**Article**

# Magnetic Particles for Sugar Separation from Sulphuric Acid Solution Generated During Nano-Crystalline Cellulose Production[†]

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## ABSTRACT

Nano-crystalline cellulose (NCC) is a renewable material having different applications ranging from drug delivery to a reinforcing filling agent in polymer synthesis. Concentrated sulphuric acid is used to hydrolyze cellulosic biomass to obtain NCC. Manufacturers are keen to reuse the diluted acid solution left after the process. However, presence of mono and oligosaccharides makes it unsuitable for repeated use. About 99 % of these compounds have been successfully separated from the acid solution by employing NaOH-treated magnetic particles developed during this investigation. It has been observed that by NaOH treatment, zeta potential of the magnetic particles could be increased from +11 mV to +37.5 mV; correspondingly, sugar removal efficiency was increased from 23.04 % to more than 99 %. Thus a direct correlation between the change in zeta potential of the particles and sugar separation efficiency has been observed. This article is protected by copyright. All rights reserved

**KEYWORDS:** nano-crystalline cellulose, magnetic particles, surfactant coating, sugar separation, zeta potential

## INTRODUCTION

Cellulose is a natural biopolymer having various commercial applications. It is renewable, biodegradable, globally available in adequate quantity, and non-toxic.[1] It is mostly composed of amorphous and crystalline structures.[2] Acid hydrolysis of cellulosic material can transform the amorphous structures to crystalline cellulose. Crystalline cellulose having a diameter of few nanometers is known as nano-crystalline cellulose (NCC) and it can be produced from a range of cellulosic biomass.[3,4] For example, utilizing wood as the cellulosic raw material, NCC of 5–10 nm in diameter and 100–200 nm in length could be obtained.[5] Compared to cellulose, NCC has higher specific strength and larger surface area.[3] Potential applications of NCC are directly related to its unique features, such as surface functionality, aspect ratio and strength, low thermal expansion, low toxicity, and favourable optical transparency, among others.[6] Applications of NCC are included, but not limited to drug delivery, synthesis of nano-composite, preparation of membrane for water treatment, preparation of films, as a template for mesoporous material synthesis, and as reinforcing filler in polymer synthesis.[3,6]

CelluForce® (Montreal, Canada) is known as the world's first commercial producer of nano-crystalline cellulose (NCC$^{TM}$).[7,8] In order to produce NCC, this industry uses concentrated sulphuric acid for pulp hydrolysis. A simplified diagram of the process presently used by the industry is presented in Figure 1. As shown in this figure, after separation of desired NCC, diluted sulphuric acid solution containing different sugars and oligosaccharides is left as liquid waste. The industry is keen to concentrate and reuse the acid in subsequent processes. However, the presence of monosaccharaides and oligosaccharides has been a problem in this reuse step. Membrane and ion exchange technologies which are being presently used to clean the acid solution could not give a foolproof solution to the problem. At present, a fraction of the solution is either being sent to biogas production plants or wastewater treatment plants (Figure 1). Thus, the industry has been looking for a technology which can completely remove the sugars present in the solution.

In this context, application of surface-modified magnetic particles has been considered in this study. Such particles can be separated from the solution by applying a magnetic field and this property will be an additional benefit for their real industrial application.[9,10] Functionalized magnetic particles are known to be used for protein purification, removal of polycyclic aromatic hydrocarbon from contaminated water, removal of methylene blue and neutral red from aqueous solution, nucleic acid separation and removal of $Ni^{2+}$, $Cu^{2+}$, $Cd^{2+}$, and $Zn^{2+}$ etc.[11-15] Therefore, the particles were modified by altering the zeta potential followed by coating with cationic surfactants dodecyltrimethylammonium bromide (DTMAB), which can bind different polysaccharides.[16] The process parameters involved in surfactant coating and binding the sugar molecules to the magnetic particles were investigated by response surface methodology. Overall, an attempt has been made to make the nano-crystalline manufacturing process greener by recycling the waste acid stream.

## MATERIALS AND METHODS

### Chemicals

Chemical such as $FeCl_3$, $FeCl_2$, NaOH, $H_2SO_4$ and ethanol were purchased from Fisher Scientific (Ontario) Canada. All these chemicals were of analytical grade. Anthrone (97 %) and dodecyltrimethylammonium bromide (DTMAB, 99 %) were purchased from Sigma Aldrich (Ontario) Canada.

### Characterization of the Sulphuric Acid Solution Received from the Industry

The sulphuric acid solution was collected from CelluForce® (Montreal, Canada), a leading manufacturer of nano-crystalline cellulose. Total carbohydrate content of the solution was determined by anthrone reagent method described in a later section. Likewise, individual sugars present in the solution were identified and their concentration was determined by LCMS method as described later.

### Preparation and Characterization of Magnetic Particles

Magnetic particles of a few hundred nanometers in diameter were prepared by modified co-precipitation method.[17] Briefly, ferric chloride (0.074 g) and ferrous chloride (0.190 g) were dissolved in 20 mL of deionized water. Under continuous bubbling with nitrogen gas and magnetic stirring, the solution temperature was increased to 60 ºC. Around 10 mL NaOH (2.5 mol/L) was added and the same temperature was maintained for next 20 min. After this period of agitation, heating was stopped, the flask containing the solution was placed on a magnetic stirrer, and prepared particles were allowed to settle for 12 h. Subsequently, supernatant was discarded and the particles were washed 3 times with distilled water. Finally, particles were separated by centrifugation (10 000 rpm or 6708 x *g*, 10 min) and dried at 105 ±1 ºC.

