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# $H_2O_2/UV-C$ and $Fe^{2+}/H_2O_2/UV-C$ treatment of a commercial naphthalene sulphonate (H-acid)

# G. Tureli, B.H. Gursoy, T. Olmez-Hanci\*, I. Arslan-Alaton

Istanbul Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, 34469 Maslak, Istanbul, Turkey Tel. +90 212 285 65 79; email: tolmez@itu.edu.tr

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### ABSTRACT

The high solubility, polarity and recalcitrant nature of naphthalene sulphonates render their treatment by conventional physicochemical and biological methods a rather difficult task. The present study aimed at investigating the treatability of a commercially important naphthalene sulphonate, e.g. H-acid, using H,O,/UV-C and Fe<sup>2+</sup>/H,O,/UV-C photochemical oxidation processes. The H<sub>2</sub>O<sub>2</sub>/UV-C process was capable of 100% H-acid, 48% COD and 27% TOC removals 180 min under the experimental conditions of 468 mg/l initial COD, 60 mM initial H<sub>2</sub>O, concentration and an initial pH of 5.9-6.0. A steady increase in the average oxidation state throughout the photochemical reaction revealed that more oxidized organic intermediates were formed during H<sub>2</sub>O<sub>2</sub>/UV-C treatment of H-acid. The effect of initial H<sub>2</sub>O<sub>2</sub> concentration on H<sub>2</sub>O<sub>2</sub>/ UV-C treatment efficiency was examined by conducting experiments at varying initial H<sub>2</sub>O<sub>2</sub> concentrations up to 200 mM. An initial H<sub>2</sub>O<sub>2</sub> concentration of 150 mM appeared to be the optimum where the highest rate constants and removal efficiencies were obtained in terms of H-acid, COD and TOC abatements. Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-C oxidation of H-acid was appreciably faster than the H<sub>2</sub>O<sub>2</sub>/UV-C process causing a significant increase in the organic carbon (COD, TOC) removal efficiency when Fe<sup>2+</sup> was applied as the photocatalyst. For the Photo-Fenton process carried out in the presence of 1.0 mM Fe2+, 96% H-acid removal was achieved in only 10 min, while 92% COD and 85% TOC abatements were attained after 60 min photochemical treatment (experimental conditions: initial COD = 463 mg/l; initial H<sub>2</sub>O<sub>2</sub> = 30 mM and initial pH =  $3.0 \pm 0.1$ ). Photo-Fenton degradation kinetics established on the basis of initial H-acid, COD and TOC abatement rates as well as treatment efficiencies followed the decreasing order of  $Fe^{2+}/H_2O_2/$ UV-C (1.0 mM Fe<sup>2+</sup>) > Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-C (0.2 mM Fe<sup>2+</sup>) > H<sub>2</sub>O<sub>2</sub>/UV-C.

*Keywords:* Naphthalene sulphonates; H-acid; Photochemical advanced oxidation process; H<sub>2</sub>O<sub>2</sub>/ UV-C; Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-C; Average oxidation state

#### 1. Introduction

Naphthalene sulfonates (general molecular structure: R-SO<sub>3</sub>H) are being frequently used as precursors for the production of sulfonated textile dyes, wetting

\*Corresponding author.

agents, dispersants, optical brighteners, pesticides, ion exchange resins, pharmaceuticals and concrete plasticizers [1]. Most of these chemicals are biologically-difficult-to-degrade, even completely refractory organics having potentially toxic and carcinogenic effects on aquatic organisms [1,2]. Some naphthalene sulphonates are strong acids ( $pK_a$  values < 1)

