Global NEST Journal, Vol 10, No 1, pp 31-38, 2008

REMOVAL OF COD FROM OIL RECOVERY INDUSTRY WASTEWATER BY THE ADVANCED OXIDATION PROCESSES (AOP) BASED ON H_2O_2

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Received: 21/06/07
Accepted: 10/09/07

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ABSTRACT

The combinations of H_2O_2/Fe^{+2}, $UV/H_2O_2/Fe^{+2}$ and UV/H_2O_2 process were investigated on treatment of oil recovery industry wastewater. Treatment of oil recovery industry wastewater, a typical high pollution strength industrial wastewater (chemical oxygen deman (COD): 21000 mg l^{-1}, biological oxygen demand (BOD): 8000 mg l^{-1}, oil and grease:1140 mg l^{-1}, total dissolved solids (TDS): 37000 mg l^{-1}, total suspended solids: 2580 mg l^{-1}), was carried out by batch oxidation processes.

The optimal mass ratio for H_2O_2/Fe^{+2} yielding the highest COD removal was found to be 8.658 corresponding to 200.52 g 1^{-1} H_2O_2 and 23.16 g l^{-1} Fe^{+2} concentrations for 60 minutes reaction time. Fenton process gave a maximum COD reduction of 86% (from 21000 to 2980 mg l^{-1}) and the combination of UV/H_2O_2 gave a COD reduction of 39% (from 21000 to 12730).

The percentage of removal, after the total reaction time (3.5h), H_2O_2: 8.4 g l^{-1} and Fe^{+2}: 0.05g l^{-1}, in the photo Fenton process, corresponded to 81 % of the total initial COD (4200 mg l^{-1}). The oxidative ability of the $UV/Fe^{+2}/H_2O_2$ process (81%) was greater than that of the UV/H_2O_2 process (55%) for 80% diluted wastewater. COD removal efficiency for UV/H_2O_2 process (COD/H_2O_2=1/2 (w/w)) was 90%, 55%, and 39 when initial COD was 1050, 4200, and 21000 mg l^{-1}, respectively, whereas COD removal was 943, 2320, and 8270 mg l^{-1}, respectively.

KEYWORDS***:*** Oil recovery industry; Fenton; Photo-Fenton; UV plus hydrogen peroxide

1. INTRODUCTION

Advanced oxidation processes (AOP) are defined as oxidation processes in which hydroxyl radicals are the main oxidants involved. Advanced oxidation processes (AOPs) are emerging and promising technology both as an alternative treatment to conventional wastewater treatment methods and enhancement of current biological treatment methods especially dealing with highly toxic and low biodegradable wastes (Chamarro *et al.*, 2001). Fenton and Photo-Fenton oxidation processes have been employed successfully to treat different industrial wastewaters, including black olive (Benitez *et al.*, 2001) and mineral oil contaminated wastewaters (Andreozzi *et al.*, 2000).

The mechanism of the Fenton reaction has been known for a long time. This oxidation method is based on the use of a mixture of hydrogen peroxide and iron salts (Fe^{+2}) which produces hydroxyl radicals ($^{\bullet}OH$) at acidic pH in ambient conditions. Both H_2O_2 and Fe^{+2} can react with $^{\bullet}OH$ and therefore both can inhibit the oxidation reactions if either of them is not in the optimal dosage (Tang and Huang, 1996). Many authors suggested Fe^{+2} to H_2O_2 mass ratio to be optimal at 1 to 10, but it must be optimised for particular wastewater to minimize scavenging effects (Torrades *et al.*, 2003). The generally accepted mechanism of the Fenton process proposes that hydroxyl radicals are produced by reaction of H_2O_2 with Fe^{+2} which is regenerated from the reaction of Fe^{+3} with H_2O_2 or intermediate organic radicals (Legrini *et al.*, 1993). This hydroxyl radical attacks organic molecules by abstracting a hydrogen atom or by adding to the double bonds. Organic molecules are then totally mineralized to carbon dioxide and water (Huston and Pignatello, 1999).

