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Fe^{III}-TAML- CATALYSED DEGRADATION OF TWO AZO TEXTILE DYES BOUND TO SILICA GEL AND CELLULOSE

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ABSTRACT

Degradation of two textile dyes, C.I.Acid Orange 7 (Orange II) and C.I. Reactive Red 2 (Procion Red MX-5B) bound to silica gel and cellulose by hydrogen peroxide catalyzed by Fe (III) complexed to Tetra-Amido Macrocyclic Ligands (Fe-TAML activators) at pH 10 was investigated. The performance of the oxidising system was characterized by conducting batch and column experiments. C.I.Acid Orange 7 and C.I. Reactive Red 2 on solid matrix after the addition of the Fe-TAML/H_2O_2 decolourize in initial time period of 10-20 minutes. The decolourisation rate of dyes on silica gel or on cellulose respectively was much slower than that in aqueous solution. On the silica gel, the degradation mechanism is the same as observed in aqueous solutions, first step is likely the formation of reactive species and the second step is the interaction of the reactive part with the desorbed dyes structure to release various species. The finding about decolourisation of the dyed cellulose leads to the conclusion that that Fe-TAML molecules must enter into the microfibril of cellulose and approach closely to the dye. Thus, the catalyst is not able to completely degrade the dye while bound to a fabric of structure such as cellulose.

KEYWORDS: Fe-TAML, hydrogen peroxide, decolourisation, azo dyes, soil contamination.

INTRODUCTION

Azo dyes exhibit environmental problems due to their ability to resist usual oxidation methods under aerobic conditions. These compounds have an azo bond (R_1-N=N-R_2), where R_1 and R_2 are aromatic groups, which in some cases can be additionally substituted by sulphonated groups at the aromatic rings. The fact that even a concentration of less than 1 ppm, can be visible in aqueous media, has made the problem even more important not only from aesthetic but also from health and environment point of view. The compounds can also contribute to the environmental processes like eutrophication by liberating by-products while oxidation, hydrolysis or other chemical reactions occurring in wastewater. Azo dyes are not readily biodegradable at aerobic conditions; in addition, under anaerobic conditions they can be reduced to potentially hazardous aromatic amines among other compounds. These by-products could be mutagenic, carcinogenic, or teratogenic and could cause long-term health effects [1-4].

Nowadays, the degradation of organic dyes has therefore attracted much attention. New technologies for wastewater decolourisation have been explored, for instance, assisted photo-catalytic degradation, photo-destruction by UV/H_2O_2, Fe (II)/H_2O_2 and soluble transition metal catalyst in combination with various oxidising agents [5-10]. Many studies have been performed on catalysed decolourisation of dyes by H_2O_2 with Fenton reagent and ozone. Ozone degrades practically all dyes, reacting rapidly with both C-N and N=N bonds. The reactions are slow at lower temperature and hence require higher catalyst and hydrogen peroxide concentrations [11].

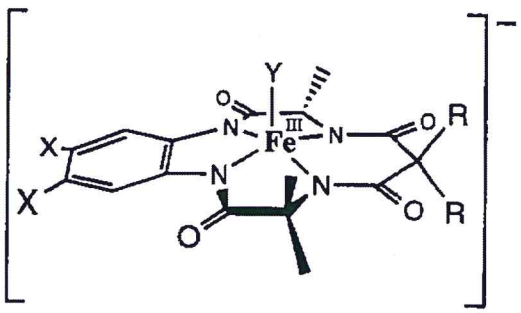


FIGURE 1 - Structures of TAML activators. 1a: X = Cl, Y = H_2O, R = CH_3, 1b: X = H, Y = Cl, R = CH_3. 1c: X = H, Y = H_2O, R = F.

