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Regeneration of Aqueous Periodate Solutions by Ozone Treatment: A Sustainable Approach for Dialdehyde Cellulose Production

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A method for easy and fast regeneration of aqueous periodate solutions from dialdehyde cellulose (DAC) production by ozone treatment is presented, along with a direct and reliable simultaneous quantification of iodate and periodate by reversed-phase HPLC. The influence of iodate and ozone concentration, solution pH, and reaction time on the regeneration efficiency was studied, as well as the reaction kinetics. Regeneration of spent periodate solutions by ozone was successfully performed in alkaline medium, which favors the formation of free $^{\bullet}$OH radicals, as supported by the addition of radical scavengers and quantum mechanical calculations. At pH 13 and an ozone concentration of approximately 150 mg L^{-1}, periodate was completely regenerated from a 100 mm solution of iodate within 1 h at room temperature. A cyclic process of cellulose oxidation and subsequent regeneration of spent periodate with 90 % efficiency has been developed. So far, commercial applications of DAC have been hampered by difficulties in reusing the costly periodate. This work overcomes this hurdle and presents a highly efficient, clean, and low-cost protocol for the preparation of DAC with integrated periodate recycling, with the possibility of scaling the process up.

Introduction

Salts of periodic acid are commonly used to oxidize vicinal cis-diols of carbohydrates in an aqueous medium through simultaneous cleavage of a carbon–carbon bond and generation of two reactive aldehyde functions, which might also be present in a masked form, for example, as a hydrate or hemiacetal. This oxidation reaction is particularly suitable for polysaccharides and has been used to oxidize starch, cellulose, and xylan, but also other glucans, fructans, and their derivatives, providing they contain vicinal diols. Periodate oxidation of cellulose involves selective attack on the anhydroglucose unit that splits the C-2–C-3 bond, causing the formation of two aldehyde groups and, at the same time, periodate is reduced to iodate.[1] The product obtained, commonly named dialdehyde cellulose (DAC), has gained much attention recently because it can be used to immobilize proteins and dyes or can serve as a starting material towards the production of biobased specialty fibers and materials.[2–5]

Sodium periodate, which is typically used as the oxidizing agent for DAC preparations, is commercially generated by electrochemical oxidation of iodate. Although electrochemical regeneration of spent iodate has been described,[6,7] the high process costs and sensitivity of the electrodes render this process less attractive in combination with DAC production. Nevertheless, iodine compounds emerging from periodate oxidation reactions (such as sodium iodate or iodine) are environmentally hazardous and cannot be removed by standard industrial wastewater treatments. Therefore, any industrial production of DAC will have to rely on effective routes for periodate recycling.

Several alternative methods for the regeneration of spent periodate, mainly from dialdehyde starch preparation, have been proposed in the literature. They mainly use secondary oxidants, such as hypochlorite and ozone, both under alkaline conditions,[8–11] or peroxosulfate under rather neutral conditions.[12] Major drawbacks of these pathways arise from high energy costs due to either elevated temperatures or long treatment times required to reach high conversion. The input of chlorinated organic compounds and corrosive halide additionally disqualifies hypochlorite usage for periodate recycling. In summary, the lack of suitable methods for efficient, large-scale, and low-cost periodate recycling was the main factor that has hampered commercial DAC production so far.

Recently, another primary oxidation agent that may offer a practicable recycling solution has been examined. In this approach, an acetic acid derivative of iodobenzene was substituted for periodate, and a regeneration route with peracetic acid

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and hydrogen peroxide was suggested, without providing a detailed protocol.[13]

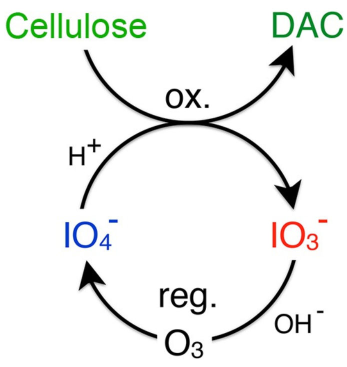
An analytical shortcoming of the above-described recycling processes is that they all rely on indirect quantification of periodate, usually performed by a titration method. An analytical method that provides direct monitoring of both iodate and periodate simultaneously would be of great importance for process optimization. To date, a variety of methods for the determination of the iodate/periodate couple have been reported in the literature.[14–19] To perform simple and reliable analysis, we used reversed-phase HPLC with direct UV detection; this is a widely available technique in standard laboratories.

A successful, large-scale implementation of periodate oxidation of cellulose requires an efficient and low-cost recycling process with direct monitoring capability. Herein, we focus on the optimization of the ozone-based regeneration method and its subsequent application in the recycling of spent periodate from DAC production. An experimental design approach was applied to elucidate the parameters governing the regeneration process. Simultaneous quantification of periodate and iodate allowed monitoring of the reaction kinetics of both cellulose oxidation and periodate regeneration. Mechanistic aspects of iodate oxidation with ozone are discussed and correlated with results from DFT calculations. The efficiency of periodate regeneration is analyzed over three recycling steps, and general considerations for method utilization are presented.

