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5,10,15,20-Tetrakis(4-sulfonato-phenyl)porphine-Mn(III) immobilized on imidazole-activated silica as a novel lignin-peroxidase-like biomimetic catalyst

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Abstract

In this study a new biomimetic lignin-peroxidase-like catalyst was investigated. Such a heterogeneous catalyst could be of potential interest for oxidative degradation of plant effluents, containing soluble lignin derivatives. 5,10,15,20-Tetrakis(4-sulfonato-phenyl)porphine-Mn(III) was coordinated to imidazole-bearing silica to give a stable adduct; by contrast, the metalloporphine did not significantly interact with plain silica gel or aminopropylsilica. The adduct showed a remarkable ability to catalyze veratryl alcohol oxidation at the expenses of H_2O_2. Kinetic and operational characterisation of the catalyst is also reported.

Keywords: Manganese porphine; Immobilization; Veratryl alcohol; Oxidation; Hydrogen peroxide

1. Introduction

The use of synthetic metalloporphines and metalloporphyrins as biomimetic compounds to catalyze oxidative degradation of a wide range of organic compounds at the expenses of hydrogen peroxide and/or other oxidants, is not new. Both iron(III) and manganese(III) synthetic metalloporphines have been already investigated with regard to their biomimetic catalytic activity [1]. In particular, several studies have been reported about cytochrome P-450-like or peroxidase-like biomimetic catalytic activity of these metalloporphines, for example, in the hydroxylation of alkanes [2–7] or epoxidation of alkenes [8–11]. Such compounds have also found applications as simplified molecular models to understand the intimate mechanism(s) of peroxidase catalytic cycle.

Furthermore, in some applications such as hydroxylations and epoxidations metalloporphines showed very promising stereo- and enantio-selective yields [7,12].

Moreover, iron(III) and manganese(III) synthetic metalloporphines could be also used as LiP biomimetic catalysts. Several studies have been performed [13–17] about oxidation of lignin-like compounds, in presence of hydrogen peroxide, catalyzed by such metalloporphines.

Degradation of lignin and ligninoids is a key step in several industrial processes and therefore the development of an inexpensive and easy-performing system for lignin degradation would have great economical effects on such processes for both lignin removal from lignocellulosics and treatment of wastewaters coming from pulp and paper plants. In fact, the current methods are based on chemical or physical approaches that are affected by low efficiency and high costs. Even enzymatic approach suffers from the drawback of difficult purification of LiP that is also unstable in the presence of oxidant excess [14,15]. Biomimetic promising methods involving polyoxometalates and

Abbreviations: APS, aminopropylsilica; IPS, (3-imidazolylpropylcarbamoyl)-3′-aminopropylsilica; SG, silica gel; VA, veratryl alcohol (3,4-dimethoxybenzyl alcohol); MnTSPP, 5,10,15,20-tetrakis(4-sulfonato-phenyl) porphine-Mn(III) chloride; LiP, lignin peroxidase, E.C. 1.11.1.7.

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iron(III)tetraamido macrocycles [18–22] have also been suggested, even if their high costs are still preventing a widespread use.

In this context, the use of synthetic metalloporphines could be an interesting solution, due to their high redox potential and resistance against oxidative degradation. The last feature is usually achieved through the electron-withdrawing groups in the *meso* positions of porphines (such as phenyl, pentafluorophenyl, *N*-methylpyridyl, 4-sulfonatophenyl groups and so on); these groups are able to increase resistance towards hydrogen peroxide in *meso*-substituted porphines, in comparison to natural porphyrins that all show unsubstituted *meso* positions [1]. Moreover, the electron-withdrawing groups from the *meso* positions increase the redox potentials of the corresponding metalloporphines.

Unfortunately, the metalloporphines, featuring the most interesting properties of catalytic efficiency and chemical robustness, usually come from complex synthetic procedures and are therefore very expensive.

Many groups have worked on iron(III) and manganese(III) porphines in solution [9,10,16]: however, this approach cannot be economically affordable on large scale. In fact, most of these catalysts are insoluble in water, and require the use of large amounts of organic solvents for exploiting their catalytic performances. Water-soluble metalloporphines are often more costly than their water-insoluble counterparts. Moreover, it was shown that when free metalloporphines work in solution several side reactions occur, such as homolytic cleavage of peroxide bond to yield Fe(IV)–OH and hydroxyl radicals, or – worse – the formation of catalytically inactive μ-oxo porphine dimers [15]. Last but not least, the problem of catalyst recovery remains largely unresolved, regardless of the solubility properties of the chosen metalloporphine. One solution could be the immobilization of these compounds on supports and some research groups have bound metalloporphines to solid supports, by using different approaches: adsorption [5,17,23,24], ion-exchange [25] and covalent bond formation [26–28].

