Degradation of Nitro-aromatic Compounds using Fenton's Oxidation

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Abstract: This paper reports on a comparative study of the degradation of para nitrophenol (PNP) and nitrobenzene (NB) of concentration of 100 ppm, 200 ppm and 500 ppm using conventional Fenton's reagent (Hydrogen Peroxide and ferrous sulphate salt). Keeping an eye on the effluent concentration of several industries, these concentrations and their controlling parameters of the reaction such as effect of pH, effect of Fe(II) to H_2O_2 molar ratio and H_2O_2:COD ratio has been proposed. For lower concentration (100 ppm) , the COD removal was found to be 81.94% and 93.22% for PNP and 83.75% and 88.6% for NB with H_2O_2:COD ratio 1:1 and 2:1 respectively and for higher concentration (500 ppm), the COD removal efficiency was found to be 80.78% and 85.69% for PNP and 84.17% and 86.08% for NB with H_2O_2:COD ratio 1:1 and 2:1 respectively which is best suited for partial degradation which enhance the biodegradation processes. All the experiments were conducted at room temperature, pH 3.25 to 3.35 having Hydrogen Peroxide and Ferrous Sulphate as the only varying parameter.

Keywords: *p*-Nitrophenol (PNP), Nitrobenzene (NB), Advanced Oxidation Process (AOP), Fenton's oxidation, COD removal

1. INTRODUCTION:

Nitrophenol and nitrobenzene are found in the effluent of industries such as rubber chemicals, dyes and paint coloring, fungicides, explosives, pesticides; prolonged exposure of these chemicals may cause serious damage to central nervous system, liver, kidney and other organs. These are highly persistent, non or less biodegradable[5] and classified as toxic (LD_{50} - 667 mg/kg oral, nitrophenol and LD_{50} -349 mg//kg oral) as per U.S. Environment Protection Agency. So, finding a cost stipulated and effective treatment system is the present demand of the society.

Due to the limitation of biological[16,23,29,30] and physical processes[4,14,12,24]; chemical processes[3,9,10,18,24] has emerged as the pathway for the degradation of these recalcitrant pollutants.

Many authors made successful attempts on removal of nitrophenol[3,5,7,19,20,29,32] and nitrobenzene[25,31,33].

However, study accomplished here suggests the removal of these compounds in a wide range of concentrations (from 100 ppm to 500 ppm) which sets it apart. The dosage of catalyst is optimized for each concentration which fulfills the requirement of effluent treatment plants which may be either partial degradation or full-fledged treatment.

A study here is conducted on the basis of literature survey and concentration 100ppm[6,8,9,19], 200 ppm[1,9,21,34] and 500ppm[5,22,34] are taken in account on a trial basis, so it can be coupled with biological treatment process (Activated Sludge Process) which is to be considered on the later stage of the study.

Fenton oxidation is known to be one of the most conventional and effective, reliable Advanced Oxidation Process for those recalcitrant organics. Advanced Oxidation Processes (AOPs) are characterized in terms of catalytic degradation reactions and oxidation potential. $^\cdot OH$ radical is known to be the next strongest oxidant ($E^\cdot = 2.87$ V)

after fluoride ($E^\cdot = 3.06$ V)[5]. During this process $^\cdot OH$ radicals are produced by the catalytic reaction of H_2O_2 and Fe^{2+}.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\cdot OH \ \ldots\ldots\ldots\ldots (1)$$

Further the produced Fe^{3+} species helps in regeneration of Fe^{2+} by reacting with hydrogen peroxide.

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + {}^\cdot HO_2 + H^+ \ldots\ldots\ldots\ldots\ldots (2)$$
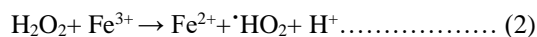
Degradation of nitrophenol and nitrobenzene occurs because of the production of these $^\cdot OH$ radicals. However, studies show that the reaction rate of (1) is much higher (rate constant changes from 63 $M^{-1}S^{-1}$ to 76 $M^{-1}S^{-1}$)[1] as compared to equation(2) which is having rate constant 0.01 $M^{-1}S^{-1}$. This implies Fe^{2+} ions are consumed at a much higher rate especially in the initial period of H_2O_2. The production of $^\cdot OH$ also degenerates Fe^{2+}.

$$Fe^{2+} + {}^\cdot OH \rightarrow Fe^{3+} + OH^- \ \ldots\ldots\ldots\ldots\ldots.. (3)$$

So, dosage of Fe^{2+} ion needs to be decided more carefully. However, it creates a problem of disposal of ferric hydroxide sludge produced. This technology is known as green technology as the concerned pollutants are broken down to CO_2 and H_2O in final step[5].

