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Research Paper

Acid mediated chemical treatment to remove sugar from waste acid stream from nano-crystalline cellulose manufacturing process

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A B S T R A C T

Nano-crystalline cellulose (NCC) is a nano-scale biomaterial derived from highly abundant natural polymer cellulose. It is industrially produced by concentrated acid hydrolysis of cellulosic materials. However, presences of as high as 5–10% of sugar monomers in spent sulphuric acid during the manufacturing process, makes it unsuitable for such recycling or reuse of sulphuric acid. Currently, the industry has been using membrane and ion exchange technology to remove such sugars, however, such technologies cannot achieve the target of 80–90% removal. In the current investigation, thermal treatment and acid mediated thermal treatment have been evaluated for sugar removal from the spent sulphuric acid. Almost complete removal of sugar has been achieved by this approach. Maximum sugar removal efficiency (99.9%) observed during this study was at $120 \pm 1\,^{\circ}C$ for 60 min using 0.8 ratio (sample: acid) or at $100 \pm 1\,^{\circ}C$ for 40 min using 1.5 ratio.

1. Introduction

Cellulose constitutes the most abundant renewable polymer resource available today. Nano-crystalline celluloses (NCCs) have garnered in the materials community a tremendous level of attention that does not appear to be relenting. These bio-polymeric assemblies warrant such attention not only because of their unsurpassed quintessential physical and chemical properties but also because of their inherent renewability and sustainability in addition to their abundance (Habibi, Lucia, & Rojas, 2010). They have been the subject of a wide array of research efforts as reinforcing agents in nano-composites due to their low cost, availability, renewability, light weight, nanoscale dimension, and unique morphology (Peng, Dhar, Liu, & Tam, 2011).

Typical procedures currently employed for the production of NCCs consist of subjecting the pure cellulosic material to strong acid hydrolysis under strictly controlled conditions of temperature agitation, and time (Brinchi, Cotana, Fortunati, & Kenny, 2013; Karim, Chowdhury, Hamid & Ali, 2016; Rhim, Reddy & Luo, 2015). The nature of the acid and the acid-to-cellulosic fibers ratio are also important parameters that affect the preparation of NCCs (Elazzouzi-Hafraoui et al., 2007; Son & Seo, 2015). A resulting suspension is subsequently diluted with water and washed with successive centrifugations (Bai, Holbery, & Li, 2009). Dialysis against distilled water is then performed to separate the NCC from the acid solution (de Souza Lima & Borsali, 2002). Additional steps such as filtration, differential centrifugation, or ultracentrifugation (using a saccharose gradient) (de Souza Lima & Borsali, 2002) have been also reported (Brinchi et al., 2013; Habibi et al., 2010).

CelluForce® (Montreal, Canada) (http://celluforce.com/en/) is a global leader in nano-crystalline cellulose (NCC™) production. NCCs manufacturing process of the industry and proposed strategy of removing sugar from the acid solution generated during the process has been presented (Kumar, Negi, Choudhary, & Bhardwaj, 2014; Sarma et al., 2016). The diluted sulfuric acid stream generated during NCCs manufacturing process is subjected to membrane based ion exchange technique to remove the remaining sugar monomer. However a significant portion of sugar is still present in the residual acid stream, which could be as high as 5–10%. Owing to strong hygroscopic nature of sulfuric acid, it makes it difficult for the manufacturer to concentrate and reuse the same acid stream in presence of such sugars during a subsequent batch. Currently, waste acid stream from manufacture industry is utilized mainly to produce biogas or sent to wastewater treatment facility at additional expense. Thus, in order to make the process more sustainable and environmentally friendly, the industry has been looking for a

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simple method to remove at least 80–90% of the sugar without neutralizing the acid solution, so that it can be concentrated for reuse. Therefore, development of a new cost-effective and efficient process for the removal of at least 80–90% of such sugar was the major objective of this study.

During acid catalyzed thermal-hydrolysis, biopolymeric assemblies (e.g. cellulose and hemicellulose) are degraded into monomers (e.g. hexoses and pentoses) and further byproducts as shown in Fig. 1 (Choudhary et al., 2013; Shen et al., 2015). However, depending on the process conditions, the conversion of these biopolymers could be directed in different directions, such as sugars monomers (e. g: glucose) (Rugg & Brenner, 1982); furfural derivative (furfural and 5-hydroxymethyl furfural) (Choudhary et al., 2013); levulinic acid (Girisuta, Janssen, & Heeres, 2007), nanostructured ceramics and nano-composites (Pang, Chin, & Yih, 2011) and others via rehydration, dehydration and other mechanism (Choudhary et al., 2013). In this context, sulfuric acid mediated heating could be a promising novel technology for sugar removal from diluted sulfuric acid stream generated during nano-crystalline cellulose (NCC™) manufacturing process. Hence, the objectives of the study were: (1) physicochemical characterization of waste acid stream from NCC manufacturing process; (2) heating at different temperatures to evaluate the effect of heating on sugar removal; (3) evaluation of acid mediated heating using different ratios of sample and acid as a novel method for sugar removal and; (4) optimization of process parameters, such as time, temperature and acid sample ratio to enhance sugar removal process. Central composite design was used for optimizing these parameters. This article will provide an alternative solution to remove residual sugar from the waste acid stream from NCC™ manufacturing process and the proposed method has the potential to be an environment-friendly solution.

