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RECYCLED PAPER PRODUCTS BLEACHING USING Fe-TALM CATALYST

The increase of brown fibres from wood and packaging products in recycled paper causes difficulties in paper recycling for newsprint production. The major reason is the dark colour of these fibres that cannot be removed by the actual bleaching methods. In this paper, the use of an iron catalyst, called Fe-TALM, was investigated with the goal of a possible boost in bleaching.

The challenge of recycled paper bleaching

Paper & pulp industry is one of the main manufacturing activities in the world, with global revenue of about 564 billion US$ [1]. The worldwide newsprint production is 6% of all paper products (around 20-25 million tons). Newsprint is the category of the paper product having the highest percentage of recycled paper (68%, approximately 16-17 million tons) [2, 3]. The Confederation of European Paper Industries (CEPI) reported that 5 million tons of recycled paper on a total amount of 49 million tons of recycled paper (≈11%) is used in the production of newsprint in Europe [4].
The recycled paper, mainly composed of wood fibres, must reach a certain brightness (55% of ISO brightness, [5]) to comply with the specifications of the market [6]. The procedure to make the recycled paper suitable for papermaking consists of four processes: pulping (process that breaks the structure of paper products and liberates the fibres), deinking (process to remove contaminants such as ink), bleaching (method used to destroy the chromophores and increase the brightness) and papermaking [7].
In almost the totality of the recycling paper mills, the bleaching process consists of one step using hydrogen peroxide in alkali conditions. The primary source of chromophores is lignin, an aromat-

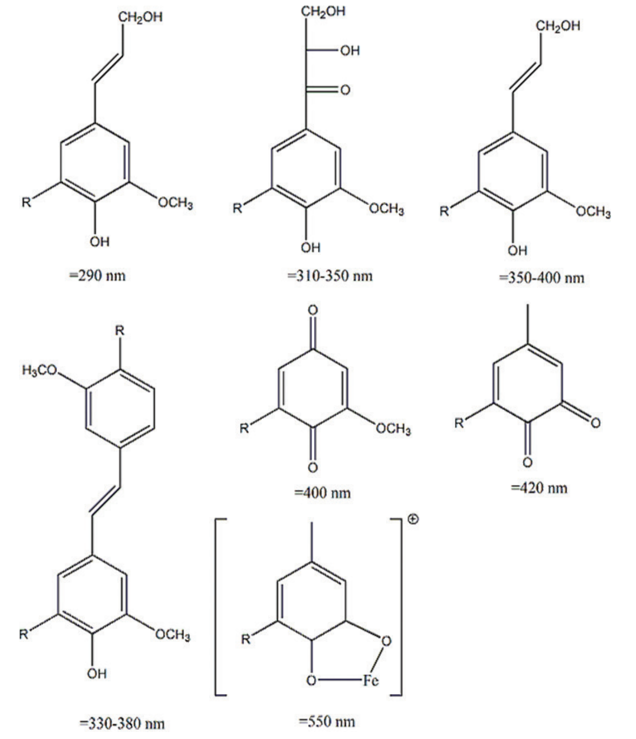


Fig. 1 - Examples of chromophores and their wavelengths in free form (R=H) or part of the lignin [9]

ic-biopolymer present in the fibres [8]. The presence of these chromophores in lignin is partially caused by metal complexes but mainly by conjugated groups. Moreover, lignin-derived chromophores can also be present in free form, linked with lignin only by hydrogen bonds and van der Waals forces (Fig. 1) [9].

In Fig. 2 an example of the reaction between the chromophore structure and hydrogen peroxide is reported. The conjugated groups present in the lignin are oxidized by the bleaching agent, forming sodium carboxylates.

The problem related to the efficient bleaching of the recycled paper has its origin in the heterogeneity of recycled paper [7]. Brown fibres cause difficulties due to their dark colour. If their relative amount in the recycled paper is too high, the target brightness cannot be reached using the actual bleaching technologies.

