Bioresource Technology 130 (2013) 278–287

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Modeling the fate and effect of benzalkonium chlorides in a continuous-flow biological nitrogen removal system treating poultry processing wastewater

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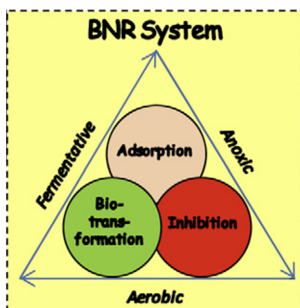
HIGHLIGHTS

- ▶ The fate and effect of BAC in a continuous-flow BNR system were simulated.
- ▶ The model considered BAC adsorption, inhibition, and resistance/biotransformation.
- ▶ BAC adsorption determines the level of its inhibitory effect.
- ▶ BAC biotransformation determines the extent of exposure of microbial communities.
- ▶ BAC inhibition is reduced/eliminated by microbial acclimation and enrichment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 September 2012
Received in revised form 18 November 2012
Accepted 25 November 2012
Available online 12 December 2012

Keywords:
Benzalkonium chlorides
Biological nitrogen removal
Kinetics
Modeling
Simulation

ABSTRACT

The fate and effect of the antimicrobial compounds benzalkonium chlorides (BACs) on the biological nitrogen removal (BNR) processes for a continuous-flow, three-stage laboratory-scale BNR system were modeled. Three kinetic sub-models, corresponding to each reactor, were developed and then combined in a comprehensive ASM1-based model. Kinetic parameters for the three sub-models were evaluated using experimental data obtained from independent batch assays. The biodegradation of BACs was modeled with a mixed-substrate Monod equation. The inhibitory effect of BACs on the utilization of degradable COD and denitrification was modeled as competitive inhibition, whereas non-competitive inhibition was used to model the effect of BACs on nitrification and inhibition coefficients were evaluated. The model simulated well the long-term performance of the BNR system treating a poultry processing wastewater with and without BACs. Enhanced BAC degradation by heterotrophs and increased resistance of nitrifiers to BACs, reflecting acclimation/enrichment over time, is a salient feature of the model.

1. Introduction

Sanitation practices in poultry and meat processing facilities generate wastewater which is combined with other wastewater streams and typically treated in biological nitrogen removal (BNR) systems comprised of a combination of fermentation, nitrification and denitrification processes. Quaternary ammonium compounds (QACs) are common antimicrobial compounds used extensively in industrial sanitizer formulations (Cross and Singer, 1994; Kummerer et al., 2002; Tezel and Pavlostathis, 2012). Among all classes of QACs, benzalkonium chloride homologs (BACs) of different alkyl chain lengths, mainly C_{12}, C_{14}, and C_{16}, are common in commercial sanitizer formulations (Sutterlin et al., 2008). The poor selectivity and target specificity of BACs could negatively impact

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0960-8524/$ - see front matter
http://dx.doi.org/10.1016/j.biortech.2012.11.103

the performance of BNR systems due to the susceptibility of BNR microbial populations to BACs. Ammonia oxidation by an enriched nitrifying culture was inhibited with increasing BAC concentration and completely ceased at 15 mg BAC/L (Yang, 2007). Nitrification was inhibited at BAC concentrations of 2 mg/L (Sutterlin et al., 2008) and denitrification was inhibited at BAC concentrations of 50 mg/L (Tezel et al., 2008; Hajaya et al., 2011).

Previous studies on the effect of BACs on BNR processes, such as nitrification and denitrification, were conducted on individual biological processes within a single environmental condition (aerobic or anoxic) and did not assess the effect of BAC on multiple processes under alternating conditions (e.g., sequence of nitrification/denitrification) as is the case in engineered BNR systems. To address this lack of information, a previously reported study investigated the fate and effect of a mixture of BACs on a continuous-flow, laboratory-scale BNR system fed with poultry processing wastewater amended with a mixture of BACs (Hajaya and Pavlostathis, 2012). Upon amendment of the system feed with BACs at 5 mg/L, complete inhibition of nitrification took place, but then the system gradually recovered within 27 days and achieved 100% ammonia removal. High nitrogen removal efficiency was achieved even after the feed BAC concentration was stepwise increased up to 120 mg/L. Batch nitrification assays performed before, during, and after BAC exposure, showed that rapid microbial acclimation and BAC biodegradation contributed to the recovery of nitrification achieving efficient and stable long-term BNR system operation (Hajaya and Pavlostathis, 2012).

In contrast to available information regarding the fate and effect of BACs on nitrification and denitrification, little to no information exists regarding nitrification and denitrification inhibition kinetics due to BACs. Three processes contribute to the overall fate of BACs within a multistage BNR system: adsorption, inhibition, and biotransformation. Modeling of the processes taking place in the three BNR system reactors (i.e., fermentation, anoxic, and aerobic) with and without BAC exposure will contribute to a better understanding of the interactions between adsorption, inhibition, and biotransformation relative to the fate and effect of BACs.

