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Process Biochemistry 42 (2007) 1398–1405

Process Biochemistry

www.elsevier.com/locate/procbio

Optimal dimethyl sulfoxide biodegradation using activated sludge from a chemical plant

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Received 22 November 2006; received in revised form 7 July 2007; accepted 17 July 2007

Abstract

Inappropriate biological treatment of dimethyl sulfoxide (DMSO) used by opto-electronics and semi-conductor industries would result in production of malodorous compounds, e.g. dimethyl sulfide, methane-thiol and hydrogen sulfide. The best sludge for DMSO biodegradation was obtained from the activated sludge of a chemical company that used to provide DMSO for the above industries. Under the optimal conditions of pH 7.0–8.5 and 30 °C, the highest removal efficiency in treatment of 500 mg l^{-1} of DMSO occurred at the rate of 0.078 g DMSO per gram suspended solids per day corresponding to 37 h for complete DMSO biodegradation in a shake-flask culture. However, the time needed for DMSO biodegradation could be reduced to 16 h at the rate of 0.153 g DMSO per gram suspended solids per day if a repeated-batch mode was adopted, indicating that an acclimation period is required by the DMSO degraders. The reaction time could further be shortened to less than 10 h with 95% removal of the 750 mg l^{-1} DMSO at the maximum rate of 0.909 g DMSO per gram suspended solids per day using an oxygen-enriched air-lift bioreactor. No malodorous compounds, such as dimethyl sulfide, were produced revealing that the biodegradation pathway is oxidative and can solve the odor problems common in the biological wastewater treatment plant of the abovementioned industries.

Keywords: DMSO; Malodorous compounds; Air-lift; Repeated-batch

1. Introduction

Dimethyl sulfoxide (DMSO) has been widely used for many industrial purposes because of its high-hygroscopic property, low flammability, good thermal stability, and versatile solubility in a range of organic and aqueous solvents, including ethanol, benzene and chloroform. DMSO is also recognized as a benign product for the environment because it can easily be recycled in a sustainable manner due to its high-boiling point. Thus, the compound has recently been considered as a good substitute for many organic solvents, and the annual sales of industrial DMSO worldwide has been on the increase. In Japan, up to 5000 tonnes of DMSO are produced per year for many industrial applications [1]. To our knowledge, the rapidly growing opto-electronic and integrated circuit (IC) packaging industries in Taiwan have used DMSO as a major photo-resist stripper and a polyimide-silylated packaging solvent, respectively. In 2001, around 900 tonnes of DMSO were imported from Japan [2], and Chang Chun Group (Miaoli County, Taiwan) has been providing the DMSO compound and its recycling service for many years.

DMSO is toxic to organisms because of its high osmolarity [3]. In addition, DMSO is transparent under room temperature and possesses a low-vapor pressure due to its high polarity, thus it can easily be accumulated in the water body without any indication of its presence [3]. The DMSO will further be biodegraded through the reduction pathway changing from odorous intermediate compounds (i.e. dimethyl sulfide (DMS) and methane-thiol (MT)) to the final malodorous hydrogen sulfide. Glindemann et al. [4] found the link between the intermittent occurrence of DMSO residues in influent of a wastewater treatment plant and the malodorous DMS in the activated sludge aeration tank.

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1359-5113/$ – see front matter
doi:10.1016/j.procbio.2007.07.013

DMS and MT also contribute to global warming and acid precipitation. Endogenously produced DMS and MT are degraded anaerobically by methanogens [5]. DMS, MT, carbonyl sulfide, dimethyl disulfide and hydrogen sulfide are the most common volatile sulfur compounds present in the biogas [6]. Most of them have a low-odor-threshold value so they are apt to exceed the odor emission standard [7]. Incubation of activated sludge with 1–10 mg l^{-1} of DMSO in bottles produced DMS in the headspace gas at concentrations exceeding the odor threshold by approximately four orders of magnitude [4].

The U.S. Environmental Protection Agency allows the discharge of wastewater containing DMSO at a concentration below 0.05 mg DMSO l^{-1}, or 100–200 mg l^{-1} according to total organic carbon (TOC) [8,9]. Therefore, DMSO must be removed or retrieved from wastewater; hence, it is of urgent need to develop relevant treatment technology for such purpose.

The method used in treatment of DMSO varies with the level of DMSO concentration in the liquor. Wastewater containing DMSO exceeding 1000 mg l^{-1} is most concentrated and can be recycled in the original processes. Wastewater derived from the washing or rinsing processes in the manufacture of semiconductors or liquid crystal display contains 10–1000 mg l^{-1} DMSO, which is comparable with that of the aforementioned DMSO-recycled liquor. Thus, the chemical decomposition and oxidation of low-concentration DMSO by UV or Fenton processes are the preferred solutions to the odor problem of wastewater treatment plant [8,10–12]. However, the huge amount of chemicals consumed by the physio-chemical process is not cost effective in treating the relatively low-concentration DMSO in discharged wastewater. Koito et al. [11] proposed a chemical oxidative pathway for oxidizing DMSO to $DMSO_2$ followed by aerobic biological treatment. Conversion of DMSO to $DMSO_2$ by chemical oxidation could avoid the malodorous problem.