The photo-Fenton process ($H_2O_2/Fe^{+2}/UV$) is one of advanced oxidation processes. This process involves the hydroxyl radical($^{\bullet}OH$) formation in the reaction mixture through photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reaction (H_2O_2/Fe^{+2}) (Fenton, 1894). The H_2O_2/UV or Fenton process alone was successful in removing COD from oil containing wastewaters. The peroxide dose is important in order to obtain a better degradation efficiency, while the iron concentration is important for the reaction kinetics (Chamarro *et al.*, 2001). The UV/H_2O_2 process uses ultraviolet radiation to cleave the O-O bond in hydrogen peroxide and generate the hydroxyl radical. When UV light is absorbed directly by hydrogen peroxide, $^{\bullet}OH$ radicals are generated by photolysis of the peroxidic bond (Bolton, 1999).

The major objective of this study was to investigate the performance of single Fenton's reagent, combination of Fenton's reagent with UV (photo-Fenton process) and combination of UV radiation with hydrogen peroxide for COD removal from oil recovery industry wastewater. The following topics were also studied: wastewater characterization, effect of H_2O_2/Fe^{+2} ratios, wastewater concentration (pollution strength) and oxidation time. The wastewater samples obtained from factory were characterized according to the procedures described in Standard Methods (APHA, 1992). It was found that the Fenton, photo Fenton and combination of UV and H_2O_2 processes have the potential to reduce the COD of oil recovery industry wastewater.

2. MATERIAL AND METHOD

2.1. Wastewater Characterization

The physicochemical characteristic of the wastewater are summarized in Table 1. The wastewater used in this work is the effluent of an actual oil recovery industry (Çorlu-Tekirdağ, Turkey).

Table1. Characteristic of wastewater (equalization tank) used in Fenton, photo-Fenton and UV/H_2O_2 processes.

Parameter	Units	Value
pH		2.5
Chemical Oxygen Demand (COD)	mg l^{-1}	21000
Biochemical Oxygen Demand (BOD_5)	mg l^{-1}	8000
Oil and Grease	mg l^{-1}	1140
SO_4^{-2}	mg l^{-1}	12400
Cl^-	mg l^{-1}	375
NO_3-N	mg l^{-1}	9.0
NH_4-N	mg l^{-1}	69
Total Suspended Solids (TSS)	mg l^{-1}	2580
Total Dissolved Solids (TDS)	mg l^{-1}	37000
Biodegradability (BOD_5/COD)		0.38

2.2. Reagents

Hydrogen peroxide were prepared using the technical grade (50.59%; density: 1.13 kg l^{-1}) H_2O_2. Ferrous sulphate heptahydrate ($FeSO_4.7H_2O$, Merck) was used as source of Fe^{+2} in the Fenton and photo Fenton treatment. All solutions of H_2O_2, Fe^{+2}, NaOH and H_2SO_4 were prepared with deionized water and were made on each experimental day.

2.3. Experimental procedure

A sketch of the laboratory reactor (Fenton process) is shown in Fig.1(b). The experiments were performed in a round-bottomed flask. In the single Fenton's reagent experiments, the UV reactor was not connected to Fenton reactor. The reaction solution was stirred with a magnetic stirrer using a constant speed at 200 rpm to maintain a well-mixed solution during the experiments. In every assay, a 300 ml sample was placed into 500 ml flask, which was submerged in a water bath for temperature control. The optimum pH for Fenton, photo-Fenton and UV/H_2O_2 for treatment of oil industry wastewater was accepted to be 3 ± 0.1 based on previous studies (McGinnis *et al.*, 2000; Garcia Montano *et al.*, 2006). In every case, the reaction was started by adding the dose of hydrogen peroxide. All experiments were carried out in batch mode.

