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Research article

Response surface methodology for optimization of cellulose extraction from banana stem using NaOH-EDTA for pulp and papermaking

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ABSTRACT

Alkaline pulping using sodium hydroxide (NaOH), also known as soda pulping, is predominantly used to extract cellulose for pulp and papermaking. The NaOH was responsible for the dissolution and removal of lignin but unfortunately, simultaneous hydrolysis of cellulose could not be avoided. Modification for improved lignin removal and cellulose stabilization are always a technical challenge for the pulp and paper industry. Therefore, ethylenediaminetetraacetic acid (EDTA) was considered as an additive to minimize cellulose hydrolysis and thus improve the total yield of cellulose pulp. Response surface methodology (RSM) with central composite design (CCD) was employed for statistical modeling and optimization of NaOH and EDTA charges for maximum pulp yield, lignin removal, and cellulose content. Analysis of variance (ANOVA) revealed a significant interaction effect of NaOH and EDTA charges on pulp yield and its cellulose content. Using the predicted optimum condition of 17.7% NaOH and 10% EDTA, pulping of banana stem at 100 ± 5 °C for 30 min resulted in increasing pulp yield, lignin removal, and cellulose content by approximately 18.5%, 1.1%, and 0.6%, respectively, as compared to pulping without EDTA. Changes in the functional groups monitored using Fourier transform infrared (FTIR) revealed the presence of ester and C–N stretching bands from cellulose extracted with NaOH/EDTA due to successful esterification of EDTA on the cellulose pulp. Further analysis on the viscosity average degree of polymerization found that the cellulose pulp extracted with NaOH/EDTA also has a higher degree of polymerization compared to the pulp extracted without EDTA. Based on these findings, it was concluded that esterification with EDTA has successfully protected the cellulose against alkaline hydrolysis by NaOH. Therefore, the addition of EDTA is a promising approach to improve the pulp yield with high degree of polymerization.

1. Introduction

Shortage in wood supply and the growing concern for sustainable resources has led to the commercialization of non-wood sources for pulp and papermaking. In 2019, around 6% of the global pulp production originated from non-wood sources (FAO, 2019). Among the commonly used non-wood sources are bagasse, straw, and bamboo (FAO, 2013). Other than that, any materials with over 34% of cellulose and less than 30% lignin are acceptable for pulp and papermaking (Nieschlag et al., 1960; Ververis et al., 2004). Banana stem is a promising alternative for pulp and paper production. Due to the high cellulose content, it was also studied for the production of dissolving pulp (Das et al., 2016), bio-composite (Srinivasan et al., 2014), and biofuel (Shimizu et al., 2018).

Chemical extraction of cellulose was usually carried out at a temperature range of 140–170 °C to deliberately remove lignin that binds cellulose fibers together (Liu et al., 2018). This process is often known as pulping or delignification process. Aside from cellulose and lignin, plants also contained hemicellulose, extractives, and ash. Hemicellulose provides additional strength to the extracted cellulose pulp despite having a different structure (Yuan et al., 2016). Extractives contain substances like waxes, fats, and resins that might render inhomogeneity and hydrophobicity in pulp (Sharma et al., 2018). Ash represents inorganic matters that might cause unwanted reactions such as with bleaching agent thus reducing its efficiency in removing residual lignin from pulping process (Dutt et al., 2009).

Extraction of cellulose from non-wood sources normally required less chemical and energy consumption due to low lignin content (Ashori, 2006; Mohieldin, 2014), as compared to woods which typically contained 40–50% cellulose and 18–35% lignin (Bajpai, 2018). A similar degree of delignification could be achieved for non-wood sources using a

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chemical charge lower than that required for woods (Azeez, 2018). Previous studies revealed that it was even possible to perform a low temperature pulping below 100 °C (Goswami et al., 2008; Rattanawongkun et al., 2020), but it is best to consider optimization of the other relevant factors such as chemical charge and pulping time to achieve satisfactory pulping efficiency (Musekiwa et al., 2020).

