ECOLOGICAL TANNING BASED ON MODIFIED CARBOHYDRATES

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ABSTRACT

This research work is based on the development of a specific class of biopolymers applied in leather tanning. From the controlled hydrolysis of starch or cellulose, polymers with a well-defined molecular weight are obtained which are subsequently modified chemically or electrochemically, thus forming glucose chains containing two or more carbonyl groups able to react with collagen and able to coordinate with other binders such as tannins, cross-linking agents and metals. With this class of biopolymers is possible to produce wet-white leathers or mixed biopolymer/metal tanned leathers, used for the production of footwear, leather goods, clothing, furniture and automotive, for their elasticity, tear resistance, low content of fog and voc, light color of the tanning which does not interfere with the light shades of the dyes. The leathers appear full and soft, very reactive to retanning agents. The characteristic buffering action of this new class of biopolymers allows to eliminate the pickel before tanning, simplifying the process that no longer require continuous pH and density checks of the processing bath. These biopolymers come from renewable sources and the production has a low energy impact and a low environmental impact given of the absence of catalysts and toxic chemical residues. The technology for the production of this kind of biopolymer is patent pending and the development is in progress.

Keywords: Oxidized Starch, Ecological Wet White, Natural based tanning

1. Introduction

Starch is the most abundant biopolymer in biosphere, produced by a large variety of plants. Due to its abundant, easy extraction method, low cost and renewable nature it became important not only for feeding but for all industrial sectors. Chemical modifications of starch, and other polysaccharides, are well studied and documented in the literature, our attention was putted on the oxidative modifications of starch at the scope to obtain a usable tanning agent that is effective in an appropriate application procedure with capping agents.

Starch is a polymer composed by monomers of D-glucose linked by an α-(1→4) glycosidic bond to obtain a long chain linear structure called amylose, chain that can be interrupted by an α-(1→6) glycosidic bond on the branched structure of the amylopectin that composes near the 75% of the mass of the isolated natural starch (Tomasik and Schilling2004). The three common and basic techniques for starch chemical modification are the etherification, esterification and oxidation.

Regarding the oxidation there are two different sites, on the starch structure, where the reaction can take place in any glucose residue: C6 carbon atom and the C2-C3 site. The C6 carbon atom shows the typical reactivity of a primary alcohol toward oxidants species. The C2-C3 site, instead, shows the reactivity of a vicinal diol that can entails the scission of the carbon-carbon bond during the oxidation. The chemical functionalities that can be generated during the oxidation of starch are two: the carboxylic function and the partial oxidation product

carbonylic function. Structure of the starch and of the possible oxidation products are showed in Fig.1, taking as example the linear structure of the amylose. The figure shows the limit structures of the possible oxidation products only for amylose, during the oxidation of the starch is also possible to have a mix of all functionality, that can be randomly located in the chain. The formation of an enolic group in C2-C3 in equilibrium with the ketonic tautomer is reported in literature but is not interesting for our purposes.

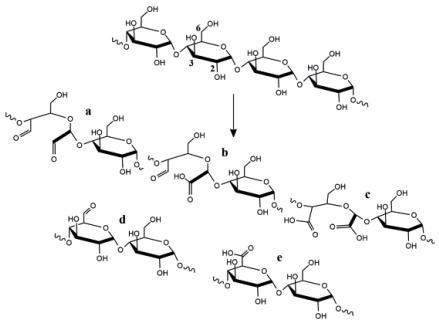


Figure 1. Representation of the possible oxidation products of the D-glucose residual in the amylose structure, a) dialdehyde starch; b), c) product of partial and complete oxidation of C2-C3; d), e) carbonylic and carboxylic product of C6. Hemiacetal form of the aldehydic groups with the alcoholic function of the unoxidized carbon atom of the starch structure are present.

In this process the origin, and therefore the nature, of the starch have a critical importance on the results. Oxidation happens on the surface of the starch granules dispersed in the liquid reaction medium and it is effective only in the amorphous regions and not in the crystalline one, so the effectiveness of the treatment depends on the amylose/amylopectin ratio, the crystallinity and the degree of polymerization of amylose (Kuakpetoon and Wang2001; Butler, Jayson, and Swallow1975). Our goal is to produce and use a carbonyl rich oxidation product of starch as a tanning agent, in combination with other tanning agent, to obtain a leather with good merceological properties. The tanning effect of these type of agents is known in the literature and the reactivity towards the collagen is supposed to be like the classical aldehydes tanning agent with the formation of an imine functionality that connect the protein structure of the hide with the polymeric structure of the oxidized starch (Wells, Filacchione and Fein 1957; Filacchione et al.1958; Kilicarislan Ozkan, Ozgunay, and Akat2019; Butler, Jayson, and Swallow1975).