The initial concentration of wastewater had 21000 mg l^{-1} COD and solution volume was 300 ml. For Fenton experiments, wastewater was used without dilution. Several set of experiments were carried out to determine the range of hydrogen peroxide and iron needed to obtain optimum results. In the first set of experiments, the amount of H_2O_2 added was changed between 22.28 and 111.4 g l^{-1} when Fe^{+2} concentration was kept constant at 7.72 g l^{-1}. In the second set of experiments, oxidation experiments were performed varying the concentration of H_2O_2 (22.28-200.52 g l^{-1}) and Fe^{+2} (2.56-23.16 g l^{-1}) and monitoring COD in samples collected at time of 60 min.

The schematic diagram of the experimental set-up used is shown in Fig.1 (a-b) for photo Fenton and UV/H_2O_2 processes. A low pressure mercury vapor lamp (model Hg F15-05, Eurotech) with a nominal power of 12 W (according to the manufacturer) was used in the UV irradiation processes at 254 nm. The UV lamp enclosed in a quartz sleeve with an inner diameter of 22 mm and a length of 225 mm was positioned within the centre of a 250 ml cylindrical stainless steel reactor as the light source.

The UV reactor was connected to the circulation tank (Fenton reactor). The circulation tank with a total volume of 500 ml is made in pyrex-glass and is equipped with an external water bath connected to tap water, for temperature control. The circulation tank is equipped with a magnetic bar, thermometer and pH meter. Circulation of the wastewater between the two tanks is made by a peristaltic pump at a rate of 2.0 l min^{-1}. The total liquid volume in the system was kept at 0.3 l (Fenton reactor) + 0.25 l (UV reactor). Samples were withdrawn from the circulation tank at t: 0, 30, 60, 90, 120, 150, 180 and 210 minutes for the COD analysis. To determine the effect of Fe^{+2} concentration on the COD removal efficiency, a series of experiments (photo-Fenton) varying the concentration of iron and keeping fixed the other parameters, were carried out. Hydrogen peroxide was employed at the concentration of 8.4 g l^{-1}, while different concentration of Fe^{+2} were tested (0.025, 0.050, 0.100 and 0.200 g l^{-1}).

In UV/H_2O_2 oxidation process, experiments were carried out at different initial COD and H_2O_2 concentrations. In the first series, three pollution strengths of wastewater such as 5, 20 and 100 % were prepared for COD removal at the fixed COD/H_2O_2 ratio of 1/2. In the second series, hydrogen peroxide was added in COD/ H_2O_2 weight ratios of 1:1, 1:2 and 1:4. The initial COD concentration was kept constant at 1050 mg l^{-1}. Immediately after the addition of the chemicals to the reactor, the UV lamp and the peristaltic pump were turned on to initiate the reaction. All the experiments were done in duplicate for the same set of conditions. The variations were systematically within ±5% of the stated values.

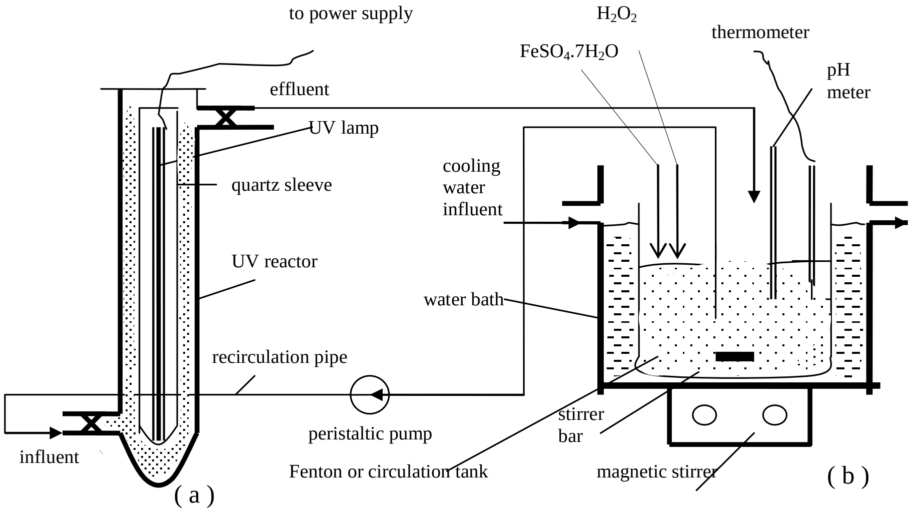

Figure 1. Schematic diagram of experimental set-up [(a) and (b)]

