

## Comparison of various advanced oxidation processes for the degradation of 4-chloro-2 nitrophenol

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### Abstract

In the present study an attempt is made efficiently to degrade USEPA listed 4-chloro-2-nitrophenol (4C-2-NP), widely available in bulk drug and pesticide wastes using various advanced oxidation processes (AOPs). A comparative assessment using various AOPs (UV, H<sub>2</sub>O<sub>2</sub>, UV/H<sub>2</sub>O<sub>2</sub>, Fenton, UV/Fenton and UV/TiO<sub>2</sub>) was attempted after initial optimization studies, viz., varying pH, peroxide concentration, iron concentration, and TiO<sub>2</sub> loading. The degradation of the study compound was estimated using chemical oxygen demand (COD) reduction and compound reduction using spectrophotometric methods and further validated with high performance liquid chromatography (HPLC). The degradation trends followed the order: UV/Fenton > UV/TiO<sub>2</sub> > UV/H<sub>2</sub>O<sub>2</sub> > Fenton > H<sub>2</sub>O<sub>2</sub> > UV. It can be inferred from the studies that UV/Fenton was the most effective in partial mineralization of 4C-2-NP. However, lower costs were obtained with H<sub>2</sub>O<sub>2</sub>. Kinetic constants were evaluated using first order equations to determine the rate constant K.

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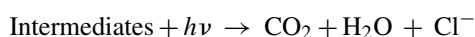
**Keywords:** 4-Chloro-2-nitrophenol; Advanced oxidation processes; Compound reduction; Comparative assessment

### 1. Introduction

Conventional wastewater treatment technologies have limitations hence demanding advanced research to tackle complex wastewater treatment. One of the promising technologies could be the use of single chemical oxidants, or the more effective destruction by the use of advanced oxidation processes (AOPs) [1]. Industrial use of phenol and its derivatives over the past decades has led to severe environmental pollution. The total waste generation comprising these hazardous substances in the southern state of Andhra Pradesh, India is estimated as 6884 t per month (TPM). Out of this around 190.3 TPM constitute phenolic wastes disposed mainly by petrochemicals, pharmaceuticals and polymer industries [2]. 4-Chloro-2-nitrophenol (4C-2-NP), which was chosen as the model compound in the present study, is recalcitrant and persistent towards biodegradation and is constituent intermediate of many industrial effluents. Well-acclimated organisms also showed ineffectiveness in treating wastewaters containing low levels of 4C-2-NP concentration due

to their low biodegradability and inhibitory nature in wastewater. The generation of 4C-2-NP containing aqueous wastes during formulation, distribution and field application of pesticides is often unavoidable. Therefore chemical oxidation methods involving advanced oxidation processes appear to be a viable alternative to destroy such compounds compared to the existing methods. Advanced oxidation process offers a highly reactive, non-specific oxidant namely hydroxyl radical (OH<sup>•</sup>), capable of destroying wide range of organic pollutants in water and wastewater [3].

- I. *UV*: Involves the interaction of light with molecules-in addition to water – to bring about their dissociation in to fragments with the following mechanistic pathway [4].



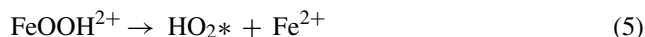
- II. *UV/H<sub>2</sub>O<sub>2</sub>*: Based on formation of OH<sup>\*</sup> radicals by means of the photolysis of hydrogen peroxide and the subsequent propagation reactions. Requires a relatively high dose of H<sub>2</sub>O<sub>2</sub>

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and/or a much longer UV exposure time.



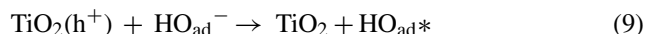
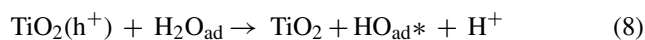
III. *Fenton process*: Production of OH radicals by Fenton reagent occurs by means of addition of  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{2+}$  salts [5]. Iron can be considered as the real catalyst. However, it cannot lead to complete mineralization of organic compounds [6].



IV. *Photo-Fenton*: An extension of Fenton process, using UV–vis light irradiation at wavelengths higher than 300 nm. The photolysis of  $\text{Fe}^{3+}$  complexes allows  $\text{Fe}^{2+}$  regeneration and the occurrence of Fenton reactions due to the presence of  $\text{H}_2\text{O}_2$  (Eq. (3)).