The common ways to obtain the oxidation of starch are the polyols oxidation technique, that require the uses of an equivalent quantity of oxidants like sodium periodate ($NaIO_4$), hypochlorite, bromate, persulfate and hydrogen peroxide, TEMPO and other N-oxoammonium compounds. In this paper we put the attention on electrochemical methods for the oxidation of the starch that can be conducted with the use of green renewable energy sources. These methods do not require equivalent quantity of oxidant. Periodate is the laboratory scale classical way to obtain the carbonylic derivates because it is pretty selective to the product known as dialdehydes starch (Fig. 1a) which is obtained through the oxidative ring opening on the C2-C3 functionality of the glucose residue (Veelaert, de Wit, and Tournois1994; Guthrie1962). The periodate is reduced to iodate, which is difficult to eliminate from the product and it is pollutant. The periodate has also the disadvantage of causing an extended depolymerization of the starch. The introduction of the electrochemical oxidation with the periodate opens the door to the use of catalytic amount of periodate thanks to the anodic regeneration of it (Dvonch and Melhtretter1951; Mehltretter1955). Hypochlorite is more interesting for industrial purpose and cause an extensive oxidation that leads only the carboxylic products (Fonseca et al.2015; Garrido et al.2014). The method is also useful in electrosynthesis where the oxidating power of the hypochlorite ion, generated in situ at the electrode, can be mediated by the catalytic effect of the bromide ion) but the toxic gas Cl_2 is produced during the treatment (Besemer and van Bekkum1994).

2. Material and methods

2.1 Material:

laboratory scale electrochemical tests are conducted in a 250 ml jacketed glass cell that can be equipped with a magnetic bar stirring system, a glassy carbon disk (GC) as a working electrode, a Pt or graphite counter-electrode and a saturated calomel electrode (SCE) or Ag/AgCl like reference. In the preparative experiment agar gel septa

was used at the scope to obtain a divided cell setup. Soluble potato starch, 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), 4-acetamonium TEMPO (ACT), D- Glucose, 35% hydrogen peroxide, sodium carbonate, sodium phosphate, concentred phosphoric acid, iron (III) ammonium sulphate dodecahydrate, disodium EDTA and solvents were purchased from Sigma Aldrich and used as received. Demineralized water was obtained by treatment with ion exchange resins. Pelt was purchased from tannery after liming and unhairing via formamidinesulfinic acid treatment. All beamhouse products are supplied by Corichem s.r.l.

2.2 Instruments:

electrochemical test was performed by an AUTOLAB potentiostat/galvanostat equipped with a booster10A and Cyclic Voltammetry accessories. FT-IR spectroscopy was performed on a Nicolet iZ10 (Thermo Scientific) in ATR mode (SeZn crystal) or in transmission (KBr table). ^{1}H- NMR, ^{13}C-NMR and 2D-NMR correlation experiments was performed on a 600 MHz instrument (Bruker). HPLC analysis was performed in an Ultimate 3000 instrument (Thermos Scientific) equipped with a DAD and a 250x4.8 mm 5µm 120 Å C18 HPLC column. Pilot scale experiments was performed on a divided-cells flow electrochemical pilot plant, the cathode act like the working electrode and is constituted by a graphite plate of the dimension of 0.04 m^2, the reservoir of the cell is constituted by a 10 L jacketed reactor. Counter electrode is an aluminium plate, the reservoir is a 10 L reactor. The two electrodes are divided by a nafion N324 selective membrane, the flow is guaranteed by two pumps equipped with flowstat. Tanning experiments were performed in a laboratory drum of 1.5 m of diameter.

2.3 Determination of the electrochemical stability window of the substrate:

a 20.6 g/L in water glucose dispersion in Na_2CO_3 0.2007 M at 25 °C was introduced in the electrochemical cell and subjected to a 0-0.2V scan cyclic voltammetry at various scan rate.

2.4 Electrochemical preparations with TEMPO and derivates:

cyclic voltammetry was conducted on a 1 mM TEMPO and Na_2CO_3 0.2 M at different pH obtained by additions 1.5 M HCl with and without the presence of glucose (5.8 g/L) or starch (21.3 g/L) at 0.100 V/s and 25 °C. For quantitative preparation two GC and one Pt electrode were used. The reaction medium is constituted by a 50 ml of a carbonate/bicarbonate 0.2M buffer solution at pH=10.5 containing 39.1 mg of TEMPO, 10 g of starch and a 0.53 V vs SCE potential is applied for 15h. Cyclic voltammetries and preparative experiment with ACT were performed in the same condition substituting it to TEMPO in equal molarity. Products were characterized by FT-IR spectroscopy and by ^{1}H-^{13}C COSY.

2.5 Electrochemical Fenton-Like oxidation with hydrogen peroxide:

Cyclic voltammetries were conducted on a 0.1 M acetate or phosphate buffer at pH=3.0 containing 1 mM iron (III) ammonium sulfate solution and to the same solution with additional 1mM disodium EDTA at 25 °C scan rate 0.100 V/s. Then 2.0 ml of hydrogen peroxide was added and another cyclic voltammetry was recorded, then 501.4 mg of glucose was added and another voltammetry was recorded. The preparative test was conducted on 50 ml of buffer solution containing 47.23 mg of iron (III) ammonium sulphate, 86.24 mg of EDTA, 2 ml pf hydrogen peroxide and 401.45 mg of glucose was added, potential of -0.25 V was applied for 11220 s. The product was freeze-dried and ^{1}H-NMR was collected.

