimum conditions: pH 3.0, 3 mg/L Fe ²⁺ , 125 mg/L $\rm H_2O_2$ and 20°C, the decolorization and COD removal of direct blue 71 were 100% and 49%, respectively.

(TOC removal % and COD removal %) is also important along with decolorization/degradation studies and there is a need to study the mineralization of organic pollutants along with the degradation of organic pollutants.

The present study has been focused on mineralization of 4-NP along with its degradation using homogeneous Fenton oxidation process. Various parameters like initial pH, reaction time, concentration of hydrogen peroxide and ferrous ions that affect the degradation and mineralization (COD and TOC removal %) of 4-NP have been optimized. Further the studies have been extended to identify the degradation products of 4-NP using LC-MS spectra technique. The results of mineralization and degradation of 4-NP have also been compared with the available studies.

2. Material and Methods

2.1. Materials

4-NP (w/w, 98% purity), ferrous sulphate heptahydrate (FeSO₄.7H₂O) (w/w, purity>99%), sulphuric acid (98% purity), mercuric sulphate (purity 99%), silver sulphate (purity > 99%), were obtained from Loba Chemie Pvt. Ltd. (Mumbai, India). Hydrogen peroxide (30% w/w) was purchased from Ranbaxy Fine Chemicals Limited (Gujarat, India). Sodium hydroxide (NaOH, 97% purity), ferrous ammonium sulphate (FAS) (99% purity) was taken from s.d. fine Chemical Limited (Mumbai, India). Potassium dichromate ($K_2Cr_2O_7$, purity > 99%) was obtained from Qualigens Fine Chemicals (Mumbai, India). All the solutions were prepared using double distilled water.

2.2. Experimental Procedure

Batch experiments for mineralization and degradation of 4-NP were performed by taking 0.05 mM ferrous sulphate solution into a 250 mL Erlenmeyer glass flask containing 100 mL of 4-NP (100 mg/L) solution. The pH of the solution was adjusted by the addition of a few drops of H₂SO₄ (0.1 N) and NaOH (0.1 N) and was measured using a pH meter (pH 700 Eutech). After the pH adjustment, 1 mM H₂O₂ was added quickly to the solution with continuous stirring at 30°C. With the addition of H₂O₂ solution, the reaction started and the samples were taken out from the flask periodically and the reaction was stopped by adding two drops of 1 M NaOH. Thereafter, the solution was filtered and the filtrate was analyzed for mineralization (TOC and COD removal %) and percentage degradation. The above experiments were repeated to study the effect of various parameters such as: pH (1 - 5), reaction time (0 - 60 min), concentration of ferrous ions (0.05 - 0.5 mM) and concentration of H_2O_2 (1 – 5 mM). All the experiments were repeated three times to get reproducibility of \pm 5%.

2.3. Analytical Methods

The 4-NP degradation (%) after the reaction was analyzed using UV/VIS spectrophotometer at λ_{max} 318 nm (Shimadzu double beam spectrophotometer Model: UV-VIS 2600/2700). The degradation efficiency was calculated as:

Degradation efficiency (%) =
$$\left(1 - \frac{C_t}{C_0}\right) \times 100$$
 (1)

Where, C_0 is the initial concentration, C_t is the concentration at any time t.

The mineralization studies, chemical oxygen demand (removal %) and total organic carbon (removal %) were also analyzed after reaction. The COD of the samples before and after the reaction, was analyzed with MAC COD digester (Model: COD-439, Karnal, India) using a standard APHA method [28]. The COD efficiency of 4-NP was calculated as:

COD removal (%) =
$$\left(1 - \frac{\text{COD}_t}{\text{COD}_0}\right) \times 100$$
 (2)

Where, COD_t concentration at any time t, and COD_0 is initial concentration at time zero.

The TOC analysis of the samples was done using a TOC analyser (Model: ASI-V and TOC-V CPN, Shimadzu, Japan) before and after the degradation of 4-NP. The non-dispersive infrared method was adopted for the detection of TOC. The TOC efficiency was calculated as:

TOC removal (%) =
$$\left(1 - \frac{\text{TOC}_t}{\text{TOC}_0}\right) \times 100$$
 (3)

Where, TOC_t concentration at any time t, and TOC_0 is initial concentration at time zero.

