

Treatment of wastewater containing pyridine released from *N,N'*-Dichlorobis (2,4,6-trichlorophenyl) urea (CC2) plant by advanced oxidation

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Abstract

Advanced oxidation is one of the most important chemical treatment methods used for complete mineralization of organic pollutants present in the wastewater. The manufacturing plant of *N,N'*-dichloro bis-(2,4,6-trichlorophenyl)-urea (CC2) produces wastewater containing pyridine, acetic acid and diphenyl urea. The effectiveness of advanced oxidation processes (AOP) for the treatment of wastewater discharged from the CC2 plant was investigated in this study. Four types of advanced oxidation processes (H_2O_2/Fe^{2+} , $H_2O_2/Fe^{2+}(Fe^{3+})/UV$, H_2O_2 (without catalyst) and $TiO_2/h\nu/O_2$) were examined. Fenton's reagent and Fenton's type reaction was able to effectively destroy pyridine and other pollutants in the wastewater. It was observed that, by advanced oxidation process, a maximum of 74.0 percent chemical oxygen demand (COD) removal was achieved. The rate of COD removal was in the order of $H_2O_2/Fe^{2+} > TiO_2/H_2O_2 > H_2O_2$ (without catalyst) $> TiO_2$.

Keywords: Advanced oxidation; Fenton's process; CC2; Pyridine; Degradation

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1. Introduction

Industrial effluents and urban municipal wastewater contain a lot of organic compounds that are harmful to the environment. The manufacturing plant of *N,N'*-dichloro bis-(2,4,6-trichlorophenyl)-urea (CC2), which is a chemical decontaminant of sulphur mustard; produces wastewater containing pyridine, acetic acid and diphenyl urea (DPU) [1-4]. Pyridine is also discharged through effluents from a variety of industries such as pharmaceuticals, dyes, pesticides and herbicides, shale oil processing, food processing and coal carbonization [5-8]. Pyridine is reported to be toxic and harmful to the environment [9-14]. Therefore, industrial wastewater containing pyridine must be treated, before discharging into the environment. Various physico-chemical methods for treatment of wastewater have been cited in the literature. These include activated carbon adsorption, incineration and aqueous oxidation [15]. But these methods give incomplete solution to the pollution problem. A lot of research has been addressed for the complete mineralization of the organic pollutants. Such research pointed out the prominent role of a special class of oxidation techniques defined as advanced oxidation

processes (AOP) which usually operate at or near ambient temperature and pressure [16-19]. Advanced oxidation is a chemical process, which aims at the mineralization of the contaminants into carbon dioxide, water and inorganic or, at least, into harmless products. Hence, this method gives complete solution to the pollution abatement. Pollutants that are not amenable to biological treatment may also be completely mineralized by adopting a proper reactive system. In such cases AOP is much more effective than those adopted in conventional treatment processes [20-22]. AOP represents a powerful means for the abatement of refractory and/or toxic pollutants in wastewater like dyes and other toxic waste materials from textile and other industries [23-26]. In the treatment by AOP, the hydroxyl radicals are first generated, which react with organic pollutants resulting in different degraded products [27, 28]. Therefore, generation of hydroxyl radical plays an important role in the chemical destruction of waste material by advanced oxidation. There are different processes of generating the hydroxyl radicals, namely, H_2O_2 photolysis (H_2O_2/UV) [29], Fenton's process (H_2O_2/Fe^{2+}) [30], photo-assisted Fenton's process ($H_2O_2/Fe^{2+}(Fe^{3+})/UV$) [31,32], photo-catalysis ($TiO_2/h\nu/O_2$) [33,34] etc. In all the reported literature, the AOP was used either for a pure compound or in case of a one component system.

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In the present study, our basic aim was to investigate the effectiveness of different AOP to degrade wastewater containing pyridine released from the CC2 manufacturing plant. Effect of different parameters such as pH, time, and dose on the degradation has been studied. This paper deals with the degradation study of the wastewater containing pyridine, acetic acid and DPU. Four types of advanced oxidation processes have been studied. These are Fenton's process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), photo assisted Fenton's process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ (Fe^{3+})/UV), photo-catalysis ($\text{TiO}_2/\text{h}\nu/\text{O}_2$) and H_2O_2 (without catalyst).

