

OXIDATIVE BREAKDOWN OF ACID AZO DYES BY MN OXIDES

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INTRODUCTION

The Kalahari manganese fields, situated in the Northern Cape province of South Africa, represents the largest body of Mn ore in the world holding up to 80% of the world's Mn reserves. As a result of ore extraction and crushing processes, large quantities of fine (< 2 mm), relatively pure Mn oxide containing tailings are generated. Manganese oxides are one of the strongest oxidising agents in natural systems, aiding in the breakdown of many organic contaminants entering soil and water systems. Despite being classified as a 'waste' the Mn oxide containing tailings material could be a valuable source of oxidising capacity for the treatment of water and soil contaminants.

The removal of azo compounds from textile waste streams is a pertinent issue in water treatment and currently there is no single, economically attractive treatment that can effectively decolorize dyes (dos Santos et al., 2007). Many biotreatment technologies achieve the reductive cleavage of the azo bond, which generates a range of aromatic amines that are colourless but significantly more carcinogenic than the parent azo compound. Advanced oxidative techniques have been successfully employed to remove colour from waste effluents (Muthukumar and Selvakumar, 2004; Gutowska et al., 2007), however, these techniques are often expensive, thus the development of an oxidative textile water treatment technique utilising Mn oxide containing mining waste is appealing.

In this investigation the Mn tailings were reacted with acid azo dyes under a range of chemical conditions typically found in textile waste waters, to establish the possibility of using the Mn mining waste in textile effluent treatment.

1. MATERIALS AND METHODS

Manganese mining waste was reacted with a number of acid azo dyes under a range of chemical conditions commonly present in textile effluent. Reaction mechanisms and final reaction products were established using a number of analytical and spectroscopic techniques including UV-visible spectroscopy, liquid chromatography mass spectrometry and high pressure liquid chromatography. Salts and organic acids are commonly found in textile effluents. Therefore the decolorization of the model dye, acid orange 7 (AO 7) was determined as a function of salt and organic acid concentration.

2. RESULTS AND DISCUSSION

The Mn tailings successfully decolorize a number of acid azo dyes through the oxidative cleavage of the azo bond. The Mn oxide component of the tailings is the active oxidant. The oxidative breakdown of acid azo dyes by the Mn oxide containing waste is inversely proportional to pH, which may relate to the change in surface charge on the oxide surfaces. Total mineralization of the azo dyes could not be achieved using the Mn tailings with quinone and hydroxybenzenesulfonate species identified as the final breakdown products of the reaction. These compounds have also been identified after treatment of dyes with white rot fungi (Zille et al., 2005). Increasing the concentration of sodium sulphate, which is commonly present in dye effluent, had the effect of increasing decolorization by the tailings. This is thought to be a consequence of compaction of the double diffuse layer allowing more intimate dye-Mn oxide contact. Increasing the concentration of acetic acid, used as a buffer in the dyeing process, also increased dye decolorization, however, this probably relates to the pH effect mentioned earlier. The decolorization potential of the Mn tailings is long lived with 96% decolorization still occurring after 60 days of continual dye replenishment. One distinct disadvantage of using Mn tailings to breakdown and decolorise dyes is the large quantities of soluble Mn that is released during the reaction. This soluble Mn would need to be sequestered if it were to become a useable technology.

3. ACKNOWLEDGEMENTS

This project was funded by BHP Billiton and the Engineering and Physical Science Council of the United Kingdom

4. REFERENCES

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