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# Conversion of cellulose into reducing sugar by solution plasma process (SPP)

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## ARTICLE INFO

## ABSTRACT

In the present study, cellulose colloids are treated with the solution plasma process in order to prepare reducing sugar. The investigated parameters are treatment time, type of electrodes, and applied pulse frequency of the bipolar supply. The reducing sugar was characterized by DNS method and the %yield of total reducing sugar (TRS) was then calculated. The crystal structure and chemical structure of plasma-treated cellulose was measured by XRD and FT-IR, respectively. The %yield of TRS was greatly enhanced by solution plasma treatment using Fe electrode. SEM and TEM micrograph indicated that Fe electrode yield the incidental Fe nanoparticles, hypothesized to catalyze the cellulose degradation during SPP treatment. The crystal structure of cellulose was destroyed. Solution plasma treatment of cellulose using Fe electrode at the high applied frequency pulse provided the highest %TRS.

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## 1. Introduction

Due to increasing population, industry, agricultural, and transportation, the demand of energy is increasing. The primary source of energy is the fossil fuel such as natural gas, oil and coal. The consumption of energy has caused the depletion of fossil fuels as well as the resulting high price of petrochemicals (Laser, Schulman, Allen, Lichwa, & Antal, 2002; Liu & Zhang, 2016; Peng, Li, & Luo, 2013; Sarkar, Ghosh, Bannerjee, & Aikat, 2012). Therefore, people are approaching towards the use of renewable source of energy. One of an alternative source of energy is biofuel such as ethanol. Ethanol can be produced synthetically from petroleum or by microbial conversion of biomass materials through fermentation. In 1995, about 93% of the ethanol in the world was produced by the fermentation method and about 7% by the synthetic method (Gupta & Verma, 2015). The ethanol production from fermentation is based from sucrose (e.g. sugar cane, sugar beet, sweet sorghum and fruits) and starch (e.g. corn (maize) grain, milo, wheat, rice, potatoes, cassava, sweet potatoes and barley) (Gupta & Verma, 2015). However, sugar-based and starch-based materials are parts of human food chain, and thus expensive. Cellulose is the most abundant and renewable biopolymer in nature. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of $\beta(1 \rightarrow 4)$ linked D-glucose units. Cellulose can be degraded into reducing sugar, predominantly glucose. The reducing sugar can be further fermented into ethanol. Therefore, degradation of cellulose to reducing sugar has received a lot of research interests. It is considered as a promising starting material for the production of ethanol (Badger, 2002; Demirbas, 2005; Taherzadeh & Karimi, 2007; Uihlein & Schbek, 2009; Xiong, Zhang, Wang, Liu, & Lin, 2014).

Recently, several methods including chemical treatment and enzymatic treatment have been reported to prepare reducing sugar (Cantero, Bermejo, & Cocero, 2013; Shuai & Pan, 2012; Wyman et al., 2005; Yang, Zhang, Liu, Li, & Xing, 2011). Among these, chemical treatment using acid is an easy process. Essentially, acid hydrolysis can be performed using both dilute and concentrated acid (Jones et al., 1984; Taherzadeh & Karimi, 2007). Dilute acid hydrolysis of cellulose requires high temperatures and long reaction time (Xiong et al., 2014). In case of concentrated acid, the process could be conducted at lower temperatures and shorter reaction times but more glucose degradation takes place (Iranmahboob, Nadim, & Monemi, 2002). Nevertheless, the chemical waste, contamination, and

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corrosion of equipment are the main drawback of acid hydrolysis. For enzymatic treatment, it is an effective method to achieve the specific cleavage of cellulose to monosaccharide. High percentage of reducing sugar was obtained (Jain & Vigneshwaran, 2012). However, the main problem of enzymatic treatment is its high cost (Orozco, Ahmand, Rooney, & Walker, 2007).

Plasma in liquid-phase or solution plasma process (SPP) technology has been recognized as an advanced oxidation process. SPP is able to produce highly active species especially hydroxyl radical (OH•). It has been widely used in many applications such as nanomaterial synthesis and water treatment (Potocký, Saito, & Takai, 2009; Takai, 2011). Our previous studies have first introduced SPP to degrade polysaccharide such as chitosan and found that the SPP treatment could reduce molecular weight of chitosan significantly and strongly promote water soluble chitosan and chitooligosaccharide products (Prasertsung, Damrongsakkul, Terashima, Saito, & Takai, 2012; Prasertsung, Damrongsakkul, & Saito, 2013). This was due to the degradation process of chitosan mainly caused by OH• radical occurred during plasma treatment. The results also showed that the crystallinity of chitosan was destroyed, resulting in amorphous structure (Pornsunthorntawee, Katepetch, Vanichvattanadecha, Saito, & Rujiravanit, 2014). As the solution plasma can be preceded using a high voltage electricity supply under mild conditions such as low temperature, atmospheric pressure and no strong chemical reagents, it is attractive to explore the possibility of using SPP to degrade cellulose, another type of polysaccharides, into monosaccharides such as sugar.