2. Materials and Methods

2.1 Chemicals

Wastewater was collected from the pilot plant of Defence Research & Development Establishment (DRDE), Gwalior, used for the production of CC-2 (Table 1). The wastewater contains acetic acid, pyridine, DPU and some other mono- and di-substituted byproducts of Hexachlorocarbonyl (HCC) and diphenyl urea (DPU). Hydrogen peroxide solution (30.0%), ferrous sulfate heptahydrate, titanium dioxide, ammonium ferrous sulfate and mercuric sulfate (all analytical grades) were purchased from M/s Qualigens India Ltd. All other chemicals used were purchased from S. D. Fine Chemicals. Triple distilled water was used for the preparation of reagent solution.

Table 1. Characteristics of the wastewater obtained from the pilot plant used for the production of CC2.	
Color	Light Yellow Brownish
pH	3.7-3.9
Total solid	1500-1800 mg L ⁻¹
TDS	1250 mg L ⁻¹
COD	11000-12500 mg L ⁻¹
Conductivity	1100-1200 micro S cm ⁻¹
BOD	7000-8000 mg L ⁻¹
Pyridine	45-65 mg L ⁻¹
Acetic acid	60-80 mg L ⁻¹
DPU	10-15 mg L ⁻¹

2.2 Experimental Setup

Experiments were carried out in a glass beaker for studying the COD removal by advanced oxidation at room temperature under sunlight. To see the effect of artificial light the chemical reactions were carried out in a laboratory photochemical reactor consisting of annular space with a net volume of 1.0 L. A 40.0 W lamp, housed in the axis of the reactor inside a glass immersion well, was used as a light source. Water coil was provided in the reactor for cooling. The experimental setup is shown in Figure 1.

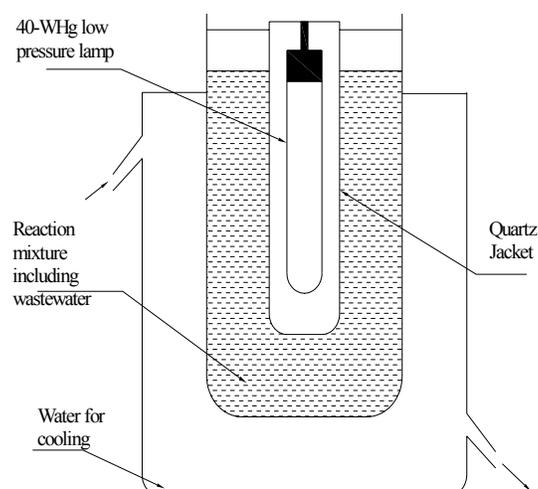


Figure 1. Experimental set up for carrying out photochemical reactions for advanced oxidation studies.

2.3 Experimental Procedure

2.3.1 Reaction at room temperature

Batch experiments were carried out in 500.0 mL beakers kept at room temperature (25 °C). The pH of the wastewater (Table 1) was manipulated by adding sulfuric acid and sodium hydroxide solution in order to perform the experiment at a particular pH. After adjusting the pH, 250.0 mL waste solution was taken in a beaker, ferrous sulfate heptahydrate (278.0 mg L⁻¹, 1.0 mM) and 30.0% (w/v) H_2O_2 (250.0 mM) were added simultaneously into the waste material. Continuous mixing was carried out by a magnetic stirrer. Samples (1.0 mL each) were withdrawn at certain time intervals (5.0, 15.0, 30.0, 60.0 and 90.0 min.) for analysis. Three samples were taken each time and were analyzed. The reactions were carried out at different pH. The same experiments were repeated with TiO_2 (1.0 mM) as a catalyst instead of Fe^{2+} and also without any catalyst.

2.3.2 Photochemical experiments under sunlight

The waste solution, 250.0 mL, (after adjusting the pH) was taken in a beaker (500.0 mL) and kept under sunlight on sunny days. The global solar radiation was measured by a radiometer. The average solar irradiation on which the experiments were carried out was 400-450 W m⁻². Fe^{2+} (1.0 mM) and 30% (w/v) H_2O_2 (250.0 mM) were added simultaneously into the waste material. The solutions were stirred occasionally and samples (1.0 mL) were withdrawn from the beaker at certain time intervals for analysis. Three samples were taken each time and were analyzed. The reactions were carried out at different pH. The same experiments were repeated with TiO_2 as a catalyst instead of Fe^{2+} and also without any catalyst.