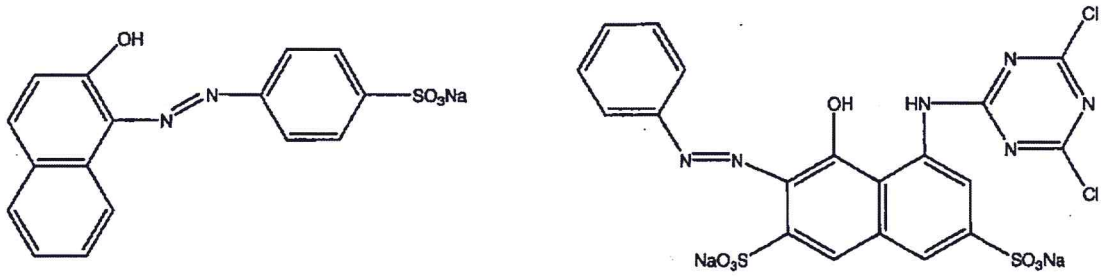
The Fe-TAML activators (Fe^{III} complexes of tetra-amido macrocyclic ligand, Fig. 1) exhibit the capacity to

marshal hydrogen peroxide to destroy organic pollutants in aqueous systems. These complexes are designed to be used under a variety of working conditions, including variable pH, temperature and solvent composition. TAML's are made from elements found in nature. Therefore, they employ non-toxic elements and yield non-toxic by-products or degradation products. They act as precursors to highly oxidised iron complexes and also as potential oxygen transfer catalysts [12]. In a recent work, a fundamental study for oxidation of the azo dyes C.I. Acid Orange 7 and other reactive dyes has been successfully performed by hydrogen peroxide catalysed by Fe-TAML in aqueous solutions at pH 9-11. The organic intermediates identified by HPLC and GC-MS were non-toxic according to the *Daphnia magna* test [13].

The contamination of soils by azo dyes represents a serious problem, and the recent research indicated that the Fenton's reagent could be applied to treating soil contaminated with hazardous organic [14, 15]. Therefore, Fe^{III}-TAML/H_2O_2 technology needs to be explored in soils.

However, in contrast to aqueous systems, soils are complex, heterogeneous, and site-specific media. The existence of ubiquitous minerals, inorganic constituents, soil organic matter, and microorganisms that can participate in the propagation reactions or trigger other abiotic and biotic processes can significantly affect Fenton-like treatments [16]. Fe^{III}-TAML/H_2O_2 technology will not be successfully developed in soils until degradation of azo dyes on the pure components of natural surfaces are better understood. Cellulose is one of the main structural components of vegetal cells, and silica is one of the major constituents of soil surfaces [17]. Therefore, a description of the degradation of azo dyes on silica gel and cellulose is the starting goal in assessing the possibility of remediation of azo dyes-contaminated soils with the TAML technique to activate hydrogen peroxide.

In this report, the potential of Fe-TAML catalyst for the degradation of dyes C.I.Acid Orange 7 and C.I. Reactive Red 2 (Fig. 2) [18] was studied in solid matrix. The aim of the research study was to observe the performance of the system at defined conditions, but also having in mind the regions where soil and sediment are contaminated by dyes like Acid Orange 7 and the reactive Procion Red 2. The study is therefore aiming at basic experimentation to initiate first investigations on direct remediation of contaminated sites.



Acid Orange 7 Procion Red 2

FIGURE 2 - Chemical structure of C.I. Acid Orange 7 and C.I.Reactive Red 2.

MATERIALS AND METHODS

Reagents and Instrumentation

C.I.Acid Orange 7 (Orange II) and C.I. Reactive Red 2 (Procion Red MX-5B) were obtained from Sigma-Aldrich Chemie GmbH without purification. The Fe-TAML complex was designed and synthesised using published methods at Canergie Mellon University and obtained from there. Hydrogen peroxide (30% w/w) was purchased from Fluka. Sodium hydrogen carbonate ($NaHCO_3$) and Sodium carbonate anhydrous (Na_2CO_3) were obtained from Merck Co. $Na_2S_2O_4$ was obtained from Sigma-Aldrich Chemie GmbH, with an approximate 85% purity. The water used for analytical purpose was Millipore water.

The instrumental analyses used for the wavescan analysis and to measure the absorbance of the treated samples were done by Ultraspec 3300 pro UV/ Visible Spectrophotometer, manufactured by Biochrom Ltd. The software used for the system's analysis is Swift II, also manufactured by Biochrom Ltd.

