



# Sustainable commercial nanocrystalline cellulose manufacturing process with acid recycling



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## ABSTRACT

Nanocrystalline cellulose (NCC) is a biomaterial having potential applications in a wide range of industries. It is industrially produced by concentrated acid hydrolysis of cellulosic materials. In this process, the sulfuric acid rich liquor can be concentrated and reused. However, removal of sugar monomers and oligomers is necessary for such recycling. Membrane and ion exchange technology can be employed to remove sugars; however, such technologies are not efficient in meeting the quality required to recycle the acid solution. As a part of the present study, activated carbon (AC) has been evaluated as an adsorbent for sugar removal from the acidic solution generated during commercial nanocrystalline cellulose manufacturing process. Almost complete removal of sugar can be achieved by this approach. The maximum sugar removal observed during this study was 3.4 g/g of AC. Based on this finding, a sustainable method has been proposed for commercial nanocrystalline cellulose manufacturing.

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## 1. Introduction

Cellulose is one of the highly abundant natural polymers, which is basically a linear polysaccharide made up of hundreds to thousands of D-glucose monomers. Wood and plant fibers such as cotton and jute are the major sources of cellulose. In addition to its traditional uses such as paper and cloth making, cellulose or its derivatives have many other applications as food, cosmetic and pharmaceutical ingredients (Shokri & Khosro Adibkia, 2013). It has also been evaluated for environmental applications such as synthetic dye removal from wastewater (Yan et al., 2011). As a result of inter molecular interactions, within the cellulose based biomass; long cellulose molecules arrange themselves as amorphous (not organized as crystal) and crystalline (having the properties of crystal) regions. Crystalline regions can be converted to nanocrystalline cellulose (NCC) by acid hydrolysis of cellulose based biomass (Brinchi, Cotana, Fortunati, & Kenny, 2013; Peng, Dhar, Liu, & Tam, 2011). NCC from wood cellulose is 5–20 nm in diameter whereas the length could be as high as in micrometer range (<http://blog.luxresearchinc.com/blog/2014/11/nanocrystalline-cellulose-production-opportunities-and-challenges/>). High specific strength and larger surface area

per unit weight of the material, surface charge, size, shape and its behavior in solution or under magnetic field distinguish this material from normal cellulose fibers (Peng et al., 2011; <http://www.celluforce.com/en/products/cellulose-nanocrystals/>). Well organized crystalline structure of the NCC makes it mechanically stronger than normal cellulose. Due to the similar reason NCC demonstrates better thermal stability. Although cellulose is the fiber of choice for conventional large scale applications such as paper or cloth manufacturing, NCC is more suitable for some high value applications such as an ingredient of strong, lightweight composite material synthesis, drug delivery, tissue engineering, antimicrobial application, in enzyme/protein immobilization, as a template for mesoporous material synthesis and green synthesis of metallic nanoparticles (Jorfi & Foster, 2015; Peng et al., 2011; Qing et al., 2016; <http://www.nrcan.gc.ca/forests/industry/products-applications/13349>). As well as, it has been found to be superior in various environmental applications, such as heavy metal removal from wastewater (Carpenter, Lannoy, & Wiesner, 2015).

During the nanocrystalline cellulose (NCC) manufacturing process, a dilute sulfuric acid stream is generated which contains different types of sugars. The manufacturing process generally employs membrane technologies for the separation of sugars, however still there is a significant portion of sugar left in the residual acid stream. The sugar components add complexity to the concentration and reuse of the acid stream. A simple method to increase the sugar removal would allow the acid to be concentrated to a

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higher degree of reuse. Therefore, developing such a method was the major objective of this study.

Activated carbon is a good absorbent which has been successfully used for removal of different organic pollutants (Hu, Shang, Heijman, & Rietveld, 2015; Ruhl et al., 2014). A highly porous structure and presence of a range of functional groups have made it an attractive material for removal of hydrophilic molecules (De Ridder, 2012). As sugars are hydrophilic compounds, activated carbon was identified as a possible candidate for sugar removal from the acid liquor generated during the nanocrystalline cellulose (NCC) manufacturing process. In order to provide a larger surface area and likely higher adsorption, activated carbon having particles at the nano-scale was used in the present investigation. The effects of different process parameters were investigated by statistical experimental design. A simplified schematic of the NCC manufacturing process and the proposed strategy for removing sugar from the acid liquor is presented in Fig. 1.

## 2. Materials and methods

### 2.1. Activated carbon (AC) and the acid sample

The activated carbon (Fisher Scientific, Canada) used in the present investigation has been characterized for particle size and zeta-potential distribution. These analyses were carried out using a zetasizer nano ZS (Malvern instruments Ltd., UK). 1000 mg/L of the particles were dispersed in distilled water. The solution was further diluted with distilled water until the sample quality was determined by the instrument to be good. Disposable folded capillary cell (DTS1070, Malvern instruments Ltd., UK) was completely filled by the sample and used for zeta-potential distribution analysis. Similarly, 1.5 mL of the sample was taken in normal disposable cuvette and used for particle size analysis.