Although immobilization minimizes the problems described above, and allows a multicyclic use of the catalyst, the first two methods lead to relatively weak interactions between metalloporphines and supports. Moreover, none of them emulate LiP active site, where Fe(III) into porphyrin is axially coordinated by imidazole-*N* of the proximal histidine. The substantial effect of a proper axial coordination towards the behaviour of metalloporphines is supported by the finding that the presence of imidazole in reaction bulk dramatically increases metalloporphine catalytic activities [1,9].

Grafting imidazole functions on solid supports in order to coordinate metalloporphine, which also leads to a higher redox potential, has been described before [29].

According to these evidences, in the perspective of setting an environmentally friendly, inexpensive treatment for wastewaters coming from pulp and paper plants, a solid, water-insoluble adduct between 5,10,15,20-tetrakis(4-sulfonatophenyl)porphine-Mn(III) chloride (MnTSPP, Fig. 1) and imidazole-functionalized silica was prepared. The obtained

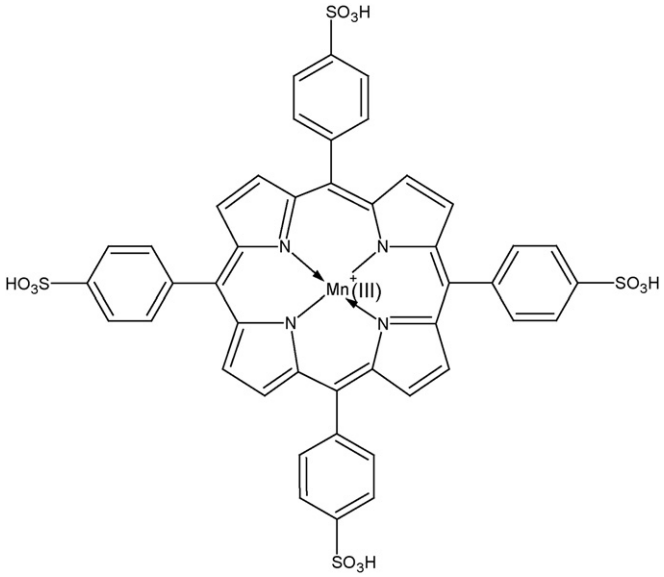


Fig. 1. 5,10,15,20-Tetrakis(4-sulfonatophenyl)porphine-manganese(III), MnTSPP.

product was tested to assess its catalytic properties as a preparation capable of mimicking fungal lignin peroxidase (LiP), E.C. 1.11.1.7 [30] using lignin model compound 3,4-dimethoxybenzyl alcohol (veratryl alcohol, VA). To our knowledge, there are no earlier study reports about an imidazole-modified support, in which the coordinating group is placed at the end of a molecular spacer, featured to impart a sharp hydrophilic character to the preparation, and long enough to minimize unspecific support/porphine interactions (Fig. 2).

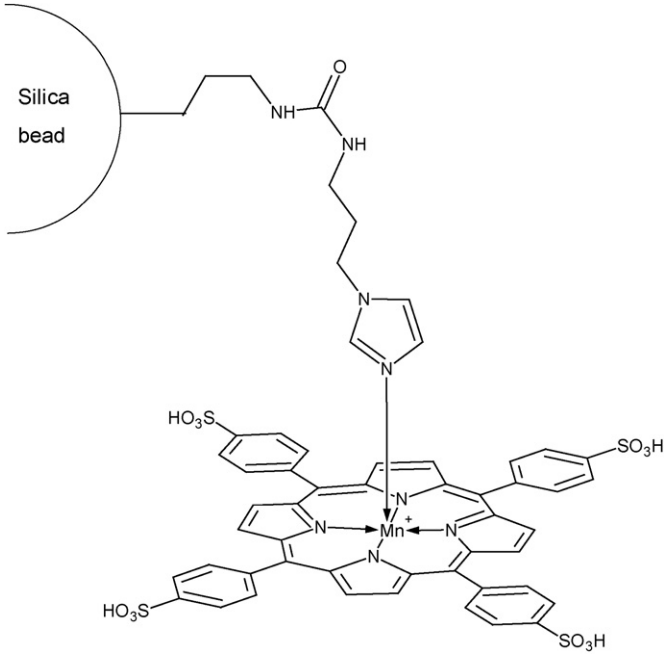


Fig. 2. Schematic representation of the proposed coordinative interaction between IPS and MnTSPP.