2.6 Pilot scale tests were conducted on the plant described above.

The flow was maintained near 5.5 L/min for both the cells, different flow was applied to maintain the pressure throw the membrane equal for both sides, and we work in galvanostatic mode. The two tanks were filled each with 7 L of a 0.1M phosphate buffer obtained mixing sodium biphosphate with phosphoric acid to reach a determined pH and iron (III)ammonium sulphate dodecahydrate. The catholyte containing also 100g/L of soluble starch. The pH and quantity of iron salts are reported in Table 1. The circulation of the solution was turned on and the anolyte was added 76 g of 35% hydrogen peroxide. Then the galvanostat was turned on and set to allow to pass 4 A of current. Periodically, a sample was collected to determine the aldehyde and hydrogen peroxide content.

2.7 Tanning experiments were performed in a laboratory drum.

After splitting and at the end of the processes, samples were taken to perform analysis.

Quantity [%]	Product	Temp. [°C]	Time [min]	Notes
100	Water	28		
0.4	NH_4Cl			pH=10.0
0.1	Soaking agent		30	Drain
20	Water	34		
0.2	Formic acid			.
0.3	Acetic acid			
2.25	Liquid deliming agent		60	
2.25	Liquid deliming agent		60	pH=8.0
0.06	Bating agent		40	Drain and wash
20	Water	20		
1	Sulfonate fatliquor		20	
10	2.6d (tanning agent)		30	
10	2.6d (tanning agent)		Overnight	pH=4.2
0.5-1	Formic acid		30-60	If required, depending from the capping agent to obtain pH=3.6
	Capping agent			
0.5-2	Sodium bicarbonate			If acid was required; quantity and time for obtain the target pH of 4.7
				Drain
100	Water	20		
0.1	EDTA		20	Drain
	Splitting, the rest of the process was conducted only on grain			
100	Water	35		
8	Filler		40	
4	Melaminic resin		30	
1.5	Neutralizing tannin		30	
4	2.6d (tanning agent)		30	
14	Mixed tannin and syntan		40	
5	Mixed Fatliquor		60	
200	Water	50		
1	Formic acid		Overnight	
2	Charge inverter		60	Drain and wash
50	Water	30		
14	Mixed tannin and syntan		60	
12	Mixed fatliquor		40	
0.5	Ammonia		5	
2.5	Dye staff		60	
4	Melamin resin		40	
200	Water	50	15	
2	Formic acid		40	Drain and wash

Table 1. Tanning procedure for the test 2.7 a, b, c, d, e.

Test 2.7a was conducted without the capping agent, for the other tests we used for the capping: 1% of oxazolidine (test 2.7b), 4% of silicate derivate (test 2.7c), 1% of Tetrakis(hydroxymethyl) phosphoniumsulfate (Test 2.7d),

3% acid polyacrylate with silica particles (test 2.7e). Test 2.7f corresponds to a performance target obtained by conventional glutaraldehyde tanning process.

2.8 Chemical oxidation tests were conducted preparing a solution of soluble starch, iron salt and a buffer, for example phosphate or acetate, in order to obtain a pH from 3 to 6. Iron salt Hydrogen peroxide is then added on top of that in small portions during several hours to maintain the temperature under 50°C, then is left to stir for 8 h. The product obtained was tested in tanning like 2.6d.

2.9 Determination of the aldehyde content in oxidized carbohydrate (CC, Carbonyl concentration) was conducted via titration according with Shmit, Whistler and Paschal(1967). 5 ml of sample was introduced into a 250 ml becher, on top of that it was added 50 ml of distilled water and the pH was adjusted to 3.2 with 0.1 M HCl and is heated to 40 °C in a thermostatic bath. Therefore 60 ml of a 0.36 M Hydroxylamine Hydrochloride and 0.1 M NaOH solution is added, the becher was covered with aluminium foil and allow to stay a 40 °C for 4h. Than the solution was pH-metrically titred to pH=3.2 with a 0.1 HCl solution. The carbonyl content, as percentage of C-OH groups converted to carbonyl groups, is calculated as sequent: $CC(\%) = \frac{(V_B - V_S)}{0.01851 \times m}$ where m is the dry weight of the sample contained in the volume titrated. Tensile strength and extension, tear propagation force and determination of distension and strength of the leather grain were performed respectively according to methods ISO 3376 [A], ISO 3377-2 [A] and ISO 3379 [A] by an external certified laboratory.

