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Study on COD removal mechanism of aminosilicone polymer microemulsion wastewater under Fenton oxidation conditions

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ABSTRACT

The present study was to investigate the COD removal mechanisms of simulated microemulsion wastewater (COD = 4000 ± 100 mg/L) contained by different aminosilicone polymers (PDMAS) under Fenton oxidation conditions. Effects of variables such as initial pH, ferrous iron concentration, and hydrogen peroxide concentration were examined by determining COD removal through batch experiments to determine the optimal operating conditions. For all three PDMAS, it was found that all the variables have the same effect trends and the maximum removal efficiencies were 85,77, and 81% for three experiment exam samples, respectively, which were named by sequence number A1, A2, and A3, under the condition of $[Fe^{2+}] = 5\,mM$ and $[H_2O_2] = 10\,mM$ at $pH = 2.5$. The variation of Fe^{2+} and H_2O_2 concentration and the evaluation of pH and oxidation-reduction potential in real-time indicated that the oxidation reaction from Fenton agents results in the removal of PDMAS polymer, the characters (viscosity and amino value) of PDMAS and their oxidative intermediates affected the Fenton oxidation process.

Keywords: Aminosilicone polymers (PDMAS); Fenton oxidation process; COD removal mechanism

1. Introduction

Aminosilicone polymer (poly(dimethyl,methyl (amino-ethyl amino-isobutyl) siloxane), PDMAS) is comprised of a group of compounds with silicon and oxygen [1] and commonly used as an antifoaming agents, fabric softener, and lubricant [2]. Its structure is usually expressed by Fig. 1 [3]. Contrast to linear polydimethylsiloxane $[CH_3\text{-}[Si(CH_3)_2O]n\text{-}Si(CH_3)_3]$ (PDMS) fluids, PDMAS fluids have some important properties, such as good washing ability, strong polarity, low surface tension, water repellence, and exceptional thermal and chemical stability because of the ammonia functional groups in side chains [2]. Therefore, it can be confirmed that the PDMAS is harder to be broken down than PDMS. The major characteristics of PDMAS polymer are chiefly viscosity and amino value. The viscosity of PDMAS stands for its molecular size (average molecular weight) indirectly, and the amino value is the milliliter value of hydrochloric acid which can neutralize one gram aminosilicone and this means the millimole value of nitrogen (including NH- and NH_2-) per gram aminosilicone [2].

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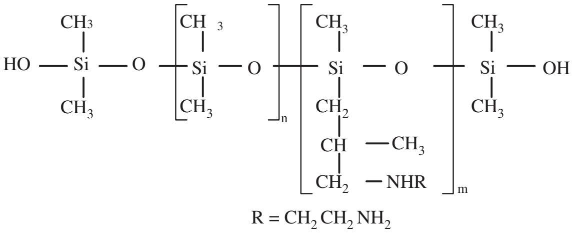

Fig. 1. Schematic diagram of the structure of PDMAS.

For the past few years, many studies have been focused on the environmental degradation pathways for the breakdown of PDMS [4,5]. Silicone compounds are essentially nonreactive, except when exposed to strong acids, bases, or oxidants [6]. PDMS is found to be resistant to hydrolytic and oxidative breakdown in wastewater treatment facilities and widely exist in sewage sludge, mainly due to that the Si–O bond is resistant to enzymatic attack [7,8] and biodegradation of Si–C bond also seems to be difficult [9]. Meanwhile, silicone polymers that enter into aquatic environment can be tightly adsorbed by sediments and accumulate, so that they are considered as environmentally persistent compounds [7,9], which could cause a potential threat to the environment [1].

Whether these characteristics of PDMAS can affect its degradation or not remains still unknown. With the increasing production and consumption of PDMAS, the treatment technologies for aminosilicone polymers in wastewater are in great demand. Studies on the COD removal mechanisms of different PDMAS (which have diverse viscosity and amino value) could have been urgent.

