



# Effective degradation of cellulose by Microwave irradiation in alkaline solution

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**Abstract** Lignocellulose biomass effectively produces chemicals and fuels, which are of importance for the establishment of a sustainable society. The conversion of cellulose, the main component of the biomass, into significant precursors that can be further converted to different chemicals or fuels under gentle conditions is a promising route. Organic acids such as acetic, glycolic and formic acid are significant examples. A novel method to produce important platform chemicals from micro-crystalline cellulose (MCC) was developed. MCC was degraded as a result of oxidation with potassium chlorate by microwave radiation in a one-pot procedure. Efficient reaction conditions such as short reaction time and full conversion of cellulose were identified. The reaction products were analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, XPS, TGA and XRD.

**Keywords** Cellulose degradation · Oxidation by  $\text{KClO}_3$  · Microwave Radiation · Basic environment

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## Introduction

Cellulose is the most abundant renewable resource of polysaccharides on earth. It is found in almost all plant sources including cotton (90%), corn cobs (45%), wood (40–45%), and bagasse (40%) and on stalks (35%) (Sundarraj and Ranganathan, 2018). Cellulose has broad applications in chemical industry due to its high availability, biocompatibility, biodegradability, and good mechanical properties. It is a linear polysaccharide composed of d-glucopyranosyl units bonded by  $\beta$  (1  $\rightarrow$  4) glycosidic linkage. Each d-glucose moiety has hydroxyl (OH) groups connected with C2, C3 and C6, which can create intramolecular hydrogen bonds within and between the cellulose macromolecules. Therefore, it is apparent that these OH groups and their intramolecular hydrogen bonds construct the crystalline structure and the rigid structure of cellulose, making it insoluble in common organic solvents and water and hindering its application (Liu et al. 2021).

The passage from nonrenewable carbon resources (petroleum) to renewable bioresources is inescapable for meeting the growing societal needs. The chemical industry is presently undergoing a paradigm shift from the utilization of fossil fuels to plants (cellulose) for the extraction of fine and bulk chemicals (Lin and Tanaka 2006). The conversion of renewable carbohydrates into important platform chemicals like levulinic, gluconic, lactic, and formic acid attracted much importance in recent years (Deng et al. 2014). These

significant organic acids are derived from cellulose, as well as isosorbide, xylitol, erythritol, glycerol, methanol, ethylene glycol, glycolaldehyde, and hydroxymethylfurfural by catalysis, hydrolysis, and oxidative cleavage (Li et al. 2018; Delbecq and Len 2018; Wang et al. 2018b). These organic acids are used in many commercial industries as food preservative, antibacterial agent in livestock feed, textiles, fuel cells, leather, cosmetics, curing and flavoring agents. Particularly, formic acid (FA) is a value-added chemical that was applied for the production of medicaments, solvents, fragrances, and fibers, as well as for the conservation of food products and forage, and was also used in the pulp and leather industries (Aguilo and Horlenko 1980). FA is a very promising substrate for the synthesis of molecular hydrogen over metal catalysts (Zacharska et al. 2015; Wang et al. 2013a, b; Zhang et al. 2013). The yield of FA from cellulose is as important as its conversion from CO<sub>2</sub> owing to the renewable nature of cellulose (Herrick and Lipták 2003).

Micro-crystalline cellulose (MCC) is mostly insoluble in water as well as in the most common organic solvents at gentle temperatures. This is an obstacle for the activation of MCC under mild conditions. Also, there are different types of bonds (C–C and C–O) in MCC macromolecules that create difficulty in its breakdown. Hence, the cleavage or oxidation of C–C and C–O bonds in MCC allows selective production of different compounds (Deng et al. 2014).

Considering the novelty of the current work, it must be pointed out that some of the oxidizing materials used in the current experiments were already attempted towards the degradation of cellulose. For example, potassium persulfate was used by Davaritouchaee and coworkers (Davaritouchaee et al. 2019) in the oxidation of wheat straw and revealed an increase in cellulose degradation temperature and a decrease in activation energy from 259 to 223 kJ/mol compared to the raw material. In another work, potassium permanganate was used to oxidize the cellulose, introducing the carboxyl groups into the oxidized polymer (Milanovic et al. 2021; Zhou et al. 2018). Cotton yarns were oxidized with potassium periodate solution with TEMPO systems. Sodium chlorite was also employed for the same purpose (Toshikj et al. 2019). However, to the best of our knowledge microwave radiation was never used in the oxidation of cellulose.

Here, MCC underwent successful oxidative degradation into important organic acids including FA, acetic acid (AA), and glycolic acid (GA) by the inorganic oxidizing reagent potassium chlorate (KClO<sub>3</sub>) using a short and facile one-step microwave-assisted method without employing any additives. The duration of microwave operation was optimized. This technique provides a novel chemistry tool that reduces the energy consumption and processing time (Scheme 1).

## Materials and methods

### Materials

The chemicals used in this study, namely MCC, KClO<sub>3</sub> and NaOH, were purchased from Sigma Aldrich (Israel). The oxidizing agents potassium permanganate (KMnO<sub>4</sub>), ammonium perchlorate (NH<sub>4</sub>ClO<sub>4</sub>), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), potassium chromate (K<sub>2</sub>CrO<sub>4</sub>), potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), potassium periodate (KIO<sub>4</sub>), potassium perchlorate (KClO<sub>4</sub>), and sodium periodate (NaIO<sub>4</sub>) were also obtained from Sigma Aldrich. The chemicals were used as received without another purification. Deionized water was used in all experiments.