Sodium hydroxide (NaOH) is the main chemical used as the pulping liquor for non-wood sources. Some previous studies on banana stem also introduced anthraquinone, sodium sulfide, or sodium sulfite into the pulping liquor to promote ether cleavage, thus improving the degradation and solubilization of lignin (Cordeiro et al., 2004; Das et al., 2016; Goswami et al., 2008). Unfortunately, treatment with NaOH also caused hydrolysis of carbohydrates which resulted in undesirable mass loss (Musekiwa et al., 2020). Plant carbohydrates are made of mostly cellulose and hemicellulose. Although cellulose is chemically stable due to its linear structure, Van Loon and Glaus (1997) mentioned that degradation of cellulose under alkaline conditions is possible through peeling-off reaction of reducing end groups and cleavage of glycosidic bonds.

Chelating agents are common additives used to improve the removal of ash. Edmunds et al. (2017) previously found that ethylenediaminetetraacetic acid (EDTA) afforded greater ash reduction than natural chelators such as acetic acid and citric acid. Furthermore, treatment with EDTA also showed the lowest extraction severity with low soluble sugars which implies minimal hydrolysis of carbohydrates. A similar finding was also reported by Islam et al. (2018) in the case of enzymatic hydrolysis where the production of soluble sugars after treatment with EDTA was lower than that of citric acid. In another study by Bicu and Mustata (2013), cellulose yield showed proportional increment with EDTA addition. Therefore, EDTA is the best candidate to protect cellulose against the degradative action of NaOH during pulp making.

In this study, the optimum NaOH and EDTA charges to achieve maximum pulp yield, lignin removal, and cellulose content were determined using response surface methodology (RSM) with central composite design (CCD). The efficiency of lignin removal was reflected by kappa number analysis. The esterification of EDTA on cellulose structure was confirmed using Fourier transform infrared (FTIR) and its performance in minimizing cellulose degradation was evaluated through analysis on the degree of polymerization.

2. Materials and methods

2.1. Material preparation

Banana stem (*Musa paradisiaca* L.) was collected approximately six months after it was planted in a designated area located in Kelantan, Malaysia (6°06′58.9″N 102°12′50.7″E). The banana stem was prepared according to a standard method provided by the Technical Association of the Pulp and Paper Industry (TAPPI); TAPPI T264 cm-97 (TAPPI, 1997). The stem was oven-dried at 105 ± 5 °C for the total removal of its moisture content as indicated by no weight change before it was ground and sieved to obtain a particle size of 0.3–0.4 mm (shown in Figure 1). Proximate chemical analysis of the sample was carried out to determine its compositions. Holocellulose content that represents carbohydrates fraction was determined according to chlorination method (Wise et al., 1946). Cellulose content was determined according to TAPPI T203 cm-99 (TAPPI, 1999a) and hemicellulose content was calculated based on the difference in holocellulose and cellulose contents. Lignin and ash contents were determined according to TAPPI T222 om-02 (TAPPI, 2002b) and TAPPI T211 om-02 (TAPPI, 2002a), respectively. Extractives content was determined according to TAPPI T204 cm-07 (TAPPI, 2007) using acetone as the solvent instead of the frequently used ethanol-benzene due to its carcinogenic effect. All reported data were in dry weight basis (wt.%) taken from an average of five replications and satisfied the statistically significant difference of $p < 0.05$.

Figure 1. Moisture-free banana stem sample.

2.2. Experimental design and optimization

One factor at a time (OFAT) design was used to evaluate the effects of pulping variables namely pulping time, NaOH charge, and EDTA charge at a fixed temperature of 100 ± 5 °C. The developed design was summarized in Table 1. The percentage of pulp yield and lignin removal were determined to justify the efficiency of NaOH in removing lignin, while cellulose content was also evaluated for pulping with EDTA to justify its efficiency in minimizing cellulose degradation.

Minitab 19 statistical software was used for experimental design, data calculation, modeling, and optimization. Response surface methodology (RSM) was employed to determine the optimum condition for the extraction of cellulose from the banana stem using central composite design (CCD) at five levels (−1.4, -1, 0, +1, +1.4). NaOH (14–20%) and EDTA (5–10%) charges were selected as the independent variables since chemical charges are the most influential factor for chemical pulping, while the pulping time and temperature were kept at 30 min and 100 ± 5 °C, respectively. The value range of each independent variable was based on the OFAT design. Under these conditions, 13 experimental runs were generated including five replications at center points, four cube points, and four axial points.

