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The effect of salt on the performance and characteristics of a combined anaerobic–aerobic biological process for the treatment of synthetic wastewaters containing Reactive Black 5

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HIGHLIGHTS

- NaCl had a time dependent effect on anaerobic decolourisation efficiency.
- First order model fitted the anaerobic decolourisation data at high salinity.
- Anaerobic decolourisation at low salinity was modelled by second order rate equation.
- Increased salinity enhanced the production of SMP and EPS by anaerobic sludge.
- Increasing NaCl concentrations retarded the autooxidation of RB5 metabolite.

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ABSTRACT

The findings of the present work showed that variation in NaCl concentration, in the range 0–100 g/l, has a significant effect on the performance and characteristics of a combined anaerobic–aerobic process used for treatment of a synthetic RB5 containing wastewater. The effect of increasing NaCl concentration on anaerobic decolourisation efficiency was time dependent and two different types of relationships were observed for the initial and the later part of the process. Anaerobic decolourisation data from runs carried out under low salinity (NaCl concentration $\leqslant$ 20 g/l) was successfully modelled using the second order kinetic rate equation, whereas at high salinity (NaCl concentration = 100 g/l) the first order kinetic model gave a better fit of the experimental data. Increase in salinity resulted in increase in Extracellular Polymeric Substances concentration throughout the anaerobic process and Soluble Microbial Products during the early stages of the process. UV–Vis spectral and FTIR analysis showed no effect of salt on the mechanism of anaerobic azo dye reduction whereas it lead to retardation or inhibition of the autooxidation of one of anaerobic RB5 reduction metabolites during the aerobic stage. The latter has implications regarding the use of the combined anaerobic–aerobic process for treatment of azo dye containing wastewaters.

1. Introduction

Azo dyes are the largest commercial class of dyes used in textile industries. An important class of these dyes – especially used for dyeing cotton yarns and fabrics – are reactive azo dyes. In order to aid the adsorption and bonding of these dyes to textile, some chemicals (mainly sodium salts) – are added to the dye bath. Furthermore, hydrolysis of the reactive azo dye molecules in the dye bath, especially at high temperatures, prevents around 15–50% of the dye molecules from fixing to the fabric [1,2]; this means that the wastewater of the dyeing operation contains significant quantities of both hydrolysed dye as well as sodium salts. Apart from the aesthetic problems caused by release of this kind of wastewaters to the environment, the mutagenic and carcinogenic nature of azo dyes themselves, or aromatic amines resulting from their anaerobic reduction, means that these dyes should be removed prior to the disposal of the wastewater [3].

The treatment of high salinity (high TDS) wastewaters has been the subject of active research [4]. Physicochemical methods have been used for treatment of these wastewaters but they suffer from high operating costs. Aerobic, anaerobic or combined anaerobic–aerobic biological processes are low cost alternative operations but, as discussed below, high Na^+ concentrations can potentially retard or inhibit microbial activity. Solutions to these problem

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are the gradual adaptation of the anaerobic or aerobic microbial populations to salt or the use of halophilic bacterial populations. Another problem sometimes reported for biological treatment of saline wastewaters is the presence of high turbidity in the effluent of these processes [4].

Recently, the combined anaerobic–aerobic biological process employing anaerobic/activated sludge has been considered for the biological treatment of wastewaters containing azo dyes [5–8]. However, the high concentrations of salt (40–100 g/l) commonly present in wastewaters of dye baths that employ reactive dyes complicates the biological treatment process; this is because sodium ions, resulting from solubilisation of sodium salts like NaCl, have been reported to affect the activity of both anaerobic as well as aerobic bacterial populations [9,10]. By increasing the osmolality of the cell's environment [11] sodium reportedly reduces the activity of bacterial populations present in anaerobic sludge and as a consequence leads to a reduction of the anaerobic COD removal performance. Previous reports, however, indicate that the different bacterial groups present in anaerobic sludge have different sensitivity to NaCl, with acidogens and acetoclastic methanogens having the highest sensitivity to the presence of sodium ions [12]. This inhibitory effect also depends on the concentration of sodium ions although different threshold levels have been reported [13–15]. Previous studies have also shown that with increasing salt concentration aerobic COD removal efficiencies decreases too [16–18].

A search of the relevant literature shows that the effect of NaCl on anaerobic decolourisation efficiency partly depends on the nature of the bacterial population employed in the anaerobic decolourisation process. For example, for halophilic bacteria it has been reported that increasing NaCl concentration initially leads to an enhancement of anaerobic decolourisation efficiency but – above a threshold value or range – the effect becomes negative [16,20]. However, there are very few reported studies on the effect of NaCl concentration on the anaerobic azo dye removal in the case of the mixed bacterial population commonly found in anaerobic and activated sludge and there is no consensus in these studies on the effect of NaCl on anaerobic decolourisation efficiency [18,21].