2. CHEMICALS USED:

Potassium dichromate, mercury sulphate, silver sulphate, Ferrous Ammonium Sulphate (FAS) chemicals required for COD estimation was acquired from Merck (India). All were of reagent grade having purity ($\geq$99%). Para nitrophenol or 4-nitrphenol and nitrobenzene used in the experiment was purchased from Sigma Aldrich (chemical formula $C_6H_5NO_4$) having molecular weight 155.11g/mol. H_2SO_4 (98% by weight), Sodium thiosulphate, potassium iodide, soluble starch, Ammonium molybdate (all reagent grade having purity $\geq$99%) used for residual peroxide measurement was collected from Merck. H_2O_2 (commercial grade 50%) was obtained from local market. All solutions were prepared with distilled water.

3. EXPERIMENTAL WORK:

3.1. Synthetic sample preparation:

Appropriate amount of para nitrophenol and nitrobenzene were added to distilled water and stirred in magnetic stirrer to ensure a homogenous mixture. Quantities of these pollutants varied depending on the reaction setup. Para-nitrophenol and nitrobenzene concentration tested in the experiment was arranged from 100-500ppm. The synthetic samples were used as soon as it was prepared for the reaction.

3.2. Analysis procedure:

All the beakers, flasks, volumetrics, pippets were procured from borosil, thoroughly washed, kept in oven for 24 hours at 100^0C before use. Hot air oven used was of LABARD, model CJ- HAO. pH meter availed was Eutech pH 510. COD digester of Merck spectragrant model TR 320 was used. Analytical balance of precision 0.001g was used. Magnetic stirrer of REMI 2ml capacity was used for continuous stirring.

All experiments were performed using unbuffered solution and in batch mode. COD was determined by closed reflux method confirming APHA standard, method no. 5220C; at 150^0C for two hours and $K_2Cr_2O_7$ was used as oxidant. Residual peroxide was measured using iodometric titration where the sample is titrated with a thiosulphate solution using starch as an indicator[15].

Solutions of nitrophenol and nitrobenzene of 100 ppm, 200 ppm and 500 ppm concentration was considered for degradation. COD of nitrophenol and nitrobenzene by close reflux method was found out to be almost same (tolerance 5%) as calculated stoichiometrically. Peroxide concentration Vs. COD graph was plotted so as to know the interference of H_2O_2 on standard COD test[13] and found out to be linear. $H_2O_2:Fe^{2+}=50:1$(by molar ratio) was taken for treatment. The requirement of H_2O_2 (50% commercial) and Ferrous sulphate was determined by assuming W/W ratio of $H_2O_2:COD$ and molar ratio of $H_2O_2:Fe^+$ respectively. In the reaction system initial time 0 minute is the time when the H_2O_2 (50%) dose is inserted to the system just after the catalyst

FeSO$_4$.7H$_2$O is dosed[5]. For each concentration the batch reaction is done with three different H$_2$O$_2$ and COD ratios (0.5:1, 1:1, 2:1) up to three hours. The reaction is performed at room temperature (23.5-25˙C) and in acidic medium (pH 3.25 to 3.35) as it has been studied that H$_2$O$_2$ is not stable in basic solution[17] and it degrades to O$_2$ and H$_2$O above pH 7. pH was adjusted using 1:20 H$_2$SO$_4$ solution so as to achieve mineralization rate. Samples were taken at regular interval for the determination of COD and residual peroxide measurement. Finally, actual COD of treated sample was found out by subtracting COD$_{RP}$ from COD at time "t".

4. RESULTS AND DISCUSSIONS:

4.1. Effect of pH:

Study shows Fenton's reaction is carried out efficiently in acidic medium (pH 2-4)[5,11,17]. When pH closes to 7, iron hydroxide and hydroxy complexes are formed which attributes to loss of efficiency of the system[1]. At a low pH (pH<2), ˙OH radicals has a tendency to add to the heterocylic ring or aromatic ring abstracting a hydrogen atom which initiates a radical chain oxidation[17]. In this study a pH range of 3.25- 3.35 is maintained throughout (Table 1 and Table 2).

