CI&CEQ
Chemical Industry & Chemical Engineering Quarterly

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Chem. Ind. Chem. Eng. Q. 28 (1) 73–84 (2022) CI&CEQ

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SCIENTIFIC PAPER

UDC 667.2:544:667.027.4/.5

ENHANCED PHOTOCATALYTIC OXIDATION OF REACTIVE DYE USING MANGANESE CATALYST COMPLEX

Article Highlights

- MnTACN as possible green catalyst showed high decolourisation potential
- The significant decolouration was observed in the first 5 min of the treatment in the UV/H_2O_2 process
- The optimum concentration ratio H_2O_2/MnTACN was 0.02 mL/L/0.001mmol/L

Abstract

In this work, the treatment efficiency of advanced oxidation processes H_2O_2/UV enhanced by the addition of a manganese catalyst complex (MnTACN) was investigated on a model dye solution and a real dye-house effluent. The experimental results were evaluated in terms of absorbance (A) and total organic carbon (TOC) reduction. The major degradation products of the model dye solution were identified by high resolution gas chromatography/mass spectrometry analyses. In addition, the toxicity of the final reaction solution after H_2O_2/UV/MnTACN treatment to Vibrio fischeri bacteria was determined. The results showed that the addition of the H_2O_2/UV/MnTACN system at different concentrations of the catalyst solution increased the decolourisation rate compared to H_2O_2/UV for both the model dye solution and real dye-house effluent.

Keywords: photocatalytic activity, advanced oxidation processes H_2O_2/UV, textile dye, manganese catalyst complex, MnTACN.

The textile industry is usually associated with strong, persistent colour, since dyes are intentionally designed to resist microbial, chemical, and photolytic degradation to satisfy consumer demands. Many acid, direct and reactive dyes are poorly biodegradable and therefore pass through wastewater treatment plants untreated. Opportunities for advanced oxidation processes (AOPs) exist for certain pollutants such as textile dyes [1], which require permanent removal rather than just phase transfer usually realised by conventional water treatment processes [2-4]. Despite their proven performances in the removal of many organic, inorganic and microbiological pollutants, some disadvantages of AOPs, namely the non-specific reactivity of hydroxyl radicals, the production of hydrophilic (and thus more difficult to treat) by-products, and the poor knowledge about the toxicity of the by-products, make them less attractive for large-scale applications [3]. AOPs in textile wastewater treatment lines plants could find large-scale application due to the presence of non-biodegradable components that cannot be removed by “phase-transfer” treatment processes, but must be permanently withdrawn. The efficiency of H_2O_2/UV processes can be enhanced by adding common catalysts such as like Fe(II), Fe(III), ZnO or TiO_2 [5-15].

In the field of wastewater treatment, using various different manganese complexes such as salen [16], porphyrin [17], 1,4,7-trimethyl-1,4,7-triazacyclononane (MnTACN) [18] and aromatic *N*-donor ligands [19] have been more or less ignored despite their obvious potential as oxidation catalysts.

MnTACN (Figure 1) catalyses many oxidations with hydrogen peroxide, including spot bleaching, alkene epoxidation and dihydroxylation, and oxidation of alkanes, phenolic substrates, alcohols, sulphides,

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Paper received: 2 December, 2020
Paper revised: 4 May, 2021
Paper accepted: 26 May, 2021

https://doi.org/10.2298/CICEQ201202019V

and DNA. The epoxidation of methyl oleate with aqueous H_2O_2 catalysed by a manganese complex and oxalic acid has been described as being an efficient and green process [19-21]. Extensive studies have also been carried out using MnTACN as a catalyst in cotton bleaching [20,22].

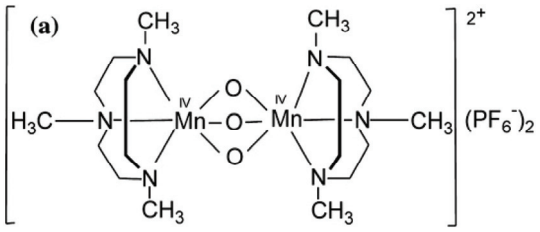

Figure 1. Chemical structure of the MnTACN catalyst.

In the field of textile dyes, Ember *et al.* [23,24] studied the oxidative degradation of various dyes by H_2O_2 catalysed by simple Mn(II) salts. The oxidation of azo dyes with H_2O_2 catalysed by manganese-1,4,7--triazacyclononane complexes in aqueous solution was also investigated [25]. The focus of the studies in all cases was on the kinetic and mechanistic studies. It was found that the active oxidant in the reactions is a very high-valent oxomanganese species rather than a free radical, such as $^{\bullet}OH$.

To our knowledge, the MnTACN catalyst has not yet been tested in the H_2O_2/UV process for decolourisation. In this configuration, additional oxidative species are formed from the hydrogen peroxide irradiated by UV. In this study, we mainly focused on reactive dyes for the following reasons: First, reactive dyes represent a significant market share due to the notable use of wool, cotton, and rayon fibres (nearly 45% of all textile dyes produced annually belong to the reactive class). Second, these dyes have low fixation rates, resulting in heavily dyed spent dye-baths that cannot be adequately treated in conventional wastewater treatment plants. Thirdly, the reactive dyeing process is particularly problematic, consuming on average ten times more water for the preparation, dyeing, washing and rinsing phases than for dyeing with other types of dyes.

The aim of the present study was to investigate the potential use of MnTACN as a catalyst in the advanced treatment of model dye solutions and real house effluents by H_2O_2/UV process. The textile dyes used in the study differ significantly in the complexity of their chemical structure and therefore have different susceptibilities to decolourisation and degradation.