2.4. Analyses

Chemical oxygen demand (the using dichromate reflux method), biological oxygen demand, oil and grease, phenol, total suspended solids, total dissolved solids, SO_4^{-2}, Cl^-, NO_3-N, NH_4-N and NO_2^- were measured in raw wastewaters by procedures described in Standard Methods (APHA, 1992). The pH measurements were performed using a pH meter (WTW340).

At selected time interval, 5 ml of reaction mixture was taken and then analyzed for COD. The samples containing H_2O_2, which interferes with the COD measurements, were eliminated by the addition of MnO_2 powder. Before each analysis, samples were centrifuged to remove MnO_2.

3. RESULT AND DİSCUSSİON

Wastewater used in this study was obtained from oil recovery industry located in Çorlu, Tekirdağ-Turkey. Composition of the wastewater used in this study is presented in Table 1. These results indicate that this wastewater contains high load of organic and inorganic matter. Therefore, this wastewater can cause serious damage to the environment when discharged directly without proper treatment.

The BOD_5/COD ratio of oil recovery industry wastewater was found to be 0.38 (Table 1). BOD/COD constitutes a good measure of the biodegradability of a wastewater. This wastewater is partially biodegradable according to Chamarro *et al*. (2001) and Garcia Montano *et al*. (2006). Contaminants with a ratio of BOD_5/COD ≥0.4 are generally accepted as biodegradable, while those with ratios situated among 0.2 and 0.3 units result partially biodegradable (Chamarro *et al*., 2001; Garcia Montano *et al*., 2006). Therefore, there was a need for advanced treatment processes to decrease pollutions from oil recovery industry wastewater.

Effluent COD concentration and COD removal efficiency in Fenton oxidation experiments under different conditions are presented in Fig.2 and Fig.3. The effect of H_2O_2 concentration on COD removal was examined by changing the H_2O_2 concentration between 22.28 and 111.4 g l^{-1} while keeping the concentration of Fe^{+2} and COD constant at 7.72 g l^{-1} and 21000 mg l^{-1}. The Fe^{+2} and H_2O_2 concentrations were varied in the mass ratio H_2O_2/Fe^{+2} from 2.886 to 14.430 (Fig. 2).

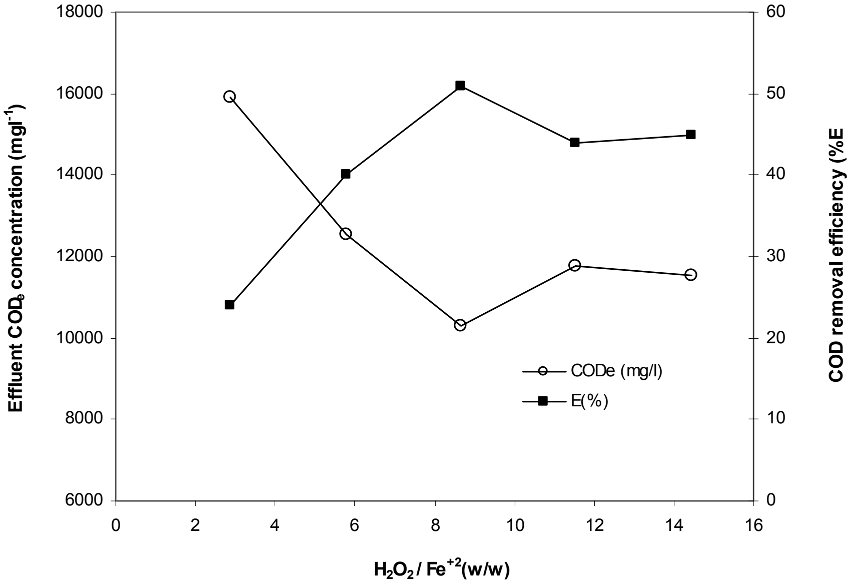

Figure 2. Effect of H_2O_2/Fe^{+2} ratios on effluent COD concentration and COD removal efficiency by Fenton process (pH=3, t=60 min, T=39-100°C)