The acid liquor sample was generated by raw material hydrolysis during nanocrystalline cellulose production and supplied by the industrial partner. The pH of the solution was about 0.6, and its total carbohydrate concentration was about 6.5 g/L. Glucose and xylose were the two major sugars present in the solution. Unidentified disaccharides and oligosaccharides were the other likely constituents of the sample (Qing, Li, Kumar, & Wyman, 2013). Identification and quantification of individual components of the solution would have provided a better understanding about removal of each compound. However, all these compounds can be collectively quantified as total carbohydrate (Martens & Loeffelmann, 2002) by a relatively simple method; therefore, identification of each constituent was not done.

### 2.2. Determination of sugar concentration in the acid stream

The sugar concentration in the acid stream was determined by the anthrone method (<http://web.itu.edu.tr/~dulekgurgen/Carbs.pdf>) and expressed as total carbohydrate. Briefly, a 1 mL sample was diluted 50 times with distilled water and then about 2 mL of chilled H<sub>2</sub>SO<sub>4</sub> (75% v/v) was added and mixed. This solution was mixed with 4 mL of chilled anthrone reagent and the resulting mixture was put in a closed COD vial and boiled for 15 min at 100 ± 1 °C. After cooling to room temperature, the absorbance was measured at 578 nm. The anthrone reagent used in this analysis was freshly prepared by dissolving 0.5 g of anthrone in 10 mL of ethanol and made up to a volume of 250 mL by using H<sub>2</sub>SO<sub>4</sub> (75%). Glucose was used as the standard compound to prepare the standard curve used for this analysis. For this purpose, five different concentrations of glucose, viz., 20, 40, 60, 80 and 100 mg/L were processed as described above and absorbance (578 nm) of resulting solutions were measured and plotted against the concentrations.

### 2.3. Investigation of the effect of activated carbon (AC) concentration on sugar removal

For this investigation, 1 g/L to 100 g/L of AC was added to the acid liquor received from the industry. The suspensions were mixed at room temperature (23 ± 1 °C) for 15 min with magnetic stirring. Immediately after mixing, the solutions were centrifuged at 10,000 rpm (6708 × g) for 10 min and AC and adsorbed sugar were separated. Supernatants were centrifuged again under the same conditions to obtain clear solutions. These solutions were analyzed to determine residual sugar concentration. The residual sugar concentration was again determined by the anthrone method as described above.

### 2.4. Investigation of the effect of reaction time on sugar removal from the acid liquor using AC

For this investigation, 50 g/L of AC was added to the acid liquor. The suspension was mixed at room temperature (23 ± 1 °C), for 15, 30, 60, 120 and 180 min with magnetic stirring. After mixing, the samples were centrifuged as before and AC and adsorbed sugar were separated. The sugar concentration in the supernatants was determined again by the anthrone method.

### 2.5. Investigation of the effect of temperature on sugar removal from the acid liquor using AC

For this investigation, 50 g/L of AC and acid liquor was mixed with magnetic stirring for 15 min at 4 ± 1 °C, 23 ± 1 °C and 45 ± 1 °C. The AC and adsorbed sugars were removed and the residual sugar concentration determined as before.

### 2.6. Investigation of the potential to reuse AC in the sugar removal process

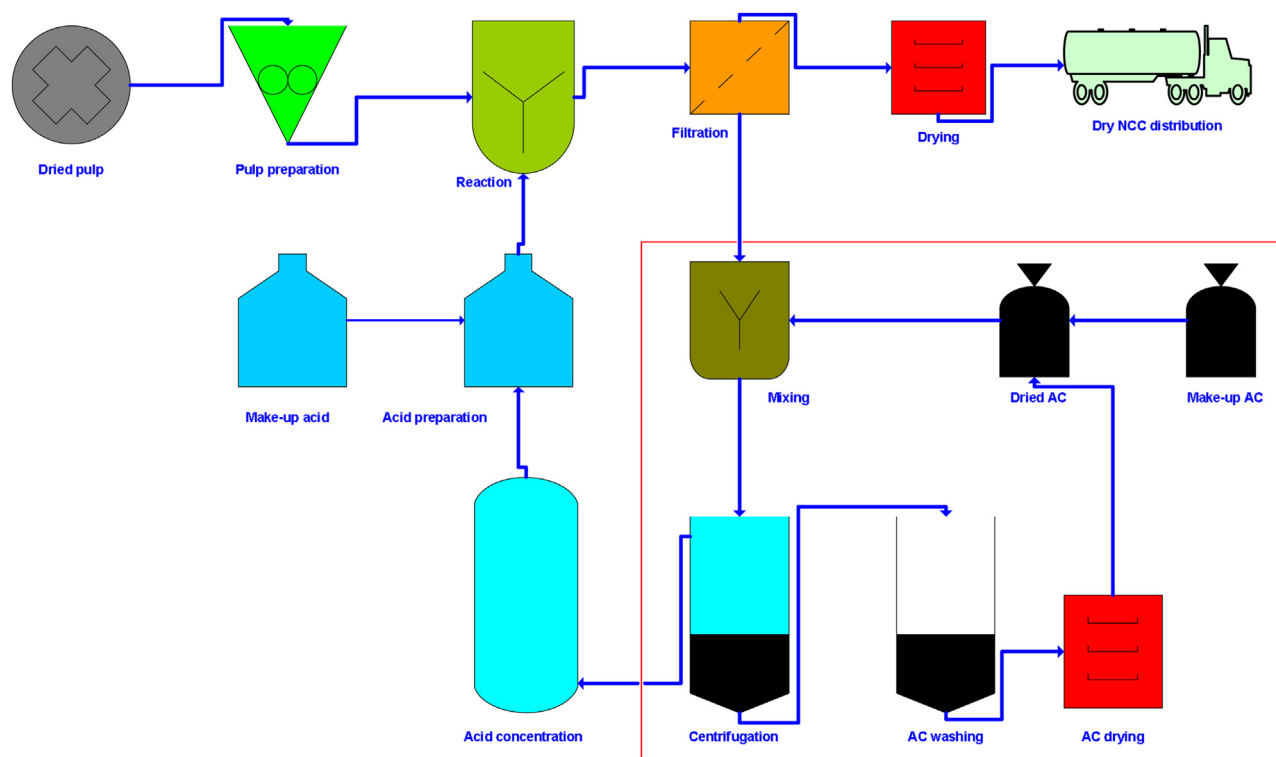
For this investigation, 50 g/L of AC was mixed with the acid liquor for 15 min at room temperature (23 ± 1 °C) and subsequently separated by centrifugation (10,000 rpm or 6708 × g for 10 min). Following separation, the AC was washed with an equal volume (1 L for 50 g) of distilled water, again separated by centrifugation (10,000 rpm or 6708 × g for 10 min) and dried at 105 ± 1 °C. The dried AC (50 g/L) was cooled down to room temperature then added back to the acid liquor and the procedure was repeated 5 times. The feasibility of using wet AC was not considered in this study but would be done so before industrial application.