The evaluated responses; pulp yield, lignin removal, and cellulose content were fitted to the second-order polynomial model. Analysis of variance (ANOVA) was applied to analyze the adequacy of the developed model, taking into consideration the significance of individual and interaction effects of each variable at a 95% confidence level. The influences of each variable and interaction between variables and

Table 1. OFAT design for evaluation of pulping variables.

Variables	Fixed conditions	Responses	References
Pulping time: 30, 60, 90, 120, 150, and 180 min	16% NaOH and 100 ± 5 °C	Pulp yield and lignin removal	(Goswami et al., 2008)
NaOH charge: 14, 16, 18, and 20%	30 min and 100 ± 5 °C	Pulp yield and lignin removal	(Finell and Nilsson, 2004)
EDTA charge: 0, 5, and 10%	16% NaOH, 30 min and 100 ± 5 °C	Pulp yield, lignin removal, and cellulose content	(Bicu and Mustata, 2013)

responses were described by three-dimensional surface plots. A numerical optimization technique based on the desirability function was carried out to achieve the maximum goal for both responses. The optimum condition predicted by RSM was then confirmed by experimental value at 95% confidence interval (CI).

2.3. NaOH-EDTA pulping

Cellulose was extracted from banana stem through laboratory-scale pulping experiments carried out in a 250 ml beaker heated on a stirring hot plate at a constant speed of 500 rpm. For each experimental run, a 10 g sample was added to 100 ml pulping liquor containing a mixture of NaOH and EDTA to ensure a liquid-to-solid ratio of 10 ml/g for complete immersion of the sample in the pulping liquor (Rattanawongkun et al., 2020). Based on the OFAT design, the maximum pulping temperature was maintained at 100 ± 5 °C for 30 min. The NaOH and EDTA charges were varied according to the central composite design. Following this pulping process, the produced pulps were thoroughly washed under running tap water, disintegrated in a three-bladed mixer for 1 min, and screened on a flat-plate screen with 0.25 mm slits. Thereafter, the screened pulps were oven-dried at 60 °C overnight for weight determination and characterization (Zainuddin et al., 2012).

2.4. Pulp characterization

For each run, the pulps were analyzed for kappa number and cellulose content in dry weight basis (wt.%) according to TAPPI T236 om-99 (TAPPI, 1999b) and TAPPI T203 cm-99 (TAPPI, 1999a), respectively. The percentages of pulp yield and lignin removal were calculated using the following Eq. 1–2;

$$\text{Pulp yield, } Y_P(\%) = m/m_0 \times 100 \quad (1)$$

$$\text{Lignin removal, } Y_L(\%) = [(L_0 - 0.13K)/L_0] \times 100 \quad (2)$$

where m_0 is the dry weight of banana stem sample in gram, m is the dry weight of pulp in gram, L_0 is the initial lignin content in dry weight basis (wt.%) determined from proximate analysis, and K is the kappa number.

In order to prove the significant role of EDTA in protecting cellulose from alkaline hydrolysis, the cellulose pulp produced at the optimum condition and a control pulp extracted without EDTA were tested for their functional groups and degree of polymerization. Fourier transform infrared (FTIR) spectra were recorded using PerkinElmer Spectrum One FTIR spectrometer within a wavelength of 4000 to 500 cm^{-1}. The spectra were analyzed for differences in absorption bands, especially around 1740 cm^{-1} attributed to ester bonding between cellulose and EDTA. A viscosity average degree of polymerization (DPv) was estimated using Morton equation (Morton, 1996) as in Eq. (3), taking μ as the pulp viscosity in mPa.s determined according to TAPPI T230 om-08 (TAPPI, 2008).

$$\text{Degree of polymerization, } DP_v = 598.4 \ln \mu + 118.02(\ln \mu)^2 - 449.6 \quad (3)$$