Results and Discussion

Utilization of ozone for periodate regeneration

Ozone is a powerful oxidizing agent. It reacts with most organic compounds containing double or triple bonds in a formal [3+2]-cycloaddition reaction with follow-up processes, and it can convert inorganic ions into oxyanions of the highest oxidation state.[20] Ozone has been widely used in the treatment of effluents from pulp and paper mills, textile dying, the pharmaceutical industry, and for water disinfection.[21–23] Herein, we employed ozone as a secondary oxidant to convert iodate formed during cellulose oxidation back into periodate (Scheme 1). The high oxidation power of ozone was no problem in this case. On the contrary, it was desired because periodate is the highest oxidation state of iodine species and no “overoxidation” would be possible.



Scheme 1. General scheme for recycling of periodate by ozone treatment in DAC production.

As mentioned above, an attempt to use ozone for the regeneration of spent periodate has already been reported in a patent application from Kesselmans,[11] which did not result in a patent being granted. In this patent application, periodate was regenerated within 5 h from 140 mM solutions of iodate at mildly alkaline pH between 8 and 10.5. However, the reaction yield of periodate was not measured, but only calculated based on the amount of ozone spent, and recycled periodate showed poor oxidation efficiency, which implied only partial regeneration.

Effect of pH on periodate recycling

In the optimization steps, fresh solutions of sodium iodate were used. All experiments were performed at room temperature with a volume of 85 mL. At first, the reaction performance was tested over the pH range of 2–14 by using a 25 mM buffered solution of iodate and moderate ozone concentration. To ensure equal pH of all samples analyzed by HPLC, the reaction solution was acidified with concentrated H_3PO_4 to pH 2 after ozonation, prior to appropriate dilution. Reaction yields of periodate were given relative to the initially measured iodate concentration. Figure 1 shows the pH dependence of the reaction yields of periodate after 30 min of reaction time at an ozone concentration of 94 mg L^{-1}.

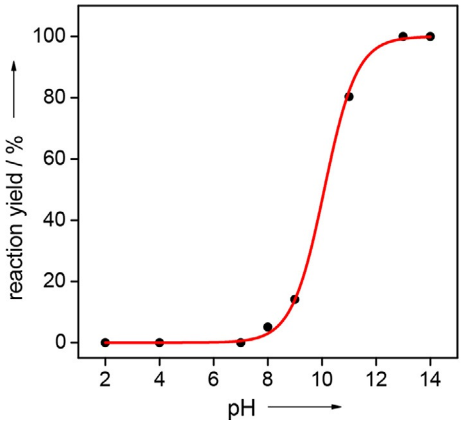


Figure 1. Effect of pH on periodate reaction yield (c_o = 25 mM $NaIO_3$, $c(O_3)$ = 94 mg L^{-1}, t = 30 min, 100 mM phosphate buffer).

Neutral and acidic conditions did not cause any formation of periodate. From pH 8 upwards, conversion was observed. Notably, the reaction yield steeply increased above pH 10 and showed full conversion at pH 13 and above, which was in stark contrast to previous findings.[11]

An experimental design approach was applied to study the influence of alkaline pH, iodate concentration, ozone concentration, and treatment time on periodate formation in more detail. Regarding the influence of pH, solutions of pH 8 and 14 were used as the lower and upper levels. Figure 2 a illustrates the reaction yields of eight sets of different reaction conditions

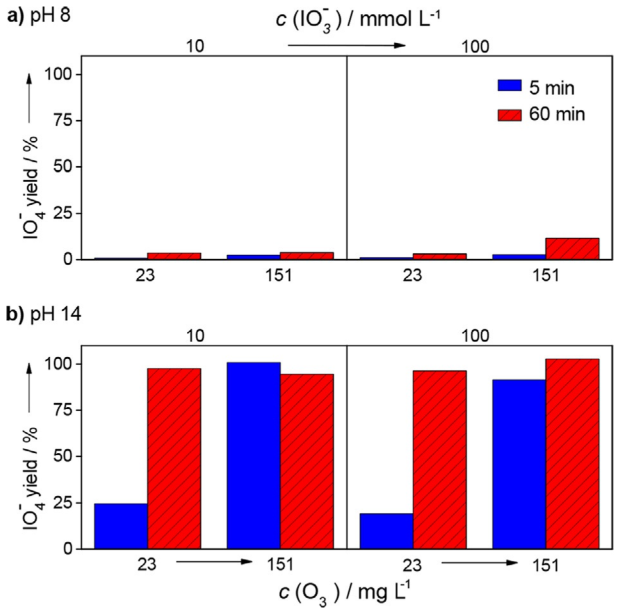


Figure 2. Experimental design approach: IO_4^- yields at a) pH 8 and b) pH 14.

at pH 8. The low periodate yield in slightly alkaline media could hardly be improved by any combination of the parameters examined. Compared with the experimental conditions at the same pH previously shown in Figure 1, a minor increase in yield from 5.1 to 11.5% was only observed when a lower iodate concentration of 10 mM was treated with a higher ozone concentration of 151 mg L^{-1} for twice as long. Strongly alkaline solutions, however, resulted in high conversion rates in the range of 94.6–102.8% after 60 min of ozone treatment for all iodate and ozone concentrations (Figure 2 b). These findings were, once more, in disagreement with data previously reported in the patent application,[11] in which pH 8.5 was claimed to give optimal regeneration conditions, whereas the reaction was allegedly not feasible above pH 10.5 due to ozone decomposition.