2.3.3 Photochemical experiments in UV reactor

Batch experiments were carried out in the UV reactor (Figure 1) with 250.0 mL wastewater sample, at a pH of 4.0. Fe^{2+} (1 mM) and 30.0% (w/v) H_2O_2 (250.0 mM) were added simultaneously into the reactor. Then UV lamp was switched on. Samples (1.0 mL each) were taken after 5.0, 15.0, 30.0, 60.0 and 90.0 min of reaction for the analysis. Three samples were taken each time, analyzed and average value was taken. The same experiments were repeated with TiO_2 (1.0 mM) as a catalyst and also without any catalyst.

2.4 Analysis

Samples of the wastewater were taken, centrifuged (model 1-15 K, Sigma, Germany) at 10000 rpm for 5 minutes, decanted and analyzed for concentration of pyridine, acetic acid and diphenyl urea using high performance liquid chromatography (HPLC), (Shimadzu, Japan, model LC-6A) fitted with C_{18} column. A UV detector (SPD-6AV) at a wavelength of 257.0 nm was used for detection. The column temperature was kept at 40 °C with mobile phase of methanol-water (70:30,v/v) at 1.5 mL/min. Ten μL of each samples was injected into the column through Reheodyne injector. Chromatopac (C-R3A) was used as integrator and recorder. The average concentration of three samples drawn at a particular time from the reactor was taken. pH was measured by a digital pH meter (model: MP220), supplied by Mettler-Toledo, GmbH, Switzerland, Germany. COD was determined as per standard procedure as described in APHA, 1998 under section 5220 [17].

3. Results and Discussion

The chemical degradation of the pollutants from the wastewater (Table 1) was studied under different operating conditions. The wastewater contains pyridine, acetic acid, DPU and some other organic compounds. The HPLC chromatogram of wastewater is shown in Figure 2. Retention times 1.782, 2.028, 2.463 and 5.428 min correspond to solvent, acetic acid, pyridine and DPU respectively. The waste also contains some mono and disubstitutes impurities of DPU. The retention time of these organic impurities were 2.97, 5.15 and 5.96 min, respectively. This complex wastewater was subjected to various experiments for degradation by AOP. It was observed that the peak corresponding to acetic acid, pyridine and PDU decreased after AOP treatment. This indicates that the degradation of organic waste was taking place by AOP treatment. Various parameters, like pH, sunlight, dose of hydrogen peroxide etc was found to effect the degradation of pollutants.

3.1 Effect of pH on degradation of waste by AOP

The effect of pH on chemical degradation of the pollutants has been studied by Fenton's process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), photo assisted Fenton's process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ (Fe^{3+})/UV) and

photo-catalysis ($\text{TiO}_2/\text{hv}/\text{O}_2$). Figure 3 shows the percent

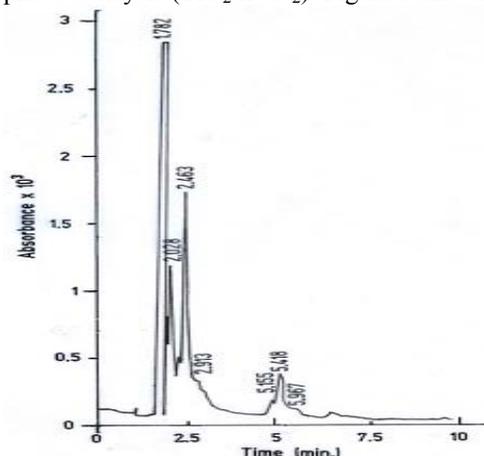


Figure 2. HPLC Chromatogram of neutral wastewater sample collected from a pilot plant of CC-2 manufacturing unit of DRDE, Gwalior, India., Column: C_{18} , Column temperature: 40.0 °C, Mobile phase: Methanol-water (70:30,v/v), Injected volume: 10 μL , λ_{max} : 220 nm, Retention time: 1.782, 2.028, 2.463 and 5.428 corresponding to solvent, acetic acid, pyridine and DPU respectively.