Cationic surfactant dodecyltrimethylammonium bromide (DTMAB) is known to bind with polysaccharides.[16] Therefore, it was decided to apply a DTMAB coating on the magnetic particles so that mono and oligosaccharides present in the acid solution could use the binding sites of the surfactant to bind to the magnetic particles. In order to apply the surfactant coating, magnetic particles (10–50 g/L) were mixed with NaOH (pH 9.4) solution and subsequently centrifuged (10 000 rpm or 6708 x *g*, 10 min) to separate the particles. Equal volume of surfactant (0.1–0.5 mol/L) solution prepared in 0.01 mol/L HCl was mixed with these particles. The reaction mixture was placed in a water bath maintained at 90 ±1 ºC and 60 rpm. Duration of this reaction, also called coating time, was varied from 30–180 min. This is an already known method for applying surfactant coating on magnetic particles.[18] After the coating period, the particles were washed 3 times with distilled water to remove unattached surfactants. Finally, surfactant coated particles were separated from the liquid by centrifugation (10 000 rpm or 6708 x *g*, 10 min) and lyophilized for 12 h. Lyophilized particles were directly used for the sugar separation study conducted using response surface methodology.

In order to determine the zeta potential distribution of the magnetic particles prepared for this investigation, they were first dispersed in distilled water. 1 mL of this sample was taken in a disposable folded capillary cell (DTS1070) and finally, the zeta potential was measured by a Zetasizer Nano ZS (Malvern instruments Ltd., UK). Likewise, a scanning electron microscope (Zeiss EVO® 50 Smart SEM system) was used to perform morphological characterization of the particles.[19] Lyophilized particles were first spread on a glass slide by using a small spatula. In order to fix the particles on SEM stub, a stub with double coated carbon conductive tab was placed on them in an inverted manner. Prior to observing the stubs in SEM, they were processed in a SPI module sputter coater to apply a gold coating on the particles fixed onto them.

## Response Surface Methodological Investigation of Sugar Separation by Surfactant-Coated Magnetic Particles

Concentration of the magnetic particles (MP), concentration of the surfactant (DTMAB), the duration of the coating reaction (coating time), and the duration of sugar binding reaction (binding time) were the four different factors considered for this investigation. As shown in

Table 1, MP concentrations considered for the study were 10–50 g/L, whereas DTMAB concentration was varied from 0.1 to 0.5 mol/L. Likewise, the duration considered for coating was 30 min to 180 min and binding time was 2 h to 24 h. Experiments were planned and the results were analyzed by a software called Design-Expert®-7 (Stat-Ease Inc. Minneapolis, MN). A two-level factorial design involving the four factors was used for this purpose. The level of each of the four factors used for the 16 different experiments conducted during the study has been presented in Table 2. As shown in Table 2, total carbohydrate removal efficiency (%) was used as the response of the study.

## Sugar Separation by NaOH-Treated Magnetic Particles

Based on the results of the previous section, NaOH-treated magnetic particles with no surfactant coating were also evaluated for sugar removal. About 50 g/L of the untreated magnetic particles (MP) were mixed with NaOH solution (pH 9.4) and the particles were subsequently separated by centrifugation (10 000 rpm or 6708 x *g*, 10 min). Treated particles were then washed with distilled water for three times and lyophilized. About 50 g/L of the lyophilized particles were mixed with the acid solution received from the industry and the solution was continuously agitated for 24 h by using a vortex. This experiment was conducted at room temperature (23 ºC). Finally, the particles were separated by centrifugation and analyzed.

## Analytical Methods

### *Total carbohydrate analysis*

Total carbohydrate content of the acid solution was determined by anthrone reagent method. For this purpose, 1 mL of the sample was taken in a glass screw cap vial followed by addition of 2 mL of 75 % (v/v) chilled $H_2SO_4$. After thoroughly mixing the solution, 4 mL of chilled anthrone reagent was added and again mixed by using a vortex mixture. Vials were then closed and placed in a heating block for 15 min and the temperature of the block was maintained at 100 ±1 ºC. Once the solution cooled down to room temperature, its absorbance was measured by a spectrophotometer at 578 nm.[20] In order to prepare the anthrone reagent for this analysis, 0.5 g of anthrone was dissolved in 10 mL of ethanol and then around 240 mL of 75 % (v/v) $H_2SO_4$ was added to make up the volume to 250 mL. Glucose was used as a standard to prepare the standard curve.

*LC-MS analysis of different sugars and their derivatives*

In order to identify different sugars and their derivatives present in the acid solution, it was characterized by LC-MS. The molecules were identified using commercially available standard compounds, such as glucose, xylose, sucrose, trehalose, furfural, and 5-hydroxymethyl furfural (5-HMF). These compounds were purchased from Sigma Aldrich (ON, Canada). Reducing sugars were analyzed by Liquid Chromatography - Mass Spectrometry (LC-MS) equipped with biobasic-18 (5 µm, 150 mm ID, 4.6 mm df) column (Agilent Technologies, USA). Internal standard used for this analysis was D-6 glucose. Sugar derivatives were analyzed by Liquid Chromatography - Tandem Mass Spectrometry (ZORBAX Carbohydrate, Agilent Technologies, USA). The column used for this analysis was biobasic-18 (5 µm, 250 mm ID, 4.6 mm df), Agilent Technologies, USA, where phenylethanol-D5 was the internal standard. Prior to the analysis, samples were centrifuged for 5 min at 7650 *x g*. For sugar analysis, samples were diluted with methanol and water mixture (8:2), whereas, for sugar derivatives, acetonitrile and water mixture (8.5:1.5) were used as the diluent. The concentrations reported in this study are averages of duplicate analysis.