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possessing low octanol-water partition coefficients  $(K_{ow} = -0.94)$ . Hence, they are very soluble in water [2,3]. They are hardly degraded in conventional treatment systems, thus easily discarded into the aquatic environment and do not significantly degrade/adsorb on biosludge and/or soil sediments [4]. Concentration of naphthalene sulphonates in European river and surface waters have been determined in the range of 2–3500 ng/1[3], whereas their concentration in industrial wastewater treatment plants, sewage treatment works receiving industrial wastewater bearing these chemicals is much higher, in the mg/l range [2]. H-acid (1-amino-8-hydroxynaphthalene-3, 6-disulfonic acid), one of the most extensively produced, commercially important naphthalene sulphonates, has a critical economic importance in textile azo dye manufacturing activities [5-7]. Production of H-acid has been recently limited since its discharge into receiving water bodies has led to serious environmental pollution problems in the main providing countries such as China and India [8,9]. In order to minimize the environmental risks arising from the production, use and discharge of several naphthalene sulphonate types, development of alternative, efficient treatment methods to eliminate them has become a priority issue [10]. More recent studies indicated that advanced oxidation processes (AOPs), involving the production of strongly oxidizing agents (free radicals such as HO<sup>•</sup>) that react rapidly and almost non-selectively with most inorganic and organic compounds, might be a good alternative for treating recalcitrant and/or toxic pollutants, including biologically-difficult-to-degrade dye intermediates [11]. Specially, photochemically induced AOPs have gained major attention due to their superior performance in organic carbon removal (mineralization) amongst others [12]. On the other hand, as far as we are concerned only one single study is available in the related scientific literature dealing with the photochemical degradation of aqueous H-acid [1].

Considering the above mentioned facts, the present work aimed at investigating the treatability of the commercial naphthalene sulphonate H-acid with H2O2/ UV-C and Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-C (Photo-Fenton) AOPs. In the first part of the study, treatment performance of the H<sub>2</sub>O<sub>2</sub>/UV-C process was evaluated in terms of parent compound (H-acid), COD and TOC removals. The effect of initial H<sub>2</sub>O<sub>2</sub> concentration on treatment efficiency was examined in detail and reaction kinetics was defined. In the s part of the study, Photo-Fenton oxidation of aqueous H-acid was performed at two different initial Fe<sup>2+</sup> concentrations. Treatment efficiencies and reaction kinetics were comparatively evaluated for H-acid degradation with the H<sub>2</sub>O<sub>2</sub>/UV-C and Fe<sup>2+</sup>/  $H_{0}O_{0}/UV-C$  processes to decide for the technically and economically more attractive treatment solution.

#### 2. Materials and methods

#### 2.1. Materials

#### 2.1.1. Aqueous H-acid solution

The commercial-grade H-acid (molecular formula:  $C_{10}O_7H_9NS_2$ ; molecular weight: 319 g/mol; 0.86 mg COD/ mg H-acid; 0.27 mg TOC/mg H-acid) was supplied by a local dye manufacturing plant [13] and used as received without any further purification. Aqueous H-acid solutions were prepared prior to each experiment with distilled water to attain a COD value of approximately 450 mg/l, considering typical textile dye manufacturing wastewater having a COD value in the range of 400–500 mg/l [14,15]. The original pH of 523 mg/l aqueous H-acid solution corresponding to 450 mg/l COD was 5.9–6.0.

# 2.1.2. Other chemicals

H<sub>2</sub>O<sub>2</sub> was purchased from Fluka as a 35% w/w stock solution. Fe<sup>2+</sup> catalyst source was freshly prepared prior to each experiment to prevent its oxidation to Fe<sup>3+</sup>. The source of Fe<sup>2+</sup> catalyst in the Photo-Fenton reaction was FeSO, 6H, O and was also obtained from Fluka. The aqueous Fe2+ source of the Photo-Fenton process was prepared in distilled water to obtain a 10% w/v stock solution. Residual/unreacted H2O2 was immediately destroyed with enzyme catalase (type: Micrococcus lysodeikticus; 100181 U/ml; Fluka grade) to quench the reaction and prevent positive interferences of H<sub>2</sub>O<sub>2</sub> with COD analyses. HNO3 and NaOH (Merck grade) solutions were prepared at different concentrations (normalities) for pH adjustment at any stage of the experiments. The mobile phase used in the HPLC measurements was analytical grade acetonitrile (Merck).