Further attention was paid to the toxicity of Reactive Blue 268 degradation products such as halogenated organic compounds. Dye analysis was carried out to study the degradation of HRGC-MS. Studies with model effluents where the parameters can be controlled and feasibility studies with real wastewater streams need to be carried out before the new promising techniques can be successfully applied.

EXPERIMENTAL

Materials

A commercially available reactive triphenodioxazine dye C.I. Reactive Blue 268 (RB268) (Cibacron Brilliant Blue FN -G, CAS No. 163062-28-0) was supplied by Ciba Specialty Chemicals and used without further purification (approximately 70-80% purity). The structure is shown in Figure 2.

In order to simulate batch-dyeing conditions, the dyes were hydrolysed as follows: 1 g RB268 was dissolved in 1 L of deionised water. The solution was heated to 60 °C, after adjusting pH to 11.0 and maintained for 4 h to allow complete hydrolysis [26].

The textile wastewater used in this work was provided by a textile company located in Slovenia. The main quality characteristics were: pH 10.1±0.2; total organic carbon (TOC) 70±7 mg/L; conductivity 6.5±1.2 mS/cm. The quality varied depending on the time of sampling.

Hydrogen peroxide solution 30% (Belinka, Slovenia) of analytical grade was used in all processes. The pH was using concentrated H_2SO_4 from Merck,

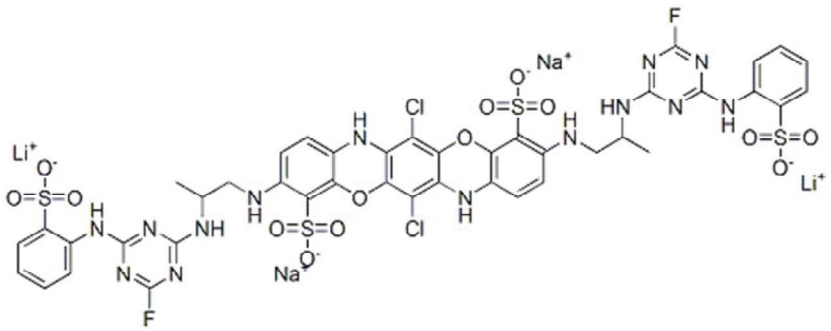

Figure 2. Chemical structure of RB268.

NaOH and HCl from Fluka, and *t*-BuOH from Sigma Aldrich.

The catalyst dinuclear tri-oxo bridged manganese(IV) complex of the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (MnTACN) was provided by Unilever R&D (Vlaardingen, The Netherlands). All solutions were prepared with deionized water (σ = 1.2 μS/cm).

Methods

Experiments on decolourisation were performed in a batch reactor (Helios ItalQuartz, Figure 3), with a maximum working volume of 1.8 L. The UV radiation source was a UV light source. The source of UV radiation was a medium pressure Hg lamp operating at 500 and 1000 W. The incident photon photonic flux was measured by H_2O_2 actinometry according to the literature [27] (I_0 = 6.0±0.1 mol/s). During the experiments, we kept the temperatures of the dye solutions constant with cooling water. The cooling water was located in a quartz cooling jacket physically separated from the surface of the UV lamp. The dye solutions were stirred with a magnetic stirrer. The reactions started when the lamp was turned on. All experiments were performed within 30 min, and samples were analysed every 5 min.

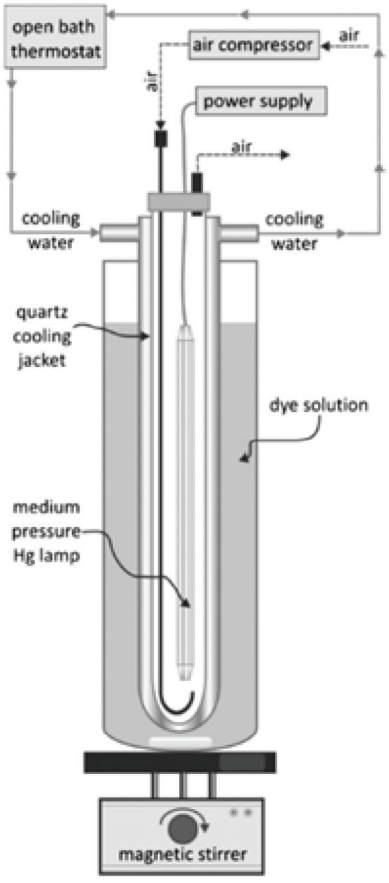

Figure 3. Photo-reactor set-up.

A comparison of decolourisation efficiencies for the dye solution RB268 with and without MnTACN as a function of reaction time was performed. The photoreactor was filled with aqueous dye solution and the indicated volume of H_2O_2 was added, based on the results of previous experiments [7].

The activity of the catalyst to decolourise RB268 was tested by varying parameters such as initial dye concentration (20-150 mg/L), MnTACN concentration (1×10^{-4}-0.02 mM), and H_2O_2 concentration of H_2O_2 (3.27-271.41 mM).

Absorbance spectra were recorded on an 8453 UV-Vis spectrophotometer (Agilent) over the range 400 to 800 nm. The absorbance decay was followed at the maximum absorbance wavelength for the RB268 at λ of 634 and at 622 nm for the real dye-house effluent. Total organic carbon (TOC) was measured using multi N/C 2100/2100S analyser (Analytic Jena, Germany) calibrated with potassium phthalate as standard solution. Conductivity was measured using conductivity meter HI 8733 (Hanna).

To evaluate the nature of decolourisation kinetics [28], the model developed by Behnajady [29] was investigated:

$$\frac{t}{1-\frac{A}{A_0}} = m + bt$$

where A and A_0 are absorbance and initial absorbance, m and b are constants concerning initial reaction rate and maximum oxidation capacity, respectively. The higher 1/m is, the faster the initial decay rate of the dye. When t is long and approaches infinity, the reciprocal of the constant b is the theoretical maximum dye removal.