## RESULTS AND DISCUSSION

### Characterization of the Sulphuric Acid Solution Received from the Industry

Acid hydrolysis is the heart of the nano-crystalline cellulose manufacturing process and the acid solution used in the present study is the fraction left after separation of nano-crystalline cellulose from the reaction mixture. This is a colourless liquid with a pH of around 0.6. Total carbohydrate content of the solution was found to be around 6510 mg/L. As presented in Figure 2, the LC-MS analysis showed that glucose (2664.5 ± 50 mg/L) was the main sugar present in the solution. It was followed by xylose (857.1 ± 50 mg/L), and trehalose (102.4 ± 45 mg/L). However, sucrose was not detected in the solution. Furfural (56.78 ± 20 mg/L), 5-hydroxymethyl furfural (5-HMF) (110.21 ± 15 mg/L), and levulinic acid (75.96 ± 32 mg/L) were the sugar derivatives detected in the solution in small quantity. Unidentified oligosaccharides could be other likely constituents of the sample.

## Preparation and Characterization of the Magnetic Particles

Magnetic particles used in this study were prepared by co-precipitation method involving ferric chloride ($FeCl_3$) and ferrous chloride ($FeCl_2$).[17] This is a well-known method, where the size of the particles can be varied by changing the type and concentration of precipitating agent. In Figure 3, size distributions of the magnetic particles (without any treatment) prepared for this investigation are presented. From Figure 3, it can be seen that the diameter of most of the particles was around 800 nm. This value is significantly higher than a typical magnetic nanoparticle having a diameter of less than 100 nm. However, the particle mixture still has a small amount of particles with a diameter of less than 200 nm. These particles can be separated from the rest by suspending them in distilled water. In this process, larger particles quickly settled down; whereas the smaller ones remained suspended for a longer time. The mixture of the particles was directly used in sugar separation experiments.

In Figures 4a and b, SEM images of magnetic particles, before and after NaOH treatment, respectively have been presented. It is evident that particles of around 200 nm to few hundred nm were mostly aggregated as larger particles. Due to mounts and pits formed by aggregation of the small particles, the surfaces of the larger particles are rough. Compared to relatively smoother surfaces, this kind of texture seems to be beneficial for adsorption of the sugar molecules. Unlike the particles shown in Figure 4a, the ones in Figure 4b were treated with NaOH; however, morphologically they were not found to be distinguishable. To the naked eye they could be distinguished, as the former was dark brown in colour, whereas the latter was light brown.

In Figure 5a, zeta potential distribution of the magnetic particles without any treatment is presented. As shown, the average zeta potential was found to be around +11 mV. A zeta potential of more than ± 5 mV indicated that particles were safe from rapid coagulation. However, since the value is within ± 30 mV, the suspension cannot be considered stable.[21] Owing to this property, it was easy to separate the particles by centrifugation. In Figure 5b, zeta potential distribution of the magnetic particles treated with NaOH is presented. Average zeta potential of NaOH treated magnetic particles was found to be around +37.5 mV, which is nearly three times more than that of the untreated particles. This change in zeta potential might be crucial in the sugar removal process. A detailed discussion regarding the role of zeta potential distribution of the particles on sugar removal efficiency is provided in a later section.

## Response Surface Methodological Investigation of Sugar Separation by Surfactant Coated Magnetic Particles

Sugar separation from the acid solution was the major objective of this research work and the purpose of this particular investigation was to study the effect of four different factors which might influence the separation process. As shown in Table 1, the amount of the magnetic particles (10–50 g/L) needed for sugar, concentration of the surfactant solution (0.1–0.5 mol/L), the duration of surfactant coating reaction (30–180 min), and the duration of the binding reaction (2–24 h) between the sugar molecules and surfactant coated magnetic particles were investigated. A two-level factorial design was used to plan the experiment and specific details of each experiment are presented in Table 2. Results were analyzed by the same software used for designing the experiments under response surface methodology.

In Figure 6a, the interaction between DTMAB concentration used for coating and the magnetic particle concentration used for sugar separation is shown. At lower DTMAB concentration (0.1 mol/L), if the amount of magnetic particles is increased from 10 to 50 g/L, sugar separation efficiency increases. It indicates that at 50 g/L, magnetic particles can offer relatively better sugar separation efficiency (70.84 %). However, at a higher DTMAB concentration (0.5 mol/L), increase in the magnetic particle concentration has a negative effect on sugar separation. It suggests that surfactant might have negative effect on the separation process. In Figure 6b, the interaction between coating time and magnetic particle concentration has been provided. From the figure, it is clear that in the case of 50 g/L of the magnetic particles, when the coating time was increased from 30 to 180 min, sugar removal decreased. However, at a lower concentration of the magnetic particles (10 g/L), coating time had no significant effect. This observation suggested that surfactant coating reduced the number of adsorption sites on the surface of the magnetic particles and the difference in the response was prominent when relatively higher concentration (50 g/L) of the particles was used.