V. *Photo catalysis*: Employs an artificial UV light and a semiconductor-like  $\text{TiO}_2$  or  $\text{ZnO}$ . It is slow compared to other AOPs and in some cases leads to incomplete mineralization of organics [7]. Absorption of the radiation with the formation of electron-hole pairs initiates the reaction and the reducing power of formed electrons allows metal reduction with the formation of the super oxide radical ion  $\text{O}_2^{\cdot-}$  whereas remaining holes are capable of oxidizing adsorbed  $\text{H}_2\text{O}$  or  $\text{HO}^-$  to reactive HO radicals.



In order to evaluate 4C-2-NP degradation capabilities using selected AOPs, a methodical study is attempted using UV,  $\text{H}_2\text{O}_2$ , UV/ $\text{H}_2\text{O}_2$ , Fenton, UV/Fenton and UV/ $\text{TiO}_2$  and the efficacy of the treatment is presented in terms of COD removal and compound degradation using instrumental methods. Further degradation rate kinetics along with cost evaluation was performed for various AOPs studied.

## 2. Materials and methods

### 2.1. Materials

4C-2-NP purchased from Aldrich is of analytical grade.  $\text{H}_2\text{O}_2$  solution (30%, w/w) is provided by Lobacheme.  $\text{TiO}_2$  in anatase form is purchased from Sigma–Aldrich.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as the source of Fe(II),  $\text{H}_2\text{SO}_4$  and NaOH are all provided by Merck. Initial concentration of 4C-2-NP in all experiments is 100 mg/l. Solutions are treated at different pH values. The adjustment of pH is made with 0.1N/1.0N solution of  $\text{H}_2\text{SO}_4$  or 0.1N/1.0N NaOH. Glass distilled water is used for the entire study.

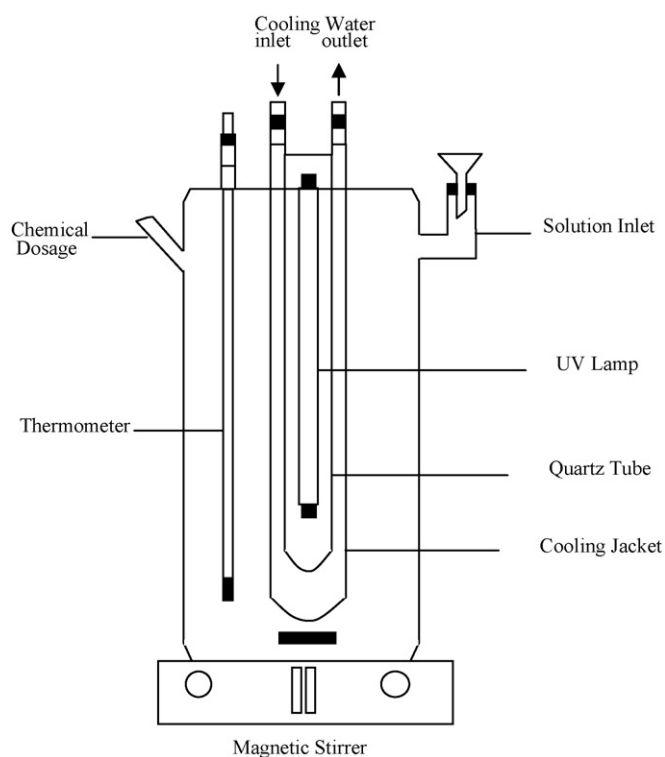


Fig. 1. Schematic diagram of the laboratory scale photochemical installation.

### 2.2. Photo reactor

All the experiments are performed in a cylindrical photo reactor with a total volume of 1.0L (diameter 12 cm and height 13.3 cm). The reactor is made of glass and covered with an aluminium sheet to prevent loss of UV light. The reactor is provided with inlets for feeding reactants, and ports for measuring temperature and withdrawing samples. The reactor is open to air with a Teflon coated magnetic stirring bar placed in the bottom for homogenization. The UV irradiation source is a 16 W low-pressure mercury vapour lamp (maximum emission at 270 nm) encased in a quartz tube. The lamp is surrounded with a water-cooling jacket to maintain a constant temperature. The lamp is axially centered and immersed in the 4C-2-NP solution. Fig. 1 shows the schematic diagram of the laboratory scale photochemical installation used in the study.