3. Results and discussion

3.1. Composition of banana stem

The banana stem has a high moisture content of approximately 90% and its composition is shown in Table 2. The values obtained from this study show a deviation of up to 31% from the previous data, with an exception for extractives and hemicellulose contents due to dissimilarity in the used solvent and analysis method. The hemicellulose content from this study was simply deduced from the difference in holocellulose and cellulose contents, while a more accurate value can be obtained using liquid chromatography (Shimizu et al., 2018) or calorimetric method (Tripathi et al., 2013). On the other hand, acetone was used to measure the extractives content in this study while the referred works used ethanol-benzene, except for Othman et al. (2020) and Shimizu et al. (2018) who did not mention their solvent. However, a significant difference was still observed although a similar solvent was used by Abdul Khalil et al. (2006), Goswami et al. (2008), and Tripathi et al. (2013). Therefore, despite the analysis method, the difference in composition is also related to the species, geographical location, age, and climate factors as suggested by Goswami et al. (2008) and Ramdhonee and Jeetah (2017). Nevertheless, this analysis confirms the high cellulose and low lignin content of the banana stem, reinforcing its potential as a good source for pulp making. Later, the values obtained from this proximate analysis were compared with the final compositions of pulp to justify the efficiency of the extraction process.

3.2. Cellulose extraction

Preliminary work was carried out based on previous studies to determine the suitable working range for this study starting with the common 16% NaOH charge used for pulping of non-wood sources (Liu et al., 2018). Since the pulping was conducted at a lower temperature of 100 ± 5 °C rather than the common temperature range of 140–170 °C (Liu et al., 2018), hence the appropriate pulping time was first to be identified. Figure 2 shows the relationship between pulp yield, lignin removal, and pulping time. The data were best fitted to an exponential function as in Eq. 4,5.

$$Y_P(\%) = 33.88 + 65.75 \exp(-0.05x), \ R^2 = 0.986 \quad (4)$$

$$Y_L(\%) = 62.45 - 62.34 \exp(-0.06x), \ R^2 = 0.991 \quad (5)$$

where Y_P is the pulp yield, Y_L is the lignin removal, and x is the pulping time.

The value of 33.88 from Eqs. 4 and 62.45 from Eq. (5) represented the points when the curves started to reach equilibrium which was close enough to the pulp yield of 33.8 ± 1.4% and lignin removal of 62.4 ± 0.8% achieved after pulping for 120 min. This finding suggested that extended pulping beyond 120 min was statistically insignificant. Previously, Wan Rosli et al. (2004) found that alkaline pulping for more than 90 min was insignificant for the removal of lignin from oil palm fronds. They reported a kappa number of 87.5 for pulping using 16.6% NaOH at

Table 2. Composition of banana stem.

Composition (%)	This study	Previous studies				
		(Abdul Khalil et al., 2006)	(Othman et al., 2020)	(Shimizu et al., 2018)	(Goswami et al., 2008)	(Tripathi et al., 2013)
Holocellulose	78.2 ± 0.3	65.2	-	-	-	69.9
Cellulose	69.4 ± 0.7	63.9	55.5	60.8	54.6	53.7
Hemicellulose	8.8 ± 0.9	-	5.4	19.6	17.5	15.5
Lignin	15.3 ± 0.1	18.6	22.3	19.3	18.2	12.4
Ash	1.6 ± 0.1	1.5	-	-	1.4	5.8
Extractives	4.9 ± 0.2	10.6	7.6	10.5	3.1	1.8