Figure 6c shows the interaction between sugar binding time and amount of particles used. It can be seen that when sugar binding time was longer (24 h), better sugar separation efficiency can be expected. In Figure 6d, the interaction between the coating time and surfactant concentration is shown. It was seen that with increase of coating time and surfactant concentration, sugar separation efficiency decreased. This observation again suggested that surfactant coating reduced sugar separation efficiency of the magnetic particles. Figure 6e shows the interaction between sugar binding time and surfactant concentration. For a shorter binding time (2 h), relatively higher surfactant concentration (0.5 mol/L) had a negative effect on sugar removal. In Figure 6f, the interaction between coating time and sugar binding time has been presented. According to this figure, a shorter coating time (30 min) followed by a longer binding time (24 h) is favourable for sugar separation from the acid solution.

Overall, magnetic particle concentration of 50 g/L and sugar binding time of 24 h are the two levels of these factors which have a positive effect on sugar separation. Prior to surfactant coating, the magnetic particles were treated with NaOH and this step might have a beneficial effect on sugar removal from the acid solution. Therefore, it was decided to conduct the following investigation.

## Sugar Separation by NaOH-Treated Magnetic Particles

The results of the study conducted using response surface methodology have suggested that surfactant molecules attached to the surface of the magnetic particles can negatively affect the adsorption of sugar molecules from the acid solution. Therefore, it was decided to conduct a sugar separation study using the magnetic particles without surfactant coating. Moreover, in order to see the effect of NaOH treatment of the particles, both NaOH-treated and untreated magnetic particles were evaluated for sugar separation. About 50 g/L of the particles was used for this investigation and the binding time was 24 h. Results of this experiment are presented in Figure 7. The results showed that the particles without NaOH treatment could remove only 23.04 % of the sugar present in the acid solution, whereas after NaOH treatment, the separation efficiency was as high as 99.62 %. Thus, NaOH treatment of the magnetic particles is a small but very crucial step for sugar separation. In contrast to this result, when magnetic particles were coated using the surfactant, 74.57 % of the sugar can be removed. This value was significantly higher than 23.04 % removal obtained for uncoated particles without NaOH treatment; however, it was lower than NaOH-treated particles. Thus, instead of surfactant coating, magnetic particles should be simply treated with NaOH for complete separation of sugar present in the acid solution. As shown in Figures 5a and b, NaOH treatment increased the zeta potential of the magnetic particles from +11 mV to +37.5 mV. This nearly threefold increase in zeta potential could be attributed to an increase in sugar separation efficiency. The most probable explanation is that the molecules present in the sulphuric acid solution received negative charge from the $(SO_4)^{2-}$ group of the acid.[22] Therefore, compared to the particles without NaOH treatment, they had a stronger electrostatic interaction with NaOH-treated particles having higher zeta potential (+37.5 mV). In Figure 8, the image of the sample kept ready for total carbohydrate analysis before and after sugar separation by NaOH treated magnetic particles is presented. It shows that the proposed approach has a visually distinguishable effect. Thus, it has been proposed that NaOH-treated magnetic particles with a zeta potential of around +37.5 mV will be useful to separate sugar molecules present in the diluted acid stream to make the stream suitable for reuse. Pilot-scale studies to be conducted in the future will shed more light on commercial viability of the technology. Our recent study suggests that by using nano-sized activated carbon, around 86 % of the sugar could be removed from the sulphuric acid solution.[23] However, it was not possible to remove the remainder of the sugar. The present finding of around 99 % removal is expected to solve this longstanding problem of the industry.

## CONCLUSIONS

Magnetic particles were prepared by the well-known co-precipitation method. These particles were coated by dodecyltrimethylammonium bromide (DTMAB), a cationic surfactant. The effects of coating time, sugar binding time, amount of magnetic particles, and amount of surfactant on sugar separation were investigated using response surface methodology. It has been observed that surfactant-coated particles can remove around 74 % of the sugar present in the acid solution. This value was significantly higher than only 23.04 % separation achieved for magnetic particles without surfactant coating. Prior to surfactant coating, the particles needed to be treated with NaOH solution. Interestingly, it has been observed that if these NaOH-treated particles without surfactant coating are used, sugar separation as high as 99 % could be achieved. Further investigations are ongoing for real industrial application of this technology.

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## CONFLICT OF INTEREST

The authors declare no competing financial interest.

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**Figure captions**

**Figure 1:** Simplified diagram of commercial nano-crystalline cellulose manufacturing process. The sample used in this investigation has been specially identified.

**Figure 2:** Different compounds present in the acid sample as identified by LC-MS analysis.

**Figure 3:** Size distribution of the magnetic particles prepared during this study.

**Figure 4:** SEM images of the magnetic particles: (a) without NaOH treatment; and (b) with NaOH treatment.

**Figure 5:** Zeta-potential distribution of the magnetic particles: (a) before NaOH treatment, where average zeta-potential was +11 mV; and (b) after NaOH treatment, where average zeta-potential was +37.5 mV.

**Figure 6**: Analysis of the responses obtained from the experiments planned using factorial design under response surface methodology framework. Detailed explanation of each of these graphs has been provided in the text.

**Figure 7**: Effect of NaOH treatment and surfactant coating on sugar removal by the magnetic particles. Dodecyltrimethylammonium bromide (DTMAB), magnetic particles (MP).

