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Implementation of fluidized-bed Fenton as pre-treatment to reduce chemical oxygen demand of wastewater from screw manufacture: Influence of reagents feeding mode

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ABSTRACT

Advanced oxidation processes (AOPs) are promising technologies to mineralize organic pollutants and reduce chemical oxygen demand (COD) from water effluents. Unfortunately, treatment of real industrial effluents is barely reported in literature and actual application is rare. One of the technology transfer limitations is associated to the identification of the most suitable stage for AOPs implementation in existing water treatment facilities of industry manufacturers. Here, we report a complete study where the most suitable stage for Fenton treatment implementation for a screw manufacture industry water treatment facility is identified. Actual wastewater effluent was collected, characterized and treated by means of Fluidized-bed Fenton (FBF) treatment to reduce COD levels. Fenton's reagents feeding mode is evaluated to better understand influence on continuous flow operational FBF performance and efficiency.

1. Introduction

Industrial manufacturing processes produce complex polluted water matrices. In order to protect our environment, generated effluents must be treated to reduce the hazardous, toxic and health impact to ecosystems and living beings. Providing clean water and sanitation is one of the grand sustainable development goals worldwide identified by United Nations [1].

Wastewater produced from industrial manufacturing processes may contain contaminants of emerging concern that are hardly removed by conventional treatment technologies [2–4]. Advanced oxidation processes (AOPs) are technologies that have proven to be efficient on the abatement of persistent organic pollutants. AOPs are methods based on the in situ generation of hydroxyl radical ($^{\cdot}OH$), an strong oxidant species ($E^{\circ}(^{\cdot}OH/H_2O) = 2.80$ V vs SHE) that reacts non-selectively with organic pollutants attaining their total mineralization [5,6]. Some of the most studied AOPs are photocatalysis [7,8], photoelectrocatalysis [9,10], advanced ozonolysis [11,12], electrochemical oxidation [13,14], H2O2/UV [15,16] and Fenton processes [17–20].

Among AOPs, the processes based on Fenton's reaction have been identified as one of the most efficient technologies to treat acidic wastewaters containing persistent organic pollutants [19,20]. Fenton process yields high amount of $^{\cdot}OH$ from the catalytic decomposition of H_2O_2 by iron(II) according to reaction (1) [20–22]. The iron catalyst is regenerated from the Fenton-like reaction (2) that releases the weaker oxidant hydroperoxyl radical ($HO_2^{\cdot}$) with a standard redox potential of $E^{\circ}(HO_2^{\cdot}/H_2O) = 1.65$ V vs SHE [23,24]. Fenton-like reaction kinetics is much slower than Fenton reaction, therefore considering a rate-limiting step [25,26].

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow H_2O + Fe^{3+} + {}^{\cdot}OH \qquad (1)$$

$$H_2O_2 + Fe^{3+} + H^+ \rightarrow HO_2^{\cdot} + Fe^{2+} + H^+ \qquad (2)$$

The Fenton process may generate iron sludge. The use of fluidized-bed reactors can minimize the formation of iron sludge since iron oxides/hydroxides crystallize onto carriers (SiO_2 particles) [22,27–29]. Crystallized iron oxides can act as heterogeneous catalyst enhancing the overall efficiency of pollutant removal by the so-called fluidized-bed Fenton (FBF) process when compared to conventional Fenton process [15,29].

Even though Fenton process performance is highly promising, actual application on the treatment of industrial effluents is barely reported. Manufacturing industries with onsite water produced treatment before disposal identify as the main implementation barrier the

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Table 1
Screw manufacturing effluent characteristics.

Parameter	Characteristics
COD	400 mg $O_2\,L^{-1}$
pH	3.05
Zn^{2+}	177.0 mg L^{-1}
Cu^{2+}	0.06 mg L^{-1}
Total Cr	0.03 mg L^{-1}
Cl^{-}	2580 mg L^{-1}

identification of the most suitable stage in their existing water treatment facilities. In this work, we identify the possible implementation of FBF as pre-treatment on the water treatment process of effluents generated from a screw manufacture industry of Kaohsiung, Taiwan. The aim is to diminish the initial COD values below 200 mg $O_2\,L^{-1}$ as desired by industry according to the effluent standards defined by the Environmental Protection Administration of the Republic of China [30]. The reduction of the initial COD values of 400 mg $O_2\,L^{-1}$ would reduce the coagulant dose required to achieve the acceptable concentration levels of heavy metals (mainly Zn^{2+}) and COD by conventional coagulation treatment prior release.