2. Experimental

All the reagents used were of the best grade available, and were used without further purification. In particular, Silica gel 100 (SG) came from Fluka (cat. No. 60746), and MnTSPP was purchased form Sigma–Aldrich (cat. No. 441813).

2.1. Preparation and analysis of silanized silicas

2.6 g (10 mmol) of (3-isocyanatopropyl)triethoxysilane and 1.4 g (11 mmol) of *N*-(3-aminopropyl)imidazole reacted in 20 mL dioxane, in order to synthesize 3-(1-imidazolyl)propylcarbamoyl-3′-aminopropyl-triethoxysilane. The mixture was allowed to react overnight, and to this newly synthesized silane 10 g of silica gel 100 was added. The slurry was kept at 80 °C overnight. The activated silica, 3-(1-imidazolyl)propylcarbamoyl-3′-aminopropylsilica (IPS), was consecutively washed with 0.5 M HCl, with H_2O, with 0.1 M NaOH and again with H_2O. The wet silica was then carefully dried overnight in a vacuum oven at 50 °C.

In control experiments, aminopropylsilica (APS) was prepared as above with the substitution of (3-aminopropyl)triethoxysilane for 3-(1-imidazolylpropylcarbamoyl)-3′-aminopropyl-triethoxysilane.

The functionalization degrees for both IPS and APS were determined by elemental analysis.

2.2. Preparation and analysis of IPS/MnTSPP adduct

Samples of 1 g of IPS were treated with different amounts of MnTSPP, ranging from 2 to 120 mg of metalloporphine, solubilized in 10 mL of H_2O, then the reaction mixtures were kept at 25 °C in the dark (because of MnTSPP photosensitivity) under stirring overnight. After this, excess metalloporphine was washed away with aqueous 1 M NaCl and finally with H_2O. The imidazole-activated silica/MnTSPP adducts were finally dried at 50 °C in a vacuum oven overnight.

Unbound MnTSPP was quantified through spectrophotometric measurement (UltroSpec 2100 pro, Amersham Bioscience) at 400 nm, by using a calibration curve obtained by using a suitably diluted solution in 25 mM potassium phosphate buffer, pH 7.0. Thus, the amounts of bound metalloporphine were determined by difference between the two measurements.

In control experiments, both SG and APS were treated with MnTSPP as described above to check their ability of binding the metalloporphine. Subsequent treatment and analysis were identical to that described above for IPS/MnTSPP adducts.

2.3. IR spectra

IR spectra (resolution 2 cm^{-1}) were recorded after the samples were obtained as KBr pellets, with a KBr beam-splitter and KBr windows on a Thermo Nicolet 5700 spectrometer at room temperature using a dry air flow.

2.4. Activity measurements

Catalytic activity of the various silica/MnTSPP adducts were measured at 20 °C through photometric assays. The assay mixture contained, in a final volume of 2 mL, 15 mg of catalyst, 8.8 mM hydrogen peroxide, 1.25 mM veratryl alcohol (VA) and 25 mM buffer.

Some buffers at different pH were used: sodium citrate (pH 3), sodium acetate (pH 4.5), potassium phosphate (pH 6 and 7) and sodium diphosphate (pH 8).

For each sample, a blank sample without catalyst was prepared.

The reaction mixture was kept under stirring for 30 min, then the absorbance increase at 310 nm was recorded (absorbance peak of the oxidation product of VA, veratraldehyde, $\varepsilon_{310} = 9300\ M^{-1}\ cm^{-1}$ [31]).

To evaluate catalyst multicyclic use, assays were repeated several times. Between cycles, IPS/MnTSPP was regenerated through exhaustive washings with H_2O, 2-propanol, and subsequent drying.

For GC–MS analysis, reaction was checked for 2 h, with further addition of 0.2 mL of 88 mM hydrogen peroxide to reaction mixture after 1 h.

Michaelis–Menten-like kinetics was assessed with the aid of Grafit 4 software (Erithacus Software Ltd.).

