Photocatalytic oxidation of a reactive azo dye and evaluation of the biodegradability of photocatalytically treated and untreated dye

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Abstract

The purpose of this study was to investigate the photocatalytic oxidation of a reactive azo dye and determine the improvement in the biodegradability when photocatalytic oxidation was used as a pretreatment step prior to biological treatment. The results obtained from the experiments adding H_2O_2/TiO_2 show that the highest decolorisation rate is provided by the combination of ($UV+TiO_2+H_2O_2$). The decolorisation efficiencies were 18%, 22%, 34% and 52% in the runs UV, $UV+H_2O_2$, $UV+TiO_2$ and ($UV+TiO_2+H_2O_2$) after approximately 100 min illumination periods, respectively. The decolorisation rate was increased significantly by initially increasing the concentration of TiO_2 in the dye solution; however, it was decreased due to the reduced light transmission when the concentration of TiO_2 was in excess. The decolorisation rate constant was $0.018 \pm 0.002 \cdot min^{-1}$ in the presence of $1\ g \cdot \ell^{-1}$ TiO_2 while it was $0.004 \pm 0.001 \cdot min^{-1}$ in the presence of $0.125\ g \cdot \ell^{-1}$ TiO_2. The results of the obtained oxygen uptake rate measurements in biological activated sludge have shown that the photocatalytically treated dye was easier to degrade than untreated dye. The ability of the activated sludge to degrade glucose was not inhibited in the presence of photocatalytically treated and untreated dye. Also, the biodegradability of photocatalytically treated and untreated dye was investigated via the biological oxygen demand (BOD) test. The results indicated that further degradation of the treated dye may take place by activated sludge in aerobic conditions.

Keywords: azo dye, photocatalytic decolorisation, biodegradability test, activated sludge

Introduction

Photocatalytic oxidation using a semiconductor such as TiO_2 as photocatalyst is one of the various advanced oxidation processes used nowadays. As TiO_2 is illuminated by light with a wavelength below 380 nm, the photons excite valence band electrons across the band gap into the conduction band, leaving holes behind in the valence band. The hydrogen peroxide absorbs only UV light with a wavelength < 300 nm (Parra et al., 2000). The holes in TiO_2 react with water molecules or hydroxide ions (OH^-) producing hydroxyl radicals ($\cdot OH$).The generation of $\cdot OH$ depends on the solution pH. In alkaline solutions, the generation of the radical $\cdot OH$ mainly involves a charge transfer between OH^- ions and valence band holes at the photocatalyst surface, whereas at neutral and acidic pH, direct hole oxidation is also possible. Organic pollutants which are adsorbed on the surface of the catalyst will then be oxidised by $\cdot OH$ (Gonçalves et al., 1999).

Photocatalytic oxidation of dyes has been investigated by a number of researchers. Photocatalytic oxidation processes can oxidise a wide variety of toxic and persistent organic compounds to harmless inorganics such as mineral acids, carbon dioxide and water (Dominguez et al., 1998). Also, this process forms some by-products such as halides, metals, inorganic acids and organic aldehydes depending on the initial materials and the extent of decolorisation (Robinson et al., 2001). The colour of dyes results from conjugated chains or rings which absorb light at visible wavelengths. The UV-degradation can be achieved by the cleavage of conjugated chains (Ma and Chu, 2001).

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The biodegradability of azo dyes has also been investigated in the past. Aromatic amines formed by biotic and abiotic conversion processes of azo dye colorants are mostly toxic. The degradability of selected amines which are detected in textile industry wastewaters has been investigated under aerobic and anaerobic conditions as well as abiotic conditions. The results show that the degradation under aerobic conditions proceeds via oxidation of the substituents located on the aromatic ring or on the side-chain (Ekici et al., 2001). The investigated azo dye metabolites are partly stable in the aqueous environment and cannot be efficiently degraded under wastewater plant conditions. Under anaerobic conditions, the azo bond is reductively cleaved, which leads to the formation of substituted aromatic amines some of which are known to be potentially toxic/mutagenic (Bromley-Challenor et al., 2000).

The chemical structures of azo dyes are based on azo benzene and the azo naphthol derivatives. They also exhibit great structural variety, therefore they are not uniformly susceptible to microbial attack. A number of authors have proposed models for the qualitative prediction of azo dye biodegradability. The quantitative relationship between the biodegradability of azo dyes and their chemical structures has been explored, and the probability for rapid aerobic biodegradation has been modeled by Suzuki et al. (2001).

Some studies have shown the utility of photocatalytic oxidation processes as a pretreatment step before a biological treatment for the improvement of biodegradability of toxic and/or non-biodegradable organic substances. The combined photochemical and biological processes were investigated for the destruction of biorecalcitrant herbicides (Parra et al., 2000) and p-nitrotoluene-ortho-sulphonic acid (Pulgarin et al., 1999). The treatability of raw and pretreated wastewater by photocatalytic oxidation was investigated. Results obtained show that the photocatalytic oxidation