Journal of Environmental Sciences 26 (2014) 566–574

Available online at www.sciencedirect.com

Journal of Environmental Sciences

www.jesc.ac.cn

Elucidating the removal mechanism of *N,N*-dimethyldithiocarbamate in an anaerobic-anoxic-oxic activated sludge system

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ARTICLE INFO

Article history:
Received 07 April 2013
revised 28 June 2013
accepted 04 July 2013

Keywords:
N,N-dimethyldithiocarbamate
hydrolysis
biodegradation
aerobic processes
anaerobic processes
wastewater treatment

DOI: 10.1016/S1001-0742(13)60448-9

ABSTRACT

N,N-Dimethyldithiocarbamate (DMDTC) is a typical precursor of *N*-nitrosodimethylamine (NDMA). Based on separate hydrolysis, sorption and biodegradation studies of DMDTC, a laboratory-scale anaerobic-anoxic-oxic (AAO) system was established to investigate the removal mechanism of DMDTC in this nutrient removal biological treatment system. DMDTC hydrolyzed easily in water solution under either acidic conditions or strong alkaline conditions, and dimethylamine (DMA) was the main hydrolysate. Under anaerobic, anoxic or oxic conditions, DMDTC was biodegraded and completely mineralized. Furthermore, DMA was the main intermediate in DMDTC biodegradation. In the AAO system, the optimal conditions for both nutrient and DMDTC removal were hydraulic retention time 8 hr, sludge retention time 20 day, mixed-liquor return ratio 3:1 and sludge return ratio 1:1. Under these conditions, the removal efficiency of DMDTC reached 99.5%; the removal efficiencies of chemical organic demand, ammonium nitrogen, total nitrogen and total phosphorus were 90%, 98%, 81% and 93%, respectively. Biodegradation is the dominant mechanism for DMDTC removal in the AAO system, which was elucidated as consisting of two steps: first, DMDTC is transformed to DMA in the anaerobic and anoxic units, and then DMA is mineralized to CO_2 and NH_3 in the anoxic and oxic units. The mineralization of DMDTC in the biological treatment system can effectively avoid the formation of NDMA during subsequent disinfection processes.

Introduction

N-Nitrosodimethylamine (NDMA) has been known as a carcinogenic and mutagenic compound since the 1960s (Patal, 1982). In recent years, NDMA has been studied widely as a novel nitrogenous disinfection by-product (Choi and Valentine, 2002; Mitch and Sedlak, 2002; Hatt et al., 2013). Research has shown that NDMA can be produced in disinfection processes using chlorine or chloramines in water or wastewater treatment plants (Sedlak et al., 2005; Yoon et al., 2011). An investigation conducted in the USA showed that the effluent of a municipal wastewater treatment plant disinfected by chlorine contained 200–400 ng/L of NDMA (Pehlivanoglu-Mantas et al., 2006). In 1998 NDMA was included in the US EPA's list of priority pollutants found in drinking water (US EPA, 1998). The California State Government has mandated that NDMA concentrations in drinking water should not exceed 10 ng/L (DHS, 2002), while the Environment and Energy Department of Ontario, Canada set a NDMA limit of 9 ng/L (MOE, 2003).

N,N-Dimethyldithiocarbamate (DMDTC) is a dimethylamide and is considered an important precursor of NDMA (Mitch and Sedlak, 2004; Padhye et al., 2013). It has been reported that the NDMA molar conversion yield from DMDTC was about 3% ((mol/L)/(mol/L)) after reaction with chloramines (Selbes et al., 2013). DMDTC is an important chemical material and organic synthetic intermediate. It is widely used in the production of rubber,

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pesticides and bactericides (Goldman et al., 2008). It is commonly used as a rubber vulcanization accelerator and as a styrene-butadiene rubber polymerization terminator. As an important bactericide, DMDTC not only is used in industrial circulating water cooling systems, but also is the intermediate species of the synthetic pesticides thiram and ziram. In addition, DMDTC is used to prepare chelating resins and mineral flotation collectors. Nearly 1400 metric tons of DMDTC is applied in the USA annually (Weissmahr et al., 1998). The US EPA (2001) estimates a peak concentration of 860 μg/L in surface water and average concentrations of 19 μg/L for ziram alone.

