Chemical Recovery in TEMPO Oxidation

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To be regarded as environmentally friendly and economical, an industrial process using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) oxidation requires recycling and/or recovery of chemicals. In this work, hypochlorite recycling *via* electrolysis was evaluated and potential means for TEMPO recovery were explored. The most important variable affecting electrochemical hypochlorite conversion was the concentration of sodium chloride in the feed solution. With 30 g/L NaCl salt, a sufficient hypochlorite concentration of 0.8% could be obtained for pulp oxidation of up to 5% consistency. The regeneration of hypochlorite in the treated TEMPO solution was possible by electrolysis and further oxidation performed with only a small addition of make-up chemicals. During electrolysis, some TEMPO degradation took place; therefore, recovery of TEMPO should be done prior to electrolysis. For the recovery of TEMPO, solid phase extraction (SPE) was tested. The best recovery of TEMPO was obtained using a combination of hydrophobic SPE resin material and distillation (yields between 52% and 87%).

Keywords: TEMPO oxidation; Recovery, Solid polymer phase; Electrolysis; Regeneration

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INTRODUCTION

Selective oxidation of primary alcohols in an aqueous solution of various carbohydrates by 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) oxidation was reported in the 1990s (Davis and Flitsch 1993; de Nooy *et al.* 1995); however, the method truly gained the attention of material science researchers when Saito *et al.* (2006a) introduced a method for preparing cellulose nanofibrils (CNFs) from TEMPO-oxidised pulp. In their procedure, the cellulose fibre suspension is oxidised by TEMPO with NaClO as the primary oxidant and NaBr as an additional catalyst at a pH of 10 to 11. TEMPO-oxidised CNFs have become one of the most industrially and scientifically promising CNF grades and have been proposed for use in a variety of applications (Fukuzumi *et al.* 2009; Fujisawa *et al.* 2012; Koga *et al.* 2013; Rebouillat and Pla 2013; Hänninen *et al.* 2014; Trygg *et al.* 2014).

The challenge in improving the environmental impact and cost efficiency of TEMPO oxidation is process development for recycling and/or recovery of TEMPO oxidation chemicals and solutions, as TEMPO and NaClO represent the major costs in biofibril production. Depending on the purity and quantity, the price of TEMPO ranges from 120 to 170 €/kg (98% purity in a 25-kg sack). The price of NaClO, according to industrial users, varies from 1500 to 2000 €/t for 100% NaClO. To improve the cost efficiency of the process, electrolysis for hypochlorite regeneration and recycling, as well as various physio-chemical methods for the effective recovery of TEMPO chemicals, should be investigated.

A patent survey revealed many alternatives for the recovery of TEMPO, *e.g.*, distillation and extraction with organic solvents or supercritical CO_2 (Miyawaki *et al.* 2010; Koji *et al.* 2011a,b). In all patents, the inventors tried to recover and reuse the expensive catalyst (*i.e.*, TEMPO) to increase profitability while maintaining stable product quality. None of the patents tried to use the reaction mixture itself for recycling purposes, probably because of the accumulated salts and the difficulty of producing consistent quality. The reuse processes for oxidising polysaccharides were not revealed or described precisely in the patents. The catalyst-containing reaction solutions were processed using several physico-chemical methods to recover the TEMPO chemical after separating the solid, oxidised polysaccharides from the aqueous dispersion.

Hypochlorite recycling can be done by electrolysis of sodium chloride, the by-products of NaClO after TEMPO oxidation (Casson and Bess 2006). The electrolysis cells are designed for low brine feed flow rates and narrow electrode gaps, to produce sodium hypochlorite concentrations approaching one percent. In this study, electrolysis for hypochlorite regeneration and TEMPO chemical recycling from the process solution was evaluated systematically and the process parameters affecting electrolysis and recovering efficiency were identified.

