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Application of Photo-Fenton-like oxidation for the degradation and detoxification of commercial naphthalene sulfonates a case study with H-acid model pollutant

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ABSTRACT

In this experimental study, the treatability of the commercially most important naphthalene sulfonate H-acid that is frequently being used as a raw material for the production of textile azo dyes with the Photo-Fenton-like (Fe^{3+}/H_2O_2/UV-A) advanced oxidation process was investigated. In the first part of the study, the above-mentioned model pollutant was subjected to Photo-Fenton treatment under different working conditions, e.g., different pH, Fe^{3+} catalyst and H_2O_2 oxidant concentrations. The treatment performance of the photocatalytic treatment process was examined on the basis of chemical oxygen demand and total organic carbon removal efficiencies. In the second part of the experimental work, untreated and Photo-Fenton-treated H-acid solutions were subjected to an activated sludge inhibition (toxicity) test using heterotrophic biomass to determine changes brought about in the acute toxicity of the naphthalene sulfonate during advanced oxidation treatment. For synthetic wastewater containing H-acid with an initial COD of 450 mg/l 82% COD and 51% TOC removals were obtained (optimized experimental conditionals: pH = 5.0; Fe^{3+} = 1.5 mM; H_2O_2 = 35 mM; reaction time = 24 min). In the case when only partial oxidation was targeted (experimental conditions: pH = 5.0; Fe^{3+} = 1.0 mM; H_2O_2 = 40 mM; reaction time = 12 min), for the same initial COD of 450 mg/l, COD and TOC abatements were obtained as 67% and 44%, respectively. Activated sludge inhibition experiments have demonstrated that no toxic advanced oxidation products were formed during Photo-Fenton oxidation.

Keywords: Advanced oxidation processes; H-acid; Naphthalene sulfonates; Photo-Fenton-like process; Activated sludge inhibition

1. Introduction

Naphthalene sulfonates (NS) are used as precursors for sulfonated azo dyes, optical brighteners, pesticides, ion-exchange resins, pharmaceuticals and concrete plasticizers. The presence of sulfonated functional groupings renders these compounds highly water-soluble, but at the same time resistant to oxidative attack by electron acceptors [1,2]. NS and their aromatic derivatives are found in river and surface waters [1,3] as well as industrial wastewater and sewage [3]. They have been detected in receiving water bodies at concentrations in the range of 20–100 µg/l [4]. However, due to their poor lipophilicity, NS are considered less dangerous than their unsulfonated analogues. Although NS exert low acute toxicity and no significant mutagenic or carcinogenic effects on the aquatic environment, their persistence and mobility in the environment due to their physical, chemical and

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transport properties (e.g., high solubility in water and low octanol-water partition coefficient) may represent a serious ecological risk. Depending their molecular structure, NS impart extreme resistance to (bio)degradation [5–7], although it has also been reported that partial degradation via specific microbial strains is possible [5]. Among NS, 1-Amino-8-naphthol-3, 6-disulfonic acid (H-acid) which is an important intermediate for the preparation of several direct, acid and reactive dyes, have great economic importance. H-acid is employed in the production of chromotrophic acid (a dyestuff intermediate), as a corrosion inhibitor and in the photography sector. Due to such diverse uses, H-acid along with its metabolites may be present at relatively high concentrations in textile/dyeing wastewater and/or dye synthesis effluent.

Conventional methods such as biological, physical and chemical processes are having several drawbacks and they are not effective for complete degradation of recalcitrant organic compounds such as H-acid [8]. So called Advanced Oxidation Processes (AOPs) are of great interest for the treatment of contaminated surface and groundwater and for the destruction of toxic and biorefractory organic pollutants found in industrial wastewaters [9]. AOPs rely on the generation of very reactive oxidizing agents, i.e., free radicals such as the hydroxyl radical (•OH). •OH can initiate oxidative degradation reactions of refractory synthetic and natural organic compounds and is capable of mineralizing them ultimately to CO_2 and H_2O owing to their high oxidation potential (+2.80 eV versus NHE) in aqueous solution. The reactions of Photo-Fenton (H_2O_2 with ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in acidic aqueous solutions), which are among the most common homogeneous systems, are potential sources of •OH generation. The use of the Fe^{3+}/H_2O_2 couple as an oxidant for wastewater treatment is attractive in many ways; iron is non-toxic, the second most abundant metal and the fourth most abundant element found in the Earth's crust and H_2O_2 is easy to handle and is environmentally being [10].