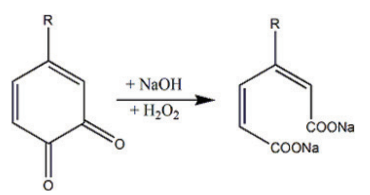


Fig. 2 - Example of the reaction between hydrogen peroxide and chromophore in free form (R=H) or part of the lignin [8]

Other chemicals can be applied for bleaching, for example, sodium dithionite, oxygen, ozone and peracetic acid [8]. Sodium dithionite has a drawback called "brightness reversion". This is by the action of air, light and heat during the process, resulting in a final paper product that shows a reduction of brightness over time [8]. Oxygen, ozone and peracetic acid are strong oxidizing agents that can destroy the lignin (process called delignification). However, they also cause the degradation of the cellulose present in the wood fibres, resulting in a mass loss [8].

It would be highly interesting to develop a process that efficiently removes the lignin while preserving the cellulose, thus allowing the production of recycled paper suitable for newspapers, while using a large quantity of brown fibres.

The Fe-TALM opportunity

The application of catalysts and activators for lignin removal was studied in paper chemistry to avoid or, at least, to reduce the use of bleaching agents that increase the mass loss during the bleaching process by degrading cellulose [10].

In literature, alternative catalysts and activators were studied to improve the bleaching process [10]. The most studied activator is "tetra acetyl ethylene diamine" (TAED) which improves the bleaching by the *in-situ* generation of peracetic

Acronym	Meaning
TAED	Tetra acetyl ethylene diamine
Fe-TALM	Iron Tetra-Amido Macrocyclic Ligand
KN	Kappa Number
LiP	Lignin peroxidase
O	Oxygen treatment
OP	Combination of Oxygen and Hydrogen peroxide
Fe	Hydrogen peroxide in combination with Fe-TALM
PD	Fe stage without the use of Fe-TALM
PB	Hydrogen peroxide bleaching
W	Washing

Tab. 1 - Tipi di biomassa in funzione dell'origine e della diversità

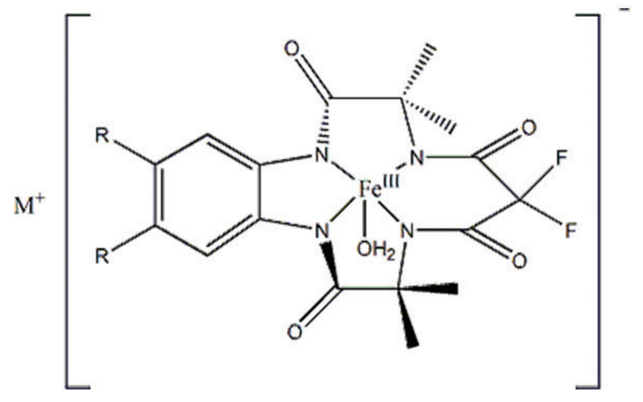
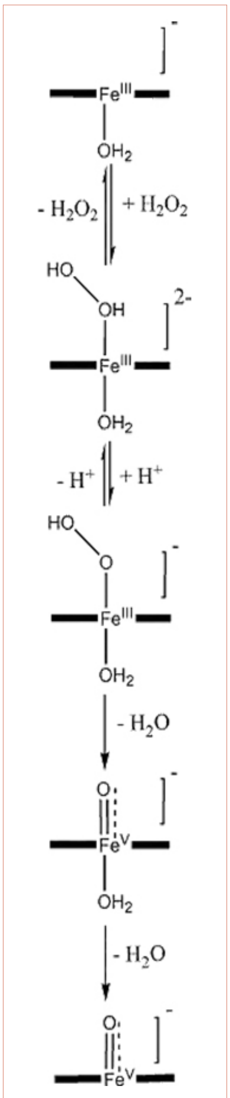


Fig. 3 - Example of a molecular structure of the complex Fe-TALM (Iron Tetra-Amido Macrocyclic Ligand) having R= H or Cl, M+= Li+ or Na+ as an example [11]



acid after reaction with hydrogen peroxide (a list of the acronyms used in this article is reported in Tab. 1). The rationale is that peracetic acid is a stronger bleaching agent than hydrogen peroxide. However, during the process, new activator must be added continuously because it is consumed. Polyoxometalates are also catalysts that have been extensively studied. These catalysts improve the reactivity of oxygen. In our work, the interest is in applying a catalyst able to improve the delignification power of hydrogen peroxide, the main bleaching chemical in paper recycling.

A group of homogeneous iron catalysts, called Fe-TALM (Iron Tetra-Amido Macrocyclic Ligand) (Fig. 3), was studied in the present research project. It is composed of one transition metal ion (iron) and a tetradentate ligand containing amide groups [11].

