Comparison Of Different Advanced Oxidation Processes For 2-Nitrophenol (2-NP) Degradation In Aqueous Solution

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Abstract

Advanced oxidation processes (likes H_2O_2/UV, Fe^{2+}/ H_2O_2/ UV, Fe^{3+}/ H_2O_2/UV, TiO_2/ H_2O_2/UV) for the degradation of 2-nitrophenol (2-NP) in aqueous solution have been studied and compared, a comparison of these techniques have been done on the basis of pH influence, kinetic constant, stoichiometric coefficient and optimum oxidant/pollutant ratio. The study of effect of temperature ($20-40$ ^{0}C) was investigated at the previously obtained optimum conditions of above stated processes and the activations energy were determined and compared for each process at their optimum condition. Out of these tested processes Fe^{3+}/H_2O_2/UV system proved to be the most efficient and occurs at a much high oxidation rate that help to reduced 100% COD by the dosing of 1.7 mmoll^{-1} of H_2O_2 and 9.3 X 10^{-3} mmoll^{-1}of Fe^{3+} and within 75 minutes of the reaction time whole process get completed.

Key words: 2-Nitrophenol; UV radiation; Photo-Fenton; Photocatalysis; Chemical oxygen demand.
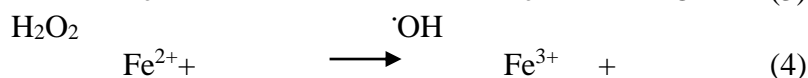
1. Introduction

The certain aromatic or phenolic compounds in wastewaters exhibit biotoxicity and recalcitrance to conventional biological oxidation process and consequently prove to be difficult to treat. In particular, 2-NP and its derivatives result from the production processes of pesticides, herbicides [1] and synthetic dyes [2].

These pollutants have high toxicity and carcinogenic characters. They have caused considerably damage to the ecosystem and largely threatening to human health. They are notified as potential toxic compounds by United States Environmental Protection Agency (USEPA) and their maximum allowable concentrations in water ranges from 1 to 20 ppb [2]. The conventional approach in industrial wastewater treatment is by chemical-physical processes: adsorption, stripping, chemical oxidation. All these processes can guarantee high removal efficiencies, but the first two have the main disadvantage that they do not provide a real degradation of the compounds but only their transfer from a diluted to a concentrated stream to be disposed on the other hand, chemical oxidation could produce intermediated characterized by a toxicity level similar to the original substance [3]. Therefore, the development of an effective degradation process for 2-NP has been investigated by numerous researchers. For example, Advanced oxidation processes (AOPs) have been proven particularly effective for the treatment of a wide variety of wastewater containing refractory organic contaminants. These methods includes among others, the use of UV, O_3, H_2O_2, Fe^{2+}, TiO_2 and their combinations [4-9], Photocatalysis [10-12], Sonolysis [13-16] and Supercritical oxidation [17-19]. These methods employ chemical, photochemical, sonochemical or radiolytic techniques to bring about chemical degradation of pollutants.

The common feature of these techniques is the generation of free hydroxyl radicals ($^.OH$), which are very reactive since they have a high oxidation potential. The oxidation potential of the hydrogen peroxide has been reported to be 1.9 V [20] while the oxidation potential for hydroxyl radicals is approximately 2.8 V, which is capable of mineralizing organic and inorganic contaminants present in drinking water and wastewaters. Reaction of hydroxyl radicals generated in the presence of an organic substrate may occur via one of the three general pathway: (1) hydrogen abstraction; (2) electrophilic addition; (3) electron transfer [21]. The homogenous advanced oxidation process employing hydrogen peroxide with UV light has been found to be very effective in the degradation of organic compound [22-24]. The formation of $^.OH$ radicals

by means of the photolysis of hydrogen peroxide and the subsequent propagation reaction requires a relatively high dose of H_2O_2 and/or much longer UV exposure time.

$$H_2O_2 + h\upsilon \longrightarrow 2\ ^{\cdot}OH \qquad\qquad (1)$$
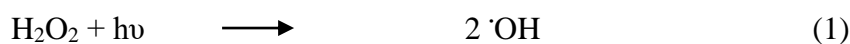
It is now common to use Fe^{2+} and H_2O_2 to generate hydroxyl radicals [25, 26] for oxidizing organics:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad (2)$$
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \qquad (3)$$
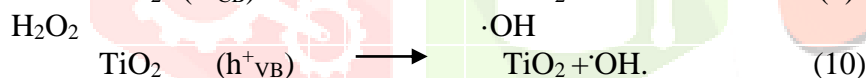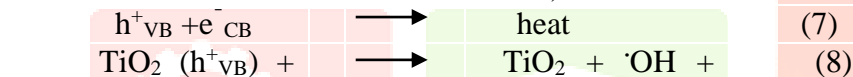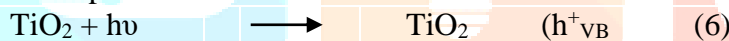$$Fe^{2+} + {}^{\cdot}OH \longrightarrow Fe^{3+} + OH^- \qquad (4)$$

However, Fenton process is not effective at pH values higher than 4.0 because Fe^{2+} easily form Fe^{3+} form which has tendency to produce ferric hydroxocomplexes. Moreover, H_2O_2 is unstable and decomposing in basic (pH >9.0) solutions [27].