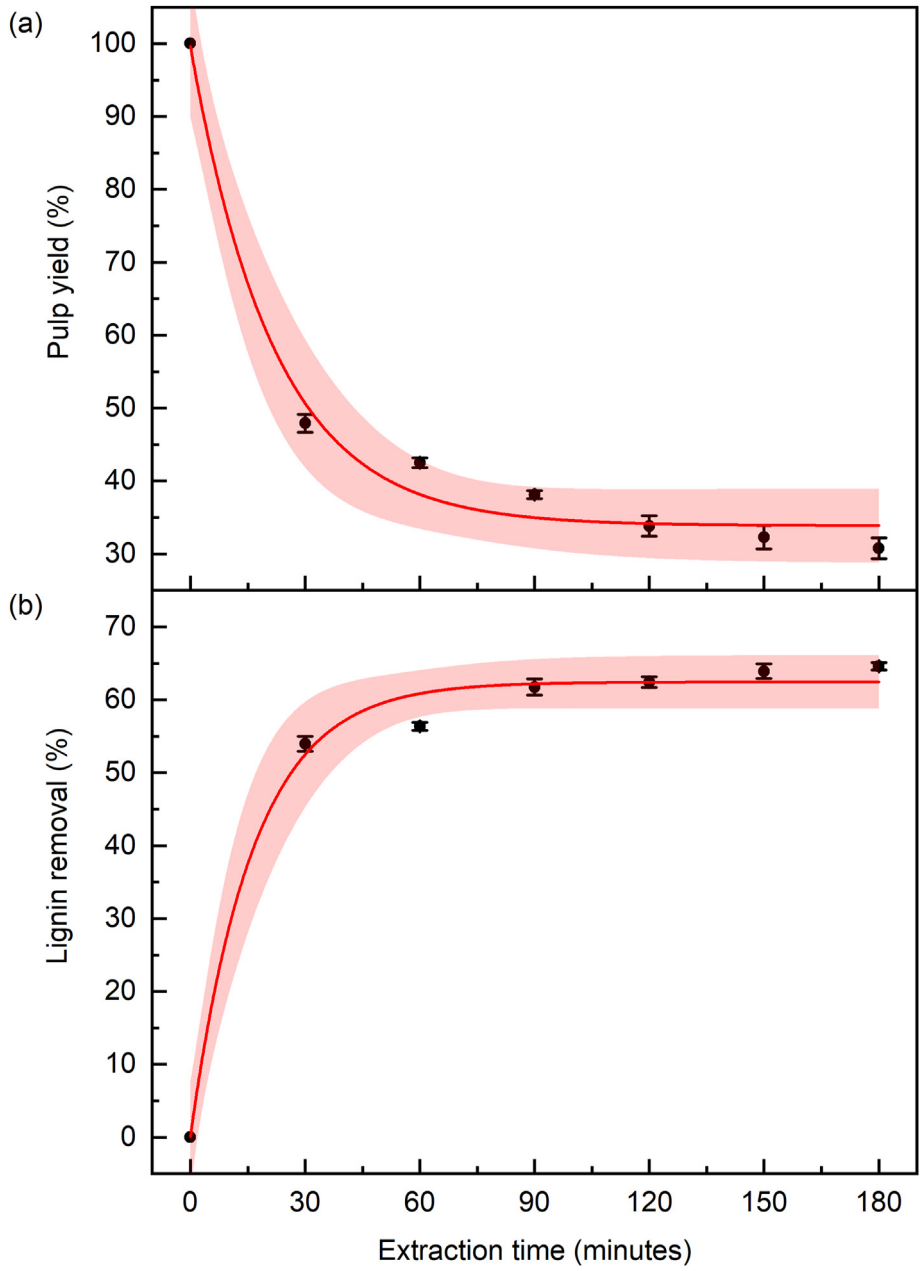

Figure 2. Plots of (a) pulp yield and (b) lignin removal as a function of pulping time with 95% confidence band.

170 °C which equals to lignin removal of approximately 23.2%. The higher removal of lignin recorded in this current study indicated that lignin from the banana stem was readily dissolved even at a lower temperature of 100 ± 5 °C.

The relative reduction in pulp yield with increasing pulping time was ascribed to the partial removal of plant components. Polowski et al. (2006) mentioned that the dissolution of soluble fractions of extractives, hemicellulose, and lignin occurred instantaneously. A fast lignin dissolution within the first 30 min using 16% NaOH has resulted in the removal of 54.0 ± 1.0% of the initial lignin content. It is known that the phenylpropane units in lignin were bonded by carbon-carbon (C–C) and ether (C–O–C) linkages. Cleavage of these linkages is fundamental for lignin removal since it produced low molecular and soluble lignin fragments (Gautam et al., 2016). Hon and Shiraishi (2000) mentioned that ether linkages are readily cleaved as compared to the more stable C–C linkages. Therefore, the steep incline in the percentage of lignin removal within this first 30 min was ascribed to the rapid ether cleavage which resulted in the fast dissolution of lignin.

