

# Detoxification and Mineralization of Nitrophenol Isomers Using Photo-assisted Processes in Batch Reactor

Arvind Kale<sup>1</sup>, M.K.N. Yenkie<sup>2</sup>

<sup>1</sup>Dharampeth M. P. Deo Memorial Science College, Nagpur

<sup>2</sup>Department of Chemical Technology, Laxminarayan Institute of Technology, Rastrasant Tukdoji Maharaj, Nagpur University, Nagpur

Author for correspondence: [arvindskale77@gmail.com](mailto:arvindskale77@gmail.com)

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**Abstract:** The kinetics of the degradation of nitro phenol isomers (2-nitrophenol, 3-nitrophenol, 4-nitrophenol) with the hydrogen peroxide photolysis, photo-Fenton and photocatalysis was investigated. The efficiency for the studied treatments were evaluated and compared. The Fenton reagent was found to be the most efficient way for the nitrophenols (NPs) degradation. The degradation of the organic compounds was determined spectrophotometrically and TOC can be identified by standard COD determination method. The degradation and detoxification of the processes have been found to adhere first order kinetics. As per refractory nature of nitrophenols the order of their mineralization was found as 4-NP>2-NP>3-NP. All the degradation processes were carried out in a batch photo reactor.

**Keywords:** AOP, Nitrophenols, UV radiation, Photo-Fenton, Photo catalysis, Hydrogen peroxide.

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## I. INTRODUCTION

The presence of nitrophenols in the environment is related both to natural processes and man-made activities. Both 2- and 4-nitrophenol are intermediates in the synthesis of azo dyes and a number of pesticides, mainly insecticides (2-nitrophenol: carbofuran, phosalon; 4-nitrophenol: parathion, parathion-methyl, fluorodifen) and herbicides (4-nitrophenol: nitrofen, bifenox). Remarkable releases of 4-nitrophenol into the water bodies may occur from the hydrolytic degradation of the insecticides parathion and although to a lesser extent from the photolytic degradation of some herbicides. Nitrophenols, particularly 2-nitrophenol and 4-nitrophenol, are also formed in the reaction of phenol with nitrite ions in water. The toxicity of 3-nitrophenol is comparatively less but it is equally refractory moiety. The reactions proceed under the influence of UV irradiation (sunlight) and in the wide range of pH values [1],[2]. Environmental reactions also lead to the formation of nitrophenols in the atmosphere. The reaction of phenol, nitrite ions and hydroxyl radical leads to the formation of 2-nitrophenol and other nitrated compounds [3]. It is considered that this phenomenon may considerably effect the presence of nitrophenols in soil environment also [4]. Its maximum allowed concentration is 20 ppb in water. Even in very low concentration it causes chronic poisoning. It takes a long time for NPs to breakdown in deep soil and in groundwater. The injurious effects of these compounds demand their priority removal from the water used for human consumption and cultivation. Nitrophenol derivatives are moderately to highly soluble in water and difficult to degrade due to their chemical stability [5]. The destruction and mineralization of it is possible by utilizing advanced oxidation processes, such as hydrogen peroxide photolysis, the Photo-Fenton and Photo-Catalysis [6]. UV-radiation alone would attack and decompose some organic molecules by bond cleavage at very slow rates. The combination of UV-light and various oxidants can decompose pollutants very effectively [7]. The decomposition of various organic pollutants using hydrogen peroxide as an oxidant under UV-illumination has been proven very effective. In all these processes formation and participation of OH radical is most important. OH radical are extremely reactive and unstable. AOP's have been defined broadly as those aqueous phase oxidation processes which are based primarily on the

intermediacy of the hydroxyl radical in the mechanism(s) resulting in the destruction of target pollutant or contaminant compound [8]. Advanced oxidation processes or photochemical oxidation processes use supplemental UV radiations with or without ozone and hydrogen peroxide to provide greater removal of toxic and refractory species. During the process of degradation it must be produced continuously “in situ” through chemical and photochemical reactions. These processes are generally,

**(1) Photolysis (UV):**

Radiation with a wavelength lower than 400nm is able to photolyse  $H_2O_2$  molecule. The mechanism accepted for the photolysis of hydrogen peroxide is the cleavage of the molecule into hydroxyl radicals with a quantum yield of two OH radicals formed per quantum of radiation absorbed [9],[10].

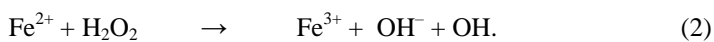


**(2) Hydrogen peroxide ( $H_2O_2$ ):  $H_2O_2 + UV$ :**

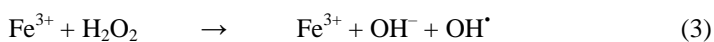
This system consists in the generation of hydroxyl radicals by means of the reaction between hydrogen peroxide and iron (II) salts [11]. The global reaction for the production of OH in acidic pH is:

**(3) Fenton system ( $H_2O_2/Fe^{2+}$ ):**

The Fenton reagent has been known for more than a century and shown to be a powerful oxidant, the mechanism of Fenton reaction is still under intense and controversial discussion. The hypothesis of 1930s, that the Fenton reaction involves formation of OH radicals has been proved by many techniques.