3. Results and Discussion

Dextrose was selected like model substrate to conduct the preliminary screening experiments. All the electrochemical processes that we use are electro-catalyzed, that mean that the electron transfers involved in the oxidation of the various carbohydrates used are conducted or mediated by species that are regenerated at the electrode, so the oxidation of the starting materials do not happen at the electrode- solution interphases but in the bulk region. The first electrocatalytic process investigate was the N- oxoammonium compounds using TEMPO and ACT. Oxoammonium compounds are very selective to the oxidation of alcohols to aldehydes, avoiding overoxidation to carboxylic groups. Cyclic voltammetries at various scan rate of the sole substrate, in Fig. 2a, reveal no redox processes affecting glucose in that window.

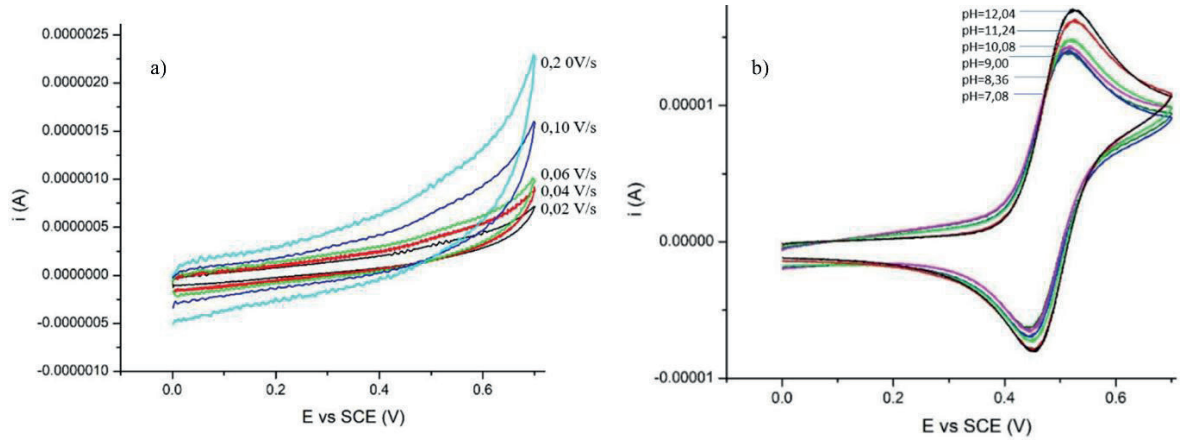


Figure 2 Cyclic voltammetries of various preliminary tests recorded according to the procedure a) 2.3; 2.4(Gennaro et al. 2018)

Subsequently the optimum pH for the catalyst is determined via cyclic voltammetry on a TEMPO solution, the analysis reveal a reversible redox process with an increasing of the anodic and cathodic peak at the increasing of the pH (Fig. 2b), same results were obtained for ACT. The addition to glucose to the system, Fig. 2c, cause a sensible increasing of the anodic current and the disappear of the cathodic peak. The introduction of a reducing species that react with the oxidized catalyst, but is not involved in a redox process at the electrode in the studied potential window, make the process clearly irreversible because the reduction of TEMPO is conducted by glucose and not by the electrode. Is also possible to observe an increasing of the peak current, because of the concentration

of the reduced catalyst in the interphase is now increased by the reducing action of glucose. More concentration means more electron transfer and consequently more current, obtaining a cyclic voltammetry that clearly shows that we have an electrocatalytic process.

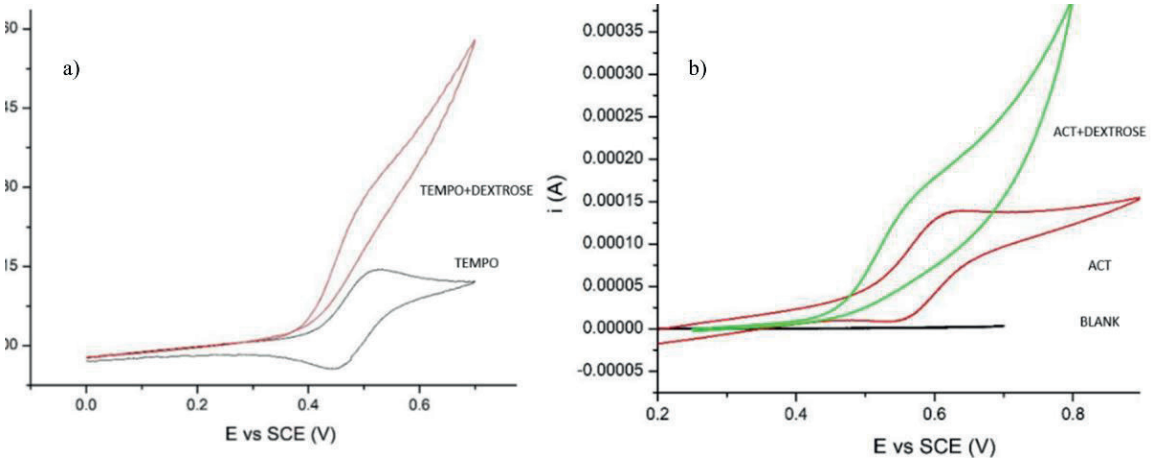


Figure 3. Cyclic voltammetries of TEMPO and ACT catalysed electrolysis of dextrose. (Gennaro et al. 2018)