Organic compounds were identified by high-resolution gas chromatography (HRGC), by separation on a HP6890GC (Hewlett-Packard, Palo Alto, CA, USA) connected to a Finnigan MAT95XP (Thermo Finnigan, Bremen, Germany), mass spectrometry (MS).

HRGC-MS analyses were performed on a RB268 sample. Prior to analyses, 10 mL of the treated sample was acidified with concentrated HCl and evaporated to dryness. A certain portion of the dry residue was derivatized with Sylon reagent (BSTFA containing 1% TMCS) in the presence of pyridine (organic base). The extract of the derivatized samples was then analysed by HRGC/MS.

The concentration of residual H_2O_2 in mg/L was determined photometrically using photometer AL250 and appropriate tablets.

The toxicity of the model dye solutions was tested in acute toxicity test with luminescent bacteria

Vibrio fischeri according to ISO 11348-1 [30]. The bioluminescence for three samples was carried out using a Dr. Lange LUMIStox 300 photometer:

Sample 1: aqueous solution of 40 mg/L RB268.

Sample 2: aqueous solution of 40 mg/L RB268 treated with H_2O_2/UV process (15 minutes and 500 W) with H_2O_2 concentration 65.29 mM.

Sample 3: aqueous solution of 40 mg/L RB268 treated with H_2O_2/UV process (15 minutes and 500 W) with 65.29 mM H_2O_2 with addition of 0.02 mM MnTACN.

The dilutions tested were 0, 0.39, 0.78, 1.56, 3.12, 6.25, 12.5, 25, 50 and 100 vool.% of the respective samples tested and were prepared with 2% NaCl.

Bacteria were first reactivated and kept at 15 °C before starting. The lyophilized bacterial reagent was reconstituted and diluted as indicated in the LUMIStox basic acute toxicity test procedure. Bacterial luminescence was then measured prior to sample addition. The decrease in bioluminescence, indicating a toxic effect of the test substance, was measured after 15 min of contact time with the samples. The analyses were performed at 15 °C. All samples were tested in duplicates. Inhibition of natural luminescence of photobacteria is considered as toxicity endpoint.

RESULTS AND DISCUSSION

MnTACN catalyst

The 1 mM stock solution of MnTACN was prepared. The pH of the 1 mM solution of MnTACN was 6.7 and the maximum absorbance was measured at λ = 485 nm. Different dilutions of the stock MnTACN solution were prepared using deionised water (1×10^{-4}--0.02 mM) and added to the reaction mixture. To check the background behaviour of the catalyst solution during the H_2O_2/UV process, 1 mM solution of MnTACN was exposed to UV irradiation (500 and 1000 W) upon addition of 22.85 mM solution of H_2O_2. Under the treatment conditions used in this experiment, MnTACN did not change its absorption characteristics according to the UV-Vis spectrum. The TOC values were measured at the same time intervals and also remained unchanged. Therefore, it could be assumed that MnTACN acted as a catalyst.

The degradation of RB268 dye solution was also studied without UV irradiation. In this experiment, the solution of RB268 of concentration 40 mg/L was magnetically stirred in the presence of MnTACN (0.001 mM) and H2O2 (65.29 mM) solution in the absence of UV light at room temperature. MnTACN is also active in the absence of UV light, but the degradation time was longer; 80% of the dye was degraded after 48h.

Degradation of RB268 under different conditions (model dye solution)

Effect of initial dye concentration

To determine the optimal conditions for the oxidation (catalyst MnTACN and H_2O_2 concentration) of textile dyes based on our previous studies we used 65.29 mM H_2O_2 and a catalyst MnTACN concentration of 0.001 mM as a starting point. Varying the initial dye concentrations, the effect of the added catalyst is apparent within the first few minutes of treatment (Figure 4). The removal of colour is one of the most important aspects in decolourisation processes. It is related to the bond cleavages of the chromophoric groups and occurs in a relatively short treatment time (≈ 5 min). Selected reaction conditions are very effective in the decolourisation of RB 286; with concentration of 40 mg/L, 60% decolourisation is

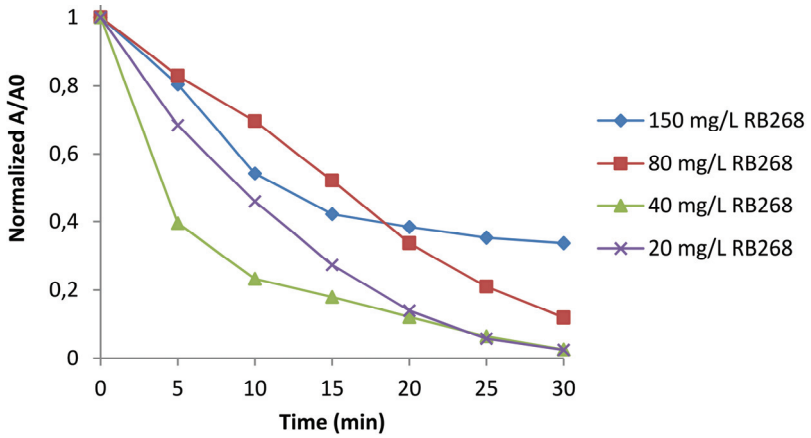

Figure 4. Effect of the addition of MnTACN on the decolouration of RB268 with different dye concentrations in photo batch reactor. Experimental conditions: concentration of RB268 was 20, 40, 80 and 150 mg/L, concentration of H_2O_2 65.29 mM, concentration of MnTACN 0.001 mmol/L.

achieved in the first 5 min. For example, only 9% decolourisation was achieved within the first 5 min when only the H_2O_2/UV process is performed.