COD removal in different processes under different pH when the reaction was carried for 2.0 h under sunlight with initial COD of 12500.0 $\text{mg O}_2 \text{L}^{-1}$, 1.0 mM Fe^{2+} , 250.0 mM H_2O_2 , and 1.0 mM TiO_2 . The degradation of the waste material under the sunlight and the COD removal in different reactions was found to dependent on pH of the solution. The results clearly indicate that the degradation of the organic pollutants decreases with increase in pH of the wastewater for all types of processes. The most effective pH for degradation by Fenton's reagent and other reaction is 2.0. A maximum of 74.0% COD removal was obtained by Fenton's reaction at a pH of 2.0. It was reported that the complete mineralization of PCP by Fenton's reagent was most effective at pH of 3.0 [35]. In one of the recent report it was mentioned that at pH between 3.0-4.0 maximum COD removal was achieved for a wastewater containing pyridine [36]. In this case our observation supports the same but here the extent of effect of pH on degradation of the waste material is less. Effect of pH on COD removal in case of photo-catalysis of the waste by TiO_2 was found insignificant.

Similar degradation studies were carried out with the actual wastewater under atmospheric condition (room temperature, 25.0 °C) without sunlight. Figure 4 represents the degradation of the waste material and removal of COD at room temperature as a function of pH where the reaction was carried out for 2.0 h with same initial concentration and dosages of Fe^{2+} , H_2O_2 and TiO_2 . It is clear from this figure that maximum COD removal was obtained at a pH of 2.0. Fenton's reagent is the most effective one in

degrading the waste material containing pyridine. A maximum of 67.0 % COD removal was obtained by Fenton's reaction at a pH of 2 and at a pH of 4.0 the maximum COD removal was 61%. This observation clearly indicates that with the reduction of pH from 4.0 to 2.0 only 9% COD removal increases. Since in large scale industrial application it is not practical to use pH of 2.0, the degradation of pollutants by Fenton's reaction can be carried out at pH of the wastewater (3.7-3.9, Table 1) where the COD removal is 60-61%.

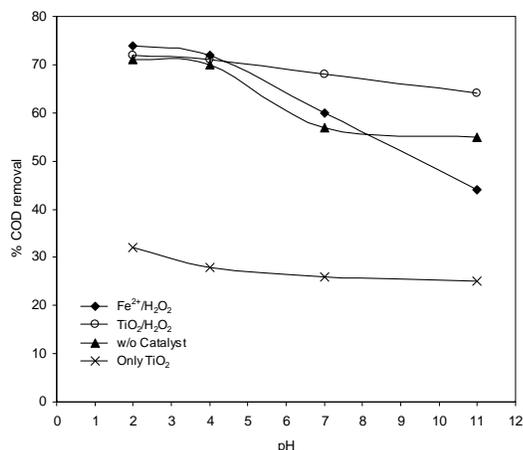


Figure 3. Removal of COD under sunlight at different pH., Initial COD: 12500.0 mg O₂ L⁻¹; Fe²⁺: 1.0 mM, H₂O₂: 250.0 mM, TiO₂: 1.0 mM and Reaction time: 2.0 h.

3.2 Effect of sunlight on degradation

Any chemical system absorbs light from the incident radiation of sun. This energy is absorbed and utilized by the system in the chemical reactions. This is obvious from the Figure 3 and Figure 4 that the percent COD removal is more in case of reaction under sunlight than reaction at room temperature for all four advanced oxidation processes when the reaction were carried out for 2.0 h with initial COD of 12500.0 mg O₂ L⁻¹; 1.0 mM Fe²⁺, 250 mM H₂O₂ and 1.0 mM TiO₂. For Fenton's reagent the extent of sunlight is understood by the results that the percent COD removal is 74.0% at pH of 4.0 under sunlight compared to 61.0% under room temperature (25.0 °C) without sunlight. This implies that almost 13.0 % extra COD removal was obtained due to sunlight in case of Fenton's reagent at a pH of 4.0 with 1.0 mM Fe²⁺.

3.3 Effect of reaction time on degradation

The effect of time on the overall degradation of the waste material by all four advanced oxidation processes was studied. The variation of percent COD removal for all reactions with time; when the reactions were carried out in an UV reactor with initial COD of 12500 mg O₂ L⁻¹, 1.0 mM Fe²⁺, 250.0 mM H₂O₂ and 1.0 mM TiO₂ at a pH of processes (Fenton's, photo Fenton's, photo-catalysis and

without any catalyst). The rate of COD removal increases 4.0; is represented in Figure 5. It is clear from this Figure that the rate of degradation follows same pattern in all