It has been noted that the final pH value of the treated solution is not dependent on the initial value after the completion of the reaction, though it varies according to the initial concentration of pollutant (both para nitrophenol and nitrobenzene). Kinetic study on degradation shows that the pollutant is transformed into a series of organic acids (mainly acetic and oxalic acids) which tends to buffer the treated solution[17].

4.2. Effect of H$_2$O$_2$ dosage on degradation efficiency

It has been noted by increasing the H$_2$O$_2$: COD ratio, removal efficiency increases drastically in all the concentration considered. For 100 ppm concentration, this increased from 59.5% to 81.94% (Table 1) in case of para nitrophenol and 58.39% to 88.6% (Table 2) for nitrobenzene, if the ratio H$_2$O$_2$: COD is modified from 0.5:1 to 2:1. For other concentration also, similar trend is followed. This can be explained by the production of OH radicals which occurs due to the catalyzation of hydrogen peroxide by ferrous ion and if the dose of catalyst (FeSO$_4$.7H$_2$O) is increased, Fe^{2+} concentration will be increased generating greater ˙OH radicals[11].

Table 1: Fenton's oxidation of PNP solution of various conc. by Fenton reaction after 180 min

| PNP conc. H$_2$O$_2$:COD	100ppm 1:1	100ppm 2:1	100ppm 0.5:1	200ppm 1:1	200ppm 2:1	200ppm 0.5:1	500ppm 1:1	500ppm 2:1	500ppm 0.5:1
COD$_{initial}$(mg/L)	192	192	192	310	310	310	760	760	760
COD$_{final}$(mg/L)	31.77	15.19	71.71	71.71	46.8	135.83	146.65	108.75	623.88
%removal	81.94*	93.22*	59.25	77.59	85.4*	52.84	80.78	85.69*	17.91
pH$_{initial}$	3.33	3.33	3.33	3.25	3.30	3.30	3.30	3.30	3.30
pH$_{final}$	2.80	2.75	2.97	2.59	2.56	2.81	2.29	2.17	2.53
RP$_{initial}$(mg/L)	650	1300	325	1200	2400	600	3260	6520	1630
RP$_{final}$ (mg/L)	68	238	85	85	300	34	102	952	34

(* These concentrations show the same efficiency after 120 min. of contact time)
(After 24hrs of contact time nearly 99% removal efficiency is achieved in each case)

Table 2: Fenton's oxidation of NB solution of various conc. by Fenton reaction after 180 min

NB conc.	100ppm	100ppm	100ppm	200ppm	200ppm	200ppm	500ppm	500ppm	500ppm
H_2O_2:COD	1:1	2:1	0.5:1	1:1	2:1	0.5:1	1:1	2:1	0.5:1
$COD_{initial}$(mg/L)	198	198	198	440	440	440	1360	1360	1360
COD_{final}(mg/L)	31.19	23.71	79.88	135.83	94.96	153.83	215.25	189.32	455.83
%removal	83.75	88.6	58.39	67.35	78.42	65.03	84.17	86.08	66.48
$pH_{initial}$	3.33	3.33	3.33	3.35	3.35	3.35	3.33	3.33	3.33
pH_{final}	2.82	2.76	2.97	2.68	2.56	2.88	2.23	2.17	2.56
$RP_{initial}$(mg/L)	424	848	212	770	1540	385	2313	4626	1156
RP_{final} (mg/L)	85	238	34	51	306	51	170	782	51

(After 24hrs of contact time nearly 99% removal efficiency is achieved in each case)

As H_2O_2 was fed in a single step in this reaction system, the concentration of H_2O_2 in the starting period would be higher and scavenged by H_2O_2 as below:

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O$$
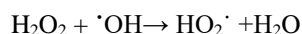
It will lead to the production of hydroperoxyl radical having pretty less oxidizing power. This theory is supported by the graphs (Fig. 1b - Fig. 6b) where the initial removal is higher and faster in every case.

The above equation also suggests that if either of the catalysts (H_2O_2 or iron salt) is increased, then inhibition of oxidation reaction occurs which leads to decrease in $^{\bullet}OH$ radicals which tends to reduce the possible attack of organic compounds[1,5]. So, intentionally H_2O_2 added was of slightly higher amount, so the residual peroxide found was not insignificant throughout the reaction (Table 1, Table 2, Fig. 1a - Fig. 6a).