General Procedure for degradation of dyes by Fe-TAML/H_2O_2 system

The matrices were first dyed with the C.I. Acid Orange 7 (Orange II) and C.I. Reactive Red 2 (Procion Red MX-5B) and then left in the oven at 27°C for 24 hours. The solid matrices selected for the experimental purpose where silica gel and cellulose. After this, the dyes were filled in the glass columns of 2.5 mm (internal diameter) x 350 mm and then eluted with Fe^{III}-TAML/H_2O_2 solution. Because of the need for a basic environment of pH 10 for the activity of the catalyst and H_2O_2, a buffer solution was prepared using Na_2CO_3 0,1M and $NaHCO_3$ 0,1M. The same

buffer solution was later used throughout all the experiments. The collected dyes samples after elution process were later scanned in the range of visible wavelengths (400-800 nm) using UV/ Visible Spectrophotometer. After using different concentrations of dyes solutions in buffer, the graphic of Abs = f (Concentration) was fixed and therefore according to the Lambert-Beer law the concentration of the dye in buffer solutions could be identified by measuring the absorbance, using the UV-spectrophotometer. The wavelength that provided maximum absorbance (λ max) for each dye solution was obtained from the scans. For different dilutions, the absorbances at optimum wavelength were plotted against corresponding concentrations of each dye to generate a standard curve for use in the analysis of dye.

C.I. Acid Orange 7

The concentration used for the experiment were, C.I. Acid Orange 7 (Hereafter referred to as AO7) = 0.5 mM, Fe-TAML = 0.001mM, H_2O_2 = 5 mM, therefore AO7/ TAML = 500 and the H_2O_2 is constantly used in excess. Silica gel matrix was used as a simplified surrogate for contaminated soil due to its simple structure and the white colour. SiO_2 was dyed with Acid Orange 7 (0.5 mM) and left in the oven. After this step dye was filled in the glass column and then eluted with catalyst and H_2O_2 solution at pH 10 and immediately scanned using UV-VIS after every 2hrs for absorbance measurements. While adding and filling processes of the dye, some part is left as unused. By adding the buffer solution we could remove it from the column and using the graphic previously mentioned we could calculate the moles that have not been used or still left in the column for the degradation process.

C.I. Reactive Red 2

Reactive Red 2 (Hereafter referred to as MX-5B) was used in the concentrations of 100mg/l (84 μM) and 50mg/L The ratio of Fe-TAML/MX-5B was 1/500. Therefore, we used Fe-TAML in the concentration of 0.17 μM. Due to the fact that the concentration of oxidant must always be high enough as not to constitute a limiting factor, the concentration of H_2O_2 was set to 5mM. Dyeing of silica gel was not possible with a reactive dye, as solid matrix had a low affinity for reactive dye. Reactive dyes are the most suitable substance to dye cellulosic fibres. Hence cotton and cellulose were dyed with MX-5B using 50mg/l concentration in buffer. After leaving for one day in dye solution, both matrices were washed with a large amount of water until the non-bound dye had been removed, subsequently by drying at 27°C in the oven. For analytical cross-check, a small amount of matrices were inserted in a column and eluted with buffer. The elution solutions were measured under UV-VIS to confirm that the bound dye is still remaining on the fibers. After that, the addition of required amount of Fe-TAML/H_2O_2 was followed and the samples were monitored every 2hrs for absorbance measurements under UV-VIS.

Decolourisation index

A decolourisation index was prepared for the dyes AO7 and MX-5B to estimate the percentage of colour removal before and after the addition of the Fe-TAML/H_2O_2.

RESULTS AND DISCUSSIONS

C.I. Acid Orange 7

C.I.Acid Orange 7 (AO7) is frequently being applied in textile industry and has already proved to be degraded successfully in aqueous environment [13]. Therefore, this research study is to observe the degradation dyes on silica gel. After addition of Fe-TAML/H_2O_2 to silica gel contaminated with dyes, the decolourisation could be observed in first few minutes replacing the initial orange colour to a very slight brownish orange colour. Interestingly, the decolourisation was intense in the area, which was in close contact with hydrogen peroxide. One explanation is disproportion bonding of the dye with Fe-TAML. The colour after the addition of Fe-TAML/H_2O_2 was compared with the decolourisation index and the percentage of removal was 55% and 85%, after 1hr and 24hrs of degradation, respectively. The UV-VIS scan was performed after 24hrs of degradation and the peak at 484 nm was no longer observed.