### 2.3. Experimental procedure

Different concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  in the ratio of 10:1 are used for optimization in Fenton and photo Fenton experiments [8,9]. In case of  $\text{H}_2\text{O}_2$  and UV/ $\text{H}_2\text{O}_2$ , the concentration of hydrogen peroxide to 4C-2-NP is maintained in the ratio of 1:1.  $\text{TiO}_2$  dosage is varied from 0.1 to 0.5 g in UV/ $\text{TiO}_2$  experiments. The reactions are stopped by adding 10% aqueous solution of  $\text{Na}_2\text{SO}_3$ . Samples are withdrawn at regular intervals during the experiment and analyzed for compound reduction and COD removal. COD is measured for each sample in accordance with standard methods. In order to decompose residual  $\text{H}_2\text{O}_2$ , which interferes with the COD

and absorbance measurements, the samples containing  $H_2O_2$  are treated with  $MnO_2$  powder [10]. Before each analysis, samples are centrifuged and filtered on  $0.25\ \mu m$  Millipore membranes to remove  $MnO_2$ . The total treatment time of the experiment is selected so that at least 90% degradation of initial compound is achieved.

#### 2.4. Analytical methods

Reduction in 4C-2-NP concentration is measured by Systronics-1272 UV-Vis Spectrophotometer (wavelength 234 nm) and further confirmed by reverse phase high performance liquid chromatography. Agilent Technologies HPLC apparatus using Chemsoft software consists of photodiode array detector. The reverse phase column used is C18. Mobile phase is a mixture of methanol and water (80:20) isocratically delivered by a pump at a flow rate of 1 ml/min. The wavelength of the UV absorbance detector is 254 nm with a retention time of 30 min.

### 3. Results and discussions

The trends in degradation capacities of 4C-2-NP using various oxidation methodologies is presented by showing the effect of pH, initial  $H_2O_2$  concentration in case of Fenton/photo Fenton and  $H_2O_2/UV-H_2O_2$ , initial  $Fe^{2+}$  concentration in case of Fenton and photo Fenton, and effect of catalyst loading in case of  $UV/TiO_2$ .

#### 3.1. Effect of pH

The effect of pH on the degradation of 4C-2-NP by different AOPs is presented in Fig. 2. In the comparison of Fenton/UV Fenton mediated degradation of 4C-2-NP, it is observed that the maximum degradation efficiency is found at a pH of 3.0

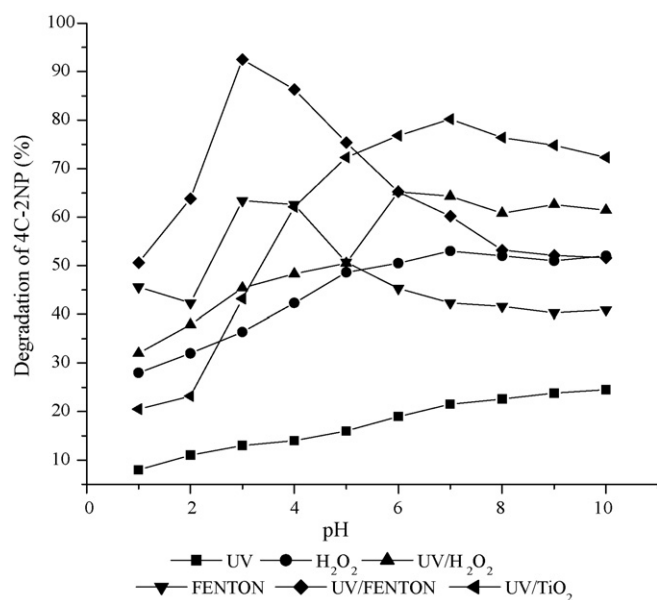


Fig. 2. Effect of pH.

and continued with similar trends till pH 4.0. The degradation dropped to 50% above pH 4.0 and thereafter no considerable change in degradation is observed. However, the degradation efficiency reached as high as 95% in the later case substantiating the fact that UV light enhanced the efficiency of Fenton reaction. This may be attributed to the precipitation of iron at this pH as  $Fe(OH)_3$  there by lowering its ability to catalyze  $H_2O_2$  [11] and also reduces the transmission of the radiation [12]. In case of  $H_2O_2$  and  $UV/H_2O_2$ , maximum degradation of 4C-2-NP is achieved at neutral pH of 7.0 and remained more or less constant when more alkaline conditions are used. A maximum degradation of nearly 80% is obtained with  $UV/TiO_2$  at a neutral pH of 7.0.

