

# Degradation and detoxicity of ethylenediamine wastewater by a continuous dosing mode sono-Fenton process

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## ABSTRACT

A continuous dosing mode sono-Fenton process was used in this study to establish an efficient treatment technology for ethylenediamine degradation. The effects of pH, dosages of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>, presence of anions and initial ethylenediamine concentrations were investigated. Experimental results showed that more than 71% of ethylenediamine was degraded by sono-Fenton process with a short reaction time. Lower pH levels and increasing dosages of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> enhanced the degradation efficiency of ethylenediamine in sono-Fenton system, but the presence of anions and higher initial ethylenediamine concentrations decreased the degradation efficiency. The toxicity of ethylenediamine wastewater was reduced by the sono-Fenton process based on the enhancement of cell viability. This study provides fundamental information about the treatment of ethylenediamine wastewater and/or other pesticides by a continuous dosing mode sono-Fenton process.

## INTRODUCTION

Ethylenediamine (C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>) is a colorless and strongly basic liquid with ammonia-like odor, which is manufactured from 1,2-dichloroethane and ammonia in an aqueous medium and is widely used in large quantities for the production of industrial chemicals. Because of its two amine functional groups, it can be used as a precursor in various polymers to readily form heterocycles such as imidazolidines or derivatives with carboxylic acids (including fatty acids), nitriles, alcohols (at elevated temperatures), alkylating agents, carbon disulfide, aldehydes and ketones [1]. Ethylenediamine is also a well-known chelating ligand for coordination compounds, and the most prominent derivative of ethylenediamine is EDTA [2-4]. However, it can release toxic and irritating vapors into its surroundings, and the vapors react with moisture in humid air to form a characteristic white mist, which is extremely irritating to skin, eyes, lungs and mucus membranes. In Taiwan, ethylenediamine is used as an

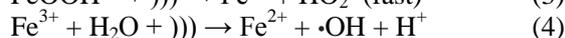
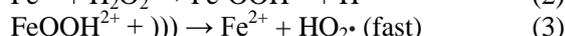
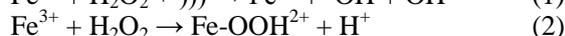
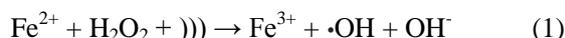
important agent in organic stripping liquid for cleaning the surface of unfinished integrated circuit plate products in the semiconductor substrate process [5]; un-reacted or residual ethylenediamine comes into the wastewater will inhibit the bioactivity of microorganisms and reduce the treatment efficiency of biological technologies in wastewater treatment plant. Therefore, effective degradation and detoxicity of ethylenediamine wastewater is investigated in this study.

Advance oxidation processes (AOPs) such as Fenton, ozone, UV light coupled with semiconductor and ultrasound are well-known since the late 20th century and have been proven as the effective treatment technology for different kinds of organic pollutants [6-8]. Even the ultrasound can effectively degrade most organic compounds, however, solving the low mineralization efficiency remains a major challenge [9]. Many studies pointed out that the addition of oxygen gas (O<sub>2</sub>) and H<sub>2</sub>O<sub>2</sub> was a useful way to enhance the formation of hydroxyl radical ( $\cdot$ OH) to degrade the organic compounds [10-12].

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Besides  $O_2$  and  $H_2O_2$ , a combination of Fenton's reagent and ultrasound, named as a sono-Fenton process, has been used for the degradation of carbofuran [13], benzene [14] and dyes [15,16]. Reaction of sono-Fenton process is shown in Eq. 1. Similar to Fenton's reaction, the  $Fe^{2+}$  is oxidized to  $Fe^{3+}$  and the produced  $Fe^{3+}$  will react with  $H_2O_2$  to produce a complex intermediate ( $Fe-OOH^{2+}$ ) as shown in Eq. 2 to lower the oxidation rate. The ultrasonic wave can decompose  $Fe-OOH^{2+}$  to  $Fe^{2+}$  and  $\cdot OOH$  (Eq. 3) and the isolated  $Fe^{2+}$  can react subsequently with  $H_2O_2$  to produce  $\cdot OH$  again (Eq. 1), and thus establishes a cyclic mechanism. In addition, the ultrasonic wave can transfer the  $Fe^{3+}$  to  $Fe^{2+}$  and produce more  $\cdot OH$  for further oxidation as shown in Eq. 4.



