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Efficient oxidative modification of polysaccharides in water using H_2O_2 activated by iron sulfophthalocyanine

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ABSTRACT

Selective and environmentally friendly oxidation of polysaccharides by hydrogen peroxide in the presence of iron tetrasulfophthalocyanine (FePcS) catalyst was studied in aqueous media. Oxidation under mild conditions led to the cleavage of the C–C bond of vicinal diols of glycoside units as a result of carbonyl and carboxyl formation. Optimized experimental conditions allowed oxidation of hydroxyethylcellulose (HEC), sodium carboxymethylcellulose (NaCMC), guar gum (GG), and inulin to the extent of 19, 30, 53, 23 carbonyl functions per 100 anhydroglucose units, respectively. Possible explanation for this relatively modest conversion is discussed. Over-oxidation phenomena appear to play an important role during the oxidation process.

1. Introduction

Natural polysaccharides with different physical properties constitute a large source of materials for increasing number of applications in the future. Their development opens a large field of applications taking advantage of their specific properties, particularly in renewability and biodegradability. Polysaccharides are especially important in many industrial domains thus acting as texture agents in foods, cosmetics and paints (Abdel-Halim, Eman, & El-Rafie, 2008; Fishman, Chau, Yadav, & Hotohkiss, 2009; Togrul & Arslan, 2003). However, the use of natural polysaccharides suffers from many drawbacks because of their thermosensitivity or uneasy water solubilization. To circumvent these limitations and to obtain specific properties, natural polysaccharides can be chemically, physically or enzymatically modified.

Derivatization of such polysaccharides leads to a variety of specialty polymers. Oxidative transformation of polysaccharides provides industrially valuable products for different applications aimed at replacing materials derived from fossil feedstock. Traditional oxidation generally involves the use of stoichiometric amounts of inorganic oxidants such as NaOCl (Floor, Kieboom, & Van Bekkum, 1989; Kuakpetoon & Wang, 2001; Nieuwenhuizen, Kieboom, & Van Bekkum, 1985; Teleman, Kruus, Ammälahti, Buchert, & Nurmi, 1999) and N_2O_4 (Kochkar, Morawietz, & Hölderich, 2001) to introduce carboxyl groups or $NaIO_4$ (Varma, Kokane, Pathak, & Pradhan, 1997) to obtain C–C bond cleavage and aldehyde functions. However, these reagents are rather expensive and/or toxic and produce a large amount of waste such as chlorinated products or nitrite and nitrate salts. Several catalytic approaches have been proposed to improve polysaccharide oxidation. Thus 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was applied in combination with NaOCl/NaBr (Bragd, Besemer, & Van Bekkum, 2002; De Nooy, Besemer, & Van Bekkum, 1995) or peroxide reagents to selectivity oxidize primary hydroxyl groups in polysaccharides. However, this method does not solve the problems associated with the use of NaOCl. Hence, from both economic and environmental points of view, alternative catalytic oxidation processes with inexpensive and environmentally friendly oxidants are desirable. Owing to its low environmental impact, hydrogen peroxide is a very attractive oxidant for industrial applications since water is the only by product.

The present work reports a study of the synthesis of oxidized products from different polysaccharides: hydroxyethylcellulose (HEC), carboxymethylcellulose sodium salt (NaCMC), guar gum (GG) and inulin. Herein we propose to use a water-soluble catalyst in the clean system iron tetrasulfophthalocyanine (FePcS)/H_2O_2/H_2O, to achieve the polymer modification. This catalyst has been

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rarely used with H_2O_2 and only once for the oxidation of starch by a dry method (Sorokin, Kachkarova-Sorokina, Donzé, Pinel, & Gallezot, 2004).

Indeed, this modification by selective oxidation of glycoside units leads to carboxyl and carbonyl functions along the polymer. We have also optimized this oxidation system and studied structural modification induced by this reaction in the carbohydrate polymer. This methodology allows for example further alkylation by reductive amination (Fredon et al., 2002).

2. Experimental

2.1. Materials

Monosodium salt of 4-sulfophthalic acid, ammonium chloride, urea, ammonium molybdate, iron sulfate heptahydrate and 35% hydrogen peroxide 35% were purchased from Acros. HEC (Cellosize QP 300), NaCMC, Guar and Inulin (Inutec N25) were purchased, respectively, from Dow Chemicals, Fluka, Sigma and Orafti. These polysaccharides were stored at room temperature, HEC, NaCMC and inulin were used without further purification.