All other decolouration experiments were conducted at a fixed dye concentration of 40 mg/L. In our experience, the concentration of the dye in real dyehouse wastewater is usually not higher than 40 mg/L.

Effect of catalyst dosage

In the first approach, catalyst concentrations were varied widely and from this the following standard conditions were chosen for the majority of our study.

In most experiments, the catalysed reactions show three distinct phases, *i.e.*, the initial induction phase followed by a fast phase and finally a slower phase.

The effect of different concentrations of catalyst was tested to determine the minimum amount still required for significant decolouration. The effect of MnTACN catalyst concentration on decolourization rates as a function of time is shown in Figure 5. The concentrations of the RB268 and H_2O_2 were 40 mg/L and 65.29 mM, respectively.

The experimental results showed two groups of decolouration profiles depending on the catalyst concentration. In all cases, a significant decrease in decolouration was observed in the first 5 min of treatment when the catalyst was added to the solution. The decolouration results after 30 min of treatment are comparable for the selected catalyst concentrations 0.02, 0.002 and 0.001 mM. The results obtained indicate that comparable decolouration rates can be achieved with a 20-fold decrease in the initial catalyst concentration. The experimental conditions indicated 0.001 mM of catalyst was to be the optimum concentration.

In the case of a catalyst concentration of 0.02 mM, the decolourisation rate decreased to 0.111 in the first 5 min of the treatment. For the same experimental conditions, but without catalyst, decolouration rate decreased very slowly and was still 0.24 after 30 min.

The highest reduction in colour was observed when 0.001 mM MnTACN was added to the batch photo reactor. After 5 minutes of irradiation, the decolouration rate reduced to 0.395, and when 0.0005 mM of MnTACN was added the decolourisation rate was 0.733.

The optimum dosage was observed at 0.001 mM of MnTACN, and complete decolourisation was observed after 30 min.

At a lower concentration of dye solution RB268, 20 mg/L we obtained better results with a lower concentration (0.0001 mM) of MnTACN (Figure 6).

Effect of H_2O_2 concentration

Once the optimal catalyst concentration was determined, kinetics were performed with different concentrations of the oxidant (Figure 7) to find the optimal dose. The catalyst MnTACN is not active without the addition of H_2O_2.

It is evident from the results that an optimal H_2O_2 dosage and consequently an optimal H_2O_2:catalyst ratio exists with large variations within the first five minutes of treatment. The decolouration profile is divided into two parts. The fast reaction occurs within the first few minutes. The second part is much slower. However, the final decolouration rate is comparable for all tested concentrations despite the H_2O_2 concen-

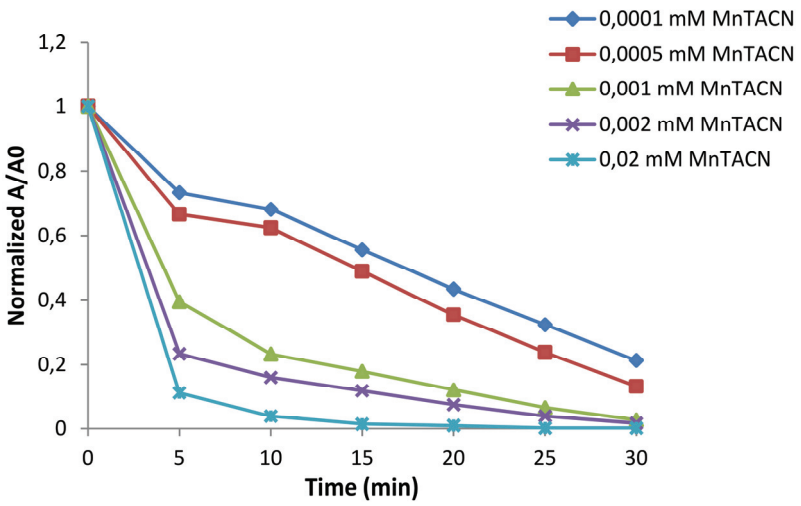

Figure 5. Decolouration as a function of time for RB268 at different MnTACN addition (dye concentration: 40 mg/L, concentration of H_2O_2 65.29 mM).

tration of 3.27 mM. From the experimental results (Figure 7), it can be seen that the highest increase in decolouration rate was observed at H_2O_2 concentration 65.29 mM. Increasing the H_2O_2 concentration above this value obviously does not increase the decolouration rate; on the contrary, the addition of a 4 times higher dose hinders the reaction [31].

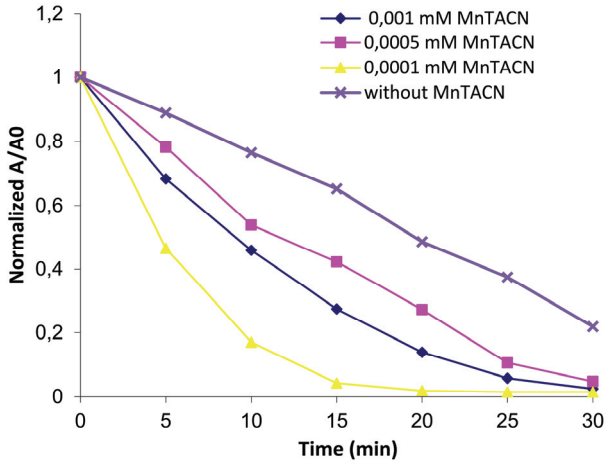

Figure 6. Effect of the addition of MnTACN on the decolourisation of RB268 in photo batch reactor. Experimental conditions: concentration of RB268 was 20 mg/L, concentration of H_2O_2: 65.29 mM.

This result suggests that the H_2O_2 concentration of 65.29 mM is the threshold for achieving maximum efficiency.

