Bioresource Technology 102 (2011) 5589–5595

Contents lists available at ScienceDirect

Bioresource Technology

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

Is the naphthalene sulfonate H-acid biodegradable in mixed microbial cultures under aerobic conditions?

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ARTICLE INFO

Article history:
Received 7 October 2010
Received in revised form 26 January 2011
Accepted 29 January 2011
Available online 5 March 2011

Keywords:
Naphthalene sulfonates
H-acid
Biodegradation kinetics
Oxygen uptake rate
Activated sludge modeling

ABSTRACT

Synthetically prepared wastewater originating from the H-acid (4-Amino-5-hydroxy-2,7-naphthalene disulfonic acid) manufacturing process was subjected to respirometric analysis for evaluating the level of achievable biodegradation in the presence of this commercially important azo dye precursor. For this purpose, H-acid was mixed with synthetic substrate having the same characteristics as sewage at a concentration and composition being typical for H-acid manufacturing wastewater. Experimental results indicated that H-acid was not biodegradable under activated sludge treatment conditions even after prolonged acclimation periods. The results were also confirmed by model evaluation of oxygen uptake rate profiles. H-acid also did not inhibit the biodegradation of synthetic sewage but accumulated as soluble inert COD in the treated wastewater.

1. Introduction

Naphthalene sulfonates are frequently used in the formulations of dispersants, surfactants, leveling, sequestering and wetting agents as well as in optical brighteners (Lange et al., 1999; Tan et al., 2005). Another major source of naphthalene sulfonates is the chemicals synthesis sector, where they serve as textile azo dye precursors (Lange et al., 1999). Due to the deactivating nature of their sulfonated ($R\text{-}SO_3H$) functional groupings, naphthalene sulfonates have an extremely low reactivity towards electrophilic addition (oxidative degradation) reactions (Rieger et al., 2002). Hence, after production and use in different industrial processes, naphthalene sulfonates are mostly discarded into waste effluent; they by-pass conventional treatment plants and accumulate in natural water bodies. Due to their polar and hydrophilic nature, they also do not significantly sorb onto sewage sludge or soil sediments (Zerbinati et al., 1997). Recently it has been reported that their concentration in European river and surface waters is detectable at ng L^{-1} and μg L^{-1} levels (Tan et al., 2005). However, their actual concentration in industrial wastewater treatment plants is much higher, usually in the mg L^{-1} range (Arslan-Alaton and Olmez-Hanci, 2010).

Among the commercially important naphthalene sulfonates H-acid is being frequently used for the synthesis of reactive and direct azo dyes (Reife and Freeman, 1996). In textile preparation and dyeing wastewater, naphthalene sulfonates are generally present in the formulations of different dispersing, solubilizing and wetting agents. On the other hand, typical H-acid production effluent has a wide COD range of 200–1000 mg L^{-1} (Reife and Freeman, 1996). The two sulfonate groupings in the molecular structure of H-acid render this napthalene sulfonate very resistant to electrophilic attack, a property that is essential for textile dyes. On the other hand, the amino and hydroxy functional groups are electron-donating moieties.

The fate of naphthalene sulfonates in biological treatment systems is not very clear since until now only limited attention has been paid towards their occurrence and degradability (Jandera et al., 2001; Song et al., 2003). Depending upon their molecular structure and/or other physicochemical properties, naphthalene sulfonates may be degradable in biological treatment systems at very slow rates and upon acclimation (O'Neill et al., 1999). In a related work, significantly higher 1,6- and 2,7-naphthalene disulfonate (5–10 μg L^{-1}) and benzothiazole-2-sulfonate (2.5–5 μg L^{-1}) removals could be demonstrated in membrane bioreactors (MBRs) than in conventional activated sludge treatment units (de Wever et al., 2007). In the same study, 1,5-naphthalene disulfonate (5–10 μg L^{-1}) could not be degraded at all both in MBRs as well as conventional activated sludge treatment systems. Although MBRs could not always make a difference in the overall pollutant

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doi:10.1016/j.biortech.2011.01.086

Nomenclature

COD (mg L^{-1}) chemical oxygen demand
DAD diode-array detector
F/M food-to-microorganism ratio
HPLC high performance liquid chromatography
HRT (h) hydraulic retention time
IC (mg L^{-1}) inorganic carbon
ISO international standardization organization
MLVSS (mg L^{-1}) mixed liquor volatile suspended solids
OUR (mg L^{-1} h^{-1}) oxygen uptake rate
SMP residual microbial products
TC (mg L^{-1}) total carbon
TOC (mg L^{-1}) total organic carbon
TSS (mg L^{-1}) total suspended solids
S_S (mg COD L^{-1}) readily biodegradable COD
S_{H1} (mg COD L^{-1}) slowly biodegradable COD fraction 1
S_{H2} (mg COD L^{-1}) slowly biodegradable COD fraction 2
X_H (mg COD L^{-1}) active heterotrophic biomass
S_o mg O_2 L^{-1} dissolved oxygen
μ_{Hmax} (d^{-1}) maximum specific growth rate for X_H
K_S (mg COD L^{-1}) half saturation constant for growth of X_H
k_{h1} (d^{-1}) hydrolysis rate for S_{H1}
k_{h2} d^{-1} hydrolysis rate for S_{H2}
K_{X1} (g COD g COD^{-1}) hydrolysis half saturation constant for S_{H1}
K_{X2} (g COD g COD^{-1}) hydrolysis half saturation constant for S_{H2}
Y_H (g cell COD g COD^{-1}) heterotrophic yield coefficient
b_H (d^{-1}) endogenous decay rate coefficient

