Journal of Hazardous Materials 169 (2009) 443–447

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Degradation of dimethyl disulfide using homogeneous Fenton's reaction

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ARTICLE INFO

Article history:
Received 8 August 2008
Received in revised form 12 February 2009
Accepted 25 March 2009
Available online 2 April 2009

Keywords:
Fenton's reaction
Odors
Dimethyl disulfide
Poultry waste
Degradation

ABSTRACT

In this work the degradation of a model odor compound (dimethyl disulfide, DMDS) using Fenton's reaction is reported. Dimethyl disulfide is present in wastewaters generated during production of poultry feather and viscera meal. Oxidation was carried out in batch reactor with temperature control. Experimental design technique was used to investigate the influence of concentration of hydrogen peroxide and Fe^{2+}, temperature and pH on degradation of DMDS. Control reactions using H_2O_2 without Fe^{2+} were carried out, but DMDS degradation could only reach 60% for a 0.025 mg L^{-1} DMDS solution, at pH 3, 60 °C using 10,000 mg L^{-1} H_2O_2 in 30 min of reaction. The Fenton's reaction could effectively remove DMDS, reaching 95% degradation at pH 3, 60 °C, 5 mg L^{-1} H_2O_2 and 1 mg L^{-1} Fe^{2+} after only 10 min of contact. A kinetic study of the Fenton's reaction was carried out, varying the concentration of hydrogen peroxide, Fe^{2+} and temperature.

1. Introduction

The increasing sensitivity of the population for odors and the demand for a clean and healthy environment have been pushing industries to a more effective control of the emission of odors and toxic pollutants in the air [1]. The conventional technologies for degradation of pollutants, excluding the biological processes, decisively do not solve the problem, since they are based on the phase transfer of these substances, transferring responsibility of the problem for future generations. The biological treatment is often the most cost effective conventional alternative for treatment of wastewaters since mineralization of the pollutants is often achieved. However, industrial wastewaters usually contain toxic and/or non-biodegradable organic substances, for which biological treatment is not efficient [2].

The poultry feather and viscera are the two major by-products generated during poultry meat production. These by-products are usually cooked in pressurized vessels to yield feather and viscera meals, which are used in the formulation of animal feed. The exhaust gases that leave the cooker are rich in malodorous compounds that are normally removed from the waste gases using wet scrubbers. The scrubbers require rather clean water for effective odor removal, and they generate a large amount of wastewater that should be properly disposed of. Thus, alternatives that could decrease water consumption are of great interest to such industries.

One of the alternatives for treatment of wastewaters and residual gases is based on chemical oxidation using Fenton's reaction (hydrogen peroxide in the presence of a catalyst, like salts of iron). Fenton's reaction is known to be very effective in the degradation of hazardous organic pollutants from water. The main advantage is the complete destruction of contaminants to harmless compounds, water and inorganic salts. The Fenton's reaction causes the formation of highly reactive hydroxyl radicals [3,4]. Hydrogen peroxide is a strong oxidant, and its decomposition generates water and oxygen [5]. In homogeneous Fenton's reaction, the iron can be recovered by alkaline precipitation after the reaction.

This work aimed to study the oxidation of a model odor compound (dimethyl disulfide) using homogeneous Fenton's reaction, proposing an alternative for odor control in poultry by-product processing plants.

2. Materials and methods

2.1. Samples

A commercial standard of the dimethyl disulfide (DMDS, 99%, Aldrich) was used in all experiments. This compound was chosen, since it is found in wastewaters from the poultry by-products industry, and for its low odor threshold (sub-μg m^{-3}) [6]. A 0.025 mg L^{-1} solution of DMDS was prepared with deionized water before every experimental run. The pH of the solution was adjusted to the pH determined in the experimental design, using a NaOH 1 M or HCl 1 M solution.

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doi:10.1016/j.jhazmat.2009.03.118

2.2. Extraction and analysis

Samples were extracted from the headspace of the standard solution by solid phase microextraction (HS-SPME) technique. The extracting fiber used was polydimethylsiloxane (PDMS), 30 μm of film thickness (Supelco, USA). The fibers were previously conditioned in the chromatograph injector for 30 min at 250 °C, according to the supplier's recommendations.

For each headspace extraction, 10 mL of sample was placed in a 20 mL amber glass vial with screw top and Teflon faced rubber septum. The vial was placed in a water bath at 50 °C. Magnetic stirring was used to increase the transfer of the volatile compound from the liquid phase to the headspace. This procedure increases the adsorption of the compounds in the SPME fibers and reduces the time necessary for the extractions [6–9]. The extraction conditions were determined in preliminary experiments (results not shown).

A gas chromatograph equipped with a split/splitless injector and a mass spectrometry detector (CG/MS Shimadzu QP5050A) was used for the instrumental analysis. The injector was equipped with a 0.8 mm i.d. SPME liner. Runs were carried out with a fused silica capillary column (DB-WAX, 30 m × 0.25 mm × 0.25 μm – polar, polyethylene glycol; J&W Scientific).

The injection was carried out in splitless mode and desorption of the compound from the fiber was achieved after 4 min of fiber exposition inside the injection port. The temperatures of the injector and MS-interface were set at 220 °C and 250 °C, respectively. Oven temperature was programmed from 50 °C to 80 °C at 20 °C min^{-1}, then to 90 °C at 5 °C min^{-1} and finally to 155 °C at 20 °C min^{-1}. Helium was used as carrier gas at a flow rate of 0.7 L min^{-1} and the detector voltage was 1.2 kV.