The mechanism of decolouration within the first 5 min: the decolouration rate was increased by the presence of MnTACN, while only OH radicals, produced with H_2O_2/UV were slower, in agreement with the literature [25].

The experiments showed very similar degradation of RB268. When the concentration of RB268 was 40 mg/L, 80% of dye was degraded after 30 min by adding 0.001 or 0.01mM MnTACN. Therefore, 0.001 mM MnTACN was used in further experiments.

The adopted model was evaluated (Bahayami). The plotted linearized adsorption kinetics curves showed excellent correlation with the model (Figure 8). The correlation factor is R^2 = 0.99788. On the one hand we have a fast reaction between UV, H_2O_2 and MnTACN, while on the other hand the scavenging of •OH slows down the reaction. This aspect shows that MnTACN can accelerate the decolourisation reactions of dyes in agreement with Santana *et al.* [29].

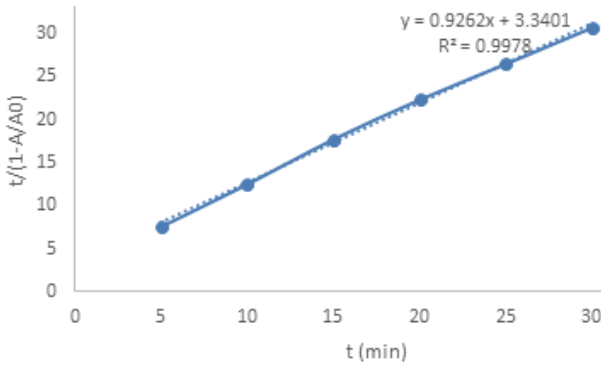

Figure 8. Kinetics for model water at optimal conditions (65.29 mol/L H_2O_2, 40 mg dye, 0.001 mM MnTACN).

Degradation of real dye-house effluent

The use of MnTACN catalyst for textile wastewater treatment processes is very interesting since t is active at pH>7. This is the advantage of the MnTACN catalyst over the Fenton reagent [7] (the optimum pH for the Fenton reaction is about 3) for textile wastewater treatment processes, since textile waste streams are mainly alkaline.

In Figure 9, decolouration was plotted as a function of time for real dye house effluent at different conditions: H_2O_2/UV, UV/MnTACN and H_2O_2/UV/MnTACN.

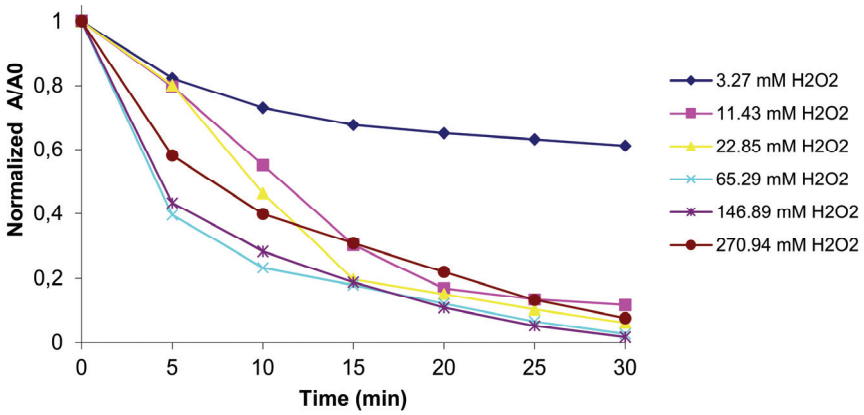

Figure 7. Influence of different concentrations of H_2O_2 on decolourisation in photo batch reactor. Concentration of RB268 was 40 mg/L, concentration of MnTACN was 0.001 mmol/L.

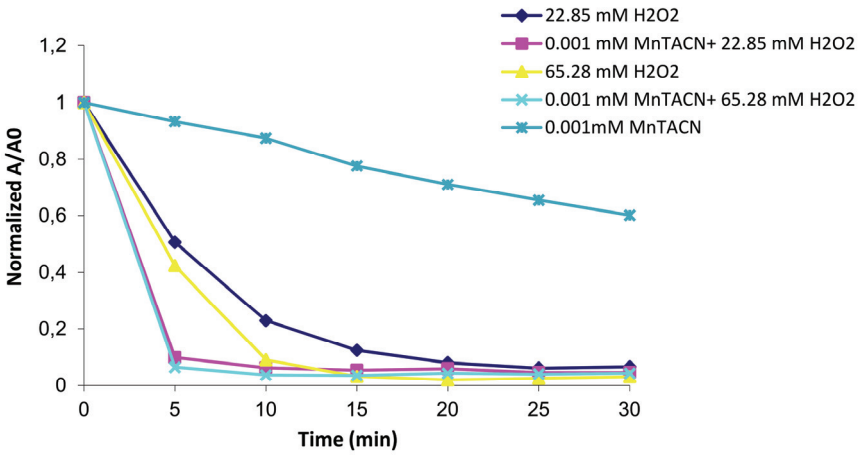

Figure 9. Decolouration as a function of time for real dye house effluent.

The fastest colour removal was achieved with a combination of H_2O_2/UV/MnTACN treatment within the first 5 min, regardless of the amount of H_2O_2, while comparable values were obtained after 10 min for H_2O_2/UV with 65.29 mM H_2O_2 addition. Thus, MnTACN accelerates the reaction rate. However, the final colour removal was comparable to the samples treated without MnTACN.

The addition of 0.001 mM MnTACN to the H_2O_2/ /UV process improved the TOC reduction for real dye--house effluent after a treatment time of 30 min. The TOC removal efficiency was higher (54%) in the case when 65.29 mM H_2O_2 was added compared to 22.85 mM H_2O_2, the TOC redaction was 43% in this case. The TOC removal efficiencies were higher when MnTACN was added to the H_2O_2/UV process. Only 29% TOC reduction was achieved with H_2O_2/UV process.