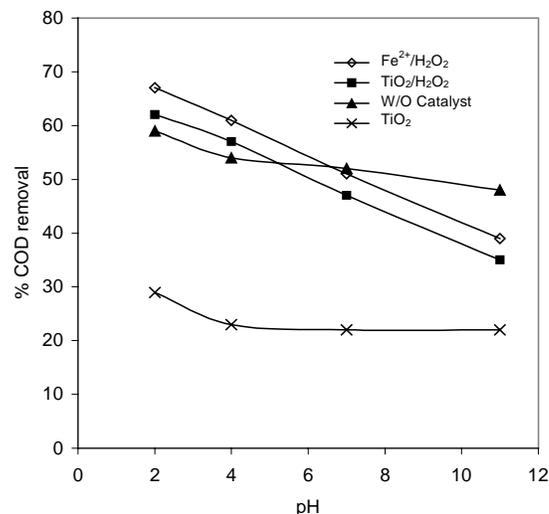


Figure 4. COD removal at room temperature at different pH., Initial COD: 12500.0 mg O₂ L⁻¹; Fe²⁺: 1.0 mM, H₂O₂: 250.0 mM, TiO₂: 1.0 mM and Reaction time: 2.0 h.

first (up to 5-6 minutes), followed by a decrease of COD removal (up to 15.0 minutes) and then the rate of removal increases again up to 60.0 minutes but finally it flattens after 60.0 minutes. The rate of COD removal was high and almost 25–30% COD removal was obtained within 5.0 minutes of reaction. Then the COD removal occurs slowly and it takes around 55.0 minutes for COD removal of another 40-46%. There was no appreciable change in COD removal after 60.0 minutes. It is likely that easily degradable compounds from the waste mixture were oxidized very fast, which might be the reason of fast removal of COD in the initial time. Thus the optimum contact time for the degradation by Fenton's and other AOPs in presence of a source of UV light was 60.0 minutes and optimum COD removal was around 71%.

Figure 6 depicts the effect of time of reaction on the removal of COD of the actual wastewater by Fenton's process at room temperature (25 °C) and 4.0 pH. It is clear from this figure that almost 35.0% COD removal was achieved within 20.0 minutes and 58% COD removal was achieved in 100.0 minutes under the condition and 66.0-67.0% COD removal was achieved with in 180.0 minutes. After 180.0 minutes there was no appreciable change in percent COD removal. Therefore the optimum contact time for the degradation of the wastewater containing pyridine in a mixture was 150 minutes when the reactions were carried out at room temperature (25.0 °C). A contact time of 180.0 minutes has been reported for the treatment of pyridine containing wastewater [36]. A contact time of

more than 2.0 h has been reported in the literature for Fenton's treatment of 4-tertiary butyl pyridine for almost complete mineralization [37]. Literature indicates a contact time of 180.0 minutes for transformation of creosote contaminated wastewater by Fenton's treatment [38]. Therefore, a reaction time of 150.0 minutes observed for Fenton's process in the present study is in well agreement with the reported time.

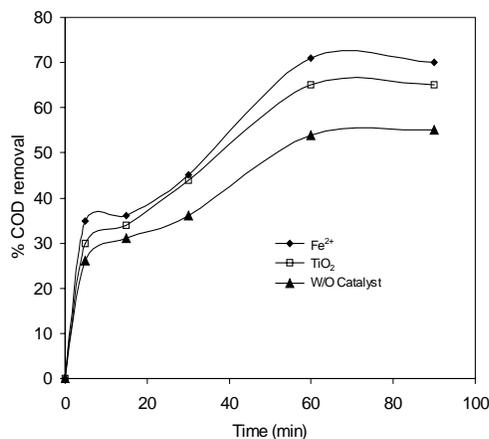


Figure 5. Rate of COD removal under UV light with different catalyst at a pH of 4.0., Initial COD: 12500.0 mg O₂/L., Fe²⁺: 1.0 mM, H₂O₂: 250.0 mM and TiO₂: 1.0 mM.

