Applicability of Fenton and photo-Fenton Processes to Combined Industrial and Domestic Wastewater

A. Arslan* **and B. Öztürk**
University of Kocaeli, Department of Environmental Engineering,
41380 Kocaeli, Turkey

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The applicability of Fenton and photo-Fenton processes as a pretreatment stage to combined wastewater was investigated. The wastewater was obtained from the inlet of the aeration tank in 42 Evler industrial and domestic wastewater treatment plant. The effects of different process variables such as initial Fe^{2+} ($c_0 = 8-33$ mmol L^{-1}) and H_2O_2 ($c_0 = 65-165$ mmol L^{-1}) concentrations, pH (3−7.75) and reaction time ($t = 5-180$ min) were evaluated. The Fenton process was investigated which under the operating conditions (pH 3, $c_{Fe^{2+}} = 12$ mmol L^{-1}, $c_{H_2O_2} = 130$ mmol L^{-1}) 100 % color and 44 % total organic carbon (TOC) removal were achieved. However, 71 % TOC removal was achieved at pH 7.75 by coagulation but color was poorly removed ($c = 20$ mmol L^{-1} Fe^{2+}, $c = 165$ mmol L^{-1} H_2O_2). In the photo-Fenton process, 84 % TOC and 87 % color removal were achieved in 30 min reaction time (pH 3, $c_{Fe^{2+}} = 26$ mmol L^{-1}, $c_{H_2O_2} = 130$ mmol L^{-1}).

Key words:
Fenton, photo-Fenton, advanced oxidation processes, industrial wastewater

Introduction

Advanced oxidation processes (AOPs) are the oxidative degradation processes for organic compounds dissolved or dispersed in aquatic media by catalytic, chemical and photo-chemical methods. These processes rely on the generation of organic radicals produced either by photolysis of organic substrate or by reaction with hydroxyl radicals.[1] Among AOPs, Fenton's reagent has been used as a chemical process for the treatment of different industrial wastewaters, including the preoxidation of pharmaceutical wastewaters,[2–3] the treatment of landfill leachate,[4] the degradation of phenol[1] and p-chlorophenol,[5] decoloration and oxidation of textile dyes[6–9] the treatment of textile effluents[10] and the treatment of olive-oil mills wastewater.[11]

The basic mechanism of the Fenton treatment process consists of chemical oxidation and chemical coagulation of organic compounds. The completion of the oxidation is dependent on the ratio of hydrogen peroxide to organic while the rate of oxidation is determined by the initial iron concentration and temperature.[12] The high removal efficiencies of Fenton process can be explained by the formation of strong hydroxyl radical (OH•) and oxidation of Fe^{2+} to Fe^{3+}. The Fenton process has dual function because the Fe^{2+} and Fe^{3+} ions are coagulants. Moreover, iron is a highly abundant and non-toxic element, and hydrogen peroxide is easy to handle environmentally.[13]

The photo-Fenton process ($H_2O_2/UV/Fe^{2+}$) is also an advanced oxidation process. This process involves the hydroxyl radical (HO•) formation in the reaction mixture through photolysis of hydrogen peroxide (H_2O_2/UV) and Fenton reaction (H_2O_2/Fe^{2+}).[14]

Successful applications of the photo-Fenton process include treatment of wastewaters contaminated with diesel,[15] the degradation of a textile biocide[16] and formaldehyde.[17]

It was reported[11] that, besides the oxidation carried out by the hydroxil radicals generated by catalytic decomposition of H_2O_2, the iron(III) ions generated during the oxidation stage promote the removal of other pollutants by coagulation and sedimentation.

Twenty different pretreated industrial wastewaters (i.e. tires, fermentation, drugs) are canalized to the combined biological treatment plant in İzmit. Also, 5 % of total flow is raw domestic wastewater. This wastewater mixture is not treated effectively in the biological system. The characterization and biological treatability of this wastewater mixture was studied previously by Arslan and Ayberk.[18] The major fraction of chemical oxygen demand (COD) in this wastewater is slowly biodegradable organic matter. Hence, chemical pretreatment is required prior to the biological system for increasing the rate of hydrolysis period. In our previous studies, color removal and improvement of biodegradability was investigated in the influent of the same plant by application of the photocatalytic oxidation process.[19]

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* Corresponding author

In this study, the oxidation of the organic compounds present in the combined wastewaters was investigated by using Fenton and photo-Fenton processes. However, there have been few studies in the literature regarding the Fenton and photo-Fenton processes conducted at neutral pH.[20] The behaviour of processes was evaluated under acidic and neutral conditions.