Fig. 4 - Example of proposed hydrogen peroxide activation mechanism using Fe-TALM [11]

This catalyst was developed to mimic the hydrogen peroxide activation of catalase-peroxidase enzymes [12]. The iron catalyst is known to react with hydrogen peroxide producing radicals (Fenton reaction, •OH). The presence of the ligands permits to form a more reactive oxygen species that is comparable to the one present in peroxidase enzymes. The proposed activation mechanism is shown in Fig. 4, where an iron(V)oxo intermediate is formed [11].

This class of coordination compounds has been demonstrated to be efficient and selective in the field of pollution reduction. For example, their ability to degrade dyes permits to apply Fe-TALM in wastewater decolouration [13, 14]. Fe-TALMs were also studied in the wastewater treatment of water coming from the paper and pulp industry [15].

Fe-TALMs are also used as bleaching boosters of virgin wood pulp [16, 17]. The catalyst transforms hydrogen peroxide in a selective delignification agent, able to preserve the cellulose. An exact delignification reaction mechanism is not reported in the litera-

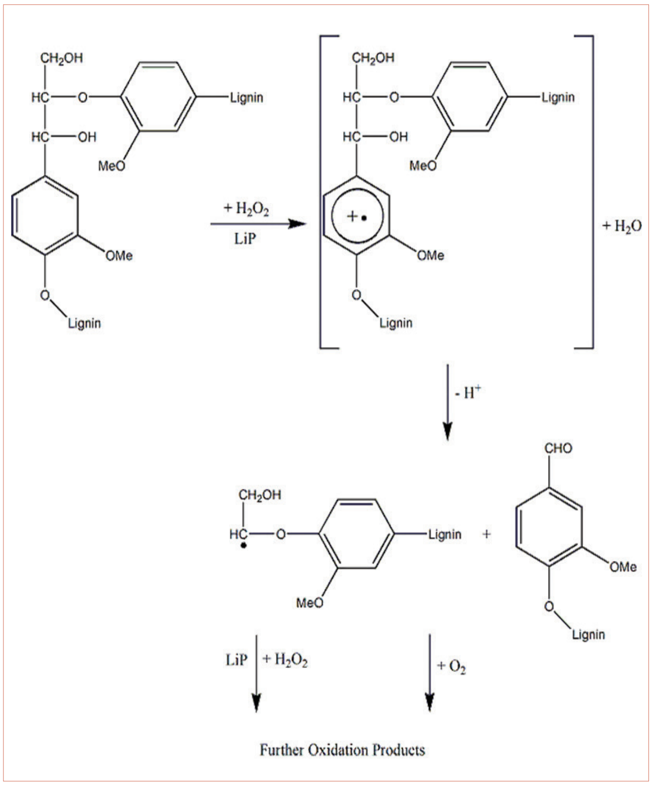


Fig. 5 - Peroxidase delignification mechanism (LiP = Lignin Peroxidase) [18]

ture yet. However, the similarity to the peroxidase enzymes leads to the following possible enzymatic lignin-degradation pathway [18] (Fig. 5).
In literature, the delignification of *Pinus radiata* wood pulp by using hydrogen peroxide in the presence of Fe-TALM (20 ppm) is described [17]. It was observed that the Kappa number (KN) (a parameter used to estimate the amount of lignin, ISO 302:2015 [19]) decreased from 22.5 to 7.3 and 13, respectively without and with catalyst. It means that the Fe-TALM removed a smaller amount of lignin. However, the viscosity (a parameter used to evaluate the cellulose degradation, ISO 5351:2010 [20]) decreased from 37.4 mPa·s to 24 and 32.8 mPa·s respectively without and with catalyst. The presence of Fe-TALM preserves the cellulose degradation reaching similar values of lignin removal. However, brightness data are not reported in that study.
The present article describes the laboratory scale study of Fe-TALM as a hydrogen peroxide boosting agent for the bleaching of deinked recycled paper with a high amount of brown fibres (50%), having a KN equal to 58 and a starting ISO brightness of 23%. The scientific purpose is to evaluate the effect of the iron catalyst to realize more efficient bleaching. A bleaching sequence composed of two or three stages was developed.