Rather slow dissolution of lignin was observed after 30 min. Approximately 8.5 ± 0.3% lignin was removed from 30–120 min, and only 2.2 ± 0.3% lignin was removed from 120–180 min. Here, the slow dissolution of lignin was believed to be associated with the less reactive lignin fraction, possible attachment to carbohydrates forming alkali-stable complex, and low alkalinity towards the process end (Hon and Shiraishi, 2000). The relatively small removal of lignin within the total 150 min suggested that pulping beyond 30 min using the current pulping conditions was inefficient for the removal of lignin. This conclusion was agreed by Dutt et al. (2009) who also found that extended pulping after a bulk removal of lignin was uneconomical. For that reason, evaluation of the other pulping variables was observed at a fixed pulping time of 30 min.

Figure 3 shows the relationship between pulp yield, lignin removal, and NaOH charge. The data satisfied a polynomial function as in Eq. 6–7.

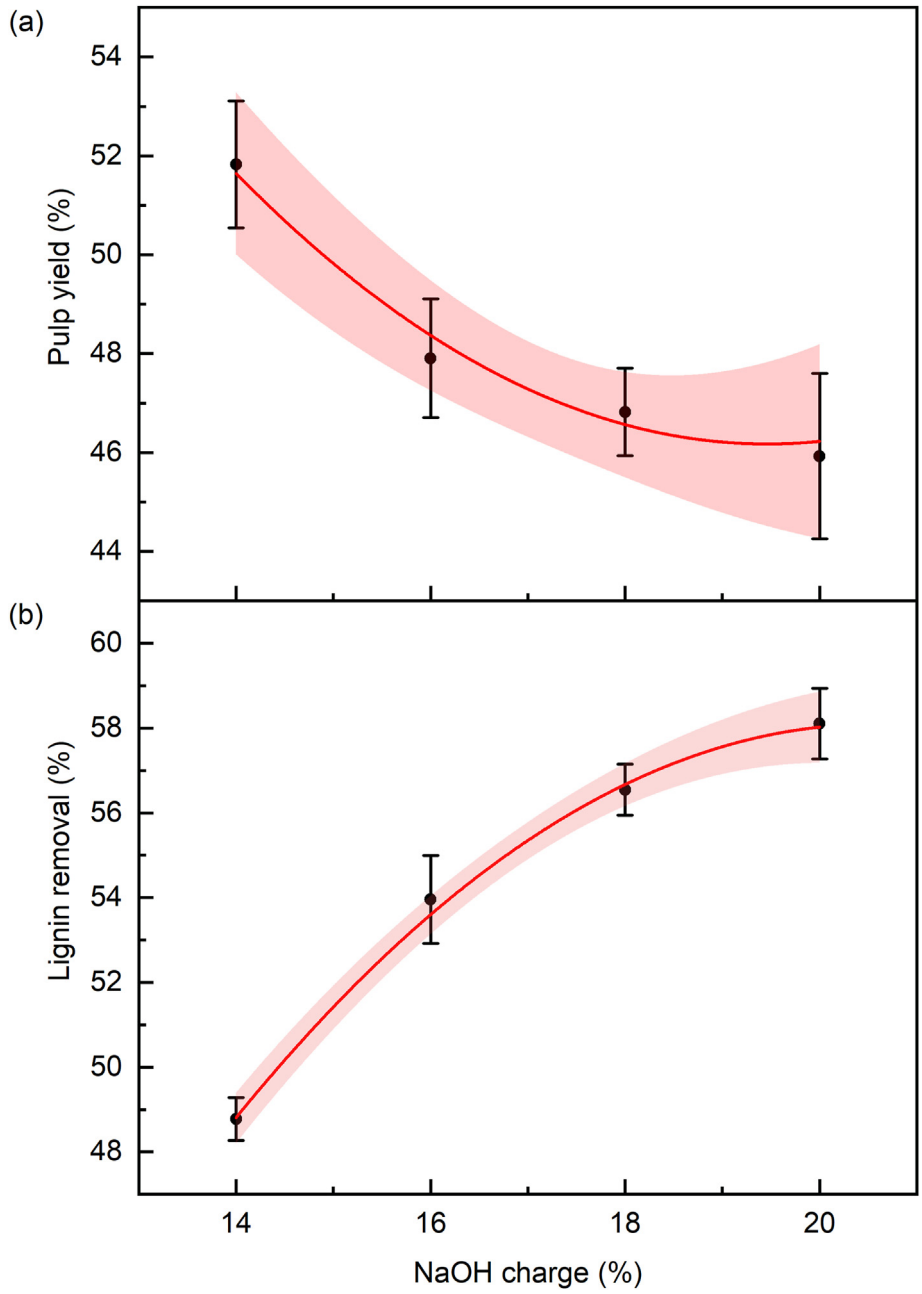

Figure 3. Plots of (a) pulp yield and (b) lignin removal as a function of NaOH charge with 95% confidence band.

$$Y_P(\%) = 115.67 - 7.14x + 0.18x^2,\ R^2 = 0.999 \quad (6)$$

$$Y_L(\%) = -32.8 + 8.83x - 0.21x^2,\ R^2 = 0.999 \quad (7)$$

where Y_P is the pulp yield, Y_L is the lignin removal, and x is the NaOH charge.