# 2.2. Photo-reactor and photochemical oxidation experiments

The H<sub>2</sub>O<sub>2</sub>/UV-C and Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-C treatment experiments were conducted at room temperature  $(20 \pm 2 \text{ °C})$  in a 3250 ml-capacity batch stainless steel photoreactor (length = 84.5 cm; width = 8 cm) equipped with a 40 W low-pressure, mercury vapor sterilization lamp that was located at the center of the reactor in a quartz glass envelope. No cooling was provided in the photoreactor, since a low pressure UV-C lamp was employed causing no rise of reaction temperature. The incident photon flux and effective light path length of the UV-C lamp were both determined via H<sub>2</sub>O<sub>2</sub> actinometry [16] at 254 nm as  $1.6 \times 10^{-5}$  einstein  $l^{-1}$  s<sup>-1</sup> and 5.1 cm, respectively. The H<sub>2</sub>O<sub>2</sub>/UV-C experiments were conducted at pH = 5.9-6.0 that is a typical pH value of textile dye manufacturing wastewater [13,14]. After H<sub>2</sub>O<sub>2</sub> addition, the reaction solution was fed to the photoreactor by means of a peristaltic pump and was continuously circulated through the photoreactor at a rate of 400 ml/min with the same pump throughout the whole experiment. After the sample t = 0 was taken, the reaction was initiated by turning the UV-C lamp on. Samples were taken at certain time intervals (i.e. 5, 10, 15, 20, 25, 30, 40, 50, 60, 80, 90, 100, 120, 150 and 180 min) for analyses of H-acid, COD, TOC, pH and residual H<sub>2</sub>O<sub>2</sub>. In case of Photo-Fenton experiments, after adjusting the pH of the H-acid solution to an initial value of  $3.0 \pm 0.1$ , e.g. the optimum pH of Fenton and Photo-Fenton oxidation processes [17], Fe<sup>2+</sup> catalyst was added. In order to eliminate the effect of the direct/dark Fenton reaction on the Photo-Fenton process, the other reactant (oxidant H<sub>2</sub>O<sub>2</sub>) was added right before to the reaction solution was totally delivered to the photoreactor by the peristaltic pump. As the whole reaction solution was fed into photoreactor, the UV-C lamp was turned on and the Photo-Fenton reaction was initiated. During the Photo-Fenton experiments, sample aliquots were taken at the time intervals t = 0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60, 80, 90, 100,120, 150 and 180 min. The UV-C doses corresponding to the above mentioned photochemical treatment periods were calculated in terms of kWh (lamp power x treatment time) divided by m<sup>3</sup> of H-acid solution (reactor volume).

#### 2.3. Analytical procedures

The sample aliquots taken at t = 0 min and during the H<sub>2</sub>O<sub>2</sub>/UV-C and Photo-Fenton experiments were analyzed for parent compound (H-acid), COD, TOC, residual H<sub>2</sub>O<sub>2</sub> and pH parameters. The residual H<sub>2</sub>O<sub>2</sub> and pH values were measured immediately, whereas H-acid, COD and TOC parameters were analyzed after pH-adjustment to around 7 to remove Fe ions via Fe(OH), precipitation and attain the most suitable pH before catalase addition for residual H<sub>2</sub>O<sub>2</sub> decomposition. After precipitation of the samples at pH 6-8, the supernatant was removed by filtering through 0.45 micron Millipore filters. The amount of H-acid in the reaction samples was monitored by high-performance liquid chromatography (HPLC, Agilent 1100 Series, USA) equipped with a Diode-Array Detector (DAD) detector (G1315A, Agilent Series) and an Atlantis C18 ( $3.9 \times 150$  mM,  $5 \mu$ M, Waters) column, at 358 nm. Acetonitrile-water solution (60:40, v/v) was employed as the mobile phase at a flow rate of 1 ml/min. The quantification limit for H-acid analysis by the chosen method was 1 mg/l. COD of the samples was determined by the closed reflux titrimetric method according to ISO 6060 [18] and TOC was measured on a Shimadzu  $V_{CPN}$ model carbon analyzer equipped with an autosampler. The pH was measured with a Thermo Orion model 720 pH-meter at any stage of the experiments.