Fenton process contains reactions of formation of hydroxyl radical by catalyzing hydrogen peroxide with ferrous iron (Eq. (1)). Comparing with other oxidants, hydroxyl radical is characteristic of high oxidation potential (E = 2.8 V) and relative lack of selectivity; thus, Fenton process is widely applied for the effective degradation of most refractory organic pollutants [10–12]. During the process, oxidation inducing ring cleavage and chain scission produces a range of intermediates, which are some organic acids and some substances with lower molecular weight [13,14].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-} \tag{1}$$

At present, more and more macromolecule compounds are artificially synthesized, and their degradation attracts much attention. Fenton process, as one of the most effective oxidation methods, is also applied for the treatment of macromolecule substances. For some water-soluble polymers, such as phospholipid polymer hydrogel (PMPC) [15], poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA) [16,17], the main chain recession is the mechanism and the degradation behavior is dependent on the H_2O_2 concentration. Meanwhile, researchers reported the treatment of emulsions containing both high and low concentrations of PDMAS using Fenton and photo-Fenton processes, with the results suggesting that PDMAS (and/or partially oxidized PDMAS) was removed from the aqueous solution as a result of the phase separation process [3]. Actually, PDMAS can be classified by molecular weight (degree of polymerization) and amine value (the amount of nitrogen in side chain also reveals the amount of side chain).Till now, there is no compared research on degradation of different PDMAS with varied molecular weight and amine value, which means that it is unclear whether the oxidation by hydroxyl radical is affected by molecular weight and amount of side chain. In our literature, we choose three different PMDAS as target pollutants and investigate the effect of initial pH, ferrous iron, and hydrogen peroxide on degradation efficiencies by Fenton process. Then, the variation of pH, ORP, ferrous iron, and hydrogen peroxide is observed in the reaction process.

2. Experimental section

2.1. Chemicals

Three concentrated emulsions containing aminosilicone polymers (PDMAS) were supplied by Transfar Group Corporation, China, with the properties shown in Table 1. Analytical grade hydrogen peroxide (30%, w/w solution), ferrous sulfate, sulfuric acid, and sodium hydrate were purchased from Sinopharm Chemical Reagent Corporation, China.

2.2. Fenton process

Synthesized wastewater (COD = 4,000 ± 100 mg/L) was prepared by diluting concentrated PDMAS emulsion with deionized water. The experimental system was comprised of a 1 L beaker filled with

Table 1
The properties of three aminosilicone polymers

Number (PDMAS)	Amine value (mg/g)	Viscosity (mPa S)
A1-LAHV	0.23–0.26[a]	20,000–50,000[a]
A2-HALV	0.50–0.60[a]	1,000–1,500[a]
A3-HAMV	0.50–0.60[a]	8,000–15,000[a]

[a] Data were provided by the manufacturer.

500 mL synthesized wastewater and mechanical stirrer agitated at speed of 250 rpm. The beaker was open to the atmosphere at room temperature (23–25℃). Certain amounts of ferrous sulfate were added into the wastewater and initial pH value was adjusted with sulfuric acid, then reaction started as hydrogen peroxides were added.

One milliliter samples was taken out at predetermined times and was immediately analyzed for Fe^{2+} and H_2O_2. Samples for analysis of COD were alkalified to 8.0 by NaOH solution at the end of reaction.

During the process, pH and ORP were online monitored every 2 s.

2.3. Analytical methods

The pH and ORP were measured with P33-pH/ORP probes (HACH, USA).

For COD measurement, the samples were heated at 40℃ for 30 min [18] to eliminate the influence of H_2O_2 on COD and analyzed according to the standard methods [19].

Before determination of hydrogen peroxide, samples were mixed with 1 ml methanol to quench the reaction [20] and then determined spectrophotometrically at 500 nm using potassium titanium (IV) oxalate [21]. The concentration of ferrous ion was measured by the o-phenanthroline colorimetric method with $\lambda = 510$ nm.