The increase on H_2O_2 concentration from 22.28 to 66.84 g l^{-1} improved the removal of organic matter. However, the extended H_2O_2 concentration above 66.84 g l^{-1} could not extended COD removal efficiency. The COD degradation decreased from 51 to 45% as the H_2O_2 dose increased from 66.84 to 111.4 g l^{-1}. This is probably due to both the auto-decomposition of

H_2O_2 into oxygen and water, and the scavenging of hydroxyl radicals by H_2O_2 (Rodriguez *et al.*, 2002). The favorable H_2O_2 to Fe^{+2} mass ratio was found to be 8.658 (w/w).

The COD removal as a function of the dosage of Fe^{+2} and H_2O_2 were illustrated in Fig.3. Different doses of H_2O_2 and Fe^{+2} were selected which yielded the same optimum H_2O_2 /Fe^{+2} mass ratio (8.658). Increasing the Fe^{+2} concentration to the parallel H_2O_2 concentration produces a higher degree of degradation. As could be seen from Figure 3, the highest COD removal efficiency was achieved after the highest addition of reagents (200.52 g l^{-1} H_2O_2 and 23.16 g l^{-1} Fe^{+2}). The COD was decreased to 2980 mg l^{-1} with 86% removal at 60 min reaction time. With 86% of COD removal, Fenton oxidation has not been found to be satisfactory for oil recovery industry with a high strength of COD. COD discharge limit to receiving waters for oil recovery industry is 250 mg l^{-1} according to Turkish Water Pollution Control regulation.

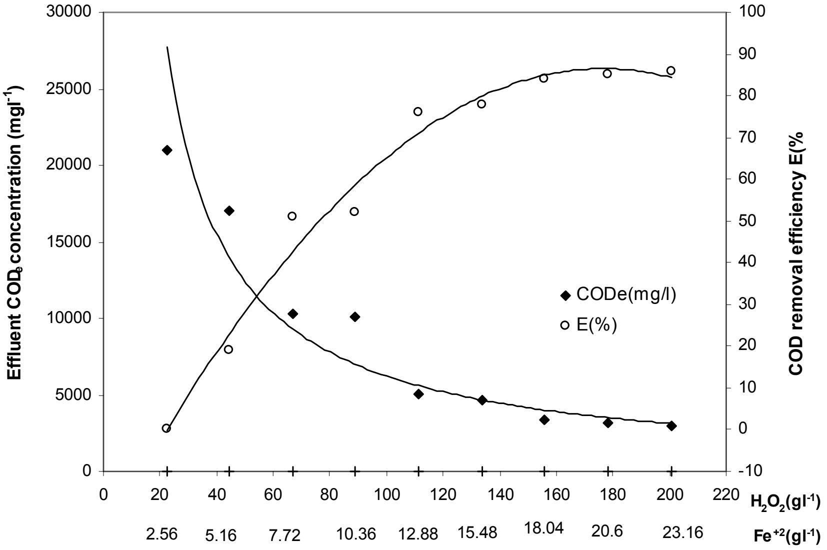

Figure 3. Effect of H_2O_2(g l^{-1}) and Fe^{+2} concentration on the effluent COD_e and COD removal efficiency (%) by Fenton process (pH=3, T=39-100oC, t=60 min)

The experimental results suggest that optimal H_2O_2 to Fe^{+2} ratio has to be maintained to achieve the maximal degradation efficient. Many authors suggested Fe^{+2} to H_2O_2 mass ratio to be optimal at 1 to 10, but it must be optimised for particular wastewater to minimize scavenging effects (Torrades *et al.*, 2003; San Sebastian *et al.*, 2003).