Our earlier study [5] has used a batch dosing mode of sono-Fenton process to degrade the non-biodegradable ethylenediamine and found that 40% of ethylenediamine was degraded with 60 min reaction. Although the biodegradability of treated ethylenediamine wastewater increased, there was still 60% of ethylenediamine remaining in the solution. Therefore, the objectives of the present study were to degrade the ethylenediamine through a continuous dosing mode sono-Fenton process and investigate the effects of different reaction parameters; toxicity of ethylenediamine wastewater before and after treatment was also investigated using cell viability method.

## MATERIALS AND METHODS

### 1. Standards and Reagents

Ethylenediamine (purity > 99.9%) was purchased from Sigma-Aldrich in analytical grade. Other chemical reagents used in this study were  $H_2SO_4$  (> 97%),  $NaOH$  (> 97%),  $FeSO_4 \cdot 7H_2O$  (> 99.5%) and an aqueous solution of hydrogen peroxide ( $H_2O_2$ , 30%, w/w in water) with the purest grade commercially available, which was used without further purification. Potassium iodide (KI), hydrogenophthalate potassium ( $C_8H_5KO_4$ ) (KHP), benzaldehyde ( $C_6H_5CHO$ ), n-hexane ( $C_6H_{14}$ ) and other chemicals were used as standard chemicals to determine the concentrations of  $H_2O_2$ , total organic carbon (TOC) and isolate the ethylenediamine from aqueous solution via a liquid-liquid derivation and extraction procedure. Six chemicals such as  $NaHSO_3$ ,  $CH_3COONa$ ,  $CaCl_2 \cdot 2H_2O$ ,  $Na_2CO_3$ ,  $Na_2SO_4$  and  $NaNO_3$  were used to prepare the reagents for investigating the effect of

anions on the degradation of ethylenediamine by sono-Fenton process.

### 2. Experimental Apparatus and Designs

A similar reactor was used by Ma and Sung [17], and a sonicator (Microson VCX 750, USA, 0-750 W) equipped with a sealed converter (Model CV 33, 63.5 mm in diameter and 183 mm in length) and titanium probe tip (No. 630-0210, 25 mm in diameter and 122 mm in length) was operated at 20 kHz in this study; the output energy of sonicator was maintained at 100 W without pulse length setup. Figure 1 shows the experimental apparatus designed for ethylenediamine degradation by sono-Fenton process. The aqueous ethylenediamine of 1,000 mL was conducted in the cylindrical reactor (working volume of 1 L, with a cooling jacket and a circulating temperature controller to maintain the reaction temperature at 25 °C) and the required reaction pH values (3-6) was adjusted using 0.1 N  $H_2SO_4$  and 0.1 N  $NaOH$ . The  $H_2O_2$  dosing rate ( $1-4 \text{ mg min}^{-1}$ ),  $Fe^{2+}$  dosage ( $5-40 \text{ mg L}^{-1}$ ) and initial ethylenediamine concentrations ( $50-400 \text{ mg L}^{-1}$ , i.e., 0.84-6.64 mM) were carried out in experiments. Concentration of each anion ( $SO_4^{2-}$ ,  $NO_3^-$ ,  $CO_3^{2-}$ ,  $CH_3COO^-$ ,  $SO_3^{2-}$  and  $Cl^-$ ) was  $50 \text{ mg L}^{-1}$ . The mixing speed of the solution was controlled at 100 rpm with a magnetic mixer to ensure the adequate mixing for all the chemicals. Aeration of air into the reactor during the reaction was maintained at  $0.2 \text{ L min}^{-1}$  to provide sufficient dissolved oxygen in solution. The oxidation reduction potential (ORP) and pH meters (Suntex PC-3200, Taiwan) were equipped with the reactor. Prior to the experiment, the ORP meter was rechecked by an ORP standard solution of 220 mV.

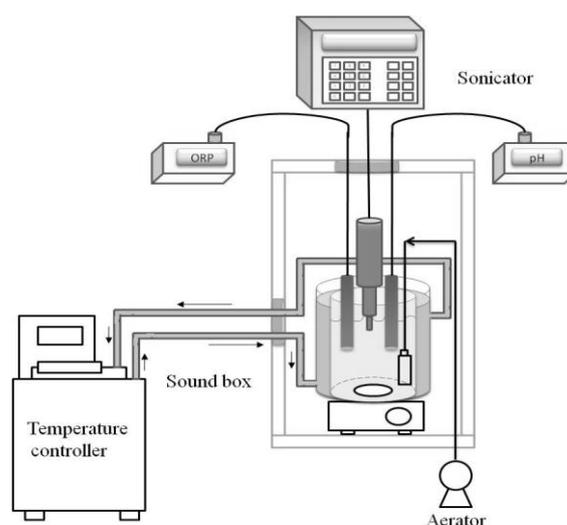


Fig. 1. Schematic diagram of experimental apparatus designed for ethylenediamine degradation by sono-Fenton process.