2. Experimental

2.1. Screw manufacturing plant wastewater

Wastewater was collected from a screw manufacture industry of Kaohsiung, Taiwan. Samples for treatment were collected prior to the coagulation treatment. The main characteristics and composition of the complex actual effluent are summarized in Table 1. The total chemical oxygen demand of 400 mg $O_2\,L^{-1}$ was associated to organic compounds used as additives during the manufacturing process. High concentration of chloride of 2580 mg L^{-1} (~73 mM) and acidic pH of 3.05 are explained by the used of acids in cleaning steps of the manufacturing process. Whereas, the high concentration of Zn^{2+} of 177 mg L^{-1} results from the effluents of the galvanization process. Minor contents of other metals such Cu^{2+} and chromium species are also found in concentrations below 0.06 mg L^{-1}. Other metals that may be found in screw manufacturing effluents such as nickel, lead, arsenic or cadmium were not identified in the wastewater samples collected.

2.2. Fluidized-bed Fenton reactor

The fluidized-bed reactor was a cylindrical glass tube reactor of 1.6 L capacity as depicted in Fig. 1. A layer of 4 mm glass beads followed by a second layer of 2 mm glass beads disposed at the bottom of the reactor as turbulence promoters and to prevent sever clogging due to the carriers. Inert SiO_2 particles of 0.5 mm (passing Sieve #30 and retaining on Sieve #40) were used as carriers. A total volume of 1.4 L of collected wastewater from screw manufacturing industry was recirculated through the fluidized-bed reactor using a peristaltic pump (Iwaki MD-10-NL12) maintaining a 50% bed expansion in the fluidized-bed reactor column. The theoretical dosage of hydrogen peroxide for removing 1 mg L^{-1} of COD by Fenton process corresponds as rule of thumb to 2.12 mg L^{-1} of H_2O_2. Therefore, the FBF treatments were conducted considering an initial concentration of 46 mM of H_2O_2 to treat 400 mg L^{-1} of COD.

2.3. Chemicals and analytical procedures

The Fenton's catalyst ferrous sulfate hepta-hydrated and H_2O_2 (35%) were purchased from Merck. The solution pH was adjusted with sulfuric acid and sodium hydroxide of analytical grade supplied by Merck. Solution pH was continuously monitored by a pH/ORP controller PC-310 from Shin Shiang Tech Instruments. Samples were taken during the FBF treatment and the Fenton reaction quenched by adding NaOH up to pH 11.0 to induce H_2O_2 removal and precipitate the iron in solution, and then filtered through 0.2 μm syringe micro-filters prior to chemical analysis. Chemical oxygen demand (COD) was analyzed according to standard methods in a closed titrimetric reflux using dichromate. Quantification of residual Fe^{2+} and H_2O_2 was conducted by the 1,10-phenanthroline and titanium oxalate standard methods, respectively, using a CT-2400 UV–vis spectrophotometer.

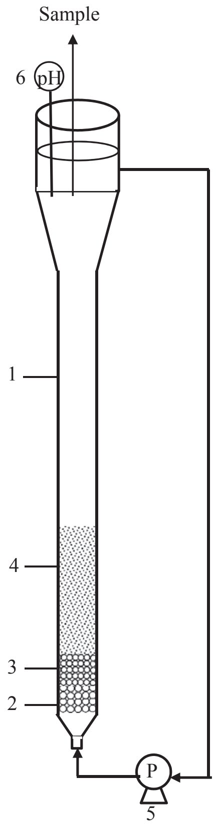

Fig. 1. Scheme of (1) fluidized-bed Fenton reactor: (2) layer of 4 mm glass beads, (3) layer of 2 mm glass beads, (4) packed bed of SiO_2 carriers prior fluidization, (5) pump, (6) pH meter.