Materials and methods

The wastewater used in this research was the influent of the 42 Evler Combined Wastewater Treatment Plant. COD, TOC and absorbance analyzes were perfermed in order to establish the efficiency of Fenton and photo-Fenton processes. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (H_2O_2, $\varphi = 30$ %) were used as the source of hydroxil radicals. The pH was adjusted by addition of concentrated sulfuric acid (H_2SO_4; Merck) and $c = 1$ mol L^{-1} sodium hydroxide (NaOH; Merck). All chemical compounds were of analytical grade.

Analysis

The COD parameter was determined according to the "Close Reflux Titrimetric Methods" as given in Standard Methods.[21] TOC was measured using a procedure described in ASTM Standards D 4129-98. Prior to the COD analysis, the residual H_2O_2 was determined via molybdate-catalysed iodometric titration.[22] A CADAS 200 spectrophotometer was used to measure the absorbance (A_λ) by scanning in the wavelength (λ) range of 200 to 500 nm. Percentage of decoloration was calculated by comparing the absorbance values of wastewater after treatment to the absorbance value of the raw sample.

Experimental equipment and procedure

Experiments of the Fenton process were carried out in 500 mL beakers with a solution volume of 300 mL that consisted of rough filtrated wastewater. The Fenton process was carried out by adding various doses of $FeSO_4 \cdot 7H_2O$ and H_2O_2 with no temperature adjustment. The solution was mixed at $n = 100$ min^{-1} for 5 min, at $n = 50$ min^{-1} for 20 min, and then standstill for 60 min. The supernatant was filtered through Millipore AP 40 filter paper with $d_p = 0.45$ μm pore diameter. All the formed flocs settled out of the wastewater by natural sedimentation and the quantity of sludge was determined by drying at $\theta = 105$ °C after dewatering.

In the photo-Fenton process, a Plexiglas reactor equipped with 4 low pressure mercury 15 W (total 60 W) lamps emitting UV-C light at $\lambda = 253.7$ nm and placed into a quartz sleeve housing was used throughout the experiments. The reaction solution ($V = 2000$ mL) was vigorously mixed from the bottom of reactor by using a magnetic stirrer at $n = 300$ min^{-1}.

Results and discussion

In present research, two samples were collected from the inlet of the aeration tank at different times. The characteristics of studied wastewater are shown in Table 1. Treatability studies by Fenton and photo-Fenton processes have been investigated. Mineralization and decoloration of wastewater were evaluated by TOC, COD and absorbance analysis. All experiments were run at pH 3 ± 0.20 and original pH (7.75) of wastewater. Fenton and photo-Fenton processes were considered as a pretreatment step in this study. It can be economic to study at original pH of wastewater instead of adjusting the pH.

Table 1 – *Characteristics of the raw wastewater*

Parameter	Sample 1	Sample 2
COD, γ/mg L^{-1}	464	669
TOC, γ/mg L^{-1}	134	171
absorbance, A_λ	3.882	3.927
pH	7.75	7.56

Experimental study of Fenton process

Efficiency of degradation

In order to determine the role of initial Fe^{2+} concentrations on Fenton oxidation of wastewater, serial experiments with varying concentrations of iron between 8 mmol L^{-1} and 20 mmol L^{-1} were carried out at a fixed $c = 65$ mmol L^{-1} hydrogen peroxide concentration for two pH values. Fig. 1 presents the effects of Fe^{2+} concentrations on the TOC removal. The TOC removal efficiencies obtained at original pH value of wastewater were higher than the TOC reduction at pH 3. Under the neutral conditions, Fenton oxidation was hindered. The coagulation with the formation of ferric hydroxide complex was more dominant than H_2O_2 oxidation. From Fig. 1, it can be seen that an increase of the Fe^{2+} concentration from 8 mmol L^{-1} to 20 mmol L^{-1} has increased TOC removal from 28 % to 63 % at original pH.

