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Comparison of biological and chemical treatment processes as cost-effective methods for elimination of benzoate in saline wastewaters

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ABSTRACT

Eight mixed cultures able to degrade benzoic acid under saline conditions were established and kinetic parameters were determined in batch processes with cultures SBM002 (0.5 g d^{-1}·g oDM^{-1}), SBM003 (0.7 g d^{-1}·g oDM^{-1}) and SBM007 (2.2 g d^{-1}·g oDM^{-1}) showing the highest degradation rates. Treatability of an industrial waste water (12 g L^{-1} benzoic acid, 82 g L^{-1} NaCl) by these cultures was proven in a fed-batch system (SBM002 & SBM003) and a continuous flow reactor (SBM007). The performance of the continuous flow reactor was 15-times higher compared to the fed-batch system due to the change of inocula, higher concentration of ammonia as nutrient and less accumulation of possibly toxic catecholic compounds. Average DOC reduction was found to be 98% at 100 g L^{-1} NaCl and 1.2 g L^{-1} benzoic acid under these conditions. Pre-treatment of the waste water via chemical precipitation by acidification to pH 3.5 diminished the concentration of benzoic acid to 2.1 g L^{-1}. In a combined chemical-biological process the volume of the bioreactor is reduced to 15% compared to a pure biological process. A comparison of operational costs for these three alternatives is presented.

1. Introduction

Benzoic acid is a major product of the chemical industry being used as starting material for chemical syntheses, artificial flavors, insect repellents, food preservatives, personal care products, medical products, antifreeze coolants and fungicides (WHO, 2005; SCCNFP, 2002). Thus, it is an important waste water component of speciality chemical industry (Li et al., 1995). Furthermore, it is a pollutant in effluents of olive oil production and black ripe olive canneries (Novachis, 2005; GE, 2011). Such waste waters typically contain 5–9% of NaCl and COD levels up to 220 g L^{-1} with mainly methoxylated and hydroxylated benzoic acids as contaminants (Etchells et al., 1966; Zouari, 1998; Di Gioia et al., 2001; Benitez et al., 2003; Fiorentino et al., 2004).

Waste water from chemical industry can contain similar concentrations of NaCl and COD. For example, acid chlorides are used during synthesis of aromatic–aliphatic ketones by Friedel-Crafts-Acylation, synthesis of esters via the Schotten-

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Baumann process and within the production of aromatic peroxides. In all three syntheses, sodium chloride is set free as well as by-products of the reaction like benzoate in case of benzoyl peroxide production. In the latter case, typical waste water shows a concentration of up to 30 g COD L^{-1}, equivalent to 12 g L^{-1} of benzoic acid, and about 8% of NaCl.

Biological treatment of saline waste waters in general is critical due to the high saline content inhibiting bioconversion processes (Piubeli et al., 2012), requiring specialized communities and treatment technologies. In contrast to non-saline conditions, especially kinetic parameters for the design of bio-treatment processes are sparsely found in literature.

Only few bacterial species are known to use benzoate as sole source of carbon and energy under saline conditions containing more than 3.5% NaCl. Rosenberg (1983) reported a *Pseudomonas halodurans* strain utilizing benzoate in media containing up to 12% NaCl. Ventosa and Del Moral described several benzoate degrading halophilic bacterial strains, but gave no information about the concentrations of NaCl and benzoate (Ventosa et al., 1982; Del Moral et al., 1988). García et al. described *Halomonas organivorans* G-16.1 degrading up to 610 mg L^{-1} benzoate at 100 g L^{-1} NaCl (García et al., 2004). Only one study dealing with the kinetics of saline benzoate metabolism was published to date (Oie et al., 2007). *Halomonas campisalis* DSMZ 15413 degraded 50 mg $L^{-1}{\cdot}h^{-1}$ of benzoate at 10% NaCl and a protein concentration of 25 mg L^{-1}.

The purpose of this study was to evaluate the treatability of a hypersaline waste water of chemical industry highly contaminated with benzoate, considering biological, chemical and combined approaches. For biological treatment, convenient bacterial communities and pure cultures were enriched and characterized with special regard to high conversion rates of benzoate and hence a compact design of a bio-treatment plant. Due to highly discontinuous formation of waste water, a batch process, a fed-batch process and a continuous flow reactor were tested as three alternatives for a bio-treatment process. Based on the low solubility of undissociated benzoic acid compared to sodium benzoate, chemical precipitation at low pH was examined as well. Finally, a sole chemical process, a sole biological process and a combined process were compared with particular regard to operational costs.

2. Materials and methods

2.1. Waste water

The waste water from industrial application showed the following parameters: COD, 30 g L^{-1}; concentration benzoic acid, 12–14 g L^{-1}; concentration NaCl, 82 g L^{-1}; pH value, 11.5–12; temperature, 25–35 °C; mass flow waste water, 2735 kg h^{-1}; total volumetric flow, 21,500 m^3 a^{-1}; freight benzoic acid, 32.5–37.5 kg h^{-1}; operation time, 8000 h a^{-1}.

2.2. Enrichment

Benzoate degrading mixed cultures were obtained from samples of salterns, sediment and activated sludge (Table 1). Cultivation conditions and sterile mineral medium with additional 1.22 g L^{-1} benzoic acid and 5–10% NaCl were used as described before (Dobslaw and Engesser, 2012). The pH value was adjusted to 7.1 by addition of 2 M NaOH. Mixed cultures were named SBM001 to SBM008.

For enrichment of single strains, mineral medium plates containing 7% NaCl were used. Grown colonies were transferred to fresh media to yield pure strains. To eliminate doubles, single strains were subjected to BOX-PCR and comparison of the band-patterns in agarose gels (Martin et al., 1992; Van Belkum et al., 1996). Pure cultures were named SBP100, SBP110, SBP175 and SBP310 based on their enrichment source (1: salterns; 3: activated sludge).

2.3. 16S rRNA gene sequencing

Genomic DNA of pure strains was obtained by thermal cracking of cells and separation of cell fragments. 16S rRNA genes were amplified by PCR using the bacteria specific primer

Table 1 – Enrichment sources and conditions of mixed cultures SBM001 to SBM008 and pure strains SBP100 to SBP310.

Name	Source	Cultured since	Concentrations of	
			NaCl (%)	Benzoate (g L^{-1})
SBM001	Mixed sample from non-saline sewage sludge, soil and river sediment	March 2010	5–10	1.22
SBM002	Saltern near Colònia de Sant Jordi on Mallorca, Spain	March 2010	10	1.22
SBM003	Derived from SBM002	March 2010	10	2.14
SBM004	Saltern "Salinas de Imón" near Sigüenza, Spain	September 2010	5–10	1.22
SBM005	Saltern near Sant Jordi de ses Salines on Ibiza, Spain	October 2010	10	1.22
SBM006	Saltern near Colònia de Sant Jordi on Mallorca, Spain	October 2010	5–10	1.22
SBM007	Saltern near Colònia de Sant Jordi on Mallorca, Spain	early June 2011	12	2.44
SBM008	Saltern near Colònia de Sant Jordi on Mallorca, Spain	late June 2011	12	2.44
SBP100	Isolated from SBM006	November 2010	7	1.22
SBP110	Isolated from SBM002	November 2010	7	1.22
SBP175	Isolated from SBM003	November 2010	7	1.22
SBP310	Isolated from SBM001	November 2010	7	1.22

Saltern samples used for enrichment were mixed samples of water and sediments from ponds of various salinities. The acronyms chosen as culture designations translate as: SBM, salt tolerant, benzoate degrading mixed culture; SBP, salt tolerant, benzoate degrading pure strain.