2.5. GC–MS analysis

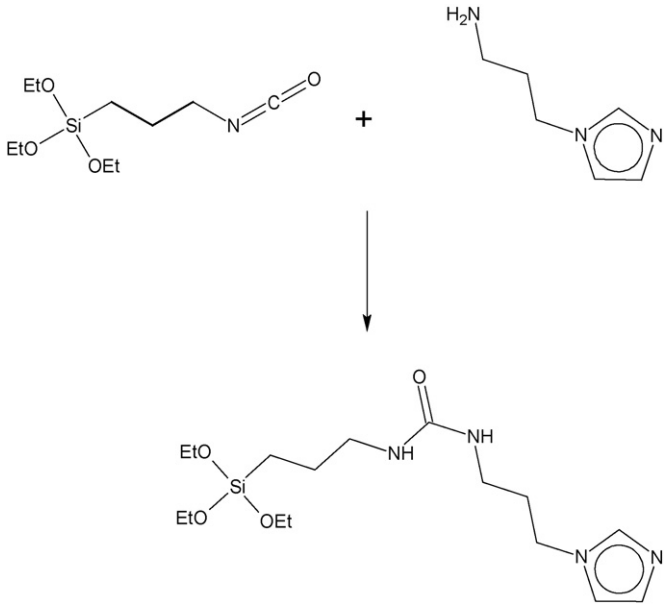
A complete analysis of the reaction products was conducted using an HP 5980 gas-chromatograph connected with an HP 5971 A mass spectrometer. The measurements were carried out by working in electronic impact at 70 eV with a source temperature of 100 °C. Gas-chromatographic separation was performed with an HP 5-MS column (length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm). Analysis conditions: initial temperature 120 °C for 15 min, then 10 °C/min gradient until 250 °C. This temperature was kept for 5 min.

3. Results and discussion

3.1. Functionalization of silica gel

The chosen commercial silica gel is easily available in large amounts at a very low price: this is why we have focused our efforts to obtain a heterogeneous catalyst based on this product.

The synthesis of the imidazolyl silane (Scheme 1) represents a case of the well-known reaction between alkyl isocyanates and aliphatic primary amines, leading to *N*,*N*′-disubstituted ureas. The obtained product was subsequently used as a silanizing agent without any need of purification (in order to synthesize IPS), and led to a functionalization degree of 0.29 mmol imidazolyl groups/g silica. In the case of the control experiment with (3-aminopropyl)triethoxysilane, APS was obtained with a functionalization degree of 0.61 mmol amino groups/g silica. This higher yield of functionalization for APS is presumably due to the sharp basic character of aminopropyltriethoxysi-



Scheme 1. Reaction between 1-(3-aminopropyl)imidazole and (3-isocyanatopropyl)triethoxysilane leading to 3-(1-imidazolyl)propylcarbamoyl-3′-aminopropyl-triethoxysilane.

lane in comparison with the weak basicity of the imidazolyl moiety.

With concern to the metalloporphine loading by IPS, a typical hyperbolic saturation curve was obtained (Fig. 3), and a proportion of 60 mg metalloporphine per gram of IPS (corresponding to a loading of 40.8 mg/g IPS) was chosen for further experimental work. With concern to control experiments, SG showed no interaction with MnTSPP, which was completely recovered by simply washing the support with distilled water. This excludes any unspecific interaction with the metalloporphine. In the case of APS, the metalloporphine was adsorbed at first and it resisted against to the water washings. However, MnTSPP was promptly and almost totally released upon washing with the NaCl solution (contrarily to that was seen with the IPS/MnTSPP adduct). These results indicate a specific, axial coordinative interaction between the imidazole nitrogen of IPS

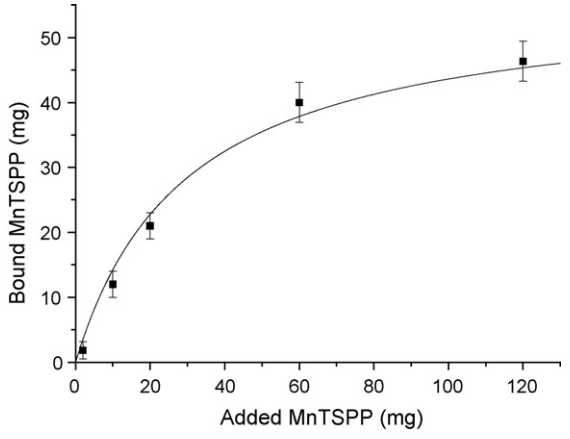


Fig. 3. MnTSPP loading vs. MnTSPP concentration. Bound MnTSPP was intended per gram IPS. Added MnTSPP was dissolved in 10 mL distilled water.