In the Fenton process, the effects of H_2O_2 concentration and initial pH on the TOC removal were studied for $c = 12$ mmol L^{-1} Fe^{2+} concentration

moval in Fenton process (pH 3, c = 65 mmol
H_2O_2)

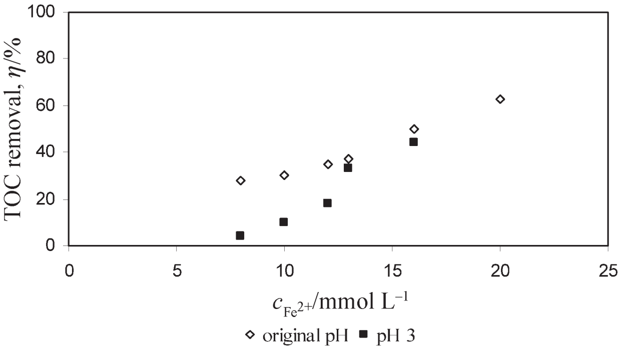

Fig. 1 – *Effect of the initial Fe^{2+} concentration on TOC removal in Fenton process ($c_{H_2O_2}$ = 65 mmol L^{-1})*

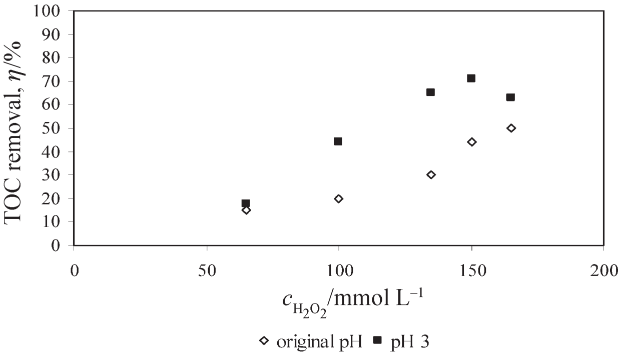

Fig. 2 – *Effects of the initial H_2O_2 concentration and pH on TOC removal in Fenton process (c = 12 mmol L^{-1} Fe^{2+})*

(Fig. 2). It was found that TOC removal efficiency increases with increasing hydrogen peroxide dose. Maximum removal efficiency was attained at H_2O_2 concentrations of c = 150 mmol L^{-1} and 165 mmol L^{-1} for pH 3 and original pH respectively. At pH 3, higher TOC removal efficiency was achived than at original pH for c = 12 mmol L^{-1} Fe^{2+} concentration. On the other hand, it was found that TOC removal efficiency increased with increasing H_2O_2 concentration up to a maximum value of η = 71 % obtained at a H_2O_2 concentration of c = 150 mmol L^{-1}. At concentrations exceeding c = 150 mmol L^{-1} H_2O_2, TOC removal decreased. If Fe^{2+} and/or H_2O_2 concentrations are overdosed •OH-scavenging reactions occur and the amount of available •OH to oxidize organic matter becomes low.[23]

For the highest TOC removal efficiency with η = 71 %, the optimum Fe^{2+} : H_2O_2 mole ratio was established as 0.125 at original pH and 0.083 at pH 3 for the Fenton process in the present study (Fig. 3). At fixed molar ratio, higher TOC removal was achieved with higher initial concentrations of Fe^{2+} and H_2O_2. When the experiment was carried out at 0.125 Fe^{2+} : H_2O_2 mole ratio, TOC removal increased from 22 % to 71 % with the increase in the concentrations of Fenton reagents.

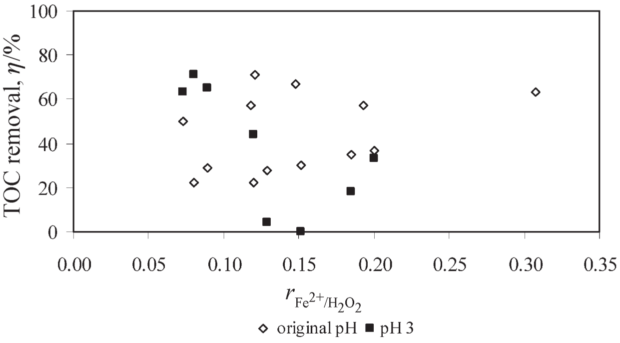

Fig. 3 – *Effect of the $[Fe^{2+}]$: $[H_2O_2]$ ratio for Fenton process*

Efficiency of color removal

The maximum absorbance of raw wastewater was observed at λ = 300 nm in an absorbance spectral scan between λ = 200−500 nm. The removal efficiencies of color were evaluated according to the absorbance values at λ = 300 nm for raw and treated wastewaters for both processes. The wavelength-absorbance scanning for raw and treated wastewater is given in Figs. 4 and 5 for original pH and pH 3.0 respectively.