# 3. Results and discusion

3.1. Effect of UV-C dose on H<sub>2</sub>O<sub>2</sub>/UV-C process

In the  $H_2O_2/UV$  system, highly reactive hydroxyl radicals (HO<sup>•</sup>) are produced by the direct UV photolysis of  $H_2O_2$  (at  $\lambda = 200-280$  nm) as displayed by Reaction 1 [19].

$$\begin{array}{c} \mathrm{H_2O_2} + \mathrm{hv} \rightarrow 2 \ \mathrm{HO^{\bullet}} \\ \Phi_{254} \ \mathrm{(quantum yield at 254 \ nm)} = 1.0 \end{array} \tag{1}$$

The generated HO<sup>•</sup> non-selectively and quickly attacks most of the organic compounds resulting in oxidative reactions in the following order; addition, ring rupture, carboxylation and mineralization reactions.

The efficiency of the oxidative process can be evaluated by the average oxidation state (AOS) parameter, which can be used to estimate oxidation in a complex solution consisting of the initial substances and their oxidation byproducts [20]. AOS was calculated from the ratio between COD and TOC as follows [21]:

$$AOS = 4(TOC - COD) / TOC$$
(2)

where COD and TOC are in molar units (in moles of C l<sup>-1</sup> and in moles of  $O_2$  l<sup>-1</sup> for TOC and COD, respectively). AOS is between +4 for CO<sub>2</sub>, the most oxidized state of C, and -4 for CH<sub>4</sub>, the most reduced state of C [22].

In the first part of this experimental study, effect of UV-C dose on  $H_2O_2/UV-C$  treatment of the aqueous H-acid solution was investigated at an initial  $H_2O_2$  concentration of 60 mM. H-acid, COD and TOC abatement rates and percent removals as well as the calculated AOS values have been reported in Fig. 1 (a) and (b) as a function of UV-C dose (in kWh/m<sup>3</sup>), respectively.

As it is shown in Fig. 1 (a), the rate and extent of parent compound removal was faster than the abatements in the COD and TOC parameters, which represent further stages of oxidation (mineralization). H-acid abatement by the H<sub>2</sub>O<sub>2</sub>/UV-C process could be fitted to 1st order reaction kinetics with a rate constant of 0.0178 min<sup>-1</sup>. H-acid was totally removed with the application of 25 kWh/m<sup>3</sup> UV-C irradiation, corresponding to a reaction time of 2 h. Reduction in the collective environmental parameters of COD and TOC were also assessed in order to evaluate the degree of oxidation. COD abatement followed the 1st order kinetics and the rate constant was calculated as  $k_{COD}$  = 0.0037 min<sup>-1</sup>, indicating a relatively slower removal rate as compared with the parent compound. Achieved COD reduction after exposure of 37 kWh/m<sup>3</sup> UV-C radiation (=180 min reaction time) was 48%. On the other hand, TOC abatement with H<sub>2</sub>O<sub>2</sub>/UV-C process followed the 0th order reaction kinetics with a rate constant of 0.3165 mg l<sup>-1</sup> min<sup>-1</sup>. 27% TOC removal was obtained at the end of the 180 min treatment period.



Fig. 1. Percent H-acid, COD and TOC removal efficiencies (a) as well as corresponding AOS values (b) versus applied UV-C dose for  $H_2O_2/UV$ -C treatment of H-acid. Experimental conditions:  $pH_0 = 5.9$ ;  $COD_0 = 468 \text{ mg/l}$ ;  $TOC_0 = 137 \text{ mg/l}$ ; H-acid<sub>0</sub> = 509 mg/l;  $H_2O_{2,0} = 60 \text{ mM}$ .

Increase in AOS values from -0.5 to 0.8 with the reaction time were obvious from Fig. 1 (b), indicating that more oxidized organic intermediates are formed during the H<sub>2</sub>O<sub>2</sub>/UV-C treatment of H-acid. As reported by Zapata et al. [20], formation of more oxidized organic intermediates changes the chemical nature of the reaction mixture and it is an indirect indication of the ability of the treatment to improve biodegradability. During the application of advanced oxidation processes, degradation intermediates being more toxic, inert and/or less biodegradable could be produced [23]. Based on our former related work no inhibitory/toxic oxidation products were formed throughout the course of the photocatalytic treatment of naphthalene sulphonates [24,25].