As for optimum dosage of reactants are concerned; for 500ppm concentration (both para nitrophenol and nitrobenzene), naturally H_2O_2: COD ratio 2:1 showed higher removal efficiency which can be co-related by reduction of COD graphs (Fig. 3b and Fig. 6b), with a contact period of 180 minutes. But for increasing biodegradability and partial oxidation ratio 1:1 was found to be economical as well as efficient; as removal efficiency for para nitrophenol and nitrobenzene was 80.78% and 84.17% respectively (Fig. 3b, Fig. 6b, Table 1 and Table 2).

Furthur it is studied that, the rate constants are inversely proportional to the initial contaminant concentration (para nitrophenol or nitrobenzene). It is because of the availability of constant amount of $^{\bullet}OH$ radicals irrespective of pollutant concentration which results in the decrease in removal rate constant compounds[1]. So, the percentage removal are found to be different at different ppm concentrations.
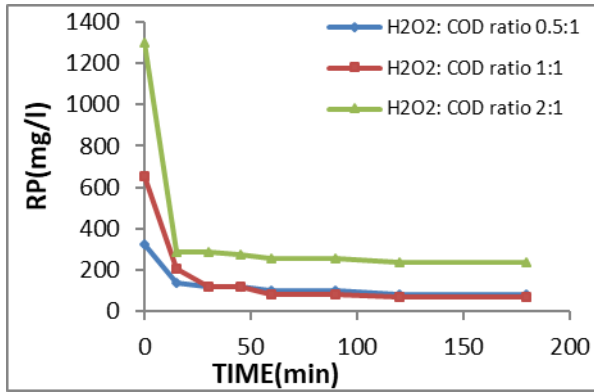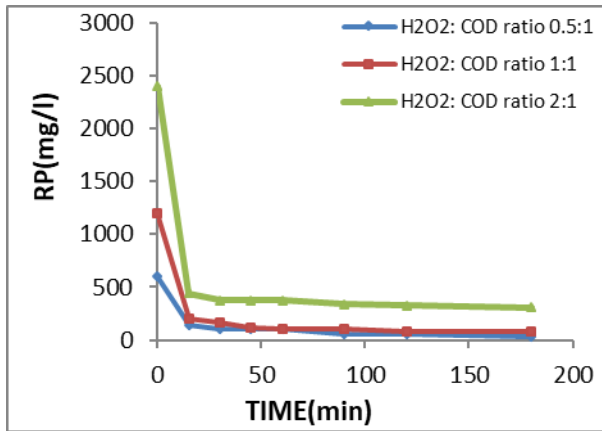
(Fig. 1a) Utilization of Hydrogen Peroxide vs.
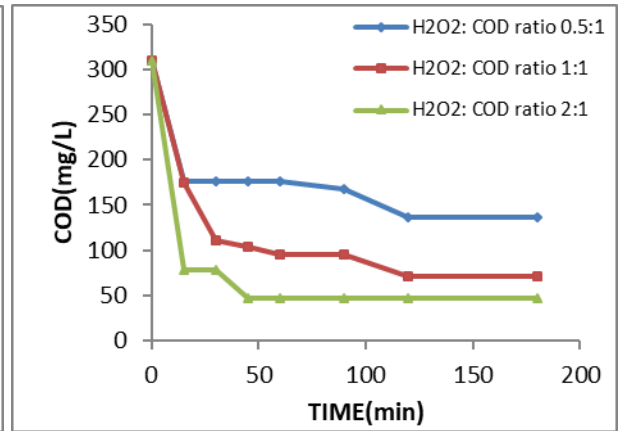Time with different H₂O₂: COD ratio
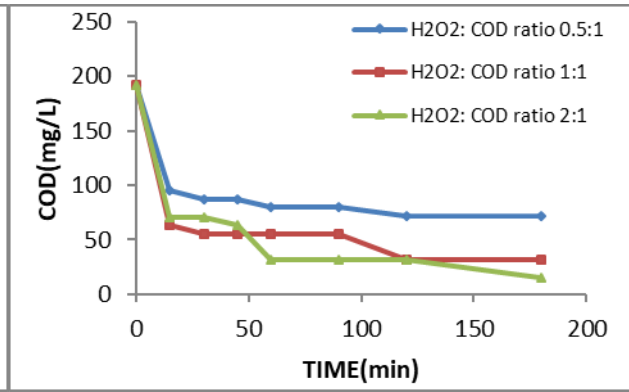
(Fig. 1b) Reduction of COD vs. Time