The reaction is fast and exothermic: temperature measured in our experiments was among 39-100 °C in the Fenton reactor. Water bath was unable to maintain fixed temperature and the system overheated up to 100 °C. Dutta *et al.* (2001) stated that there was practically no difference in the rate and extent of degradation of the reaction in the temperature between 40 and 75 °C. Rodriguez *et al.* (2002) reported that a significant enhancement of DOC reduction efficiency during the photo-Fenton treatment was verified when the temperature was increased from 40 to 60 °C. A plateau is reached above 60 °C.

The recently developed photo Fenton treatment is based on the hydroxyl radical generation by a mixture of H_2O_2 to Fe^{+2} ions.

Fig.4 shows the COD removal by the photo-Fenton process with a variation of H_2O_2 /Fe^{+2} mass (w/w) ratios for a reaction time of 30, 60, 90, 120,180 and 210 min. A turbidity in the solutions during the photo treatment hinders the absorption of the UV light for the photo Fenton process (Rodriguez *et al.*, 2002). Therefore, wastewater was diluted (80%) and used in photo Fenton and UV/ H_2O_2 experiments. The wastewater temperature in the circulation tank varied in the range of 39-43 °C (photo Fenton and UV/ H_2O_2).

When H_2O_2 dose was fixed at 8.4g l^{-1} and as Fe^{+2} concentration was increased sequentially from 25, 50, 100 and 200 mg l^{-1}, the removal efficiency increased from 75% to 81% and then decreased to 71% and 51%, respectively. This increasing trend is due to that the higher the ferrous dosage, the more the $OH^{\bullet}$ can be formed through reaction, thus leading to a high COD removal. The best COD removal efficiency was obtained with Fe^{+2} concentration of 50 mg l^{-1}. The highest percent COD removal was 81% after 210 min of oxidation with a H_2O_2/ Fe^{+2} mass ratio of 168. The dosage of ferrous ions over 50 mg l^{-1} does not increase the COD removal efficiency. This may be due to the increase of a brown turbidity in the wastewater during the photo-treatment, which hinders the absorption of the UV light required for the photo fenton process and excessive formation of Fe^{+2}, which can compete with the organic carbon for $OH^{\bullet}$ radical and also fixed H_2O_2 concentration can become the limiting factor (Rodriguez *et al*., 2002).

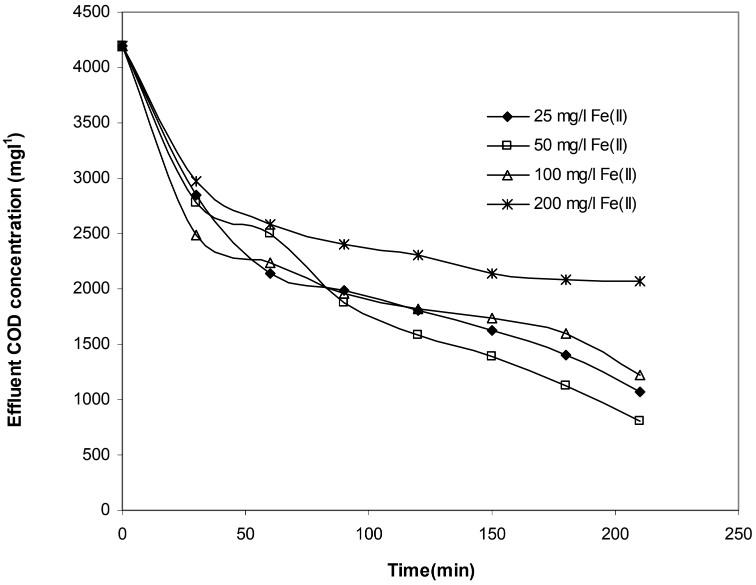

Figure 4. Variation of effluent COD concentration with time different Fe (II) concentration by photo-Fenton process (H_2O_2=8400 mg l^{-1}, pH=3.0, T=39-43, COD_o=4200 mg l^{-1})