Murakami-Nitta et al. [13] have isolated a new DMSO-degrading microorganism, *Cryptococcus humicolus* WU-2, using an oxidative biodegradation pathway. However, Kino et al. [14] found that the efficiency of biodegradation of the odorless intermediate, dimethyl sulfone ($DMSO_2$) using strain WU-2 was too low. Other microorganisms were further isolated to help complete the whole DMSO odorless degradation process. If a feasible biological treatment technology for DMSO removal can be developed, both the odorous DMS problem and the wastewater pollution problem would be solved simultaneously for opto-electronic and IC packaging industries. Thus, the main goal of this study was to achieve optimal DMSO biodegradation without producing odorous compounds using activated sludge selected from many sources. Many influencing factors including pH, temperature, oxygen supply and acclimation were examined. The air-lift bioreactor was employed to supply dissolved oxygen for DMSO biodegradation.

2. Materials and methods

2.1. Chemicals

DMSO, KH_2PO_4, K_2HPO_4, $CaCl_2$ and Sucrose were purchased from Sigma–Aldrich Co. (St. Louis, USA). $MnSO_4$, $FeCl_3$, NH_4NO_3 and $MgSO_4$ were obtained from Merck & CO., Inc. (Whitehouse Station, USA). All other chemicals were of reagent grade or above.

Table 1
Composition of medium used for acclimated culture and as DMSO-simulated wastewater

Compounds	Concentration (mg l^{-1})
DMSO	500
Sucrose	50
$(NH_4)_2SO_4$	120
$MgSO_4{\cdot}7H_2O$	25
$FeCl_3{\cdot}6H_2O$	0.15
$MnSO_4{\cdot}H_2O$	2.50
$CaCl_2$	1.82
KH_2PO_4	2.72 g l^{-1}
K_2HPO_4	5.23 g l^{-1}

2.2. Acclimation of activated sludge

The potential DMSO-degrading microbial consortium was selected from activated sludge and lake mud. About 100 l of sludge collected from activated sludge of a chemical plant or lake mud were prescreened through a metallic sieve (No. 60 mesh) to remove a high portion of non-degradable suspended solids. It was aerated in an open-top tank and regularly fed with simulated wastewater containing DMSO (Table 1) as a nutrient medium according to the report of Yang and Myint [9]. The activated sludge was precipitated, collected and then washed with the simulated wastewater every month. The settled activated sludge was occasionally wasted to maintain a constant quantity, 10% (v/v) in the tank. The activated sludge was incubated for at least 3 months before the experiment started.

2.3. Background study and DMSO aeration

In order to check if the DMSO under aeration was evaporated into air or absorbed into nutrient colloids, two 500-ml Erlenmeyer flasks fed with 300 ml of 100- and 900-mg DMSO l^{-1} sterilized simulated wastewater containing DMSO were immersed in a shaking water bath (30 °C; 120 rpm) and aerated at a rate of 0.5 l h^{-1} through 0.22-μm Optiseal Cartridge Filters (Millipore, Billerica, MA) using a magnetic diaphragm air pump (Hiblow, Taipei County, Taiwan). The DMSO concentration was measured at regular time intervals. Moreover, the background study was also carried out in the air-lift experiment at an aeration flow rate of 10 l min^{-1}.

2.4. DMSO biodegradation tests

The DMSO-degrading shake-flask culture was incubated on an orbital shaker at a speed of 120 rpm using activated sludge from various sources and DMSO concentrations under different temperatures and pH levels. One hundred ml of acclimated activated sludge from different sources were centrifuged for 5 min at 5000 rpm and 4 °C. The supernatant was poured out and the precipitated biomass was then re-suspended with 100 ml of sterilized simulated wastewater containing no DMSO. The cleaning procedures were repeated twice to wash out any DMSO residues and other impurities, and the sludge was then used as an inoculum. A 10% seeding ratio (i.e. 30-ml inoculum fed into 270-ml sterilized simulated wastewater containing DMSO) was chosen. The initial DMSO concentration, pH, and temperature in the simulated wastewater were 500 mg l^{-1}, 7.0 and 25 °C, respectively, for all experiments, unless otherwise stated. The different operating conditions include temperatures of 20, 25, 30, 35 and 40 °C, pH of 3.0, 5.0, 7.0, 8.5 and 10, and DMSO concentrations of 200, 400, 600, 800 and 1000 mg DMSO l^{-1}. McIlvaine, and Clark and Lubs buffer solutions were used for the pH adjustment in the range of 2.6–7.6 and 8.0–10.2, respectively [15].

2.5. Fed-batch and repeated-batch experiments

Among different cultural sources, 200 ml of the activated sludge (suspended solids (SS) about 6000-mg l^{-1}) that performed best in DMSO biodegradation in