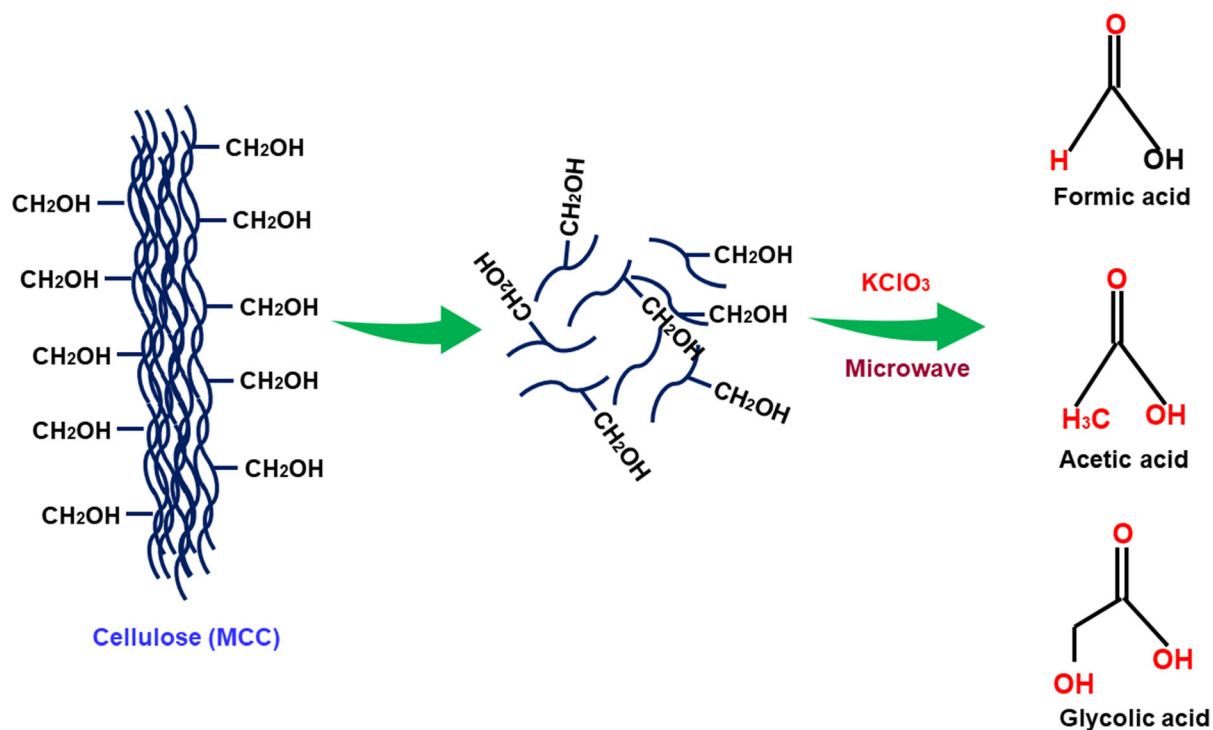
### Sample preparation

#### *Dissolution of MCC in aqueous NaOH*

Cellulose (0.5 g) was suspended in 26.9 mL of water, and 2.5 g of NaOH was added to the suspension. The mixture was shaken to dissolve the NaOH at room temperature. The suspension was cooled and held in a refrigerator until it became a solid frozen mass, which was allowed to thaw at room temperature and was transformed into a gel-like mass. 20.6 mL of water was added, and after gentle shaking, a clear cellulose solution was obtained (Isogai and Atalla 1998).

#### *Oxidation and degradation of MCC*

Oxidation of MCC was attempted using different oxidizing reagents with microwave and hydrothermally. The various oxidation agents used in this study are presented in Table 1. It is notable that all experiments were carried out under basic conditions



**Scheme 1** Schematic illustration of the conversion of MCC into organic acids by oxidation using the microwave-assisted method

**Table 1** Products of MCC oxidation with microwave under alkaline conditions for 1, 3 or 5 min

Reagent	Solvent	PH	Time (min)	Final products
Potassium permanganate	Alkaline solution	Basic	1,3, and 5	–
Ammonium perchlorate	Alkaline solution	Basic	1,3, and 5	–
Potassium persulfate	Alkaline solution	Basic	1,3, and 5	–
Potassium chromate	Alkaline solution	Basic	1,3, and 5	–
Potassium dichromate	Alkaline solution	Basic	1,3, and 5	–
Potassium periodate	Alkaline solution	Basic	1,3, and 5	–
Sodium periodate	Alkaline solution	Basic	1,3, and 5	–
Potassium perchlorate	Alkaline solution	Basic	1,3, and 5	–
Potassium chlorate	Alkaline solution	Basic	1,3, and 5	FA, AA and GA

(pH = 12), and the domestic microwave oven (Sharp) was operated for 1, 3 or 5 min at a power of 1100 W. Potassium chlorate (0.1 g) was added to a 250 mL round bottom flask that contained 50 ml of the clear cellulose solution, and the flask was subjected to microwave irradiation for 5 min. The resulting product was centrifuged at 8000 rpm for 30 min. The formation of the gel-like product was allowed for all characterizations.