Recently, it was shown that a treatment process using Fe^{3+} and H_2O_2 with the aid of UV radiation (Photo-Fenton like process) is an effective alternative for the degradation of organic pollutants present in the soil or ground water [28,29]. It facilitates the photolysis of aquated Fe^{3+} ions to give *OH and regenerate Fe^{2+} for Fenton's reaction
(Eq. (2))

$$Fe\,(OH)^{2+} + h\upsilon \longrightarrow Fe^{2+} + {}^{\cdot}OH \qquad (5)$$

However, this reaction is pH and wavelength dependent [28,30] at which the quantum yield of *OH and ferrous ion formation decreased at longer wavelengths. Hydroxyl radicals can also be generated with a solid semiconductor TiO_2 or ZnO that absorbed radiation (according to its band-gap) when in contact with water and generates pairs of valance-band holes and conduction-band electrons.

$$TiO_2 + h\upsilon \longrightarrow TiO_2\ (h^+{}_{VB} + e^-{}_{CB}) \qquad (6)$$
$$h^+{}_{VB} + e^-{}_{CB} \longrightarrow heat \qquad (7)$$
$$TiO_2\ (h^+{}_{VB}) + H_2O \longrightarrow TiO_2 + {}^{\cdot}OH + H^+ \qquad (8)$$
$$TiO_2\ (e^-{}_{CB}) + H_2O_2 \longrightarrow TiO_2 + {}^{\cdot}OH + {}^{\cdot}OH \qquad (9)$$
$$TiO_2\ (h^+{}_{VB}) + OH^- \longrightarrow TiO_2 + {}^{\cdot}OH. \qquad (10)$$

Electron/hole pairs ($e^-{}_{CB} + h^+{}_{VB}$) are generated by the absorption of photons with energy greater than necessary to move an electron from the valance band to the conduction band of the semiconductor. When electron / hole pairs are generated, the electron move away from the surface to the bulk of the semiconductor as the hole migrates towards the surface. If the solvent is oxidoreductively active (water) it also act as a donor and acceptor of electrons. Thus, on a hydrated and hydroxylated semiconductor surface, the holes produce $^{\cdot}OH$ radicals whenever different semiconductor have been tested under comparable conditions for the degradation of the same compounds, TiO_2 has generally been demonstrated to be the most active.

Many studies were published on the degradation of organic pollutants, in particular phenols and nitrophenols, in water. In this study 2-NP was chosen as a model compound. It is one of the 114 organic pollutants listed in EPA. In this work, homogenous and heterogeneous photoxidative degradation of 2-NP, with particular emphasis on the operational parameters, decrease of the pollutant concentration, stoichiometric coefficient and optimum oxidant/pollutant ratio have been studied.

2. Methodologies

2.1 Materials
All chemicals were used as it's received, from the various vendors, in which 2-NP, $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.2H_2O$ were purchased from Merck. All stock solutions were prepared in deionized distilled water, and 2,4-D was prepared at 0.3mM and directly used for reaction study $FeSO_4.7H_2O$ and hydrated $Fe_2(SO_4)_3$ were freshly made in diluted sulphuric acid both 0.01mM Hydrogen peroxide (30% w/w) was purchased

from Merck, Titanium dioxide (Degussa P25) was utilized as a photocatalyst. Its main physical data are as follows: average primary particle size around 30 nm and purity ~97% with 80:20 anatase to rutile. Sodium hydroxide and Hydrochloric acid were used for pH adjustment. All these chemicals were analytical grade.

2.2 *Installation*

All experiments were carried out in a 1.0 liter jacketed thermostatic photo reactor (diameter 81 mm and height 320 mm,) equipped with low pressure mercury lamp (8 W, UV-C, manufacture by Philips, Holland) it was placed in the center of photoreactor. The reactor is equipped with a magnetic stirrer used a Teflon coated magnetic needle for homonisation of test samples at the constant rate of 600 rpm achieved by using dimmerstat. All the photo oxidation reactions were performed at atmospheric pressure. The temperature was maintained at 30± 0.2 °C by circulating water from a cryostat bath (Fourtech systems, Mumbai, India).