EXPERIMENTAL

Materials

Never-dried, bleached birch pulp (UPM, Pietarsaari Mill, Finland) was used in all oxidations throughout this work. In all cases, Saito’s TEMPO-mediated oxidation was performed at room temperature, 2% consistency, pH 10, for 90 min (Saito *et al.* 2006b). The concentrations of TEMPO and NaBr in the reaction solutions were 125 mg/L and 1.25 g/L, respectively. All of these were industrial grade.

After TEMPO oxidation and washing cycles, fibre separation was completed using filter cloths with small pore size (50 to 100 µm). The used filter cloths were made of either polyamide or polypropylene. The separation of water from the pulp became more difficult when the pH of the solution was reduced from pH 10 to pH 8. The separated filtrates obtained before pulp washing were used for the regeneration and recycling experiments. The concentrations in the filtrates were typically 90 to 110 mg/L of TEMPO and 0.9 to 1.1 g/L of NaBr because of adsorption losses to the fibres during washing. The oxidation ratio was from 2.5 and 7.5 mmol NaOCl/g pulp, depending the desired oxidation level of 700 to 1300 COOH mmol/kg pulp.

After the separation of fibres, the pulp was washed. Every batch was washed at least two times with 5 L of water, which decreased the pH to 8.5. Pulp charge densities were determined by conductometric titration (Metrohm 712 Conductometer, Herisau, Switzerland, method applied by SCAN-CM 65:02 (2002)).

Electrolysis of Processed TEMPO Solutions

Electrolysis was performed with a filter press type EC-Electro MP (multipurpose)-cell, purchased from Electrocell (Denmark). The cell contained two compartments. Electrolysis took place in an undivided compartment and the other compartment, next to the anode, was used to control the temperature of the anode by circulating thermostatically controlled water in it. The projected electrode areas of anode and cathode were 200 cm^2. The anode was a DSA (dimensionally stable anode), and the cathode material was titanium.

A Switch-Kraft Type SK 075B (Kraftelektronik AB, Sweden) rectifier was used as a power source for electrolysis. The maximum current and voltage were 50 A and 15 V, respectively. All of the electrolysis experiments with the MP-cell were run in controlled current mode.

Figure 1 shows the experimental setup. The temperature of the product as well as cell voltage and electric current were recorded.

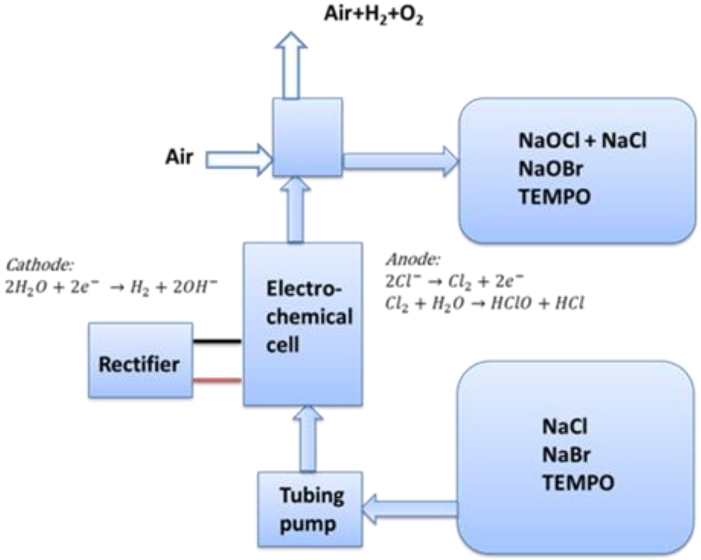


Fig. 1. Experimental setup with one compartment MP-cell, single-pass hypochlorite electrolysis with DSA anode, and titanium cathode