Liquid chromatography—mass spectroscopy (LC–MS) analysis of the reacted 4-NP samples was made to identify the intermediate products over the mass range of 40–400 amu. (model: Q-TOF micro waters, Waters, USA). The reacted sample was analyzed for determination of intermediate products using negative mode electrospray ionization (ESI) technique.

3. Results and Discussion

3.1. Effect of pH

The pH value of solution influenced the generation of hydroxyl radicals and thus the oxidation efficiency of 4-NP. It is known that the Fenton's reaction is active in acidic medium. Thus, the effect of pH on the degradation of 4-NP was carried out by varying the pH in the range 1 to 5 at the initial reaction conditions of H_2O_2 concentration of 2 mM, Fe^{2+} concentration of 0.2 mM at 30°C and 40 min of reaction time. The effect of pH on oxidation of 4-NP i.e. degradation efficiency, COD removal (%) and TOC removal (%) is presented in Fig. 1.

It is observed that the degradation (%) of 4-NP increased from 28% to 84% with an increase in pH from 1 to 3 and thereafter it decreased to 65% with an increase in pH from 3 to 5. Similarly, the COD and TOC removal (%) of 4-NP has increased from 16% to 42% and 23% to 53%, respectively with increase in pH from 1 to 3 and it decreased to 32% and 40%, respectively with further increase in pH from 3 to 5. The maximum degradation of 84 % was obtained for 4-NP at pH 3. The COD removal (%) and TOC removal (%) for 4-NP, at 3 pH were 42% and 53% respectively. Therefore, the optimum pH for the degradation along with mineralization of 4-NP was 3. Below pH 3, the degradation (%) of 4-NP

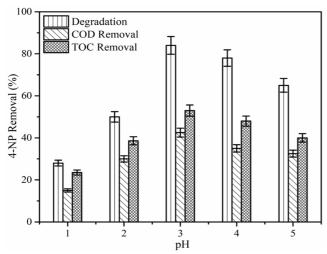


Fig. 1. Effect of pH on the degradation of 100 mg/L of 4-NP at reaction conditions: $[H_2O_2] = 2$ mM, $[Fe^{2+}] = 0.2$ mM and time = 40 min.

was low because very less 'OH radicals were produced as hydrogen peroxide was not decomposed by Fe²⁺ ions due to the stable oxygen concentration [29]. At very low pH, H⁺ ion acts as 'OH radical scavengers according to Eq. (4) [30].

$$HO^{\bullet} + H^{+} + e^{-} \rightarrow H_{2}O$$
 (4)

Inhibition of 'OH radical generation at low pH is due to the formation of complex species $[Fe(H_2O)6]^{2+}$ which reacts very slowly with hydrogen peroxide. In addition, the H_2O_2 gets solvated in the presence of high concentration of H^+ ions at low pH to form stable oxonium ion $[H_3O_2]^+$. The oxonium ion makes H_2O_2 electrophilic to enhance its stability, thus reducing the reactivity with Fe^{2+} ions [31]. At pH 4 and 5, due to the formation of ferrous and ferric oxy-hydroxides complexes, lesser amount of the 'OH radicals were generated which might have resulted in lower degradation and mineralization of 4-NP [11]. De Luis et al. [32] study has also observed maximum degradation of phenols (ortho, meta and para-cresol) at pH 3 using a homogeneous Fenton oxidation process. Meric et al. [22] achieved COD removal of 78.6% for Reactive Black 5 (RB5) dye at pH 3.

3.2. Effect of Reaction Time

The degradation of 4-NP was analyzed by varying the reaction time from 4 min to 1 h and is shown in Fig. 2. The reaction time needed for the degradation of 4-NP will depend on various parameters like pH, initial concentration of 4-NP, concentrations of ferrous ions and $\rm H_2O_2$. For the initial reaction of 100 mg/L of 4-NP, 2 mM of $\rm H_2O_2$, 0.2 mM of $\rm Fe^{2^+}$ concentration and at pH 3, it is observed that the degradation of 4-NP increased linearly up to 8 min of reaction time and then followed the non-linear increase up to 40 min. The degradation of 4-NP was increased from 35% to 84% with increase in reaction time from 4 min to 40 min and thereafter no further degradation of 4-NP has been noticed. Therefore, the optimum reaction time for the degradation of 4-NP was observed to be 40 min for further studies.