The rate constant for the reaction of ferrous ion with hydrogen peroxide is high and Fe (II) oxidises to Fe (III) in a few seconds to minutes in the presence of excess amounts of hydrogen peroxide. Hydrogen peroxide decomposes catalytically by Fe (III) and generates again hydroxyl radicals according to the reactions:



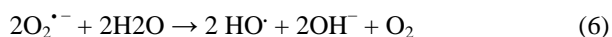
For this reason, it is believed that most waste destruction catalysed by Fenton's reagent is simply a  $Fe^{3+}-H_2O_2$  system catalysed destruction process, and Fenton's reagent with an excess of hydrogen peroxide is essentially a  $Fe^{3+}-H_2O_2$  process (known as a Fenton-like reagent). Thus, the ferrous ion in Fenton's reagent can be replaced with the ferric ion [12]. Iron salts act as a catalyst for hydrogen peroxide decomposition, further reactions regenerate iron (II). The use of  $Fe^{2+}/H_2O_2$  as an oxidant for wastewater treatment is attractive due to the facts that: (i) iron is a highly abundant and non-toxic element, and (ii) hydrogen peroxide is easy to handle and environmentally benign or friendly. Thus, the Fenton process is very effective for OH radicals' generation; however, it involves consumption of one molecule of  $Fe^{2+}$  for each OH radical produced, demanding a high concentration of  $Fe^{2+}$  [13].

**(4) Heterogeneous photo catalysis with  $TiO_2$ :**

When  $TiO_2$ , an n-type semiconductor is irradiated with light of wavelength  $\lambda \leq 390$  nm, an electron jumps from the valence band (VB) to the conduction band (CB), leaving a hole behind. The electron-hole pairs, thus generated, are capable of initiating oxidation and reduction reactions on the surface of  $TiO_2$  particles. In the presence of oxygen, these pairs migrate to the interface to yield oxidizing species. In aqueous suspension systems, holes ( $hVB^+$ ) react with surface  $OH^-$  groups and produce  $HO^\cdot$  radicals



radicals which are known to be the most oxidizing species [14], whereas electrons ( $eCB^-$ ) are trapped at surface defect sites and removed by reactions with adsorbed molecular  $O_2$  to produce superoxide anion radical, which then forms more  $HO^\cdot$  radicals[15].



The reactions of HO<sup>•</sup> radicals with the organic pollutants lead to the mineralization of the compounds.

## II. EXPERIMENTAL AND METHODOLOGY

### a) Materials:

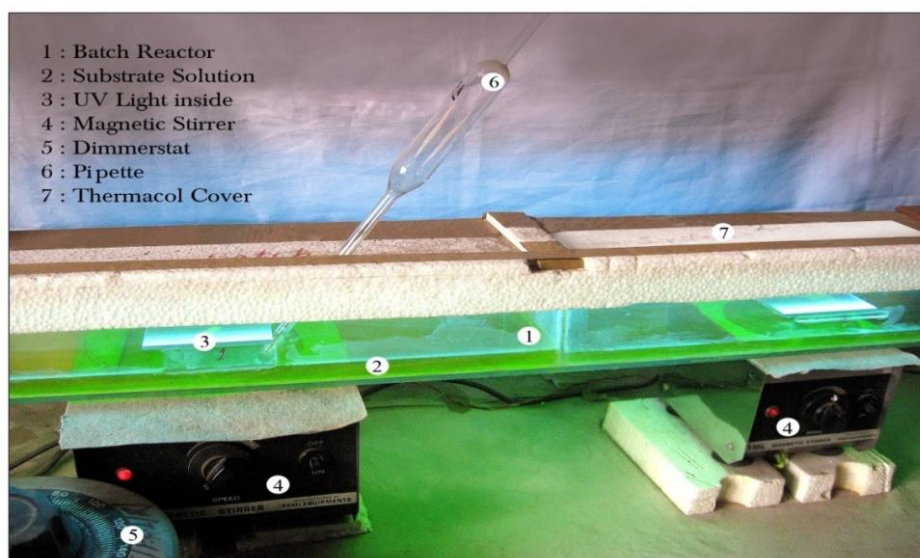
All the chemicals used in the present investigation were of highest purity grade available and were directly obtained from suppliers and were used as such without further purification. The aqueous phase solubility data of all substrates used in the studies was available in the Merck Index and are given in the *Table 1*. The stock solutions of the pollutants were prepared in freshly boiled and cooled distilled water and were stored in amber coloured bottles. 0.005 M stock solutions of 2-nitrophenol, 3-nitrophenol and 4-nitrophenol were prepared by dissolving the required amount of these compounds in freshly boiled and cooled distilled water and diluting to 1000 ml in a volumetric flask.  $3 \times 10^{-4}$  M solutions of substrates were then used as the initial reactant concentration for treatment using different AOPs as given below:

**TABLE 1: The Physico-chemical properties of the substrates studied.**

No.	Compound	Molar mass	Solubility (Mol/L at 25-30 <sup>o</sup> C)	$\lambda_{Max}$ , nm	$\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup>
1.	2-Nitrophenol	139.11	0.0143	277	5495.6
2.	3-Nitrophenol	139.11	0.0970	272	5680.3
3.	4-Nitrophenol	139.11	0.1294	318	9549.5
4.	Hydrogen peroxide	34	-	420	875.78