Wastewater treatment plants (WWTPs) are a potential source of DMDTC pollution in the environment (Mitch and Sedlak, 2004). A previous survey demonstrated that DMDTC concentrations were between 277–1358 μg/L in the influent of a typical municipal WWTP in Shanghai, China (Cao and Li, 2012). That WWTP did not process any industrial wastewater, indicating that the concentration of DMDTC may be even higher in WWTPs accepting industrial wastewater. Research has shown that NDMA-contaminated DMDTC-containing treatment chemicals and fungicides contribute to pulses of high concentrations of NDMA in raw sewage (Mowbray, 2002). Therefore, it is of interest to study the removal of DMDTC in WWTP. To date, reports investigating the removal of DMDTC in WWTP are limited. Mitch and Sedlak (2004) investigated the fate of NDMA precursors in municipal WWTP, indicating that although secondary biological treatment effectively removed dimethylamine (DMA), secondary treatment was less effective at removing other NDMA precursors, including dimethylamides. Therefore, elucidating the fate of DMDTC in secondary biological treatment processes is beneficial for better understanding the removal of dimethylamides as NDMA precursors.

The main purpose of this study was to investigate the removal of DMDTC in biological wastewater treatment processes. First, the hydrolysis of DMDTC at different pH values was investigated. Then sorption experiments were performed with sterilized sludge, as was DMDTC biodegradation under anaerobic, anoxic and oxic conditions. Finally, a laboratory-scale anaerobic-anoxic-oxic (AAO) system was constructed to investigate the removal of DMDTC in WWTP with nutrient removal. The effects of operational parameters such as hydraulic retention time (HRT), sludge retention time (SRT), mixed-liquor return ratio (MLRR) and sludge return ratio (SRR) were evaluated. Based on the above investigation, the removal mechanism of DMDTC during activated sludge processes was elucidated.

1 Materials and methods

1.1 Reagents

DMDTC (purum, 40% in H_2O), acetonitrile and methanol (HPLC grade, ⩾ 99.9%) as high performance liquid chromatography (HPLC) mobile phase, sodium bicarbonate (analytical reagent, ⩾ 99.5%), and phenyl isothiocyanate (GC grade, ⩾ 99.0%) as derivative reagents were purchased from Sigma-Aldrich Company (USA). DMA (37%, *W/W*, in H_2O) was purchased from Chem Service, Inc. (West Chester, USA). Sodium carbonate (analytical reagent, ⩾ 99.8%), iodine (analytical reagent, ⩾ 99.8%) and potassium iodide (analytical reagent, ⩾ 99.0%) as derivative reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

1.2 Seed sludge and synthetic wastewater

The seed sludge was obtained from the return activated sludge tanks at the Quyang Municipal Wastewater Treatment Plant, Shanghai, China. It was washed three times, using tap water, to remove unnecessary organic substrate residues. After settling and drawing the supernatant, the final mixed liquor suspended solids (MLSS) of the seed sludge was in the range of 8000–10000 mg/L.

Synthetic wastewater was used for all the experiments. The synthetic wastewater was prepared using tap water and supplemented with nutrients, trace elements, and buffering compounds. The synthetic wastewater composition is listed as follows (mg/L): $C_6H_{12}O_6$ 150, peptone 150, NaAc 80, NH_4Cl 80, $KH_2PO_4{\cdot}2H_2O$ 26.3, $MgSO_4{\cdot}7H_2O$ 20, $CaCl_2$ 10.6, $NaHCO_3$ 80, $FeCl_3{\cdot}6H_2O$ 0.45, H_3BO_3 0.045, $CuSO_4{\cdot}5H_2O$ 0.009, KI 0.054, $MnCl_2{\cdot}4H_2O$ 0.036, $ZnSO_4{\cdot}7H_2O$ 0.036, EDTA 3. The main characteristics of the synthetic wastewater were: chemical organic demand (COD) = 300–350 mg/L, NH_3-N = 20–30 mg/L, PO_4^{3-}-P = 5–6 mg/L. The initial concentration of DMDTC introduced into the synthetic wastewater was 5000 μg/L.

1.3 Effects of pH on DMDTC hydrolysis

Some research indicates that substances containing dithio groups are not stable in aqueous solution, and would hydrolyze under both acidic and alkaline conditions (Watanabe et al., 2004; Brunner, 2009). The hydrolysis is faster when the carbon atom is connected to a nitrogen atom or oxygen atom (Duan et al., 2010). To investigate the effect of pH on DMDTC hydrolysis, experiments were carried out at initial pH values ranging from 2.0 to 13.0. In total 12 sets of 500 mL brown glass bottles with stoppers were prepared. Each set was performed in triplicate, for which a solution (250 mL) containing 11 mg/L DMDTC was dosed, and pH was adjusted by NaOH or H_2SO_4 as appropriate. All the bottles were kept in an incubator at 30 ± 1°C in the dark. At a predetermined time each set was sampled and analyzed for DMDTC and DMA contents by