UV–vis spectra were recorded on a Perkin Elmer Lambda 25 spectrophotometer. ^{1}H NMR spectra were realized on a Brüker DPX-400 spectrometer, IR spectra Perkin Elmer 310 FT-IR, titration by TitraLab® TIM 845.

2.2. Methods

2.2.1. Preparation of iron tetrasulfophthalocyanine FePcS

The sodium salt of iron tetrasulfophthalocyanine was prepared according to a modified method developed by Weber and Bush (1965). Monosodium salt of 4-sulfophthalic acid (6.4 mmol), ammonium chloride (3.5 mmol), urea (38.6 mmol), ammonium molybdate (0.02 mmol), and iron sulfate heptahydrate (1.2 mmol) were ground together in a mortar until a homogenous powder is obtained. Then the mixture was heated to 280 °C during 2 h (yield 82%). The solid cake was characterized by UV–vis (water), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 328 (55 700), 630 (65 200).

2.2.2. GG treatment

GG was purified by dissolution in water (1 g/L) at room temperature followed by filtration under vacuum. The solution was concentrated to 3 g/L by evaporation at 40 °C under reduced pressure and then the polymer was precipitate by ethanol (50% v/v) (Frollini, Reed, Milas, & Rinaudo, 1995).

2.2.3. HEC oxidation by the dry method

An aqueous solution (1 mL) containing 2 μmol of FePcS catalyst was mixed with HEC (3.50 g, 13 mmol AGU) and 0.25 mL of 35% H_2O_2 (2.9 mmol) were added. Resulting mixture was mixed and allowed to react at 60 °C during 14 h. The oxidized colorless product was solubilized in water, precipitated in acetone and dried to give 2.50 g of product (71% yields). IR (KBr): 3439 cm^{-1} (υ O–H); 2 870 cm^{-1} (υ C_{sp3}–H); 1734; 1620; 1456; 1354; 1064; 891 cm^{-1}.

2.2.4. HEC oxidation in aqueous media

Catalyst (10 μmol, 13 mg) was mixed with polysaccharide (13 mmol AGU, 3.5 g) in 25 mL of water until complete solubilization, and then an aqueous solution containing 1.1 mL of 35% H_2O_2 was added. Resulting mixture was stirred and allowed to react at 60 °C during 18 h. After complete consumption determined by iodometric method, the colorless product was precipitated in acetone and dried. IR (KBr): 3439 cm^{-1} (υ O–H); 2870 cm^{-1} (υ C_{sp3}–H); 1734; 1620; 1456; 1354; 1064; 891 cm^{-1}.

2.2.5. Determination of carbonyl and carboxyl degrees of substitution

Carboxylic degrees of substitution (DS) were determined by a titration with sodium hydroxide. Carbonyl DS was performed by a measure of aldehyde mole number using a method adapted from Pommerering, Rein, Bertram, and Müller, 1992 consisting in an acid–base titration after a Cannizarro reaction.

2.2.6. HPLC analyses

HPLC was performed on a Dionex P680 HPLC system consisting of a pump and the Chromeleon© software. The detection system consisted of a refractive index detector (RI 101 Shodex) at 35 °C. Separation was performed on 2xPL aquagel-OH MIXED 8 μm columns (300 × 7.5 mm). Injection volume of 2% solutions (w/v) in 30% methanol and 70% 0.2 M $NaNO_3$, 0.01 M NaH_2PO_4, pH 7 in ultra pure water and filtered on Minisart RC 4 0.2 μm, was 100 μL. The mobile phase was 70% 0.2 M $NaNO_3$, 0.01 M NaH_2PO_4, pH 7, 30% methanol at the flow rate 1.0 mL/min and the columns were operated at 25 °C.

2.2.7. Formaldehyde titration

Formaldehyde was quantified according to the Mimura, Kanebo, Nishigams, Fukui, and Kanno (1976) method. This spectrophotometric method consist in forming a purple triazin from a specific reaction between formaldehyde and AHTT (4-amino-3-hydrazino-5-mercapto-1,2,4-triazole). Absorbance of the resulting colored solution was measured at 550 nm, Calibration curves relating the absorbance at 550 nm to formaldehyde concentration was plotted and regression analysis of the results were computed.