3. Results and discussion

3.1. Effect of initial pH

Initial pH, as one of the important factors, is in the range of 2–4 that strongly favors the oxidation of Fenton process. Fig. 2 plots the effect of pH on the COD removal efficiency of different PDMAS microemulsion simulated wastewater systems under the experimental condition of 5 mM Fe^{2+} and 10 mM H_2O_2. It clearly reveals that, for all the three systems, maximum efficiencies were obtained at 2.5, and the increase or decrease in the initial pH could cause the reduction in COD efficiency. Therefore, it may be indicated that the most ideal pH for generation of $HO^{\cdot}$ is 2.5 for treatment of PDMAS microemulsion simulated wastewater. The amount of generated $HO^{\cdot}$ is dependent on the available amount of Fe^{2+} and H_2O_2 in Fenton system. As we known, formation of $(Fe(II)(H_2O))^{2+}$ at low pH, as well as instability of Fe^{2+} that is due to transformation from Fe^{2+} to Fe^{3+} at a pH > 4.0 and precipitation of $Fe(OH)_2$ at high pH, can reduce the available amount of Fe^{2+}. Meanwhile, the reduction in H_2O_2 occurs when self-decay [22] and decomposition catalyzed by $Fe(OH)_3$ happens at higher pH [23]. In addition, the availability of H_2O_2 is limited for the species of $H_3O_2^+$ in low acid condition [24]. Hence, the concentration of $HO^{\cdot}$ would decrease with reduction in available Fe^{2+} and H_2O_2, resulting in lower removal efficiency at high and very low pH.

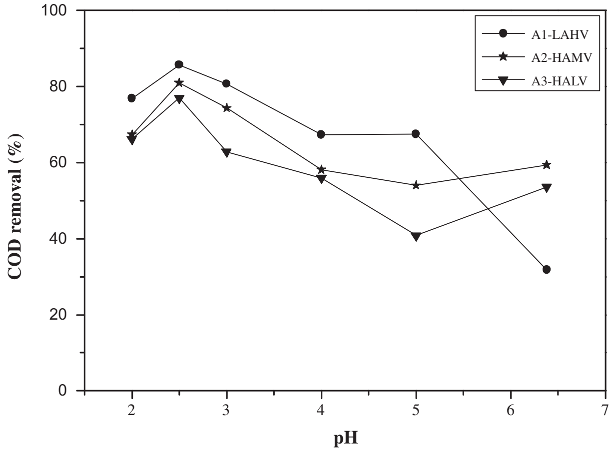

Fig. 2. Effect of initial pH on COD removal efficiency for PAMAS microemulsions. (conditions: $(Fe^{2+}) = 5$ mM, $c(H_2O_2) = 10$ mM).

In all the three systems, their COD removal efficiencies' ranking was A1 > A2 > A3. Taking the different amine value and molecular weight of PDMAS into consideration, when microemulsion wastewater contained PDMAS of similar amine value, it can be seen that better efficiencies were attained with higher molecular weight than with lower molecular weight. On the other hand, amine value has the same effect on removal efficiency of PDMAS.

3.2. Effect of Fe^{2+} concentration

Ferrous iron acted as a catalyst has great influence on the amount of generated $HO^{\cdot}$ through Eq. (1) so as to affect the removal efficiency. Fig. 3 illustrates the COD removal efficiency for microemulsions at varied concentrations of Fe^{2+} for fixed H_2O_2 concentration of 10 mM and at pH of 2.5. At lower Fe^{2+} concentrations varied from 0.5 to 5.0 mM, the COD removal efficiency sharply increased and maximum efficiency was achieved at 5.0 mM Fe^{2+} for all the three systems. The increase in Fe^{2+} concentration could produce more amount of $HO^{\cdot}$ [Eq. (1)], so that the degradation efficiency increases with more PDMAS reacted with $HO^{\cdot}$. In addition, due to insufficient Fe^{2+} to reacted with H_2O_2, residual H_2O_2 would consume the $HO^{\cdot}$ [Eq. (2)] so as to the reduction on amount of $OH^{\cdot}$ that could reacted with PAMAS. At higher Fe^{2+} concentrations, little drops in efficiency happened with further