### 2.7. Two step treatment of the acid liquor with fresh AC for sugar removal

At room temperature, 50 g/L of AC was mixed with the acid liquor for 15 min and adsorbed sugar was separated as before (by centrifugation at 10,000 rpm or 6708 × g for 10 min). The supernatant containing residual sugar was subjected to a second treatment using 50 g/L of fresh AC. All other reaction conditions of the second treatment were similar to that of the first treatment. Sugar removal efficiency was determined by the same method as described before.

### 2.8. Investigation of the effect of sample pre-concentration on sugar removal from the acid liquor using AC

The acid liquor samples were concentrated by evaporating the liquid at 100 ± 1 °C. A specified concentration of AC (Table 1) was added to the concentrate and the suspension was mixed for 15 min at room temperature (23 ± 1 °C). Samples were processed and sugar concentrations were determined as mentioned before.



**Fig. 1.** Schematic representation of nanocrystalline cellulose (NCC) manufacturing process presently employed by the industry. Different steps of the proposed sugar removal approach are within the red outlined box. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**  
Investigation of the effect of sample pre-concentration on sugar removal from the waste acid stream using AC.

Sl. No.	First Treatment			Second Treatment			Cumulative removal (%)
	Pre-concentration	Activated Carbon	Centrifugal separation	Pre-concentration	Activated Carbon	Centrifugal separation	
1	–	50 g/L	Yes	–	–	–	86.79
2	2 times	100 g/L	Yes	–	–	–	44.55
3	4 times	200 g/L	Yes	–	–	–	NONE
4	–	50 g/L	Yes	3 times	50 g/L	Yes	91.24

### 2.9. Investigation of the effect of autoclaving on sugar removal from the acid liquor using AC

Two sets of experiments were conducted. In the first set, AC (50 g/L) was added to the acid stream and the solution was autoclaved at 121 °C for 20 min. In the second set, the acid stream was autoclaved under the same conditions and then AC (50 g/L) was added. The remaining procedures were as before. The removal efficiency in these experiments was compared with that of an experiment carried out without autoclaving.

### 2.10. Statistical experimental design to investigate sugar removal by the proposed method

AC concentration (g/L) and mixing time (min) were investigated by statistical experimental design. The ranges of the two factors used are shown in Table 2. Table 3 shows the central composite design used to plan 13 different sets of experiments. The design matrix used in the study was constructed using Design-Expert®-7 software (Stat-Ease Inc. Minneapolis, MN), where sugar removal efficiency was used as the response. Based on ANOVA, a response surface linear model was found to be appropriate (p value: 0.013) to explain the responses.

## 3. Results and discussion

### 3.1. Activated carbon (AC): characterization and properties

Particle size and zeta-potential distributions of the activated carbon used in the present study are presented in Fig. 2a and b, respectively. Particles were found to be around 120 nm in diameter. Three zeta-potential peaks were found at  $-1.88$  (51.7%),  $-24.3$  (10%) and  $23.7$  (38.3%) mV, indicating the presence of particles belonging to three distinct surface charge groups (<http://ncl.cancer.gov/NCL.Method.PCC-2.pdf>; Patravale, Dandekar, & Jain, 2012 (Chapter 3)). Roles of the particles belonging to each surface charge group on sugar removal could be a subject of further fundamental investigation; however, it was not considered during this study.