2.2.8. Results and discussions

Several transition metal catalysts, including ruthenium (Bressan, Forti, Ghelfi, & Morvillo, 1993), manganese and iron (Parovuori, Hamunen, Forssell, Autio, & Poutanen, 1995) have been proposed to activate hydrogen peroxide. Especially, related metal sulfophthalocyanines (Fig. 1) have been successfully used in combination with H_2O_2 for oxidative degradation of chlorophenols (Sorokin & Meunier, 1996; Sorokin, Séris, & Meunier, 1995). Oxidation of simple alcohols and ketones using water-soluble iron tetrasulfophthalocyanine (FePcS) as catalyst in aqueous media has also been described by Alessandro, Liberatore, Tonucci, Morvillo, and Bressan (2001). Such oxidations lead to the formation of aldehydes, carboxylic acids and ketones. Recently, native potato starch has been oxidized by a dry method using FePcS/H_2O_2, but this dry system provides only small amounts of aldehydes and carboxylic acids (Kachkarova-Sorokina, Gallezot, & Sorokin, 2004). Indeed, resulting degrees of substitution in aldehyde (DS_{CHO}), and carboxyl (DS_{COOH}) expressed as the number of carbonyl and carboxyl groups per 100 anhydroglucose units (AGU) were, respectively, DS_{CHO} = 8.0% and DS_{COOH} = 4.0%, whereas the maximum DS in starch is DS_{CHOmax} = 200%.

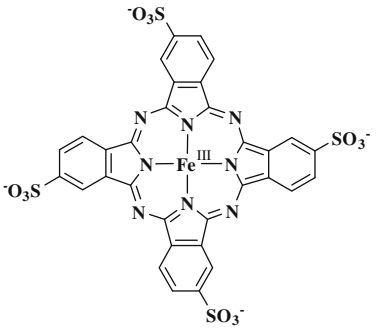

Fig. 1. Iron tetrasulfophthalocyanine.

In connection with our research program on parietal polysaccharide valorization, the aim of this work is the oxidation of four water-soluble polysaccharides using the green system FePcS/H_2O_2 in aqueous media. Firstly, we decided to investigate a thorough study on the oxidation of a well-known and widely used water-soluble polymer; hydroxyethylcellulose (HEC). This polymer is derived from cellulose by grafting ethylene oxide units onto the sugar backbone. Then, the catalytic system FePcS/H_2O_2/H_2O was applied to the other polysaccharides (Fig. 2). The oxidation reaction occurs at the vicinal diols of the glycoside unit leading to a cleavage of the C–C bond giving carbonyl and carboxyl functions.

Polysaccharide oxidation easily leads to overoxidation and depolymerisation, consequently, a careful investigation of this reaction using the FePcS/H_2O_2/H_2O system was achieved, to form a maximum amount of carbonyl groups.

The modification of rheological properties of these polysaccharides can be improved for specific applications by the introduction of hydrophobic groups (Karam et al., 2008). Our aim herein is to modify these polymers in order to endow them with amphiphilic properties by grafting long alkyl chains on the polysaccharide backbone. This requires the formation of aldehydes functions on the glycosides units which could further react with fatty amines.

2.2.9. Study of HEC oxidation by the FePcS/H_2O_2/H_2O system as reference

Firstly, HEC oxidation was performed according to the Sorokin dry method for starch oxidation (Kachkarova-Sorokina et al., 2004). Thus, a small amount of aqueous solution of FePcS was mixed with HEC with 1.5×10^{-4} catalyst/substrate molar ratio. Then hydrogen peroxide solution with 1/4.5 oxidant/substrate molar ratio, was added to the impregnated solid under continuous mixing. Resulting degrees of substitution in carboxyl (DS_{COOH}) and carbonyl (DS_{CHO}) per 100 AGU were, respectively, DS_{COOH} = 2.6% and DS_{CHO} = 6.3%, with a molar yield of 71%. Considering these moderate values we decided to perform the reaction in aqueous media. Indeed, homogenous conditions should improve the yield of oxidized HEC. Furthermore hydrogen peroxide quantity has been increased to be introduced into stoichiometric amount, and FePcS amount was also increased to 2.3×10^{-3} catalyst/substrate molar ratio. In these conditions, HEC was firstly dissolved into 25 mL water, then catalyst and oxidant quantities were successively added. In this case, the oxidation reaction provided 4.0% carboxyl, and 10.7% carbonyl groups with the same molar yield as in the dry method. DS of oxidized HEC were slightly increased but remained to be optimized. Therefore, in order to determine optimized experimental conditions and to let us identify the most important factors we decided to investigate a Latin square design of experiments.