Multivariate analysis showed correlation coefficients of 0.91, −0.12, 0.12, and 0.13 for the four abovementioned variables—pH, iodate concentration, ozone concentration, and treatment time—revealing the highest impact of pH on ozonation performance. High ozone concentration at pH 14 caused 91.5% regeneration of periodate from a 100 mM solution of iodate, and 100% regeneration from a 10 mM solution of iodate, after only 5 min. A decrease in ozone concentration slowed down the conversion process to some extent, necessitating longer reaction times to attain comparable yields. Interestingly, prolonged ozone treatment of a 10 mM solution of iodate resulted in a slight decrease of periodate yield. This suggests that severe alkaline conditions cause side reactions that initiate decomposition of periodate. Because this reaction must be a reduction, it is reasonable to assume the involvement of intermediate hydrogen peroxide or superoxide anion radicals as reductants.

Another downside of working at pH 14 was the lowered solubility of $NaIO_4$, which caused periodate precipitation during or after the reaction. Neutralization of the solution with concentrated H_3PO_4 dissolved the precipitate, but, in turn, introduced an extra quantity of salts that interfered with iodate sampling during HPLC analysis. This precipitate formation made accurate online monitoring of the reaction kinetics impossible. To prevent possible side reactions and perform reliable iodate/periodate analysis, we tested whether the use of less alkali could avoid precipitate formation without a decline in reaction yields. At the same time, applying less alkali would be more economical for the whole recycling process.

Reaction kinetics

Having identified pH as the most important parameter that governed the formation of periodate, we continued investigating the iodate to periodate conversion in alkaline media with a high ozone input. We examined, in particular, the correlation between iodate concentration and available alkali, the role of oxygen radicals, and the effect of higher temperature in the conversion process. For this purpose, aliquots were taken at distinct time intervals, immediately diluted for chromatographic analysis to avoid the formation of sodium periodate precipitate, and directly measured by HPLC. Furthermore, changes of pH over time were monitored. The reaction was terminated at 1 h or sooner, if considerable amounts of precipitate were formed in the reaction flask, which indicated complete oxidation. Blank reactions were performed by excluding one of the components (O_3, NaOH, or $NaIO_3$).

Effect of iodate concentration

The use of diluted alkali indeed delayed precipitate formation to a certain extent, which allowed for the recording of iodate and periodate concentration over time. Figure 3 shows the yield of $NaIO_4$ for various initial concentrations of iodate in alkaline solutions when a maximum ozone concentration of 151 mg L^{-1} was applied. At pH 13, periodate was completely regenerated from a 10 mM solution of iodate already after 10 min. Up to 100 mM iodate could be converted within 1 h. Interestingly, if the concentration of iodate was higher than

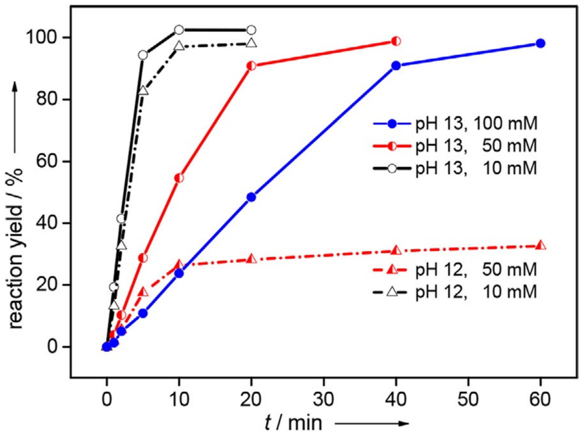


Figure 3. Effect of initial iodate concentration in alkaline media on periodate reaction yield ($c(O_3) = 151$ mg L^{-1}, $T = 25$ °C, unbuffered system).

the initial hydroxide concentration (i.e., 150 mм), complete periodate regeneration was not possible even at prolonged reaction times (data not shown).

Similar to pH 13, complete periodate regeneration was observed at pH 12 for an iodate concentration of 10 mм within 10 min. However, when an iodate concentration of 50 mм was used, thus exceeding the amount of hydroxide ions in solution, a yield of only 26 % was reached in the first 10 min of the reaction, after which time the concentration of periodate leveled off. These observations indicated a strong correlation between the starting iodate concentration and solution alkalinity.

The pH of the (unbuffered) reaction solution during ozonation was followed. At an initial pH of 13 and an iodate concentration of 100 mм, the pH of the solution mixture decreased over time as the periodate concentration increased, whereas no change of pH was observed for 10 and 50 mм iodate. In less alkaline media, at pH 12, this initial value stayed constant only in the case of a 10 mм solution of iodate. Using a 50 mм solution of iodate, we observed a pH drop from 12 to 8 within the first 5 min of the reaction, thereby stopping the regeneration process. No change in pH was observed when ozone was purged through alkaline solutions in the absence of iodate. These results showed that the consumption of hydroxide ions stemmed from the oxidation of iodate and might have had a strong impact on the performance of the ozone reaction.