It is therefore of our interest to apply solution plasma to treat cellulose in order to investigate the effects of solution plasma on the preparation of reducing sugar. The investigated parameters are treatment time, type of electrodes, and applied pulse frequency of the bipolar supply. Several types of electrodes materials including tungsten (W), copper (Cu), and iron (Fe) are employed. The morphology of electrode surface and sputtered solid metal particles are characterized by SEM and TEM, respectively. The plasma-treated cellulose was characterized including total reducing sugar by DNS method, hydroxyl radicals content by salicylic acid method, crystal structure by XRD, and chemical structure by FT-IR.

## 2. Materials and methods

### 2.1. Materials

Microcrystalline cellulose powder (particle size of 150 μm) was purchased from Hemidia, India. Salicylic Acid (SA) was purchased from Sigma Aldrich. Phosphoric acid, nitric acid, sulfuric acid, and hydrogen peroxide were used as received. All of the chemicals, reagents, and solvents used were of analytical grades.

### 2.2. Solution plasma experiment

The setup of solution plasma system, modified from our previous study products (Prasertsung et al., 2012; Prasertsung et al., 2013), is shown in Fig. 1. Briefly, one gram of cellulose powder was suspended in 100 mL of 0.04 M sulfuric acid to obtain cellulose colloid in a glass reactor. The solution plasma is generated at the voltage, and pulse width of 1.6 kV, and 3 μs, respectively. The different type of electrodes including tungsten, copper, and iron were used. The treatment time of solution plasma and applied pulse frequency were varied in the range of 0–300 min and 15–30 kHz, respectively. During plasma treatment, the cellulose colloid was continuously stirred and the temperature of the colloid was 60 °C. In addition, hydrolysis of cellulose colloid without plasma treatment using sulfuric acid at 60 °C was conducted as a control.

### 2.3. Characterization of plasma-treated cellulose

After hydrolysis, the liquid fraction (hydrolysate) was separated from the solid by vacuum filtration. The remained cellulose was washed with water and dried for further analysis. The XRD analysis of cellulose powder before and after SPP treatment was performed using X-ray diffractometer (Shimadzu Lab XRD-6000, Japan). Each sample was pressed into a lamellar container (20 mm in diameter). X-ray diffraction patterns of the plasma-treated and untreated cellulose were measured over diffraction angle ($2\theta$) of 10° to 40° with a CuKα target at 40 kV and 50 mA. The degree of relative crystallinity of cellulose samples was calculated as follows (Zhang, Liu, & Zhao, 2012).

$$\text{Degree of relative crystallinity}(\%) = \frac{I_{(200)} - I_{(am)}}{I_{(200)}} \times 100 \qquad (1)$$

where $I_{(200)}$ is the adsorption peak intensity of the (200) reflection (at $2\theta = 22.3°$), and $I_{(am)}$ is the minimum adsorption intensity between (110) and (200) peaks (at $2\theta \approx 18°$).

FT-IR (Digilab, FTS 7000 Series, USA) was used to characterize the chemical composition of plasma-treated and untreated cellulose powder. FT-IR spectra of samples prepared with KBr were collected using 64 scans in the range of 4000–400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

The hydrolysate of plasma-treated cellulose was centrifuged to recover the sputtered metal particles. The obtained particles were dried overnight prior to characterize the morphology by transmission electron microscope (TEM) using a Philips EM208 microscope operating at an accelerating voltage of 120 kV. The morphology of electrodes surface was studied using scanning electron microscopy (SEM, JEOL, JSM-6400). The remained hydrolysate was then analyzed for total reducing sugar, degraded product and hydroxyl radicals.