Analysis of Liquid Phase

The concentrations of chlorine and bromine ions (Cl-, ClO_3-, Br-, BrO_3-) were monitored by capillary electrophoresis (CE, Beckman Coulter P/ACE MDQ, Brea, USA) before and after electrolysis. The CE separations were carried out using an electrolyte solution consisting of 15 mM 2,3-pyrazinedicarboxylic acid, 30 mM N-cyclohexyl-3-aminopropanesulfonic acid (CAPS), and 0.5 mM hexamethonium hydroxide at pH 10.5 (adjusted with NaOH). Capillary length (Ldet/Ltot) was 100/110 cm, and internal diameter was 50 µm. The separation voltage was adjusted to -20 kV, and the detection wavelength was 281 nm in indirect detection mode. Samples were injected using pressure injection at 3,5 kPa for 15 s. Capillary and sample storage temperatures were set to 20 °C. Prior to analysis, the samples were diluted 1:50 (v/v) with 10 mM NaOH. Hypochlorite was determined by iodometric titration.

The glass columns in the SPE trial were filled with octadecyl silane sorbent (C18) with a particle size of 40 µm and nominal porosity of 60 Å (Bakerbond Phase (C18)). During packing, the sorbent was wetted with water to ensure dense packing.

The TEMPO concentration of these solutions was 160 mg/L, quantified by LC/MS (Waters Acquity UPLC connected with Waters Xevo TQ MS triple quadrupole mass spectrometer, Milford, USA). The solution was milky because of colloidal material (estimated particle size: 1 to 40 µm), so the process started with the removal of colloidal material using a decanter centrifuge. The used centrifugation was typically 6000 rpm and 15 minutes.

Solid Phase Extraction (SPE)

The SPE extraction tests were carried out using preparative HPLC (Shimadzu LC-8A, Kyoto, Japan) equipped with two pump units (max flow 150 mL/min in each pump) and a glass column (Büchi). To avoid jamming, all in-line filters (1 to 2 µm) were off or out-of place in the liquid delivery system. In the separation column, the in-line and out-line filters were on.

Two columns with capacities of 886 cm^3 (narrow and long column, length 47 cm, diameter 4.9 cm) and 1806 cm^3 (thick and short column, length 23 cm, diameter 10 cm) were used in the experiments. The elution of bound TEMPO was carried out either with ethanol or with acetone, and the pumping direction was downward. The collection of organic solvent in a chilled (4 °C) reservoir prevented volatilization of TEMPO.

The organic solvent was distilled using a vacuum distillation apparatus with a cool trap to recover the extracted TEMPO. UV-VIS spectroscopy (Shimadzu, Kyoto, Japan) was used in all cases as a simple and fast method to determine the TEMPO concentration in filtrates before and after recovery. The concentration of TEMPO in the process solutions was determined using standard solutions with a known amount of TEMPO.

RESULTS AND DISCUSSION

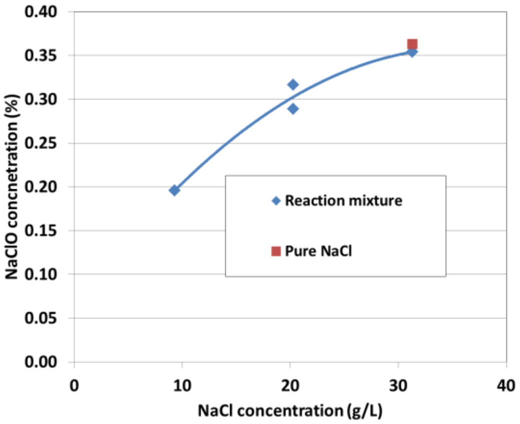
Electrolysis of the solutions with sodium chloride and sodium bromide has been mostly unexplored. On the other hand, electrolysis of sodium chloride to produce hypochlorite solutions has been studied in detail (Ibl and Vogt 1981). It is well known that the current efficiency for hypochlorite formation is dependent on various factors, including the concentration of sodium chloride (which affects mass transfer and reaction rate at the anode) and hypochlorite (which decomposes at the anode, cathode, and bulk), current density, and temperature. These variables are extensively interrelated, and were thus investigated in more detail in regard to recycling TEMPO oxidation chemicals.