The change in pH during the reaction was assumed to be caused by the presence of different periodate species in the solution. It is known that, in aqueous media, periodate is predominantly hydrated and found in different ionic forms or dimers of orthoperiodic acid H_5IO_6 ($pK_1=1.64$, $pK_2=8.36$, $pK_3=14.98$).[24] Under alkaline conditions, in particular, from pH 9 onwards, the dominant periodate species is $H_3IO_6^{2-}$. Because the ozone oxidation of iodate stoichiometrically leads to the formation of $H_4IO_6^{-}$, the subsequent transition towards equilibrium is followed by a release of protons. Therefore, we can assume that the decrease in pH is caused by periodate generation, as shown in Equations (1)–(3):

$$IO_3^- + O_3 \rightarrow IO_4^- + O_2 \tag{1}$$

$$IO_4^- + 2\,H_2O \rightarrow H_4IO_6^- \qquad K = 29 \tag{2}$$

$$H_4IO_6^- \rightarrow H_3IO_6^{2-} + H^+ \qquad pK_2 = 8.36 \tag{3}$$

Due to the decrease in pH during the ozonation process, the alkalinity of the reaction solution should be carefully adjusted according to the concentration of iodate to be converted. Based on our study, we propose that the appropriate hydroxide concentration for efficient periodate regeneration should be at best equal to the initial concentration of iodate.

Mechanistic studies

It is known that ozone is highly reactive in aqueous media, and therefore, rather unstable. The ozonation process can follow two general pathways: ozone reacts by direct oxidation as molecular ozone or by indirect reaction through the formation of secondary oxidants. The mechanism of ozone decomposition includes a multitude of successive reactions, generating a vast number of radicals;[25,26] all of them potent oxidants with different oxidative power. However, only the oxidation potential of hydroxyl radicals would be sufficiently high to effect oxidation of iodate to periodate. The rate of decomposition is greatly enhanced at increased pH due to the catalytic effect of hydroxide ions [Eqs. (4)–(8)]:[27,28]

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{4}$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2 \tag{5}$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \tag{6}$$

$$O_3^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^- + O_2 \tag{7}$$

$$O_3 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + O_2 \tag{8}$$

Thus, in reactions that involve ozone above a certain pH, oxidation is an indirect process, according to radical-type reaction mechanisms.[29,30] The observed efficient periodate regeneration through ozone under alkaline conditions suggests that reactive oxygen species, such as hydroxyl radicals, which are even more powerful oxidants than molecular ozone itself, are the active species involved in iodate oxidation.

To shed more light onto this issue, we performed ozonation of 10 mм iodate at pH 13 in the presence of *t*BuOH as a radical scavenger. *t*BuOH reacts rapidly with $^{\bullet}OH$ radicals and only very slowly with ozone [Eqs. (9) and (10)]:[31,32]

$$t\text{BuOH} + {}^{\bullet}OH \rightarrow t\text{BuO}^{\bullet} + H_2O \qquad k = 5\times 10^{8}\ \text{M}^{-1}\,\text{s}^{-1} \tag{9}$$

$$t\text{BuOH} + O_3 \rightarrow \text{products} \qquad k = 0.03\ \text{M}^{-1}\,\text{s}^{-1} \tag{10}$$

A possible hydrogen-transfer reaction involving ozone and *t*BuOH, according to Equation (10), is strongly unfavored compared with the hydrogen-transfer reaction shown in Equation (9), which is largely exothermic because of much higher stability of $t\text{BuO}^{\bullet}$ than that of $HO^{\bullet}$.[33,34] Direct ionic oxidation of tertiary alcohol *t*BuOH by ozone can also be ruled out.[35]

The gas was dispersed through a 2 mm inner diameter (i.d.) tube instead of a frit because small amounts of *t*BuOH already induced foam formation that made the reaction difficult to handle. Without a gas disperser and without adding a radical scavenger, periodate regeneration was complete after 40 min (Figure 4). After the addition of 100 mм *t*BuOH, the reaction significantly slowed down to consume only 29 % of iodate within 60 min. A further increase of *t*BuOH completely impeded iodate oxidation, which indicated that excess scavenger promptly trapped all $^{\bullet}OH$ radicals. These findings strongly support the assumption that $^{\bullet}OH$ radicals are the active oxidant species, or are at least strongly involved in the periodate regeneration process.