### b) UV Photo reactor:

In this work, an innovative batch photo reactor is used for this investigation. This reactor was designed and fabricated in the laboratory. The batch reactor (1m x 0.12m x 0.1m) was fabricated using soda-silica glass of 5 mm thickness. A 30W low pressure mercury UV lamp (Philips) was mounted lengthwise in the reactor such that the contaminant solution present in the reactor was directly irradiated by UV radiation. During the experimental runs was covered with a parabolic lid made up of inert material lined internally by using aluminum foil to avoid external exposure of harmful UV radiation and quantitative reflection of radiation in the solution of reactor. During each run, 1L of solution containing known amount of pollutant was loaded in the reactor and was exposed to UV radiations for about 240 min with constant stirring using magnetic stirrers placed below reactor. At desired intervals of time, the aliquots of solution were withdrawn from the reactor for analysis (Fig: 1)



**Fig 1: Batch reactor with 30 W UV lamp.**

**c) Method:**

All the chemicals used were AR grade. The sample for treatment was prepared in distilled water from stock solutions of 2-NP, 3-NP and 4-NP. The initial concentration of NPs in all experiment was  $3 \times 10^{-4}$  M. the pH value was adjusted by 0.01M NaOH and 0.01M H<sub>2</sub>SO<sub>4</sub>. Degradation rate of NPs in aqueous solution during Photo-oxidation, Photo-Fenton treatment and Photo-catalytic process using batch systems. Different concentrations of H<sub>2</sub>O<sub>2</sub> were utilized for optimizing the dose by using different H<sub>2</sub>O<sub>2</sub>/COD ratios. The doses of Fe<sup>2+</sup> were varied from 0.01mM – 0.05mM. In the Photo-Catalysis the TiO<sub>2</sub> doses were varied from 0.2g/L – 0.6g/L. with optimized dose of TiO<sub>2</sub>. During the system run, the concentration changes of the substrate and oxidant were monitored at desired intervals of time by withdrawing 10ml aliquot of solution from reactor. The analysis was done using UV-visible spectrophotometer. The degradation and hence the decolourisation of the substrate compound is observed. In certain cases the substrate solution turned from colorless to light brown to pale yellow, probably due to the formation of certain colored intermediates thereby interfering with the spectrophotometric analysis. The intermediates formed were short-lived as the UV scan of the reactor contents taken from time to time did not show any characteristic peaks indicative of particular compounds. In such cases the change in the concentration or a decrease in the concentration of the reacting substrate was carried out by determining the chemical oxygen demand (COD) of the samples taken out from time to time. The UV exposure time during the experiment was about 240 min. Experiments in the batch reactor were carried out at different pH, oxidant concentration doses of Fe<sup>2+</sup> and TiO<sub>2</sub> to optimize these process parameters for achieving efficient mineralization of contaminants studied.

**d) Analytical Technique:**

Spectrophotometer (GBC 911A) was used for determination of concentration of substrate. Calibration plots of NPs and H<sub>2</sub>O<sub>2</sub> were prepared for determination of molar extinction coefficient, which was used for determination of concentration of NPs, and H<sub>2</sub>O<sub>2</sub>. The values of molar extinction coefficient for NPs and H<sub>2</sub>O<sub>2</sub> were obtained as given in (Table-1). At different interval of time the aliquots were withdrawn and concentration was determined. The COD of samples was also determined by standard method to observe the extent of mineralization of NPs. To ascertain the concentration of substrate at desired interval of time, samples were withdrawn for determination of optical density as well as COD. In spectrophotometric determination decrease in the concentration of NPs is observed but presence of intermediates formed during the degradation process shows the incomplete mineralization of the sample. Therefore to observe the actual decay of the substrate, COD of the samples was determined to allocate the percentage oxidation of the sample substrate. Final comparative degradation profile is interpreted by using COD parameter.

### III. RESULTS AND DISCUSSION

The study discussion on UV photolysis, photo-peroxidation, photo-catalysis and photo-Fenton processes investigated for the mineralization and detoxification of wastewater containing nitrophenols in the batch reactor. The reasons for the selecting nitrophenols as pollutants is due to their refractory property towards decomposition. The results also describe the relative effectiveness and merits and demerits of various advanced oxidation processes studied under similar conditions. An effort has also been made to describe the kinetics of oxidative degradation of substrate and decay in oxidant concentration with time.

**Kinetics of the process:**

The decrease in the concentration of nitrophenols as a function of time for UV, UV-H<sub>2</sub>O<sub>2</sub>-Fe<sup>2+</sup>, UV-TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>, processes investigated showed a typical linear or exponential decay. The concentration decay of H<sub>2</sub>O<sub>2</sub> against time was linear and followed 1<sup>st</sup> order kinetics. The concentration decay profile gives good idea of order of reaction and in order to evaluate the same for oxidation of nitrophenols, the experimental data obtained were fitted in the following rate expression,

$$- d[C]/dt = k [C]^n \quad (1)$$

For a first order reaction the integrated form of Eqn. (1) becomes,

$$n \{ [C] / [C]_0 \} = - k_1 t \quad (2)$$

where,  $k_1$  (min<sup>-1</sup>) is the first order rate constant.