removal efficiencies achieved, they showed reduced lag phases of biodegradation kinetics and a stronger memory effect as contrasted to conventional activated sludge systems. Ultimately, naphthalene sulfonate removal in MBRs also appeared to be less sensitive towards system operational variables.

Related studies in the literature only yield arbitrary and empirical results on the biodegradation of naphtalene sulfonates mostly reporting achieved removals in a *black box* approach. This traditional approach is now replaced by respirometric evaluation which gives not only biodegradation characteristics in terms of relevant process kinetics but also inhibitory impacts of the tested chemical on the available organic substrate (Orhon et al., 2010; Karahan et al., 2010). The experimental evaluation relies on dissolved oxygen as the main parameter and essentially measures the oxygen uptake rate (OUR) profile, i.e. OUR variation with time under testing conditions (Spanjers and Vanrolleghem, 1995; Orhon et al., 2007). The experimental OUR profile can be interpreted by activated sludge models which now incorporate dissolved oxygen as a key model parameter and kinetic assessment is performed by the calibration of the selected model with the experimental data. This new approach is now successfully implemented for assessing the biodegradation kinetics for domestic sewage (Koch et al., 2000; Orhon et al., 2002), industrial wastewaters (Orhon et al., 1999, 2009a) and specific chemicals (Cokgor et al., 2009). It is also applied for the kinetic determination of the inhibitory impact of these chemicals on substrate utilization (Orhon et al., 2010).

In this context, the main objective of the study was to explore the fate and biodegradation of H-acid in aerobic microbial culture by means of on-line respirometric tools. The study also evaluated the inhibitory impact of the selected chemical on substrate utilization. H-acid was selected as the model naphthalene sulfonate for the present study due to its high abundance, production rates, frequent use and commercial importance, as aforementioned.

2. Methods

2.1. Materials

The commercial grade H-acid ($C_{10}O_7H_9NS_2$; M_W: 319; purity: >95%; CAS: 90-20-0) was provided as a gift sample by a local textile dye manufacturing plant and used as received. Aqueous H-acid solutions were prepared daily in distilled water to attain the COD values used in the acclimation and biodegradation experiments as well as in respirometric studies. All other chemicals used in this study were of at least reagent grade.

2.2. Experimental approach

The experiments were essentially designed to observe and evaluate the fate and impact of H-acid to a mixed microbial culture sustained with synthetic substrate under aerobic conditions. A peptone-meat extract mixture, referred as *peptone mixture* in the text for simplicity was selected mainly because it is the standard organic carbon source for the ISO inhibition tests (ISO 8192, 2007) and it may be used with the same characteristics in the experiments. The biodegradation characteristics of the *peptone mixture* are well tested and documented in the literature and quite similar to those associated with domestic sewage (Insel et al., 2006; Katipoglu et al., 2010).

All experiments were conducted in two parallel bioreactors; the first one, called the *control reactor,* was fed only with the selected organic substrate – *the peptone mixture*, whereas the second reactor, namely the *H-acid reactor was* fed the mixture of H-acid and synthetic substrate (sewage). The experimental evaluation essentially relied on respirometric tests measuring the oxygen uptake rate (OUR) profile resulting from the activity of the microbial culture. These tests were conducted twice, before and after the acclimation period allowed to the culture for H-acid feeding. They were conducted in parallel batch reactors, one used for OUR measurements and the other for the assessment of the resulting COD profile. The OUR profiles were used for the calibration of the selected model, to assess the biodegradation characteristics of the synthetic substrate utilized in the experiments by identifying the values of model coefficients corresponding to best-fit situation.

2.3. Acclimation experiments

For the acclimation experiments, activated sludge obtained from the aeration basin of a domestic advanced wastewater treatment plant located in Pasakoy, Istanbul was used as the seed source at an average concentration of 3000 mg L^{-1} mixed liquor volatile suspended solids (MLVSS). The H-acid and control reactors had a working volume of two liters and were continuously operated in a fill-and-draw mode. Control and H-acid reactors were operated at a temperature of 20 ± 1 °C and the air supply to the reactor was adjusted to secure a dissolved oxygen concentration of $\geqslant$3.0 mg L^{-1}. The total COD was kept constant at 1000 mg L^{-1} during the acclimation period for both reactors. The acclimation process lasted for eight months and during this period the H-acid concentration was increased stepwise from 114 mg L^{-1} (corresponding to 100 mg L^{-1} COD) to 580 mg L^{-1} (corresponding to