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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].

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

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

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.

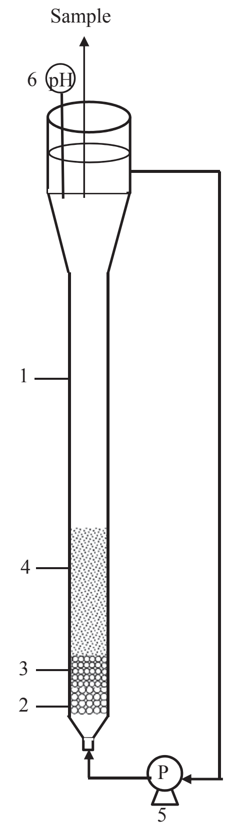

Fig. 1. Scheme of (1) fluidized-bed Fenton reactor: (2) layer of 4 mm glass beads, (3) layer of 2 mm glass beads, (4) packed bed of SiO_2 carriers prior fluidization, (5) pump, (6) pH meter.

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