In order to determine the total reducing sugar, DNS method was used. The DNS reagent was prepared as described elsewhere (Zhang et al., 2012). In brief, dinitrosalicylic acid (DNS), potassium sodium tartrate, and 2 M NaOH were mixed in hot deionized water (50 °C). After the mixture was completely dissolved, phenol and sodium sulfite were added. The solution was used as DNS reagent. In order to determine the total reducing sugar of plasma-treated cellulose, 0.5 mL of DNS reagent and 0.5 mL of hydrolysate sample was mixed and heated for 5 min. Then the mixture was cooled to room temperature. The absorbance intensity of the final solution was measured using a Shimadzu UV-9100 spectrophotometer at 540 nm. The calibration curve was performed using glucose as standard reagent. The percentage of total reducing sugar (%TRS) was calculated as follows:

$$\%TRS = \frac{amount\ of\ total\ reducing\ sugar}{amount\ of\ cellulose} \times 0.9 \times 100 \qquad (2)$$

For sugar determination, the hydrolysate was filtered with a 0.45 μm syringe filter prior to analyze by High-performance liquid chromatography (HPLC) (Alltech ELSD 2000, USA). The chromatographic separations were carried out using a Rezex RPM-Monosaccharide Pb2+ column and RI detector. The mobile phase was deionized water with the flow rate of 0.6 mL/min and 20 μL of samples were injected.

To quantify hydroxyl radicals produced during plasma treatment, the modified salicylic acid (SA) method has been used according to previously reported (Peralta & Roa, 2014). 1 mL of a $1 \times 10^{-3}$ M SA solution was mixed with 1 mL of liquid fraction of plasma-treated and untreated cellulose. The concentration of the hydroxylated products including 2,3-dihidroxybenzoic acid and 2,5-dihydroxibenzoic acid was determined using a UV–vis Spectrophotometer (Shimadzu UV-9100, Japan). The calibration curve
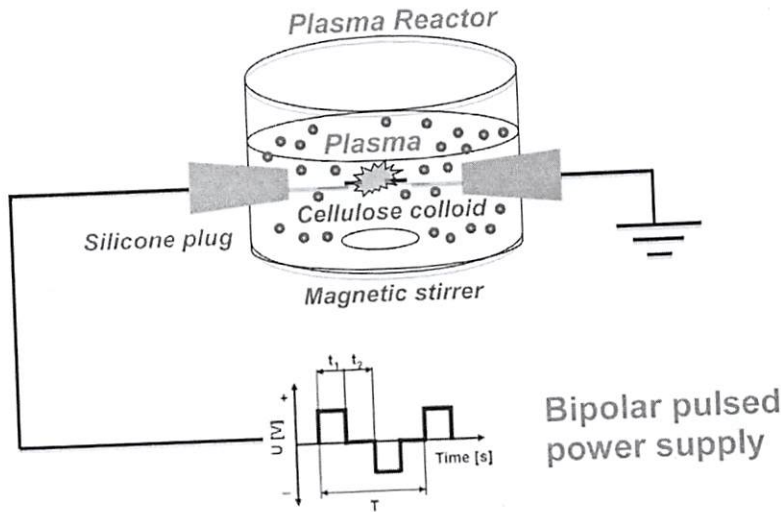
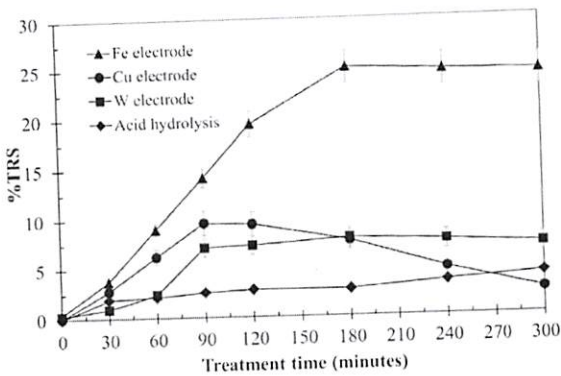Fig. 1. Schematic diagram of solution plasma treatment of cellulose colloid.



Fig. 2. Effects of types of electrodes on %TRS of plasma treatment of cellulose colloid using sulfuric acid as solvent.

was performed using SA solution as standard reagent. The concentration of hydroxyl radical was then calculated.