Table 1
Choice of parameters.

Factors	Modes		
	1	2	3
Temperature	40 °C	50 °C	60 °C
Reaction time	6 h	12 h	18 h
FePcS eq.	7.4×10^{-4}	2.2×10^{-3}	4.4×10^{-3}
H_2O_2 eq.	0.2	0.6	1

The variations of DS_{CHO}, DS_{COOH} and weight yields were studied as a function of factors like FePcS (7.4×10^{-4}–4×10^{-3} equivalents), H_2O_2 (0.2–3 equivalent per AGU) and reaction times (6–22 h). After this screening, we then defined, for an optimization study, a new experimental field where factors have the largest influence on DS_{CHO}. The choice of factors and their modes are given in Table 1. So, 3^4 (or 81) experiments should be done in order to explore the complete experimental field. In order to reduce the number of experiments, we built a Latin square design of experiments (Lochner & Matar, 1990). Hence, nine experiments are sufficient to determine optimized conditions and identify the influential factor modes. For all oxidized HEC, DS_{CHO} DS_{COOH} and weight yield have been measured.

The results have been analyzed according to Lochner and Matar (1990). Fig. 3 represents the average effect of the factors on weight yields, DS_{CHO} and DS_{COOH}. When analyzing this figure, the four factors considered seem to have a significant influence on DS_{CHO}. In the experimental field, weight yields do not seem to be linked to FePcS and H_2O_2 molar ratio. On the contrary, low temperatures and short reaction times increase considerably weight yields (90% at 40 °C and 6 h, against 60% at 60 °C and 18 h).

Bearing in mind that our aim herein is requiring the best value of DS_{CHO}, optimal conditions were related with higher temperatures, longer reaction times, and the higher H_2O_2 molar ratios. Moreover, DS_{COOH} did not seem to be influenced by any of these factors and did stay at a low value. Surprisingly, the lower catalyst amount was the factor leading to the higher DS_{CHO} value. Indeed, a decrease in FePcS eq. leads to an increased aldehyde formation (from 3% up 11% with, respectively, 4.4×10^{-3}–7.4×10^{-4} eq. FePcS). This tendency might arise from a degradation of hydrogen peroxide caused by FePcS. So, to be optimal the catalytic reaction can be also successfully carried out with a small HEC/FePcS molar ratio.

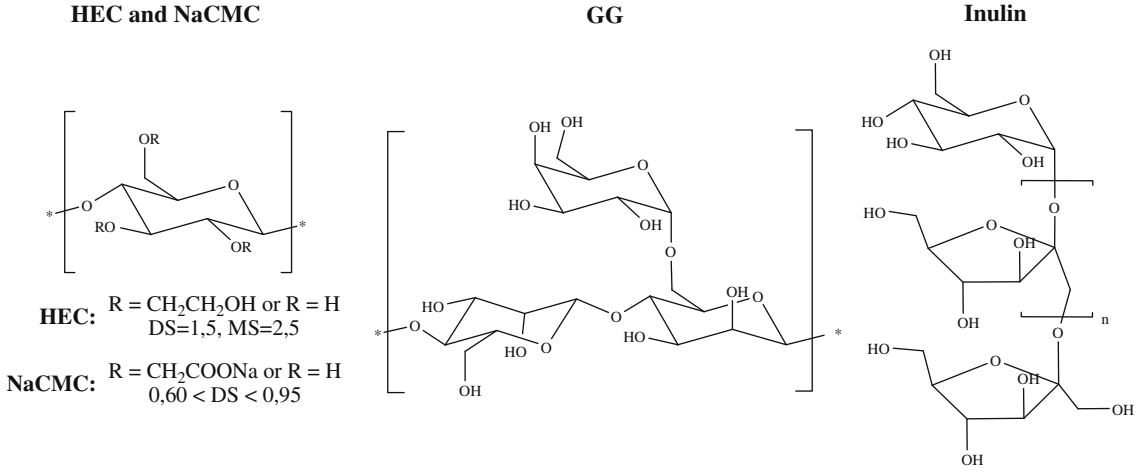

Fig. 2. Polysaccharides.