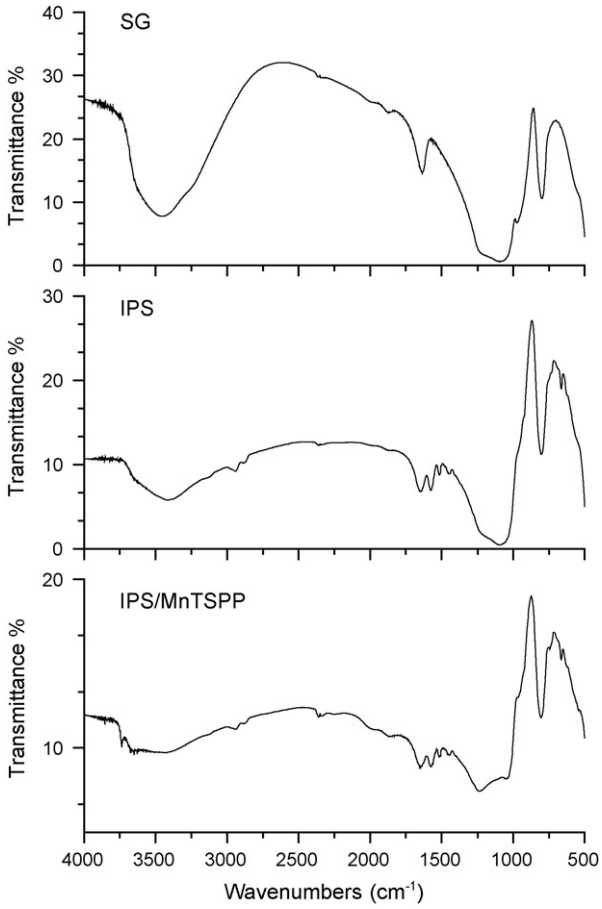


Fig. 4. IR spectra of SG, IPS and IPS/MnTSPP.

side-chains and the Mn(III) chelated within the porphine macrocycle (Fig. 2). This interaction is therefore insensitive to the rise of ionic strength caused by NaCl. Moreover, this specific interaction seems to be rather strong and therefore prevents imidazole protonation (and concomitant MnTSPP release) unless pH drops below 3 (not shown). On the other hand, the interaction between APS side-chains and MnTSPP would be ionic in nature (APS amino groups and MnTSPP sulfonato moieties should be involved), which explains its lability.

The changes of the support from the commercial SG to IPS and to IPS/MnTSPP adduct could be checked by inspection of the IR spectra (Fig. 4): the reaction of 3-(1-imidazolyl)propylcarbamoyl-3′-aminopropyl-triethoxysilane with silica led to decrease of –OH band at 3500 cm^{-1}, and two new bands appeared at 1450–1550 and 700 cm^{-1}, too. Further differences were also noted after metalloporphine complexation: in particular the bands at 1250 and 3750 cm^{-1}.

It is worth noting that the amount of bound MnTSPP (about 45 μmol/g under saturating conditions) is by far lower than the imidazolyl moieties (290 μmol/g). This finding could be explained by the above observation on SG structure: the majority of the imidazolyl moieties, although bound at the ends of flexible chains, would be unable – because of sterical hindrance – to properly interact with manganese ions that are firmly complexed within the rigid and bulky tetraphenylporphine structure.

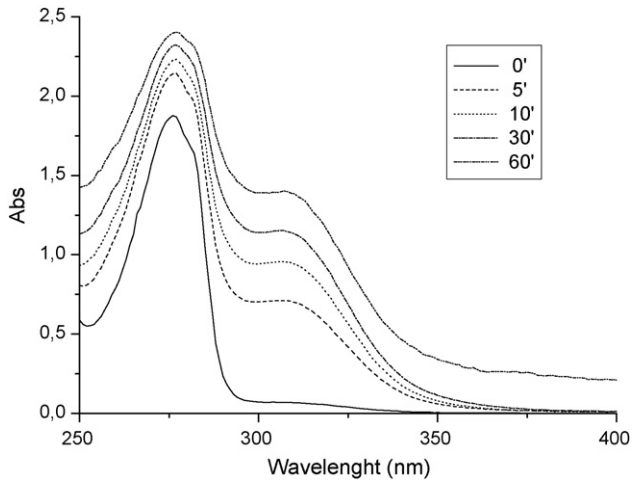


Fig. 5. Spectral changes of VA oxidized by H_2O_2 in the presence of the IPS/MnTSPP adduct.