3. Results and discussion

3.1. Conventional treatment of screw manufacturing industrial effluent

The industrial effluent from the screw manufacturing process consists of a complex mixture of heavy metals and organic matter (cf. Table 1). Before disposal, the generated wastewater is treated by conventional physico-chemical treatment of coagulation following several treatment steps. As summarized by the scheme of Fig. 2, the water matrix contained concentrations of 193.6 ppm of Zn^{2+} and total COD of 463.68 mg $O_2\,L^{-1}$ at highly acidic pH of 1.7 undergoes through a rapid mixing tank where sodium sulfide and iron (III) chloride are added as precipitant and coagulants prior entering the flocculation tank. The gentle stirring in the flocculation tank brings the suspended particles together that form larger flocs during the pH alkalization, where the pH is raised up to optimum coagulation conditions of pH 8.3. The precipitation of some heavy metals by the precipitation of their metal hydroxides or entrapped by the iron hydroxide flocs reduces the concentration of Zn^{2+} down to 11.63 ppm and the COD till 287.12 mg $O_2\,L^{-1}$. After these initial steps, the effluent follows an additional coagulation process by the addition of polyaluminum chloride as coagulant. The suspended solids are removed in the sedimentation

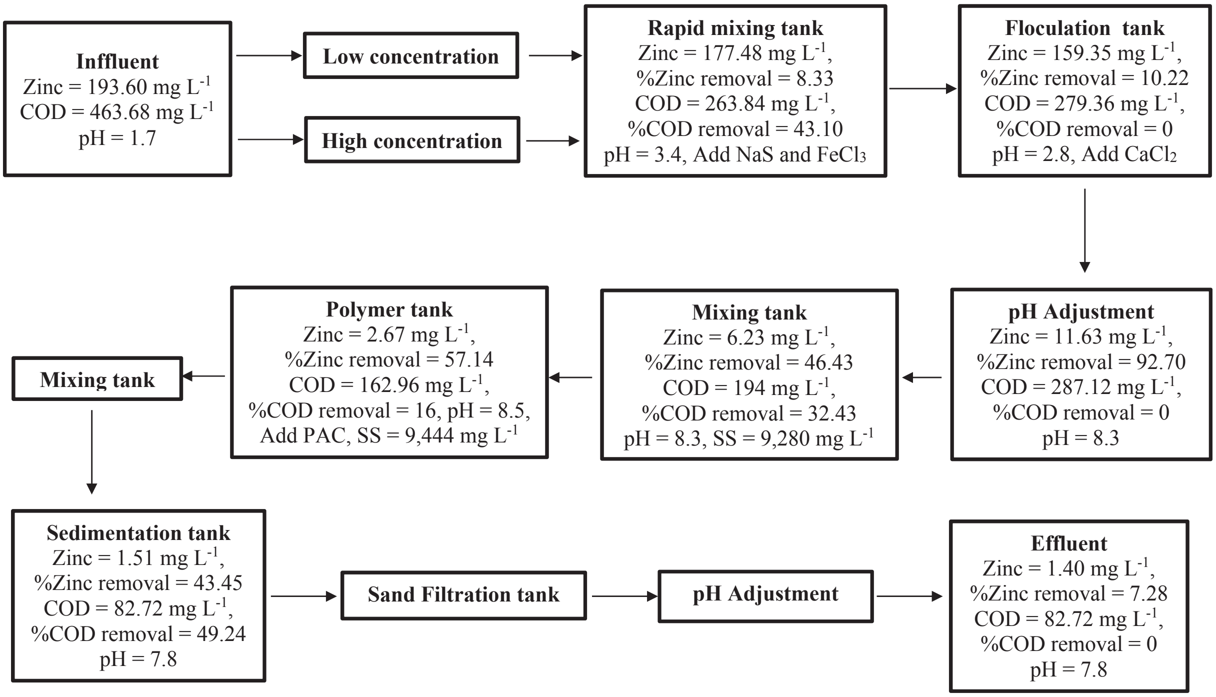

Fig. 2. Scheme of the conventional treatment followed prior to water disposal.

tank followed by a conventional sand filtration tank. Effluent pH is readjusted by carbonization to acceptable values ranging between pH 7.0-8-0. The treated industrial effluent contains low concentrations of Zn^{2+} 1.4 ppm and COD values of 82.7 mg O_2 L^{-1}, below the COD limits of 200 mg L^{-1} recommended by law before industrial wastewater release to the environment [30]. However, the use of AOPs as pre-treatment can contribute to reduce the initial COD value through the mineralization of organics and/or the formation of negatively charged organic species (e.g. carboxylic acids) [31,32] that can be easily removed by complexation or entrapment by coagulation treatment [33]. Fenton process has an optimum pH requirement of 3.0 which is coincident with the natural pH found in the rapid mixing tank where Fe^{3+} is added (Fenton-like catalyst) [24]. In this context, FBF process may be applied as pre-treatment prior to the rapid mixing tank by adding Fe^{2+} as Fenton catalyst (1), while the Fe^{3+} produced may be used as coagulant in the following treatment steps described above (Fig. 2). The following sections consider the treatment of wastewater collected at the rapid mixing tank prior to the addition of iron (III) chloride with 400 mg O_2 L^{-1} of COD and 177 ppm of Zn^{2+}.