Since NaOH was responsible for the dissolution of lignin, hence the removal of lignin increased proportionally with increasing NaOH charge. Consequently, the value of pulp yield reduced proportionally. Estimation using the polynomial function suggested that a maximum lignin removal of 60% could be achieved through pulping using approximately 21% NaOH. Therefore, the studied range of 14–20% NaOH was suitable to be applied in the five-level central composite design.

Moreover, NaOH charge of more than 20% was afraid to cause severe degradation of cellulose while NaOH charge of less than 14% was expected to be insufficient for the pulping of banana stem (Cordeiro et al., 2004; Deniz et al., 2004). In a previous pulping of banana stem using 18% NaOH at 90 °C for 30 min, Cordeiro et al. (2004) achieved a kappa number of 58 which equals to lignin removal of approximately 37.2%. Here in this current study, a better lignin removal of 56.5 ± 0.6% which equivalent to kappa number of 51.2 ± 0.7 was recorded for pulping using the similar NaOH charge and pulping time. This finding indicated a good efficiency of NaOH in removing lignin at the currently used pulping conditions.

The effects of EDTA charge are shown in Figure 4. The pulping was performed using a mixture of NaOH and EDTA which was responsible for the dissolution of lignin and minimization of cellulose degradation, respectively. Efficiency of the pulping process was thus evaluated in terms of pulp yield, lignin removal, and cellulose content. Eq. 8–10 show the polynomial function for all evaluated responses.