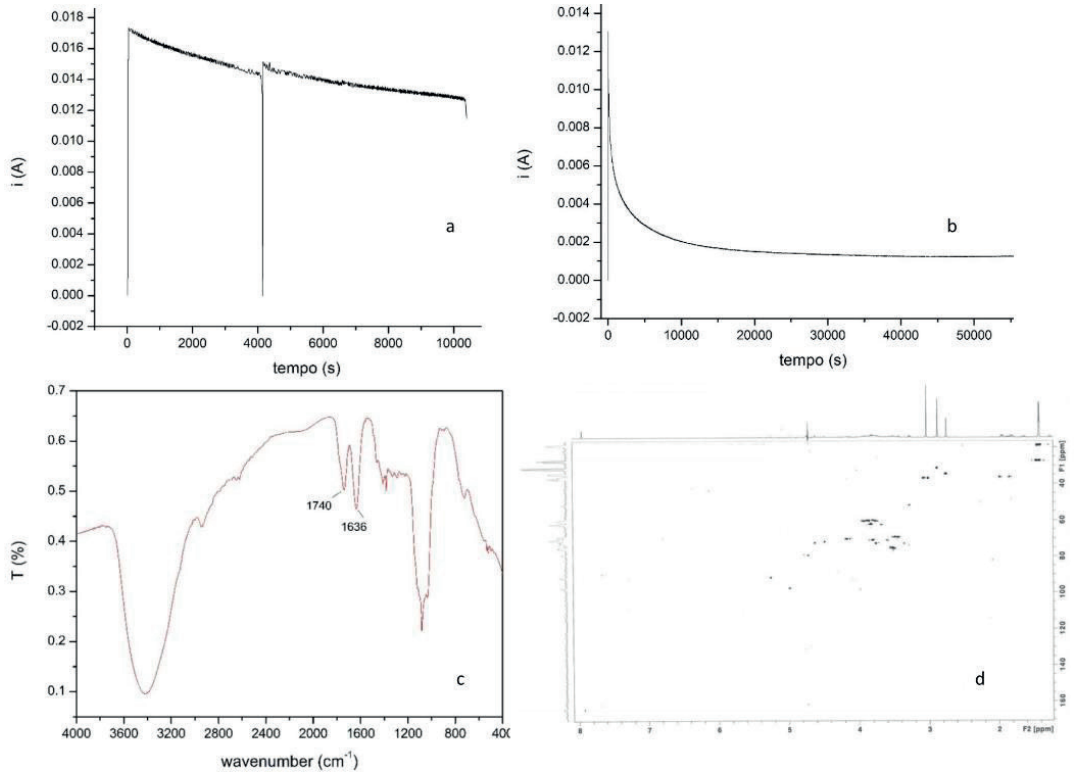


Figure 4. Graphix of current versus time of the preparative tests of oxidation of dextrose with a) TEMPO, spike is caused by operator error; b) ACT. c) and b) show respectively the FT-IR ATR and ^{1}H- ^{13}C COSY experiments on the TEMPO oxidized freeze-dried products. (Gennaro et al. 2018)

The preparative test is designed according to the information obtained by the previous experiments. Results in Fig.4 show that the TEMPO acts like a better catalyst because in 1000 s it allows to pass 149.21 C against ACT that only passes 98.01 C, so it need more time to obtain the same results. Infrared analysis (Fig.4c) reveals the formation of aldehydic group because of the peak at 1740 cm^{-1}, only an amount of the -OH groups involved in the oxidation process are oxidized to carbonyl group, another part remains unreacted and another portion is

overoxidized to carboxylate, identified by the peak at 1636 cm^{-1}. NMR experiment confirms these results and shows the presence of carboxylic hydrogen revealed by the signal at 7.93 ppm on the F1 channel in Fig.4d.

The possibility of use a much strong oxidating method to obtain the oxidation of starch was also investigated, an oxidating method called electro-Fenton reaction, a technique based on Fenton chemistry. Simplifying the mechanism of the conventional Fenton reaction Fe (II) is oxidized by hydrogen peroxide to Fe (III) producing the hydroxide radical, a strong oxidating species, and a hydroxide ion, therefore the Fe (III) is reduced back by hydrogen peroxide to Fe (II) producing hydroperoxide radical and an hydronium ion, restarting the catalytic cycle. That means that a quantity of hydrogen peroxide is consumed to restore Fe (II) in a slow step that produce a lesser oxidizing species. In addition, other reactions which require the presence of Fe (III) that are not described here, contribute to depress the reactivity of Fenton oxidation (Brillas, Sirés, e Oturan 2009). The idea is to continuously reduce the Fe (III) at the electrode in order to maintain its concentration as low as possible to prevent undesired reactions, promote the reactivity and, eventually, electrogenerated the hydrogen peroxide. Because the reduction of Fe (III) in this system is not performed by hydrogen peroxide there is not the production of H^+ ion that neutralizes the OH^- ion produced by the Fe (II) oxidation, so there is the necessity of a buffer to maintain stable the pH. We conduce cyclic voltammetries on a Fe (III) solution with and without the presence of disodium EDTA. As we see in Fig. 5a the presence of a complexing agent makes the process more reversible and it is possible that the complexation makes the Fe (II) a more powerful reducing agent because of the shift of the cathodic peak to more negative potential.