Table 1 reveals that only  $\text{KClO}_3$  successfully oxidized the cellulose.

### Characterization

The chemical structure of the oxidized MCC was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) on a 300 MHz spectrometer (Bruker) using  $\text{NaOH}/\text{D}_2\text{O}$  as the solvent. The elemental composition and chemical bonding were analyzed using X-ray photoelectron spectroscopy (XPS) using a Nexsa (England) spectrometer. The detection and identification of the degradation of MCC were also measured by thermogravimetric analysis (TGA) on a

Perkin Elmer Clarus 680/Clarus SQ 8C instrument. The flow rate of nitrogen was 20 mL/min, and the temperature rate was increased at 10 °C/min, the samples (MCC and oxidized MCC) were heated from 30 to 950 °C. The difference in the morphology of the surface and the size of the pure MCC particles and the degraded MCC (DMCC) was characterized by environmental scanning electron microscopy (E-SEM) using a *Quanta* FEG 250 (FEI) device at 5 kV. The crystalline nature of the MCC and DMCC composites was assessed using an X-ray diffraction (XRD) technique measured by a Bruker (Germany) AXS D8 Advance diffractometer.

## Results and discussion

### NMR spectrum of the attained product

The NMR spectra of the oxidized MCC in aqueous solution are given in Fig. 1. The evidence for the successful oxidation of MCC was obtained from both  $^1\text{H}$  (Fig. 1a) and  $^{13}\text{C}$  (Fig. 1b) NMR. Significant differences are observed between the initial and final MCC after oxidation in aqueous solution. The  $^{13}\text{C}$  NMR spectrum of the initial material was obtained from the literature (Heinze and Koschella 2005). The NMR spectra of the starting compound and product obtained after oxidation of the MCC are compared.

Figure 2 displays the  $^{13}\text{C}$  solid-state NMR (SSNMR) spectrum of the cellulose. The spectrum matches very well recently published spectra (Hussin et al. 2018; Okushita et al. 2012; Newman et al. 1996; Wang et al. 2013a, b). The main peaks of the cellulose appear at 65.3, 71.8, 72.6, 75.2, 89.1, and 105.36 ppm are assigned to C6, C2, C3, C5, C4 and C1, respectively (Fig. 2). It is clear from Fig. 1a and b that these peaks disappeared in the product, indicating the successful oxidation and elimination of the cellulose, corroborated by the changes in the peaks of the final product.

Figure 1a illustrates results for the aqueous  $^1\text{H}$  NMR of the NaOH treated product. Figure 1b presents the corresponding  $^{13}\text{C}$  NMR of the solution in  $\text{D}_2\text{O}$  of the NaOH solution of the product. The disappearance of the cellulose peaks is the most remarkable feature, indicating the successful oxidation of the cellulose.

Figure 1b shows the peaks of the  $^{13}\text{C}$  NMR spectrum located at 24 and 172 ppm which represent

the carbons of acetic acid. The two peaks at 62 and 182 ppm represent the carbons of glycolic acid, and the peak at 169 ppm is attributed to formic acid. Moreover, the peaks of the proton NMR spectrum also match the hydrogens of FA, AA and GA, which are found in H (t) at 1.811, 1.837 and 1.847 ppm (AA), 8.111 ppm (FA), and 3.586 ppm (GA) (Table 2).

Moreover, in previous studies, the oxidizing materials that were used for cellulose degradation such as vanadium (V)-containing catalyst, a high-cost material, usually undergo at least two reactions (Lu et al. 2018). Another oxidizing catalyst, Mo-V-P heteropoly acids, have a long catalytic synthesis (Gromov et al. 2016). Carbon electrodes modified by gold nanoparticles (Sugano et al. 2016) are also expensive, and TEMPO-mediated oxidation system requires preparation step (Isogai et al. 2018) The oxidation of cellulose with the catalytic aqueous mixture of  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} + \text{H}_2\text{SO}_4$  with molecular oxygen (Lu et al. 2016) is a very slow process compared to our method.