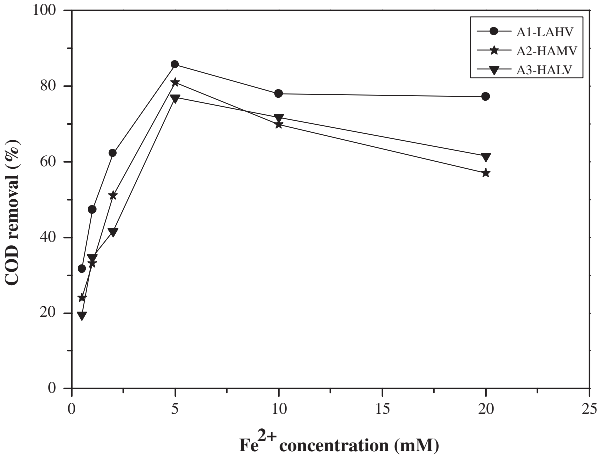

Fig. 3. Effect of Fe^{2+} concentration on COD removal efficiency for PAMAS microemulsions (conditions: pH = 2.5, c(H_2O_2) = 10 mM).

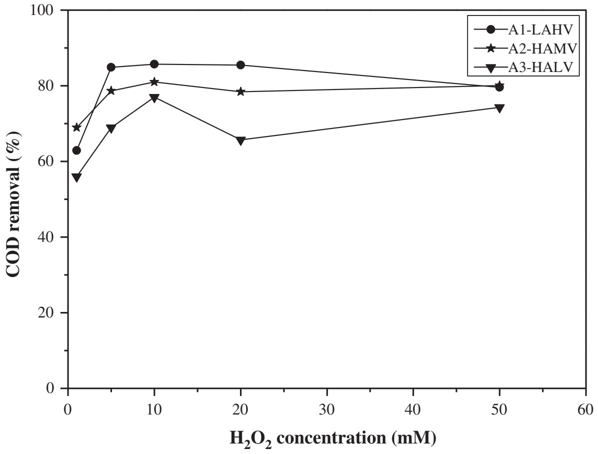

Fig. 4. Effect of H_2O_2 concentration on COD removal efficiency for PAMAS microemulsions. (conditions: pH = 2.5, c(Fe^{2+}) = 5 mM).

increasing to 10 and 20 mM in Fe^{2+} concentration. As an scavenger of $OH^{\cdot}$, Fe^{2+} could reacted with $OH^{\cdot}$ due to excess amount of Fe^{2+} remained in solution at high initial Fe^{2+} concentration [25].

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad (2)$$

Comparing the COD removal efficiency of three systems, similar phenomenon occurred that the sequence of efficiency was nearly A1 > A2 > A3.

3.3. Effect of H_2O_2 concentration

H_2O_2 is an oxidizing agent as well as the precursor of $HO^{\cdot}$ in Fenton reaction. To study the effects of H_2O_2 concentration on the COD removal efficiency of three microemulsions, experiment was performed by varying the initial H_2O_2 concentration from 2.5 to 50 mM. The experimental result is shown in Fig. 4. It is obvious to find the different effects of H_2O_2 on removal efficiency for the three systems. The same tendency that the efficiencies increased with increasing H_2O_2 concentration from 2.5 to 10 mM and dropped a little at higher concentration of H_2O_2 was gotten for treatment of A1, A2, and A3. Usually, the removal efficiency of the pollutant rises with the increase in the amount of H_2O_2 due to an increase on the amount of $HO^{\cdot}$ through Eq. (1). Nevertheless, the accumulation of H_2O_2 could consume the $HO^{\cdot}$ and react with Fe^{3+} to form weaker $HO_2^{\cdot}$ that is not active as $HO^{\cdot}$ toward pollutant degradation [26].