2.3. *Experimental procedure*

All the experiments were carried out in batch mode. In each experiment a 2-NP solution of 41.73 mgl^{-1} (0.3 mM/L) was prepared with double distilled water by using stock solution of 2087 mgl^{-1} (0.015 M). The solutions were perfectly mixed to guarantee that all 2-NP was dissolved, and the required concentrations of iron salt $FeSO_4.7H_2O$ ($Fe_2(SO_4)_3$ in case Fe(III)) were added when necessary. The required pH of solution was adjusted initially by using dilute 0.01 N HCl or NaOH whenever its required. Every time the photo-reactor was charged with 800ml solution. A 30% aqueous hydrogen peroxide solution was injected into the reactor at different concentrations and the UV-light was switched on at the same time. During the experiments, samples were withdrawn from the reactor at several time intervals, filter through 0.45 µm membrane filter and directly used for further analysis without quenched of the reaction.

2.4 *Analytical methods*

The change in 2-NP concentration was measured with UV-visible spectrophotometer (Spectrascan UV 2600, Chemito,India) at 276.5 nm, the quartz cuvette of 1 cm of pathlength was used while recording the spectra. A calibration plot based on Beer-Lambert's law was established by relating the absorbance to the concentration. COD measurements were conducted in accordance with the titrimetric open reflux method [31]. Total organic carbon (TOC) was measured by direct injection of the filtered sample into a Shimazu 5000A, TOC analyzer.

3. Results and discussion

3.1 *Decrease in the pollutant concentration in the various AOPs processes*

Different variables (likes pH, oxidant concentration and catalyst dosages) were studied in order to find the optimum conditions for each process, in accordance with the percentage of degraded 2-NP (Table 1). These results are summarized in Fig.1.

For comparison, the best experimental conditions were selected. It can be observed that in the photo-Fenton process the best results were obtained at acidic pH value less than 4.0. As regards the $Fe^{3+}/H_2O_2/UV$, at pH 3.0 and at 1.7 mmoll^{-1} of H_2O_2 with 9.3 X 10^{-3} mmoll^{-1} of Fe^{3+} concentrations, this combination gave excellent result as shown in table 1. Judging from table 1, it is interesting to note that $Fe^{3+}/H_2O_2/UV$ showed higher improvements in terms of decay rate and overall removal than UV/H_2O_2, in an aqueous solution, Fe^{3+} undergoes spontaneous hydrolysis with water to form $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_2^{4+}$ and $Fe(OH)_3^0$ in absence of other chelating ligands [32]. At our investigated pH level of 3.0, the predominant species is the monohydroxy complex, $FeOH^{2+}$, which is the most photo-sensitive species of the four, and such a complex is capable of producing hydroxyl radicals directly [33] through photosensitization reaction (see Eq.(4))

In addition, the generation of Fe^{2+} in eqn.(4) indirectly induced the Fenton's reaction, which gave more hydroxyl radicals. This assumption can be father justified by Fig.1, where the $Fe^{3+}/H_2O_2/UV$ process is initially slower than $Fe^{2+}/H_2O_2/UV$. However, the former will overrule the latter afterwards because it takes time for the $Fe^{3+}/H_2O_2/UV$ to generate Fe2+ as indicated in Eq.(4). The $Fe^{3+}/H_2O_2/UV$ process gave a faster rate and a better overall removal of 2-NP (i.e. 100%) then did the $Fe^{2+}/H_2O_2/UV$ process. This is likely due to the abundant $[Fe^{3+}]$ in the solution, which induced photo-sensitization and, accordingly the generation of ˙OH radicals.

In the H_2O_2/UV process, the best result were found in acidic condition at pH 3.0 and the optimum H2O2 dose was 1.4 mmoll^{-1} for the oxidation process, UV light play very vital role in H_2O_2/UV process, the yield of ˚OH radicals increases as seen (Eq.(1)) but when pH was increase quantum yield diminished because of secondary reactions. While in $TiO_2/H_2O_2/UV$ process the degradation rate increase with the catalyst concentration up to a value of 0.3 g/L at pH 7.0 and further addition of TiO_2 showed adverse effect

this is due to the aggregation of TiO$_2$ particles, which reduced the interfacial area between the reaction solution and the photocatalyst. The rate of degradation with TiO$_2$/UV largely induced by presence of small amount of H$_2$O$_2$ (1.3 mmoll^{-1}) Eq.(8).

TOC decrease was measured for some processes. In the experiment RP4, a 36.61 % of TOC depletion was achieved after 120 min of treatment; 92.13 % of TOC decrease in FP3 and 96.47 % in FP13 after 75 min and 42.26 % in 120 min in the experiment RT8.