In combined anaerobic–aerobic biological processes used for treatment of azo dye containing wastewaters usually anaerobic and/or activated sludge, as opposed to pure halophilic bacteria, are employed and, furthermore, the majority of colour removal occurs through the biologically mediated reduction of the azo bond in the anaerobic stage or phase of the process [8]. This means that the elucidation of the nature of the effect of NaCl on anaerobic decolourisation efficiency of reactive azo dyes by anaerobic sludge is of utmost importance if these processes are to be considered for the biological treatment of reactive azo dye containing wastewaters from the textile or dyeing industries.

Reactive Black 5 is a bifunctional dye containing two sulfatoethylsulphone groups and is the biggest selling dye in the world for producing navy blue and black shades [22]. The kinetics of bacterially mediated anaerobic RB5 decolourisation process employing anaerobic sludge has been the subject of some previous studies but in all of these studies synthetic wastewaters lacking NaCl have been employed [23–26]. What complicates the kinetic modelling of such a process is the presence of two azo bonds in RB5 which reportedly have different reactivities [27]. For this reason, some researchers [23–25] have fitted two first order rate equations through the data, one using the data obtained during the initial part of the anaerobic decolourisation process and another using the data pertaining to the later part of this process. As a result, in these studies two different rate constants have been reported for the same process. On the other hand, Isik and Sponza [26] claimed a satisfactory fit between the RB5 anaerobic decolourisation data and the first order model for the data throughout the anaerobic process and subsequently reported only one rate constant for a given initial dye concentration. Therefore, it seems that further work in this area – especially in media containing NaCl – is necessary.

Another important aspect of processes aimed at biological treatment of saline industrial wastewaters concerns the production of extracelluler polymeris substances (EPSs) and soluble microbial products (SMPs) during the process. This is important because a great fraction of the residual COD in biologically treated effluents potentially relate to SMP produced during the process rather than to un-degraded pollutants [28]. Also, in some previous reports production of EPS have been associated with better pollutant removal efficiency [1]. According to Zou et al. [29] bacterial cells produce SMP and EPS in response to the presence of salinity in the growth environment. However, there are only limited studies on the production of EPS/SMP in saline wastewaters by the mixed bacterial population in anaerobic sludge [12,29–31], and none of these have considered the effect of the presence of azo dyes.

The objective of the present study was the systematic study of the effect of NaCl concentration, in the range 0–100 g/l, on the dye and COD removal performance of a combined anaerobic–aerobic process for decolourisation of an RB5 containing synthetic wastewater. During the anaerobic stage, anaerobic sludge was employed and the effect of NaCl on the kinetics of anaerobic decolourisation, as well as the production of SMP and EPS, was studied in detail. The fate of dye and anaerobic dye reduction metabolites during both the anaerobic and aerobic stages in runs employing various salt concentrations was also followed using UV–Vis spectral and FTIR analysis.

2. Material and methods

2.1. Biomass

The anaerobic sludge used in the anaerobic decolourisation runs was initially collected from anaerobic treatment unit of the Tondgooyan petrochemical unit of Mahshahr city in south of Iran. When not employed in anaerobic decolourisation experiments, the anaerobic sludge was kept in 500 ml serum bottles at 35 °C, and, every 48 h fed with nutrient media and flushed with nitrogen gas. After each anaerobic decolourisation experiment, the anaerobic sludge from the 100 ml serum bottles were pooled together and kept in 500 ml serum bottles until the next set of experiments.

The activated sludge used in aerobic runs was obtained from the activated sludge unit of the Gheytariye municipal wastewater treatment plant in Tehran. The activated sludge was aerated through a porous ceramic diffuser in a tank immersed in a water bath at 30 °C and the rate of aeration was adjusted such that the dissolved oxygen concentration in the tank was always above 3 mg/l. The activated sludge was fed every 24 h with a nutrient media in which the ratio of carbon, nitrogen and phosphor was adjusted to 100:5:1.

2.2. Chemicals

Azo dye Reactive Black 5 was purchased from Ciba dye manufacturer and used without any further purification. A hydrolysed stock solution (5 g/l) was prepared according to the method described by Lourenco et al. [32]. A concentrated solution of the dye was prepared, the pH was adjusted to 12 and the solution was stirred for 1 h at 80 °C. The solution was allowed to reach room temperature and was then neutralised and diluted to 1 l. The nutrient media used in the maintenance of the anaerobic sludge, as well as in the anaerobic decolourisation experiments, had the following composition (mg/l) [26,33,34]: glucose (937), NH_4Cl (400), $NaHCO_3$ (5000), $MgSO_4{\cdot}7H_2O$ (400), Cystein (10), KCl (400), $CaCl_2{\cdot}2H_2O$