3.2. Defining Fenton's catalyst effect on COD abatement

The initial concentration of Fe^{2+} defines the kinetics of ${}^{\cdot}OH$ production from the Fenton's reaction (1) since H_2O_2 is usually added in excess [23]. The experimental determination of the optimum Fe^{2+} dosage is especially relevant on the treatment of actual effluents where the available catalyst in the Fenton's reagent may be compromised by the complexation of Fe^{2+} and Fe^{3+} ions with other species in solution that precipitate the catalyst (e.g. phosphates, sulfide) or form complexes with the metallic ion (e.g. carboxylic acids, EDTA) both limiting its reactivity on the decomposition of H_2O_2 [34,35].

Addition of H_2O_2 to the effluent in absence of iron showed a slight decrease of COD of ~2.0%. The slight abatement of COD may be associated to the production of ${}^{\cdot}OH$ from the Fenton-like reactions with Cu^{2+} acting as catalyst according to reactions (3) and (4) [24,36,37], which are feasible due to the presence of small amounts of copper in solution (see Table 1). Since other metallic ions that may act as Fenton-like catalysts such as cobalt ions were not present in solution, alternative sources of ${}^{\cdot}OH$ are not considered herein. Even though, certain organic compounds may be directly oxidized by H_2O_2 as a weak oxidant with an $E^{\circ}(H_2O_2/H_2O) = 1.76$ V vs SHE.

$$H_2O_2 + Cu^{2+} + H^+ \rightarrow HO_2^{\cdot} + Cu^+ + H^+ \quad (3)$$

$$H_2O_2 + Cu^+ + H^+ \rightarrow H_2O_2 + Cu^{2+} + {}^{\cdot}OH \quad (4)$$

Higher and faster abatement of COD was observed when Fe^{2+} was added as Fenton catalyst (1). As can be deduced from Fig. 3, there is an optimum concentration of Fe^{2+} that allows attaining higher COD abatement with a reduction from 400 mg L^{-1} down to 120 mg O_2 L^{-1} (70% removal) after 15 min of FBF treatment when using an initial Fe^{2+} dose of 5.0 mM. Further increases of Fe^{2+} decreases the overall efficiency of the FBF treatment since lower percentages of removal of 66%, 64%, and 49% were attained for 7.5 mM, 10.0 mM and 25.0 mM, respectively. This trend can be mainly associated to the scavenging effect of Fe^{2+} at higher Fe^{2+}:H_2O_2 ratios due to reaction (5), which consumes the generated ${}^{\cdot}OH$ diminishing the rate of organic events decreasing the COD abatement rate [38,39]. Whereas, the major

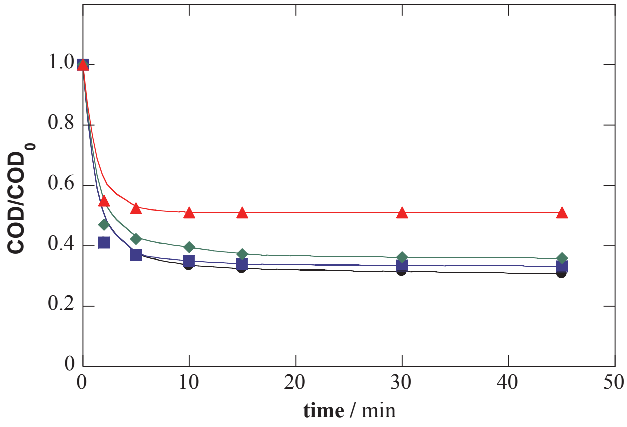

Fig. 3. Chemical oxygen abatement of screw manufacturing wastewater during Fluidized-bed Fenton treatment with 46.0 mM of H_2O_2 at different iron catalyst dosage: (●) 5.0 mM, (■) 7.5 mM, (◆) 10.0 mM, and (▲) 25.0 mM.