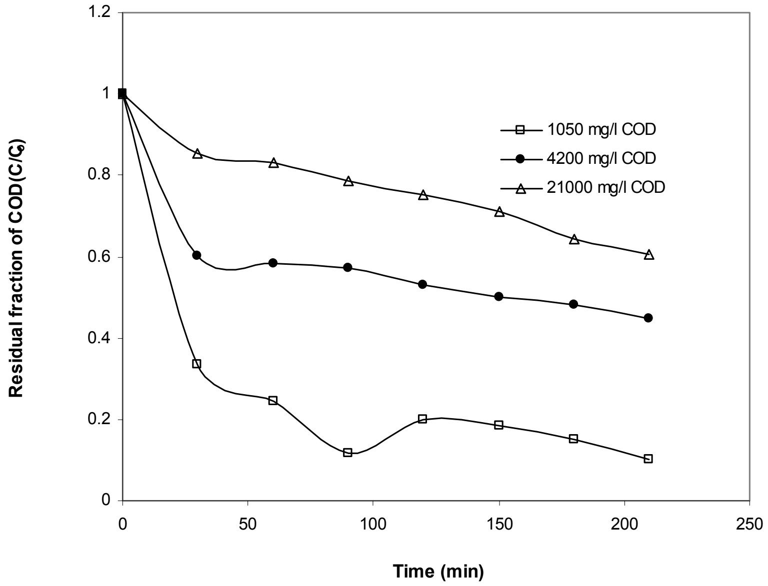

Figure 5. Variation of fraction COD with time different initial COD concentration by UV/H_2O_2 process (COD/H_2O_2:1/2(w/w), T=39-43°C, pH=3)

Ultraviolet photolysis combined with hydrogen peroxide was found appropriate oxidation process for treatment of low pollution strength wastewater. The efficiencies of the UV/H_2O_2 process in the fix dosage ratios of COD/H_2O_2 are illustrated in Figure 5. The UV/H_2O_2 process was able to mineralize 90% of the initial COD (COD_o:1050 mg l^{-1}). Lower COD removals were observed when the initial COD concentration exceeded 4200 mg l^{-1}. High initial COD (≥21000 mg l^{-1})containing wastewaters did not suffer any appreciable oxidation with the combination of UV radiation and hydrogen peroxide. Reductions of COD can only be as high as 39% when the initial COD is 21000 mg l^{-1} and the initial concentration of hydrogen peroxide is 42 g l^{-1}. High COD wastewaters absorb most of the incident UV radiation, while for lower COD wastewaters hydrogen peroxide is the main absorber (Beltran *et al.*, 1997).