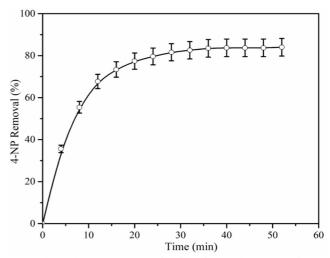


Fig. 2. Effect of reaction time on the degradation of 4-NP; Conditions: [4-NP] = 100 mg/L, $[H_2O_2] = 2 \text{ mM}$, $[Fe^{2+}] = 0.2 \text{ mM}$, pH = 3 and time 60 min.

3.3. Effect of H₂O₂ Concentration

The dosage of H_2O_2 is an important parameter as it affects the generation of OH radicals. The H_2O_2 concentration was varied from 1 mM to 5 mM to study the mineralization and degradation of 4-NP. The effect of H_2O_2 on the degradation, COD removal and TOC removal of 4-NP is shown in Fig. 3. It is observed that the degradation, COD removal and TOC removal of 4-NP increased with increase in concentration of H_2O_2 from 1 mM to 4 mM and thereafter decreased. The H_2O_2 concentration of 4 mM, degradation, COD removal (%) and TOC removal (%) of 4-NP were obtained to be 93.6, 50% and 60.3%, respectively. Increased concentration of H_2O_2 from 1 mM to 4 mM have resulted in more 'OH radicals, which might have increased the degradation and mineralization of 4-NP. Further at higher H_2O_2 dosage, i.e. 5 mM the decrease in degradation, COD removal and TOC removal of 4-NP might

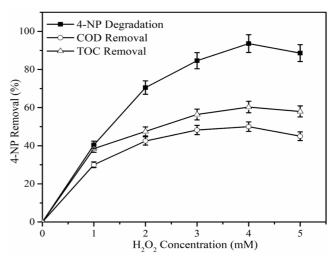


Fig. 3. Effect of H_2O_2 concentration on the degradation of 4-NP, COD removal and TOC removal; Conditions: [4-NP] = 100 mg/L, $[Fe^{2+}] = 0.2$ mM, pH = 3, time = 40 min.

be due to the scavenging of generated 'OH radicals i.e. the 'OH radicals may react with H₂O₂ to generate HO₂' radicals and which are less reactive than 'OH radicals [18, 33].

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$$
 (5)

Also the unused portion of H_2O_2 during the Fenton process contributed to COD and hence the excess amount was not recommended [34, 35].

3.4. Effect of Fe2+ lons Concentration

It is utmost important to analyze the optimum loading of Fe²⁺ ions to mineralize and degrade 4-NP, because at low Fe²⁺ ion concentrations, the degradation and mineralization of 4-NP are less due to insufficient amount of Fe²⁺ ions. But higher quantities of Fe²⁺ ions lead to an unutilized quantity of iron salt, which further contributes to increase the total dissolved solids content in the solution [36, 37]. The range of Fe²⁺ ion concentration was selected by performing initial experiments. The concentration of Fe²⁺ ions was varied from 0.05 mM to 0.5 mM and keeping the rest of the parameters constant and the results are shown in Fig. 4. It was found that the degradation and mineralization (TOC and COD removal) rate increased with an increase in the Fe²⁺ ion concentration up to 0.2 mM of aqueous solution and after that the degradation and mineralization rate decreased (Fig. 4). The maximum degradation of 4-NP (93.6%) was observed at Fe²⁺ ion concentration of 0.2 mM.

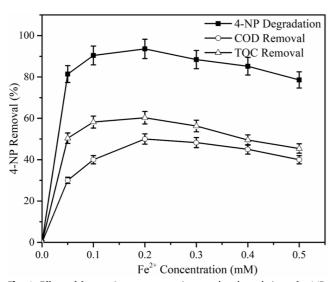


Fig. 4. Effect of ferrous ions concentration on the degradation of 4-NP, COD removal and TOC removal; Conditions: [4-NP] = 100 mg/L, $[H_2O_2] = 4$ mM, pH = 3, time 40 min.