Stage/ Sequence nr.	1	2	3	4	5	6	7	8	9
Pre-treatment	/	/	/	O(W)	O(W)	O(W)	OP(W)	OP(W)	OP(W)
Fe-TALM delignification	/	P_D(W)	Fe(W)	/	P_D(W)	Fe(W)	/	P_D(W)	Fe(W)
Peroxide bleaching	P_B(W)	P_B(W)	P_B(W)	P_B(W)	P_B(W)	P_B(W)	P_B(W)	P_B(W)	P_B(W)

Oxygen (O): 3% K (fibre consistency), 5.42% NaOH, 0.76% $MgSO_4$, 10 bar O_2, 100 °C, 1 h; Oxygen with Hydrogen peroxide (OP): (O step) + 10%H_2O_2; Fe-TALM (Fe): 5% K, 90 °C, pH=10.6 buffer: Na_2CO_3/HCl, H_2O_2 5.5%, 60 min, Fe-TALM 20 ppm on dry fibres; Fe step without catalyst (PD): 5% K, 90 °C, pH=10.6 buffer: Na_2CO_3/HCl, H_2O_2 5.5%, 60 min; Hydrogen peroxide (PB): 2% K, pH=10.5, 10% H_2O_2, 80 °C, 90 min.; Washing (W) after each step [21]

Tab. 2 - Bleaching sequences

The effects of Fe-TALM on recycled paper bleaching

Different bleaching sequences were explored, composed of the following steps, all acronyms are reported in Tab. 1:

1. an optional pre-treatment to reduce the amount of lignin (KN) before the use of Fe-TALM catalyst. This stage was used to observe the selectivity of the catalyst stage, in the presence of different quantities of lignin in the sample. Two different pre-treatments were explored. In the first one, only oxygen (O) was applied. In the second one, oxygen in combination with hydrogen peroxide (OP) was used;
2. a selective delignification step using Fe-TALM (Fe) in combination with hydrogen peroxide. The selectivity of the catalyst was evaluated comparing the Fe-TALM stage with a blank reaction (PD) performed at the same reaction conditions but without the use of the catalyst;
3. a final hydrogen peroxide bleaching (P_B).

The bleaching sequences studied in this work are reported schematically in Tab. 2.
Generally, 2% of hydrogen peroxide (w/w versus dry fibres) is used at an industrial scale, working at

Sequence nr.	Step	ISO Brightness (%)	ISO STD	KN
Starting material	/	23	1	58
1	P_B(W)	29	1	52
2	P_D(W) P_B(W)	25 30	2 1	46 44
3	Fe(W) P_B(W)	24 30	1 1	42 41
4	O(W) P_B(W)	32 46	1 1	40 38
5	O(W) P_D(W) P_B(W)	32 34 48	1 2 1	40 34 32
6	O(W) Fe(W) P_B(W)	32 35 47	1 1 1	40 29 28
7	OP(W) P_B(W)	40 50	1 1	30 28
8	OP(W) P_D(W) P_B(W)	40 41 51	1 1 1	30 27 27
9	OP(W) Fe(W) P_B(W)	40 41 57	1 1 1	30 22 21

Tab. 3 - ISO Brightness and Kappa number values obtained during the bleaching sequences

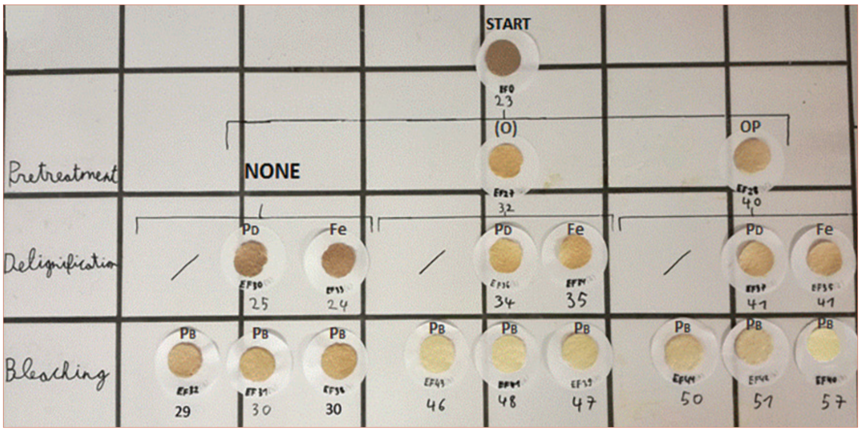


Fig. 6 - Recycled paper samples during the bleaching sequences

a fibre consistency of 30%. In this work, a higher amount of hydrogen peroxide (10% on dry fibres) was used in the last bleaching step. This amount was used to compensate for the lower consistency (2%) used at the laboratory scale. The major reason to study the system at a consistency of 2% is that higher values did not permit a homogeneous stirring and, consequently, homogeneous values of temperature and pH.