### 3. Analytical Methods

Ethylenediamine was first qualified by a gas chromatography equipped with mass spectrometry (GC-MS-QP2010, Shimadzu, Japan) using a DB-5MS column (30 m in length, 0.25  $\mu\text{m}$  in thickness, and 0.25 mm in diameter) and quantified by a gas chromatography with flame ionization detector (GC/FID-Varian GC 3400, Mulgarve, Victoria, Australia) using a DB-1 column (30 m  $\times$  0.53 mm i.d., 1.50  $\mu\text{m}$ ). Before being analyzed by GC/MS and GC/FID, 5 mL ethylenediamine water sample was collected into a vial and three drops of NaOH was added to adjust the pH in a neutral level. Then 1 mL of benzaldehyde solution was added to derive the ethylenediamine and followed by 1 mL n-hexane extraction for 30 min with a mixing speed of 150 rpm. After this extraction procedure, 1  $\mu\text{L}$  of upper solvent layer was collected and injected to the GC in splitless mode. The GC oven temperature in GC/MS and GC/FID was programmed from 70  $^{\circ}\text{C}$  (holding time 2 min) to 230  $^{\circ}\text{C}$  (holding time 5 min) at a ramp of 20  $^{\circ}\text{C min}^{-1}$ . The injector and detector temperatures for GC/MS and GC/FID were same at 230 and 280  $^{\circ}\text{C}$ , respectively. Nitrogen gas (carried gas, 15  $\text{mL min}^{-1}$ ), hydrogen gas (33  $\text{mL min}^{-1}$ ) and air (400  $\text{mL min}^{-1}$ ) were used for GC-FID. High purity (99.99%) helium gas was used as a carrier gas (1.5  $\text{mL min}^{-1}$ ) for GC-MS. Mass spectra were obtained by electron-impact at 70 eV using the full-scan mode. Figure 2 shows the mass spectrum of ethylenediamine determination in GC/MS analysis. Based on the appearance of the mass spectrum including peak 91, 104 and 133 and upon comparison with the mass spectra library in GC/MS, the substance was identified as 1,2-(dibenzylideneamino)ethane, which was the derivate of ethylenediamine through the addition of benzaldehyde. Prior to sample analysis, a calibration curve was plotted with known concentration of ethylenediamine (between 0 to 400  $\text{mg L}^{-1}$ ). The  $\text{H}_2\text{O}_2$  concentration was measured using KI titration method. Mineralization of ethylenediamine was investigated by TOC with a TOC analyzer (TOC-500, Shimadzu, Japan); method detection limit of TOC was 0.04  $\text{mg L}^{-1}$ .

Toxicity measurements of samples (before and after sono-Fenton treated) were performed by the cell counting procedures. The water samples were first sterilized by filtration through a 0.25  $\mu\text{m}$  Millipore membrane filter (Millipore, Bedford, USA). The rat liver cell line Clone-9 was maintained in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% (v/v) fetal bovine serum, 100  $\text{U mL}^{-1}$  penicillin and 100  $\mu\text{g mL}^{-1}$  streptomycin at 37  $^{\circ}\text{C}$  in a humidified incubator under 5%  $\text{CO}_2$ . Confluent cultures were passaged by trypsinization. The cells were washed twice with warm DMEM (without phenol

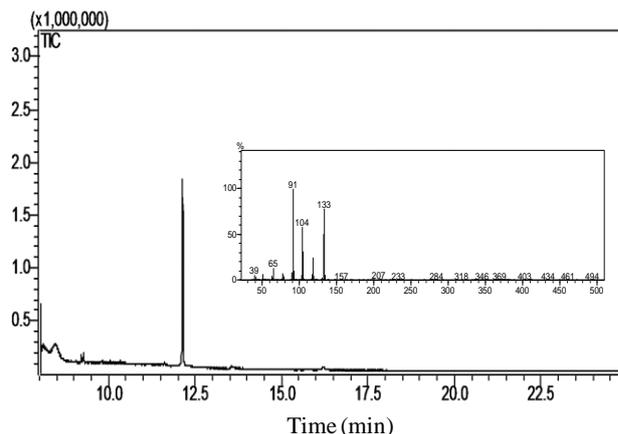


Fig. 2. Total ionic chromatography (TIC) and mass spectrum of ethylenediamine derivation product (1,2-(dibenzylideneamino)ethane) determination in GC/MS analysis.

red) and then treated in a serum-free medium. In all experiments, cells were treated with alachlor water samples for 24 h before and after sono-Fenton treatment. Cell viability was determined using a blue formazan assay in which colorless 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide is metabolized to a blue product by mitochondrial dehydrogenases. Absorbance was recorded at 540 nm using SpectraMAX 340 reader. The data were expressed as the mean percent of viable cells compared to the control.