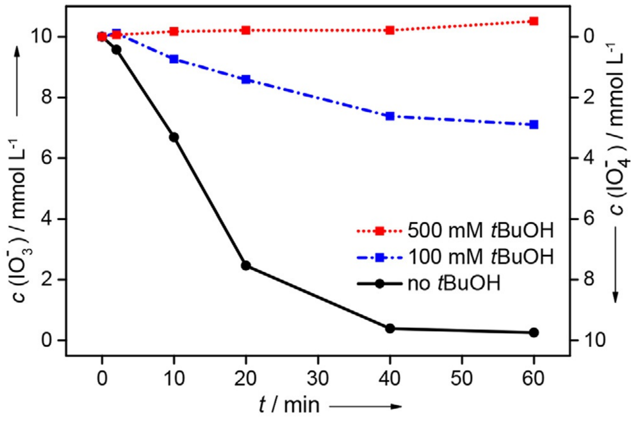


Figure 4. Effect of *t*BuOH on the ozonation of iodate ($c_o = 10$ mM $NaIO_3$, $c(O_3) = 151$ mg L^{-1}, pH 13, unbuffered system).

To lend further support to this theory, computations were carried out on the interactions between iodate and the above-mentioned chemical species that arose from ozone decomposition. Figure 5 shows potential energy curves regarding the O–I distances in the interactions between iodate and $^{\bullet}OH$ radical, and iodate and ozone, calculated at the DFT(UM06-2X) level. It became clear that, among all chemical species present in the system, only the $^{\bullet}OH$ radical had an energy minimum in the interaction with iodate, with a binding energy of around 7 kcal mol^{-1} (for details, see the Supporting Information). It is thus likely that the $^{\bullet}OH$ radical reacts with iodate with no activation barrier for the initial step, whereas the reactions of the other species exhibit significantly higher barriers. Without investigation of further elementary steps towards periodate formation, these computational results corroborate our assumption of an $^{\bullet}OH$ radical based reaction mechanism in the ozone oxidation of solutions of iodate; this is in agreement with our experimental results. The computational results are also reasonable when considering the difference in oxidation potentials of the five oxidants: their standard redox potentials are 2.6, 0.78, 2.2, 1.5, and 2.1 V for the $^{\bullet}OH$ radical, $O_2^{\bullet-}$ radical, $O_3^{\bullet-}$ radical, $HO_2^{\bullet}$ radical, and ozone, respectively, in which the potential of the $^{\bullet}OH$ radical is clearly the highest, and hence, this radical is the strongest oxidant.[36–39]

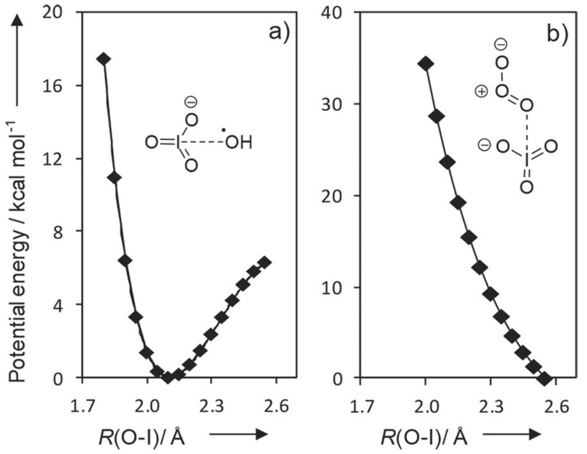


Figure 5. Potential energy curves in the interactions between iodate and a) $^{\bullet}OH$ radical and b) ozone, as calculated at the DFT(UM06-2X) level of theory. The 6-311+G(d), 6-311G(d), and 6-311G (d, p) basis sets were employed for O, I, and H atoms, respectively.

Temperature effect

Finally, regeneration efficiency was tested at increased temperatures, which have been shown to accelerate the rate of ozone decomposition and, in turn, to be conducive to faster cellulose oxidation.[40] A temperature of 55 °C was chosen to mimic the conditions for DAC preparation. Only 60 % of periodate was formed at 55 °C in 10 min, before the concentration of periodate leveled off (see the Supporting Information). Compared with complete conversion at RT within the same time, elevated temperatures proved to be rather disadvantageous for periodate regeneration. This observation is explained by very poor solubility of ozone in water at 55 °C and possible side reactions.[41,42]

Recycling of periodate from DAC preparation

To investigate whether ozone treatment could be utilized for the recycling of periodate in DAC production, the efficiency of periodate regeneration and its impact on cellulose oxidation was examined over three cycles (Scheme 1).

Fresh periodate was used as an initial oxidant for the cellulose pulp in the first cycle. Periodate consumption and iodate formation during oxidation of cellulose at 55 °C to a degree of oxidation (DO) of 2 % is shown in Figure 6. The pH of the solution decreased over time from 4.3 to 3.3. The absence of periodate after 2 h was taken as indication of the reaction being completed. A linear dependence was observed from the semi-logarithmic plot of concentration over time, showing that the kinetics of cellulose oxidation to a low DO followed a pseudo-first-order rate law with respect to periodate concentration (see the Supporting Information). We observed the same kinetic model in a recent study in which the oxidation of cellulose to a DO of 50 % was monitored at RT over a longer reaction time.[43]

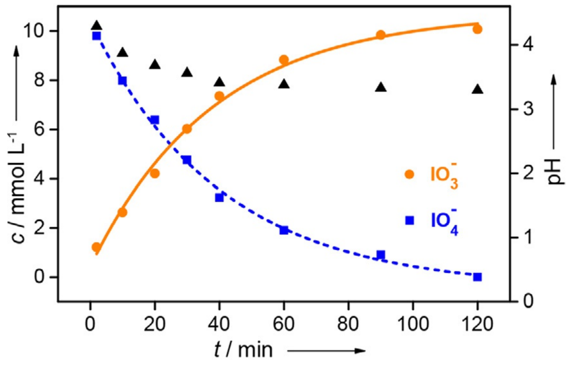


Figure 6. Reaction kinetics of periodate oxidation of cellulose ($c_o = 10$ mM $NaIO_4$, $T = 55$ °C) and observed decrease in pH over time.