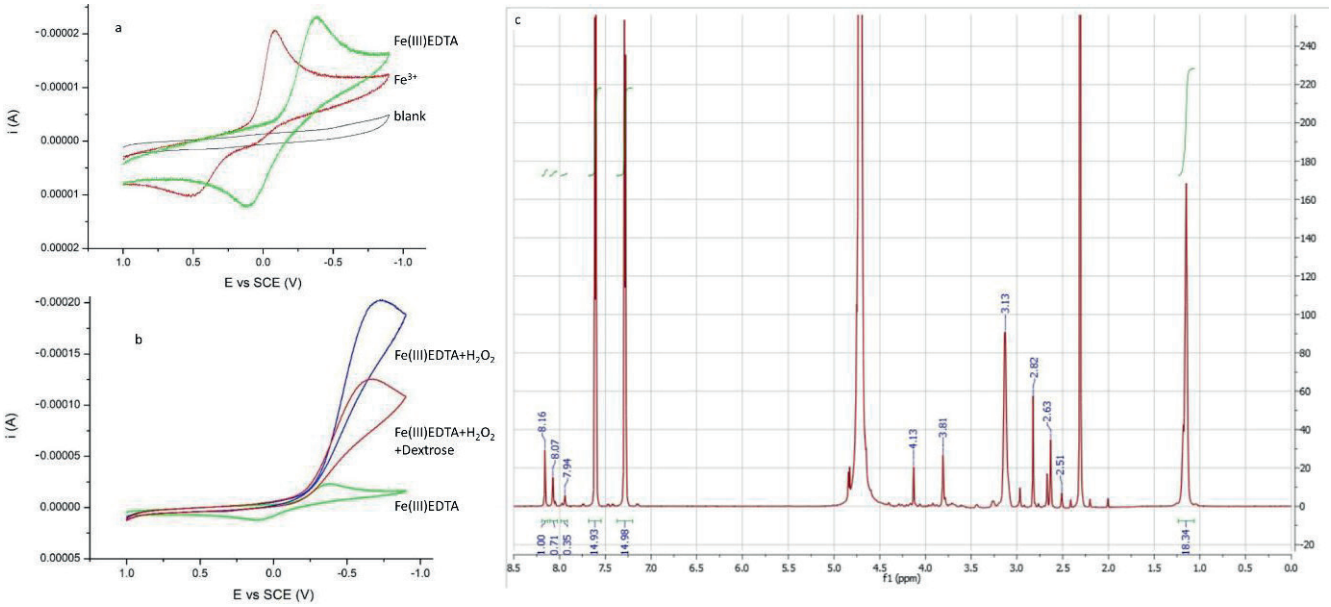


Figure 5 cyclic voltammetries and ^{1}H-NMR (D_2O, 400 MHz) obtained from the procedures 2.5 (Gennaro et al. 2018)

A more reversible shape is obtained substituting the acetate buffer, used to collect the voltammogram Fig. 5a, with phosphate buffer, in Fig. 5b, because the acetate interferes in the complexation of iron with EDTA acting like a competitive ligand. The addiction of hydrogen peroxide changes the cyclic voltammetry from a reversible shape to the irreversible one shown in Fig. 5b because of the Fe (II) is not oxidized back at the electrode anymore but by hydrogen peroxide, increasing the Fe (III) concentration in the interphase and consequently increasing the peak current. The addition of dextrose drops the cathodic peak current because of the hydroxy radical now react with the carbohydrates and do not involve in the possible side reaction of oxidation of Fe (II) to Fe (III), causing the decreasing of the concentration of the last one at the electrode; this prove that dextrose is involved in the process. Analyzing the voltammetries, an applied potential of E_{app}=-0.250 V was selected for preparative scale experiment in order to obtain the reduction of iron but not the hydrogen peroxide one. In the test 145.4 C were passed to the cell with an initial current of 21.0 mA that drop to 6.3 mA near to the end of the experiment. The ^{1}H-NMR of the product of the test permits to qualitative identify the aldehyde groups formed during the test that correspond

to the signals at chemical shift of δ=7.94, 8.07, 8.16 ppm. This result permits to pass with this setup to the pilot scale experiment.

