

The degradation pathway of aminosilicone polymer in aqueous microemulsion by Fenton process

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ABSTRACT

This research systematically studied the degradation pathway of aminosilicone polymers (PDMAS) by Fenton process in aqueous microemulsion. We show that the optimum parameters of Fenton process for degradation of PDMAS and COD reduction in aqueous microemulsion (COD = 4500 mg/L) are pH of 2.5, ferrous iron of 5 mM, and hydrogen peroxide of 10 mM. Under optimal reaction conditions and with pH modified to 8 after Fenton reactions, 42 mg/L NH_4^+ was produced along with 76.8% COD removal, in which oxidation and coagulation contributed 10.6% and 66.2%, respectively. Yet, COD removal of PDMAS emulsion by same amount of ferric ions at pH 8 was only 5.7%, indicating the major removal of COD was through precipitation of PDMAS and its oxidation intermediates from Fenton reaction due to the destabilization of the microemulsion resulted from surfactant degradation. Comparison of the FTIR spectra before and after treatment by Fenton process revealed the absence of amine groups on side chains, which suggested the complete break down of the C–N bonds by hydroxyl radicals. GPC results further showed that the backbone of PDMAS was likely broken down randomly, resulting in intermediates with lower molecular weights.

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1. Introduction

Aminosilicone polymers (PDMAS) are known as poly(-organosiloxanes), which are comprised of a group of compounds with silicon and oxygen [1]. Linear polydimethylsiloxane $[\text{CH}_3\text{—}[\text{Si}(\text{CH}_3)_2\text{O}]_n\text{—Si}(\text{CH}_3)_3]$ (PDMS) fluids are the simplest and most important industrial silicones [2]. Contrast to the linear PDMS, PDMAS have some side chains with amine functional groups, which give these polymers some important properties, such as good washing ability, strong polarity, low surface tension, water repellence, and exceptional thermal and chemical stability [1]. As a result, aminosilicone-in-water emulsions are commonly used as antifoaming agents, fabric softener and lubricants [2]. The structure of PDMAS can be expressed by Scheme 1 [3].

Silicone compounds are essentially nonreactive, except when exposed to strong acids, bases, or oxidants [4]. PDMAS are 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 [5,6] and biodegradation of Si–C bond also seems to be difficult [7].

Meanwhile, silicone polymers that enter into aquatic environment can be tightly adsorbed by sediments and accumulate. Therefore, PDMAS are considered as environmentally persistent compounds [5,7], which could cause a potential threat to the environment [1].

In China, the consumption of PDMAS is significant. PDMAS are typically used as water emulsions (microemulsion) since its microemulsion form (oil-in-water) is very stable [8]. The aminosilicone-in-water emulsions exist in effluent of aminosilicone chemical plants and textile dyeing factories. Like PDMS, there was no observed degradation of PDMAS in conventional bio-based wastewater treatment processes. With the increasing production and consumption of PDMAS, the treatment technologies for PDMAS in aqueous emulsions are in great demand.

Fenton reagent consisting of H_2O_2 and ferrous iron has been widely used in the treatment of industrial wastewater [9–11]. Hydroxyl radicals produced from the activation of H_2O_2 by ferrous iron (Reaction (1)) have very high standard redox potential ($E^\circ = 2.8 \text{ V SHE}$) and are able to attack most organic pollutants.



The main advantage of Fenton process is its ability to degrade many pollutants to harmless compounds such as water, CO_2 , organic acids and possibly other inorganic species under moderate reaction conditions and at relatively low cost [12,13].

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Few researches reported the treatment of emulsions containing both high and low-concentrations of PDMAS using Fenton and photo-Fenton processes [3]. The limited results suggested that PDMAS were removed from the aqueous solution as a result of the phase separation process. Whether or not the PDMAS oxidized remains unclear. The main objective of this research was to study the PDMAS's degradation pathway during Fenton process through characterizing the reaction intermediates and to optimize this process for its possible future application in PDMAS wastewater treatment.

2. Experimental section

2.1. Materials and methods

Concentrated PDMAS-in-water emulsion was obtained from Transfar Group Corporation (Hangzhou city, China). The emulsion contained ~50% PDMAS with hydroxyl end groups and ~16% of a non-ionic surfactant (fatty alcohol-polyoxyethylene ether, $C_{12}H_{25}O(CH_2CH_2O)_9H$). The sizes of PDMAS are between 38,843 and 357,133 Da and the amine content is ~0.4 mmol/g. Analytical grade H_2O_2 solution (30%, w/w), $FeSO_4 \cdot 7H_2O$, H_2SO_4 and NaOH were purchased from Sinopharm Chemical Reagent Corporation (Shanghai city, China).

For COD measurement, the samples were pre-heated at 40 °C for 30 min to eliminate the influence of hydrogen peroxide [14], then the COD was determined using dichromate titrimetric method [15]. The H_2O_2 concentration was determined spectrophotometrically at 500 nm using potassium titanium (IV) oxalate [16]. Before determination of hydrogen peroxide concentration, samples were mixed with 1 ml methanol to quench the Fenton reaction [17]. Ammonia nitrogen (NH_4^+-N) was determined according to the standard method [15].