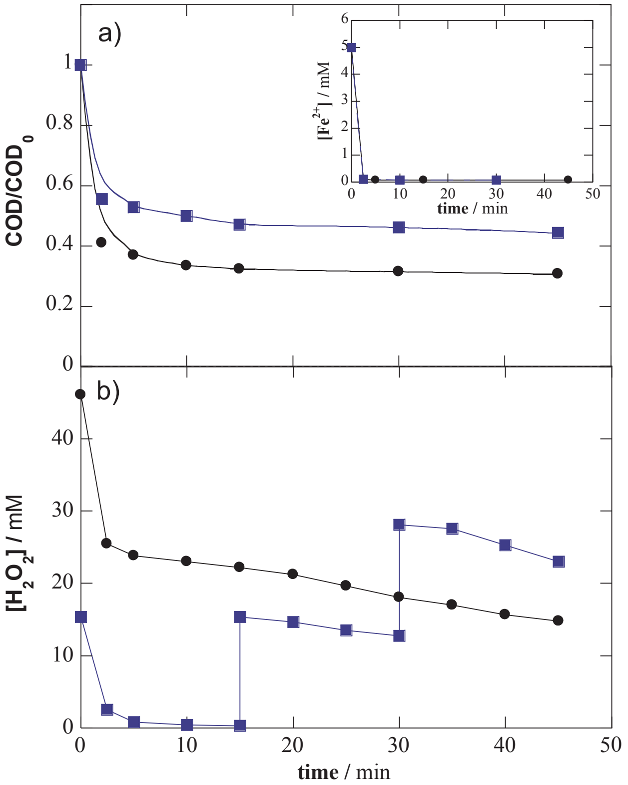

Fig. 4. (a) COD abatement and (b) H_2O_2 concentration profile during FBF treatment using different H_2O_2 feeding modes: (●) single dose, (■) three-dose steps. The inset panel depicts the concentration of Fe^{2+} during the treatment.

concentration of Fe^{3+} also contributes to consume higher amount of H_2O_2 by the Fenton-like reaction (2) that releases the weaker oxidant $HO_2^{\cdot}$, which cannot reduce COD as efficiently as $^{\cdot}OH$ [39,40].

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^- \tag{5}$$

Experimental result suggest that the optimum dosage of Fe^{2+} is 5.0 mM since allows attaining COD values below maximum contents recommended by law of 200 mg L^{-1} [30]. The remaining COD may be associated to low molecular weight carboxylic acids that form stable complexes with Fe^{3+} and Fe^{2+}, as observed during the treatment of model pollutants by Fenton processes [24,35,41]. It is important to remark that the dose of Fe^{2+} added as a pre-step is considerably lower than the usual dosages required for coagulation treatment and the added iron can be re-used as coagulant after FBF process in the subsequent coagulation steps.

3.3. Evaluating hydrogen peroxide feeding mode influence on FBF performance

Reagents feeding mode in continuous operation may influence the overall performance and reduce operational costs of FBF treatment. Fig. 4 demonstrates the influence of the feeding mode of H_2O_2 on the COD abatement. Noticeable is the lower COD abatement of 55% attained by the supply divided in three dosing stages of 15.3 mM in comparison to the 70% COD removal of single supply mode. This trend can be explained by further analyzing the evolution profiles of H_2O_2 and Fe^{2+} concentrations during FBF process for both feeding modes.

As can be seen in the inset panel of Fig. 4a, Fe^{2+} concentration depicts an identical profile in both feeding situations. Fenton's catalyst (Fe^{2+}) is quickly consumed by reaction (1) with an average constant of 55 $M^{-1}\,s^{-1}$, yielding high amounts of $^{\cdot}OH$ [35,36]. After this initial stage, a residual pseudo-constant concentration of Fe^{2+} of ca. 0.05 mM remains in solution due to the Fenton-like reaction (2) that slowly regenerates the catalyst with a rate constant of $2.0 \times 10^{-3}\,M^{-1}\,s^{-1}$ [23,36]. These two differentiated stages can be also observed in the H_2O_2 profiles of Fig. 4b. The initial dramatic decay of H_2O_2 is associated to the quick reaction with Fe^{2+} according to the Fenton's reaction (1). Meanwhile, the slower abatement of H_2O_2 is defined by the slower regeneration of Fe^{2+} by Fenton-like reaction (2). During this second stage, H_2O_2 is consumed by (i) the Fenton-like reaction that regenerates Fe^{2+}, and (ii) the consumption of the regenerated Fe^{2+} by Fenton's reaction; although the kinetics is defined by the rate-limiting step (reaction (2)). Thus, the two differentiated stages on COD abatement kinetics are defined by Fe^{2+} availability.