The plot of  $\ln [C_0/C]$  against time will be linear and 1<sup>st</sup> order kinetics are operative (Table-2). In the present investigation, the plots were carried out using MS-excel that provides the facility for linear and non-linear regression of the data. The

reliability of the kinetic data is understood by closeness of linear regression coefficient to 1. The possibility of adherence of rate data to 2<sup>nd</sup> order kinetics was also explored but none of the system obeyed the 2<sup>nd</sup> order kinetics. The Photo-Fenton system seems to followed 1<sup>st</sup> order kinetics for  $t_{1/2}$  of the degradation of nitrophenols, but later the rate becomes very slow and steady due to interference of intermediates; therefore the overall order of the process may be fraction which could be explored theoretically.

**TABLE 2: Order of reaction and regression coefficient for AOP.**

No.	Substrate	System Type	1 <sup>st</sup> order ( $k_1$ ) min <sup>-1</sup>	R
1.	2-Nitrophenol	Photo-Fenton	0.0086	0.9966
		Photo-catalysis with TiO <sub>2</sub>	0.0033	0.9530
2.	3-Nitrophenol	Photo-Fenton	0.0095	0.9260
		Photo-catalysis with TiO <sub>2</sub>	0.0035	0.9618
3.	4-Nitrophenol	Photo-Fenton	0.0086	0.9913
		Photo-catalysis with TiO <sub>2</sub>	0.0027	0.9578

**Optimization of pH and H<sub>2</sub>O<sub>2</sub> in Photo-oxidation:**

The aqueous solutions of nitrophenols were subjected to the process of photo-oxidation by UV + H<sub>2</sub>O<sub>2</sub> combination. The required amount of oxidant was added to the reactor contents and the same was irradiated using the 30 W UV source. The oxidant used was H<sub>2</sub>O<sub>2</sub>. Since the rate of photolysis of hydrogen peroxide forming HO· free radicals is strongly pH dependent [19], the pH of the reactor contents was maintained constant by adding calculated quantity of sulphuric acid or NaOH. As stated earlier that oxidation process being highly pH dependent, the rate of substrate degradation was determined at optimized pH 4.5. The various stoichiometric ratio used were H<sub>2</sub>O<sub>2</sub>/COD = 2.0, 2.5, 3.0, 3.5, 4.0. The rate of degradation was highly pH dependent.

In case of UV + H<sub>2</sub>O<sub>2</sub> combination, there will be competition for UV light between H<sub>2</sub>O<sub>2</sub> and substrate and, depending upon the concentrations and molar absorptivities of the two compounds at the wavelength emitted by UV lamp, a relative distribution of light will take place. Absorption of light by H<sub>2</sub>O<sub>2</sub> will lead to its decomposition, giving HO· radicals with a quantum yield of two [16]. The HO· radical then attacks the aromatic ring leading to the degradation of substrate [17].

Degradation studies of different substrates were performed by adding a definite amount of H<sub>2</sub>O<sub>2</sub> to the substrate solution at different pH. The obtained results show that more effective degradation was observed at acidic pH 4.5. Results of oxidation of nitrophenol by different photo-oxidative processes were studied by conducting the degradative experiments at various of H<sub>2</sub>O<sub>2</sub>/COD ratios equal to 2.0, 2.5, 3.0, 3.5 and 4.0. Degradation studied at stoichiometric ratio higher than 3.0, that is at H<sub>2</sub>O<sub>2</sub>/COD = 3.5 and 4.0 showed decrease in oxidative degradation efficiency and it decreased from 97% to 96%. During the initial one hour of the contact time no substantial decrease in substrate concentration was observed but as the reaction time progressed to two hours the rate of degradation increased to 62%, 64%, 72%, 68% and 73% at the H<sub>2</sub>O<sub>2</sub>/COD ratio of 2.0, 2.5, 3.0, 3.5 and 4.0 respectively. At the end of four hours the rate of degradation further increased to 92%, 96%, 97%, 96% and 96% for H<sub>2</sub>O<sub>2</sub>/COD ratio of 2.0, 2.5, 3.0, 3.5 and 4.0 respectively. It is thus obvious that at optimum oxidant to substrate ratio of 3.0, the substrate degradation was highest [Fig 2.].

In order to optimise the solution pH, experiments were carried out at pH 4.5, 7.0 and 9.5 keeping the H<sub>2</sub>O<sub>2</sub>/COD ratio constant. The photodegradation proceeded slowly and no major change in the concentration was observed in the initial one hour of reaction time which was the case with other pollutants also. Thereafter the reaction proceeded at a faster rate and maximum mineralisation of the substrate was noticed within four hours of contact time. The observed results indicate the photo-oxidation works efficiently at pH 4.5 for NPs.

**Photo-Fenton process:**

The oxidative decomposition and transformation of organic substrates by H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> has been known for nearly a century. This method has the advantage that hydrogen peroxide, used as an oxidant, is soluble in water in all proportions and fairly cheaper than other oxidants. It also has the advantage of using iron as catalyst which is the second most abundant metal and the fourth most abundant element on earth. In water it is present as ferric or ferrous ions, which form complexes with water and hydroxyl ions depending on solution pH and temperature. This technique has been suggested to be feasible and

promising to remove pollutants from natural and industrial wastewaters. On addition of Fenton's reagent to the reacting solution, a pale yellow colour developed immediately which gradually disappeared after 30 to 60 minutes of exposure. This colour development may be attributed to the formation of intermediates in the reacting solution.