#### 3.2. Influence of initial hydrogen peroxide concentration

The effect of initial hydrogen peroxide concentration on the removal of 4C-2-NP is shown in Fig. 3. Experiments are conducted by varying  $H_2O_2$  from 100 to 700 mg/l. When the concentration of  $H_2O_2$  is increased from 100 to 400 mg/l the degradation efficiency increased from 36 to 54% in case of  $H_2O_2$  alone, but the combination of  $UV/H_2O_2$  improved the degradation from 39 to 75% when the concentration of  $H_2O_2$  increased from 100 to 200 mg/l, which may be due to the production of additional  $OH^\bullet$  radicals emanated from UV enhanced  $H_2O_2$ . Maximum degradation of 88% is achieved at an optimum of 100 mg/l of  $H_2O_2$  with  $UV/Fenton$  and 70% with Fenton at an optimum of 200 mg/l. Addition of  $H_2O_2$  exceeding 200 mg/l did not improve the degradation efficiency. This may be attributed to auto decomposition of  $H_2O_2$  to oxygen and water, and the recombination of  $OH^\bullet$  radicals. Moreover, higher concentrations of hydrogen peroxide act as free-radical scavenger itself, thereby decreasing the concentration of hydroxyl radicals and reducing compound elimination efficiency [13]. Therefore,  $H_2O_2$  should be added at an optimum concentration to achieve the best degra-

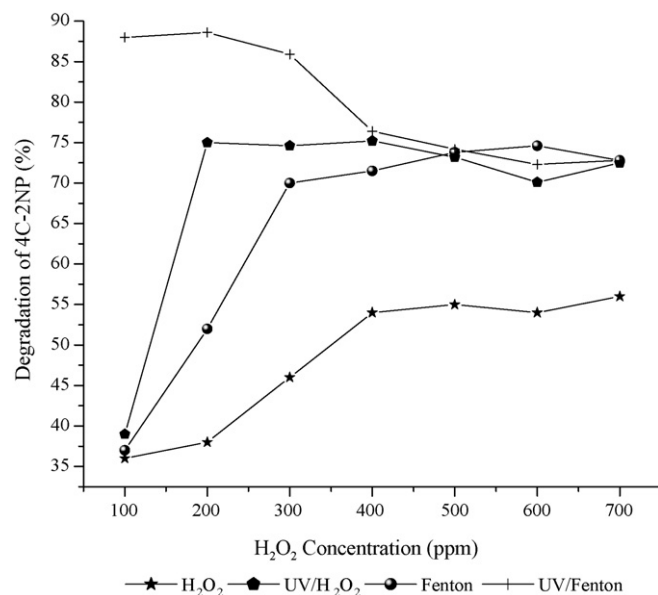


Fig. 3. Influence of  $H_2O_2$  concentration.

dition. However not all the added  $\text{H}_2\text{O}_2$  was consumed. When 250 mg/l is used, at least 60 mg/l of  $\text{H}_2\text{O}_2$  remained in the reactor at the end of the reaction. This could be due to the absorption spectrum of  $\text{H}_2\text{O}_2$ . Photolysis of  $\text{H}_2\text{O}_2$  requires  $<360$  nm. It has a favorable absorption spectrum around 250 nm, which leads to the efficient  $\text{H}_2\text{O}_2$  photolysis generating more  $\text{OH}^\bullet$  radicals [14,15]. The low residual concentration of  $\text{H}_2\text{O}_2$  is essential advantage of photo Fenton over the Fenton and especially with  $\text{H}_2\text{O}_2$  alone, where the residual concentration of  $\text{H}_2\text{O}_2$  was much higher.