It is important to notice that when considering the H_2O_2 supply divided in three dosing stages, the H_2O_2 consumption after the initial dose is governed by the Fenton-like kinetics since Fe^{2+} has been already consumed (cf. Fig. 4). In this context, the major COD removal is defined by the $^{\cdot}OH$ production during the first stage of FBF process, which is smaller in the three dosing steps scenario because of three main reasons. First, the initial concentration of H_2O_2 is completely consumed in the first 10 min of treatment stopping the extension of the Fenton and Fenton-like reactions (1) and (2). Second, the lower initial H_2O_2 results in slower yield and smaller accumulation of $^{\cdot}OH$, which reduces the rate of organic events. Finally, the parasitic consumption of $^{\cdot}OH$ by Fe^{2+} according to reaction (5) became more notorious because of the higher initial Fe^{2+}:H_2O_2 ratio in comparison to the single feeding mode.

These results suggest that the optimum feeding mode of H_2O_2 must consider a single supply stage of required H_2O_2 concentration because allows achieving higher COD abatement. Lower residual concentrations of H_2O_2 remain in solution (see Fig. 4b) in comparison to multiple-feeding mode, which suggests a higher FBF treatment efficiency.

3.4. Optimizing Fe^{2+} feeding mode enhances FBF performance

Availability of Fe^{2+} is paramount to ensure the in situ generation of $^{\cdot}OH$ from Fenton's reaction (1). Feeding mode of Fe^{2+} (Fig. 5a) plays a governing role in FBF, where H_2O_2 is added in excess. As discussed above, abatement of COD by FBF process presents two differentiated kinetic stages: An initial fast stage defined by quick yield of $^{\cdot}OH$ from Fenton's reaction (1), followed by a second stage rate limited by Fe^{2+} regeneration from Fenton's like reaction (2). Analyzing the H_2O_2 profile in solution after initial catalyst feeding (inset panel of Fig. 5a) evidences that excess H_2O_2 remained in solution. When considering the Fe^{2+} catalyst feeding divided in different dosage steps, higher concentration remains in solution after the addition of smaller amounts of catalyst. Therefore, subsequent additions of Fe^{2+} catalyst doses can initiate a new first FBF stage and contribute to COD removal. On top of that, subsequent additions of Fe^{2+} doses can consume completely the H_2O_2. The total consumption of H_2O_2 is quite relevant since it is an indicative that a post-treatment to remove remaining excess in treated water prior release will not be required. Total consumption of H_2O_2 achieved by the same total concentration of Fe^{2+} added demonstrates that Fe^{2+} is partially consumed by parasitic reaction (5) during monodose operation mode [39,42]. Therefore, feeding mode contributes to enhance the overall efficiency of FBF process.

The COD abatement depicted in Fig. 5b shows that using a three-stage feeding of Fenton catalyst enhances the FBF efficient use of reagents and allows achieving higher removals of ~80%. This trend can be justified by the minimization of the parasitic reaction (5) by the decrease of the initial Fe^{2+}:H_2O_2 ratio along with the production of $^{\cdot}OH$ from Fenton's reaction (1) after each dose addition at 0 min, 15 min and 30 min of treatment [23]. Noteworthy is the lower COD removal differential attained after the third dosage. This trend may be explained by the higher recalcitrant character of by-products released from the parent organic compounds in the effluent. It is well known that the breakage of aromatic compounds and degradation of organic species results in the release of short molecular weight carboxylic and