## 3. Results and discussion

In this study, the SPP was introduced to treat crystalline cellulose in diluted sulfuric acid in order to degrade cellulose and prepare reducing sugar. Fig. 2 shows the %total reducing sugar (TRS) analyzed by DNS method, as a function of treatment time and types of electrodes. The results showed that the %TRS of acid hydrolysis of cellulose without plasma treatment was measured to be 3%. However, the %TRS was increased when the SPP was applied. After solution plasma treatment using the tungsten (W) electrode for 90 min, the %TRS of plasma-treated cellulose was slightly increased up to 7.8%. Then, it seemed to be consistent until the treatment time reached 300 min. The degradation reaction can be predominantly induced by free radical such as hydroxyl generated by plasma treatment. As previously reported by Baroch, the generation of hydroxyl radical could be existed during solution plasma treatment via the reaction of oxygen radical and water in the system (Baroch, Anita, Saito, & Takai, 2008).

$$O^\bullet + H_2O \rightarrow 2OH^\bullet \tag{3}$$

The degradation mechanism of cellulose in the presence of hydroxyl radical has been proposed (Wang, Li, Yang, Chen, & Gao, 2011). Hydroxyl radicals could react with glucose unit of cellulose

and generate a carbon radical. This led to a cleavage of glycosidic linkage by the oxidation reaction of superoxide anion and carbon radical. Thereafter, cellulose was subsequently degraded to reducing sugar. In addition, this result was in good agreement with our previous studies which found the degradation of polysaccharides polymer such as chitosan during solution plasma treatment (Prasertsung et al., 2012; Prasertsung et al., 2013). The β-1-4 glycosidic linkage of chitosan could be subsequently broken by the generated hydroxyl radicals, resulting in low molecular weight chitosan. As known that chitosan and cellulose material are recognized as polysaccharides, therefore cellulose could be degraded to reducing sugar by hydroxyl radical generated in the system with the similar degradation reaction to that of chitosan. When the solution plasma treatment using copper (Cu) electrodes was employed, it was found that the %TRS was slightly increased to 11% after plasma treatment for 90 min. After that a continuously decrease in %TRS was noticed until the treatment time reached 300 min. The %TRS of plasma-treated cellulose colloid using Cu electrode was higher than that of W. The improvement of %TRS caused by using Cu electrode could be attributed to the copper ions generated by the erosion of copper electrode via electrolysis during plasma treatment (Potocký et al., 2009). As previously reported by Friedrich, copper ions can also act as a catalyst and enhance the Fenton reaction (Cupro-Fenton reaction) (Friedrich, Silva Zanta, Machulek, Silva, & Quina, 2012). Therefore, the decomposition of the H$_2$O$_2$, generated in the system during plasma treatment by recombination reaction of hydroxyl radical, could occur and provided high amount of hydroxyl radical as follow.

$$H_2O_2 + Cu^+ + H^+ \rightarrow OH^\bullet + Cu^{2+} + H_2O \tag{4}$$
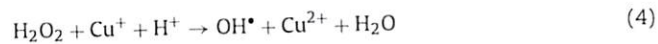
Considering the reduction of %TRS after plasma treatment using Cu electrode for 90 min, it could be caused by the side reaction which could exist during plasma treatment. The reducing sugar product obtained from the degradation of cellulose could react with copper ions (Cu$^{2+}$) and hydroxyl radical to produce copper oxide, as previously described by Chandraju (Chandraju, Venkatesh, & ChidanKumar, 2014). As a result, the reducing sugar product in the system was consumed, resulting in lower %TRS.