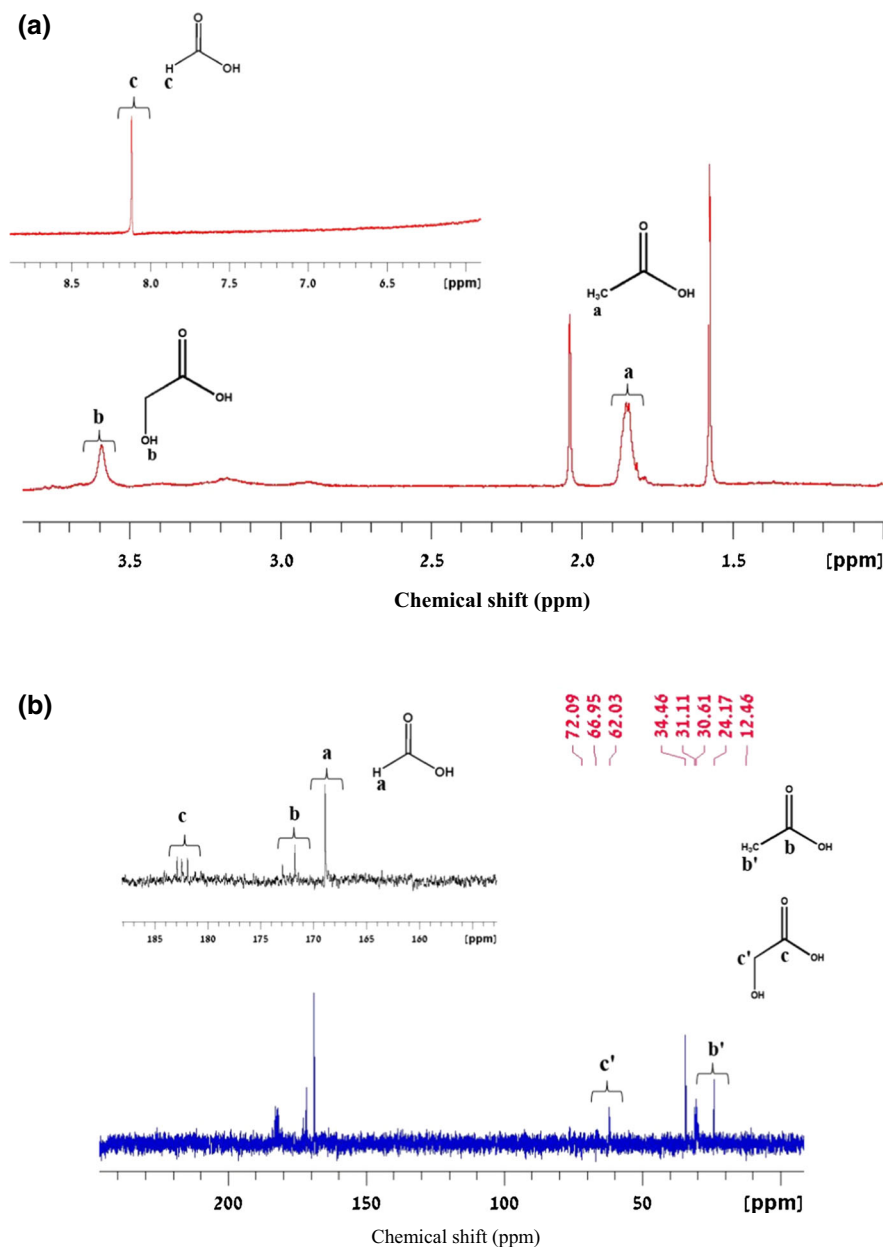
Thermochemical conversion of cellulosic materials can also be achieved by microwave heating (Motasemi and Afzal 2013; Al Shra'Ah and Helleur 2014; Wang et al. 2008). In conventional thermal heating, the energy is transferred from the source to the center of material via radiation, convection, and conduction, while in the microwave or dielectric heating the electromagnetic energy is converted to thermal energy from inside the sample.

The microwave-assisted reactions can be completed more efficiently in comparison with other thermal methods due to efficient heat transfer profiles. For this reason, microwave heating appears as one of the promising techniques for carrying out the biomass pyrolysis process, accelerating chemical reactions and reducing the processing costs. The combination of microwave radiation and  $\text{KClO}_3$  is novel and was apparently not reported previously.

### Thermogravimetric analysis (TGA) of thermal degradation of oxidized MCC

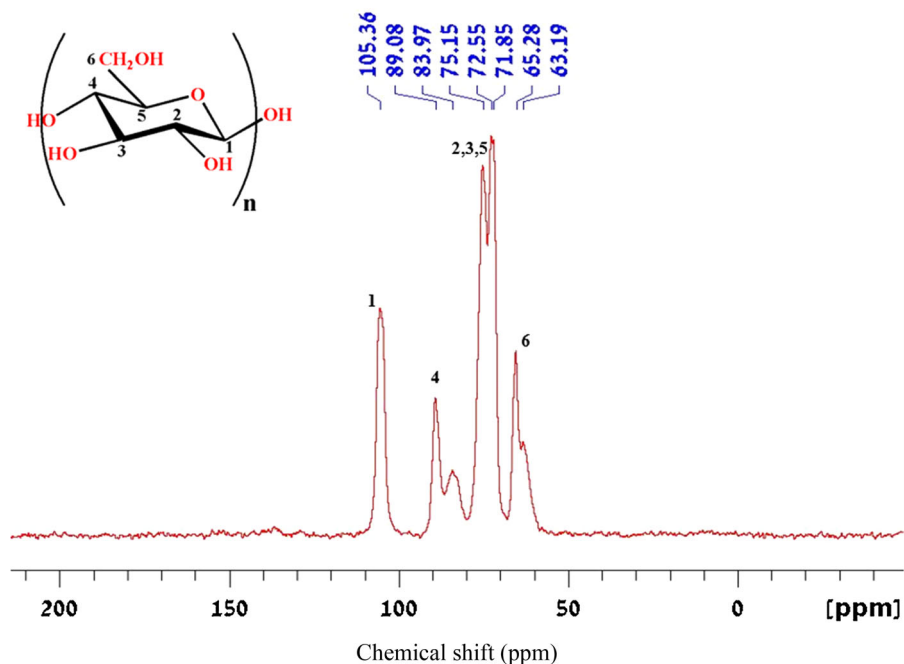
The TGA analysis in Fig. 3 shows the curves of the thermal decomposition of MCC and DMCC obtained after potassium chlorate treatment under microwave conditions. The thermal decomposition ( $T_d$ ) point of the DMCC was approximately 38 °C, which was lower than the original decomposition temperature of pristine cellulose (300 °C). From 30 to 300 °C, the