The Effect of Variables on Current Efficiency

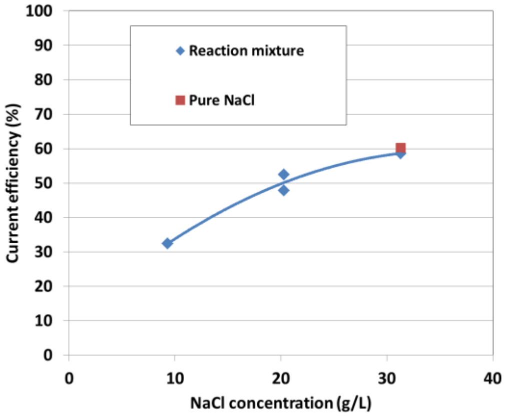
The effects of NaCl concentration, pH, temperature, electric current density, and flow rate on the current efficiency of NaClO regeneration in recycled process solutions were studied. The amount of hypochlorite in the product was measured by titration as soon as possible after electrolysis.

As expected, the NaClO concentration and current efficiency increased when the amount of NaCl was increased in the feed. The addition of NaCl was required to produce a sufficient concentration of NaClO for TEMPO oxidation (Figure 2). The reaction mixture containing NaBr and TEMPO resulted in almost the same current efficiency as the pure NaCl solution.

The current efficiency with as-received anode and pure NaCl at 20 g/L concentration was 63%, but after two rounds of electrolysis with the recycling solutions only 50% current efficiency was obtained with 20 g/L of pure NaCl, as shown in Fig. 2. It is possible that organic material in the filtrates partly inactivated the anode surface, resulting in lower current efficiency. However, no further deactivation of the anode was observed.



(a)



(b)

Fig. 2. The influence of NaCl concentration on the (a) NaClO concentration and (b) current efficiency at 30 A electric current and 6.9 mL/min flow rate

An increase in the electric current and current density at a constant flow rate and a decrease of the flow rate at a constant electric current decreased the current efficiency. The main reason for this was the increase in sodium hypochlorite concentration and its decomposition at the anode and cathode (Ibl and Vogt 1981).

In the recycling experiments, the hypochlorite concentration was increased by circulating the TEMPO solution two or three times through the electrochemical cell, but circulation did not offer any benefits in terms of current efficiency. With a single pass and 30 A current, the current efficiency was approximately 50% and the NaClO concentration 0.3% v/v (Fig. 2). When the electric current was 15 A and the solution was passed two times through the cell, the current efficiency was 48% and the NaClO concentration was 0.29% v/v.

The effect of the temperatures of the cooling water of the anode and the product solution on current efficiency was not clear, nor was the effect of pH in the feed solution. The current efficiency and the concentration of hypochlorite were insensitive to the cooling water and product temperature until the product temperature reached 35 °C. After that point, the current efficiency started to decrease. The pH of the feed solution was not important, and only minor changes in the current efficiency were observed when the pH was varied between 8.5 and 13. The concentration of sodium hypochlorite was around 0.3% in all experiments.

Figure 3 shows the relationship between the NaClO concentration and current efficiency for all measurement points. As the concentration of NaClO increased, the current efficiency decreased. The effect of NaCl concentration in the feed solution at constant hypochlorite concentration was decisive.