Table. 1 Experimental condition for 2-NP degradation

Exp. no.	Process	pH	C_{H2O2} (mM/L)	C_{Fe2+} (mM/L)	C_{Fe3+} (mM/L)	C_{TiO2} (g L^{-1})	Time of treatment (min)	% Removal of 2-NP
RP1	UV/H$_2$O$_2$	free(6.7)	1.2	0	0	0	120	69
RP2	UV/H$_2$O$_2$	free(6.7)	1.4	0	0	0	120	82.1
RP3	UV/H$_2$O$_2$	free(6.7)	1.6	0	0	0	120	73.11
RP4	UV/H$_2$O$_2$	init.(3.0)	1.4	0	0	0	120	84.62
RP5	UV/H$_2$O$_2$	init.(5.0)	1.4	0	0	0	120	76.93
RP6	UV/H$_2$O$_2$	init.(7.0)	1.4	0	0	0	120	68.69
RP7	UV/H$_2$O$_2$	init.(9.2)	1.4	0	0	0	120	42.69
FP1	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0.0027	0	0	75	97.37
FP2	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0.0067	0	0	75	98.62
FP3	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0.0093	0	0	75	99.31
FP4	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0.012	0	0	75	98.87
FP5	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.0)	1.0	0.0093	0	0	75	98.19
FP6	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.0)	1.4	0.0093	0	0	75	98.94
FP7	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.0)	2.0	0.0093	0	0	75	99.06
FP8	Fe^{2+}/ H$_2$O$_2$/UV	init.(2.5)	1.7	0.0093	0	0	75	98.37
FP9	Fe^{2+}/ H$_2$O$_2$/UV	init.(3.5)	1.7	0.0093	0	0	75	98.31
FP10	Fe^{2+}/ H$_2$O$_2$/UV	init.(4.0)	1.7	0.0093	0	0	75	97.06
FP11	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0	0.0027	0	75	98.06
FP12	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0	0.0067	0	75	98.44
FP13	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0	0.0093	0	75	100
FP14	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.0)	1.7	0	0.012	0	75	98.62
FP15	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.0)	1.0	0	0.0093	0	75	97.87
FP16	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.0)	1.4	0	0.0093	0	75	98.25
FP17	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.0)	2.0	0	0.0093	0	75	99.18
FP18	Fe^{3+}/ H$_2$O$_2$/UV	init.(2.5)	1.7	0	0.0093	0	75	98.93
FP19	Fe^{3+}/ H$_2$O$_2$/UV	init.(3.5)	1.7	0	0.0093	0	75	99.31
FP20	Fe^{3+}/ H$_2$O$_2$/UV	init.(4.0)	1.7	0	0.0093	0	75	98.12
RT1	TiO$_2$/ H$_2$O$_2$/UV	free(6.7)	1.4	0	0	0.1	120	67.87
RT2	TiO$_2$/ H$_2$O$_2$/UV	free(6.7)	1.4	0	0	0.2	120	82.31
RT3	TiO$_2$/ H$_2$O$_2$/UV	free(6.7)	1.4	0	0	0.3	120	93.44
RT4	TiO$_2$/ H$_2$O$_2$/UV	free(6.7)	1.4	0	0	0.4	120	80.3
RT5	TiO$_2$/ H$_2$O$_2$/UV	free(6.7)	1.4	0	0	0.5	120	73.17
RT6	TiO$_2$/ H$_2$O$_2$/UV	init.(3.0)	1.4	0	0	0.3	120	65.68
RT7	TiO$_2$/ H$_2$O$_2$/UV	init.(5.0)	1.4	0	0	0.3	120	83.69
RT8	TiO$_2$/ H$_2$O$_2$/UV	init.(7.0)	1.4	0	0	0.3	120	95.56
RT9	TiO$_2$/ H$_2$O$_2$/UV	init.(9.2)	1.4	0	0	0.3	120	62.18

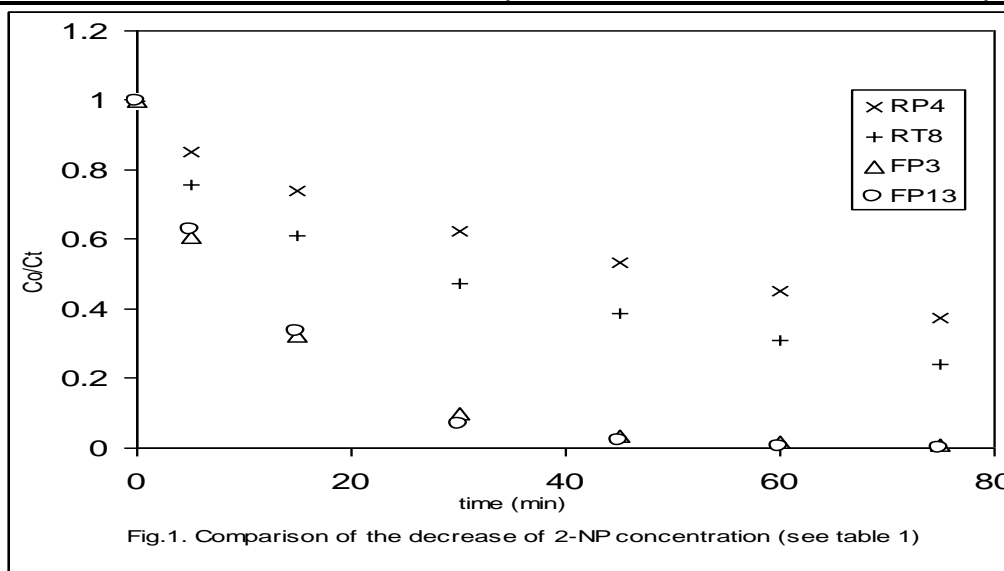Fig.1. Comparison of the decrease of 2-NP concentration (see table 1)