## RESULTS AND DISCUSSION

### 1. Effect of pH

A suitable pH level is a key parameter in the degradation of organic pollutants by AOPs and biological systems. Most studies have proposed that the lower pH level was good for the degradation of organic pollutants [16-18]. In this study, initial pH levels were first set at pH 3 to 6 and the reaction temperature, initial ethylenediamine concentration,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  dosages were conducted at 25  $^{\circ}\text{C}$ , 100  $\text{mg L}^{-1}$ , 20  $\text{mg L}^{-1}$  and 4  $\text{mg min}^{-1}$ , respectively, and the results are shown in Fig. 3. The change of pH during 60 min reaction at pH 3 and 4 were decreased to 2.97 and 3.72, respectively. At pH 5 and 6, the final pH values were 4.48 and 5.49. This decrease could be explained by the addition of  $\text{FeSO}_4$  as the source of  $\text{Fe}^{2+}$ . Clearly, the degradation of ethylenediamine increased with lower pHs at the optimal pH 3. In addition, a progressive increase of the ethylenediamine degradation (Fig. 3a) was observed with reaction time, which was significantly different from our earlier research. The results shown in Ma [5] indicated that the degradation of ethylenediamine was almost terminated after the reaction time of 15 min,

indicating  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  could not be effectively contributed to the formation of  $\cdot\text{OH}$  so that the degradation was insignificant. Figure 3b also shows the profiles of ORP values during the reaction at different pH levels. At pH 3, the maximum ORP value was 578 mV at 60 min, and was much higher than the data observed in other pH levels. Higher ORP values indicate a higher oxidation potential for the oxidation system; thus the optimal degradation and mineralization efficiency of ethylenediamine took place at pH 3. In addition, at these four pH levels, the ORP values apparently increased with reaction time. Therefore, it is concluded that this continuous dosing mode sono-Fenton process can provide sufficient oxidation potential for the degradation of organic pollutants than a batch dosing mode one. Many researchers also found out that the increase of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  dosages were effective on the enhancement of organic compound degradation but further increases in  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  dosages were worthless [15,16,19]. Thus, this study adjusted the  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  reagent dosing mode as a continuous mode, i.e., these reagents were dosed into the solution drop by drop so that the  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  will not be overdosed and the sono-Fenton process can be readily carried out during the reaction.

Figure 4a shows the results of ethylenediamine degradation and mineralization at different pH levels within 60 min reaction. It was found in Fig. 4a that the degradation and mineralization efficiencies of ethylenediamine were 61 and 54% at pH 3, which were higher than other pH levels. As the initial pH increased to pH 6, degradation and mineralization efficiency of ethylenediamine decreased to 23 and 21%, respectively. This fact is comparable to other studies where the lower pH level is good in the degradation of organic compounds by sono-Fenton process or other AOPs [18,20].

## 2. Effect of $\text{Fe}^{2+}$ Addition

Figure 4b shows the results of ethylenediamine degradation and mineralization by sono-Fenton process at pH 3 and  $\text{H}_2\text{O}_2$  of  $1 \text{ mg min}^{-1}$  with different  $\text{Fe}^{2+}$  dosages. The degradation and mineralization efficiencies of ethylenediamine increased with an increase of  $\text{Fe}^{2+}$  dosages; however, as the  $\text{Fe}^{2+}$  dosage was greater than  $20 \text{ mg L}^{-1}$ , degradation and mineralization efficiencies decreased. Ghodbane and Hamdaoui [21] used the sono-Fenton process to degrade the Acid Blue 25 dye and found that the rate of dye degradation was significantly enhanced by the addition of  $\text{Fe}^{2+}$ , mainly due to the highly produced  $\cdot\text{OH}$ . It was also observed that further increase in  $\text{Fe}^{2+}$  concentration from 10 to  $50 \text{ mg L}^{-1}$  decreased the initial degradation rate slightly [21]. This is due to the fact shown as Eq. 5 that at high  $\text{Fe}^{2+}$  concentrations, the solution undergoes self-quenching