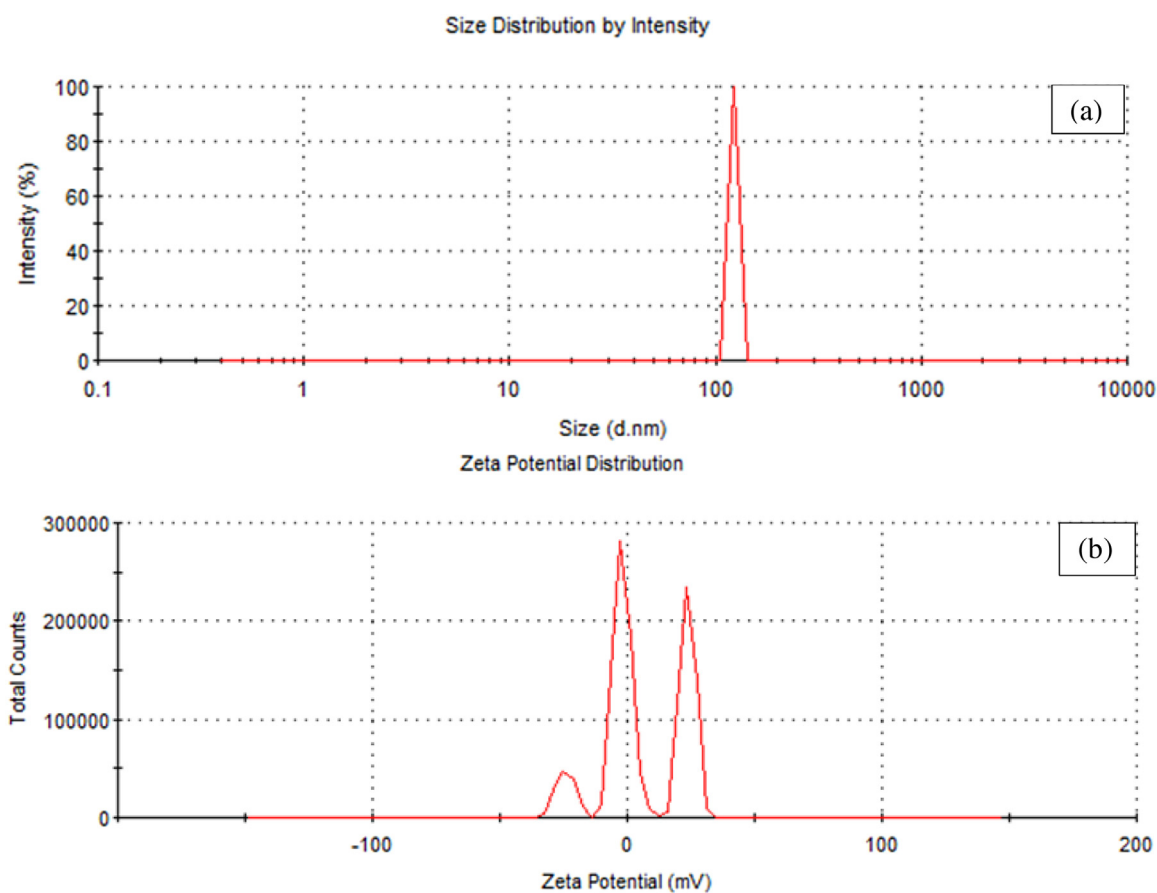
Although activated carbon can be produced from any carbon rich substance; wood, charcoal, and bituminous coal are some of the materials mostly used due to their low inorganic constituents (Dąbrowski, Podkościelny, Hubicki, & Barczak, 2005). Li, Lee, and Gullett (2003) have investigated the effect of oxygen-containing functional groups present on the surface of AC on adsorption of mercury (Li et al., 2003). According to the authors, lactone and carbonyl groups present in the surface of AC might have played a positive role in the adsorption process, whereas phenolic

**Table 2**  
Various factors and their limits considered for the study using response surface methodology.

Factor	Unit	Coded factor	$-\alpha$	Lower limit	Upper limit	$+\alpha$
AC concentration	g/L	A	39.64	50	100	110.36
Reaction time	min	B	20.59	120	600	699.41

**Table 3**  
Different experimental runs conducted using response surface methodology and their corresponding responses.

Run	Factors		Response Removal efficiency (%)
	A:AC concentration (g/L)	B:Reaction time (min)	
1	75	360.00	80.65
2	75	360.00	82.18
3	100	600.00	92.16
4	50	600.00	83.72
5	110	360.00	90.63
6	75	699.41	82.95
7	75	360.00	84.49
8	75	20.59	84.49
9	75	360.00	83.72
10	50	120.00	81.41
11	100	120.00	91.4
12	75	360.00	88.33
13	39.64	360.00	82.95