2.3. Oxidation runs and analysis of the results

A control run was carried out for each experimental run of DMDS degradation. The control conditions were the same as the sample, however, without the addition of H_2O_2 and Fe^{2+}. Percent of DMDS degraded was calculated based on the blank runs.

The evaluation of the effects of the variables (H_2O_2 and Fe^{2+} concentrations, pH and temperature) on the degradation of DMDS was carried out using experimental design technique. The results were analyzed with the aid of the software Statistica 6.1 (StatSoft Inc., Tulsa, OK, USA). All the tests were carried out in duplicate, and the central points in triplicate. The statistical analyses were carried out using pure error, identifying the significant regression coefficients with a confidence level of 95%.

2.3.1. Oxidation with hydrogen peroxide

The studies of chemical oxidation of DMDS with hydrogen peroxide were carried out with aqueous hydrogen peroxide (H_2O_2) 30% (Merck, Brazil). The levels of the factors investigated are presented in Table 1, for the first complete experimental design, which consisted in a two level, three-factor experimental design (2^3), with one experimental point at the center of the cube of the experimental space. The DMDS solution (10 mL, 0.025 mg L^{-1}) was placed in 20 mL vials with magnetic stirring, and H_2O_2 was added to reach the required concentration. The vials were immediately closed and kept under the reaction conditions for 30 min.

Table 1
Levels of the factors studied in the 2^3 experimental design.

Level	H_2O_2 (mg L^{-1})	Temperature (°C)	pH
−1	500	25	3
0	5250	42.5	7
+1	10,000	60	11

Table 2
Levels of the factors studied in the second experimental design.

Level	H_2O_2 (mg L^{-1})	Fe^{2+} (mg L^{-1})	Temperature (°C)
−1	5	0.1	25
0	27.5	0.55	42.5
+1	50	1	60

2.3.2. Oxidation with homogeneous Fenton's reaction

The runs were carried out in the same way as described in the previous item, though adding a solution of ferrous sulfate (Merck, Brazil). The initial pH was kept at 3. The levels of the factors studied in the 2^3 experimental design are presented in Table 2. These levels were chosen based on the results of preliminary experiments (results not shown). The aim of the designs was to maximize the degradation of DMDS with the lowest possible amounts of H_2O_2 and Fe^{2+}.

2.3.3. Kinetic study of the oxidation of DMDS for the homogeneous Fenton's reagent

This study was carried out to determine a relationship between the reaction rate and the concentrations of H_2O_2 and of Fe^{2+}. An expression for the calculation of the rate constant of the reaction (k) was obtained following the approach proposed by Lin et al. [10]. For the kinetic study, the concentration of peroxide was kept constant (5 mg L^{-1}), while varying Fe^{2+} concentration (0.5 mg L^{-1}, 1 mg L^{-1}, 5 mg L^{-1} and 10 mg L^{-1}). Then, this latter was kept constant (1 mg L^{-1}) and peroxide amount varied (1 mg L^{-1}, 5 mg L^{-1}, 10 mg L^{-1} and 50 mg L^{-1}). DMDS concentration was monitored as a function of time of reaction.

The effect of the temperature in the oxidation of DMDS with the homogeneous Fenton's reagent was evaluated at 1 mg L^{-1} of Fe^{2+} and 5 mg L^{-1} of H_2O_2, pH 3 and time of reaction of 30 min. Temperatures studied were 25 °C, 40 °C, 55 °C and 60 °C.

3. Results and discussion

3.1. Oxidation with hydrogen peroxide

The matrix of the first experimental design and the respective responses in terms of degradation percentage (oxidation) of DMDS, using H_2O_2 is presented in Table 3.

The results of the analysis of variance validated the coded empiric model presented in Eq. (1), since the calculated F-test (Fisher distribution) is 6.8 times higher than the tabulated F, with a correlation coefficient $R = 0.90$, for the analysis of the regression in relation to the residues.

$$\%\text{Removal} = 31.7 + 14.8 \times T - 6.1 \times \text{pH} + 1.4 \times \text{per} + 4.4 \times T \times \text{per} - 4.5 \times \text{pH} \times \text{per} \quad (1)$$

where T is the reaction temperature, pH is the pH of the solution and per is the concentration of H_2O_2.

Table 3
Matrix of the 2^3 experimental design (real and coded values) and the respective responses in terms of degradation of DMDS. Runs without addition of Fe^{2+}.

Run	Temperature (°C)	pH	H_2O_2 (mg L^{-1})	% Degradation
1	25 (−1)	3 (−1)	10,000 (+1)	22.4 ± 4.0
2	60 (+1)	3 (−1)	10,000 (+1)	59.7 ± 0.2
3	25 (−1)	11 (+1)	10,000 (+1)	0
4	60 (+1)	11 (+1)	10,000 (+1)	39.5 ± 1.4
5	25 (−1)	3 (−1)	500 (−1)	19.3 ± 2.0
6	60 (+1)	3 (−1)	500 (−1)	39.2 ± 1.6
7	25 (−1)	11 (+1)	500 (−1)	15.0 ± 1.6
8	60 (+1)	11 (+1)	500 (−1)	37.0 ± 1.6
9	42.5 (0)	7 (0)	5250 (0)	53.3 ± 2.2