The mineralization i.e. COD removal and TOC removal increased from 30% to 50% and 50.4% to 60.3%, respectively, with increase in $\mathrm{Fe^{2+}}$ ion concentration from 0.05 mM to 0.2 mM. The higher dosage of $\mathrm{Fe^{2+}}$ ions (>0.2mM) may result to scavenging effect with 'OH radicals present in solution as per the following reaction [22]:

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^{-}$$
 (6)

$$H_2O_2 + HO^- \rightarrow HO_2^{\bullet} + H_2O^+$$
 (7)

3.5. Reaction Mechanism Showing the Degradation Pathways of 4-NP

The 'OH radicals were generated during the reaction between Fe²⁺ ions and hydrogen peroxide. The 'OH radicals reacted with 4-NP compound and led to the formation of intermediate products. The reaction products of the degraded 4-NP were identified using LC-MS spectra at a retention time of 3.542 min (Fig. 5). 3,4-dihydroxynitrobenzene, 1,2,4 trihydroxylbenzene, 1,2-dihydroxyaminophenol, 4-aminophenol, Hydroquinone, p-benzoquinone, 3,4,5-tridydroxynitrobenzene, 1,2,6-trihydroxy-4-aminophenol and acetic acid were identified as the some of the intermediate products by the following reactions:

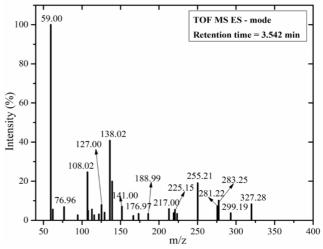


Fig. 5. LC-MS spectra analysis after degradation of 4-NP at optimized reaction conditions: 4 mM of H_2O_2 concentration, 0.2 mM of Fe^{2+} concentration, 40 min reaction time.

$$C_6H_5NO_3 + HO^{\bullet} \rightarrow C_6H_5NO_4 + H^+$$
 (8)
4-Nitrophenenol 3,4-dihydroxynitrobenzene

$$C_6H_5NO_4 + HO^{\bullet} \rightarrow C_6H_6NO_3 + NO_2$$
 (9)
1,2,4-trihydroxylbenzene

$$C_6H_5NO_3 + 2H^+ \rightarrow C_6H_7NO + O_2 + e^-$$
 (10)
4-aminophenol

$$C_6H_5NO_4 + H^+ \rightarrow C_6H_7NO_2 + e^-$$
 (11)
1,2-dihydroxyaminophenol

$$C_6H_7NO + HO^{\bullet} \rightarrow C_6H_8NO + e^{-}$$
 (12)
4-aminophenol

$$C_6H_8NO + HO^{\bullet} \rightarrow C_6H_6NO_2 + NH_3$$
 (13)
Hydroquinone

Table 2. The Various Intermediate Products Formed After The Degradation of 4-NP

Intermediate name	Chemical formula	Structure	Molecular weight
		ОН	
4-nitrobenzene-1,2-diol	$C_6H_5NO_4$		155
(3,4-dihydroxynitrobenzene)			
		NO_2	
		OH OH	
Benzene-1,2,4-triol (1,2,4 trihydroxylbenzene)	$C_6H_6O_3$		126
(1,2,4 umydroxylbenzene)		OH	
		ОН	
4-aminobenzene-1,2-diol	CHNO	OH	106
(1,2-dihydroxyaminophenol)	$C_6H_7NO_2$		126
		$^{N}H_{2}$	
		OH I	
4-aminophenol	C ₆ H ₇ NO		109
•		VIII.	
		$\dot{\sf N}\sf H_2$	
		OH 	
Hydroquinone	$C_6H_6O_2$		110
		ОН	
		О П	
		Ĭ	
p-benzoquinone	CHO		100
1,4- benzoquinone	$C_6H_4O_2$		108
		\downarrow	
		Ö	
- '']		OH OH	
5-nitrobenzene-1,2,3-triol (3,4,5-tridydroxynitrobenzene)	$C_6H_5NO_5$		171
o, i,o diayaroxyimrobonzonoj		$ ho_2$	
		ОН	
5-aminobenzene-1,2,3-triol	CHNO	ОН	4.44
(1,2,6-trihydroxy-4-aminophenol)	$C_6H_7NO_3$	4	141
	a v c	NH ₂	
Acetic acid	$C_2H_4O_2$	н₃ССООН	60
$C_0H_0O_0 \leftrightarrow C_0HNO_0 + 2H^+$	(14)	$C_0H_1O_0 + 2HO^{\bullet} \rightarrow C_0$	$C_cH_cO_c + 2H^+$ (1)