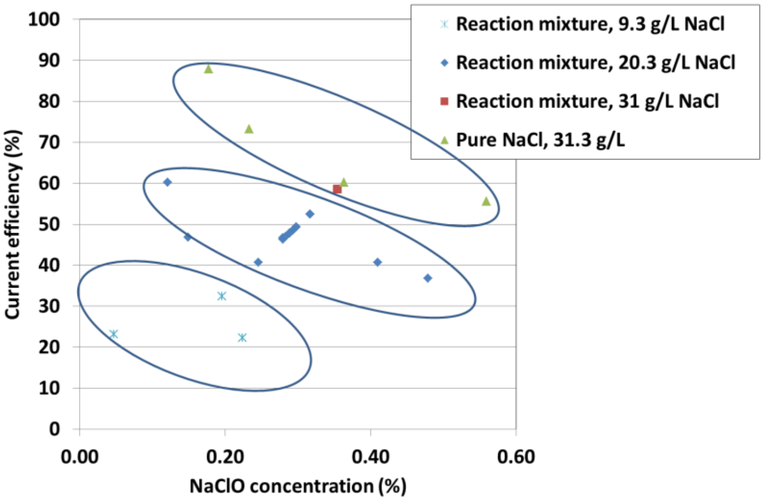


Fig. 3. Current efficiency *vs.* NaClO concentration

Recycling Experiments

Based on the obtained results, a NaCl concentration of 30 g/L was used in the recycling experiments. The target hypochlorite concentration was 0.75%, which should be sufficient for TEMPO oxidation up to 5% consistency. In the first two recycling series, the main objective was to monitor the salt species formed through electrolysis. The last two recycling tests aimed at optimising the oxidation efficiency.

To monitor the chlorine and bromine components, a CE method was developed. As shown in Fig. 4, the separation between Br^- and Cl^- was, in many cases, inadequate, and they could not be fully distinguished.

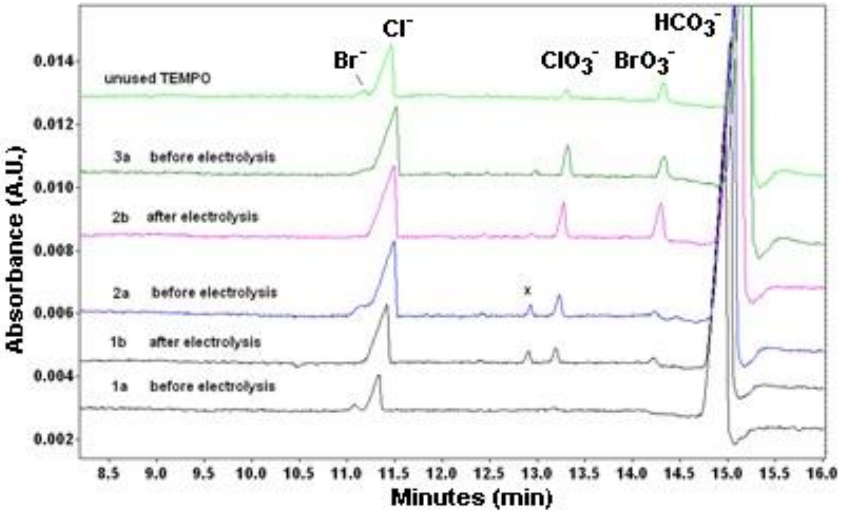


Fig. 4. The effect of electrolysis and recycling on chlorine and bromine ions in sample series 1: X denotes an unidentified compound

The salt species, chlorates, and bromates could be easily measured from the electropherograms. Chlorite and perchlorate anions were not found in samples. The hypochlorite anion (ClO^-) was not observed by CE in the samples either, although the pH of samples and the electrolyte content were high enough to ionise the analyte (pKa value of ClO^- is 7.53). In addition, the lack of a stable solution for quantitation standards is detrimental to analysis by CE. Thus, the hypochlorite was quantified by titration, as previously discussed. The pH dependence of the salt species was very small (not shown here).

The amount of chlorates increased systematically during the recycling cycles. The amount of bromates oscillated between increasing and decreasing, probably because of the effects of adsorption. The variation in the concentration of NaClO was probably a result of the used pH of the recycled solution, which was not standardised. Additionally, the dry contents of the pulp changed slightly during the recycling tests.