**Fig. 1** **a**  $^1\text{H}$  NMR of degraded MCC (DMCC).  
**b**  $^{13}\text{C}$  NMR spectrum of DMCC



mass of cellulose was almost unchanged. In contrast, the onset decomposition temperature for DMCC was 38 °C, and the weight loss continues until 90 °C. The difference between the two curves is clear indicating the absence of cellulose from DMCC. The difference between MCC and DMCC is also reflected in their stability. The highest boiling point of the degradation products (AA, FA and GA) is 118 °C which belongs to AA. The curves of DMCC show a continuous weight loss at temperatures below 200 °C. At 450 °C, MCC

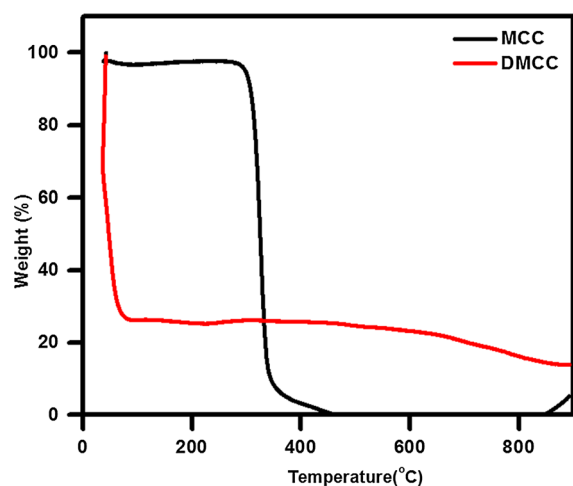
and DMCC show residual weights of 0 and 23%. DMCC was collected from the reaction mixture after the completion of the oxidation process (Rosli et al. 2015). The 18% of DMCC after heating to 800 °C is perhaps carbon char that was left from the decomposition of the degradation products.



**Fig. 2**  $^{13}\text{C}$  Solid-state NMR (SSNMR) spectrum of cellulose

**Table 2**  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift ( $\delta$ , ppm) values of the decomposition products of cellulose

Compound	$^1\text{H}$ chemical shift ( $\delta$ , ppm)	$^{13}\text{C}$ chemical shift ( $\delta$ , ppm)
Formic acid	$^1\text{H}$ (singlet) at 8.111	169
Acetic acid	$^1\text{H}$ (triplet) at 1.811, 1.837, 1.847	24, 172
Glycolic acid	$^1\text{H}$ (singlet) at 3.586	62, 182

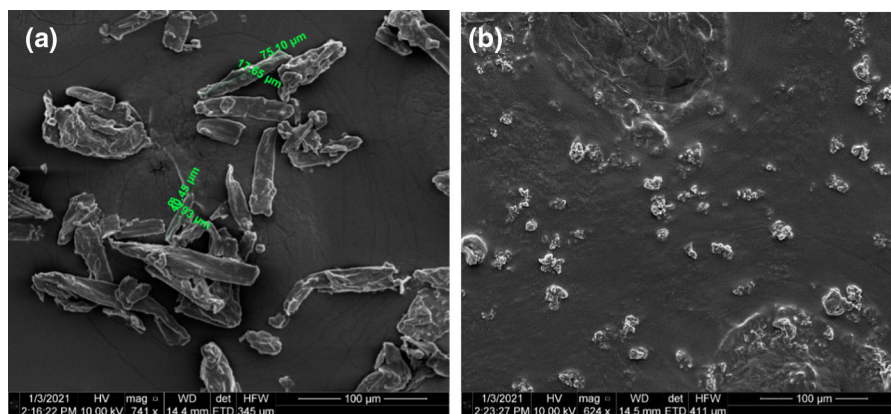


**Fig. 3** TGA curves of MCC and DMCC

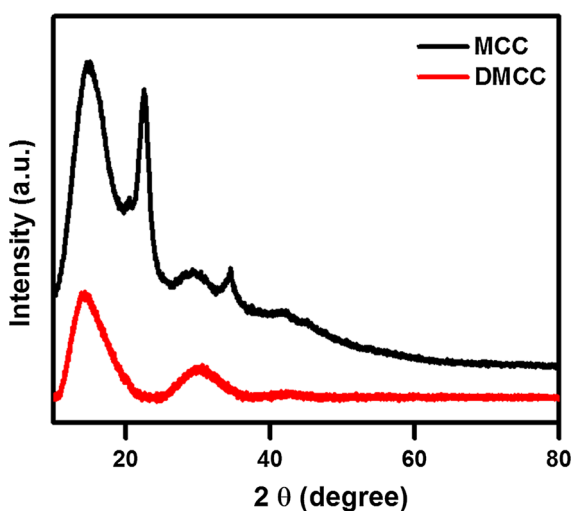
#### Scanning electron microscope (SEM)

SEM helps to reveal the morphological and topographical features of the precursors and the resulting carbon composites. The E-SEM images of cellulose are presented in Fig. 4a (before) and Fig. 4b (after) oxidation. Before oxidation and degradation, the cellulose particles resembled blocks and logs of wood. After degradation, the original crystallinity of the cellulose particles is lost. The morphology of the cellulose crystals changed after oxidation, which substantiates the TGA results on the successful degradation of the cellulose.