The purpose of the present study was to evaluate the effect of Photo-Fenton-like oxidation on the treatability of a NS frequently used for the production of direct and reactive azo dyes, namely H-acid. For that purpose, iterative experiments were conducted to examine the effect of different process variables playing an important role in Photo-Fenton-like oxidation (e.g., catalyst and oxidant concentrations, as well as reaction pH) on the oxidation efficiency and abatement rate of aqueous H-acid. Relative changes in the inhibitory (biotoxic) effect of H-acid degradation intermediates on heterotrophic biomass (sewage sludge) during the application of photochemical oxidation were also examined by conducting activated sludge inhibition experiments.

2. Materials and method

2.1. Materials

The commercial-grade H-acid (HA, $C_{10}O_7H_9NS_2$; MW:319 g/mol) was supplied by a local dye manufacturing plant [11] and used as received without any further purification. 35% w/w H_2O_2 (Fluka) was used as received without any dilution. The ferrous iron catalyst source was prepared for daily use by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ (Fluka), in distilled water to obtain a 10% w/v stock solution. Several concentrations of HNO_3 and NaOH (Merck) solutions were prepared for pH adjustment at any stage of the experiments. HPLC grade acetonitrile was purchased from Merck.

2.2. Photoreactor and photochemical oxidation experiments

Photo-Fenton-like oxidation (Fe^{3+}/H_2O_2/UV-A) experiments were conducted in a 100 ml capacity cylindrical pyrex glass reaction vessel. Aqueous HA solutions were daily prepared by distilled water to attain an approximate chemical oxygen demand (COD) value of 450 mg/l, considering typical textile dye manufacturing wastewater having COD in the range of 400–500 mg/l [11]. HA solution of 100 ml in reaction sample glass (batch photoreactor) was exposed to Photo-Fenton-like process by black light bulb (150 W) which emits UV-A light between 310–390 nm as well as it has maximum light emission at 360 nm. The incident light flux of the UV-A lamp was already determined as 2.6×10^{-5} einstein/min by ferrioxalate actinometry [12]. The photoreactor was located inside a box (60 × 40 × 55 cm) with its three inner sides covered by mirrors enabling efficient UV-A light distribution across the reaction vessel. The solution in photoreactor was mixed by magnetic stirrer to provide effective mixing during the reaction. To obtain fixed light emission, lamp was opened before 20 min from starting the Photo-Fenton-like oxidation experiments. After the sample including Fe^{3+} $t = 0$ was taken, the reaction was initiated by adding H_2O_2. In order to determine treatment performance of the Photo-Fenton-like process, samples were taken at regular time intervals for analyses up to 60 min and analyzed for COD, total organic carbon (TOC) and HA measurements.

2.3. Analytical procedures

The amount of HA in the reaction samples was monitored by HPLC (Agilent 1100 Series, USA) equipped with a Diode-Array Detector (DAD) detector (G1315A, Agilent Series) and a Atlantis C18 (3.9 × 150 mM, 5 µm, Waters) column, at 358 nm. Acetonitrile/water solution (60:40, v/v) was employed as mobile phase at a flow rate of 1 ml/min. The quantification limit of the instrument is 10 mg/l. Residual H_2O_2 was destroyed with enzyme catalase derived from *Micrococcus lysodeikticus* (100181 U ml^{-1}, Fluka grade) to quench the reaction and prevent positive interferences with the COD measurements. COD of the samples was determined by the closed reflux titrimetric method according to ISO 6060 [13] and TOC was measured on a Shimadzu V$_{PCN}$ model carbon analyzer. All analytical measurements were performed after filtration of the treated samples though a 0.45 µm membrane filter (Millipore) in order to remove the settled $Fe(OH)_3$ sludge. The pH was measured with a Thermo Orion model 720 pH-meter at any stage of the experiments.

2.4. Activated sludge inhibition experiments

Acute toxicity tests were conducted in accordance with a test procedure described in ISO 8192 [14] at a constant temperature of 20 ± 2 °C. The heterotrophic biomass, obtained from Paşaköy Urban Waste Water Treatment Plant and used in the activated sludge inhibition test, was daily fed with synthetic sewage prepared according to the ISO 8192 guidelines [14]. All experiments were run at a constant heterotrophic active biomass concentration of 2000 mg/l. The COD of the synthetic sewage was adjusted to 480 mg/l and used as the "readily biodegradable substrate" in the toxicity experiments. The test samples were prepared with a defined amount of treated/untreated HA solutions. The blank sample was prepared using the same amounts of activated sludge inoculum and synthetic sewage solution as the test samples. The decrease in dissolved oxygen concentration (DO, in mg/l) in the blank as well as in different dilutions of raw and pre-treated synthetic HA effluent samples was monitored for 15–180 min (incubation period) using a WTW Oxi Digi 2000 model oxygen meter. Oxygen uptake rates (OUR, expressed in mg l^{-1} h^{-1}), were calculated on the basis of the linear part of the decreasing DO concentration curves versus time. Percent inhibition of OUR, i.e., I_{OUR}, for every test and blank samples, was calculated using the following equation:

$$I_{OUR}\,(\%) = [(R_B - R_T)] \times 100/R_B \qquad (1)$$

where R_T is the OUR in the effluent sample mixture (Synthetic HA effluent + synthetic sewage) and R_B stands for the OUR in the blank sample (synthetic sewage only).