### 3.3. Effect of Fe(II) concentration

To ascertain the effect of ferrous ion in oxidizing 4C-2-NP, a series of experiments are conducted by varying Fe(II) concentration from 10 to 60 mg/l and presented in Fig. 4. The degradation rate of 4C-2-NP increased with increasing amounts of iron salt. A maximum of 90% degradation of 4C-2-NP was achieved with 30 mg/l of initial concentration of  $\text{Fe}^{2+}$  in UV/Fenton whereas 68.2% with 50 mg/l of  $\text{Fe}^{2+}$  in Fenton process. Addition of iron salt above 50 mg/l did not affect the degradation, even when the concentration was doubled. This is due to the fact that, at a Fe(II) concentration higher than the optimum, the initial formation rate of hydroxyl radicals originated mainly from the decomposition of  $\text{H}_2\text{O}_2$  was so high that much of hydroxyl radicals were consumed by the side reactions before they could be utilized effectively for the removal of the compound [16]. Moreover, it resulted in brown turbidity that hindered the absorption of the UV light required for photolysis and caused the recombination of OH radicals [17]. After the Fenton and photo Fenton treatments, the residual iron was removed by alkalinization of the solution [18]. The residual concentration of total iron after alkalinization and subsequent filtration remained only 0.3–0.2% of the initial value, when the 90% degradation of 4C-2-NP was achieved.

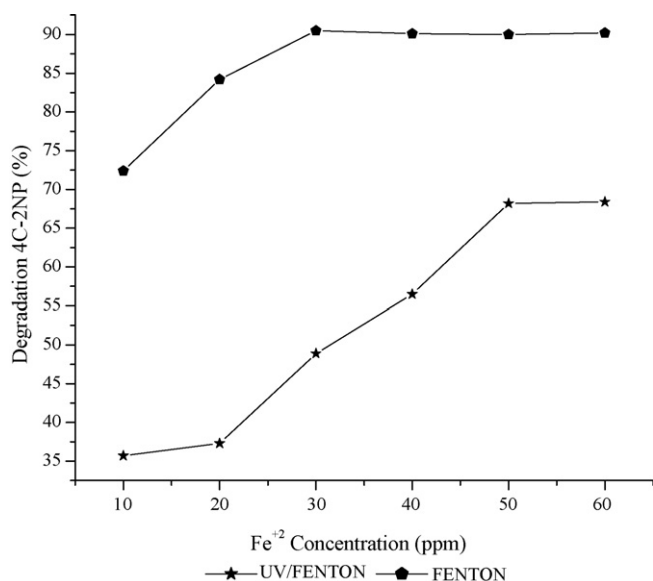


Fig. 4. Effect of Fe(II) concentration.

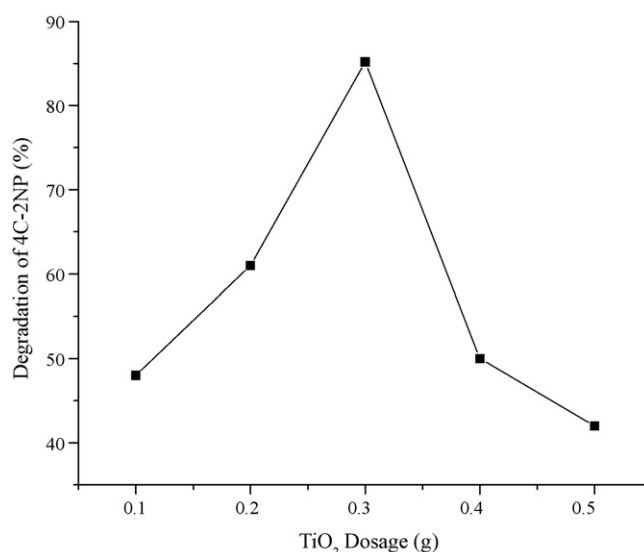


Fig. 5. Effect of catalyst ( $\text{TiO}_2$ ) loading.

### 3.4. Effect of catalyst loading

Suspensions at  $\text{pH } 7.0 \pm 0.2$  and 100 mg/l 4C-2-NP concentration are used to study the effect of catalyst loading by varying the amount of  $\text{TiO}_2$  from 0.1 g to 0.5 g/L. The curve in Fig. 5 shows the degradation of 4C-2-NP with the catalyst. Initial reduction of the compound may be due to the adsorption of compound on to the  $\text{TiO}_2$  particles but after the adsorption–desorption equilibrium is established, the actual degradation of the compound is seen. As the concentration of  $\text{TiO}_2$  increased, the rate of degradation increased up to a certain point, and then decreased slowly. Maximum degradation occurred at a  $\text{TiO}_2$  concentration of 0.3 g. Addition of excess of  $\text{TiO}_2$  above this dosage did not significantly enhance the degradation. This is due to the aggregation of  $\text{TiO}_2$  particles, which reduced the interfacial area between the reaction solution and the photo catalyst. The increase in opacity and light scattering by the particles may be the other reasons for the decrease in the degradation rate [19].