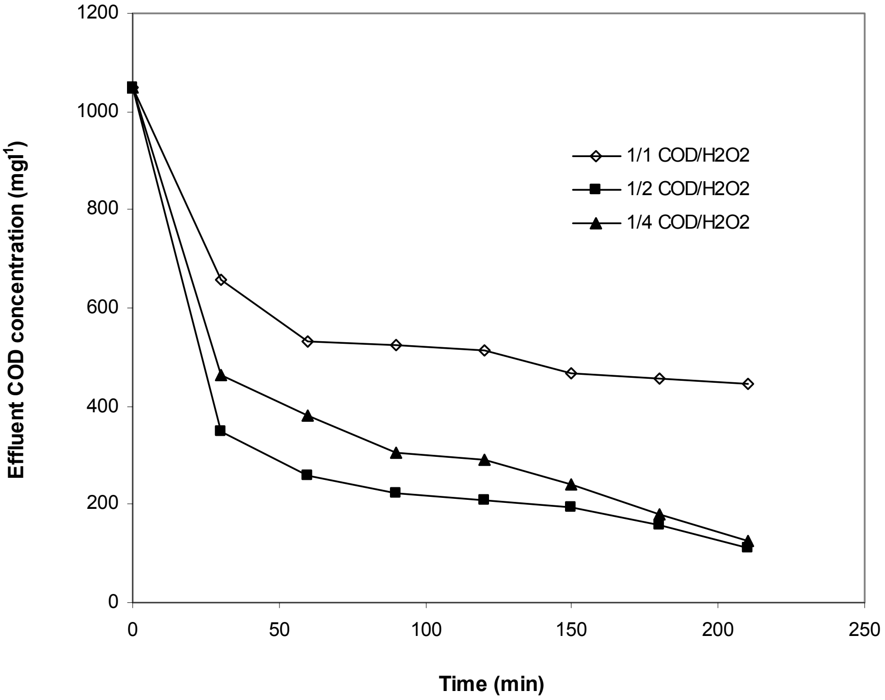

Figure 6. Variation of effluent COD concentrations with time different COD/H_2O_2 ratios by UV/H_2O_2 process (pH=3, T=39-43°C, COD=1050 mg l^{-1})

Fig. 6 depicts variations of COD removal with the different COD/H_2O_2 ratios at a constant initial COD of 1050 mg l^{-1} for the reaction time of 210 min. The COD/H_2O_2 ratio (w/w) was found approximately 1/2 for maximum COD removal (initial COD:1050 mg l^{-1}). No improvment on COD removal was obtained when higher H_2O_2 concentration was employed, as shown in Fig.6. The contribution of COD/ H_2O_2 ratio to COD removal reached 58%, 90% and 88% for the dosage ratios of COD/ H_2O_2 as 1:1, 1:2 and 1:4, respectively. As seen from fig.6, at 1050 mg l^{-1} H_2O_2, COD removal was 58% and it increased to 90% when H_2O_2 was raised to 2100 mg l^{-1} due to increase in the formation of $OH^{\bullet}$. Further increase in H_2O_2 dosage (4200 mg l^{-1}) lead to the decrease of COD removal efficiency (88%). Excessive amounts of H_2O_2 could be attributed to the formation of much less powerful $HO_2^{\cdot}$ radicals.

As a result in this study, efficiency of the UV/H_2O_2 process for COD removal is dependent on initial wastewater pollution strength or dilution of wastewater, hydrogen peroxide concentration and reaction time. It was found that the oxidative ability of UV/H_2O_2 (55%) is less than that of the $UV/Fe^{+2}/H_2O_2$ (81%) process alhough both processes destroy 80% diluted wastewater (COD/H_2O_2=1/2 w/w).

Fenton's reagent commonly requires a relatively short reaction time compared with other AOPs. Thus, Fenton's reagent is frequently used when a high reduction of COD is required (San Sebastian *et al.*, 2003). Bubling was observed in all trials and a rapid boil was observed for tests using higher reagent concentrations. Gas production was more intense when higher reagent concentrations were used.

4. CONCLUSIONS

The degradation of wastewater from oil recovery industry was investigated by the Fenton, photo Fenton and UV/H_2O_2 processes. The COD removal efficiency was strongly affected by many factors such as the concentration of H_2O_2, Fe^{+2} and the ratio of organic materials to the Fenton reagents.

The optimum operating conditions of the Fenton oxidation process involve 200.52 mg l^{-1} H_2O_2, 23.16 mg l^{-1} Fe^{+2}, 21000 mg l^{-1} initial COD and 60 min of treatment time. Under these conditions, the COD removal efficiency was observed to be 86 %.

The optimum operating conditions for the photo Fenton oxidation of wastewater was carried out at the given operating conditions (pH3 ± 0.1, Fe^{+2}: 50 mg l^{-1} and H_2O_2: 8400 mg l^{-1}, T: 39-43 ^{o}C). The optimal ratio H_2O_2/Fe^{+2} (w/w) was 168, which produced a COD removal of 81% for 80% diluted wastewater (COD_o: 4200 mg l^{-1}).

As a result of this study, a low COD removal efficiency (39 %) was found for the photo treatment process (UV/H_2O_2) without dilution of wastewater. In addition, more COD was removed at higher COD strengths than lower COD with the same mass ratio ($COD/2\ H_2O_2$) though COD removal efficiency decreased with initial COD.

ACKNOWLEDGEMENTS

The authors wish to thank the Diktaş Oil Factory for the supporting this study (Çorlu-Tekirdağ-Turkey).

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