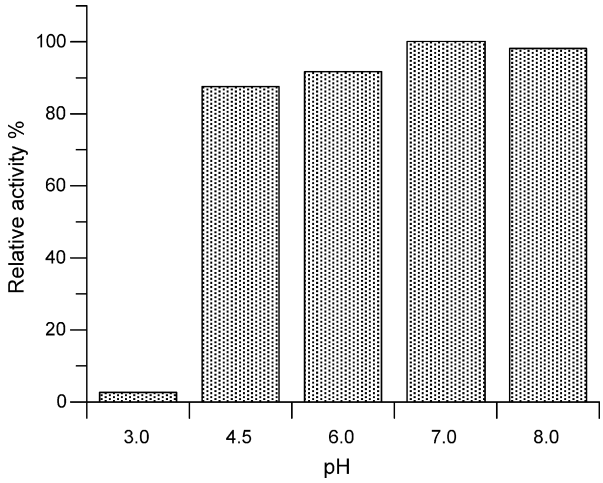


Fig. 6. Catalytic dependence on pH for the IPS/MnTSPP adduct.

3.2. Catalytic activity of IPS/MnTSPP adduct

Whereas SG and APS were almost unable to load MnTSPP, IPS support bound a noticeable amount of metalloporphine, as revealed by the blackish-brown color of the adduct. Accordingly, only this preparation could catalyze the oxidation of veratryl alcohol at the expenses of hydrogen peroxide at a significant rate (3.2 μmol veratraldehyde released per minute under the experimental conditions described in Section 2.4). Consequently, further characterization was mainly focused on the IPS/MnTSPP adduct.

3,4-Dimethoxybenzyl alcohol (veratryl alcohol, VA) is commonly used as a convenient substrate to assess the LiP activity [31–34]. In fact, preparation of pure lignin samples is not easy, and the physicochemical properties of the obtained products widely vary depending on both the chosen plant sources and the purification protocols; therefore the results are hardly reproducible. So, various model compounds have been proposed to carry out photometric LiP assays [34], and chosen to avoid interference by other enzymes that often come with LiP, such as peroxidase(s) and laccase. Among these compounds, VA is inexpensive and enough water-soluble to obtain aqueous solutions, and thus it is suitable for photometric measurements. In fact, the compound is oxidized by LiP to form the corresponding aldehyde which can be detected by virtue of its adsorption at λ_{max} of 310 nm. VA simply behaves as a nonsubstrate for both peroxidase and laccase, although being oxidized – at the expenses of molecular oxygen and with concomitant H_2O_2 release – by another fungal enzyme, veratryl alcohol oxidase (VAO, E.C. 1.1.3.7) [35]. In the present work, we have chosen VA also because its adsorption by the adduct – as well as that one of the corresponding aldehyde – is negligible (not shown). Product formation could be checked by UV spectrophotometry (Fig. 5).

Among the wide variety of oxidants proposed for use with metalloporphine catalysts [1,9,36,37], hydrogen peroxide has been chosen in the present study for various reasons: (i) the substance is easily available in large amounts at a relatively low price, and is suitable for safe transport and stocking; (ii) it is completely miscible with water thus avoiding the need of using any organic solvent; (iii) the only degradation products are water and molecular oxygen, which are harmless and obviously do not imply any recovery process of the exhausted oxidant. In conclusion H_2O_2 is the oxidant of choice for catalytic oxidative processing of wastewaters, and was the sole oxidant used throughout this study.

Addition of more hydrogen peroxide when veratraldehyde production ceased, produced no effects on the absorption spectra, thus showing that under the tested conditions no further oxidation of the aldehyde took place, and also suggesting that VA was almost totally consumed. The same inertness of the compound was seen when veratraldehyde was directly subjected to H_2O_2 action in the presence of the catalyst: the former could be regarded as a dead end product of VA oxidation, as confirmed also by the failure of detecting veratric acid by GC–MS (the expected oxidation product of veratraldehyde) as a result of the catalytic oxidation of both VA and veratraldehyde. On the contrary, VA addition to the reaction mixture where the substrate had been apparently exhausted, caused a significant rise of the aldehyde peak, therefore indicating that the aromatic alcohol had been almost entirely consumed whereas an excess of hydrogen peroxide was still present (not shown).