The pilot scale test was performed in the pilot plant showed in Figure 6. The results of the various experiments are showed in Table 2. As we can see pH and catalyst content are determinant, less acid pH increases the Fenton reactivity but it is not possible to increase the pH a lot, in order to avoid hydrogen peroxide self-degradation and iron compounds precipitation. The optimum pH range is determined to be between 3.2 and 4 by the use of speciation diagrams of iron in water. With the increasing of the catalyst concentration there is an increment of the aldehyde content.

Test	pH	Iron salt content [g]	Aldehyde content [%]
2.6a	3.2	6.3	4.5
2.6b	3.2	20	8.19
2.6c	4	6.3	5.67
2.6d	4	20	9.45

Table 2. pH, iron salt and aldehyde content of the final product of the four tests performed on the pilot scale plant.

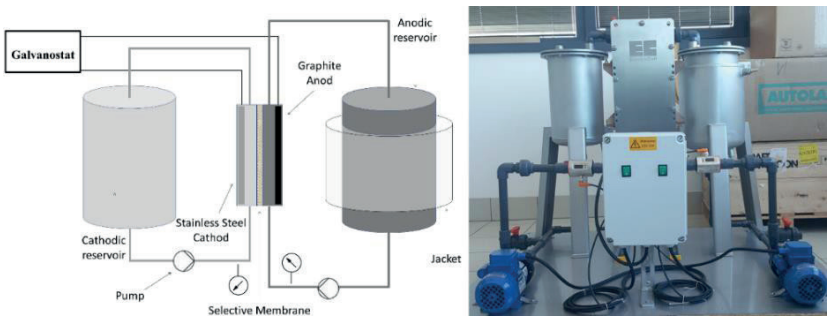


Figure 6 Schematic representation and picture of the pilot scale plant.

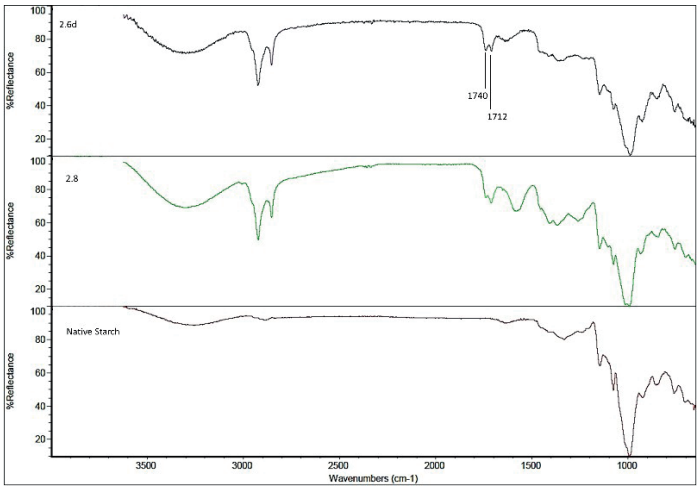


Figure 7. Comparison between the normalized FT-IR spectrum of 2.8, 2.7d and native starch.

We cannot abuse in its quantity because is difficult to remove from the final product and imparts a red colour that is transferred to the hide during tanning and can increase the presence of iron defect. The better results are obtained with the test 2.6d that is repeated 10 times for producing materials for the subsequent tanning tests and for proof the reproducibility of the preparation. The classical Fenton chemistry, used in experiment 2.8, gives

quantity of carbonyl group of 5.42 % or higher obtained in our tests. However, this type of reaction appears to be difficult to control due to the exothermic character, with overoxidation to carboxyl. Fig. 7 puts in evidence the different ratio between the carbonyl (1740 cm^{-1}) and carboxyl (1712 cm^{-1}) signals. It is possible to see the high degree of oxidation produced by classical Fenton approach where the carboxyl signal is higher than carbonyl one, that means the problem is overoxidation. Obtained results in term of leather quality are reported in Table 3 and 4. As we can see the leather tanned with 2.6d tanning agent possess a good thermodynamic stability, near to the standard wet white 2.7f, and this permits to be workable. As can be appreciated in Table 3, chemical-physical properties of the obtained leathers are less than the target glutaraldehyde benchmark 2.7f except for silicate derivate one that is completely comparable and possess a sufficient thermodynamic stability. On the other hand 2.7c has unsatisfactory merceological properties that could be greatly enhanced by the improvement of the retanning process. It is notable that the application of the tanning agent 2.6d do not require a pikling procedure with the consequent saving of chemical agents and time.

Sample	Tg after tanning [°C]	Tg crust [°C]	Tear propagation force [N]	Tensile Test		Distension and Strength			
				Tensile Strength [N/mm^2]	Elongation at max. force [%]	Grain distension [mm]	Load at grain crack [N]	Distension at crack [mm]	Load at crack [N]
2.7a	65	75	87.0	9.64	40.9	7.8	221	9.0	274
2.7b	74	79	79.9	10.3	37.3	6.9	196	9.20	333
2.7c	71	81	127.0	16.2	53.2	8.8	341	11.1	532
2.7d	74	79	85.1	13.2	60.5	8.4	239	10.1	319
2.7e	67	77	54.1	9.16	33.8	6.2	174	7.9	260
2.7f		81	108	15.1	64.0	9.4	356	11.7	488

Table 3. Chemical-physical property of obtained leathers.