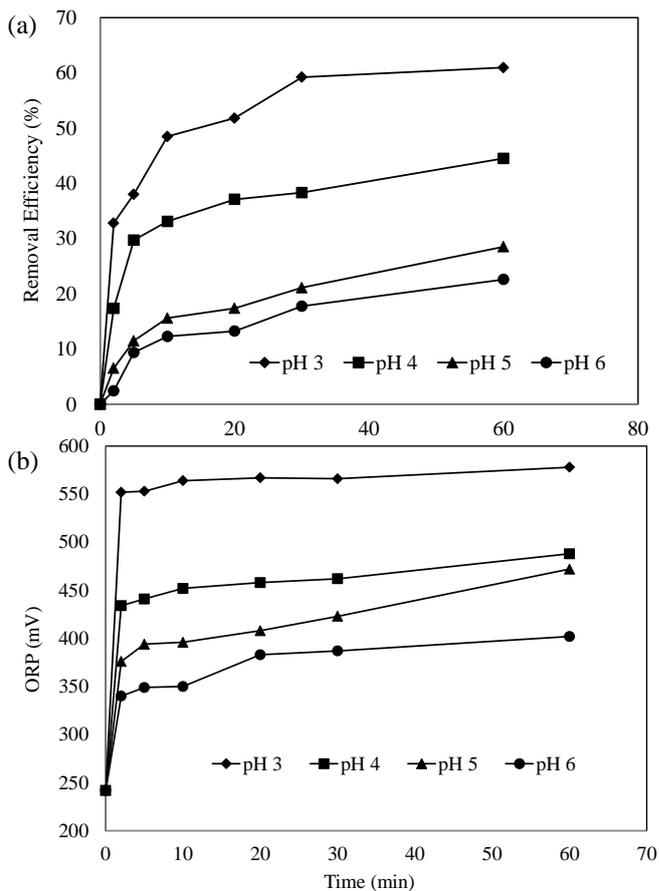


Fig. 3. (a) Degradation of ethylenediamine (b) ORP profiles by sono-Fenton process at different pH levels.

of  $\cdot\text{OH}$  by the added amounts of  $\text{Fe}^{2+}$  to produce  $\text{Fe}^{3+}$ . Qiu et al. [22] and Pradhan and Gogate [23] also found a comparable result, where the excess addition of  $\text{Fe}^{2+}$  would react with the  $\cdot\text{OH}$  and decrease the amount of  $\cdot\text{OH}$  in the system. Even the excessive addition of  $\text{Fe}^{2+}$  led to the decrease of degradation efficiency, reasonably higher iron dosages only would be beneficial under certain conditions [14,16,24].



## 3. Effect of $\text{H}_2\text{O}_2$ Addition

In this study, the major consideration of a continuous  $\text{H}_2\text{O}_2$  dosing mode in sono-Fenton process is to avoid excess  $\text{H}_2\text{O}_2$  addition resulting in the  $\cdot\text{OH}$  self-competition (Eq. 6) during the oxidation reaction (including the recombination of two  $\cdot\text{OH}$  to form  $\text{H}_2\text{O}_2$  and one  $\cdot\text{OH}$  with one  $\cdot\text{OOH}$  to form  $\text{O}_2$  and  $\text{H}_2\text{O}_2$ , shown as Eq. 7 and 8, respectively) as [14,19].