**Fig. 4** Scanning electron microscopy (SEM) images of **a** commercial MCC and **b** DMCC



**Fig. 5** XRD patterns of microcrystalline cellulose before and after oxidation and degradation

#### X-ray diffraction (XRD)

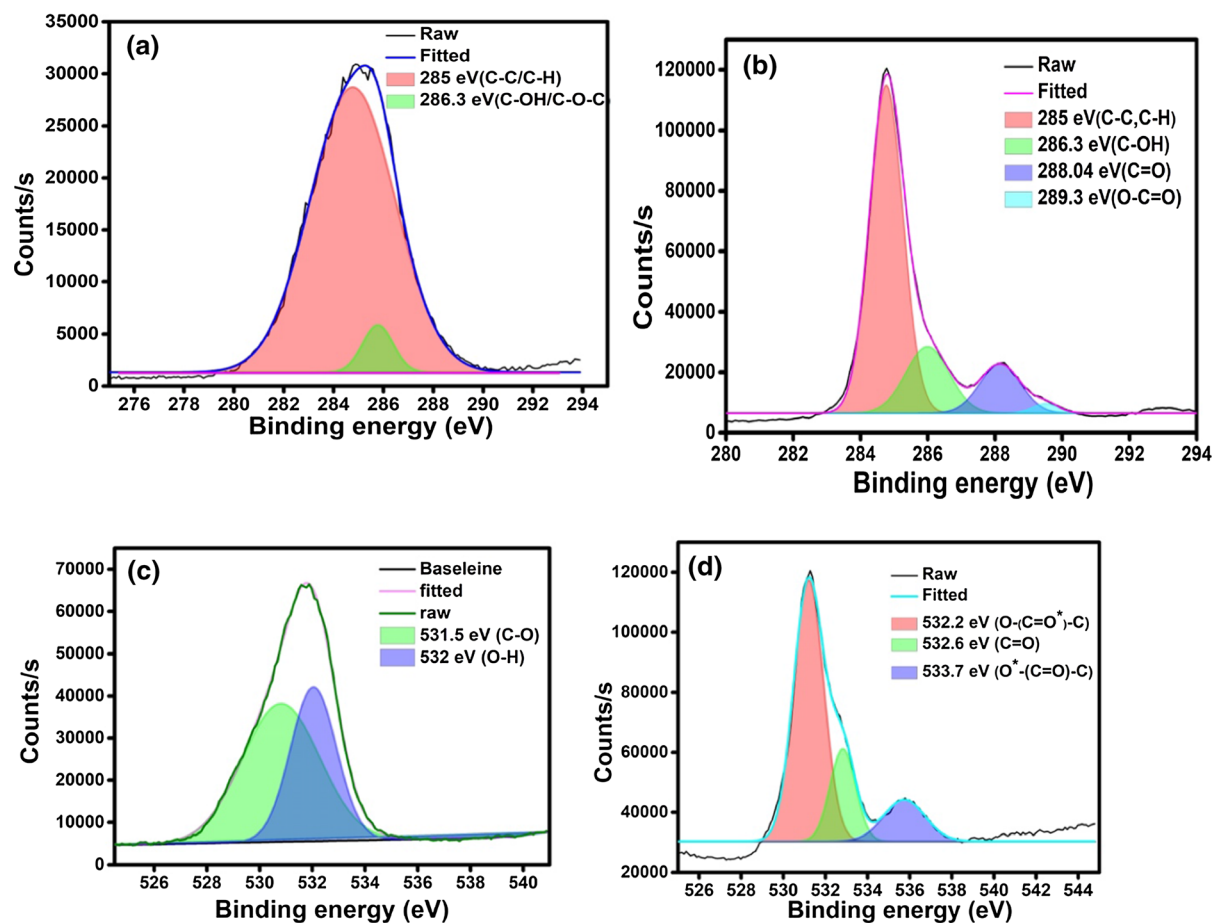
To further determine the change in crystallinity, the XRD patterns of MCC and DMCC are shown in Fig. 5. For MCC there are crystallographic diffraction peaks around  $2\theta = 34.45^\circ$ ,  $22^\circ$  and  $15^\circ$  (Pang et al. 2014), indicating the characteristic cellulose I crystal structure. After oxidation and degradation, the crystalline peaks near  $22^\circ$  and  $35^\circ$  disappeared, and the peak around  $2\theta = 15^\circ$  widened and became less sharp. These results demonstrate that the crystallinity of cellulose was noticeably decreased. The peak at  $30^\circ$  belongs to the holder, as it can be seen in the curve of the empty holder that contains peaks around  $2\theta = 30^\circ$  and  $41^\circ$ . This result is in accordance with the SEM

results, confirming that the oxidation reaction decomposes the cellulose polymer and diminishes its crystallinity.