The objectives of the research reported here were to: a) develop kinetic sub-models for the processes occurring in the three reactors in a BNR system; and b) develop and validate a comprehensive, dynamic model capable of simulating the fate of BACs and their effect on the overall BNR system performance.

2. Methods

2.1. Laboratory-scale BNR system

The BNR system consisted of three reactors: a fermentation reactor (R_1), an anoxic reactor (R_2), and an aerobic reactor (R_3) (Fig. S1, Supplementary Data). The BNR system was operated at room temperature (22–23 °C). BAC-free, dissolved air flotation (DAF) underflow wastewater collected periodically from a local poultry processing facility and stored at 4 °C was used as the feed to the BNR system. Operation of the BNR system involved three phases as follows. In Phase I, the system was operated continuously for 30 days, treating BAC-free wastewater. In Phase II, the system was operated for 510 days with the feed poultry processing wastewater amended with a BAC mixture, its concentration stepwise increased from 5 to 60 mg/L, followed by a sharp increase to 120 mg BAC/L. In Phase III, the system was operated for 130 days with the same, BAC-free poultry processing wastewater without any BAC amendment (referred to as post BAC exposure period). A mixture containing three BAC homologs (Barquat MB80) obtained from Lonza Inc. (Williamsport, PA, USA) was used in this study, composed of (%, w/w): C_{12}BAC, 32; C_{14}BAC, 40; C_{16}BAC, 8; ethanol, 10; and water, 10. A 10 g/L BAC stock solution in de-ionized water (DI) was prepared and used throughout the study. Further details on the BNR system, its operation and performance, as well as analytical procedures, were previously reported (Hajaya and Pavlostathis, 2012).

2.2. BAC partitioning and phase distribution

Because the chemical composition and concentration of the solids in the feed poultry processing wastewater and the three reactors in the BNR system were significantly different, the BAC equilibrium phase distribution in these four compartments was evaluated by performing an adsorption assay. Triplicate series were prepared in 250-mL Erlenmeyer flasks with azide-amended wastewater (1 g NaN_3/L), mixed liquor at a fixed initial solids concentration, and BACs at an initial concentration range between 5 and 60 mg/L. The flasks were sealed with stoppers and agitated with an orbital shaker at 190 rpm for 24 h at 22 °C. The phase distribution of BAC was determined at the end of the batch adsorption assay by quantifying both the total and liquid-phase BAC concentration, and then the BAC mass adsorbed on the solids was calculated by difference.

The Freundlich isotherm was used to describe the BAC adsorption equilibrium data. The Freundlich model, which was originally developed as an empirical expression that accounts for surface heterogeneity and exponential distribution of sites and their energies, is an appropriate model when more than one sorption mechanism applies (Ismail et al., 2010), which is the case with BAC (Ren et al., 2011). The Freundlich isotherm equation is as follows:

$$q_e = K_F C_e^n \quad (1)$$

where q_e is BAC concentration on the biomass at equilibrium (mg/g VSS); C_e is BAC concentration in the liquid-phase at equilibrium (mg/L); K_F is the adsorption capacity factor ((mg/g VSS)(L/mg)^n); and n is the Freundlich intensity parameter. The BAC concentration data were fitted to the Freundlich isotherm equation and the adsorption parameter values (K_F and n) were estimated by non-linear regression analysis performed using SigmaPlot, Version 10 software (Systat Software Inc., San Jose, CA, USA).

In order to accommodate the difference in BAC phase distribution in the BNR system model, the adsorption behavior of BAC was included in the sub-models (see below). However, the nonlinear Freundlich adsorption isotherm results in an implicit equation when the liquid and solid phase BAC concentrations are correlated with the total BAC concentration. On the other hand, a linear adsorption relationship results in an explicit equation, which can be easily incorporated in the BNR system model (see Section 2.4, below). Thus, the BAC phase distribution was assumed to be linear in two BAC liquid-phase concentration domains, as follows:

$$\text{For } C_e \le C_e^I \qquad q_e = K_p^I C_e \quad (2)$$

$$\text{For } C_e > C_e^I \qquad q_e = K_p^I C_e^I + K_P^{II} C_e \quad (3)$$

where C_e^I is the upper value of the BAC liquid-phase equilibrium concentration (mg/L) of the lower BAC concentration domain; K_P^I and K_P^{II} are the linear partition coefficients (L/mg) for the lower and upper BAC liquid-phase concentration domains, respectively.

2.3. Model development

Kinetic expressions for processes taking place in the three BNR system reactors (i.e., fermentation, anoxic, and aerobic reactor) were first developed as sub-models and kinetic parameters and coefficients were evaluated using experimental data obtained from independent batch assays. Then, a comprehensive, dynamic model