**Fig. 2.** (a) Size distribution and (b) zeta-potential distribution of the AC particles used in the present study.

groups showed negative effect (Li et al., 2003). Tessmer, Vidic, and Uranowski (1997) have investigated the role of oxygen-containing functional groups of AC on adsorption of phenol (Tessmer et al., 1997). The authors have concluded that oxygen-containing basic functional groups, such as chromene and pyrrole are crucial for irreversible adsorption of phenol by activated carbon (Tessmer et al., 1997). According to Moreno-Castilla (2004), adsorption of

organic compounds from aqueous solution by any carbonaceous material is a complex and cumulative response of both non-electrostatic and electrostatic interaction (Moreno-Castilla, 2004). Although the natures of the adsorbent and solution chemistry are the two important factors, carbon surface chemistry is the most crucial one to control both electrostatic and non-electrostatic interactions (Moreno-Castilla, 2004). As a part of present investigation,

sugar removal potential of AC has been demonstrated. However, no attempt has been made to discern the type of interaction or functional groups involved in the adsorption process. Porosity of AC is another factor that affects the adsorption of organic molecules (Huang, Chou, & Teng, 2002). The zeta potential of the particles was found to be within  $\pm 30$  mV, so that coagulation would be slow. During coagulation, however, binding with sugar molecules is also possible. Therefore, functional groups, porosity and coagulation are all factors that should be considered in determining the observed response.

### 3.2. Investigation of the effect of activated carbon (AC) concentration, reaction time and temperature on sugar removal

The total carbohydrate concentration of the acid liquor was 6.5 g/L, with glucose and xylose being the two major constituents. As a part of this study, the effect of AC concentration on sugar removal was investigated and the results are shown in Fig. 3(a). It is clear that the technique is capable of removing sugar from the acid liquor. By increasing the AC concentration from 1 g/L to 100 g/L, sugar removal efficiency was increased from 52% to 93%. However, if the amount of sugar removed per gram of AC is considered, the AC concentration of 1 g/L showed the highest sugar removal efficiency (3.4 g sugar/g of AC). The purpose of this study was to remove at least 80% of the sugar present in the acid solution so a much higher AC application (50 g/L of AC) was needed. Therefore, 1 g/L of AC was not considered for further investigation.

Results of the investigation of the effect of reaction time on sugar removal are shown in Fig. 3(b). The time of mixing with the acid solution was found to be a crucial factor for sugar removal. Increasing the reaction time from 15 to 180 min increased the sugar removal from 87 to 93% and it was decided to further increase the reaction time to 600 min. It was used as a factor for the investigation conducted using statistical experimental design as discussed in a later section. Both adsorbent dose and contact time are crucial for adsorption (Teka and Enyew, 2014). The reason behind considering the mixing time for further investigation was to find out if the amount of AC required to achieve desired 80% of the sugar removal could be reduced by increasing the contact time.

Likewise, temperature is another factor that affects sugar removal. The results of this investigation are shown in Fig. 3(c). The results show that better removal is achieved when the reaction is conducted at low temperature. When the temperature was increased from  $23 \pm 1$  °C to  $45 \pm 1$  °C, sugar removal efficiency was decreased from 87% to 71%. This type of effect of temperature has been explained as being caused by an increase in the kinetic energy of the adsorbing molecule (Chiang, Chiang, & Huang, 2001). Possible as well, however, is the polymerization of sugar derivatives in the acid liquor which, in turn, might affect the adsorption process. This hypothesis might offer another method to separate the sugar molecules from the acid solution and attempt will be made to investigate this possibility as a separate study.

The possibility of reusing the AC was also investigated. The results of this investigation are shown in Fig. 4. The results show that there is a decrease in the response particularly after the second reuse but that activity remains even after the fifth use. Fig. 5(a–f) shows SEM images of the AC before and after sugar adsorption. The surfaces of the AC particles have long ridges and grooves (Tansel & Nagarajan, 2004) and they are considered to aid adsorption (Riaz Ahamed, Chandrasekaran, & Arun Kumar, 2013). Prior to application for sugar removal, the ridges were more prominent and sharper (Fig. 5a). However, after first use, there is mechanical degradation (Fig. 5b–f), although ridges and grooves were present and distinguishable even after the 5th use. Overall, any significant changes in the appearance of the AC particles surfaces have not been noticed. Surface pores could neither be clearly seen