MnTACN cannot decolourise wastewater without H_2O_2. It can only accelerate the decolourisation process, *e.g.*, active mononuclear Mn(II) or dinuclear Mn(IV)-O-Mn(IV) [32] in the presence of H_2O_2/UV. The addition of t-BuOH (9 mL) as radical scavenger to the H_2O_2/UV process with aqueous solution of 40 mg/L RB268, 22.85 mM H_2O_2 and 0.001 mM MnTACN didn't inhibit the decolourisation process. This proves that the active oxidant in the reactions is a highly-valent oxomanganese species and not $^{\bullet}OH$.

However, the catalyst retains its structure after the decolourisation process and gives the identical UV-Vis spectrum as before the decolourisation process (Figure 10). The same results were reported in the study of oxidation of organic substrates by MnTACN [33]. In agreement with the proposed mechanism, it was reported [34] that the bridged-oxo-Mn complex exhibited catalase activity when H_2O_2 was the oxidant.

The kinetics for real dyehouse effluent were studied using the adopted model (Behnajady). The model has been plotted in Figure 11. The R^2 is practically equal to 1.

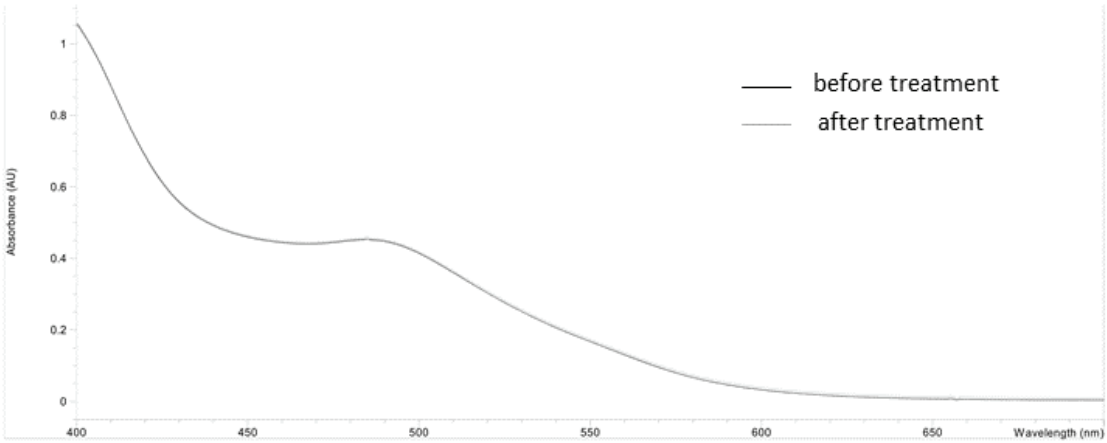

Figure 10. UV-Vis spectra of MnTACN solution before and after treatment in H_2O_2/UV reactor.

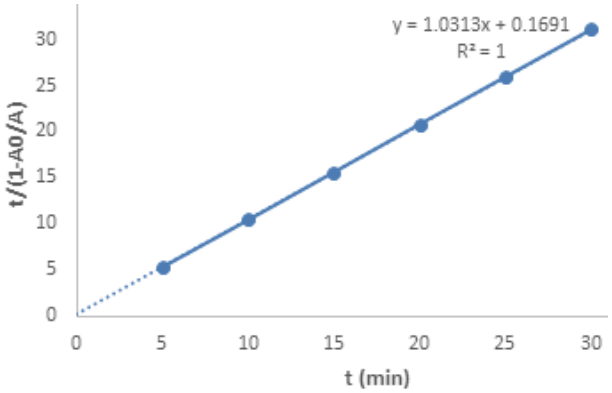

Figure 11. Kinetics for real dye-house effluent.

The model describes such a reaction system very well, which is confirmed by the results found here. Based on the results for the model solution and the real dyehouse effluent, we can assume that MnTACN increases the decolourisation, and the decolourisation in the real dyehouse effluent (lower intercept *m* in Figure 11) was even faster than in the model solution (Figure 8). In another study, it was found that there could be a certain compound in the dyeing solutions which could interact with UV/H_2O_2 and enhance decolourisation [7].

The different dosages of reagents, catalysts, and target dyes, were studied and it was found that the most appropriate suitable kinetic model may change from one reaction system to another [29].

Comparative studies of degradation products

The degradation intermediates of RB268 dye solution with a concentration 100 mg/L treated with MnTACN (concentration 0.002 mM) and without MnTACN catalyst under H_2O_2/UV conditions (1000 W, 22.85 mM H_2O_2) were analysed. HRGC/MS chromatograms confirmed the formation of volatile intermediates, which were identified using AMDIS – Automated Mass Spectral Deconvolution and Identification System software. Mass spectra of the detected compounds were compared with mass spectra from the standardized mass spectra library NIST and Wiley. Various hydroxylated compounds of the fluorotriazine ring were detected. The proposed degradation pathways are shown in Figure 12. One of the most obvious is cyanuric acid with a retention time (RT) of 13.641 min. In addition, some compounds related to cyanuric acid were also detected, such as ammelide at RT 16.461 min, and ammeline at RT 18.726 min. The concentrations of these compounds increase with processing time and were not present in the untreated solution. HRGC/MS analysis of the RB268 dye solutions indicate the presence of halogenated organic compounds. The decrease in the concentration of halogenated organic compounds was observed after 5 min of treatment of RB268 dye solutions by H_2O_2/UV process. Halogenated organic compounds were not detected after 30 min. MnTACN enhances the degradation of the dye solution, no detection of the halogenated organic compounds was observed after 5 min of treated time.

