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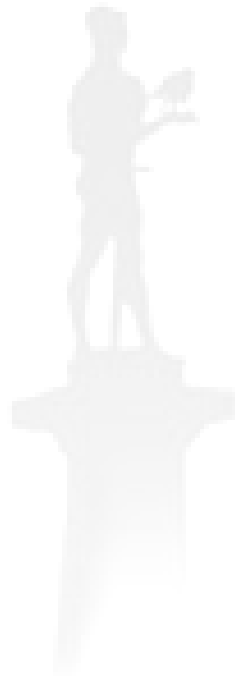
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Section  
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## Efficient Bleaching of Cotton With Hydrogen Peroxide Using a New $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$ Catalyst Reaction System

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This study outlines fundamental aspects of the performance of  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$  catalyst (dinuclear  $\mu$ -oxo bridged Mn(IV) complex of the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane) as a process intensifier for bleaching of cotton with  $\text{H}_2\text{O}_2$ . This catalyst and related complexes have proven to be very active in the catalysed, and often selective, oxidation of organic substrates with  $\text{H}_2\text{O}_2$  in non-aqueous systems [1a] and provide stain bleaching activity in detergent formulations under alkaline conditions [1b].

Catalytic bleaching of cotton takes place in a heterogeneous aqueous reaction system in which it is difficult to study physical and chemical phenomena. To study intrinsic kinetics and chemical mechanism, it is necessary to exclude the influence of transport phenomena that exist in such a heterogeneous reaction system. In order to eliminate these effects, we have developed homogeneous model system containing specific polyphenolic substrates (mainly flavonoids) as model compounds to mimic cotton fibre coloured matter. The primary model pigment chosen is morin, owing to its presence in native cotton fibre.

The oxidation of model compounds over  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$  catalyst is carried out in batch mode. The influence of reactant and catalyst concentrations, reaction temperature and reaction pH is investigated. The results show that the addition of very small quantities of  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$  leads to a tremendous increase of the reaction rates at lower temperatures (30-40°C) by providing a new mechanism with lower activation energy of bleaching.

Through the use of a homogeneous system, we have revealed the ability of  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$  to use  $\text{O}_2$  present in the aqueous system as ultimate oxidant. Figure compares the reaction profiles of the uncatalysed ( $\text{H}_2\text{O}_2$ ) and  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$  catalysed morin oxidation by  $\text{H}_2\text{O}_2$  or  $\text{O}_2$  recorded by UV-Vis spectrophotometry at 410 nm (25°C and pH 10). A decrease of absorbance with time corresponds to oxidative degradation

and can be considered as a measure for the catalytic activity of  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$ .

The catalytic oxidation activity of  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$  is confirmed to be superior compared to the activity of "free" manganese catalyst [Mn(II)]. Reaction rates are pH dependent, reaching a maximum value at *ca.* pH 10.5 and without significant change until *ca.* pH 11. Generally, the results obtained from both systems (heterogeneous and homogeneous) correlate well. When  $[\text{Mn}_2\text{O}_3(\text{tmtacn})]^{2+}$  is present in the bleaching system, the process efficiency is improved, the oxidation proceeds

rapidly even at ambient temperatures, whereas bleaching system with hydrogen peroxide only, shows almost no reaction under the same conditions.

We thank Dr. R. Hage (Unilever Research, the Netherlands) and Dr. W. R. Browne (University of Groningen, the Netherlands) for helpful discussions on the reaction mechanisms.

- (a) C. Zondervan et al., *Chem. Comm.* (1997) 419; (b) R. Hage et al., *Nature* 369 (1994) 637.