**Figure 8**: Photograph of the samples processed with anthrone reagent for total carbohydrate analysis. It indicates that nearly complete removal of sugar can be achieved by treating the sample with surface modified magnetic particles developed during this study.

## Tables

**Table 1: Different factors and their levels considered for planning the experiments using factorial design**

| Factors | | Lower level | Upper level |
|---|---|---|---|
| A | MP (g/L) | 10 | 50 |
| B | DTMAB (M) | 0.1 | 0.5 |
| C | Coating time (min) | 30 | 180 |
| D | Binding time (h) | 2 | 24 |

*Dodecyltrimethylammonium bromide (DTMAB), magnetic particles (MP)

**Table 2: Experiments planned using the factorial design considered for response surface methodological investigation of sugar separation from the acid solution**

| RUN | MP (g/L) | DTMAB (M) | Coating time (min) | Binding time (h) | Removal (%) |
|---|---|---|---|---|---|
| 1 | 10.00 | 0.50 | 180.00 | 2.00 | 70.47 |
| 2 | 50.00 | 0.50 | 180.00 | 2.00 | 51.51 |
| 3 | 10.00 | 0.10 | 180.00 | 2.00 | 70.47 |
| 4 | 10.00 | 0.10 | 180.00 | 24.00 | 60.39 |
| 5 | 10.00 | 0.50 | 30.00 | 24.00 | 74.16 |
| 6 | 50.00 | 0.10 | 180.00 | 2.00 | 70.84 |
| 7 | 10.00 | 0.10 | 30.00 | 2.00 | 58.17 |
| 8 | 50.00 | 0.10 | 30.00 | 2.00 | 70.84 |
| 9 | 10.00 | 0.50 | 30.00 | 2.00 | 62.2 |
| 10 | 50.00 | 0.10 | 180.00 | 24.00 | 69.72 |
| 11 | 50.00 | 0.50 | 180.00 | 24.00 | 56.39 |
| 12 | 50.00 | 0.50 | 30.00 | 24.00 | 75.69 |
| 13 | 10.00 | 0.10 | 30.00 | 24.00 | 69.35 |
| 14 | 50.00 | 0.50 | 30.00 | 2.00 | 60.83 |
| 15 | 10.00 | 0.50 | 180.00 | 24.00 | 69.27 |
| 16 | 50.00 | 0.10 | 30.00 | 24.00 | 74.57 |

*Dodecyltrimethylammonium bromide (DTMAB), magnetic particles (MP)

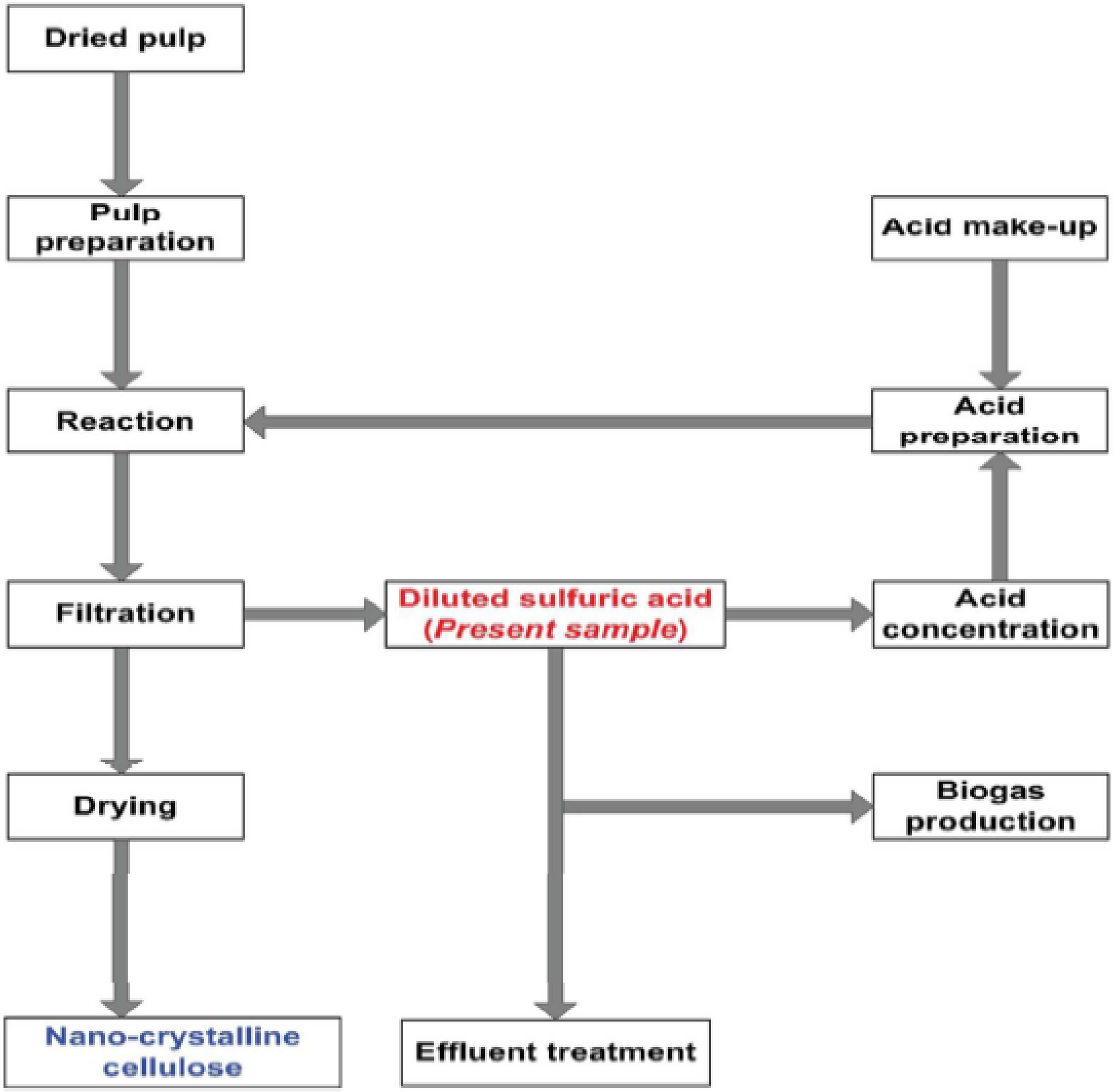
Dried pulp
Pulp preparation
Reaction
Filtration
Drying
Nano-crystalline cellulose
Acid make-up
Acid preparation
Diluted sulfuric acid (*Present sample*)
Acid concentration
Biogas production
Effluent treatment