The brightness and kappa number values after each step were measured and reported in Tab. 3. The samples taken during the analysis are shown in Fig. 6. The efficiency of the catalyst is evident after an OP step as the KN is reduced by almost 50%.

Sequence 9 permits to reach a brightness within the specification for newspaper production (ISO 57). If the catalyst is not used, the final brightness is 51 (sequence 8). When the selective delignification step is not used (sequence 7), an ISO brightness of only 50 was achieved.

There was no clear difference between Fe(W) and P_D(W) in terms of brightness (sequences 2, 3, 5 and 6) when oxygen was used as pre-treatment. The same result was obtained when the pre-treatment of the starting material was absent. Moreover, there is no palpable difference when the selective delignification step is missing (sequences 1 and 4).

If the KN is too high, the selective delignification step is not evident. It means that the Fe-TALM is useful when kappa number is close to or less than 30. To proof this hypothesis, a study on the selectivity of the delignification step was done, and results are reported in Tab. 3.

The selectivity of the Fe-TALM process was further evaluated by measuring the mass loss and the KN change during the selective delignification step. The results are reported in Tab. 4. The amount of lignin removed during the reaction was calculated following the formula [22]:

%Lignin=0.15xΔKN

Afterwards, the removed lignin amount was divided by the mass loss to estimate the selectivity of the catalyst to lignin in comparison to its action towards other components such as cellulose (expressed as%).

The selectivity of the catalyst to degrade the lignin in comparison to cellulose increases from 52% (no pre-treatment, KN=58) to 92% (OP pre-treatment, KN=30). Instead, the selectivity of the P_D reaction decreases from 51% (no pre-treatment) to 20% (OP pre-treatment). KN influences the selectivity of the catalyst; as a matter of fact, the selectivity increases when KN decreases.

Sequence Nr.	Mass loss (%)	Starting KN	ΔKN	Lignin removed* (%)	Selectivity* (%)
2. (P_D)(W).(P_B)(W)	3.5	58	12	1.8	51
3. (Fe)(W).(P_B)(W)	4.6	58	16	2.4	52
5. (O)(W)(P_D).(W)(P_B)(W)	2.9	40	6	0.9	31
6. (O)(W)(Fe)(W)(P_B)(W)	2.2	40	11	1.65	75
8. (OP)(W)(P_D)(W)(P_B)(W)	2.3	30	3	0.45	20
9. (OP)(W)(Fe)(W)(P_B)(W)	1.3	30	8	1.2	92

Tab. 4 - Fe-TALM selectivity at the variation of the starting KN

Conclusions

Fe-TALM seems to be an attractive delignification agent for brown fibres because it improves the final brightness of the recycled paper and reduces the cellulose degradation, a drawback typically present

during the most known delignification process. However, pre-steps to reduce kappa number are necessary.
The proposed new method is promising but requires additional intensive studies to evaluate its applicability to the bleaching of recycled paper at an industrial scale.
The study of recovery, recycling and catalytical stability of the Fe-TALM is also crucial.
If pre-treatment turns out to be too expensive, this new method would be limited to starting materials having a low kappa number.
In conclusion, this work is a starting point for future research in the field of recycled paper bleaching, where major studies are still to be done.

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Sbiancamento di prodotti in carta riciclata utilizzando un catalizzatore Fe-TALM

L'aumento delle fibre marroni, provenienti dai prodotti di imballaggio e legno, nei rifiuti di carta sta causando difficoltà nel riciclo per la produzione di giornali a causa del loro colore scuro che non può essere rimosso dagli attuali metodi di sbiancamento. In questo articolo, è stata sviluppata una sequenza di sbiancamento con l'impiego di un catalizzatore di ferro, chiamato Fe-TALM, per valutarne l'effetto sulla lucentezza.