Interestingly, the %TRS of plasma-treated cellulose colloid was dramatically enhanced when iron (Fe) electrode was used. The %TRS of plasma-treated cellulose using Fe electrodes was remarkably increased up to 27.0% after plasma treatment for 180 min and tended to be constant until the treatment time reached 300 min.
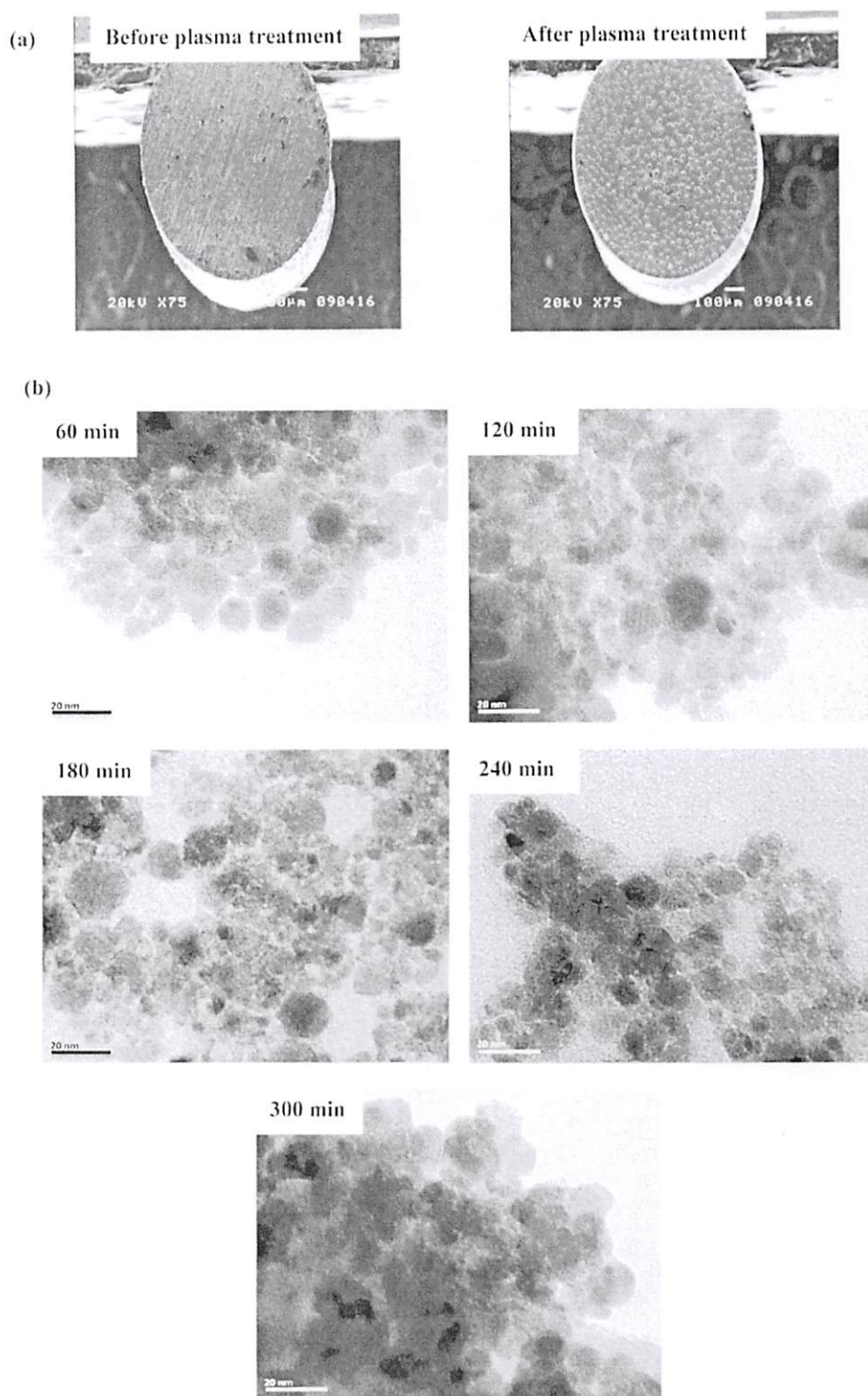
**Fig. 3.** (a) Scanning electron micrographs of iron electrode surface before and after plasma treatment, and (b) Transmission electron micrographs of sputtered iron nanoparticles during plasma treatment for 60–300 min.

The maximum%TRS of plasma-treated cellulose using Fe electrodes was relatively high in comparison to those using W and Cu electrodes. Fig. 3a shows SEM micrograph of iron electrodes before and after plasma treatment. The results showed that before plasma was applied, the smooth surface of iron electrode was observed. However, the electrode surface became rough when the plasma was applied. This revealed that the erosion of iron electrode via material sputtering occurred during plasma treatment. Fig. 3b shows TEM micrographs of iron particles generated by electrode material sputtering during plasma treatment for 60–300 min. It was evident that the spherical shape of iron nanoparticles with the size of 10–20 nm was observed when solution plasma was applied for 300 min. In
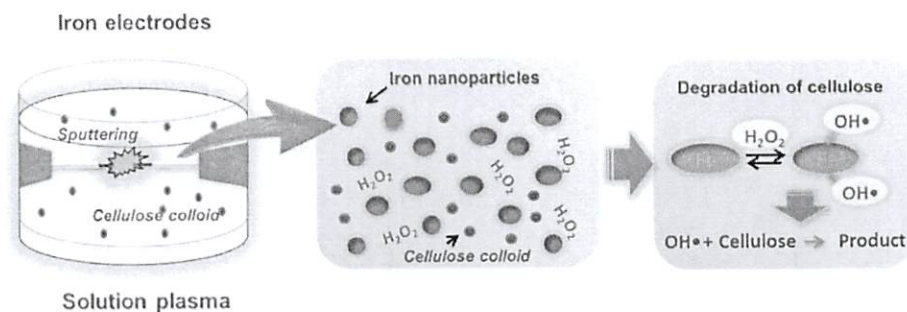
Iron electrodes