Fig. 1   Comparision of the decrease of 2-NP concentration

Fig.2. Neperian logarithm of the relative concentration vs. time.

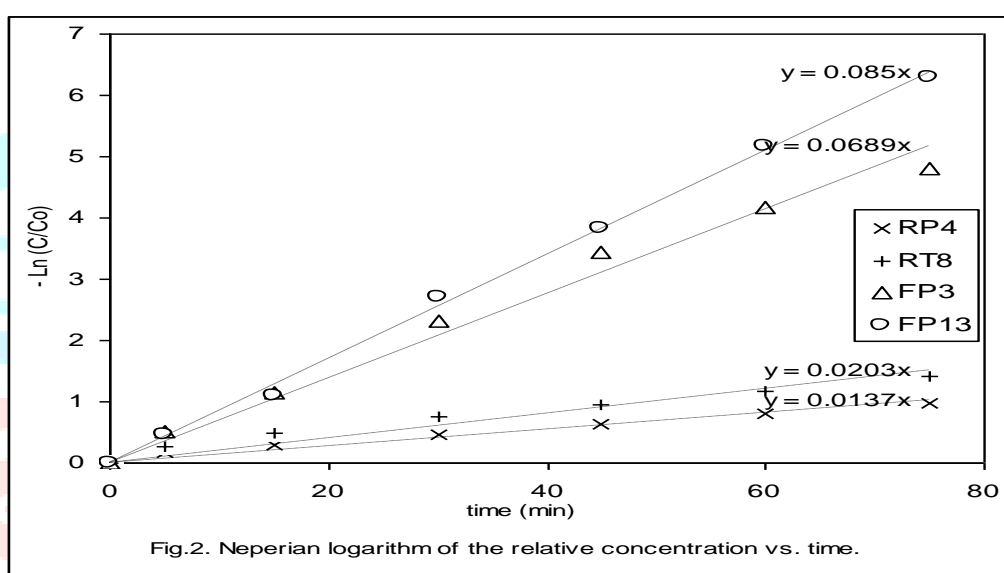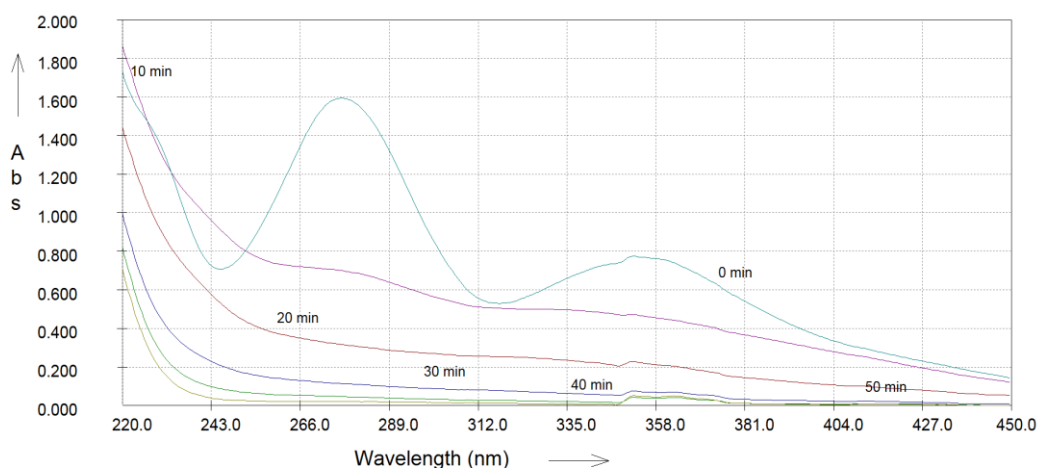**Fig. 2   Neperian logarithm of the relative concentration vs time**

Fig. 3   UV-Visible absorption spectra of 2-nitrophenol subjected to $Fe^{3+}/H_2O_2/UV$ process.