$$C_6H_6O_2 \leftrightarrow C_6HNO_2 + 2H^+$$
 (14)
1,4- benzoquinone

$$C_6H_5NO_4 + HO^{\bullet} \rightarrow C_6H_5NO_5 + H^+$$
 (15)
 (3,4,5-tridydroxynitrobenzene)

$$C_6H_5NO_5 + 2H^+ \rightarrow C_6H_7NO_3 + O_2$$
 (16)
1,2,6-trihydroxy-4-aminophenol

$$C_6H_4O_2 + 2HO^{\bullet} \rightarrow C_6H_4O_4 + 2H^+$$
 (17)

$$C_2H_4O_2 + 8HO^{\bullet} \rightarrow 2CO_2 + 2H_2O$$
 (18)
Acetic acid

Details of identified intermediate products formed after the degradation of 4-NP are given in Table 2.

3,4-dihydroxynitrobenzene, 1,2,4-trihydroxylbenzene, 3,4,5 trihydroxynitrobenzene, hydroquinone, p-benzoquinone, CO_2 and

Table 3. Comparison of Present Study for The Degradation of 4-NP with Previous Studies

Reference	Pollutant	Initial operating conditions	Degradation (%)	COD removal (%)	TOC removal (%)	DOC removal (%)	Kinetic study
Ma et al., 2000 [18]	4-Nitrophenol	$\begin{aligned} &[4\text{-NP}]_0 &= 1 \text{ mM,} \\ &[H_2O_2] &= 1 - 10 \text{ mM,} \\ &[Fe^{2^+}] &= 1 - 10 \text{ mg/L,} \\ &pH &= 3 \end{aligned}$	99	-	-	30.6	4-NP degradation profiles fit- ted well into a pseudo first- order kinetic equation.
Kavitha and Palanivelu, 2005 [20]	2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (DNP), 2,4,6- trinitrophenol (TNP)	$\begin{split} [2\text{-NP/4-NP}]_0 &= 1.43 \text{ mM}, \\ [H_2O_2] &= 17.3 \text{ mM}, \\ [Fe^{2^+}] &= 0.45 \text{ mM}, \\ [DNP] &= 1.08 \text{ mM}, \\ [TNP] &= 0.87 \text{ mM}, \\ pH &= 3 \end{split}$	-	-	-	32	Degradation of NPs obeys a pseudo-first-order kinetics. Treatment efficiency for the NPs followed the sequence: NP > DNP > TNP.
Present Study	4-NP	$\begin{split} [4\text{-NP}]_0 &= 0.72 \text{ mM}, \\ [H_2O_2] &= 1-5 \text{ mM}, \\ [Fe^{2^+}] &= 0.05-0.5 \text{ mM}, \\ pH &= 3 \end{split}$	93.6	50	60.3	-	The degradation of 4-NP followed second order kinetics.

 $\rm H_2O$ were identified as the intermediate products by Ziang et al. [38]. Daneshvar et al. [39] study has identified 3,4-dihydroxynitrobenzene, 1,2,4 trihydroxylbenzene, hydroquinone as the intermediate products using photo-oxidative degradation of 4-NP. Jiang et al. [40] carried out electrochemical degradation of 4-NP and resulted in the formation of hydroquinone, p-benzoquinone, 4-aminophenol as the intermediate products. Sun and Lemley [41], Zhao et al. [42] and Minz et al. [43] studies have reported the formation of 3,4-dihydroxynitrobenzene, 1,2,4-trihydroxylbenzene, hydroquinone, p-benzoquinone, as the intermediate products after degradation of 4-NP. Some of the residual fragments against molecular weights 76.96, 188.99, 217.0, 225.15, 255.21, 281.22, 283.25, 299.19 and 327.28 remained unidentified may be due to the complexity of their formation in the solution phase.