Solution plasma

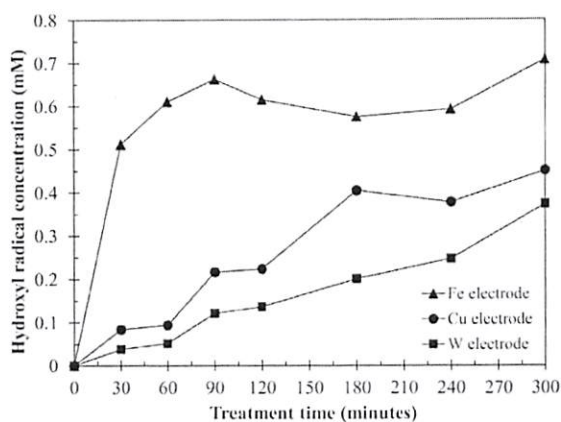**Fig. 4.** Schematic diagram of degradation mechanism of cellulose colloid via iron nanoparticles.



**Fig. 5.** Effects of types of electrodes on OH radical concentration of plasma treatment of cellulose colloid using sulfuric acid as solvent.

addition, the aggregate of iron nanoparticles was noticed after plasma treatment for 120 min. The improvement of %TRS of plasma-treated cellulose colloid by iron nanoparticles could be described as follows. Firstly, oxidation reaction at the electrode surface could transform these nanoparticles into ferrous ions and induce Fenton reaction during plasma treatment. This could increase the amount of hydroxyl radicals in the system, as previously described by Tantiplapol (Tantiplapol et al., 2015). For the second reason, generated iron nanoparticles could act as a metal solid catalyst in cellulose degradation (Ndolomingo & Meijboom, 2015). The mechanism of cellulose degradation induced by iron nanoparticles was shown in Fig. 4. The degradation of cellulose is predominantly affected by the decomposition of hydrogen peroxide, which is generated during plasma treatment by the recombination reaction of hydroxyl radicals. The peroxide can react on the surface of iron nanoparticles leading to transform into the reactive species especially hydroxyl radicals. Thereafter, the cellulose can react with hydroxyl radicals, resulting in the decomposition of cellulose and providing reducing sugar product. Therefore, enhanced %TRS of plasma-treated cellulose colloid using iron electrode could be predominantly caused by the decomposition of $H_2O_2$ induced by ferrous ions and the presence of metal solid catalyst in system.

In order to confirm the degradation mechanism as described above, the amount of hydroxyl radical generated during plasma treatment was determined. Fig. 5 shows the concentration of hydroxyl radicals generated during plasma treatment as a function of type of electrode and treatment time. It was found that the amount of hydroxyl radical produced after plasma treatment using W and Cu electrodes were slightly increased with increasing treatment time. This result corresponds with the result on the %TRS of plasma-treated cellulose colloid, as showed in Fig. 2. The use

of both W and Cu electrodes provided low amount of hydroxyl radical. This led to a limit in the degradation reaction of cellulose induced by hydroxyl radicals in the system, resulting in low %TRS. Interestingly, the amount of hydroxyl radical generated during plasma treatment was dramatically enhanced when Fe electrode was applied. At the first 90 min of plasma treatment, the concentration of hydroxyl radical was rapidly increased. The increase of hydroxyl radicals could be attributed to the decomposition of $H_2O_2$ in the system. In other words, the generated $H_2O_2$ during plasma treatment could be reduced into hydroxyl radicals again by the mechanism described above. As a result, the amount of hydroxyl radical was greatly generated and subsequently the degradation of cellulose was enhanced. Therefore, the decomposition reaction of $H_2O_2$ could also be responsible for the enhancement of cellulose degradation. Considering the concentration of hydroxyl radicals after plasma treatment for 90 min, it was found that it seemed to be consistent until the plasma treatment time reached 300 min. This was possibly due to the decrease in catalyst efficiency. As observed in Fig. 3b, the iron nanoparticles were obviously accumulated at the treatment time in the range of 120–300 min. This could reduce the surface area and the active site of catalyst for $H_2O_2$ in the system (Liu & Zhang, 2016). As a result, the amount of the hydroxyl radical products was subsequently unchanged.