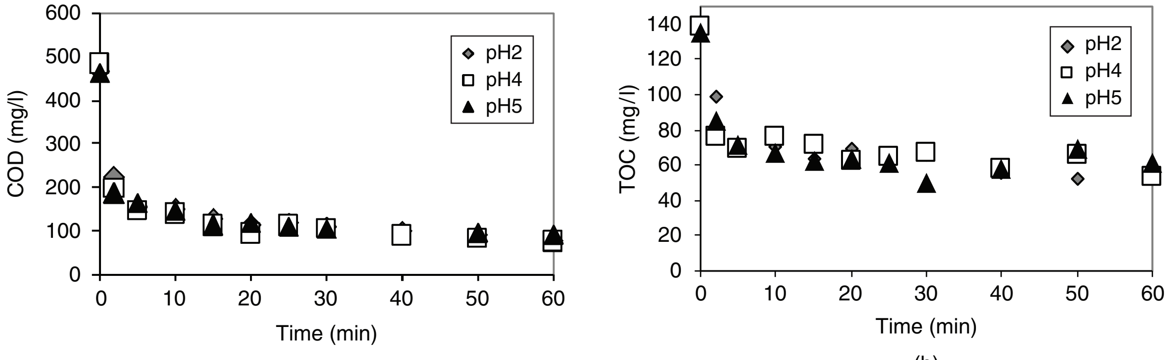
3. Results and discussion

3.1. Effect of pH

It is well known that pH has a significant effect on the performance of Fenton's reagent [15]. Fenton, Photo-Fenton and Photo-Fenton-like oxidation rates are strong function of reaction pH and being favored under acidic pH conditions (2–5) with an optimum range of pH = 2.8–3.0 [16]. The effect of pH on COD and TOC abatements during Photo-Fenton-like oxidation of synthetic HA solution having COD of 450 mg/l was examined at constant Fe^{3+} concentration of 1.5 mM and H_2O_2 concentration of 35 mM. The COD and TOC abatements by Photo-Fenton-like treatment as a function of studied pH values (2, 4 and 5) are shown in Figs. 1(a) and 1(b) respectively. As can be seen from the Fig. 1 COD and TOC abatements were not affected by the reaction pH in the range of 2–5. Hence, the less acidic and technically more feasible value of pH = 5 is recommended as the optimum pH for Photo-Fenton-like treatment of aqueous HA.

3.2. Effect of Fe^{3+} concentration

Fe^{3+} concentration has an integral role in the rate and efficiency of the Photo-Fenton reactions, since it catalyzes the decomposition of H_2O_2 to produce •OH [17]. The presence of ferric iron is important for the formation of photo-active ferri-hydroxo complexes



(a) (b)

Fig. 1. Effect of pH on COD (a) and TOC (b) abatements at pH values of 2, 4 and 5 (COD_0 = 450 mg/l; Fe^{3+} = 1.5 mM; H_2O_2 = 35 mM).

that absorb UV or even near UV-visible light. During their photoreduction additional •OH are produced, enhancing the Photo-Fenton reaction appreciably. In order to evaluate the effect of Fe^{3+} concentration on COD and TOC removal rates, Photo-Fenton-like oxidation experiments with different Fe^{3+} concentrations (0.5–3.5 mM) were carried out at a constant H_2O_2 concentration of 30 mM (Fig. 2). COD removal efficiencies increased from 68% to 80% with increasing Fe^{3+} concentration from 0.5 to 1.5 mM. COD and TOC removal efficiencies were obtained as 80% and 52%, respectively, at 1.5 mM Fe^{3+} concentration and 60 min reaction time. Further increase in Fe^{3+} concentration to 3.5 mM resulted in a slight decrease in COD removal efficiencies to 73% which may be attributed to the free radical scavenging effect of excessive (overdosed) Fe^{3+}/Fe^{2+} concentrations [18];

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad k = 3.0\times10^8\ M^{-1}s^{-1} \qquad (2)$$