Condition: Exp. (pH 3, 1.7 mM/L of H_2O_2, 9.3 X 10-3 mM/L of Fe^{III}, 800ml; 0.3 mM of 2-NP, 50 min, Temp- 30ºC)

Fig.3 shows the representative UV- Visible spectra of 2-NP degraded during AOPs. The two peaks at 276.5 nm and 349.5 nm are observed on the UV-Visible spectra of the freshly prepared 2-NP. These peaks gradually diminished along with the proceeding of the $Fe^{3+}/H_2O_2/UV$ process. These spectra results indicate

the degradation of the 2-NP and the formation of intermediates. At 20 min, the character peaks (276.5, 349.5) of 2-NP disappears and its absorption elsewhere also decreases. So all 2-NP have been oxidized at this time and the formed intermediates are being further oxidized to CO_2 and H_2O. The possible intermediates which are formed during the process are shown in scheme1.

3.2 Comparison of first order kinetic constant

Parameters chosen for comparison are the kinetic constants and $t_{1/2}$, which are global parameters that include all the phenomena involved in the studied processes. This means that these parameters include kinetic and radiation influences, and also reactor design effects, on the global reaction rate. Thus, this allows the overall comparison between the different AOPs tested. The value of the first order kinetic constant was obtained by fitting the experimental data shown in Fig.1 to a straight line (see Fig.2). These results are summarized in Table 2. In this table is also presented the value of half-life, that is, the time required to decrease the concentration of the reactant to half the amount present before the reaction. As the values of $t_{3/4}$ are equal to $t_{1/2}$ x 2 in most of the cases, is possible to say that reactions obey a first order rate constants, in the experimental conditions tested.

Table. 2 Pseudo-first order kinetic and half-time for the different processes

Process	k (min^{-1})	$t_{1/2}$ (min)	$t_{3/4}$ (min)
UV/H_2O_2	0.0137	50.58	100.73
$Fe^{2+}/H_2O_2/UV$	0.0689	10.06	20.03
$Fe^{3+}/H_2O_2/UV$	0.085	8.15	16.23
$TiO_2/H_2O_2/UV$	0.0203	34.14	67.98

As can be observed, the process exhibiting the highest k is $Fe^{3+}/H_2O_2/UV$, 6.20 times higher than the UV/H_2O_2 and 4.19 times higher than $TiO_2/H_2O_2/UV$ process.

3.3 influence of the amount of oxidant on the kinetic constant

In this section the effect of pH, the amount of hydrogen peroxide and the catalysts (Fe^{2+}, Fe^{3+} and TiO_2) on the kinetic constant (k) is presented. In Fig.4 k vs. the various pH and TiO_2 is presented, and in Fig.5 and Fig.6 shows k vs. H_2O_2 and Fe^{2+} and k vs.H_2O_2 and Fe^{3+} respectively.
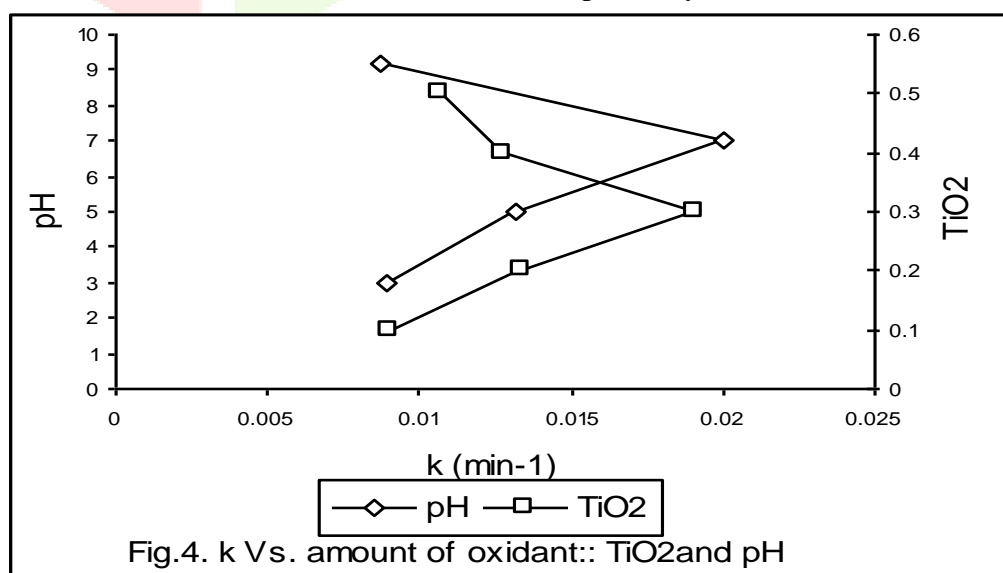