# 3.2. Effect of initial H<sub>2</sub>O<sub>2</sub> concentration on H<sub>2</sub>O<sub>2</sub>/UV-C process

 $H_2O_2/UV-C$  oxidation of aqueous H-acid solutions was carried out at different initial  $H_2O_2$  concentrations in order to investigate the effect of  $H_2O_2$  concentration on parent compound and organic matter (COD, TOC) removal rates. The studied initial  $H_2O_2$  concentration levels were chosen considering our previous photochemical treatability studies conducted with industrial pollutants having the same initial COD levels [25]. H-acid and COD abatements followed 1st order reaction kinetics at all studied  $H_2O_2$  concentrations in the experimental range, whereas TOC abatements did not fit to any reaction kinetics for most of the experiments, especially those performed at the lower initial  $H_2O_2$  concentrations, since noticeable TOC removals could not be obtained during these experiments. Determined rate constants ( $k_{H-acid}$  and  $k_{COD}$ ) were presented in Fig. 2 as a function of initial  $H_2O_2$  concentration.

As can be seen from Fig. 2, an optimum value for initial H<sub>2</sub>O<sub>2</sub> concentration (150 mM) existed, where maximum rate constants were achieved for both parent compound and COD abatements. Reaction rate constants for H-acid removal slightly increased up to a concentration of 50 mM H<sub>2</sub>O<sub>2</sub>. A rapid acceleration in the H-acid abatement rate constants was observed particularly in the range 50-100 mM H<sub>2</sub>O<sub>2</sub> and reached a peak value of 0.0236 min<sup>-1</sup> at 150 mM H<sub>2</sub>O<sub>2</sub>. 73% H-acid abatement was achieved after 120 min reaction time at an initial H2O2 concentration of 150 mM. A slight decrease in H-acid removal rate was observed when the initial H<sub>2</sub>O<sub>2</sub> concentration was increased to 200 mM. This efficiency decrease could mainly be attributed to the free radical scavenging effect of excessive H2O2 concentrations  $(H_2O_2)$  overdosing effect) which is shown in Reaction (3). This observation can be explained by the fact that an excessive amount of H2O2 will compete with the organic pollutant for the HO<sup>•</sup> [26];

$$\begin{array}{l} H_2O_2 + HO^{\bullet} \to HO^{\bullet} + H_2O \\ HO^{\bullet} = 1.2 - 4.5 \cdot 10^7 \, m^{-1} s^{-1} \end{array}$$
(3)

COD abatement rate constants showed a similar trend with H-acid abatement rate constants and reached a value of 0.0048 min<sup>-1</sup> at the optimum  $H_2O_2$  concentration of 150 mM. For this case, 45% COD reduction was



Fig. 2. H-acid and COD abatement rate constants under different concentrations of  $H_2O_2$  for  $H_2O_2/UV$ -C treatment of H-acid. Experimental conditions:  $pH_0=5.9$ ; average  $COD_0=461 \text{ mg/l}$ ; average  $TOC_0=141 \text{ mg/l}$ ; average H-acid $_0=512 \text{ mg/l}$ ; UV-C dose=37 kWh/m<sup>3</sup> corresponding to a reaction time of 180 min.

obtained after 120 min reaction time. The highest TOC removal was achieved at 150 and 200 mM initial  $H_2O_2$  concentrations as 32% after 120 min treatment.