Generally, the crystalline structure of cellulose is one of important factors that affect the degradation of cellulose. In order to investigate an alteration of crystal structure of cellulose during plasma treatment, XRD was performed. Fig. 6a shows the X-ray diffraction patterns of untreated and plasma-treated cellulose at the treatment time of 300 min. It was observed that the untreated cellulose sample displayed two characteristic peaks at $2\theta = 15.1°$ and 22.5°, which are referred to cellulose-I structure (Jinbao, Xiangrong, Meiyun, Huijuan, & Hang, 2015). After plasma treatment using W and Cu electrodes for 300 min, the diffraction peak located at both $2\theta = 15.1°$ and 22.5° shows less intensity in comparison to those of untreated sample. This suggested that the crystalline region of the cellulose sample was destroyed during plasma treatment. When the Fe electrode was applied, the intensity of diffraction peak at $2\theta = 15.1°$ and 22.5° of the degraded cellulose products was the lowest in comparison to those of W and Cu electrodes. The use of Fe electrodes could enhance the disruption of the crystalline structure of the cellulose more than W and Cu electrodes. Fig. 6b shows the calculated degree of relative crystallinity of untreated and plasma-treated cellulose as function of treatment time and type of electrodes. The degree of relative crystallinity of untreated cellulose was approximately 64%. The degree of relative crystallinity of cellulose was increased when the solution plasma treatment using W, Cu, and Fe electrodes were applied for 60 min. The increase of degree of relative crystallinity of plasma-treated cellulose could be attributed to the destruction of amorphous region of cellulose structure (Jinbao et al., 2015). After 60 min of plasma treatment, the degree of relative crystallinity of
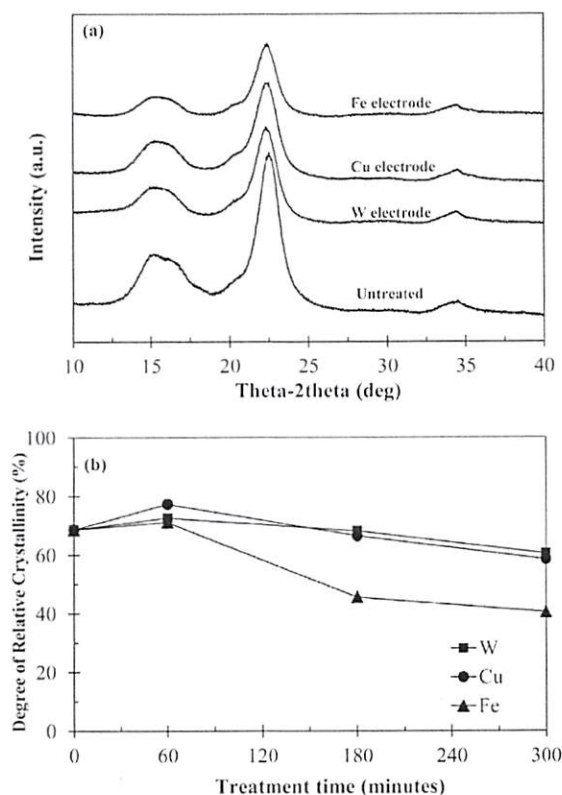
**Fig. 6.** (a) X-ray diffraction patterns of untreated and plasma-treated cellulose at the treatment time of 300 min and (b) degree of relative crystallinity of untreated and plasma-treated cellulose.



**Fig. 7.** FT-IR spectra of untreated and plasma-treated cellulose.



**Fig. 8.** Effects of applied pulsed frequency on%TRS of plasma treatment of cellulose colloid using sulfuric acid as solvent.

cellulose treated by W and Cu electrodes was slightly decreased. In case of Fe electrode, it tended to be decreased at the treatment time of 180 min and slightly decreased until the treatment time reached 300 min. A more disrupted crystal structure of cellulose treated by Fe electrode may be caused by the high amount of hydroxyl radical generated in the system, as showed in Fig. 5. As previously reported by Le, the hydroxyl radical could effectively break the hydrogen bonds and crystal structure of cellulose (Le et al., 2015). This also corresponds to the%TRS results, shown in Fig. 2. The reduced crystal structure of cellulose to amorphous favors the degradation process of cellulose by increasing an accessibility of hydroxyl radicals. As a result, the%TRS of plasma-treated cellulose product was increased.

The FT-IR spectra of untreated and plasma-treated cellulose samples are shown in Fig. 7. The characteristic peaks of untreated cellulose appeared at 2900, 1373 cm$^{-1}$, 1158cm$^{-1}$, and 1158 cm$^{-1}$, which corresponded to C—H stretching, C—H deformation, and C—O—C stretching vibration at glycosidic linkage, respectively (Jinbao et al., 2015). After the solution plasma was applied, the characteristic peaks of plasma-treated cellulose mostly exhibited the same bands as the untreated sample. However, there was a new band at 1710 cm$^{-1}$, which corresponded to the C=O stretching vibration (Tong et al., 2013). This result indicated that aldehydes and ketones were formed after the degradation of cellulose by plasma treatment.