3.4 Optimum operating dose

The degradation of pyridine and other organic pollutants present in the wastewater depends on the dose of Fenton's reagent, namely, ferrous sulphate and hydrogen peroxide. Hence, in order to get maximum efficiency in the effluent treatment facility of a manufacturing unit, it is essential to operate the plant at optimum dose of both ferrous sulphate and hydrogen peroxide. Various reports are available, where the dose has been optimized for different type of pollutants. In a recent report, ferrous sulphate was varied from 40.0 mg L⁻¹ to 240.0 mg L⁻¹ and the optimum dosage was found out to be 200.0 mg L⁻¹ at pH 4.0 [36]. A ferrous sulphate dose of 55.847 mg L⁻¹ has been reported for more than 90.0% transformation of creosote-contaminated wastewater [38]. Fenton's reagent has also been reported for atrazine transformation, which is also a nitrogenous pollutant and a ferrous sulphate dose of 150.0 mg L⁻¹ was used for effective degradation of 16.1 mg L⁻¹ atrazine [39]. Experiments were conducted with the actual wastewater (initial COD of 12500.0 mg L⁻¹) in presence of sunlight at 25.0 °C at a pH of 4.0 by varying the dosages of ferrous sulphate from 40.0 to 350.0 mg L⁻¹. In our study the optimum dosage of ferrous sulphate was found to be 280.0 mg L⁻¹ (1 mM).

Similarly, the dose of hydrogen peroxide is also important for the degradation of pollutants. With increase

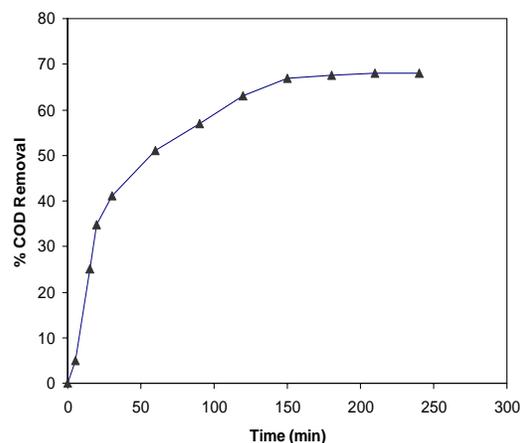


Figure 6. Rate of COD removal when the reaction was carried out at room temperature and at a pH of 4.0., Initial COD: 12500.0 mg O₂ L⁻¹, Fe²⁺:1.0 mM, H₂O₂ and 250.0 mM.

in dose of hydrogen peroxide, the percent COD removal increases up to a certain limit, after which there is no improvement with the dose. In our present study the dose of H₂O₂ was varied from 30.0 to 400.0 mM and we have observed that the optimum dose of hydrogen peroxide was 250 mM. It was earlier reported that a dose of 87 mM of hydrogen peroxide was found to be optimal to have an effective COD removal of 67.65% for pyridine containing wastewater [36]. An optimum dose of 9.0 mM and 480.0 mM were reported for creosote and atrazine contaminated wastewater, respectively [38,39]. This indicates that our observation of the optimum dose of H₂O₂ for the degradation of pyridine containing wastewater was in the same range. Therefore, in all our study we have used a dose of H₂O₂ of 250.0 mM in Fenton's reaction.

4. Conclusion

The degradation of pyridine along with other organic pollutants present in the effluent water of CC-2 manufacturing plant has been studied by four AOP's namely, UV/H₂O₂, Fenton's and photo-Fenton's processes and photo-catalytic (TiO₂/hv) processes. The efficacy of these processes for removal and mineralization of the pollutants have been studied. In the photo-Fenton's process a maximum of 74.0% COD removal was obtained at a pH 2.0. The rate of COD removal was in the order of H₂O₂/Fe²⁺ > TiO₂/H₂O₂ > H₂O₂ (without catalyst) > TiO₂. pH was found to affect the COD removal and it was observed that at lower pH (<4.0) the rate of degradation and removal of COD was higher for all the cases. But, only 6 % increase in the COD removal was obtained with the decrease of pH from 4.0 to 2.0. Since in large scale industrial application it is not practically and economically viable to use pH 2.0, the degradation of pollutants by

Fenton's reaction can be carried out at pH of the wastewater i.e 3.7-3.9, where the COD removal is 61% at 25.0 °C. The effect of pH on COD removal was found less when the degradation reaction was carried out without a catalyst. When the degradation of the waste solution was carried out with TiO₂ and without H₂O₂ no significant effect of pH on COD removal was obtained. In the degradation by Fenton's process the optimum dose of H₂O₂ was found to be 250.0 mM and that of Fe²⁺ was 1.0 mM for COD removal of the wastewater.

5. Future Study

In the present study the degraded products have not been identified. Also the reaction pathway has not been established. In future study the degradation products will be identified and the reaction pathways will be studied. The probable reaction mechanism of degradation by AOP will be investigated. The kinetics of the degradation reactions will also be studied in details.

6. References

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