Figure 1

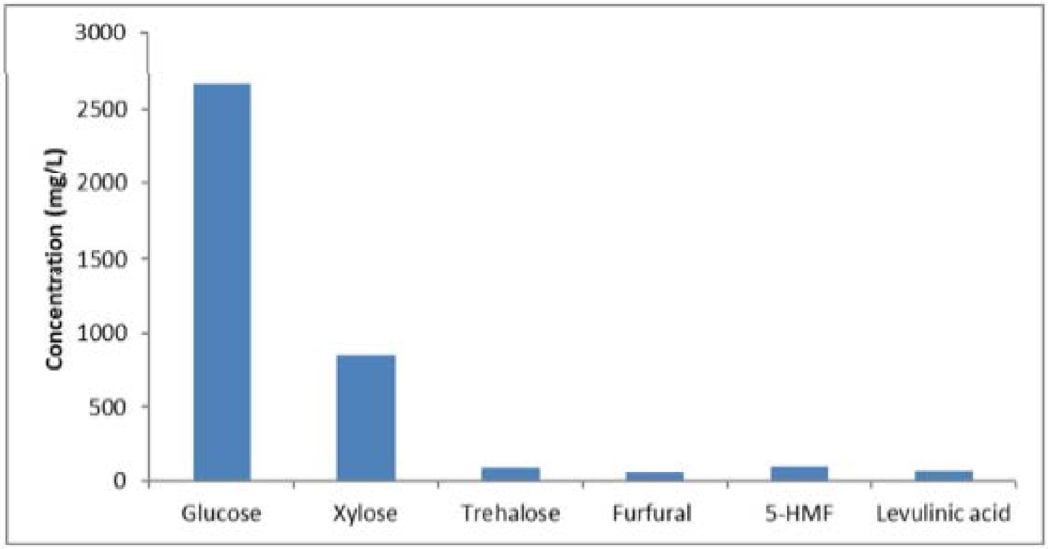
3000
2500
2000
1500
1000
500
0
Concentration (mg/L)
Glucose
Xylose
Trehalose
Furfural
5-HMF
Levulinic acid

Figure 2

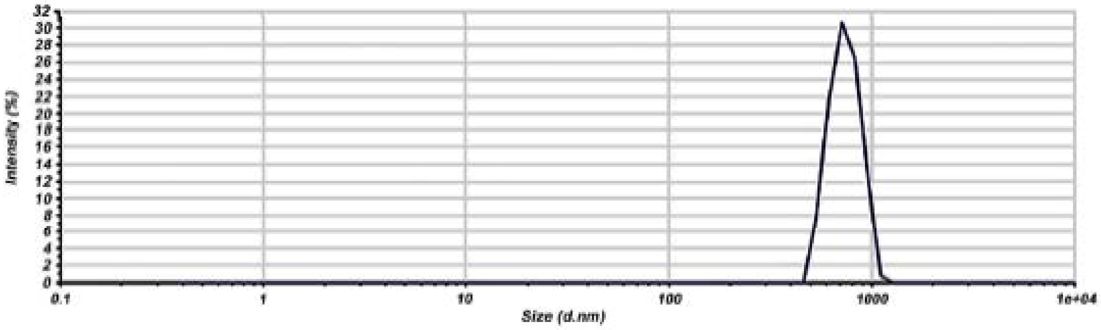
Intensity (%)
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.1
1
10
100
1000
1e+04
Size (d.nm)