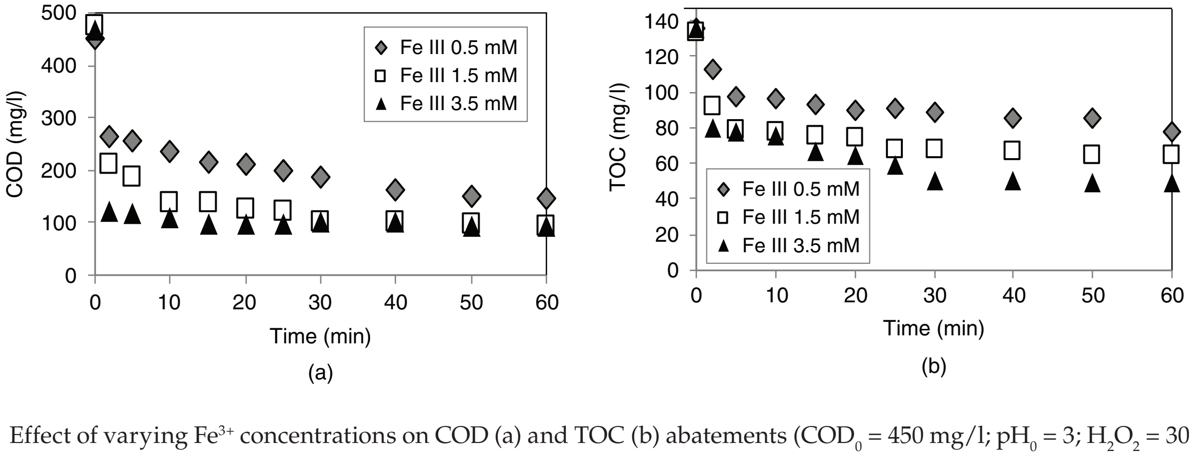
Photo-Fenton-like treatment at a concentration of 0.5 mM Fe^{3+} resulted in 42% TOC removal after a treatment time of 60 min, whereas 51% TOC removals occurred at Fe^{3+} concentrations of 1.5 mM and 3.5 mM, respectively. These results demonstrated that a further increase in the concentration of Fe^{3+} did not affect the TOC removal efficiency as expected.

3.3. Effect of H_2O_2 concentration

From the scientific literature it is well-known that the concentration of H_2O_2 directly influences the degree of oxidation and its overdosing may result in inhibitory free radical scavenging effect. Figs. 3(a) and 3(b) illustrates the effect of varying H_2O_2 (15–35 mM) concentrations upon COD and TOC abatements for an initial Fe^{3+} concentration of 1.5 mM at $pH_0 = 3$. As is obvious from Fig. 3, COD and TOC abatements increased with an increasing initial H_2O_2 concentration. The highest COD and TOC removal efficiencies were obtained as 82% and 54% at an initial H_2O_2 concentration of 35 mM, respectively, at 60 min treatment time.

3.4. Effects on toxicity (activated sludge inhibition)

Information about the toxicity of degradation intermediates as well as model compounds appears to be critical for information about the practical applicability of an AOP [19,20]. Furthermore, in most cases the final goal of AOP is to improve the biocompatibility (reduce the toxicity) of the effluent by converting inhibitory/refractory pollutants into more degradable and/or less harmful compounds. The objective of this part of the study is to assess the effect of HA and its oxidation intermediates formed during the Photo-Fenton-like treatment on bacterial communities present in the aquatic environment especially in aerobic biological treatment systems. In this respect, four sets of respirometric experiments corresponding the treatment period of 2, 6, 12, 24 min were performed. The percent of inhibition caused by oxidation intermediates formed during the Photo-Fenton-like oxidation of HA samples on heterotrophic biomass was calculated for samples treated at operational conditions of $COD_0 = 450$ mg/l, $Fe^{3+} = 1$ mM, $H_2O_2 = 40$ mM and pH = 5 for 15 min incubation period. The inhibition HA ($COD_0 = 450$ mg/l) on heterotrophic biomass respiration rate relative to a control (in our case synthetic sewage) was found as 17% indicating that the original HA is not seriously biotoxic (inhibitory) towards heterotrophic biomass. However, the toxic/inhibitory effect of oxidation intermediates also needs to be considered to judge whether photocatalytic treatment should be applied to treat HA. The percent inhibition of OUR in untreated and Photo-Fenton-like



(a) (b)

Fig. 2. Effect of varying Fe^{3+} concentrations on COD (a) and TOC (b) abatements ($COD_0 = 450$ mg/l; $pH_0 = 3$; $H_2O_2 = 30$ mM).