# 3.3. Effect of $Fe^{2+}$ on $H_2O_2/UV-C$ process

The oxidation rate and efficiency of the organic pollutants can be improved with the addition of Fe<sup>+2</sup>/Fe<sup>+3</sup> to photochemical H<sub>2</sub>O<sub>2</sub>/UV oxidation system, namely by applying the Photo-Fenton advanced oxidation process. H<sub>2</sub>O<sub>2</sub> decomposition catalyzed by Fe<sup>+2</sup> or Fe<sup>+3</sup> ions generates additional HO<sup>•</sup>, as shown for Fe<sup>+2</sup> ions in Reaction (4). Under UV light irradiation ( $\lambda$  = 200-400 nm) photoreduction of Fe<sup>+3</sup> to Fe<sup>+2</sup> occurs (Reaction (5)) producing more HO<sup>•</sup> [27].

$$Fe^{+2} + H_2O_2 \rightarrow FeOH^{+2} + HO^{\bullet}$$
  $k = 76.5 \text{ m}^{-1} \text{ s}^{-1}$  (4)

$$Fe(III)OH^{+2} + h\nu \rightarrow Fe^{+2} + OH^{-} + HO^{\bullet}$$
(5)

In Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-C process, in addition to the above reactions, formation of hydroxyl radical also occurs by Reaction (1) [27].

In this part of the present study,  $Fe^{2+}/H_2O_2/UV-C$  oxidation experiments were conducted with aqueous H-acid solution at different initial  $Fe^{2+}$  concentrations at pH 3.0 ± 0.1 (which was defined as optimum pH for Photo-Fenton processes) [17]. In Fig. 3, H-acid, COD and TOC removal efficiencies were displayed for  $Fe^{2+}/H_2O_2/UV-C$  oxidation at 0.2 and 1.0 mM initial  $Fe^{2+}$  concentrations, together with the abatements obtained for  $H_2O_2/UV-C$  process. Initial concentration of  $H_2O_2$  was kept at 30 mM in these experiments.

It is clear from Fig. 3 (a) that parent compound removal rate in case of Photo-Fenton process was significantly faster than the H2O2/UV-C oxidation, as expected. For both of the studied Fe2+ concentrations, H-acid levels decreased down to below 25 mg/l, indicating more than 95% removal after an exposure to 3 kWh/m<sup>3</sup> UV-C irradiation (corresponding treatment time = 15 min). On the other hand, the remaining H-acid concentration for the same treatment period was measured as high as 360 mg/l in case of H<sub>2</sub>O<sub>2</sub>/UV-C process, corresponding to only 28% removal instead of almost complete removal observed with the Photo-Fenton oxidation process. As it is shown in Fig. 3 (b), the highest COD removal was obtained when the higher initial Fe<sup>2+</sup> concentration was selected (1.0 mM), followed by 0.2 mM Fe2+ and finally H2O2/UV-C. The difference between the observed removal efficiencies and reaction kinetics of Photo-Fenton as compared with H<sub>2</sub>O<sub>2</sub>/UV-C oxidation is moreevident in terms of the COD parameter. The Photo-Fenton treatment process performed with 1.0 mM Fe<sup>2+</sup> reduced the original COD of 468 mg/l to 37 mg/l after a UV dose of 12.3 kWh/m<sup>3</sup> (corresponding



Fig. 3. (a) H-acid; (b) COD; and (c) TOC abatements versus UV-C dose, for  $H_2O_2/UV$ -C and  $Fe^{2+}/H_2O_2/UV$ -C oxidations of H-acid. Experimental conditions:  $pH_0=2.9$ ; average  $COD_0=463$  mg/l; average  $TOC_0=140$  mg/l; average H-acid\_0 = 500 mg/l;  $H_2O_{2,0}=30$  mM. •  $H_2O_2/UV$ -C; Photo-Fenton (0.2 mM Fe<sup>2+</sup>); and Photo-Fenton (1.0 mM Fe<sup>2+</sup>).

to a treatment period of 60 min); while effluent COD values were obtained as 240 mg/l and 378 mg/l for Photo-Fenton treatment in the presence of 0.2 mM Fe<sup>2+</sup> and with  $H_2O_2/UV$ -C only, respectively. Trends in TOC abatement were found to be similar to those of COD (Fig. 3 (c)). The rate and extend of TOC removal was considerably high for the Photo-Fenton experiment carried out with 1.0 mM Fe<sup>2+</sup> as compared with the other selected oxidation systems (0.2 mM Fe<sup>2+</sup> and with  $H_2O_2/UV$ -C only). The initial TOC of 161 mg/l was reduced down to 25 mg/l after 60 min by applying 12.3 kWh/m<sup>3</sup> UV-C radiation in the presence of

