Production of cellulose nanocrystal from Israeli paper mill sludge by ozonation pretreatment followed by recyclable maleic acid hydrolysis

Roi Peretz[1], Elizaveta Sterenzon[1], Yoram Gerchman[2], Vinod Kumar Vadivel[1], Thomas Luxbacher[3], Hadas Mamane[1]

[1] School of Mechanical Engineering, Faculty of Engineering and Water Research Center, Tel Aviv University, Tel Aviv 69978, Israel
[2] Department of Biology and Environment, Faculty of Natural Sciences, University of Haifa-Oranim, Tivon 3600600, Israel
[3] Anton Paar GmbH, Anton-Paar-Str. 20, 8054 Graz, Austria

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Presenting author email: peretzroi10@gmail.com

Introduction

In Israel, ~ 4.8–6.2 million tons of MSW are generated annually, composed of 34% organic material, 16% paper and 8% cardboard. The combined paper and cardboard wastes amount to 1.15–1.49 million ton/year, yet only 20% is currently being recycled, with a target of 35% by 2020. Thus, 80 thousand tons of paper and 150 thousand tons of cardboard are recycled in Israel, producing 0.32 million tons of packaging paper and recycled white paper annually. The waste generated from the recycling of cardboard results in 31,000 tons of recycled paper sludge (RPS),

A valuable product that can be derived from these paper wastes are cellulose nanocrystals (CNC). These rod-like cellulose whiskers can serve as key building blocks in many industrial applications for the development of materials including thin films, nanocomposites, biomedicines, water-treatment materials and smart materials. However, lignin removal is necessary step in the production process as lignin reduces the separation efficiency of wood materials into their components. Ozonation has been examined as a technology for delignification due to its high oxidative capacity, low generation of inhibitory compounds, reduced pollution and savings in cleaning efforts. However, in the practices for which it was used, it was criticized for being costly and energy-demanding. The goal of this study was to determine the feasibility of ozone as a pretreatment process on recycled paper sludge (RPS) followed by recyclable maleic acid hydrolysis to produce CNC.

Materials and methods

RPS

RPS material was received from the Hadera Paper mill in Hadera, Israel. The RPS was dried, ground in a 250W laboratory blade mill (MRC Ltd., Israel) and sieved (450W, ALS Ltd., Israel) for the removal of most of the plastic, sand and dirt.

Ozonation treatment

Ozone experiments were performed in semi-continuous batch reactors that allow continuous addition of ozone to a fixed batch of water with suspended RPS. Ozone gas was generated using an oxygen-fed ozone generator (up to 4 g/h; BMT 802N, Germany) and the oxygen– ozone gas mixture was bubbled directly into the glass reactors. The reactor was filled with a suspension of RPS in DIW and operated under ambient conditions, with a constant gas flow of 0.35 L/min.

CNC recovery

After ozonation treatment, acid hydrolysis was conducted using 10 g oven-dried RPS fibers in 70 wt% maleic acid solution at 100°C for 90 min with stirring. The reaction was terminated and immediately vacuum-filtered and dried overnight in an oven. Dried RPS (1 g) was mixed in 100 mL DIW, sonicated and washed several times. The suspension was dialyzed against DIW for several days, centrifuged to separate large fibers, and was sonicated again for 20 min to obtain a colloidal suspension of CNC.
The total amount of recovered CNC was determined by chemical oxygen demand (COD), using COD tubes (Lovibond, England). Calibration curve was prepared using a known CNC powder (Nanografi, Turkey).

Maleic acid extraction and recovery after hydrolysis

After separation of the hydrolyzed RPS material from the acid liquor, the maleic acid was recovered by liquid–liquid solvent extraction method using ethyl acetate and NaCl. Ethyl acetate and the highly acidic wastewater were mixed

1:1 (v/v) in a separating funnel. A pinch of NaCl was added and vigorously mixed for a few more minutes before allowing phase separation. The upper layer (ethyl acetate) was collected and evaporated, resulting in a crystalline powder that was compared with standard maleic acid powder using attenuated total reflection–Fourier transform infrared (ATR–FTIR) spectroscopy (Tensor 27-IR, Bruker, USA).

Results and discussion

Ozonation of RPS was examined to determine the impact of ozone on the RPS characteristics. Lignin content (ABSL), was reduced by 43% from no ozone to 120 min of ozone during the ozonation process. This is reasonable as ozone has a high reaction rate constant with phenols (e.g., lignin) (1300 $M^{-1}s^{-1}$ for phenol). An increase in total phenol content in the liquid phase with increasing ozonation time was also observed suggesting ther release of phenols from the biomass. As RPS is the only material present during the ozonation experiment, these results strengthen the hypothesis of lignin's degradation to smaller phenolic substances during ozonation

At pH 5, the zeta potential is ζ = -6.5 mV for raw RPS and ζ = -7.7 mV, ζ = -9.6 mV and ζ = -12.4 mV after ozone treatment for 15 min, 60 min and 120 min, respectively. The increase in the negative zeta potential is linearly correlated with ozonation time. Upon ozone treatment, the IEP of RPS remained almost unaffected, while the apparent zeta potential shifted toward more negative values. Since the fiber structure and the swelling property are less likely to be affected by the ozone treatment, the shift in the apparent zeta potential is mainly assigned to a change in the fibers' surface charge. Ozone treatment induces the removal of non-cellulosic impurities and the oxidation of hydroxyl groups. The former enhances accessibility of readily available acidic groups, whereas the latter increases the number of these surface functional groups. XRD analysis showed a slight increase in CI with ozonation time and increase in crystallinity was observed after 55 min ozonation, from 80.33% to 86.53%, yet longer ozonation did not result in any other change in crystallinity. This is reasonable, as ozonation's effect on the crystalline regions of cellulose fibers has been found to be very limited

Recovery of CNC as determined by CNC concentration was demonstrated. Increased ozonation times (and hence accumulated ozone dose) resulted in an increase in the total CNC produced from the RPS, however total CNC only amounted to ~80 mg/L or 0.8% w/w. A reduction in total acid recovery was demonstrated with longer RPS ozonation pretreatments, varying from 31.25% acid recovery for RPS samples without ozone treatment to only 8.77% recovery for samples that were reacted with ozone for 120 min. It is assumed that the ozonation process affects the fiber composition or conformation (i.e., lignin removal or improved accessibility of acid to cellulose), enabling higher hydrolysis rates with the cellulose fibers, and resulting in less acid remaining for recovery and further recycling.

Conclusions

The ozonation process was examined as a pretreatment stage for CNC recovery from RPS, due to previous studies showing the high reaction rate constant of ozone with lignin components, which might result in delignification of the biomass or lead to other processes that allow access to cellulose fibers for further processing. Ozonation showed an increase in lignin removal from RPS materials with increasing ozone dose. This was also suggested by zeta potential analyses which showed that while the cellulose fibers were barely affected, the ozonation process stimulated the removal of lignin and other impurities. This resulted in higher accessibility of the cellulose fibers. Increased ozone doses resulted in an increase in CNC production; however, the total yield remained low at 0.8%, even at high ozone doses. Maleic acid may not be sufficiently strong for cellulose hydrolysis due to the high crystallinity value of RPS, and application of stronger acids should be examined. Despite low conversion yields, this work demonstrates the potential of ozonation as a pretreatment stage for CNC production from cellulose-rich wastes such as RPS.

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