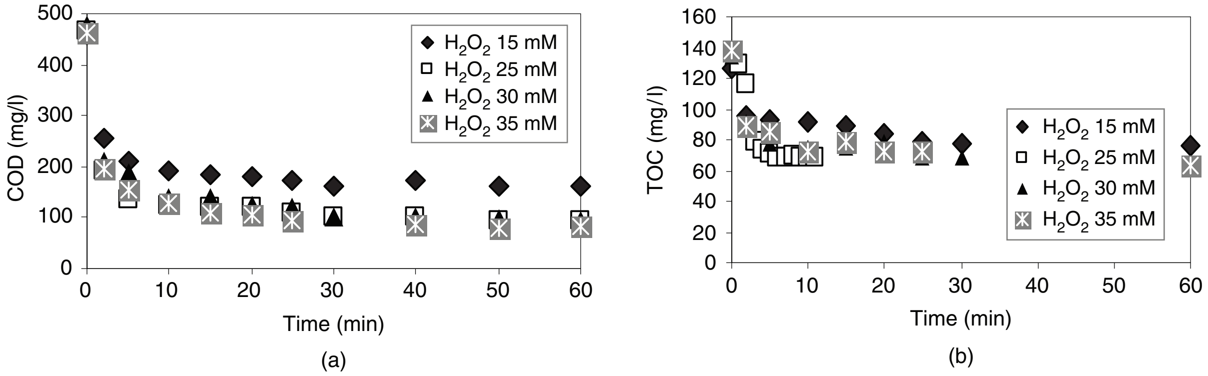


Fig. 3. Effect of varying H_2O_2 concentrations on COD (a) and TOC (b) abatements (COD_0 = 450 mg/l; pH_0 = 3; Fe^{3+} = 1.5 mM).

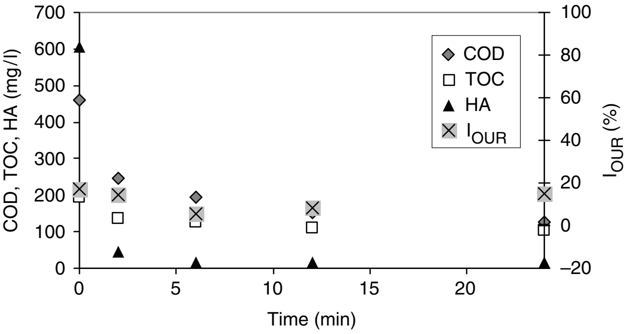


Fig. 4. Changes in I_{OUR} values as well as HA, COD and TOC abatements as a function of Photo-Fenton-like partial treatment for a 15 min activated sludge incubation time (COD_0 = 450 mg/l; pH = 5; Fe^{3+} = 1 mM; H_2O_2 = 40 mM).

treated reaction samples which were measured in parallel after an incubation period of 15 min are presented in Fig. 4. As is evident from Fig. 4, the slightly inhibitory effect of HA decreased in parallel to the decrease in COD, TOC and HA content of the effluent. HA was also measured in these experiments to assess the relationship between parent pollutant removal and changes in toxicity. The I_{OUR} value measured after for 24 min photochemically treated HA solution was 15%, while COD and TOC removals were 72% and 46%, respectively. Hence it can be concluded that no harmful oxidation intermediates were formed during Photo-Fenton-like oxidation of HA.

4. Conclusions

In this experimental study the treatability of aqueous HA, the commercially most important naphthalene sulfonate, with the Photo-Fenton-like ($Fe^{3+}/H_2O_2/$UV-A)dvanced oxidation process was investigated. In addition, the acute toxicity of raw and treated HA samples on heterotrophic biomass was evaluated. pH had no effect on COD and TOC abatements in the range of 2 to 5. For synthetic wastewater containing HA with an initial COD of 450 mg/l (Experimental conditions: pH = 5; Fe^{3+} = 1.5 mM; H_2O_2 = 35 mM; t_r = 60 min) resulted in 82% COD and 54% TOC removals, for highest treatment efficiencies. In the case when partial oxidation was targeted (Experimental conditions: pH = 5; Fe^{3+} = 1.0 mM; H_2O_2 = 40 mM; t_r = 12 min), COD and TOC abatements were obtained as 67% and 44%, respectively. Furthermore, activated sludge inhibition test revealed that photochemically treated HA solution did not exert a significant inhibitory effect during and at the end of advanced oxidation with the Photo-Fenton-like process. In the other words, oxidation intermediates or end products produced were not significantly inhibitory/toxic to heterotrophic biomass. In conclusion, Photo-Fenton-like oxidation is an efficient process for the fast removal of refractory HA from wastewater bearing this pollutant.

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