Fig.1. Profile of RP and COD reduction during degradation of PNP (100 ppm) at various time using Fenton's reagent
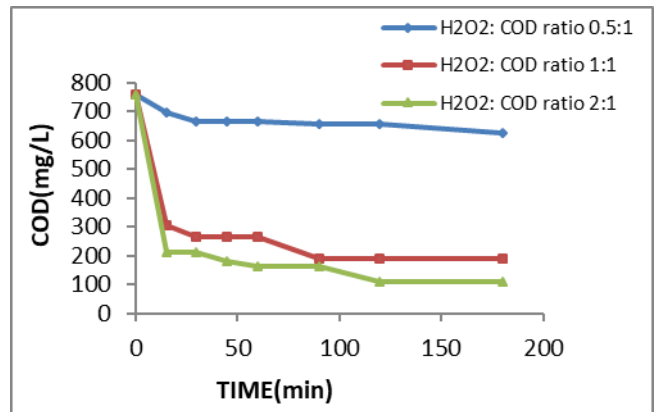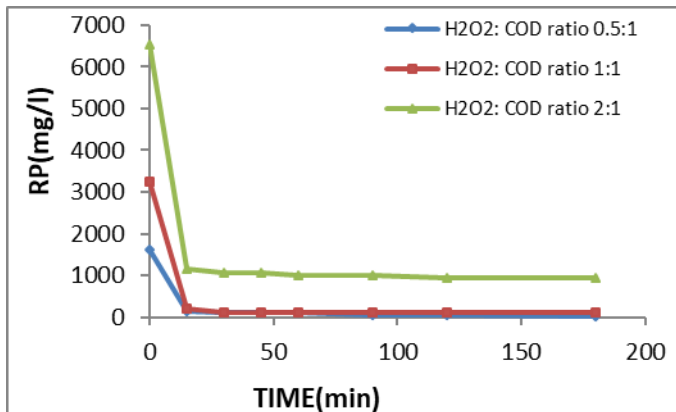

(Fig.2a) Utilization of Hydrogen Peroxide vs.
Time with different H₂O₂: COD ratio
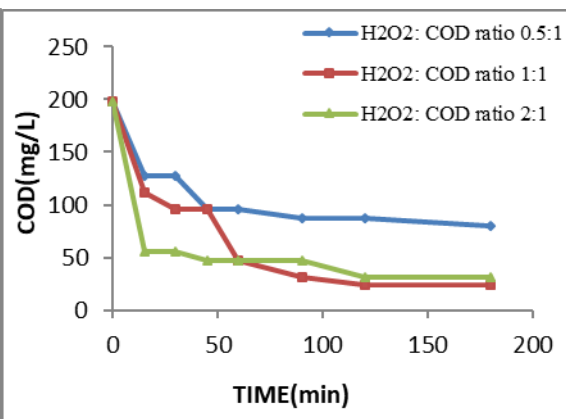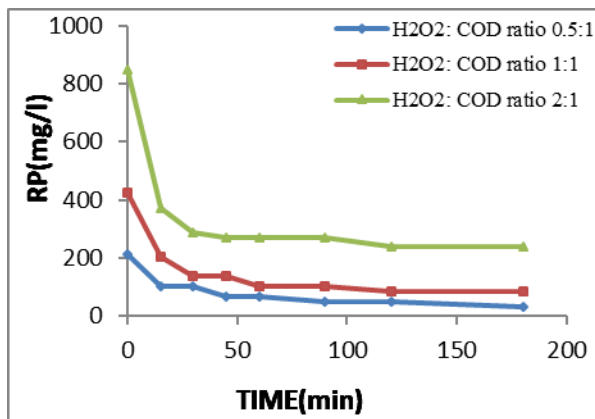
(Fig. 2b) Reduction of COD vs. Time

Fig.2. Profile of RP and COD reduction during degradation of PNP (200 ppm) at various time using Fenton's reagent