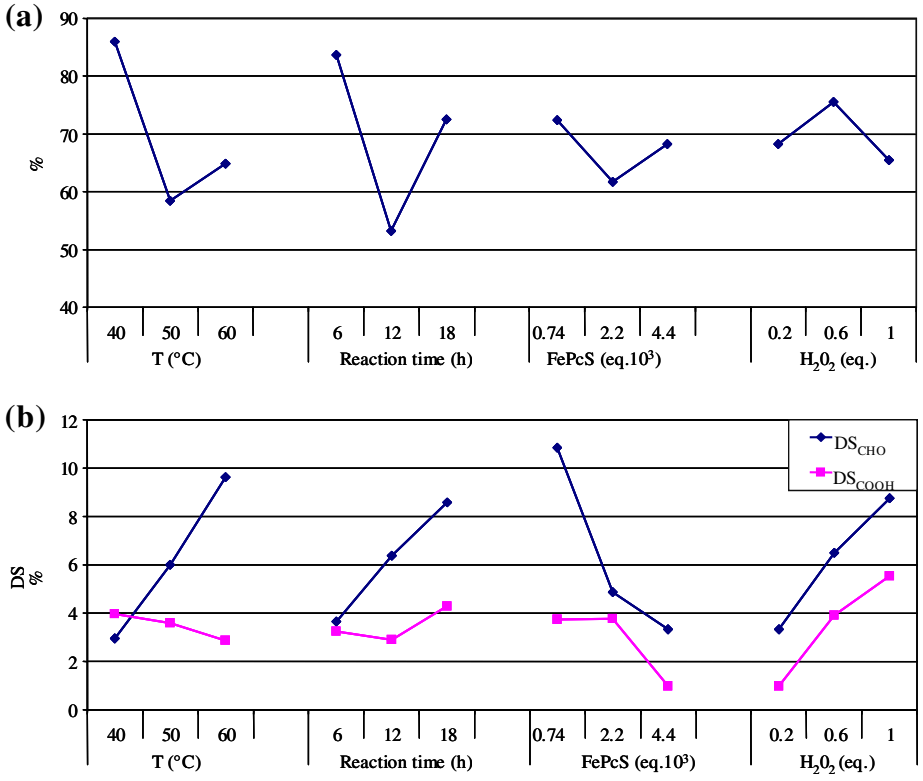

Fig. 3. Average effect of temperature, reaction time, HEC/FePcS and HEC/H_2O_2 molar ratios on: (a) weight yield, (b) DS_{CHO} and DS_{COOH}.

We investigated an experiment consisting in a combination of all the factors giving the maximal DS_{CHO} to validate our Latin square design of experiments (60 °C, 18 h, 7.4×10^{-4} eq. FePcS and 0.2 eq. H_2O_2). Resulting DS_{CHO} value should to be higher than any previous experiment. In our case, the reaction has been successfully optimized leading to 5% carboxyl and 19% carbonyl functions (4–10% previously observed).

2.3. NaCMC oxidation

Whereas FePcS/H_2O_2/H_2O catalytic oxidation system has been greatly improved on HEC model substrate, we decided to extend this process to NaCMC which is also a cellulose derivative. Like HEC, the NaCMC structure is based on the β-D-glucopyranose polymer of cellulose; some hydroxyls are substituted by carboxymethyl functions. The reaction occurs the same way as mentioned above with HEC; α-diols on carbons 2 and 3 of glucidic units are cleaved by the FePcS/H_2O_2 system leading to carbonyl and carboxyl functions.

Firstly, the reaction was performed at 60 °C in same experimental environment as HEC optimized oxidation reaction. Unfortunately, these conditions were not compatible with this polysaccharide. Indeed, weight yields obtained were modest (about 55%), and consumed H_2O_2 value was only 50%. Furthermore oxidized NaCMC precipitated as slime and was rather difficult to isolate. Consequently, some reactions conditions needed to be modified. We decided thus to decrease reaction temperature to favor better weight yields and oxidized products were precipitated in ethanol in place of acetone.

As we mentioned above, after 18 h reaction time only 50% of H_2O_2 was consumed so we decided to investigate a kinetic study of NaCMC oxidation. Fig. 4 shows the consumed H_2O_2, weight yield, DS_{CHO} and DS_{COOH} as a function of time.