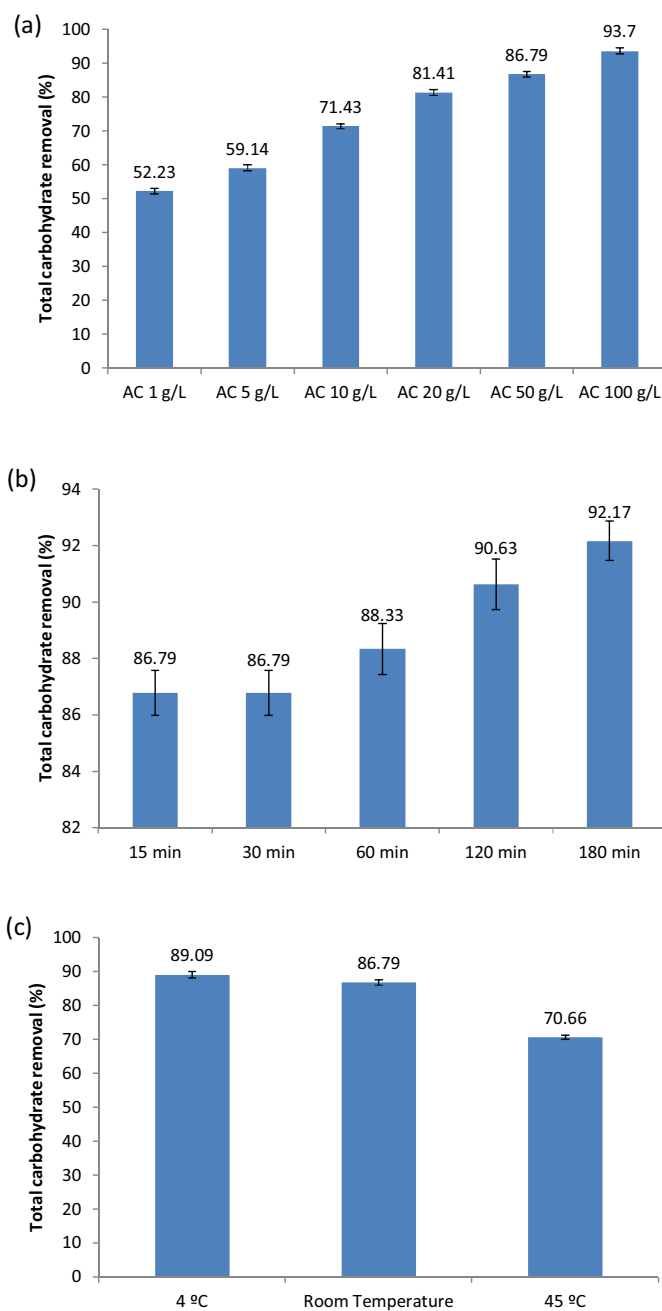


Fig. 3. (a) Effect of activated carbon (AC) concentration on sugar removal from the waste acid stream, (b) effect of reaction time on sugar removal from the waste acid stream using AC (50 g/L) and (c) effect of temperature on sugar removal from the waste acid stream using AC (50 g/L).

before nor after the adsorption study. This observation indicates that change in the appearance of the surfaces has very less to do with sugar adsorption by the particles. Probably surface charges and functional groups were mostly responsible for sugar adsorption whereas porous structure was mostly responsible for increasing the total surface area. Adsorbed molecules might have homogeneously distributed over the surfaces without creating any visually distinguishable changes.

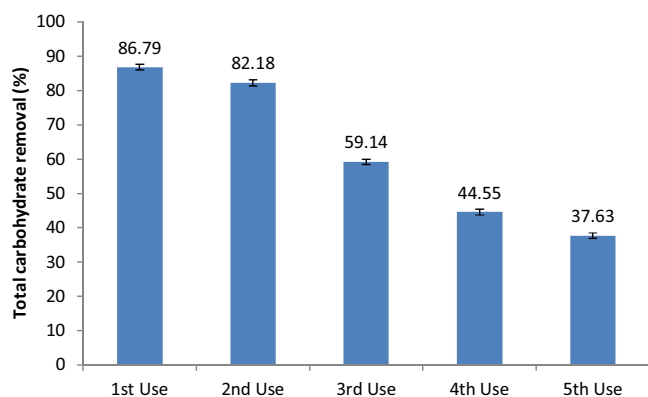


Fig. 4. Sugar removal from the waste acid stream with AC (50 g/L) recycling.

### 3.3. Two step treatment of the acid liquor with AC for sugar removal

The results from the 2 step treatment of acid liquor with AC for sugar removal are presented in Fig. 6(a). The second treatment only improved the overall sugar removal from 87% to 90%. As might be expected, sugar concentration is a key factor in achieving effi-

cient removal. During the first treatment 87% of the sugar was removed leaving only 13% in the solution. This concentration is too low to allow efficient removal of the remaining sugars by AC. Initial concentration of the adsorbate is a crucial factor to determine the adsorption capacity of AC ([http://www.jstor.org/stable/41293528?seq=1#page\\_scan\\_tab\\_contents](http://www.jstor.org/stable/41293528?seq=1#page_scan_tab_contents)).

Thus, pre-concentration of the residual sugar to achieve better removal efficiency was evaluated.

### 3.4. Investigation of the effect of sample pre-concentration and autoclaving on sugar removal

Results of this investigation are shown in Table 1. From the table it can be concluded that sample pre-concentration by heating has a negative effect on removal efficiency by AC. However, the results from this investigation indicate that heating may be able to initiate humin formation from the sugars (Herzfeld et al., 2011; van Zandvoort et al., 2015; van Zandvoort et al., 2013) and it might be possible to remove such products by a suitable membrane. Likewise, the results of the investigation of the effect of sample autoclaving on sugar removal are shown in Fig. 6(b). The results show that removal was negatively affected by autoclaving. As mentioned in the experimental section, the purpose of this study was to hydrolyze any disaccharides or oligosaccharides which might