(Fig. 3a) Utilization of Hydrogen Peroxide vs.
Time with different H₂O₂: COD ratio
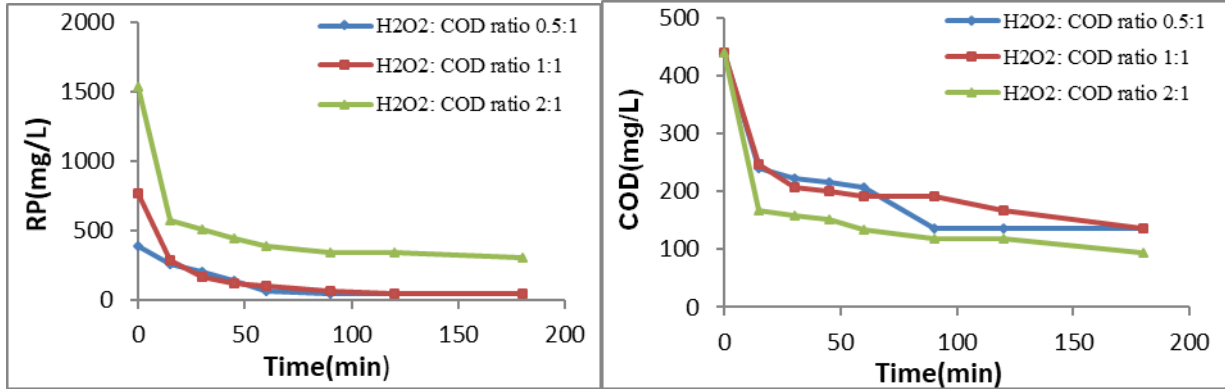
(Fig. 3b) Reduction of COD vs. Time

Fig.3. Profile of RP and COD reduction during degradation of PNP (500 ppm) at various time using Fenton's reagent

(Fig.4a) Utilization of Hydrogen Peroxide vs.
Time with different H₂O₂: COD ratio
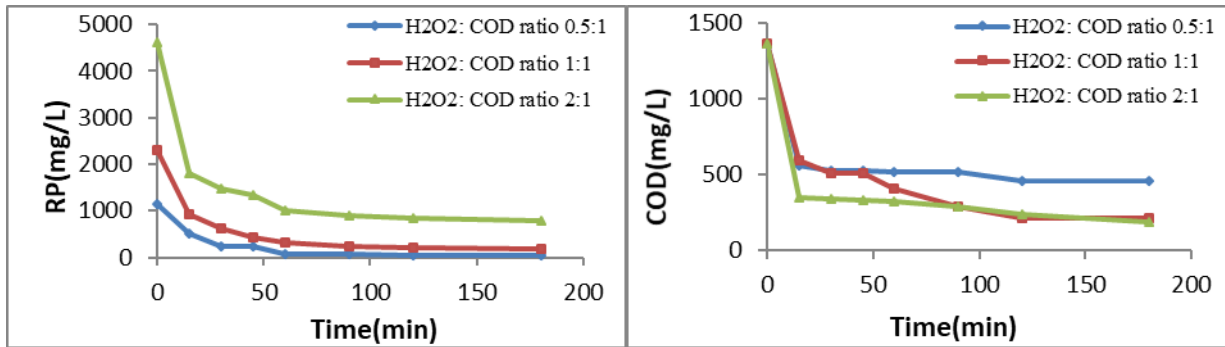
(Fig. 4b) Reduction of COD vs. Time

Fig.4. Profile of RP and COD reduction during degradation of NB (100 ppm) at various time using Fenton's reagent

(Fig.5a) Utilization of Hydrogen Peroxide vs.   (Fig.5b) Reduction of COD vs. Time
        Time with different H₂O₂: COD ratio

Fig.5. Profile of RP and COD reduction during degradation of NB (200 ppm) at various time using Fenton's reagent

(Fig. 6a) Utilization of Hydrogen Peroxide vs.   (Fig.6b) Reduction of COD vs. Time
        Time with different H₂O₂: COD ratio

Fig.6. Profile of RP and COD reduction during degradation of NB (500 ppm) at various time using Fenton's reagent

5. CONCLUSION:

Conventional Fenton's reaction method is found to be one of the efficient and cost effective methods for the degradation of nitro aromatic compounds such as para nitrophenol and nitrobenzene. It is considered eco friendly or green technology as the pollutant is broken down to stable carbon dioxide and water and secondary pollutant generation is also avoided but the intermediate product formation during mineralization process is yet to be considered. For concentration upto 100 ppm, H_2O_2: COD ratio 0.5:1 can be taken into consideration as per the process requirement as the removal efficiency meets nearly 60% (Fig. 1b and Fig. 4b) for both Para-nitrophenol and nitrobenzene. But for higher concentrations (200 ppm and 500 ppm),H_2O_2: COD ratio 0.5:1 is to be discarded and only ratio 1:1 can be considered for partial degradation and ratio 2:1 for >85% removal efficiency (Fig. 2b, Fig. 3b, Fig. 5b and Fig. 6b). It is also possible to recycle the iron sludge by raising the pH, separating the floc and acidifying the iron sludge which is not included in this study.

6. ACKNOWLEDGMENT:

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