**Optimization of Fe<sup>2+</sup>:**

Fe<sup>2+</sup> dose was varied from 0.01 mM/L to 0.05 mM/L at optimum H<sub>2</sub>O<sub>2</sub> dose of evaluated earlier by photo-oxidation using H<sub>2</sub>O<sub>2</sub> + UV combination. The pH of the solution was maintained between 4.5 - 4.6. The results for the optimisation of Fe<sup>2+</sup> concentration for nitrophenol solutions are presented in [Fig.3]. It has been observed that the maximum degradation has been achieved at optimized dose of Fe<sup>2+</sup> equal to 0.03mM/L, whereas over dosing of iron affects the effective degradation adversely, when optimised amount of H<sub>2</sub>O<sub>2</sub> was 11 mM/L. The kinetic profile of photo-Fenton process at optimized dose of iron and hydrogen peroxide shows the degradation of m-nitrophenol, p-nitrophenol and o-nitrophenol as 94%, 98% and 99% respectively, after 240 min. [Fig.4,5].

**Photo-Catalysis:**

Results of addition of photo-catalyst TiO<sub>2</sub> with UV/H<sub>2</sub>O<sub>2</sub> for degradation of substrates are studied. The photo degradation efficiency was observed to increase rapidly with increase in the amount of TiO<sub>2</sub> dose from 0.2 g/L to 0.4g/L and then decreases on further increase of TiO<sub>2</sub> concentration to 0.6 g/L with 11mM/L of H<sub>2</sub>O<sub>2</sub>, for the substrate concentration of 3x10<sup>-4</sup> M in 240 min. of irradiation time. During the first hour of the reaction, no appreciable decay in COD was observed but as the reaction continued an appreciable decrease in substrate COD was seen which at the end of four hours was 62%, 54% and 54% for 0.2 g/L, 0.4 g/L and 0.6 g/L dose of catalyst added respectively. Thus the maximum efficiency was found to be for 0.2 g/L of catalyst. The results of COD decay in NPs are summarised in [Fig 6, 7 and 8]. The concentration decrease of NPs using 0.2-0.3 g/L of semiconductor photo catalyst TiO<sub>2</sub> is reported in [Fig. 9] that showed optimum decay of p-nitrophenol, o-nitrophenol and m-nitrophenol as 73%, 73% and 64% respectively.

The result of degradation of nitrophenols was also observed keeping the COD parameter under study. It has been seen that the rate of COD decay was enhanced due to use of oxidant. COD of substrates used in different photo-oxidative process were determined. The consequent result clearly shows that photo-Fenton process can effectively and fast degrade the nitrophenols under study. The effective degradation after photo-Fenton is followed by UV+H<sub>2</sub>O<sub>2</sub>.

Added H<sub>2</sub>O<sub>2</sub> reacts with conduction band electrons to generate HO· radicals which are necessary for the photo degradation reactions. Being an electron acceptor, H<sub>2</sub>O<sub>2</sub> does not only generate HO· radical but it also inhibits electron-hole recombination process, which is one of the most important practical problem in using TiO<sub>2</sub> as a photocatalyst. In this study, the results of photocatalytic oxidation with TiO<sub>2</sub> seem to be poor over photo-oxidation and photo-Fenton processes.

**TABLE 3: Comparison of efficiency of degradation of NPs in batch system.**

No.	Substrate	AOPs in Batch	% Degradation
1.	2- Nitrophenol	Photo-peroxidation	97
		Photo-Fenton	99
		Photocatalysis with H <sub>2</sub> O <sub>2</sub>	73
2.	3- Nitrophenol	Photo-peroxidation	93
		Photo-Fenton	94
		Photocatalysis with H <sub>2</sub> O <sub>2</sub>	64
3.	4-Nitrophenol	Photo-peroxidation	96
		Photo-Fenton	98
		Photocatalysis with H <sub>2</sub> O <sub>2</sub>	73

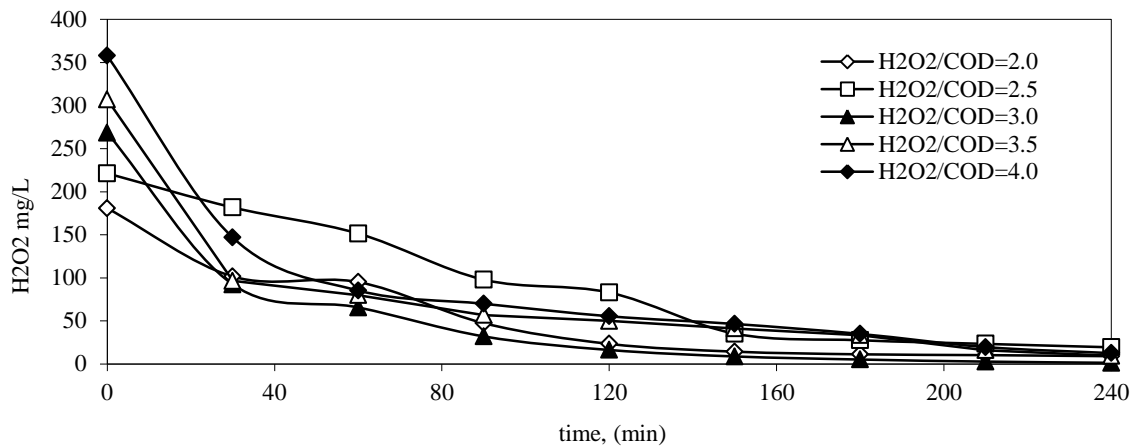


Fig 2: Retention of H<sub>2</sub>O<sub>2</sub> concentration during degradation of substrate