Based on above experimental results, a more appropriate Fenton reaction conditions were pH = 2.5, $[Fe^{2+}]$ = 0.5 mM, $[H_2O_2]$ = 10 mM. Compared with the above three different reaction condition experimental results, analysis COD removal trends of PDMAS microemulsion samples found that the COD removal rate of three different systems showed a basic trend.

In addition, the experiment results also can reflect that certain molecular size of aminosilicone polymer and COD removal efficiency has a relative law: The higher molecular weight PDMAS samples show slightly higher removal efficiency. The reason to explain the mechanism of COD removal would be that the main contribution of COD removal comes from the flocculation after the oxidative degradation. Because the higher molecular weight means the longer molecule chain, the flocculation of macromolecule pollutants would be better. From another perspective, even the same equivalent flocculation formatting, a higher molecular weight of the sample also means the more quality of COD removed.

3.4. Variation of Fe^{2+} and H_2O_2 concentrations

Fenton reaction is consisting of Fe^{2+} and H_2O_2, so the variation of concentrations of that two reagents could indicate how the pollutant added influence Fenton reaction. Under the condition of fixed pH 2.5, Fe^{2+} concentration 5 mM, and H_2O_2 concentration 10 mM, control experiments based on whether the PDMAS was added or not were conducted and the results were compared.

A consistent trend was found that the Fe^{2+} concentrations with the initial value at 5 mM decreased quickly to the minimum within the first minute of reaction and kept at a relatively stable value, which were 0.06, 0.17, 0.27, and 0.28 for none PDMAS, A1, A2, and A3, respectively (Fig. 5). For the PDMAS microemulsions, some intermediates produced through Eq. (2) can reacted with Fe^{3+} to form Fe^{2+} [Eq. (3)], which lead to the higher Fe^{2+} concentration in PDMAS microemulsion than that with none PDMAS added solution. Comparing the different COD removal efficiency, it can be deduced that lower COD removal efficiency could also mean less amount of produced intermediate in A1 microemulsion so less Fe^{3+} was oxidized to Fe^{2+} by intermediates.

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \tag{3}$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \tag{4}$$

H_2O_2 is not only the precursor of $HO^{\bullet}$ but also an oxidant that could reacted with some substances followed by Eqs. (4) and (5). Thus, the H_2O_2 concentration is affected by this side reaction and the amount of residue H_2O_2 would reflect the probable reactions occurring in Fenton system when the PDMAS exists.

$$R^{\bullet} + H_2O_2 \rightarrow ROH + HO^{\bullet} \tag{5}$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HOO^{\bullet} \tag{6}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^{+} + HOO^{\bullet} \tag{7}$$

The results of variation of H_2O_2 concentration are depicted in Fig. 6. Of all Fenton systems, H_2O_2 was consumed sharply within the first minute. Contrast to the higher residue H_2O_2 concentration of 6.45 mM in Fenton solution without PDMAS added, lower H_2O_2 concentrations were found in all other three microemulsions, which were 3.66, 4.02, and 2.73 for A1, A2, and A3, respectively. With PDMAS added, some intermediates generated from the attack of PDMAS by $HO^{\bullet}$ may react with H_2O_2 and impact the reaction of Fe^{2+} formation through Eq. (6). According to the COD removal efficiency, although the amount of H_2O_2 consumed in A2 and A3 microemulsions was nearly the same, the efficiencies for degradation of PDMAS were different.