The results presented in Figs. 4 and 5 demonstrate that the optimum concentration of Fe^{2+} was

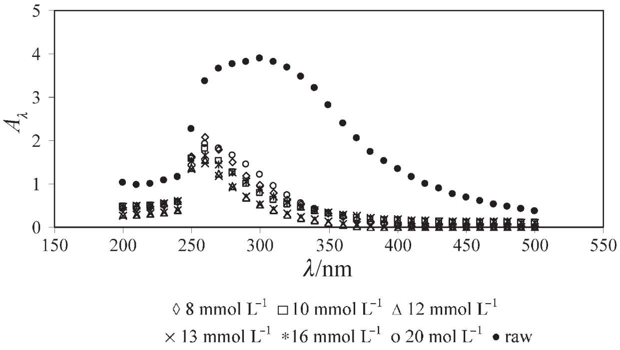

Fig. 4 – *Effect of initial Fe^{2+} concentrations on color removal in Fenton process (original pH, c = 65 mmol L^{-1} H_2O_2)*

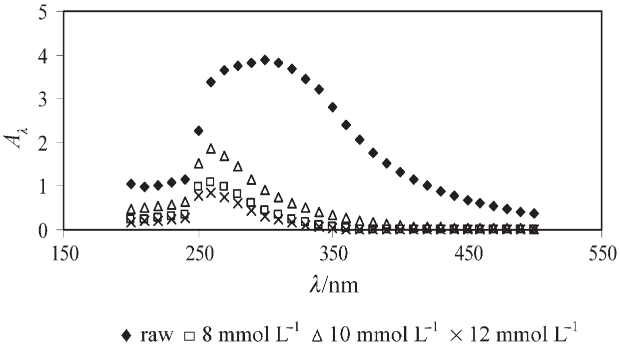

Fig. 5 – *Effect of initial Fe^{2+} concentrations on color removal in Fenton process (pH 3, c = 65 mmol L^{-1} H_2O_2)*

c = 12 mmol L^{-1} for both the original pH and pH 3, corresponding to 87 % and 92 % color removal, respectively. For the optimum concentration of Fe^{2+}, Fenton experiments were carried out to define effectiveness of the experimental conditions for different initial H_2O_2 concentrations (Fig. 6).

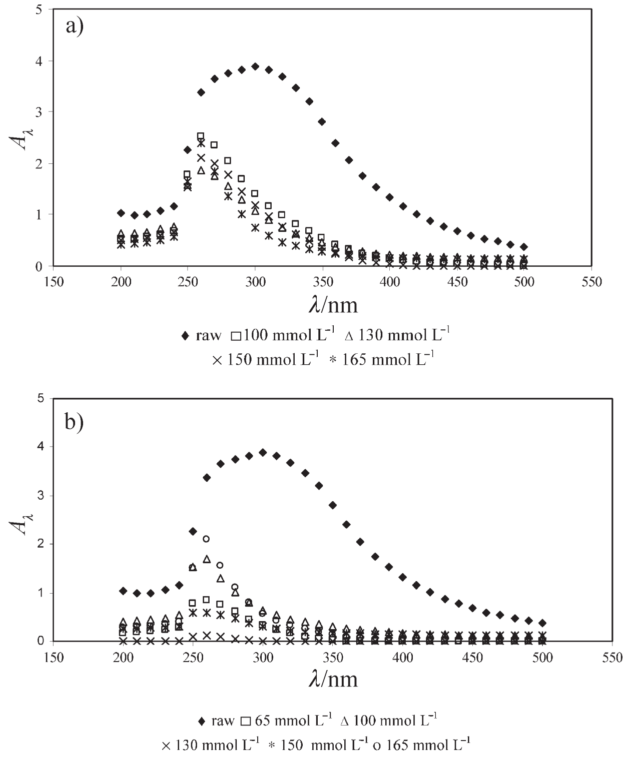

Fig. 6 – *Effect of H_2O_2 dosage on color removal in Fenton process at c = 12 mmol L^{-1} Fe^{2+} concentration (a) original pH (b) pH 3*

In the Fenton studies carried out with initial concentrations of c = 12 mmol L^{-1} Fe^{2+} and c = 130 mmol L^{-1} H_2O_2, 72 % and 100 % color removal were achieved for original pH and pH 3 respectively. Without pH adjustment for the neutral wastewater, 28 % sacrifice might be more worthwhile by operating the Fenton process at pH 7.75 instead of operating it at pH 3.