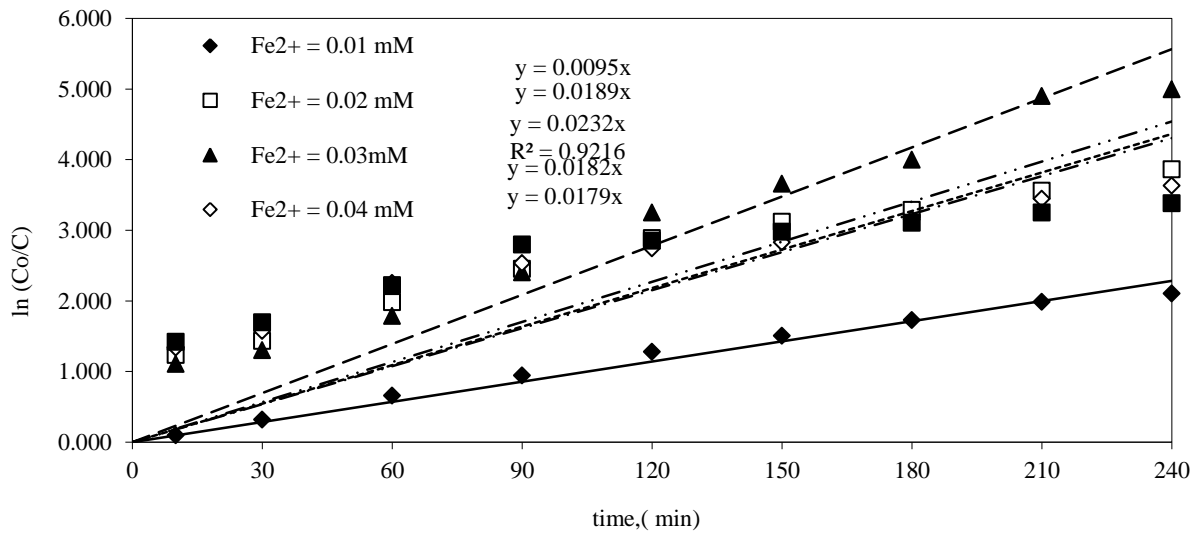


Fig 3 : Concentration decrease in nitrophenols as a function of time in Photo-Fenton

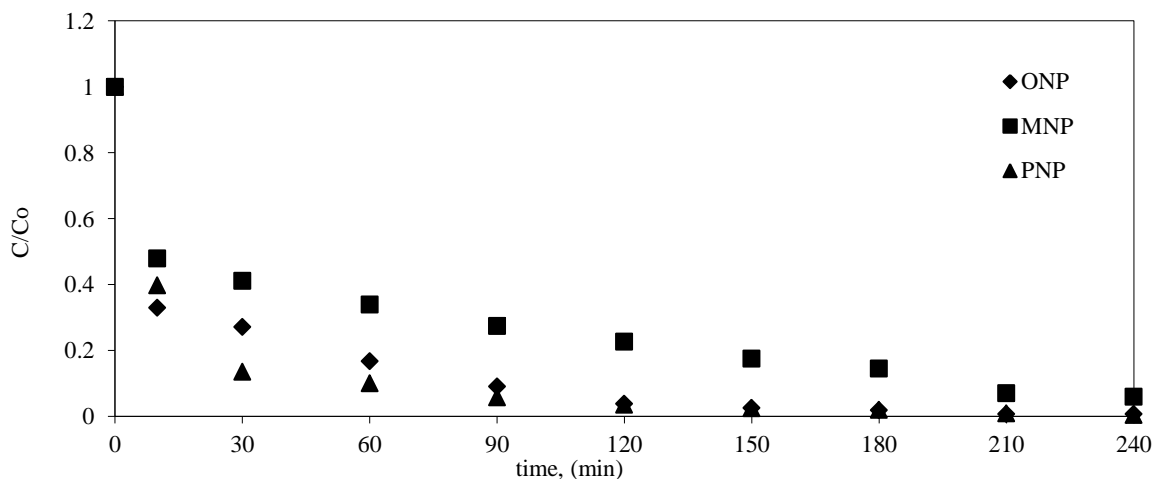


Fig 4: Comparative degradation of o, m, and p-nitrophenol in Photo-Fenton Process