C.I. Reactive Red 2

C.I. Reactive Red 2 (MX-5B) are highly reactive due to the two chlorines built into the triazine ring. They are named dichlorotriazinyl dyes and its characteristic absorbance wavelength is 538nm. The degradation of MX-5B has been already performed in aqueous solution [19] and it is now a challenge to observe the degradation percentage in solid matrix. As for reactive dye, it is impossible to bind to silica gel and hence during dyeing all the dye generally comes out without dyeing the silica gel.

In these regards, dyed cotton and cellulose were subjected to the treatments of Fe-TAML/ H_2O_2. In case of dyed cotton, after the addition of optimised ratio of Fe-TAML/ H_2O_2, incomplete decolourisation was observed. The initial red colour was not completely decolourised and after application of the decolourisation index the colour removal was fixed at 85%.The wave scan was performed after one hour and after 24hrs and the peak at 538 nm was observed. Cotton is the purest natural form of native cellulose with cellulose I polymorphic structure. The reason for partial decolourisation could be the possibility of incomplete degradation of C.I. Reactive Red 2 due to steric hindrances of the bond to the cellulose. There might be the formation of some bonds between the first and the last -OH, but also some bonds may be formed to the inner -OH of the chain and therefore, Fe-TAML/ H_2O_2 might be sterically hindered to degrade the dye molecule bound there. In case of dyed cellulose, after the addition of Fe-TAML, the system was left for 24hrs so that the matrix could react with Fe-TAML and this was followed by addition of H_2O_2. After some time, decolourisation of Procion

MX-5B occurred, but was not completely. The slight decolouration of cellulose after comparing with the decolourisation index was fixed at 70%.

After dyeing process, some of the dye molecules have penetrated into submicroscopic pore. Due to the adsorption and chemically bound of dyes, cellulose provides protection of dyes from Fe-TAML. Therefore, assuming that the first degradation step is forming of reactive species Fe^{III}-OOH, dyes must leave from submicroscopic pore.

According to A. Sugane et al's research results [20] that the dye loss from cellulose was attributed to three contributions, namely, (1) alkaline hydrolysis of dye-fibre bond, (2) oxidative fading of the dye chromophore by peroxides, and (3) the extent of cellulose degradation. In our experiment, only situation (1) is possible. During degradation process, the cellulose chains can be open by the water and water can decrease the physical interaction between dye and cellulose, which results in mobility in wet cellulose. Therefore, some decolourisation of C.I.Reactive 2 occurred.

However, when some of C.I.Reactive 2 were bound to cellulose by a nucleophilic substitution reaction between cellulose and physisorbed dye, the covalent bond between dye and cellulose fibre is evidently similar to an ester [21] and the hydrolysis of covalent dye-fibre bond was not easy in our experiment condition. Thus, decolourisation of C.I. Reactive 2 occurred, but not completely. Therefore, it can be concluded that Fe-TAML was not able to interact with the dye properly (Fig. 3).