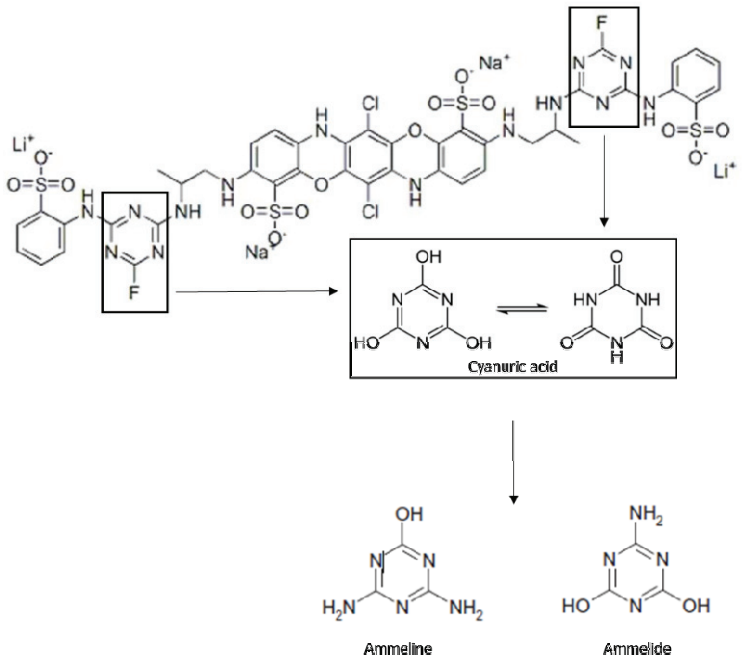

Figure 12. Proposed degradation pathways.

The dye degradation products of the fluorotriazine dye RB268 were detected in the extract of the derived samples treated with the H_2O_2/UV procedure. Cyanuric acid was present in the initial samples at RT of 13.614 min. In addition, some compounds related to cyanuric acid such as ammelide at RT 16.461 min and ammeline at RT 18.726 min were also detected [35]. The concentrations of these compounds (cyanuric acid, ammelide, ammeline) increased with processing time and were not present in the untreated solution. Therefore, it could be concluded that the compounds are the degradation products of the Reactive Blue dye RB268.

The comparison between catalysed (Figure 13a) and uncatalysed process (Figure 13b) shows that the concentrations of the degradation compounds were higher without the MnTACN catalyst.

Toxicity test results

Toxicity test results for *Vibrio fischeri* were expressed as EC_{50}, which represents the volume percent concentration of 3 samples.

Bacterial bioluminescence is used as an indicator of water toxicity, in that bioluminescence decreases as toxicity increases.

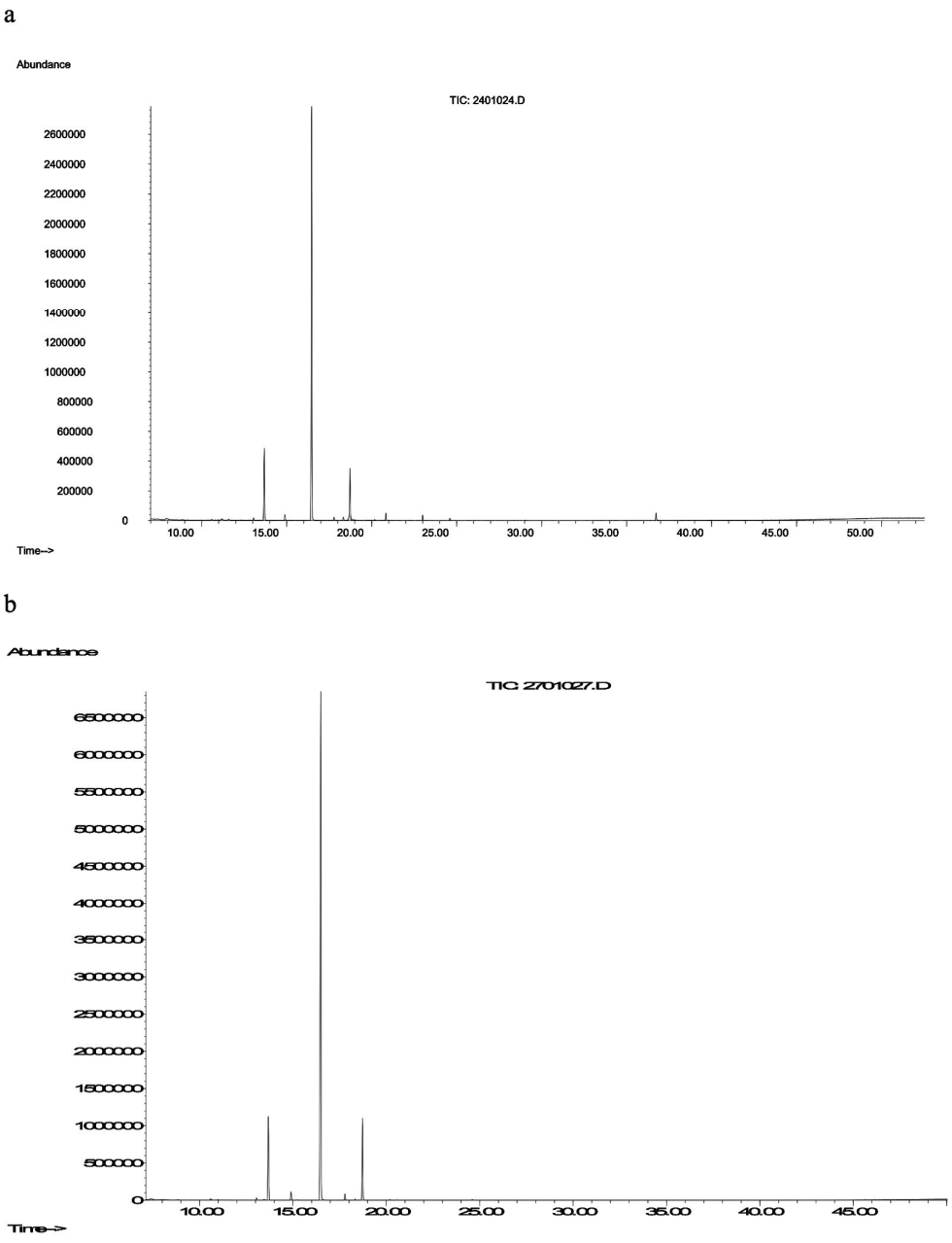

Figure 13. HRGC-MS chromatograms of samples taken after 30 min of H_2O_2/UV with (a) and without MnTACN (b).