#### X-ray photoelectron spectroscopy (XPS)

XPS analysis provides information about the surface elemental composition and functional groups. The images in Fig. 6 obtained from XPS patterns of MCC and the DMCC present the difference in the functional groups that appear in the product. Both products consist mainly of carbon and oxygen. The cellulose polymer has two types of functional groups—the multiple hydroxyl groups per unit of the polymer had one primary and two secondary alcohols, and one ether group. Figure 6a shows the C1s spectra of MCC which is deconvoluted into two peaks located at 285.0 and 286.3 eV, representing C–C/C–H and C–O–C/C–OH groups. However, the C1s spectrum of DMCC reveals additional peaks at 288.0 and 289.3 eV, corresponding to C=O and COO<sup>−</sup> as well as a shoulder at 286.3 eV assigned to C–OH. These peaks belong to the organic acids after degradation (FA, AA and GA). Figure 6c and d compare the oxygen (O1s) spectra of MCC and DMCC and reveal the new bonds in the product. The peaks in the O1s spectrum of DMCC disclosed three main classes of oxygen bonds: (Table 3).

All the characterization experiments lead to the same conclusion—the DMCC product differs from the cellulose. In this work, we found that only potassium chlorate was able to oxidize the MCC. The other nine well-known oxidizing agents were not successful in this oxidation process neither by microwave nor



**Fig. 6** XPS patterns of the C1s and O1s spectra of **a, c** MCC and **b, d** DMCC

**Table 3** XPS peaks of DMCC

Bond	Peak value (eV)
O-(C=O*)-C bonds peaks	532.2 in GA and AA
O*-(C=O)-C bonds peaks	533.7 in GA and AA
Carbonyl, organic C = O bonds	532.6

hydrothermally. Even for the chlorate ions, negative results were obtained when the reaction was carried out hydrothermally at 80 °C for 8 h. No degradation of cellulose was detected for the other oxidizing agents. We are therefore left with two major questions: 1) why only  $\text{ClO}_3^-$  can oxidize the MCC under microwave (MW) radiation and 2) why these products are obtained only by MW irradiation?

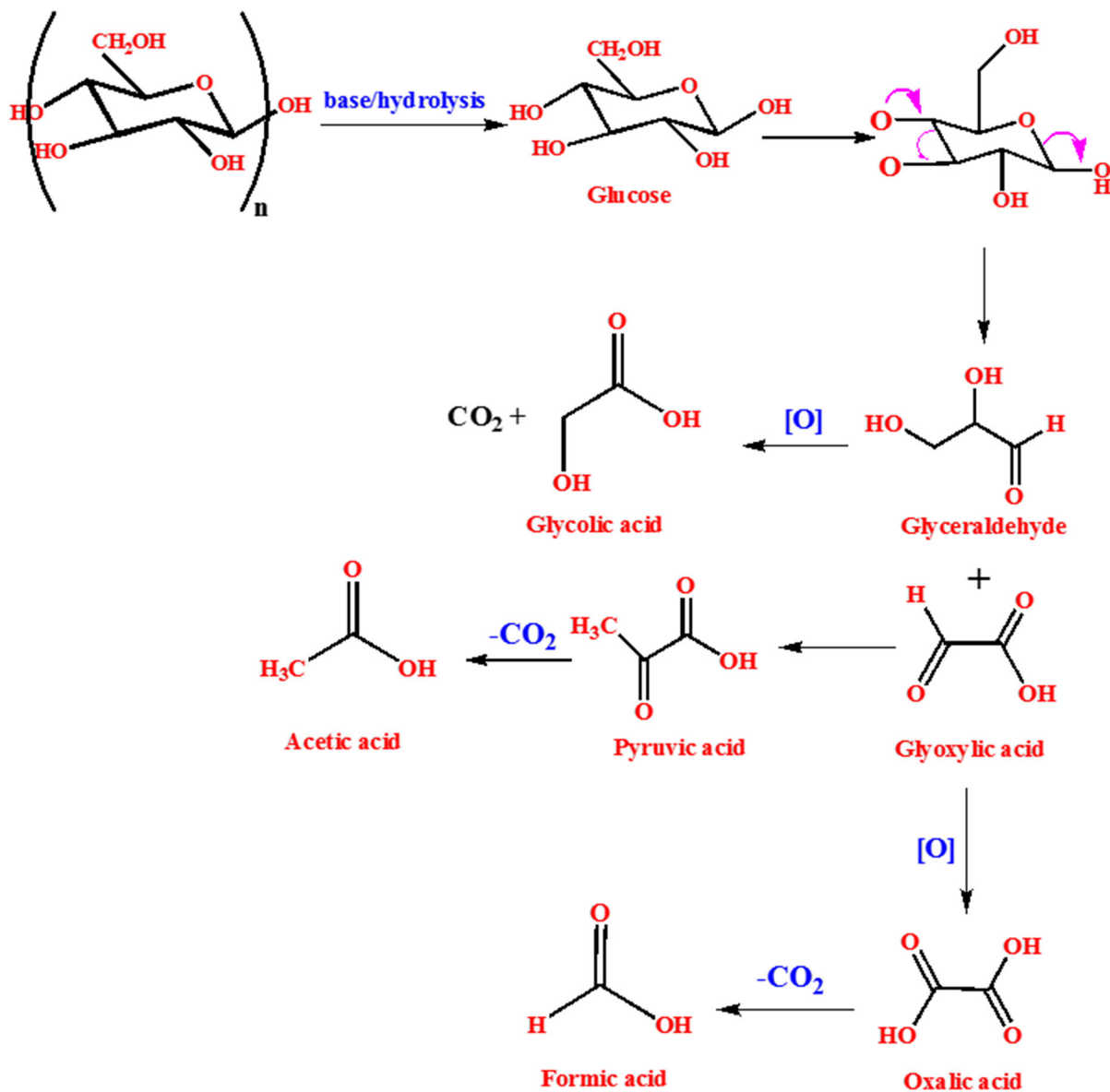
First, we tried to correlate the oxidizing power to the standard oxidation potential (Table 4). The