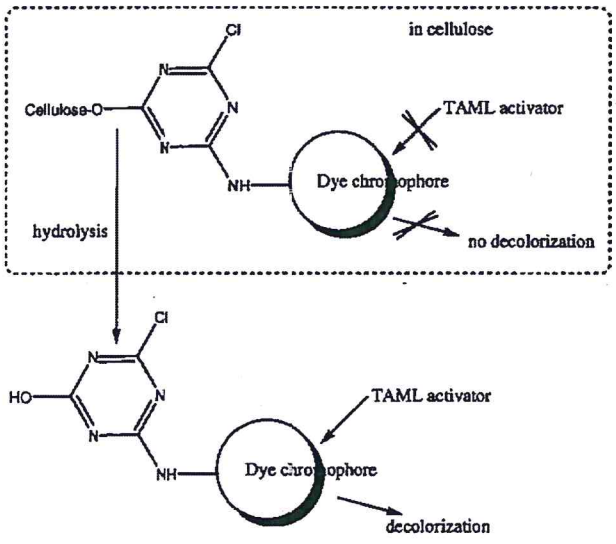


FIGURE 3 - Schematic representation of partly decolization of C.I.Reactive 2

In order to clarify the findings about incomplete reactivity due to insufficient interaction of Fe-TAML with the dye molecules, an independant experiment was performed in a beaker with similar conditions. The only difference was that Fe-TAML was added during dyeing process and the ingredients were mixed thoroughly. After drying, the process followed by addition of H_2O_2 and at the end of reaction complete decolourisation within 1hr duration was observed. The decolourisation observed was better than in previous experiments and could be interpreted as a strong justification for the reason of improper reaction of the dye with Fe-TAML if added after dyeing and drying processes. The visual difference could be observed after 1hr and 24hrs of degradation which was fixed at 70% and 0%, respectively. Therefore, if Fe-TAML was added during the dyeing process and the ingredients were mixed thoroughly, Fe-TAML catalyst entered into the microfibril of cellulose and attacked dyes bonded to cellulose. Thus, decolourisation of C.I.Reactive 2 occurred completely (Fig. 4).

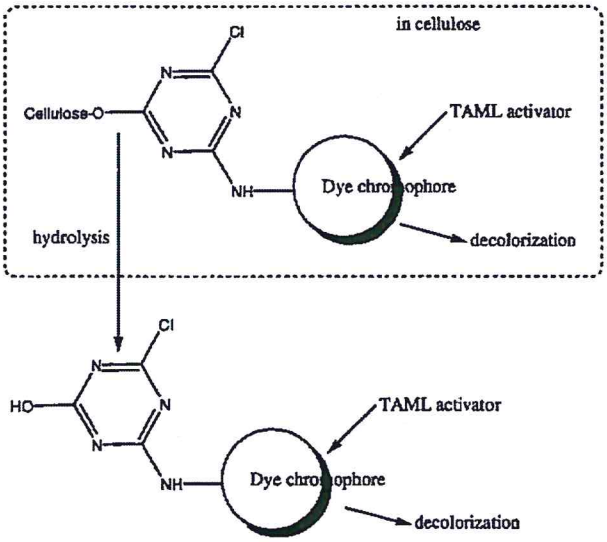


FIGURE 4 - Schematic representation of completely decolization of C.I.Reactive 2

The question then arises why Fe-TAML can not enter into submicroscopic pore of cellulose during the degradation process. It may be attributed to the aggregation of C.I. Reactive 2 on cellulose, which blocks space between cellulose and prevents Fe-TAML from cellulose. The aggregation of reactive dyes on cellulose was also reported [22].

Different Reactivity of Dissolved Dyes Compared to Adsorbed and Chemically Bound Dyes

To date, the oxidation of dyes were studied in solution where the dyes were dissolved in water [13]. In this paper, we looked for the oxidation of dyes with H_2O_2 in the presence of TAML, which are either adsorbed on silica or chemically bound to cellulose.

In contrast to aqueous system, silica gel and cellulose are heterogeneous medias. The reaction is apparently much slower and not complete, depending on the pre-treatment. It might be that the dye must be desorbed from silica to become oxidized. There will be an equilibrium of adsorbed and dissolved dye. The adsorption/ desorption of silica gel on azo dyes can significantly affect Fenton treatments. Factors that can affect the adsorption/desorption are: (1) elec-

trostatic, (2) hydrogen bonding, (3) hydrophobic interactions between dye and silica gel [23]. When pH 10 was applied, the dyes anion was the reactive species. Also, silica gel had the surface of hydroxyls and the silica gel surface is negatively charged at pH 10. Thus, electrostatic interaction between silica gel and azo dyes could be negligible. Hydrogen bonding and hydrophobic interactions between azo dyes and silica gel are more common mechanism in adsorption/desorption process. However, Procion Red 2 was not possible to adsorb on silica gel whereas acid orange 7 can adsorb on silica gel. Comparing with octanol-water partition coefficient (K_{ow}) of two kinds of dyes, it can be found that AO7 > MX-5B. This shows that hydrophobic interaction play an important role in adsorption and desorption.These sorption and desorption might contribute to the relative slow degradation rate of dyes on silica gel compared to the aqueous solution. The degradation mechanism is similar as those observed in aqueous solution: the first step is forming of reactive species Fe^{III}-OOH, which then reacts with the desordyes to give the various species.