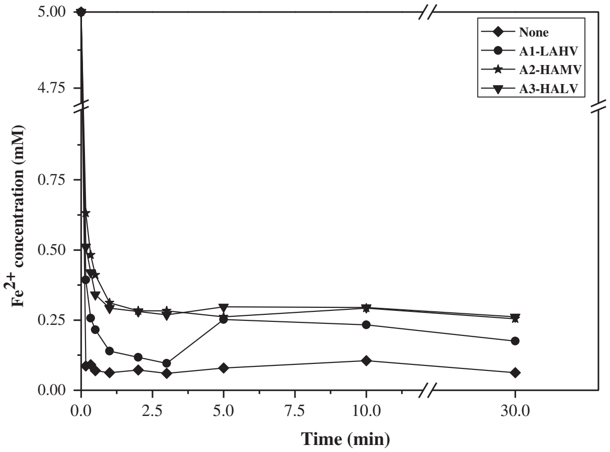

Fig. 5. Variation of Fe^{2+} concentration during Fenton process (conditions: pH = 2.5, $c(Fe^{2+}) = 5$ mM, $c(H_2O_2) = 10$ mM).

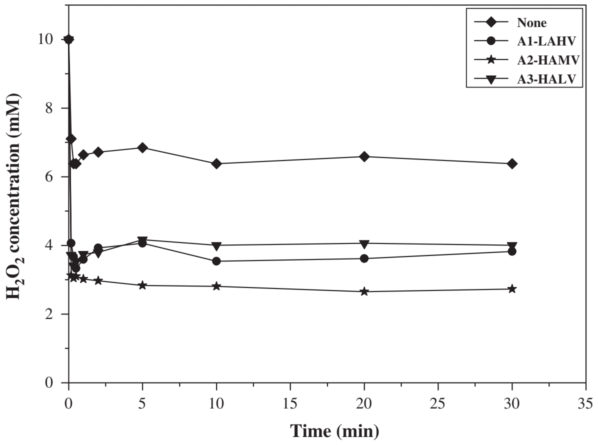

Fig. 6. Variation of H_2O_2 concentration during Fenton process (conditions: pH = 2.5, $c(Fe^{2+}) = 5$ mM, $c(H_2O_2) = 10$ mM).

The experiment also found that the higher ammonia value and the lower molecular weight of aminosilicone polymer samples could consume more H_2O_2. Aminosilicone polymer's degradation mechanism can explain this phenomenon. The consumptions of $HO^{\bullet}$ were mainly used to attack the side chain ammonia alkyl group and the main chain ring. The higher ammonia values mean more side chains of the equivalent aminosilicone polymers, the smaller molecular weight means more main chain ring s of equivalent aminosilicone. So, the higher ammonia values and lower molecular weight aminosilicone polymer samples will consume more of $HO^{\bullet}$. The variation of H_2O_2 concentration in the Fenton reaction, from another aspect, also verifies the reliability of the aminosilicone polymer's degradation pathway which was proven in another paper.

We can get the conclusion from the above results: The ammonia value of the aminosilicone and molecular weight affect the consumption of the concentration of H_2O_2 in the Fenton oxidation process and demonstrated the law of the higher ammonia values and low molecular weight will be more consumption of H_2O_2.

3.5. Evolution of ORP and pH

The parameters such as ORP and pH, which could reflect the reactions indirectly, were monitored real-time. Fig. 7 describes the typical evolution of ORP and pH during all Fenton systems (initial pH = 2.50; [Fe^{2+}] = 5 mM; [H_2O_2] = 10 mM).

It can be seen that, at an early stage, ORP values, with initial value of approximately 460 mV for the different experiments, increased suddenly to achieve values of about 610 mV within 1 min after the addition of H_2O_2, which indicate that substances with high oxidation potential were generated. Due to the high rate of reaction (1), a great deal of HO· and Fe^{3+} with high oxidation potential was produced and made the increment on ORP values. In the second stage, compared with *None* PDMAS sample's variation on ORP value in Fenton system, the ORP values of Fenton systems with added PDMAS decreased gradually in 5 min. In Fenton system, the reaction products remained stable in the early stage to keep a stationary ORP level. However, as the PDMAS added in to Fenton system, $HO^{\bullet}$ was consumed by oxidation with PDMAS so that the more oxidative species decreased and ORP dropped accordingly [27]. In a final stage, due to some oxidative intermediates coming from the oxidation of PDMAS, ORP value increased again.