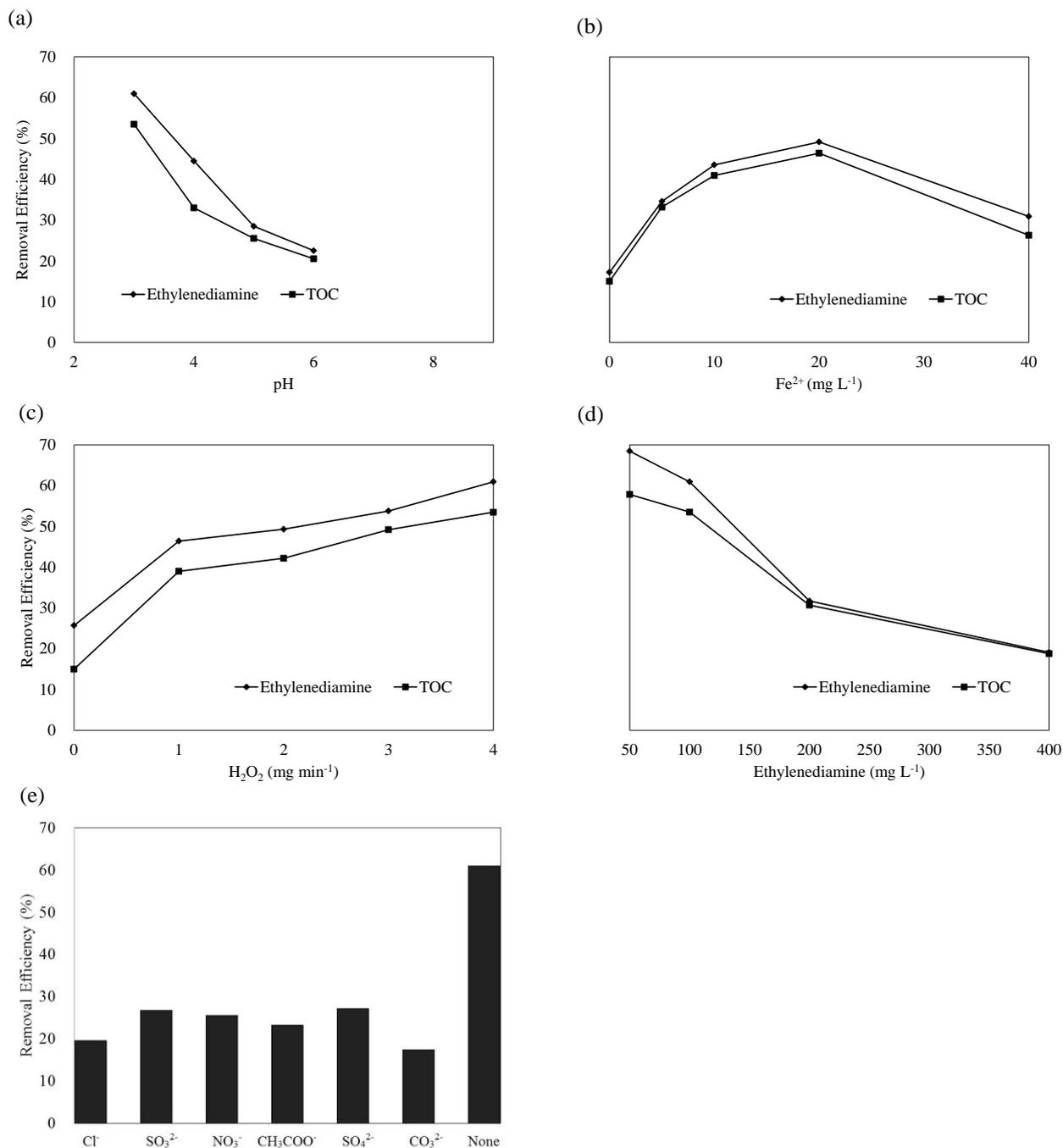


Fig. 4. Degradation and mineralization of ethylenediamine by sono-Fenton process at (a) different pH levels, (b) different  $Fe^{2+}$  concentrations, (c)  $H_2O_2$  dosing rates, (d) different initial ethylenediamine concentrations and (e) different anion additions.

Therefore, in Fig. 4c, as the  $H_2O_2$  dosing rate increases, the degradation and mineralization of ethylenediamine increases, which indicates that the addition of  $H_2O_2$  is effective on the enhancement of  $\cdot OH$  to oxidize the ethylenediamine. Degradation of ethylenediamine was only 26% by ultrasound/ $Fe^{2+}$  process (without  $H_2O_2$ ) and increased from 46 to 61% while the  $H_2O_2$  dosing rate increased from 1 to 4 mg min<sup>-1</sup>. In our earlier research [5], four  $H_2O_2$

concentrations such as 50, 100, 150 and 200 mg L<sup>-1</sup> were conducted and optimal dosage was found at 100 mg L<sup>-1</sup>  $H_2O_2$  to degrade 50 mg L<sup>-1</sup> ethylenediamine (degradation efficiency was 40%); as the  $H_2O_2$  concentration was over 100 mg L<sup>-1</sup>, degradation efficiency of ethylenediamine decreased. Babuponnusami and Muthukumar [14] used the sono-photo-Fenton process to degrade phenol and found that increasing the  $H_2O_2$  concentration was valuable