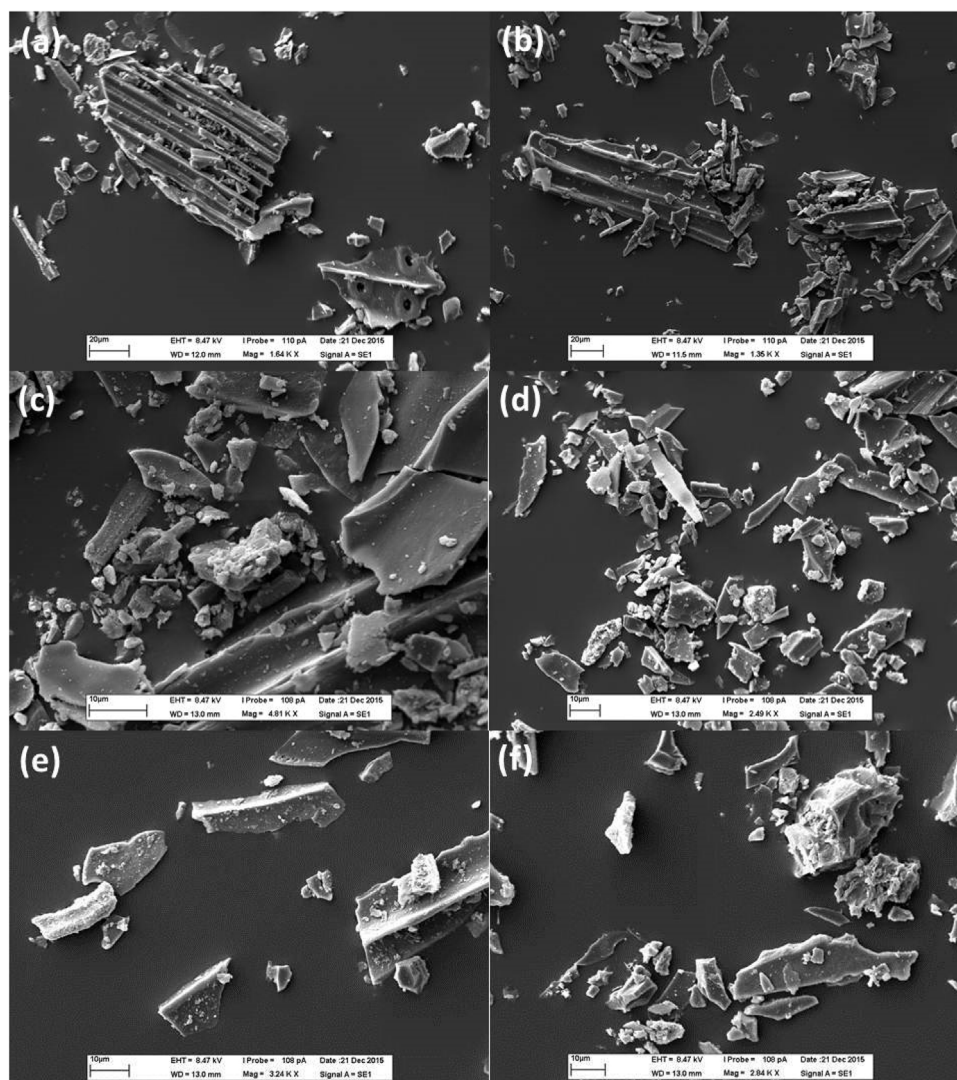


Fig. 5. SEM images of the AC particles: before using for sugar separation (a), after 1st use (b), 2nd use (c), 3rd use (d), 4th use (e) and 5th use (f).

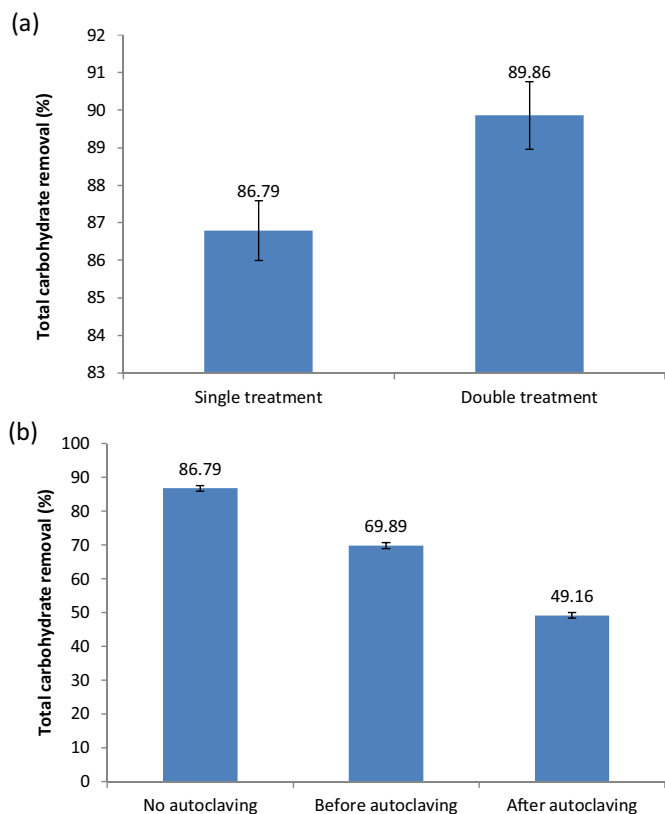


Fig. 6. (a) Sugar removal from the waste acid stream by two-step treatment using fresh AC (50 g/L), (b) effect of autoclaving on sugar removal using AC (50 g/L).

have been in the solution, to their monosaccharides so that they could easily access the pores of the activated carbon particles. However, as it is evident from Fig. 6(b), when 50 g/L of AC is mixed with the solution which is already autoclaved; sugar removal efficiency decreased from 87% to 49.16%. This observation indicates that if

the sample is processed at high temperature, sugar removal efficiency is reduced and it supports the result presented in Fig. 3(c) and Table 1. As mentioned in the discussion related to Fig. 3(c) and Table 1, heating might lead to humin formation making it difficult to remove by adsorption.