Table 1 Reaction rate constants for H-acid removal and percent removal efficiencies for COD and TOC parameters

Treatment processes	$k \text{ or } k_{i}$ (min <sup>-1</sup> )	COD removal @ 60 min (%)	TOC removal @ 100 min (%)
H <sub>2</sub> O <sub>2</sub> /UV-C	0.015	18	18
Fe <sup>2+</sup> /H,O,/UV-C	0.437	48	53
(initial $Fe^{2+} = 0.2 \text{ mM}$ )			
Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /UV-C	0.443	92	87
(initial $\overline{Fe^{2+}} = 1.0 \text{ mM}$ )			

1.0 mM Fe<sup>2+</sup>. On the other hand, in case of 0.2 mM Fe<sup>2+</sup>, the same reduction could be obtained after the reaction solution was subjected to 24 kWh/m<sup>3</sup>, corresponding to approximately 120 min photochemical oxidation. In case of  $H_2O_2/UV$ -C process, the effluent TOC obtained after 120 min was found as high as 131 mg/l obviously revealing a dramatic decrease in treatment performance.

Since abatement curves representing the Photo-Fenton treatment could not be fitted well to any reaction kinetic, the majority analysis of reaction kinetics was focused on the initial reaction rates ( $r_i$ ; mgl<sup>-1</sup> min<sup>-1</sup>), derived from the slope of the response curve within the time period over the first few min of oxidation.

$$r_i = \Delta C / \Delta t \tag{6}$$

where *C* refers to the H-acid concentration (in mg/l) and *t* stands for treatment time (in min). The initial reaction rate constants ( $k_i$ ) were calculated by dividing the  $r_i$  to the initial H-acid concentration ( $C_i$ ).

$$k_i = r_i / C_i \tag{7}$$

In Table 1, 1st order reaction rate constants (*k*) obtained for  $H_2O_2/UV$ -C oxidation were provided together with the initial reaction rate constants (*k<sub>i</sub>*) calculated for the Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV-C processes, for comparison purposes. Percent COD and TOC removals were also displayed in the table, for 60th and 100th min of treatment, respectively.

#### 4. Conclusions

In the present work,  $H_2O_2/UV$ -C and  $Fe^{2+}/H_2O_2/UV$ -C (Photo-Fenton) treatment of aqueous H-acid solutions at typical azo dye production effluent loads were comparatively investigated. The effect of the initial  $H_2O_2$  concentration on  $H_2O_2/UV$ -C treatment efficiency and optimum initial  $H_2O_2$  concentration were determined considering the parent compound, COD and TOC abatement rates. Proper selection of the optimum initial

H<sub>2</sub>O<sub>2</sub> concentration appeared to be key factor to achieve highest possible treatment efficiencies for H<sub>2</sub>O<sub>2</sub>/UV-C oxidation of H-acid under the studied experimental conditions. An initial H<sub>2</sub>O<sub>2</sub> concentration of 150 mM appeared to be the optimum where the highest rate constants and removal efficiencies were obtained. Treatment performance and reaction kinetics of the H<sub>2</sub>O<sub>2</sub>/ UV-C process were improved considerably when subjecting H-acid to Photo-Fenton treatment under varying Fe<sup>2+</sup> concentrations. From the reaction rate constants it can be seen that  $Fe^{2+}/H_2O_2/UV-C$  oxidation is about 30 times faster than the  $H_2O_2/UV-C$  treatment process in terms of parent compound removal. In case of organic carbon removal a five fold enhancement was observed for Photo-Fenton oxidation of aqueous H-acid as compared to plain H<sub>2</sub>O<sub>2</sub>/UV-C treatment, emphasizing the superiority of the Photo-Fenton process for the degradation of naphthalene sulphonates.

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