Figure 3

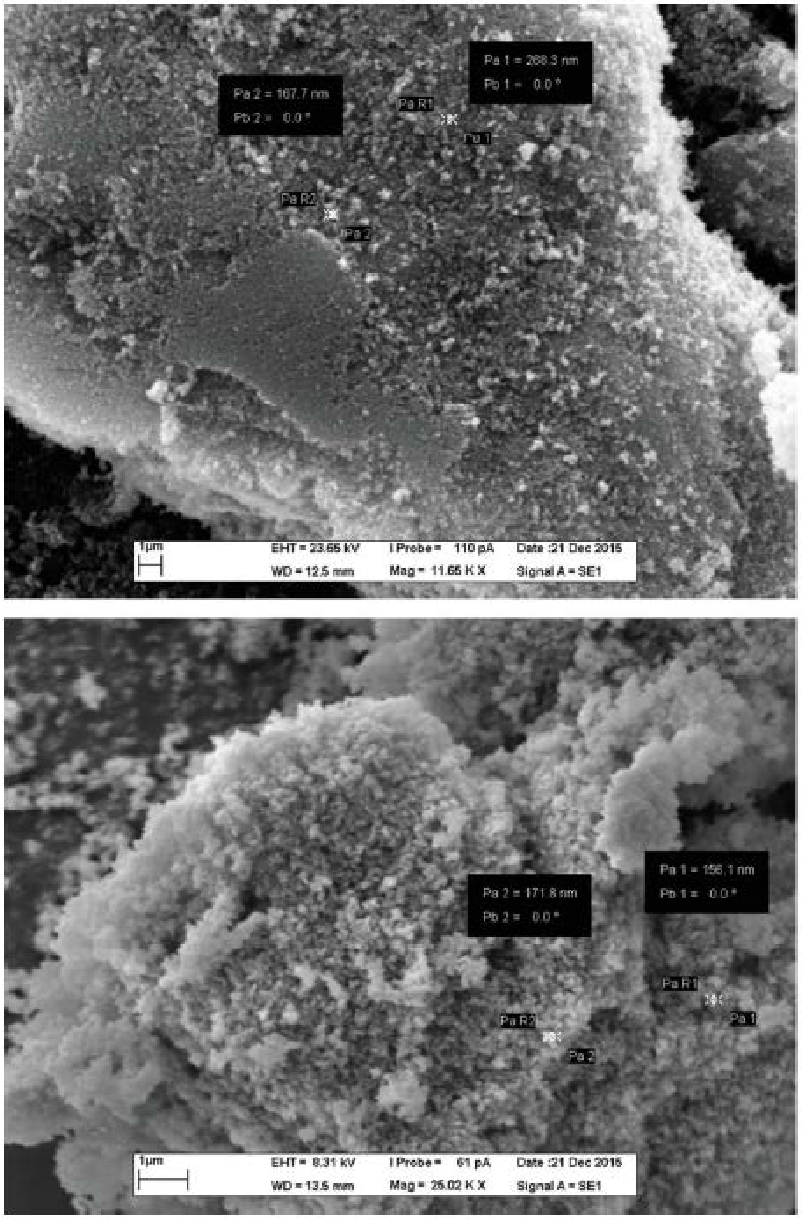
Pa 2 = 167.7 nm
Pb 2 = 0.0 °
Pa 1 = 268.3 nm
Pb 1 = 0.0 °
Pa R1
Pa 1
Pa R2
Pa 2
1µm
EHT = 23.65 kV
I Probe = 110 pA
Date :21 Dec 2016
WD = 12.5 mm
Mag = 11.65 K X
Signal A = SE1
Pa 2 = 171.8 nm
Pb 2 = 0.0 °
Pa 1 = 156.1 nm
Pb 1 = 0.0 °
Pa R1
Pa 1
Pa R2
Pa 2
1µm
EHT = 8.31 kV
I Probe = 61 pA
Date :21 Dec 2016
WD = 13.5 mm
Mag = 26.02 K X
Signal A = SE1

Figure 4

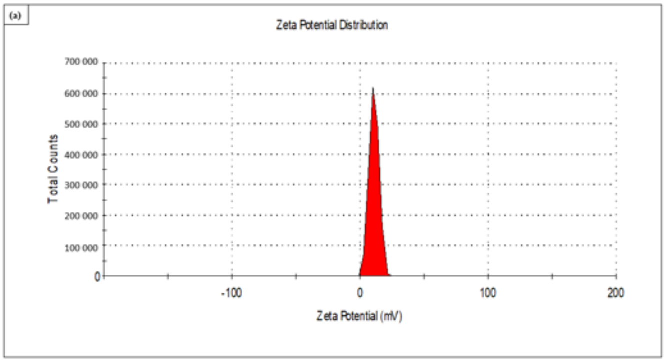

Figure 5(a)

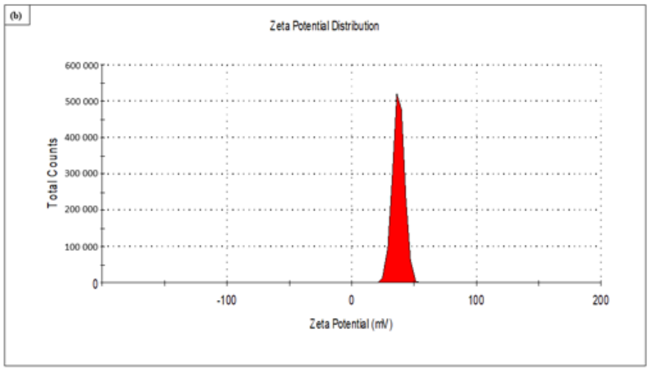

Figure 5(b)

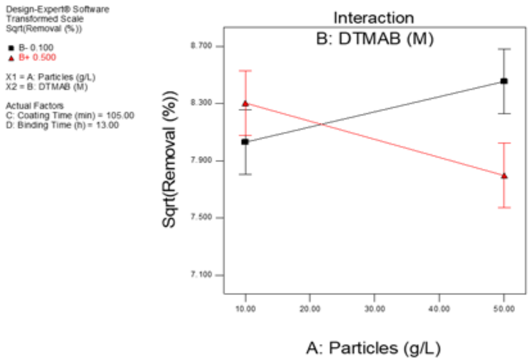

Figure 6(a)