### 3.5. Results of the investigation conducted using statistical experimental design

From the different experiments conducted during this study, AC concentration and reaction time are found to be the two factors which influence sugar removal from the acid liquor positively. Sugar concentration is another important factor; however the acid solution has been subjected to treatment without any dilution and hence it was always constant. Based on the results from the preliminary experiments, an AC concentration range between 50 and 100 g/L and a reaction time range of between 120 and 600 min were chosen for the investigation using statistical experimental design. Results of this investigation are shown in Fig. 7. From this figure it can be concluded that AC concentration is the dominant factor and there is no benefit of increasing the reaction time from 120 min to 600 min. Likewise, by increasing the AC concentration from 50 g/L to 100 g/L only around 10% increase in sugar removal could be achieved. Based on this observation it has been concluded that AC concentration of around 50 g/L will be sufficient to achieve required level of sugar removal and there is no need to extend the mixing time beyond 120 min.

It is evident that the activated carbons used in the present study can remove as much as 3.4 g of sugar per g of AC. The high acidic pH (0.6) of the medium could be one important factor responsible for such high removal efficiency. At such a pH, the sugar molecules are expected to receive small amount of charge either due to protonation or may be because of the  $\text{SO}_4^{2-}$  group of the sulfuric acid (Roman & Winter, 2004). In fact, due to high acidic pH of the solution adsorption behavior of AC particles were expected to be different from conventional adsorption studies conducted for heavy metal or other pollutant removal from wastewater at near neutral pH (Attia, Khedr, & Elkholy, 2010; Budinova, Petrov, Minkova, & Gergova,

Design-Expert® Software

Removal

● Design points above predicted value

○ Design points below predicted value

92.16

80.65

X1 = A: AC

X2 = B: Time

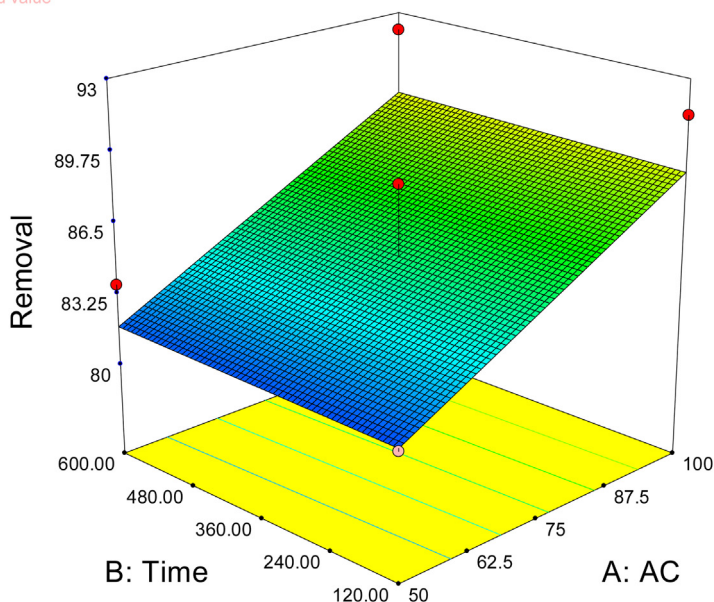


Fig. 7. Response surface 3D plot showing the effect of mixing time (min) and AC concentration (g/L) on sugar removal.

1994; Chen, Huang, Li, & Wu, 2012; El Khames Saad, Khiari, Elaloui, & Moussaoui, 2014; Khalkhali & Omidvari, 2005; Mohan & Singh, 2002; Ma, Gao, Chu, & Li, 2013). It should be noted that this is the first report on sugar separation by AC. Had there been any previous sugar separation study using AC, it would have been better to compare the efficiency of the present process.

#### 4. Conclusions

AC can be used as an adsorbent for sugar removal from the waste acid stream of the nanocrystalline cellulose (NCC) manufacturing process. The approach may help efficient recycling of the acid used in the process. Of the factors evaluated, increasing sugar concentration, AC concentration and time aided adsorption while increasing temperature had a negative effect. Additionally, the AC used in this approach can be recycled for at least 4–5 subsequent batches of reaction. Investigation using response surface methodology has shown that among AC concentration and reaction time, the former is the dominant factor to control sugar removal. By increasing the AC concentration, it would be possible to increase the sugar removal efficiency, considering the cost and possible loss of the acid solution, application of more than 50 g/L should not be considered.

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