Consumed H_2O_2 evolved linearly nearly to 90 h and reached 100%. At this time all oxidant was consumed but DS_{CHO} continued to increase yet slowly and the weight yield to decrease. Moreover, DS_{CHO} curve presents a sudden slope break well before the total disappearance of H_2O_2, (20 h were only necessary to DS_{CHO} to reach a plateau, and 90 h for consumed H_2O_2). It has to be noted that DS_{COOH} began to increase only after arrest of H_2O_2 consumption, but very slowly (maximum 3% AGU). When the oxidant has been entirely consumed, it could be possible that an intermediate has been formed, which then react with NaCMC to form carboxyls and carbonyls, but its kinetic being slower than H_2O_2 consumption.

Weight yields curve seem to be directly linked to carbonyl formation. Thus, a large decrease of weight yields has been observed in the first hours of reaction (50% in 24 h). In the same time, aldehydes curve inversely rise (up to 30% AGU). This observed drop in weight yields could be explained by an over-oxidation of the polysaccharide which could be responsible for the degradation of the polymer. These fragments which have a smaller degree of polymerization should not precipitate in ethanol; involving a decrease in weight yields. Hence, temperature reaction was not an increasing factor of weight yields. Taking into consideration that some hydroxyls of NaCMC are substituted, about 30% DS_{CHO} of oxidized NaCMC is a quite good oxidation rate. Furthermore, when reaction is stopped after 24 h, no carboxyl groups were yet formed. This fact is very important, especially when the aldehydic functions are to be used for subsequent reactions such as reductive amination.

2.4. GG oxidation

Having demonstrated that cellulose ethers could be successfully oxidized by FePcS/H_2O_2/H_2O catalytic system, we decided to extend this process to GG. This gum is a high molecular weight natural carbohydrate polymer consisting of a polymannan backbone with single galactose unit side chains.

As shown with NaCMC, HEC optimized oxidation process could not be exactly applied. Therefore, like NaCMC we investigate a kinetic study of the oxidation reaction of GG in FePcS/H_2O_2/H_2O catalytic system at 60 °C (Fig. 5). In this case oxidation occurs differently than with NaCMC reaction because carboxyls were formed the same time as carbonyls groups. It has been noted that oxidation reaction seems to be done after 30 h, DS_{CHO} reach then about 55%. As we expected, better oxidation DS are obtained. Indeed, in GG all glycoside units contain vicinal hydroxyl groups, so oxidation could be performed at each AGU contrary to HEC and NaCMC where some hydroxyls are substituted. Thus, the DS_{CHO} expected should be higher. An explanation of this observation could be due to the GG conformation in water (Wang & Somasundaran, 2007). The helical structure of GG is relatively compact, and prevents the accessibility of many OH groups to H_2O_2 oxidation. Consequently, this carbonyl degree of substitution seems to be the maximum.

2.5. Inulin oxidation reaction study

Polysaccharides like of HEC, NaCMC, and GG have a high molecular weight, around 1000000 D. We hypothesized that since the FePcS/H_2O_2/H_2O catalytic oxidation system was efficient on high molecular weight polysaccharides, it would also work on low molecular weight polysaccharides. Inulin is a low molecular natural weight polysaccharide consisting of a chain of fructose units with a terminal glucose molecule. The average degree of polymerization (DP) of inulin depends on the source of inulin, but is generally comprised between 22 and 60. Here we worked with an inulin with a DP 30, its average molecular weight is thus about 5000 D which is quite low compared to HEC, NaCMC and GG (300000 D–2000000 D).

Oxidation process developed with HEC applied to inulin at 60 °C provided results rather different than previous polysaccharides. Indeed, contrary to all other oxidizing results DS_{COOH} value is largely higher than DS_{CHO} (43% AGU carboxyl and 7% AGU carbonyl functions). Furthermore weight yield is very modest; 39% (assay 1, Table 2). Taking into account that inulin is a low molecular weight polysaccharide; high reaction temperature might lead to overoxidation and depolymerisation of the polymer. Indeed, in this case, reaction conditions must be too strong leading to overoxidation of carbonyl groups into carboxylic functions. Thus to avoid this phenomenon, reaction was then realized at a lower temperature (assay 2, Table 2). DS_{CHO}, and DS_{COOH} were, respectively, 23% AGU and 8% AGU. In this case DS_{COOH} value is largely lower than DS_{CHO} value, so 40 °C seems to be a temperature favoring the formation of carbonyl functions.