Chemical sludge

The quantity of chemical sludge produced from the Fenton process is shown in Table 2. Although the quantity of formed sludge in the process varied with the concentrations of used Fe^{2+} and H_2O_2, it was γ = 10 g L^{-1} as mean value for optimum concentrations. Benatti *et al.*[12] showed that the optimization of COD removal led to minimal formation of iron sludge that has to be removed after treatment.

Table 2 – *Chemical sludge formed during the Fenton process*

$c_{Fe^{2+}}$/mmol L^{-1}	$c_{H_2O_2}$/mmol L^{-1}	pH	sludge, γ/g L^{-1}
8	65	7.75	6.34
12	65	7.75	9.02
13	65	7.75	6.50
13	100	7.75	9.46
13	135	7.75	9.99
13	150	7.75	8.94
13	165	7.75	8.75
20	135	7.75	19.70
26	135	7.75	14.76
33	135	7.56	15.80
8	65	3	7.79
12	65	3	5.31
13	65	3	7.14
12	100	3	9.46
12	135	3	8.84
12	150	3	14.79
12	165	3	16.30

Experimental study of photo-Fenton process

Efficiency of degradation

The efficiency of photo-Fenton process as a pretreatment step of combined wastewater was investigated. The effects of pH and irradiation time were studied. Control samples were also conducted without Fe^{2+} addition. Fig. 7 presents the efficiencies of COD removal for sample 1 in the presence of c = 26 mmol L^{-1} Fe^{2+} and 130 mmol L^{-1} H_2O_2. The experimental results obtained from the photo-Fenton process show that a major part of the oxidation reaction was completed in the first 5 minutes. At pH 3,

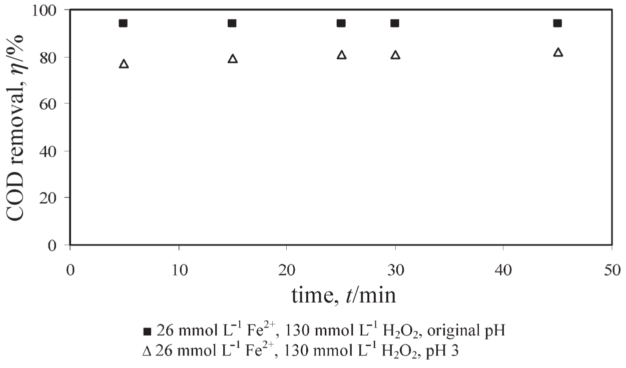

Fig. 7 – *Effect of the initial pH value on the COD removal efficiency for sample 1*

the maximum removal efficiency (η = 77 %) was achieved within 5 min. For sample 2, the photo-Fenton treatment was carried out at pH 3, with c = 26 mmol L^{-1} Fe^{2+} and c = 130 mmol L^{-1} H_2O_2 (Fig. 8). Under these operating conditions, the maximum COD removal efficiency was 97 % after t = 150 min treatment. Due to the sample 2 being stronger than sample 1, the oxidation of wastewater was completed with extended treatment time.

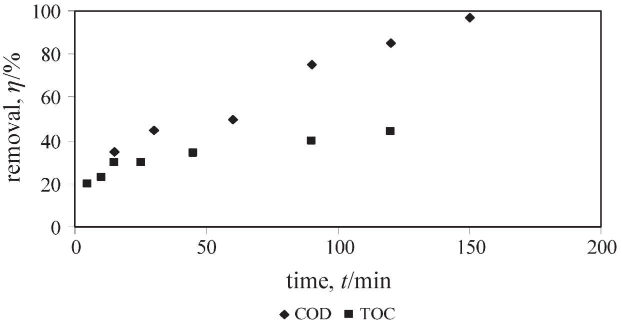

Fig. 8 – *Removal efficiencies of COD and TOC for sample 2 (pH 3, c = 26 mmol L^{-1} Fe^{2+} and 130 mmol L^{-1} H_2O_2)*

Efficiency of color removal

The photo-Fenton process was conducted to evaluate its applicability on the decoloration of combined wastewater as was the Fenton process. The wavelength-absorbance scanning for raw and treated wastewater is given in Fig. 9 for pH 3.0.