The reaction solution of about 10 mᴍ iodate after cellulose oxidation was treated with ozone at pH 12 for 20 min. Recycled periodate solutions were reused for the subsequent oxidation of cellulose pulp over three cycles, as illustrated in Figure 7. Thereby, the starting amount of cellulose was adjusted after each recycling step to keep the DO of the final product constant and, at the same time, preserving a pulp consistency of around 7.3 %. Adding wet cellulose to a recycled solution led to a slight decrease of periodate concentration (and pulp consistency) in every oxidation step.

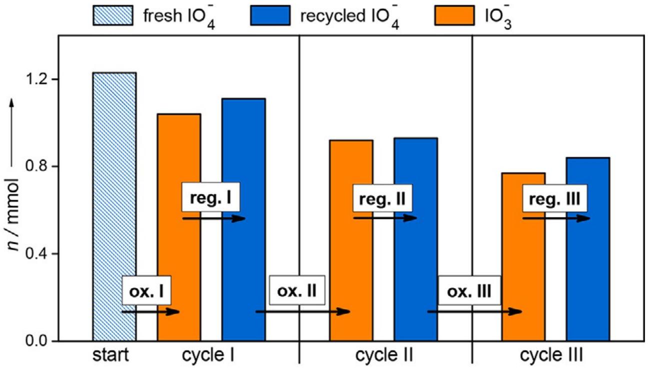


Figure 7. Periodate regeneration by ozone treatment over three recycling steps.

In all experiments, the final concentration of iodate after oxidation corresponded to the initial (diluted) concentration of periodate within the error of measurement. However, about 10–15 % of iodate remained trapped in the wet DAC fibers after they were pressed out at the end of the oxidation. This amount of iodate, corresponding to "fresh/recycled IO_4^-" minus "IO_3^-" given in Table 1, was accounted for as oxidation loss.

The efficiency of three consecutive regeneration steps, taken as the ratio of "recycled IO_4^-" and "IO_3^-" amounts, was found to be 107, 101, and 109 %. These somewhat higher values are due to small amounts of unconsumed periodate that adds to the regenerated periodate. Clearly, ozone treatment resulted in full periodate recovery throughout all recycling steps.

Carbonyl group labeling of all DACs prepared was carried out to see if recycled periodate might have any hitherto unknown effects on the produced DAC. Parallel to cellulose oxidation with recycled periodate, control reactions were performed with equal stoichiometric amounts of fresh periodate. A comparison of control reactions and those run with recycled oxidant showed no influence of the periodate origin on iodate–periodate interconversion (Table 1). Likewise, fluorescence labeling revealed comparable carbonyl group contents of DACs in all cases. An average carbonyl content of 100 μmol g^{-1} showed good oxidation performance, thus confirming successful utilization of ozone for periodate recovery in the process of DAC production.

General considerations

The overall efficiency of the process for three consecutive recycling steps was 90, 84, and 90 %, respectively. The observed losses exclusively result from the workup procedure after oxidation. In industrial applications, the loss of iodate in the wet, solid product could be minimized, if the solutions from subsequent washing steps of DAC fibers were collected and residual iodate was concentrated, for example, by vacuum evaporation. This step was not considered necessary for the proof of concept in our approach. The decrease of periodate concentration and pulp consistency, emerging from the addition of the wet cellulose pulp at the start of oxidation, could be compensated for by the addition of fresh periodate to a recycled solution.

Sodium hydroxide and sulfurous/sulfuric acid, which may be used for pH adjustment in the recycling process, are already readily used in pulp and fiber production. The drop in pH observed during ozonation proved to be beneficial for the recycling process because it decreased the amount of acid required for the next oxidation step. Due to the limiting gas–liquid mass transfer, an excess of ozone has to be applied in the range that is dependent on the particular setup in use. Ozonation time cannot be reduced through the use of increased amounts of alkali due to the formation of periodate precipitate, which can be dissolved only below pH 2; this, in turn, causes additional consumption of acid and dilution of the solution.