Sample	Merchandise evaluation (from 1 to 10)			
	Softening	Firmness	Roundness	Tinctorial yield
2.7a	5.3	8.3	8.0	5.6
2.7b	7.7	6.3	7.7	5.3
2.7c	5.7	5.7	5.9	7.3
2.7d	4.3	4.0	5.0	3.7
2.7e	7.3	7.3	7.7	5.7
2.7f	8.2	5.2	8.2	5.8

Table 4 Merchandise evaluation of obtained leathers.

3. Conclusion

In conclusion this work proves the possibility of obtaining oxidized starch by the use of electro-Fenton approach that gives better results, in terms of carbonyl content, than classical Fenton or electrocatalytic TEMPO oxidation. The method does not produce toxic species and do not need further purification like chlorine or periodate methods. The product of the oxidation has proven to be a useful tanning agent if it is applied with an appropriate tanning procedure that involve the use of capping agent. In this sense the better agent is proven to be the silicate derivate that provide a leather that possess chemical-physical properties very similar to standard glutaraldehyde tanned leather.

4. Acknowledgement

We thank Giovanni Dalla Valle, M.D. (Corichem s.r.l.; ricerca@corichem.it) for the help on the writing of this manuscript.

5. Bibliography

1. Besemer, A.C., Bekkum, H. van, Dicarboxy-Starch by Sodium Hypochlorite/Bromide Oxidation and Its Calcium Binding Properties, Starch – Stärke, 46, 95–101, 1994.

2. Brillas, E., Sirés, I., Oturan, M.A., Electro-Fenton Process and Related Electrochemical Technologies Based on Fenton's Reaction Chemistry, Chemical Reviews 109, 6570–6631, 2009.

3. Butler, J., Jayson G.G., Swallow A.J., The Reaction between the Superoxide Anion Radical and Cytochrome c, Biochimica Et Biophysica Acta 408, 215–22, 1975.

4. Dvonch, W., Melhtretter C.L., Electrolytic preparation of periodate oxypolysaccharides, US PATENT 2,648,629, 1953

5. Filacchione, E.M., Harris E.H., Fein M.L., Korn, A.H., Haghiski, J., Wells, P.A., Tanning studies with dialdehyde starch, J. Am. Leather Chem. Assoc., 53, 77-89, 1958.

6. Fonseca, L.M., Gonçalves, J.R., El Halal, S.L.M., Pinto, V.Z., Guerra Dias, A.R., Jacques, A.C., da Rosa Zavareze. A., Oxidation of Potato Starch with Different Sodium Hypochlorite Concentrations and Its Effect on Biodegradable Films, LWT - Food Science and Technology, 60, 714–20, 2015.

7. Garrido, L.H., Schnitzler, E, Boff Zortéa, M.E., de Souza Rocha, T., Mottin Demiate, I., Physicochemical Properties of Cassava Starch Oxidized by Sodium Hypochlorite, Journal of Food Science and Technology 51, 2640–2647, 2014.

8. Gennaro, A., Isse A. A., Pavan S., Bianchin L.Processo innovativo per la realizzazione di pelli oleo/idrorepellenti esenti da metalli e da PFAS. Bando per il sostegno a progetti sviluppati da aggregazioni di imprese Regione del Veneto POR FESR 2014-2020 ASSE 1 e ASSE 3. Azione 1.1.4. 2018.

9. Guthrie, R.D., The "Dialdehydes" from the Periodate Oxidation of Carbohydrates, Advances in Carbohydrate Chemistry, 16,105–58, 1962.

10. Kilicarislan O., Ozgunay, H., Akat, H., Possible Use of Corn Starch as Tanning Agent in Leather Industry: Controlled (Gradual) Degradation by H2O2, International Journal of Biological Macromolecules, 122, 610–18, 2019.

11. Kuakpetoon, D., Wang Y-J., Characterization of Different Starches Oxidized by Hypochlorite, Starch – Stärke, 53, 211–18, 2001.

12. Mehltretter, C.L., Electrochemical production of periodate oxypolysaccharides, US Patent US2713553A, 1955.

13. Shmit, R. J., Whistler, R. L., Paschal, U. F., Starch: Chemistry and technology, 620–25, Elsevier, 1967.

14. Tomasik, P., Schilling, C.H., CHEMICAL MODIFICATION OF STARCH, Advances in Carbohydrate Chemistry and Biochemistry, 59, 175–403, 2004.

15. Veelaert, S., de Wit, D., Tournois, H. An Improved Kinetic Model for the Periodate Oxidation of Starch, Polymer, 35, 5091–97, 1994.

16. Wells, Percy A, Edward M Filachione, e Martin L Fein., Tanning with periodate oxypolysaccharides, US Patent US2886401, 1957.

Note