The catalytic activity depended on pH of reaction medium, being the optimum centered at pH 7 (Fig. 6).

A Michaelis–Menten-like kinetics was found for both hydrogen peroxide consumption and veratraldehyde formation (Table 1), showing that the catalyst could be saturated by both H_2O_2 and VA.

The catalyst was suitable for repeated use: catalytic activity remained over 90% of the starting one for the first three cycles, but it quickly decreased below 20% after eight cycles. Results are summarized in Table 2. This activity drop is concomitant with a color fading of the adduct, and is perhaps depending on an oxidative degradation of the porphine ring due to a prolonged action of relatively concentrate hydrogen peroxide.

As concerns the reaction mechanism, it was observed that the amount of aldehyde production is far to be stoichiomet-

Table 1
Kinetic parameters of the IPS/MnTSPP adduct in the presence of the substrates, H_2O_2 and VA

Substrate	Kinetic parameter	Value
VA	K_M	5.5 ± 0.9 mM
VA	k_{cat}	18.6 ± 0.9 min^{-1}
H_2O_2	K_M	10.3 ± 2.1 mM
H_2O_2	k_{cat}	16.5 ± 1.4 min^{-1}

The assay mixture contained, in a final volume of 2 mL, 15 mg of catalyst, 8.8 mM hydrogen peroxide, 1.25 mM VA and 25 mM potassium phosphate buffer pH 7. Absorbance increase at 310 nm was then read after 30 min of stirring reaction ($n = 3$).

Table 2
Catalytic activity of the IPS/MnTSPP adduct upon multicyclic use in the presence of 15 mg of catalyst, 8.8 mM hydrogen peroxide, 1.25 mM VA and 25 mM potassium phosphate buffer pH 7 (final volume 2 mL)

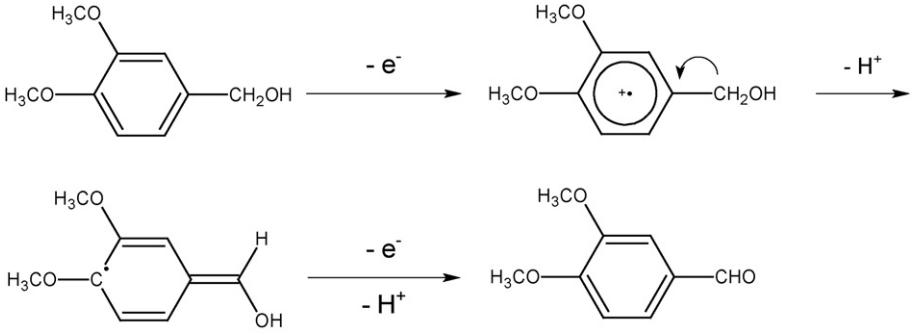
Cycle number	Catalytic activity (%)
1	100
2	97.5
3	92.5
4	88.3
5	80.1

After 30 min of stirring reaction, absorbance increase at 310 nm was detected. Between cycles, catalyst was regenerated through washings with H_2O and 2-propanol.

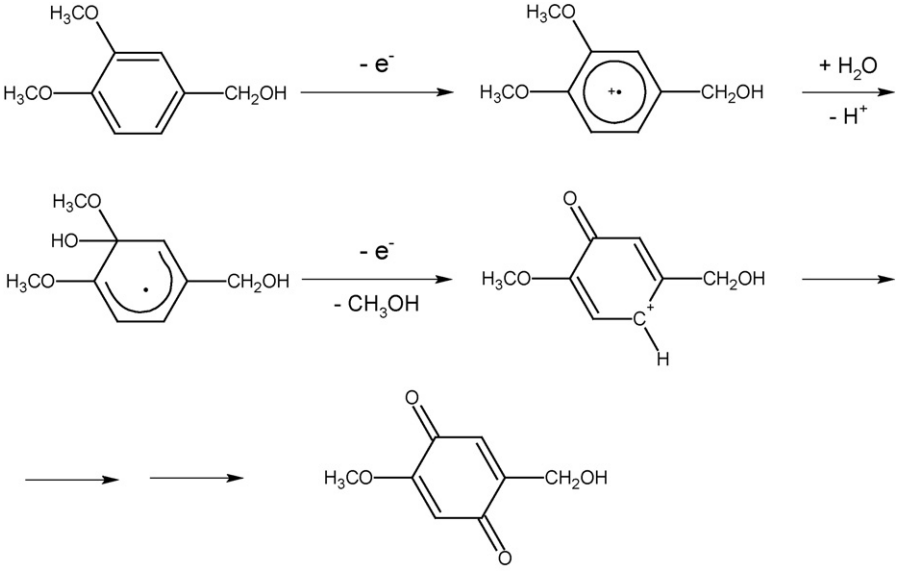
ric: after 2 h of reaction, the absorption peak at $\lambda = 310$ nm reached a maximum which corresponds to a conversion of about 17%, indicating that the reaction did not proceed further.