All recycling methods so far utilize a higher pH for the per iodate regeneration than that for the oxidation reaction. This is necessary due to the pH dependency of the redox potential of the periodate/iodate couple: with 1.6 V at a low pH versus 0.7 V at high pH, the oxidation of iodate is facilitated under alkaline conditions. Therefore, accumulation of salt cannot be avoided in any recycling scenario. Other inorganic secondary oxidants would end up as salts in the regeneration process

Table 1. Effect of ozone treatment on cellulose oxidation performance. Controls 1 and 2 represent reactions with fresh solutions of IO_4^- run in parallel to those with recycled periodate.[a]

Sample	Start cellulose c(C=O) [μmol g^{-1}]	n(IO_4^-) [mmol]	Cycle I ox.[b] I n(IO_3^-) [mmol]	DAC c(C=O) [μmol g^{-1}]	reg.[c] I n(IO_4^-) [mmol]	Cycle II ox.[b] II n(IO_3^-) [mmol]	DAC c(C=O) [μmol g^{-1}]	reg.[c] II n(IO_4^-) [mmol]	Cycle III ox.[b] III n(IO_3^-) [mmol]	DAC c(C=O) [μmol g^{-1}]	reg.[c] III n(IO_4^-) [mmol]
Recycling	26	1.23[a]	1.04	98	1.11	0.92	103	0.93	0.77	92	0.84
Control 1					1.11[a]	0.93	109	0.93			
Control 2								0.93[a]	0.82	103	0.83

[a] Fresh IO_4^-. [b] Oxidation. [c] Regeneration .

themselves. Thus, with oxygen as the only byproduct, ozone keeps salt generation at a minimum. Nevertheless, a small amount of salt has been shown to improve the oxidation efficiency by disrupting the hydrogen-bond network of cellulose, and thereby, making some of the hydroxyl groups better accessible to periodate. For example, Sirvio et al. performed salt-assisted oxidation with an amount of NaCl that corresponded to the concentration of salt which would accumulate from IO_4^- recycling after 17 cycles.[44] This indicates that the presence of salt could be tolerated to a certain extent, after which periodate would be precipitated and recovered as a salt, given a sufficient amount of alkali, or purified by other means.[6]

Another particular benefit of using ozone in alkaline medium is the removal of organic impurities, such as low-molecular-weight acids and hydroxyacids from cellulose or polysaccharide degradation, by oxidation. These impurities are completely oxidized, that is, converted into CO_2 and water, under the strongly oxidizing conditions. They would thus not further contribute to the total organic carbon (TOC) content in the effluents and also could not undergo any side reactions, such as condensation to chromophoric substrates, with cellulose or DAC.

Regardless of the change in pH, recycling of periodate evidently has to be carried out separately from cellulose oxidation to prevent side reactions of the polymer with the secondary oxidation agent, for example, cellulose degradation or further oxidation of aldehydes to carboxyl groups. Recycling of periodate with ozone also allows the preparation of DAC of various degrees of oxidation by using higher periodate concentrations.[43] In our study, we evaluated the regeneration of periodate up to 100 mm solutions of iodate. If desired, even saturated solutions of iodate (e.g., 400 mm) can be recycled by ozone treatment, providing the pH is kept high enough, if only in the form of precipitated salt.

The proposed ozone-based regeneration method should be suitable for recycling of spent periodate not only from oxidation of cellulose, but also from oxidation of starch and other glucans. If the oxidation product was soluble, for example, fully oxidized DAC or low-molecular-weight carbohydrates, the precipitation of iodate prior to regeneration could be achieved by the addition of metal ions or organic solvents.[9]

Conclusions

This study demonstrates efficient periodate recycling by ozone treatment with a great potential for large-scale applications in DAC production. Alkaline conditions that promote the formation of oxygen radicals and a high ozone concentration at room temperature proved to be most beneficial for high conversion efficiency. Direct monitoring of reaction kinetics showed that 100% yields were attained when the concentration of alkali was at least equal to the initial iodate concentration to be converted, or higher. Insight into the mechanism of ozone oxidation, by means of hydroxyl radical scavengers and DFT calculations of potential energies, assisted better understanding of the recycling process and confirmed that hydroxyl radicals were centrally involved in the oxidation system.

Spent periodate from DAC preparation was completely regenerated by ozone treatment over three consecutive recycling steps. The observed consumption of hydroxyl ions during ozonation could be an advantage in the recycling process because it decreased the amount of acid necessary to return to the acidic conditions desired for cellulose oxidation. Minor losses of iodate in the recycling process result from the workup procedure after the oxidation step, which can be overcome by collection of the DAC washing solutions. Recycled periodate maintained good oxidation performance throughout subsequent DAC preparations, and showed no differences from fresh periodate. The presented recycling process for periodate offers an environmentally friendly, economically feasible, and sustainable pathway for the production of oxidatively functionalized celluloses and other polysaccharides.

Experimental Section

Materials

All chemicals used for optimization of the regeneration process were obtained as p.a. grade from Sigma–Aldrich (Schnelldorf, Germany) and were used as received. Acetonitrile and phosphoric acid (85%) were of the highest purity available and obtained from Merck (Vienna, Austria) and Roth (Graz, Austria), respectively.