### 3.5. Comparison of various AOPs studied

A comparison of UV,  $\text{H}_2\text{O}_2$ , UV/ $\text{H}_2\text{O}_2$ , Fenton, UV/Fenton and UV/ $\text{TiO}_2$  processes in terms of COD removal and CNP degradation is illustrated in Fig. 6 and Table 1.

Table 1  
Pseudo-first-order rate constants

S. no.	Oxidants	$K$ ( $\text{min}^{-1}$ )	$r^2$
1	UV/Fenton	$1.46 \times 10^{-3}$	0.99
2	UV/ $\text{TiO}_2$	$0.8 \times 10^{-3}$	0.98
3	UV/ $\text{H}_2\text{O}_2$	$0.72 \times 10^{-3}$	0.97
4	Fenton	$0.47 \times 10^{-3}$	0.96
5	$\text{H}_2\text{O}_2$	$0.34 \times 10^{-3}$	0.91
6	UV	$0.32 \times 10^{-3}$	0.91

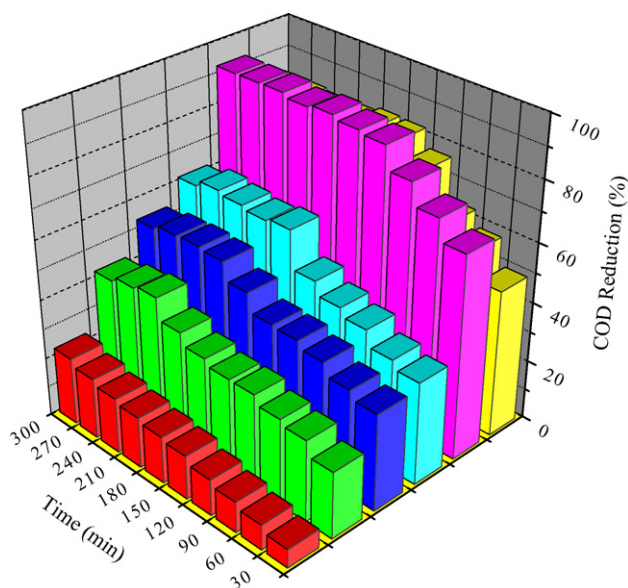


Fig. 6. Reduction in COD using various oxidants.

### 3.5.1. Mineralization of 4C-2-NP

Total mineralization of the compound should be considered since the intermediate products of some compounds can sometimes be more toxic than the original compound itself. Therefore, reduction of COD is also monitored along with 4C-2-NP concentration. Percentage reduction of COD with different AOPs is shown in Fig. 6. Neither UV nor  $\text{H}_2\text{O}_2$  alone could totally remove COD. But UV in combination with  $\text{H}_2\text{O}_2$  showed considerable reduction in COD (50%). However, in the presence of  $\text{TiO}_2$  as catalyst, UV enhanced the reduction of COD (80%) compared to  $\text{H}_2\text{O}_2$  as catalyst. The COD reduction with photo Fenton process is found to be more efficient (90%) compared to Fenton where 65% reduction is seen. This can be explained by the complete oxidation of all  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  enhanced by UV [20].

Mineralization achieved by UV process is very little because the compound undergoes photochemical reaction as a consequence of light absorption and rarely these transformations contribute to compound removal. In this sense, the light absorbed by the compound can be generally considered as wasted light [21]. Removal of 4C-2-NP by  $\text{H}_2\text{O}_2$  and UV/ $\text{H}_2\text{O}_2$  is also very slow and incomplete. The major drawback of UV/ $\text{H}_2\text{O}_2$  is due to the small molar extinction coefficient of  $\text{H}_2\text{O}_2$ , which is only  $18.6 \text{ M}^{-1} \text{ cm}^{-1}$  at 254 nm; only a relative small fraction of incident light is therefore exploited for 4C-2-NP removal [22]. Fenton process is able to destroy 4C-2-NP effectively but rather have difficulty in mineralizing the compound completely. In photo Fenton and UV/ $\text{TiO}_2$  process, 92.7% and 85.2% mineralization of 4C-2-NP is observed within 120 min of the reaction time.