**Table 4** Standard oxidation potential of the reagents

Reagent	Oxidation potential (V)
$\text{K}_2\text{S}_2\text{O}_8$	2.1
$\text{KMnO}_4$	1.49
$\text{KClO}_4$	1.39
$\text{NH}_4\text{ClO}_4$	1.39
$\text{K}_2\text{Cr}_2\text{O}_7$	1.36
$\text{KClO}_3$	1.15
$\text{NaIO}_4$	- 0.7
$\text{KIO}_4$	- 1.65
$\text{K}_2\text{CrO}_4$	- 6.5

table indicates that the chlorate is not the strongest oxidizing agent. However, to this table, we must add the basic conditions under which the reaction is

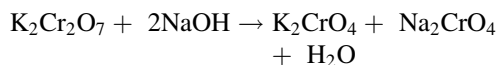




**Scheme 2** The oxidation and degradation mechanism of cellulose

performed, namely  $\text{pH} \sim 11$ . Under these basic conditions, chlorate is the strongest oxidizing agent, while for example  $\text{K}_2\text{S}_2\text{O}_8$  decomposes fast under these conditions to  $\text{HSO}_4^-$ . Potassium permanganate is also a stronger oxidizing agent than  $\text{ClO}_3^-$  but this is only true for acidic medium; it is a weak oxidant in both neutral and alkaline medium (Peroxide et al. 2019). Potassium dichromate acts as an oxidizing agent only in an acidic medium. It does not act as oxidizing agent in basic medium, which involves a

non-redox reaction whereby it forms chromate ion. In basic medium, Cr has a + 6 oxidation state in both dichromate and chromate forms and reacts according to the following reaction:



The main products in the one-step oxidation of cellulose by chlorate ions were FA, GA and AA.

The proposed mechanism is speculative. To comprehend the mechanism of the cellulose degradation, we examined whether the degradation mechanism involves first the decomposition of the cellulose to glucose. This was done by a control experiment in which identical conditions were used to oxidize the glucose as for the cellulose. The NMR results (Fig.S1) display a different spectrum compared with the peaks in Fig. 1b. The NMR peaks indicate that different products such as glucuronic acid and glucose were obtained in the oxidation of glucose. Moreover, unlike cellulose the glucose was not completely degraded. It is still speculated that glucose is an intermediate product, but perhaps it is formed in its excited state and therefore leading to different products. These results show that the degradation of cellulose does not proceed via glucose.

Returning to the second question regarding why MW radiation, MW is a well-known means for accelerating chemical reactions especially for reactants or catalysts with a dipole moment. The ability to accelerate a chemical reaction is attributed to heating effect in which the “real” temperature is higher than the measured temperature. This is frequently termed superheating (Tao et al. 2021) or the existence of hot spot (Liu et al. 2020). The other explanation is a drastically reduced activation energy allowing the reaction to progress along a new mechanistic route. This is particularly useful when the transition state has a dipole moment which strongly interacts with the MW radiation. These two factors play an important role in accelerating the reaction. The presence of many  $\text{ClO}_3^-$  and  $\text{OH}^-$  ions plus their counter ions helps to absorb the radiation and leads to hot spots. In addition, the transition state of the reaction also has a dipole moment and speeds up this chemical reaction. In the first step, the base hydrolysis forms the glucose. In the next step, the glucose oxidizes by  $\text{KClO}_3$  and forms a different product with MW condition, shown in Scheme 2. The formation of the acids was confirmed by NMR techniques (Wang et al. 2018a).

## Conclusion

In conclusion, we presented a fast and facile method to convert the highly micro-crystalline commercial cellulose into a precious and significant product like formic, acetic, or glycolic acid. The novelty of this

strategy for decomposing cellulose comprises two concepts: (1) to use an inorganic oxidizing reagent to oxidize the cellulose and (2) expose the degradation of cellulose by microwave irradiation for a maximum of 5 min. Therefore, the practicability of using cellulose as a feedstock for extraction of important chemicals is demonstrated.

## Declarations

**Conflict of interest** The authors have no conflicts of interest to declare that they are relevant to the content of this article.

**Human and animal rights** This article does not contain any studies with human participants or animals performed by any of the authors.

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