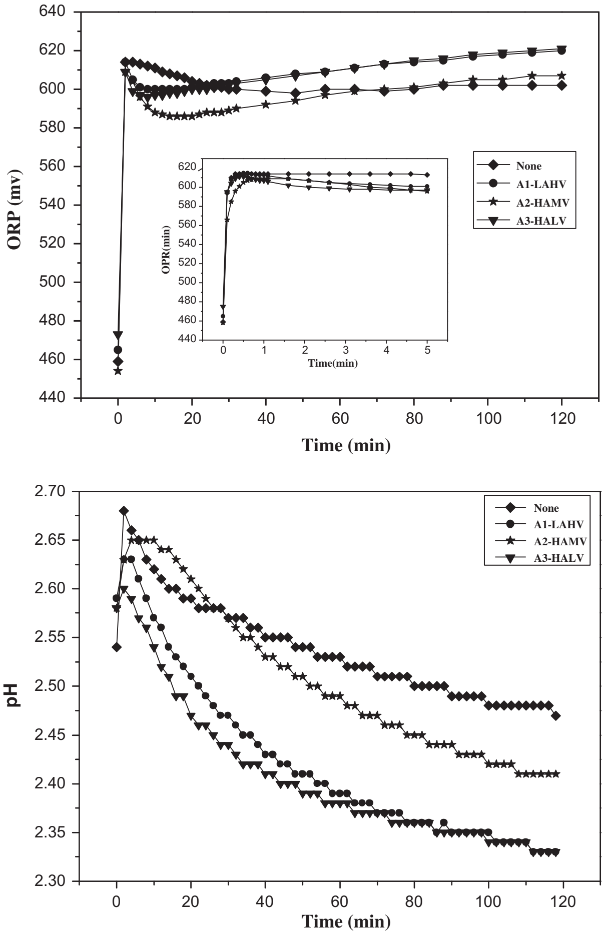

Fig. 7. Variation of ORP and pH during Fenton process.

The pH variation of Fenton systems was determined in the experiments. The pH values of solutions were all set at 2.50 and began to record at the addition of H_2O_2. It is apparent that all the pH came to the maximum within 1 min and declined as the reaction proceeded. Contrast to pH 2.70 of Fenton system alone, all the other pH values of PDMAS added systems were about 2.60 and lower at the latter reaction. When PDMAS was oxidized by $HO^{\bullet}$ and some organic acids would formed, the pH value could dropped. In addition, the hydrolysis of the ferrous ion and ferric ions also caused the decrease in pH.

4. Conclusions

Fenton process is an effective method for treatment of the PDMAS microemulsion wastewater with different molecular weights and amine values. For all three PDMAS, it was found that all the variables have the same effect trends, and the higher molecular weight aminosilicone polymer samples show slightly higher removal efficiency. Under the optimum operating condition (initial pH = 2.5, [Fe^{2+}] = 5 mM, and [H_2O_2] = 10 mM), the highest removal efficiencies were achieved to 85, 77, and 81% for A1, A2, and A3, respectively.

The variation of Fe^{2+} and H_2O_2 concentration and the evaluation of pH and ORP in real-time indicated that the oxidation reaction of Fenton agents result in the removal of PDMAS, and the characters of PDMAS and their oxidative intermediates affected the Fenton oxidation process. The Fe^{2+} and H_2O_2 concentrations were decreased rapidly with the oxidative process. And the molecular weight and ammonia values of the PDMAS have affected the consumption of the concentration of H_2O_2 and showed that the higher ammonia values and lower molecular weight would consume more of H_2O_2. In the Fenton reaction of the three different PDMAS, Fe^{2+} concentration and ORP, pH trends confirmed that the intermediates also affect the process of Fenton reaction with the degradation of PDMAS.

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