The results of the recycling series indicated that the amount of TEMPO catalyst and NaBr co-catalyst were very important in terms of the reaction efficiency. Because of the chosen recycling procedure, *i.e.*, the addition of extra NaCl to the feed solution, the produced charge densities were higher than in the original TEMPO oxidation, mostly because of the higher NaClO concentrations reached in regeneration. With increasing recycling stages, the concentration of TEMPO decreased markedly. A low concentration of TEMPO increased the reaction time dramatically (from 120 min for the original oxidation to 613 min for the third recycled oxidation), but because of the high concentration of NaClO, the charge density level was still higher than in the original oxidation (825 mmol/kg *vs.* 981 mmol/kg). The concentration of NaBr was unknown, and therefore the need for make-up chemicals was not precisely known. The concentration of TEMPO in the oxidation solution only decreased by approximately 12% to 15% because of water retention in the filtration process. The greater decrease may indicate degradation of TEMPO during electrolysis.

Analytical Evidence of the Diminishing Concentration of TEMPO

The concentration of TEMPO decreased notably during the electrolysis cycles. Water retention during the filtration process alone cannot explain the changes in the TEMPO concentration. Therefore, LC/MS analysis was performed to reveal the fate of TEMPO during recycling. The LC/MS chromatograms from recycled samples revealed three peaks that occurred at 1.96, 3.15, and 4.57 min (not shown). The corresponding molar masses were 158, 216, and 156 g/mol, respectively. The peak at 4.57 min is the TEMPO peak, which correlates with the peak at 1.96 min. The peak at 4.57 min is the TEMPO peak (M = 156 g/mol) which possibly correlates with the peak at 1.96 min (M = 158 g/mol). The retention time difference, however, between TEMPO and this molecule is quite high, about 2.5 min (column phase of C18 was used). One speculation is that the peak observed at 1.96 min is some kind of open-ring structure of TEMPO. The open-ring of “TEMPO” could occur in a cationized form, which would make it elute from C18-column notably earlier than TEMPO. In the article of Ma *et al.* (2011), it has been presented that the thermal decomposition of TEMPO *via* ring opening mechanism can be possible in acidic media. Speculation for the peak at 3.15 min (M = 216 g/mol) is that the oxidation compound is sodium salt of glucuronic acid.

The stability of TEMPO in the process solution after electrolysis was also evaluated. Process samples were stored at room temperature for nine days, after which the concentration of TEMPO was measured by LC/MS (Fig. 5). The TEMPO concentration in the untreated sample was 403 mg/L, in the 10 A sample it was 12 mg/L, and in the 50 A sample it was only 5.1 mg/L. After three more days of storage, the weak signals of TEMPO molecules disappeared from the LC/MS chromatograms. It is likely that the TEMPO radical was decomposed during electrolysis treatment.