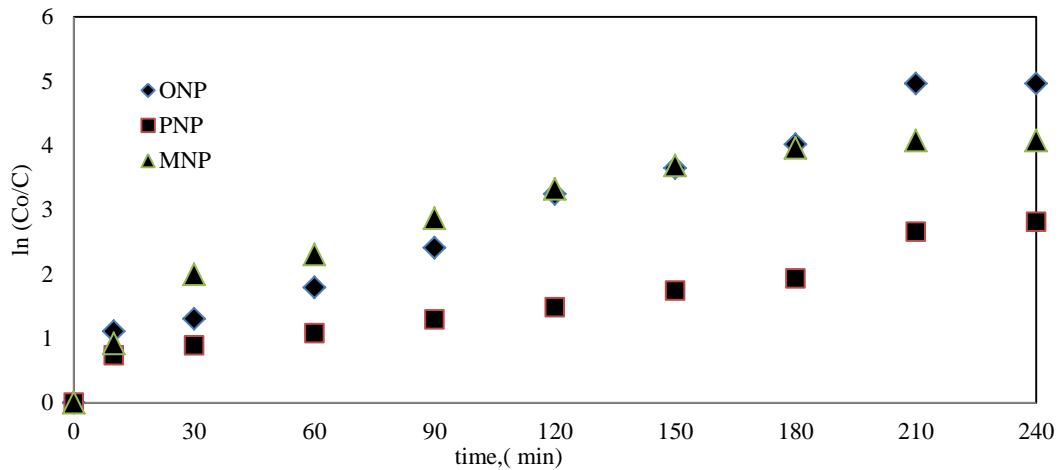


Fig:5-Comparative degradation of o, m, p-nitrophenol in Photo-Fenton process in Batch System