PDMAS and reaction products for infrared analysis were prepared by casting the dried polymer evenly onto a clean KBr disk. FTIR spectrophotometer (Nicolet, AVA TAR370) recorded infrared absorbance spectra ranged from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . Gel permeation chromatography (Waters, 1525/2414) was employed to identify PDMAS and reaction products in order to find out the change of number-average molecular weights (Mn), weight-average molecular weights (Mw), peak position of molecular weight (Mp) and molecular weight distributions during the degradation process. The standard sample was polystyrene. Tetrahydrofuran (THF) was used as the mobile phase that flowed at 1.0 ml/min with column temperature at 25 °C.

2.2. Fenton experiments

Synthesized wastewater was prepared by diluting concentrated PDMAS emulsion with deionized water. The mass concentration of PDMAS emulsion was 12.8 g/L, COD value of the wastewater was 4500 ± 100 mg/L, and the pH value was 7.2 ± 0.1. The experimental system was comprised of a 1 L beaker filled with synthesized wastewater volume of 500 mL and mechanical stirrer agitated at speed of 250 rpm. The beaker was open to the atmosphere at room temperature (23–25 °C). Certain amount of ferrous sulfate was added into the wastewater and the initial pH was adjusted using sulfuric acid, then reaction started as hydrogen peroxide was added.

Samples were taken out at predetermined times. The sample was treated by adjusting pH value to 8.0 with sodium hydroxide and sit for 30 min to precipitate PDMAS and the intermediates produced by oxidation of PDMAS with iron hydroxides. The supernatant was then filtered through a 0.45 μm filter for analyses of COD and NH_4^+-N concentration. In some cases, samples were

taken and treated by adjusting pH value to 1.0 with sulfuric acid and then analyzed for COD. Control experiments were performed by employing only H_2O_2 , Fe^{2+} or Fe^{3+} at pH 2.5 to evaluate their efficiency in COD removal. The samples were treated by adjusting pH to 8.0 after reaction and the supernatant was subjected to COD measurement.

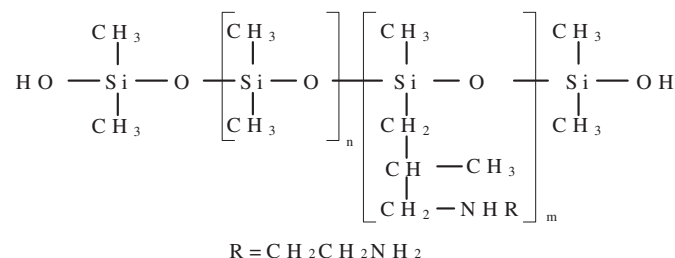
The initial PDMAS microemulsion and the reaction micro-emulsion samples were demulsified by adding excess amount of NaCl, with the help of magnetic stirring at 500 rpm. Then the organics on the surface of aqueous solution were transferred to beakers and dried at 105 °C for 24 h for FTIR and GPC analyses.

3. Results and discussion

3.1. COD removal by oxidation and coagulation

Control experiments were designed to investigate the COD removal efficiency by different processes, with the results shown in Fig. 1. It is obvious that the COD removals by hydrogen peroxide and ferrous ion only are negligible. Therefore, it is clear that the oxidation of PDMAS emulsion by hydrogen peroxide and coagulation of PDMAS emulsion by ferrous ion at pH 8 have little ability in removing COD. The Fenton process combining with coagulation at pH 8, at the other hand, resulted in as high as 76.8% removal of COD. Therefore, with the hydroxyl radical and ferric iron produced, Fenton process (followed with coagulation) is an efficient method to remove COD from PDMAS wastewater. It is well known that ferrous and ferric iron cannot cause coagulation at pH lower than 2 [18]. In our study, pH value of reaction mixture after Fenton reaction was also adjusted to 1 to completely eliminate the coagulation effect, and the COD reduction caused by hydroxyl radical oxidation was determined to be 10.6%. The COD removal caused by precipitation/coagulation of PDMAS and its reaction intermediates by iron hydroxide was then estimated to be 66.2%, which was much higher than that by oxidation. Therefore, coagulation plays a key role in COD reduction of microemulsion.

Interestingly, coagulation of PDMAS emulsion by ferric hydroxide without the oxidation only removed 5.7% COD, much lower than that caused by coagulation after Fenton reaction. Therefore, it can be deduced that the degradation of surfactant molecules by hydroxyl radicals and consequent breakdown of PDMAS emulsion could be a critical step in COD removal. Indeed, Teixeira et al. (2005) reported that during Fenton reaction PDMAS and/or partially oxidized PDMAS were removed from the aqueous solution through phase separation as a result of surfactant breakdown. The surfactant used in our PDMAS emulsion is fatty alcohol-polyoxyethylene ether ($C_{12}H_{25}O(CH_2CH_2O)_9H$), a non-ionic surfactant, which can be efficiently degraded by hydroxyl radicals [19]. It has been suggested that the oxygen in the EO groups ($-CH_2CH_2O-$) is prone to be attacked by hydroxyl radicals during oxidation process [20,21]. The hydroxyl radical attack will result in products with less EO groups and eventually organic acids and carbon



Scheme 1. Schematic diagram of the structure of PDMAS.

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