Fully bleached sulfite dissolving pulp (beech) from Lenzing AG (Lenzing, Austria) was used as the cellulosic test substrate. The weight-average molar mass of the pulp was 290 $kg\,mol^{-1}$ with a starting carbonyl content of 24.3 $mmol\,kg^{-1}$. Full characterization of this pulp was previously reported by our group.[45]

Preparation of DAC

Air-dried cellulose sheets (10 g) were torn into small pieces of 1–2 cm^2 and disintegrated in water by using a kitchen blender. After removing excess water by filtration with a Büchner funnel, the water content of the cellulosic pulp was approximately 50%wt. The wet cellulose was immersed in a solution of sodium periodate (0.26 g) to a total volume of 120 mL and was oxidized at 55 °C to a DO of 2%, according to a method reported previously.[43] Aliquots were taken every 10 min to monitor both periodate consumption and iodate formation, by measuring their absorbance at $\lambda = 290$ nm after ion separation on a reversed-phase column. When all periodate was consumed, the reaction solution was filtered off, and the pulp was thoroughly washed with deionized water to remove residual iodate. Pulp samples were frozen without drying and stored for further analysis by gel permeation chromatography (GPC).

Recycling of periodate

After cellulose oxidation, the reaction solution containing about 10 mm iodate was allowed to cool and the pH was adjusted to 12 with 4.5 m NaOH. An amount of about 100 mL was treated with ozone for 20 min at room temperature. Finally, 12 m HCl was used to acidify the regenerated solution of periodate to pH 4.5, which was required for the next oxidation cycle (Scheme 1). Recycled periodate was reused to repeatedly oxidize cellulose to DAC, as described above. Control reactions with fresh solutions of periodate were run in parallel. The starting amount of cellulose was adjusted to keep the DO of the final product constant. Dilution of recycled periodate caused by the water content of the cellulosic pulp was accounted for in each oxidation step.

Ozone treatment of iodate

An oxygen-based ozone generator (Anseros COM-AD-04, Tübingen, Germany) was used. Ozone concentration in the gas phase was in the range from 0.1–151.3 mg$\,L^{-1}$ and was controlled by the generator power level, according to product specifications from the manufacturer, which we verified by an iodometric titration method.[46] The ozone treatment was performed in a 100 mL glass bottle with a three-way dispenser (ozone gas inlet and outlet, sampling inlet). The ozone generator was equilibrated under oxygen flow for 1 h before the ozone gas stream was switched on to indicate the start of the reaction.

The ozone-containing gas was purged at a constant flow of 50 L$\,h^{-1}$ through a polytetrafluoroethylene (PTFE) frit (20×9 mm) with a pore size of 10 μm to ensure a high number of small bubbles, that is, a large reactive surface area. Furthermore, the reaction solution was vigorously mixed with a magnetic stirrer to enhance mass transfer into the liquid phase.

Design of experiments

Four variables were explored to probe the conversion efficiency: pH, iodate concentration, ozone concentration, and reaction time. Thus, a two-level full factorial design of given variables was applied, that is, 4^2 experiments were carried out in total to determine the effect of the parameters selected and their respective interactions. The lower and higher levels of the reaction variables are given in Table 2. The response variable evaluated was the reaction yield of periodate. The software JMP 12.0.1 was used for multivariate analysis.

Table 2. Reaction variables used in the experimental design.

Level	pH	$c(IO_3^-)$ [mmol$\,L^{-1}$]	$c(O_3)$ [mg$\,L^{-1}$]	t [min]
lower	8	10	23	5
upper	14	100	151	60

GPC analysis

Carbonyl group profiling of DACs produced with fresh and regenerated solutions of periodate, as well as of the nonoxidized reference sample, was achieved by selective labeling of the aldehyde groups with the marker carbazole-9-carboxyloxyamine followed by size exclusion chromatography multiangle laser light scattering (SEC-MALLS) fluorescence analysis (CCOA method), as described previously.[47]

HPLC analysis

An Agilent 1100 Series HPLC system (Agilent Technologies, Waldbronn, Germany) was used. Samples were separated on a J'sphere ODS-M80 reversed-phase column (250×4.6 mm, 4 μm particle size) with a precolumn, both from YMC (Dinslaken, Germany). Identification and quantification of iodate and periodate were performed by direct UV detection at $\lambda = 220$ nm, according to the method outlined by Sajonz et al. with a few modifications.[17] Optimum separation was achieved with a mobile phase consisting of 0.15% aqueous H_3PO_4 (≈pH 2) and acetonitrile (90/10, v/v), and isocratic elution at a flow rate of 1 mL$\,min^{-1}$. The column temperature was kept at 25 °C. The injection volume was 5 μL. All samples for HPLC analysis were prepared with 0.15% H_3PO_4 as the diluent and filtered through a 0.45 μm filter prior to injection. The system was controlled by ChemStation software Rev B.04.03 SP1.

The iodate/periodate quantification method was analytically validated (see the Supporting Information). The limit of detection and limit of quantification for iodate were 0.02 and 0.06 mM, respectively, and 0.03 and 0.09 mM, respectively, for periodate. The average relative standard deviations were 1.6 and 1.9% for iodate and periodate, respectively.

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Keywords: biomass · iodine · ozone · radicals · reaction mechanisms

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