Fig.4. k Vs. amount of oxidant:: TiO2and pH

Fig.4 K vs. amount of oxidant: TiO2 and P^H

Fig.5. k Vs. amount of oxidant: H2O2 and Fe3+ (Fe3+ = 0.0093 mM/L)
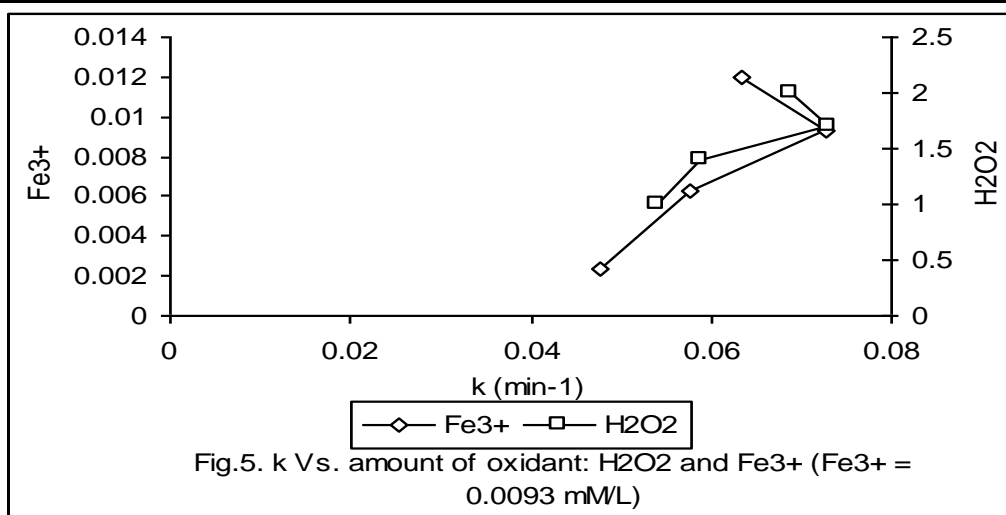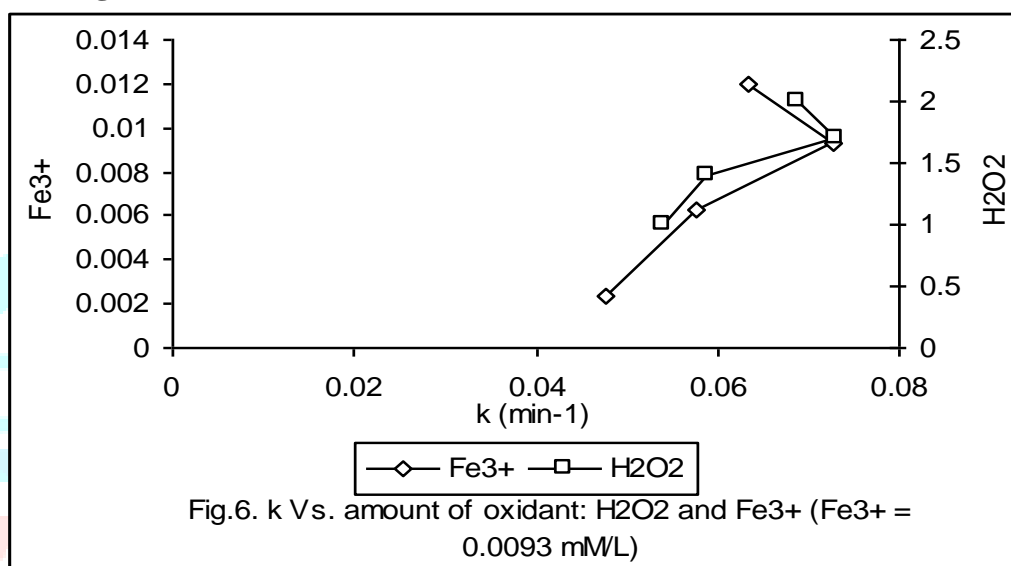
Fig.5 K vs. amount of oxidant: H2O2 and Fe^{2+} (Fe^{2+}=0.0093mM/L)

Fig.6. k Vs. amount of oxidant: H2O2 and Fe3+ (Fe3+ = 0.0093 mM/L)

Fig.6 K vs. amount of oxidant: H2O2 and Fe^{3+} (Fe^{3+}=0.0093mM/L)

3.4 Activation energy

In order to understand how much energy required to obtaining the maximum degradation of the contaminants the activation energy was calculated by the following Arrhenius equation [34].

$$\ln k = \ln A - (E_a/RT)$$

where Ea (KJ/mol) is the Arrhenius activation energy of degradation; k is the first order rate constant; A is the Arrhenius factor; R(J/molK) is the gas constant and equal to 8.314 J/molK and T(K) is the operated temperature.