Cellulose is a linear arrangement of ß-linked glucose units, presenting a uniform distribution of -OH groups on the outside of each chain. When two or more chains make contact, the hydroxyl groups are ideally situated to "zip" the chains together by forming hydrogen bonds [17]. Reactive Procion MX-5B can bind to cellulose by physisorbtion and chemisorption. The physisorbtion is driven by the binding enthalpy, which is ascribed to van der Walls forces [24]. The hydrogphobic dye core (conjugated aromatic part) should be close to cellulose and the hydrophilic sulfonates are hydrated in water pools in the bulk amorphous regions, in this way, the binding enthalpy is small. However, Whiting et al. [25] found that Reactive Red 2 dye molecules do not prefer to be oriented in relation to the cellulose matrix by molecular dynamics simulations analysis with Qunanta 97. Bird et al. [26] also found that physisorbed dye showed no orientation dependence using a NEXAFs spectroscopic analysis. Chemisorption of the Reactive Procion MX-5B on cellulose can take place by a nucleophilic substitution reaction between cellulose and physisorbed dye (Fig. 5). The covalentaly bonded species showed angle dependence. There are no reports regarding the attachment of a particular OH group to the dye but most likely it is bound to the primary OH group at C6 because it being sterically free. The chemically bound dye is difficult to oxidize. The reactive species is a higher valent Fe^{III}-OOH within the TAML cage [13]. The oxidant must withdraw electrons from dyes, nevertheless it is difficult to approach the dye, since the dye is in the microfibril of cellulose, which has a helical ("Bündel-Structure") structure. Hence, due to the adsorption and chemically bound to dyes, the degradation reaction of dyes is possibly diffusion-controlled. Therefore, ultrasonic mixing or some catalysts to accelerate hydrolysis of dye-fibre bond are required to be introduced into the system in order to improve degradation of dyes in contaminated soil and sediment. Although this research is in its initial stage of development, Fe^{III}-TAML/H_2O_2 technology has been potentially an effective remediation technology for the azo dyes contaminates soils.

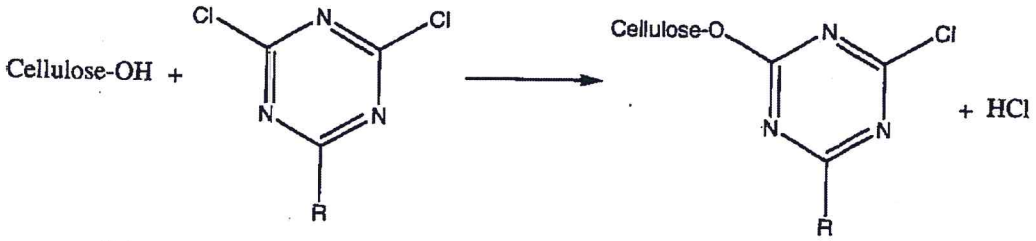


FIGURE 5 - Schematic representation of C.I.Rective Red 2 covalently bonded to cellulose

CONCLUSIONS

Degradation of two textile dyes, C.I.Acid Orange 7 (Orange II) and C.I. Reactive Red 2 (Procion Red MX-5B) bound to silica gel and cellulose by hydrogen peroxide catalyzed by Fe (III) complexed to Tetra-Amido Macrocyclic Ligands (Fe-TAML activators) at pH 10 was investigated. C.I.Acid Orange 7 and C.I. Reactive Red 2 on solid matrix after the addition of the Fe-TAML/H_2O_2 decolourize in initial time period of 10-20 minutes. The decolourisation rate of dyes on silica gel or on cellulose respectively was much slower than that in aqueous solution. Oxidation of azo dyes adsorbed to silica is much easier compared to bound to cellulose. It is likely that the azodye is desorbed into aqueous solution, where it will become oxidized. Therefore, contamined soils can be effectively treated by the H_2O_2/TAML system. The finding about decolourisation of the dyed cellulose leads to the conclusion that that Fe-TAML molecules must enter into the microfibril of cellulose and approach closely to the dye. Thus, the catalyst is not able to completely degrade the dye while bound to a fabric of structure such as cellulose. The information collected is very important in cases where soil contaminated with dyes or other chemicals should be treated directly with Fe-TAML/H_2O_2 at alkaline conditions.

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