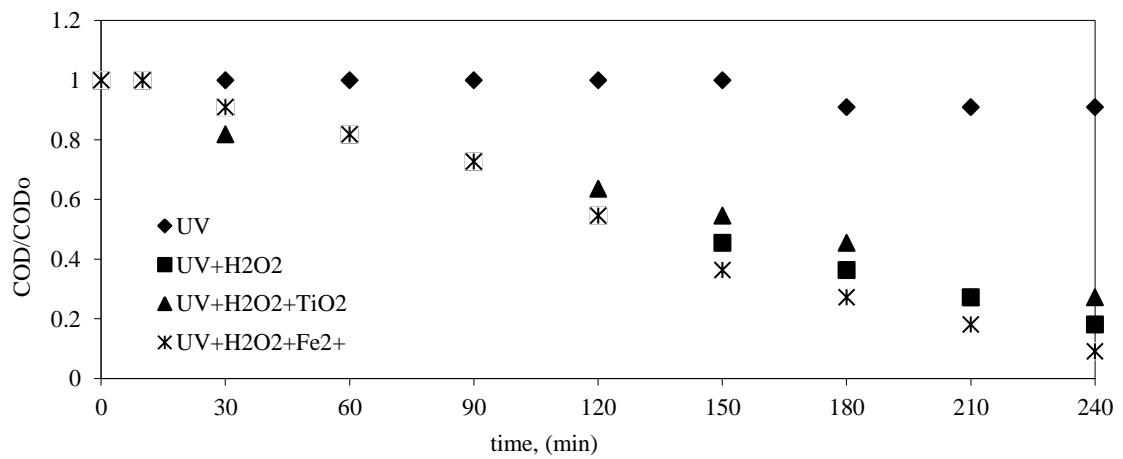


Fig 6 : COD decay profile of o-nitrophenol for various AOPs in Batch

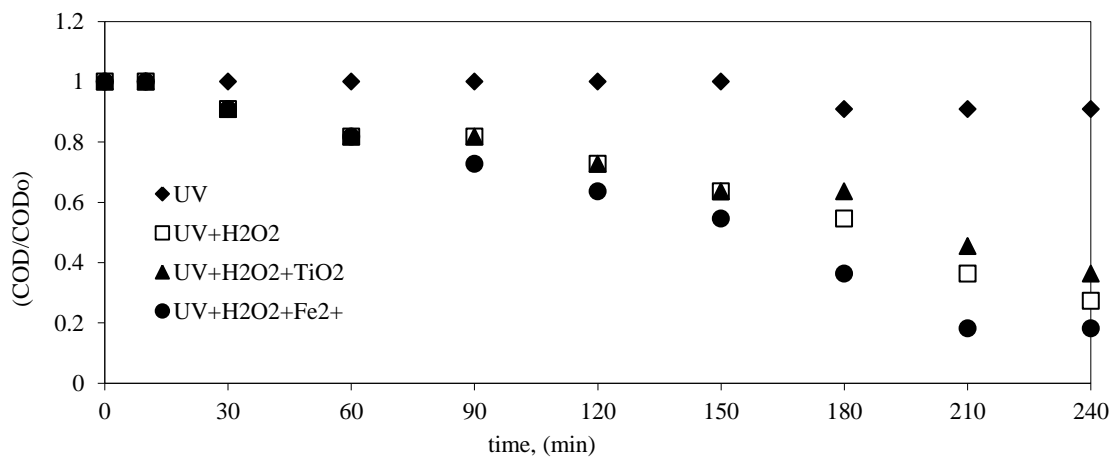


Fig 7: COD decay profile in m-nitrophenol in various AOPs in Batch



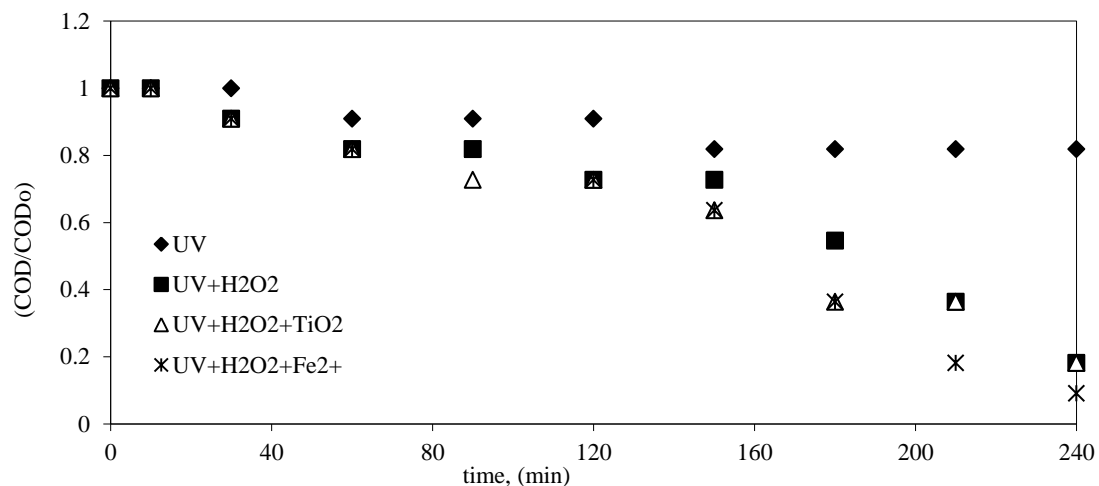


Fig 8: COD decay profile of p-nitrophenol in different AOPs in Batch

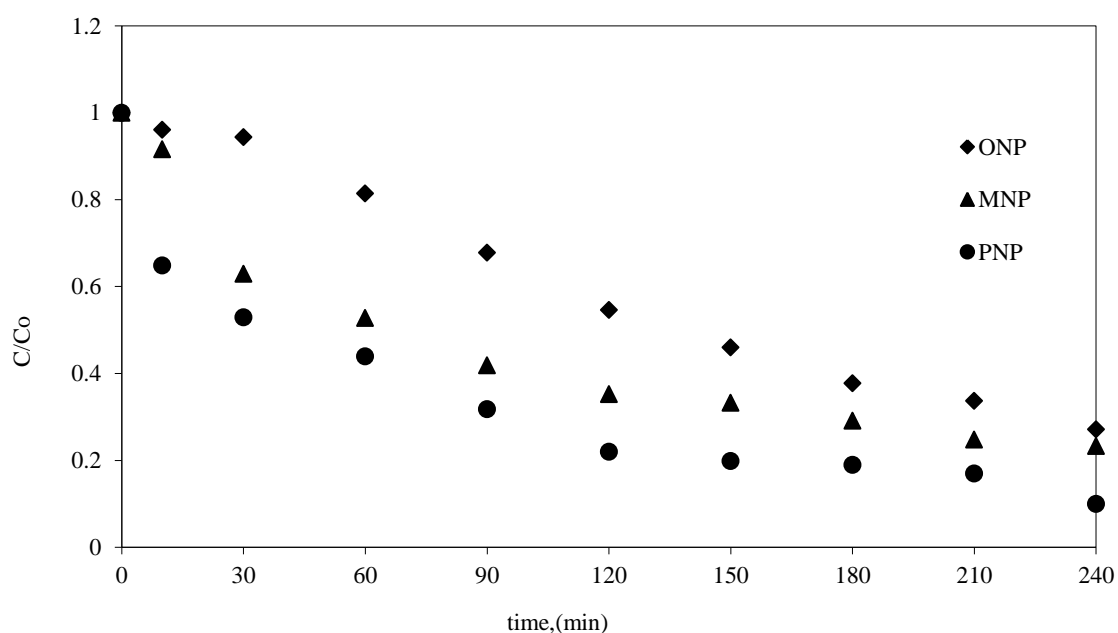


Fig 9: Comparative degradation of o, m, and p-nitrophenol in Photo-Catalysis

#### IV. CONCLUSION

In the present investigation, detoxification and mineralization of isomers nitrophenols using different advance oxidation processes was studied in a novel batch reactor. The degradation of 4-nitrophenol is found to faster and more efficient than 2-nitrophenol and 3-nitrophenol. The rate of  $\text{OH}^\cdot$  oxidation are about the same for both but seems to be lower in case of 3-nitrophenol. Among the studied AOPs the photo-Fenton process in acidic pH is more efficient than photo-peroxidation and photo-catalysis with  $\text{TiO}_2$ . The estimated degradation percentage observed in these processes using spectrophotometric determinations and COD determinations show nearly equal degradation pattern. Use of  $\text{H}_2\text{O}_2$  with UV+ $\text{TiO}_2$  increases the generation of  $\text{HO}^\cdot$  radicals responsible for the degradation of the contaminant also inhibits electron-hole recombination process, which enhances the rate and percentage of degradation of the substrate, at the same time the turbid solution thereby decreasing the reaction rate due to the retardation of light penetration, which is a prerequisite for catalysing the reaction. As per refractory nature of nitrophenols the order of their mineralization was found as 4-NP>2-NP>3-NP. All the degradation processes were carried out in a batch photo reactor.

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