to increase the degradation efficiency of phenol and the optimal  $\text{H}_2\text{O}_2$  concentration was  $700 \text{ mg L}^{-1}$ . As the  $\text{H}_2\text{O}_2$  concentration was over  $700 \text{ mg L}^{-1}$ , degradation efficiency of phenol decreased. Li and Song [19] used a sono-Fenton process to decolorize dye Acid Red 97 and found that increased  $\text{H}_2\text{O}_2$  concentration was effective on the enhancement of decolorization. However, additional amount of  $\text{H}_2\text{O}_2$  in solution would react with the  $\cdot\text{OH}$  leading to the decrease of decolorization. Bagal and Gogate [18] used the ultrasound coupled with  $\text{H}_2\text{O}_2$  to degrade alachlor and found that the degradation efficiency increased with increasing  $\text{H}_2\text{O}_2$  concentrations. At higher loadings of  $\text{H}_2\text{O}_2$ , however, the scavenging action of un-dissociated hydrogen peroxide also contributed to the overall action and hence it resulted in a marginal increase in the extent of degradation.

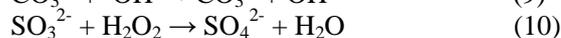
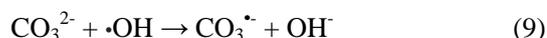
#### 4. Effect of Ethylenediamine Concentration

Most researches have proposed that higher initial concentration of pollutants will decrease the degradation efficiencies of organic pollutants in ultrasonic or sono-Fenton systems, which is due to the increase in pollutant load and the amounts of  $\cdot\text{OH}$  produced is insufficient to destruct the pollutants completely [15,19,23,25]. Therefore, as illustrated in Fig. 4d, degradation and mineralization efficiencies of ethylenediamine decrease with the increasing initial ethylenediamine concentrations; degradation efficiencies decrease from 69 to 19% when the initial ethylenediamine concentrations increase from 50 to  $400 \text{ mg L}^{-1}$ . There is a comparable phenomenon with the ethylenediamine mineralization. Figure 4d indicates that the degradation and mineralization results at higher initial ethylenediamine concentration are much closer than lower ones, which indicates that most degraded ethylenediamine is mineralized. The results shown in Fig. 4d indicates that the degradation efficiency decreases with the increasing concentrations and the removal amounts of ethylenediamine are linearly dependent on the initial ethylenediamine concentration. As it is observed, the sono-Fenton process degrades more ethylenediamine at high ethylenediamine concentration even the reaction is carrying out at the optimal condition for low ethylenediamine concentration wastewater.

#### 5. Effect of Anions Addition

The presence of anions such as chloride, sulphate, carbonate, and bicarbonate is common in industrial effluents [26]. Wang et al. [27] degraded 2-chloro- and 2-nitrophenol by photocatalytic method and found that the presence of  $\text{Cl}^-$  would significantly inhibit the degradation efficiency. Bhatkhande et al. [26] summarized the effect of four anions on the degradation of organic compounds and found the

following order:  $\text{SO}_4^{2-} < \text{HCO}_3^- < \text{NO}_3^- < \text{Cl}^-$ . Sun et al. [15] studied the reactions between anions and  $\cdot\text{OH}$  and found the effect of various inorganic anions was in the following order:  $\text{SO}_3^{2-} > \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{CO}_3^{2-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ , which indicated that  $\text{SO}_3^{2-}$  had a strong inhibition on the degradation of pollutants in ultrasonic system. Typically, effects of anions on the degradation of organic compounds depend on the type of treatment method and characteristics of target compounds. Figure 4e shows the degradation of ethylenediamine by sono-Fenton process in the presence of six anions. After 60 min reaction, degradation efficiency was 61% without anion and was significantly decreased to lower than 18 to 27% with different anions; presence of  $\text{CO}_3^{2-}$  significantly inhibited the ethylenediamine degradation efficiency with only 18%. This fact is comparable to the other studies [29-31] and can be explained by Eq. 9 that  $\text{CO}_3^{2-}$  reacts rapidly with  $\cdot\text{OH}$  to quench the  $\cdot\text{OH}$  so that the inhibition of ethylenediamine degradation is significant. The effect of various inorganic anions in this study is in the following order:  $\text{CO}_3^{2-} > \text{Cl}^- > \text{CH}_3\text{COO}^- > \text{NO}_3^- > \text{SO}_3^{2-} = \text{SO}_4^{2-}$ , which is different from Sun et al. [15] but comparable to Bhatkhande et al. [26]. Sun et al. [15] proposed that  $\text{SO}_3^{2-}$  had a significant inhibition on the degradation of dye, which might be that  $\text{SO}_3^{2-}$  either reacted with  $\text{H}_2\text{O}_2$  to decrease the amount of  $\text{H}_2\text{O}_2$  available for  $\cdot\text{OH}$  production, or quenched the  $\cdot\text{OH}$  directly as shown in Eqs. 10 and 11. In this study,  $\text{H}_2\text{O}_2$  was dosing into the reactor drop by drop so that the  $\text{H}_2\text{O}_2$  easily reacted with  $\text{Fe}^{2+}$  to produce  $\cdot\text{OH}$  and the effect of Eq. 10 might be ignored. In addition, this study used the  $\text{FeSO}_4$  to prepare the  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  was always present in samples. This might be the reason that the effect of adding more  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  on the inhibition of ethylenediamine degradation was lower than other anions. However, the effect of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  are still important, due to more than 50% of ethylenediamine degradation was inhibited.