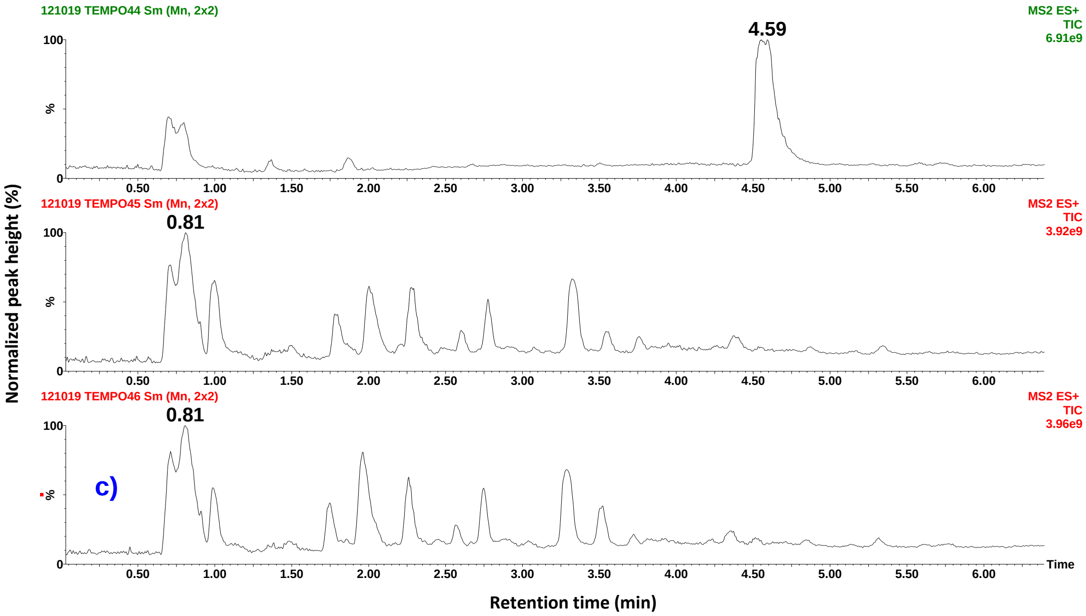


Fig. 5. LC/MS chromatograms of the decomposition spectra of TEMPO after decomposition test: a) is the original solution, b) is the 10 A sample, and c) is the 50 A sample after 9 days storage at room temperature.

Electrolysis for hypochlorite recovery has thus proved to be a feasible method for recycling the TEMPO oxidation filtrates. In these optimised conditions, the used TEMPO oxidation solution can be recycled and further oxidation performed cost effectively with just a small addition of make-up chemicals. However, TEMPO degradation occurs during electrolytic regeneration of hypochlorite. Thus, recovery of TEMPO before electrolysis should be considered and studied.

Solid Phase Extraction for Recovery of TEMPO

The trapping ability of the hydrophobic solid phase extraction material for TEMPO recovery was tested. This would be a new TEMPO recovery method, and in contrast to ion-exchange resins, should not adsorb inorganic salts or hydrophilic pulp degradation products.

Seventy litres of process water that was used in TEMPO oxidation was treated. The process began with the removal of colloidal material using decanter centrifuge. After that, the solution was pumped through a C18 column, where TEMPO molecules were bound to sorbent material. The unit operations are presented in Fig. 6.

A volume of 1.2 L of ethanol was enough to extract the TEMPO from the narrow column. Inactive precipitates, which were wood-based materials, were found in some extraction solutions (ethanol and ethanol-water solutions after solvent extraction). The same precipitate was formed in the clear ethanol solution during storage.

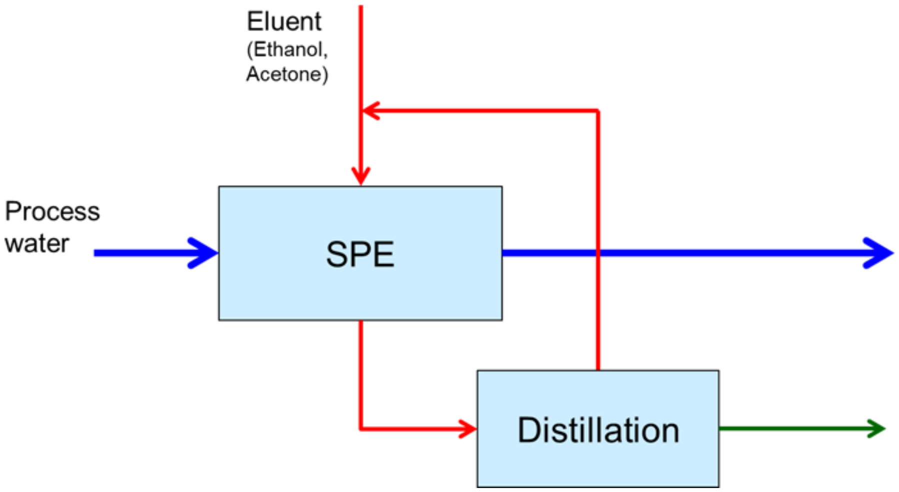


Fig. 6. TEMPO recovery method and the unit operations

Extraction Efficiency with Ethanol or Acetone

After the separation efficiency was determined, the TEMPO concentration of the various solutions was measured. The initial concentration of TEMPO was 160 mg/L in the process solution, and after the column treatments the TEMPO concentration in process water decreased to 0.05 mg/L. This means that the trapping efficiency of TEMPO to C18 sorbent material was almost 100%. The TEMPO concentration in ethanol was 9300 mg/L. Thus, the extraction efficiency was 93% and the enrichment factor was 70 : 1.2 = 58. Only a relatively small amount of ethanol was needed to remove TEMPO from the SPE material.