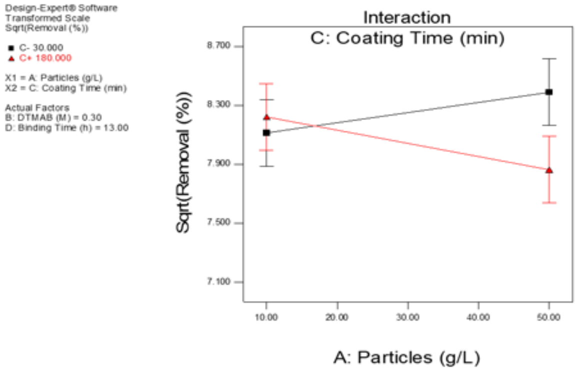

Figure 6(b)

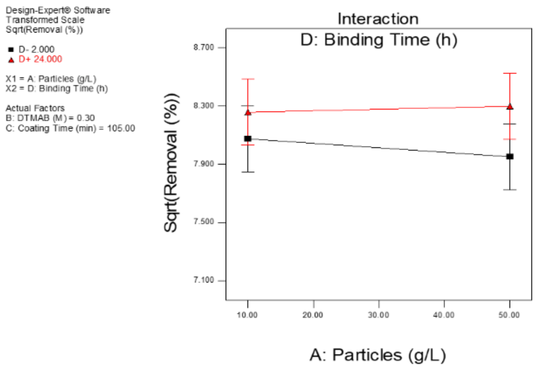

Figure 6(c)

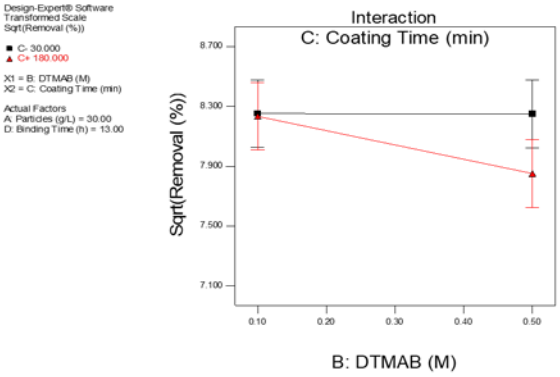

Figure 6(d)

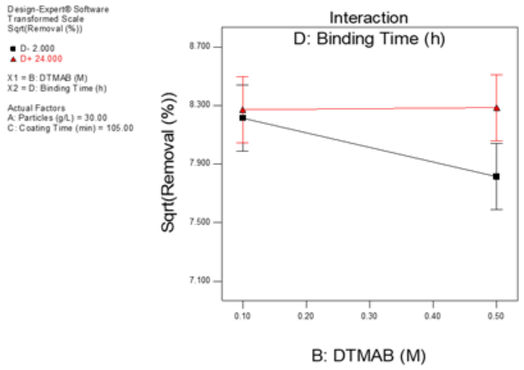

Figure 6(e)

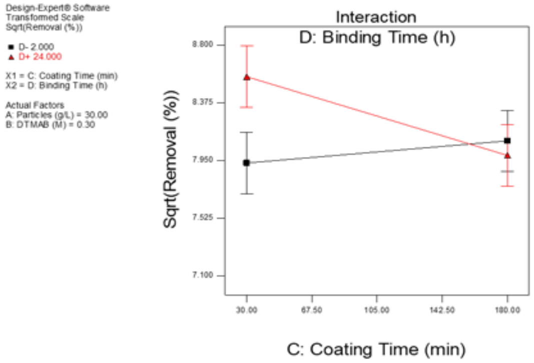

Figure 6(f)

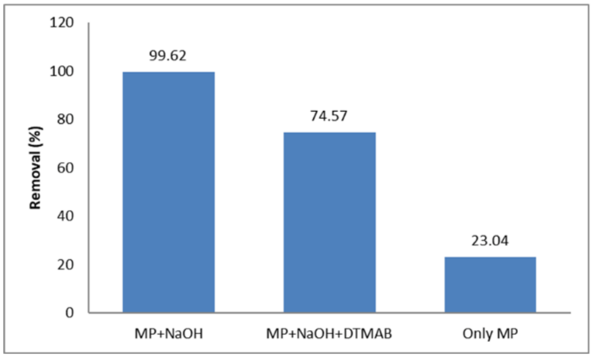
Removal (%)
120
100
80
60
40
20
0
99.62
74.57
23.04
MP+NaOH
MP+NaOH+DTMAB
Only MP

Figure 7

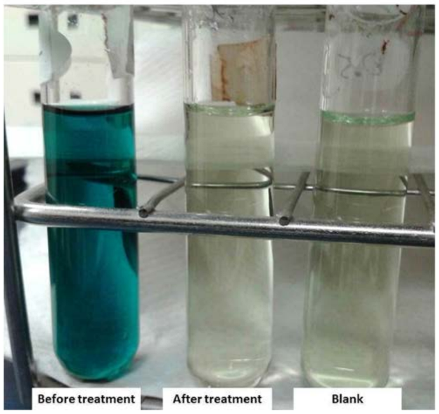

Figure 8