#### 6. Cell Viability

In our earlier research [5], we have used the ratio of biochemical oxygen demand/chemical oxygen demand (BOD/COD) as the "biodegradability" to propose the change in toxicity of ethylenediamine wastewater. However, this ratio is well-known as an indirect index for understanding the toxicity, due to the interferences present in the analytic process for high-strength nitrogenous wastewater. In this study, the cell viability was used to reveal the change in toxicity of ethylenediamine wastewater before and

after treatment. Figure 5a shows the results of cell viability of blank (Reverse Osmosis water, defined as 100%), untreated ethylenediamine wastewater, treated wastewater with 30 and 60 min reaction. The sono-Fenton process was conducted at pH 3, 20 mg L<sup>-1</sup> of Fe<sup>2+</sup>, 4 mg min<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub>, 100 mg L<sup>-1</sup> of ethylenediamine and 25 °C. As it is observed, cell viability (ethylenediamine : DMEM = 1:9) increases by sono-Fenton oxidation with decreased toxicity with time. After 60 min reaction, cell viability increased from 70% (un-treated ethylenediamine) to 86% (based on blank test). In addition, as the ratio of ethylenediamine : DMEM = 9:1 (data not shown), the cell viability of un-treated ethylenediamine wastewater decreased to less than 40%, which was estimated to be toxic. In Fig. 3a, 59% of ethylenediamine was degraded within 30 min reaction, and slightly increased to 61% at 60 min with 39% of ethylenediamine still present. In Fig. 5b, almost a linear relationship was observed and the increase of cell viability was obviously resulting from TOC removal, which indicated that the mineralization of ethylenediamine was the key in toxicity reduction. Therefore, based on the results shown in this study, a continuous dosing mode sono-Fenton process is more effective on ethylenediamine wastewater degradation and detoxicity than the batch dosing mode.

### CONCLUSIONS

The degradation of ethylenediamine in aqueous solution was investigated by a continuous dosing mode sono-Fenton process under different experimental conditions, including pH, dosages of H<sub>2</sub>O<sub>2</sub> and

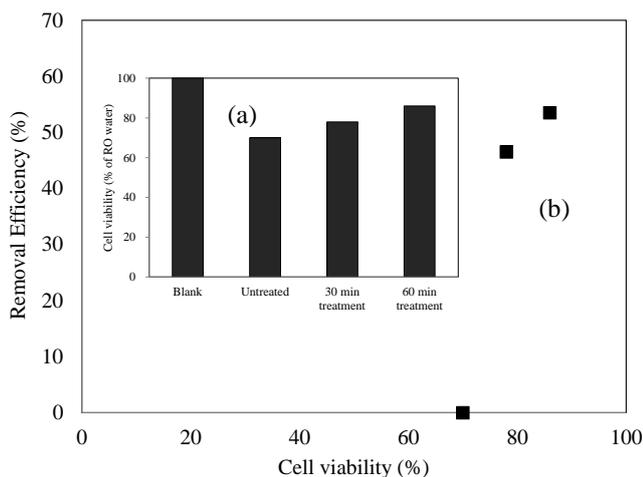


Fig. 5. (a) Enhancement cell viability and (b) relationship between TOC removal and cell viability of treated ethylenediamine wastewater by sono-Fenton process.

Fe<sup>2+</sup>, anions and a range of initial ethylenediamine concentrations. More than 71% ethylenediamine degradation efficiency combined with 58% mineralization was achieved after 60 min of treatment at optimal condition. Degradation efficiency increased through an increase of Fenton reagents and a decrease of initial ethylenediamine concentration. Presence of CO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup> significantly inhibited the degradation of ethylenediamine in sono-Fenton system. The cell viability study indicated that the toxicity of ethylenediamine wastewater was reduced by the sono-Fenton process and the mineralization of ethylenediamine was closely related to the reduction of toxicity.

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