2. Materials and methods

2.1. Chemicals and waste acid stream sample

Chemicals, such as sulfuric acid, sodium hydroxide, acetone, methanol, acetonitrile, NH_4OH etc. were purchased from Fisher Scientific (Ontario, Canada). Glucose, xylose, fructose, treholose, furfural, hydroxymethyl furfural, levulinic acid, acetic acid, among others have been purchased from Sigma Aldrich (USA). All the standards used for analytical methods are of analytical grade. Waste acid stream from NCC manufacturing process was received from CelluForce® (Windsor, Quebec).

2.2. Heating experiment on sugar removal from waste acid stream of manufacturing process

Heat mediated in-situ acid catalyzed the hydrolysis of cellulose was performed to reduce sugars and further conversion of other byproducts to reuse the acid. For this investigation, heating at different temperatures, such as 40 °C, 60 °C, 80 °C and 100 °C have been carried out using about 10 mL of sample from the sulfuric acid stream received from CelluForce® (Windsor, Quebec). Each sample was heated to the aforementioned temperatures in a closed COD vial and boiled for 120 min. After heating, each sample was cooled to room temperature and total reducing sugars, total carbohydrates and byproducts were analyzed using different analytical methods (Maiti et al., 2016; Miller, 1959) (http://web.itu.edu.tr/~dulekgurgen/Carbs.pdf).

2.3. Acid mediated heating experiment on sugar removal from waste acid stream of manufacturing process

During the transformation of the biopolymer, such as cellulose to sugar monomer and other byproducts, several operational variables interact and influence the process (Zhang, Xin, Liu, & Ge, 2015). Slight change in process condition could lead the entire process in a definite direction (Choudhary et al., 2013). Thus, in order to enhance the sugar removal and by-products removal, different ratios of (sample: sulfuric acid) have been used at different temperatures as mentioned earlier in a closed COD vial and boiled for 120 min. After heating, each sample was cooled to room temperature and total reducing sugars, total carbohydrates and byproducts were analyzed using different analytical methods. Sugar was finally converted to black nanoparticles. These particles were removed from the solution by the method described in Section 3.7.

2.4. Experimental design and sugars and byproducts removal optimization through response surface methodology (RSM)

During acid hydrolysis of cellulose, several operational variables interact and influence the response. Determination of the optimum point can be achieved with a limited amount of experiments through statistical analysis. Response surface methodology (RSM), a compilation of mathematical and statistical techniques, can be used to interpret and evaluate the combined effects of all the factors in the hydrolysis process (Zhang et al., 2015). Central composite design (Zhang et al., 2015) was applied to investigate sugars and byproducts removal (dependent variable) as a function of three independent variables: reaction time (A), temperature (B) and sample & concentrate sulphuric acid ratio (C). Design-Expert-7 software (Stat-Ease Inc. Minneapolis, MN) has been used to construct the experimental design and the design has been extended up to +α and −α level (Maiti et al., 2015). The experimental design resulted in a set of 20 experiments, comprising three different code levels (low (-1), middle (0) and high (+1)). The ranges of the variables investigated and responses were reported in terms of sugars (glucose, xylose, and trehalose) and by-products (levulinic acid, 5-HMF) removal as shown in Tables 1 and 2.

A quadratic polynomial equation (Eq. (1)) was proposed to interlink the effects of the three independent variables on sugar removal as follows:

$$(\text{Sugar/Byproducts})_{\text{removal}} = X_0 + \sum_{i=1}^{n} X_i Y_i + \sum_{i=1}^{n} X_{ii} Y_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} X_{ij} Y_i Y_j \quad (1)$$

where, $(\text{Sugar/Byproducts})_{\text{removal}}$ is the dependent variable; Y_i and Y_j are the independent variables (n = 3 (A, B and C); X_0 is the intercept constant and X_i, X_{ii} and X_{ij} correspond to the regression coefficients. The same software (Design-Expert®-7) employed for test-matrix design was used to check the experimental responses obtained. An analysis of variance (ANOVA report) was performed to fit the quadratic polynomial equations. Final values of code factors (A, B, C, A^2, B^2, C^2 etc.) were considered to be statistically significant at $p < 0.05$. The quality of the model fit was evaluated by the coefficient of determination (R^2) and the adjusted coefficient of determination (R^2_{Adj}).

2.5. Total reducing sugar analysis by standard DNS method

Total reducing sugar concentration was analyzed by di-nitro salicylic acid (DNS) method (Miller, 1959). Briefly, 200 μL solutions of the sample were taken each time. It was mixed with 800 μL water and 2 mL of 3, 5 di-nitro salicylic acid reagents (alkaline) and placed in water bath for 10 min at 100 ± 1 °C and cooled to room temperature. Later, about 7 mL water was added and the solution was vortexed for 30 s. The optical density was measured at 540 nm using 200 μL of resulting solution in 96 well polystyrene assay plate