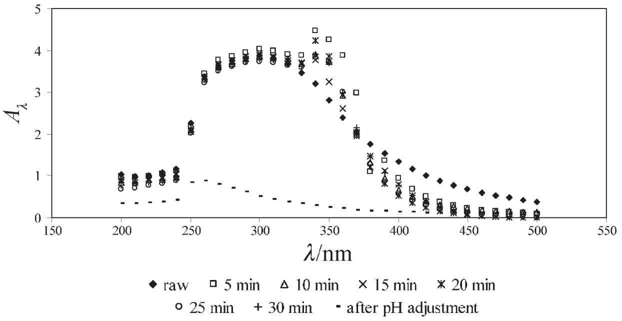

Fig. 9 – *Wavelength-absorbance scanning for sample 1 in photo-Fenton process (pH 3, c = 26 mmol L^{-1} Fe^{2+}, c = 130 mmol L^{-1} H_2O_2, t = 30 min)*

As discernable from Fig. 9, 87 % of color removal was obtained at pH 3 after 30 min. This indicates that the pH value affects the amount of HO·formed through the photo-Fenton process. Fig. 10 shows the wavelength-absorbance scanning for sample 2.

Under the acidic conditions, the maximum color removal was 86 % in 120 min. This reaction time was 4 times longer than with sample 1.

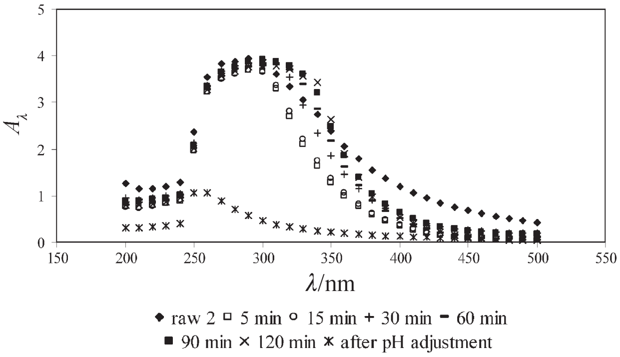

Fig. 10 – *Wavelength-absorbance scanning for sample 2 (pH 3, c = 26 mmol L^{-1} Fe^{2+}, c = 130 mmol L^{-1} H_2O_2, t = 120 min)*

Conclusions

The Fenton experiments conducted at original pH value of wastewater showed that coagulation played a more important role than oxidation. The color removal was achieved with oxidation, but the removal of organic matter was achieved by coagulation in Fenton treatment. In the Fenton process, optimum Fe^{2+} and H_2O_2 concentrations to achieve the highest TOC removal efficiency (η = 71 %) have been established as c = 12 and 150 mmol L^{-1} at pH 3, c = 20 and 165 mmol L^{-1} at original pH respectively. In addition, 100 % color removal was achieved at pH 3 with concentrations of c = 12 mmol L^{-1} Fe^{2+} and c = 130 mmol L^{-1} H_2O_2. The best treatment results were obtained with the Fenton process, under the given operating conditions (pH 3, $c_{\mathrm{Fe}^{2+}}$ = 12 mmol L^{-1}, $c_{\mathrm{H_2O_2}}$ = 150 mmol L^{-1}). Under these conditions, 92 % color removal and 71 % decrease in TOC was achieved. For the photo-Fenton process, 87 % color and 82 % COD removal was obtained under the experimental conditions; at pH 3, with c = 26 mmol L^{-1} Fe^{2+} and c = 130 mmol L^{-1} H_2O_2 in 30 min.

According to the experimental results, each process has its optimum performance at different pH values. Especially for color removal, the photo-Fenton process must be run under acidic pH values. According to Kang *et al.*[14] the optimal pH range for the photo-Fenton removal of color can be controlled at 3–5.

Fenton and photo-Fenton processes can be applied to the pretreatment of such combined wastewaters. The investigations should be continued on the cost effectiveness of the processes.

Nomenclature

TOC – total organic carbon
COD – chemical oxygen demand
AOPs– advanced oxidation processes

A_λ – absorbance
c – concentration, mmol L^{-1}
d_p – pore diameter, μm
n – stirring speed, min^{-1}
r – mole ratio
t – time, min
V – volume, L
γ – mass concentration, g L^{-1}
η – efficiency, %
θ – temperature, °C
λ – wavelength, nm
φ – volume fraction, %

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