This finding was confirmed by GC–MS analysis: a conversion of 87.9% was obtained after 2 h, whereas veratraldehyde concentration was only 12.9% of initial VA concentration. No other products were detected by this technique. Therefore, oxidation of VA under the described conditions must go to other products, undetectable by GC–MS, but affecting the absorbance at 310 nm, which explains the observed discrepancy of conversion to veratraldehyde between UV and GC–MS data.

A discussion about the nature of the high valent (most probably oxoferryl Fe(IV)=O) heme intermediate [3,38,39] arising from the action of hydrogen peroxide on ferriheme – and by analogy, on Mn(III)porphines and porphyrins – is beyond the scope of this article. However, the attitude of Mn to exist in the Mn(V) state has been underlined by Powell et al. [36],



Scheme 2. Putative reaction pathway from veratryl alcohol to veratraldehyde.



Scheme 3. Putative reaction pathway from veratryl alcohol to 2-hydroxymethyl-5-methoxy-1,4-benzoquinone.

and therefore a Mn(V)(=O)TSPP intermediate could well be the first product arising by hydrogen peroxide action. Much work has been spent to the identification of reaction products arising by LiP action on methoxybenzenes and among these on veratryl alcohol [33,40,41]. A general agreement nowadays exists on the idea that the first product of LiP-catalyzed oxidation of methoxybenzenes and related compounds, of course including lignin and congeners and derivatives, is an aromatic radical cation, which could evolve in different manners, depending on its chemical nature and on the experimental conditions. In particular, veratraldehyde is the main product in the case of LiP catalysis (Scheme 2), where deprotonation and rearrangement of the cation radical lead to veratraldehyde. A very different pathway could be observed when model metalloporphines have been used [39]. In particular, work with H_2O_2 and electron-deficient Fe(III)-porphines produced high yields of 2-hydroxymethyl-5-methoxy-1,4-benzoquinone (Scheme 3), whose formation is not surprising when taking into account that the catalytic center is freely accessible by water molecules. Therefore, hydration of the intermediate cation radical prevails over deprotonation. By analogy, this could explain why, also in the case of MnTSPP, only a minor fraction of VA was converted to the corresponding aldehyde even if VA was almost totally consumed. The same quinone could well be the prominent product of the IPS/MnTSPP catalyst; unfortunately it anyway escaped the GC–MS analysis adopted along the present study, perhaps being further oxidized to even more hydrophilic, polar products such as dicarboxylic acids. Or maybe oligomerized or polymerized products arose from VA.

On the contrary, a significant difference was found between the above-mentioned Fe(III)-porphines and MnTSPP used here: the former cleave veratraldehyde to muconic dimethylesters [39] while the latter showed no action towards the aldehyde.

4. Conclusions

The IPS/MnTSPP adduct appears to be a very promising heterogeneous catalyst, that could be well suitable for the oxidative degradation – by means of hydrogen peroxide – of water-soluble lignin derivatives such as those coming from pulp and paper plants. The presented data suggest a deep oxidative action which is a favourable prerequisite for a further mineralization. Preliminary studies (Sanjust, 2007, unpublished) have shown that other aromatic compounds, such as anthraquinone derivatives, and alkaline extracts of wood, that are well different from VA but even more environmentally relevant, are oxidized by H_2O_2 in the presence of the described catalyst. These findings will conceivably broaden the application fields of the catalyst, such as treatment of various industrial wastewaters.

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