3.6. Kinetic Study

The kinetics of the reaction helps to study the factors which influence the rate of reaction like reactant concentration, oxidant concentration and composition of the reaction mixture [44] and provides useful information about the mechanism and rate of chemical reaction. Kinetic study for the degradation of 4-NP was done as a function of time at optimum reaction conditions, i.e. initial 4-NP concentration 100 mg/L, [H_2O_2]: 4 mM, [Fe^{2+}]: 0.2 mM and pH 3. The degradation data of 4-NP was analyzed for 1st order and 2nd order rate expressions as:

First order kinetics

$$\ln \frac{C_0}{C_t} = kt$$
(17)

Second order kinetics

$$\frac{1}{C_t} = \frac{1}{C_o} + k't \tag{18}$$

Where, C_0 is the initial concentration of 4-NP and C_t is the

concentration of 4-NP at any time t, k and k' represents the rate constants of first and second order reactions respectively.

Kinetic rate constant for the degradation of 4-NP for 1st order and 2nd order rate expression are 0.0829 min⁻¹ and 0.0037 L mg⁻¹ min⁻¹. The higher value of the regression coefficient (0.974) for 2nd order reaction as compared to 1st order reaction (0.853) shows that the degradation of 4-NP obeys 2nd order reaction rate with rate constant of 0.0037 L mg⁻¹ min⁻¹. Ghosh et al. [26] also observed second order rate for the degradation of 4-chlorophenol (4-CP) and nitrobenzene using Fenton reagent. The degradation of 2,6-dimethyl aniline using 'OH radicals also showed that the data was well fitted to second order kinetic model [45].

3.7. Comparison with Earlier Studies

A comparison of homogeneous Fenton process for the degradation of 4-NP for the present and available reported studies has been made and is shown in Table 3. Ma et al. [21] achieved 99% degradation of 4-NP using 5 mM of $\rm H_2O_2$ concentration, 5 mg/L of $\rm Fe^{2+}$ at pH 3 in 2 h. Also, the dissolved organic carbon (DOC) removal efficiency was 30.6%, i.e. only one-third of 4-NP was mineralized. Another study on the degradation of nitrophenols: 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (DNP) and 2,4,6-trinitrophenol (TNP), the maximum mineralization (DOC) for mono-nitrophenols was 32% [23]. However, in the present study, 93.6% degradation of 4-NP was achieved with 50% COD removal and 60.3% TOC removal efficiency in the short reaction period of 40 min. The mineralization efficiency achieved is higher than the previous studies.

4. Conclusions

The mineralization studies on 4-NP along with degradation have been made using homogeneous Fenton's oxidation.

The present study revealed that homogeneous Fenton's oxidation process can be used for the mineralization and degradation of 4-NP. The optimum reaction conditions for 4-NP degradation and mineralization are observed at pH 3, H₂O₂ concentration of 4 mM, Fe²⁺ concentration of 0.2 mM in 40 min of reaction time. At optimal condition, 93.6% of 4-NP were degraded within 40 min with COD removal (%) and TOC removal (%) of 50% and 60.3%, respectively. The kinetic study revealed the degradation of 4-NP by second order kinetics with rate constant of 0.0037 L mg⁻¹ min⁻¹ and correlation coefficient 0.974. The higher mineralization efficiency of 4-NP (50% COD removal and 60.3% TOC removal) has been observed in the present study as compared to the previous reported studies. Based upon the LC-MS spectra analysis 3,4-dihydroxynitrobenzene, 1,2-dihydroxyaminophenol, 1,2,6-trihydroxy-4-aminophenol, 3,4,5-trihydroxynitrobenze, 4-aminophenol, hydroquinone, p-benzoquinone, acetic acid etc. have been identified as the intermediate products. The present study indicated that the Fenton process was a feasible method to treat acidic wastewaters. This method could also be used in combination with other AOPs for better results.

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Author Contributions

S.M. (Ph.D student) conducted all the experimental work under the joint supervision of Dr. R.G. (Associate Professor) and Dr. S.G. (Associate Professor).

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