The extraction procedure was also done using acetone as solvent. The organic solvent was pumped at the speed of 90 mL/min and the direction of flow was downward. One litre of acetone was enough to extract TEMPO from the long and narrow column and the extractant contained 11.2 g of TEMPO. The extraction efficiency was 93% and the enrichment factor was 70 : 1 = 70. The higher enrichment factor means that less solvent is needed to elute bound TEMPO.

A trial with a wide, short column revealed that the amount of extractants decreased, probably due to asymmetric elution and poor flow properties. With this type of column, the enrichment factor was only 32.

Distillation of Extraction Solvents

The purpose of the distillation stage was to recover extracted TEMPO from the organic solvent. The distillate was colorless at the beginning of the distillation procedure (about half of the original amount), but when the concentration of TEMPO increased, the colour of the distillate became more yellow. At this point, 85% to 90% of the initial volume was removed. Significant differences in distillation efficiency were not observed when neutral and acid distillations were compared. The extractant was distilled with vacuum at 33 to 40 mbar and at a temperature of 16 to 19 °C.

After distillation of the readily distillable fraction of the ethanol, the residue ethanol solution-containing TEMPO was transferred to a petri dish and solvent was evaporated in a fume hood under atmospheric pressure and at room temperature with airflow. During the evaporation, crystallisation of TEMPO molecules was observed. The recovery of solid TEMPO was 5.3 g, which means there was 47% recovery of solid TEMPO.

The vacuum distillation of TEMPO from acetone solution was more efficient than from ethanol. The amount of recovered solid TEMPO was 9.1 g, which means there was an 81% recovery yield of solid TEMPO.

It was also observed that during 2 to 3 weeks storage at 6 to 8 °C, TEMPO crystals started to appear in the ethanol solution, even at low TEMPO concentrations, but this method was not efficient, and the recovery of TEMPO was poor.

CONCLUSIONS

1. Electrolysis for hypochlorite recovery was shown to be a feasible method for recycling TEMPO oxidation filtrates. The most important variable affecting hypochlorite conversion was the concentration of sodium chloride in the feed solution. Sufficient hypochlorite concentrations of 0.75% for the pulp oxidation at 5% consistency could be obtained with 30 g/L salt concentration. The effect of pH, when ranging from 8.5 to 13, was minor. Additionally, the effect of temperature was not important when it did not exceed 35 °C. An increase of electric current decreased the current efficiency due to the increase in sodium hypochlorite concentration. By decreasing the volumetric flow rate, the concentration of hypochlorite could also be increased, although the current efficiency decreased due to the increased dwell time and hypochlorite concentration. In these conditions, the used TEMPO oxidation solution can be recycled and further oxidation performed cost effectively using a small addition of make-up chemicals. However, TEMPO degradation occurred during electrolytic regeneration of hypochlorite. Additionally, the changes in the concentrations of chlorates and bromates should be taken into account in the recycling schedule.
2. Solid phase extraction (SPE) is a potential method for TEMPO recovery. These trials included testing commercial extraction agent materials in different conditions and re-using of the recycled TEMPO. The TEMPO solutions had to be rid of colloidal substances using decanter centrifuge, and all filters (suction and in-line) had to be off or out of place due to jamming problems. Ethanol and acetone were used as extraction solvents in the recycling tests. The distillation of acetone was very effective. The recovery of solid TEMPO was 81%, the extraction efficiency was 93%, and the enrichment factor was 70. The recycled TEMPO samples proved to be as active in the oxidation trial as the native TEMPO. Two patents have been written based on this work (Nuopponen *et al.* 2014, 2015).

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