The observed small value of Ea clearly indicates that all the below reported processes occurs through photocatalyticaly and these are more efficient for degradation of all the types of recalcitrant pollutants.

Table. 3 Activation energy of various AOPs Processe

Process	Ea(KJ/mol)	lnA	R^2
UV/H_2O_2	10.62	0.0083	0.9875
$Fe^{2+}/ H_2O_2/UV$	20.03	5.3054	0.9047
$Fe^{3+}/ H_2O_2/UV$	22.32	6.2345	0.9314
$TiO_2/ H_2O_2/UV$	15.47	2.4232	0.9994

3.5 Reaction mechanism

The reaction of hydroxyl radicals with aromatic groups occurred via electrophilic addition reaction shown at scheme 1. The intermediate were cathecoal, 1,2,4 benzene triol and 1,2,4,6 benzene tetrol because of unusual behaviors of hydroxyl radical that it continuously added to benzene ring till all the position are occupied by .OH. Further reaction of the primary intermediates with hydroxyl radicals lead to ring opening and formation of oxygenated aliphatic compounds like muconic acid, malic acid, glyoxylic acid, oxalic acid, acetic acid etc., [35,36]. and eventual producing mineralization products it can also be understand by observing of vanishing of peaks in Fig. 3.

Scheme.1 degradation mechanism of 2-NP
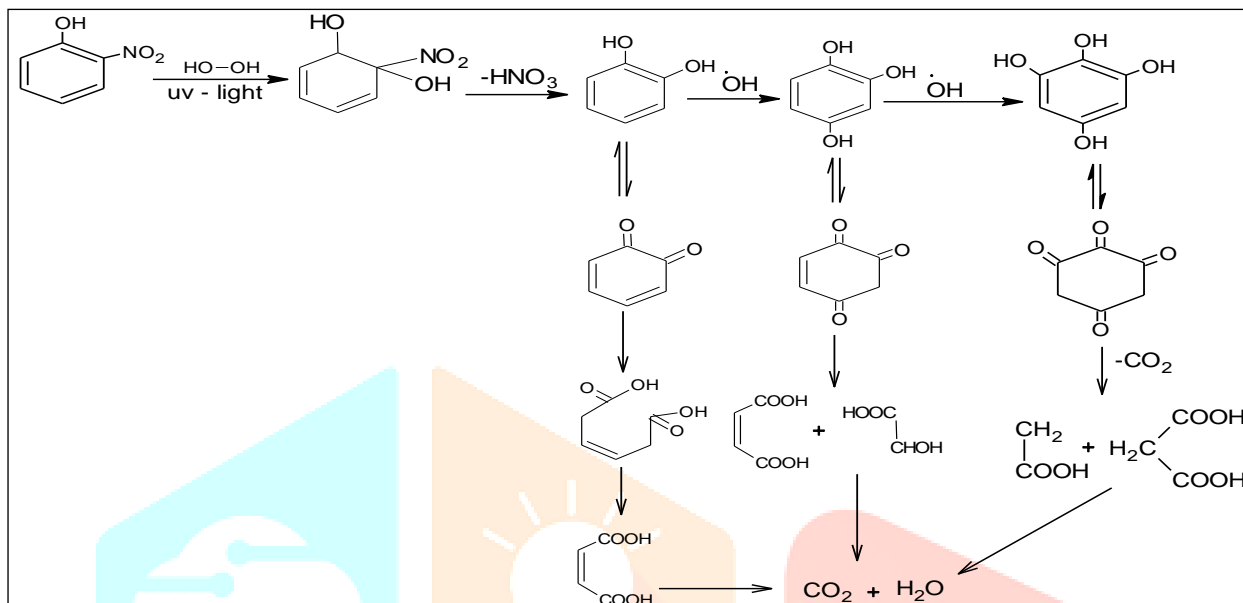
4. Conclusions

Different AOPs (H_2O_2/UV, Fe^{2+}/ H_2O_2/ UV, Fe^{3+}/ H_2O_2/UV, TiO_2/ H_2O_2/UV) have been studied and compared for the degradation of 2-NP in aqueous solution. It has been found that the degradation of 2-NP was strongly accelerated by the photochemical oxidation processes. The H_2O_2/UV and TiO_2/ H_2O_2/UV process enhanced 2-NP degradation rate but still required relatively long reaction periods with poor COD and TOC minimization efficiency.

The optimum conditions obtained for the best degradation with Fe^{3+}/ H_2O_2/UV process were pH 3, initial reactant concentration of 9.23 X 10^{-3} mM/L Fe^{3+} and 1.7 mM/L H_2O_2 for an initial 2-NP of 0.3 mM/L and the result was obtained to the loss 100 % COD and 96.47 % TOC after 75 min of reaction.

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