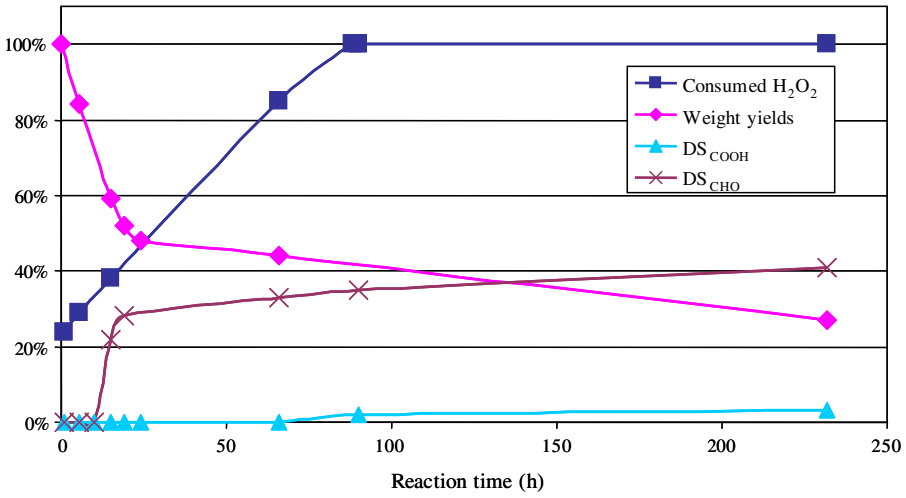

Fig. 4. Oxidation kinetic of NaCMC.

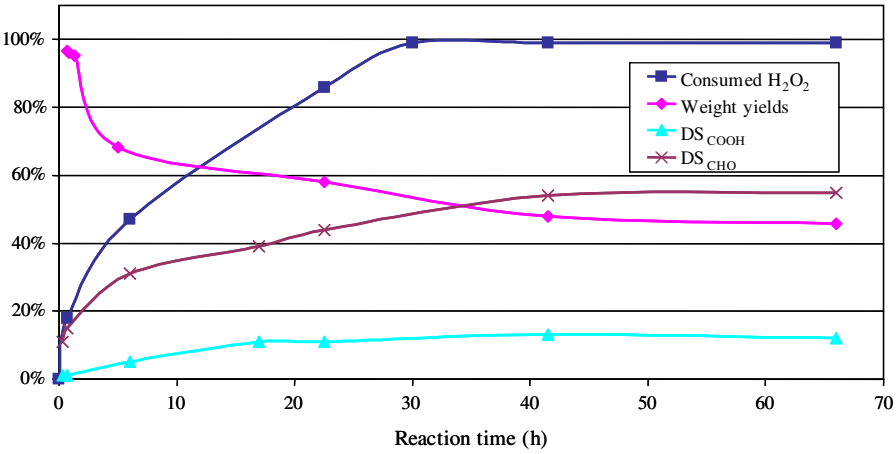

Fig. 5. Kinetic study of pre-treated GG oxidation.

Table 2
Inulin oxidation results.

Assay	T (°C)	Reaction time (h)	Consumed H_2O_2 (%)	Weight yield (%)	DS_{COOH} (% AGU)	DS_{CHO} (% AGU)
1	60	18	86	39	43	7
2	40	18	80	76	8	23
3	T_{amb}	24	57	78	4	15
4	T_{amb}	72	61	74	4	16

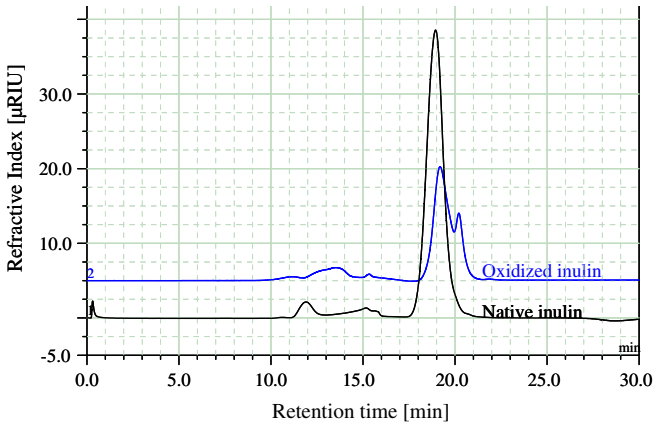

Fig. 6. HPLC chromatograms of native and oxidized inulin.