Fig. 8 shows the effects of applied pulse frequency on%TRS of plasma-treated cellulose colloid. It was evident that the%TRS of plasma treatment of cellulose at applied pulse frequencies of 15 kHz and 22.5 kHz were increased when the plasma treatment was applied for 180 min. Then it seemed to be constant. In case of the applied pulse frequency of 30 kHz, the%TRS was continuously increased until the treatment time reached 300 min. The
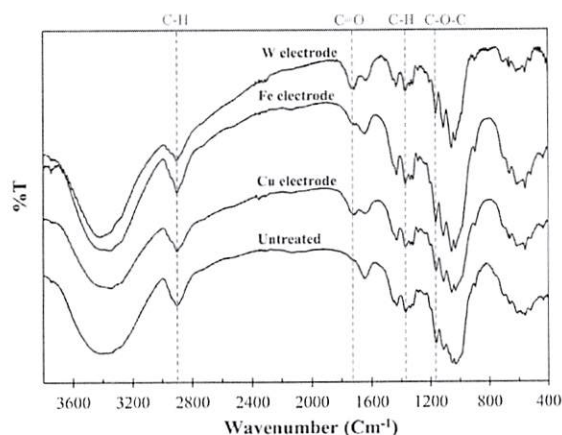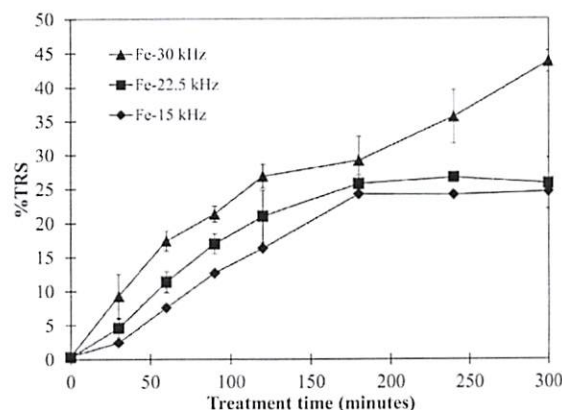
maximum%TRS of plasma-treated cellulose after plasma treatment at the applied pulse frequencies of 15 kHz, 22.5 kHz, and 30 kHz were measured to be 25, 27, and 42, respectively. The improvement on the%TRS at applied pulse frequencies of 30 kHz could be attributed to the increased energy input in the plasma system. An increase of energy may accelerate an erosion of iron electrodes during plasma treatment, provided high amount of solid particles. In addition, the amount of hydroxyl radical during plasma treatment could be enhanced by increasing the energy input of power supply in the plasma system (Kang, Li, & Saito, 2013). As a result, degradation process of cellulose could be enhanced, resulting in a high%TRS of plasma-treated cellulose.

Additionally, the result clearly suggested that high plasma energy strongly promoted the degradation of cellulose, but it might further cause the degradation of degraded products such as glucose as it is known that the glucose degradation into 5-hydroxymethylfurfural is the main side reaction during degradation of cellulose (Xiong et al., 2014). High reaction temperature can accelerate the degradation of glucose product (Xiong et al., 2014). In this work, HPLC analysis of plasma-treated cellulose hydrolysate showed that the sugar products in hydrolysate were mainly composed of maltose, glucose, xylose and mannose (see supported data). 5-hydroxymethyl furfural was not presented in hydrolysate product. This indicated that the degradation of cellulose by solution plasma treatment did not induce the degradation of glucose product, possibly due to low temperature of solution plasma treatment.

## 5. Conclusion

In this study, a solution plasma system was introduced to treat cellulose colloid in order to prepare reducing sugar. The plasma-treated cellulose colloid was degraded during plasma treatment and provided the reducing sugar product. The%TRS was greatly affected by the types of electrodes and the applied pulse frequency. The plasma treatment of cellulose colloid using Fe electrode and high pulse frequency strongly promoted the%TRS. We found that the incidentally co-generated iron (Fe) nanoparticles via Fe electrode erosion could be investigated during solution plasma treatment and strongly promoted the degradation of cellulose. Degradation process of cellulose caused by plasma treatment has an effect on the crystal structure. These results implied that the Fe was suitable electrode for degradation of cellulose by solution plasma treatment.

## Acknowledgements

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2017.05.025.

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