Sample 1, aqueous solution of 40 mg/L RB268 showed no inhibitory effect on *V. fischeri*, even without any dilution. Sample 2, aqueous solution of 40 mg/L RB268 treated with H_2O_2/UV process (15 min and 500 W) with H_2O_2 concentration of 65.29 mM caused a decrease in luminescence. The results show that after the H_2O_2/UV step, the toxicity increases. The EC_{50} value was determined at 0.25 vol.%. The inhibition of *V. fischeri* bioluminescence (%) for the dilutions of Sample 2 are shown in Table 1. In the solution, the remaining H_2O_2 was measured at 25 % of the initial concentration. The toxicity of Sample 2 can be explained by the presence of H_2O_2 in wastewater which is toxic even at low concentrations [36,37].

Table 1. The inhibition of Vibrio fischeri bioluminescence (%) for the dilutions of Sample 2

c (%)	Inhibition (%)
0.39	53.22
0.78	65.18
1.65	67.23
3.125	70.40
6.25	76.12
12.5	81.09
25	84.33
50	87.88
100	90.62

Sample 3, an aqueous solution of 40 mg/L RB268 with 65.29 mM H_2O_2 with the addition of 0.02 mM MnTACN by the H_2O_2/UV process (15 min and 500 W), also showed no inhibitory effect on *Vibrio fischeri.* The addition of MnTACN even had a positive effect on the survival of *Vibrio fischeri*. No residual H_2O_2 was present in the solution and it was suggested that MnTACN additionally activated H_2O_2 degradation without changing its structure during the decolourisation process.

Usually, AOPs are used for the degradation of targeted pollutants or groups of pollutants such as textile dyes; in some cases AOPs lead to the formation of toxic by-products that pose a potential environmental risk. From the toxicity test, it can be concluded that RB268 degradation products don't have an inhibitory effect on *Vibrio fischeri.*

Residual H_2O_2 should be removed from treated wastewater before discharge or reuse. To avoid the presence of residual H_2O_2 in the treated water, two main approaches were implemented, namely the addition of relatively low concentrations of H_2O_2 (which can be completely consumed during the process) and filtration through activated carbon [38]. The addition of the catalyst MnTACN to H_2O_2/UV has no negative effect on *V. fischeri* bacteria.

CONCLUSIONS

The potential use of MnTACN as a catalyst in the advanced treatment of model dye solutions and real dye-house effluent by H_2O_2/UV process was investigated. The formation of a highly efficient and reusable catalyst for the oxidative decomposition of various stable organic dyes by H_2O_2 under mild reaction conditions was observed. The results showed that manganese-containing compounds are environmentally acceptable as possible catalysts in bleaching. The addition of different concentrations of the catalyst solution increased the decolourisation rate compared to H_2O_2/UV alone. The ratio between oxidant and catalyst needs to be determined for optimum efficiency. The results showed that the optimum concentration ratio was H_2O_2/MnTACN = 65.29 mM/0.001 mM. Moreover, the catalyst additive significantly improved the decolouration rate within the first 5 min of treatment and reduced the treatment time required for decolouration. The degradation mechanism is still unclear, but no halogenated organic compounds were detected after a treatment time of 30 min.

MnTACN was successfully used for the first time as an H_2O_2/UV catalyst for decolourisation of a model solution. Moreover, the decolourisation rate was also improved in the real dyehouse effluent.

Acknowledgements

This work was supported by the Slovenian Research Agency under the research programme P2--0118 Textile Chemistry and P2-0032 Process Systems Engineering and Sustainable Development.

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NAUČNI RAD

POBOLJŠANA FOTOKATALITIČKA OKSIDACIJA REAKTIVNE BOJE KORIŠĆENJEM KOMPLEKSA KATALIZATORA NA BAZI MANGANA

U ovom radu je istražena efikasnost naprednih oksidacionih procesa H_2O_2/UV pojačanih dodatkom kompleksa manganskog katalizatora (MnTACN) na modelnom rastvoru boje i stvarnom efluentu iz procesa bojenja. Eksperimentalni rezultati su procenjeni u smislu redukcije apsorbancije i ukupnog organskog ugljenika. Glavni proizvodi degradacije modelnog rastvora boje identifikovani su analizama gasne hromatografije/masene spektrometrije visoke rezolucije. Pored toga, utvrđena je toksičnost finalnog reakcionog rastvora nakon H_2O_2/UV/MnTACN tretmana na bakterije Vibrio fischeri. Rezultati su pokazali da se dodavanjem sistema H_2O_2/UV/MnTACN u različitim koncentracijama rastvoru katalizatora povećava brzina dekolorizacije u poređenju sa H_2O_2/UV i za modelni rastvor boje i za stvarni efluent iz procesa bojenja.

Ključne reči: fotokatalitička aktivnost, napredni oksidacioni procesi H_2O_2/UV, tekstilna boja, kompleks manganskog katalizatora MnTACN.