It has to be noted a drop in weight yield between 60 °C and 40 °C, (39% vs 52% at 40 °C), it confirmed that the polysaccharide had been degraded. Hence, smaller fragments of oxidized polysaccharide should not precipitate in acetone. Over-oxidation is also observed at the reductive end groups of most polysaccharides (Cantley, Hough, & Pittet, 1963). To demonstrate that this phenomenon took place in this oxidation we decided to achieve HPLC comparisons between native and oxidized inulin. Thus Fig. 6 represents the signal of the RI detector versus the retention time. Native inulin exhibits a single peak, although oxidized inulin curb shows two peaks with retention times inferior to native inulin (retention times of 19.19 and 20.21 min, respectively). Previous column calibration indicates that the majority peak corresponds to a DP 25 and the other peak to a DP value of 1.6. These results demonstrate that the polysaccharide has been cut into small fragments and it is possible that this over-oxidation phenomenon conduct to a liberation of mono and disaccharides, which could explain the 1.6 DP value.

Having shown the fragmentation of native inulin, we investigated the characterization of the generated over-oxidation fragments in the filtrate. Indeed, as mentioned above only 39% of weight was retrieved, its means that 61% of inulin has been degraded. Table 3 shows the mass balance and molar quantities of carbonyl and carboxyl functions in the precipitate and in the filtrate. The weight of the filtrate was retrieved after vacuum evaporation.

Table 4
Oxidation of the different polysaccharides.

Polysaccharide	T (°C)	Reaction time (h)	Weight yield (%)	DS_{CHO} (per 100 AGU)
HEC	60	18	71	19
NaCMC	50	24	52	30
GG	60	40	49	53
Inulin	40	18	76	23

Furthermore aldehyde and carboxylic acid functions were quantified before precipitation. Firstly a loss in weight was observed between the total mass of the reaction substrate before precipitation (1.62 g) and the system precipitate/evaporated filtrate (1.42 g). Secondly, we observed that the sum of quantified aldehydes in the system {precipitate + filtrate} was not equal to the quantified aldehydes before precipitation. These observations could be explained by the evaporation of volatile products that could be created during over-oxidation. One possible volatile aldehydic substance is formaldehyde (Perlin, 1980).. A specific colorimetric titration of this substance showed that only 0.1% of formaldehyde has been formed during the reaction (2 mg HCHO for 1.62 g inulin). The loss of weight was in fact due to oxidized monosaccharides fragments that were collected during the filtrate evaporation.

Formation of formaldehyde has also been quantified in the other polysaccharides oxidations. Hence, further industrial application will require this information, because formaldehyde is a highly toxic organic substance. In all cases, not more than 0.1% of formaldehyde was formed.

3. Conclusion

In this work, we have developed a new way for the chemical modification of four polysaccharides (HEC, NaCMC, GG and inulin) by the clean and cheap $FePcS/H_2O_2/H_2O$ oxidation system. Indeed this new system avoid the use of *per*iodate which is usually used for polysaccharide oxidation, the allergenic properties of iodine forbid its use in the cosmetic industry. Our results prove that it is possible to obtain in homogenous aqueous media oxidized polysaccharides with DS_{CHO} = 53% (Table 4). Design of experiments and statistical analysis are powerful tools allowing evaluation of the most significant factors (Time, Temperature, FePcS and H_2O_2 molar ratio). We showed that this process could be applied to other polysaccharides with different molar weights. On the other hand, modest weight yield of oxidized inulin has been explained by an over-oxidation phenomenon.

This catalytic system is very interesting, indeed no waste are formed because the process does not involve any acid, base or buffer solutions. Long alkyl chains could then be grafted on modified polysaccharides in order to endow them with amphiphilic properties.

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Table 3
Mass balance and molar quantities of inulin oxidation*.

	Mass (g)		COOH (mol)		CHO (mol)	
Before precipitation		1.62		3.7×10^{-3}		14.2×10^{-3}
Precipitate	0.740	=1.429	2.9×10^{-4}	=3.69 × 10^{-3}	1.7×10^{-3}	=6 × 10^{-3}
Filtrate	0.689		3.4×10^{-3}		4.3×10^{-3}	

* 1.62 g inulin, 1.2×10^{-4} eq. FePcS, 1.1 eq. H_2O_2, 40 °C, 18 h.

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