### 3.5.2. Degradation rate

From the experimental results kinetic constants are derived by fitting the experimental data using Pseudo first order kinetics. Since reaction mechanisms are complex for the photo catalytic

Table 2  
Cost of the reagents

S. no.	Reagent	Basis	Cost (\$)
1	$\text{H}_2\text{O}_2$	kg	0.74
2	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	kg	14.2
3	$\text{TiO}_2$	kg	0.98
4	Electricity	kWh	0.0765

degradation of organic compounds, a rigorous kinetic study cannot be performed. However, when the experimental data is plotted it looked like a first order reaction with respect to 4C-2NP degradation. Therefore, an approach to this kinetic study is performed by assuming that the photodecomposition reaction followed first order kinetics. This approach is in coincidence with similar studies by several authors [23,24].

In order to evaluate these rate constants, the terms  $\ln C_t/C_0$  versus reaction time are plotted, and after linear regression analysis, the first order rate constants are determined.

$$\ln \frac{C_t}{C_0} = -k_0^* t$$

where  $C_0$  and  $C_t$  are the concentration of 4C-2-NP at times 0 and  $t$ ,  $k_0^*$  is a pseudo-first-order rate constant and  $t$  is the time in minutes. The results confirm the significant accelerating effect of photo Fenton and UV/ $\text{TiO}_2$  reactions on 4C-2-NP degradation in comparison with other AOPs studied (Table 1). Almost all the processes followed the pseudo first order kinetics except  $\text{H}_2\text{O}_2$  and UV, which showed a slight deviation from linearity ( $r^2 = 0.91$ ). The degradation rate of 4C-2-NP followed the order:

$$\text{UV/Fenton} > \text{UV/TiO}_2 > \text{UV/H}_2\text{O}_2 \\ > \text{Fenton} > \text{H}_2\text{O}_2 > \text{UV}$$

### 3.6. Cost estimation

Cost evaluation is one of the important aspects in the treatment of waste. The overall costs are represented by the sum of the capital costs, the operating costs and maintenance. For a full-scale system these costs strongly depend on the nature and the concentrations of the pollutants, the flow rate of the effluent and the configuration of the reactor [25]. An estimation of costs has been made in this section (Tables 2 and 3) regarding the operating costs for the treatment processes used for the degradation of 4C-2NP. Cost evaluation for UV processes was based on electrical energy per order (EE/O) [10] using the following

Table 3  
Operating costs of the treatment methods

S. no.	Process	Treatment cost (\$/kg)
1	UV	250.5
2	$\text{H}_2\text{O}_2$	5.8
3	UV/ $\text{H}_2\text{O}_2$	58.6
4	Fenton	7.4
5	UV/Fenton	28.7
6	UV/ $\text{TiO}_2$	78.5

formula:

$$EE/O \text{ (kWh/m}^3\text{)} = \frac{Pt \times 1000}{V \times 60 \log(C_{\text{ini}}/C_{\text{fin}})}$$

where  $P$  is rated power (kW),  $V$  is the volume (in liters) of water treated,  $t$  is the time (min),  $C_{\text{ini}}$  and  $C_{\text{fin}}$  are the initial and final concentrations of the compound to be treated. Among all the treatment processes studied, operating costs of photo catalysis and UV are considerably more expensive than others. However, costs can be decreased considerably for photo catalytic treatments when solar light is used [26].

#### 4. Conclusions

- The results of this study showed that the degradation of 4C-2-NP was strongly accelerated by the photochemical oxidation processes.
- Neither UV nor  $\text{H}_2\text{O}_2$  alone could degrade 4C-2-NP. The combination of UV to the system i.e., UV/ $\text{H}_2\text{O}_2$  process enhanced 4C-2-NP degradation rate but still required relatively long reaction periods with poor minimization efficiency.
- The optimum conditions obtained for the best degradation with Photo Fenton were pH 3, initial reactant concentration of 30 mg/l  $\text{Fe}^{2+}$  and 100 mg/l  $\text{H}_2\text{O}_2$  for an initial 4C-2-NP of 100 mg/l.
- The degradation rate can be accelerated using high-pressure mercury vapour lamps instead of medium pressure lamps.
- The advantages of the photo-Fenton process as an oxidative pre-treatment step over other photochemical treatment processes are easy handling of the method, because no specific technical equipment is necessary, low investment, less energy demand, and harmless process products.
- This study has proven that UV/Fenton can be a successful pretreatment before biological remediation.

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