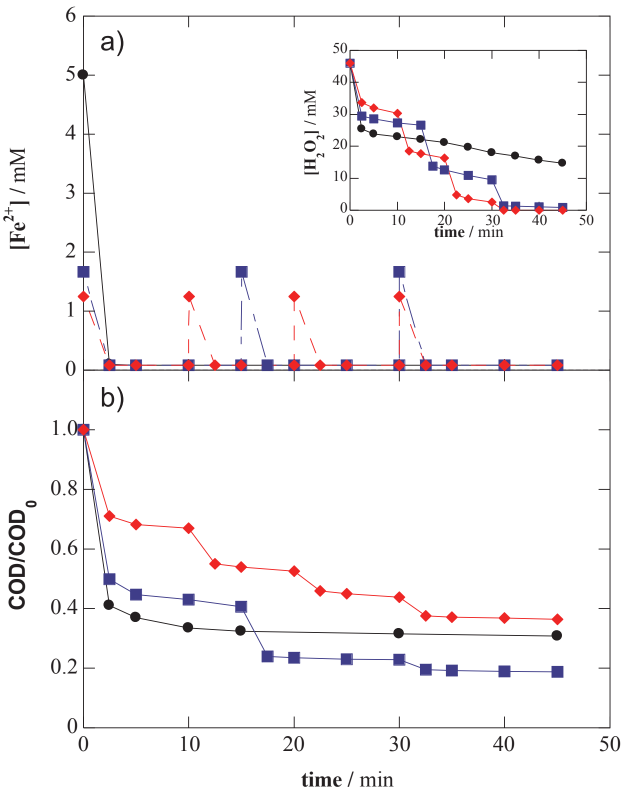

Fig. 5. (a) Fe^{2+} concentration profile and (b) COD abatement during FBF treatment using different Fe^{2+} feeding modes: (●) single dose, (■) three-dose steps, (◆) four-dose steps. The inset panel depicts the concentration of H_2O_2 during the treatment.

dicarboxylic acids that are barely removed by Fenton reaction [6,41]. Moreover, these carboxylic acids may form iron-carboxylate complexes reducing the extent of Fenton-like regeneration kinetics [35].

Noteworthy is the detrimental effect observed when increasing dosage steps from three to four catalyst doses, being solely attained a COD abatement of ~64% (inferior to the 70% of conventional mono-dose treatment). This trend can be explained by the consumption of $^{\cdot}OH$ by H_2O_2 according to reaction (6), which occurs for small Fe^{2+}:H_2O_2 ratios [39].

$$H_2O_2 + {}^{\cdot}OH \rightarrow HO_2^{\cdot} + H_2O \quad (6)$$

These results demonstrate the relevance of the feeding mode and how operational mode and reactor design can contribute to enhancing water treatment performance. Implementing FBF process with three steps Fe^{2+}-dosage operational mode would allow reducing initial COD of screw manufacturing effluent far below the 200 mg $O_2\,L^{-1}$ maximum limit defined by law.

4. Conclusions

Actual implementation of Fenton processes as water treatment technology face as one of the most relevant challenges, the identification of the most suitable stage fit in existing water treatment facilities of manufacturing industries. Understanding operation units in existing on site water treatment facilities is paramount to identify implementation opportunities. Fluidized-bed Fenton treatment has been proposed as chemical oxygen demand treatment of acidic screw manufacture industry effluents. . Actual wastewater samples were treated achieving up to 80% COD reduction in 40 min of Fenton treatment, attaining COD effluent content of 80 mg $O_2\,L^{-1}$ below the maximum 200 mg $O_2\,L^{-1}$ level defined by environmental protection agencies.

On top of that, effect of Fenton's reagents (H_2O_2 and Fe^{2+}) feeding mode have been evaluated in order to envision the most competitive possible continuous flow operational fluidized-bed reactor. Supplying required H_2O_2 divided in three dosing stages was detrimental because the COD abatement kinetics became defined by the slower Fenton-like kinetics since Fenton's catalyst (Fe^{2+}) was already consumed after first H_2O_2 dose addition. Dividing Fe^{2+} requirements in three steps Fe^{2+}-dosage operational mode enhances the overall efficiency of FBF and allows attaining higher COD abatement percentages. Whereas, increasing dosage steps from three to four catalyst doses resulted in lower COD abatement due to the enhancement of parasitic reaction (6) that occurs at small Fe^{2+}:H_2O_2 ratios. These results demonstrate the relevance of the feeding mode, which must be considered in FBF reactor design.

Implementation of FBF treatment prior to the conventional treatment followed at the effluent treatment platform of the screw manufacturing industry would allow achieving lower COD characteristic values prior effluent release. Moreover, reduction of initial COD values prior coagulation treatment may reduce coagulant dose requirement minimizing sludge production and coagulation water treatment cost.

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