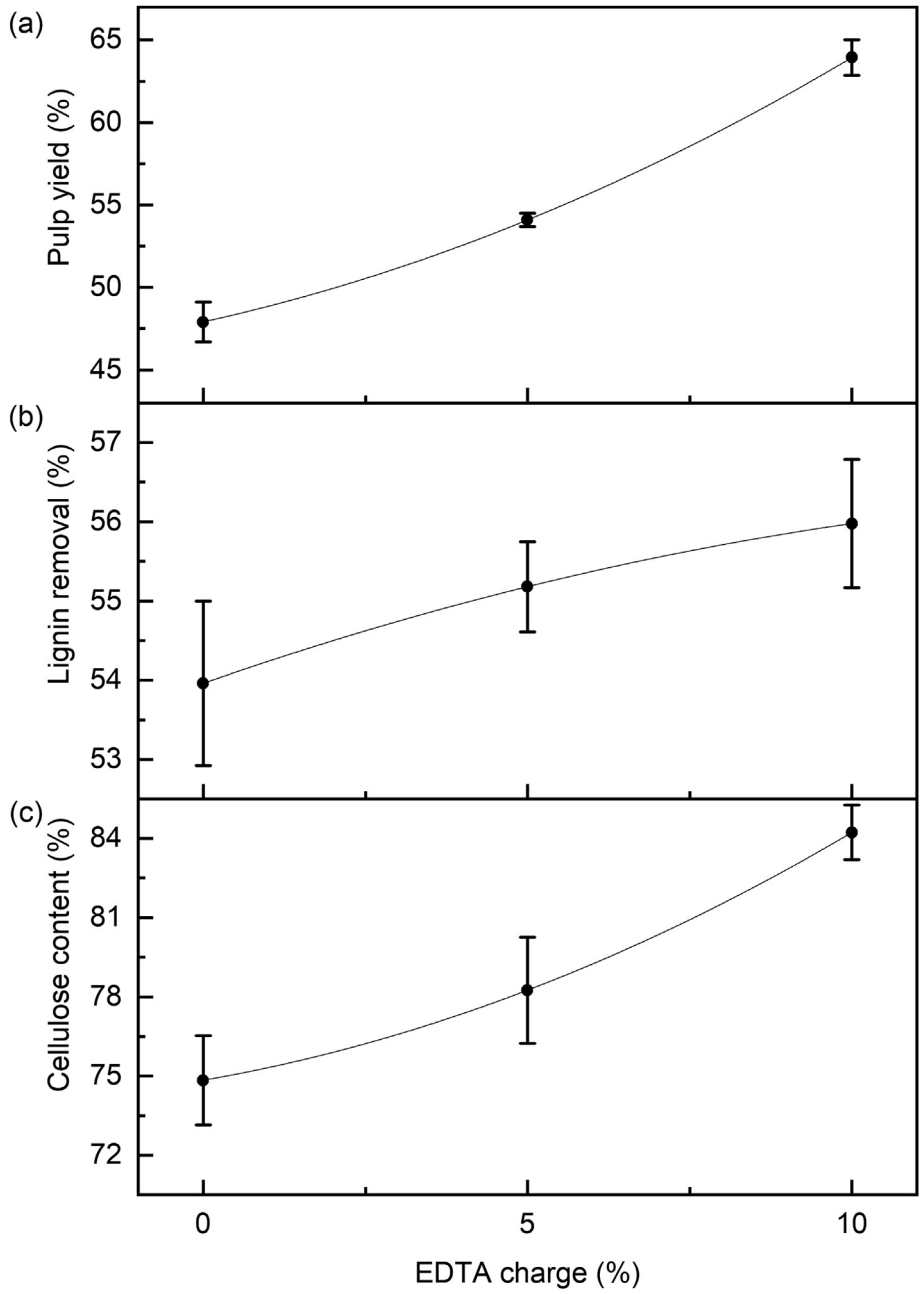

Figure 4. Plots of (a) pulp yield, (b) lignin removal, and (c) cellulose content as a function of EDTA charge.

$$Y_P(\%) = 47.91 + 0.87x + 0.07x^2,\ R^2 = 1 \quad (8)$$

$$Y_L(\%) = 53.96 + 0.29x - 0.008x^2,\ R^2 = 1 \quad (9)$$

$$Y_C(\%) = 74.84 + 0.43x + 0.05x^2,\ R^2 = 1 \quad (10)$$

where Y_P is the pulp yield, Y_L is the lignin removal, Y_C is the cellulose content, and x is the EDTA charge.

Introduction of EDTA has generally improved the removal of lignin and consequently increased the cellulose content of the produced pulp. However, the effect of EDTA on the removal of lignin is relatively small and it was corroborated by the increasing pulp yield. This slight improvement of 1.2–2.0% lignin removal was likely related to an increase in lignin reactivity under basic conditions (Edmunds et al., 2017; Mosier et al., 2005). Estimation using the polynomial function suggested that a maximum lignin removal of 56.6% could be achieved with an addition of 18% EDTA. The estimated value is close enough with 56.0 ± 0.8% lignin removal recorded after pulping with 10% EDTA. Therefore, the studied range of 5–10% was fixed for the central composite design.

The increasing pulp yield by 6.2 ± 1.3% with addition of 5% EDTA and 16.0 ± 0.5% with addition of 10% EDTA could also related to the improvement in cellulose stability. This was later confirmed through FTIR and DPv analysis. In general, degradation of cellulose was possible through a fast peeling-off reaction at reducing end groups of cellulose (Van Loon and Glaus, 1997). Esterification with EDTA through substitution of hydroxyl group from cellulose with carboxylic group from EDTA was believed to be responsible for the stabilization of the reducing ends and thus minimizing the degradation of cellulose. A similar improvement in cellulose yield was also reported during NaOH/EDTA pulping of orange peel by Bicu and Mustata (2013).

Table 3. Central composite design for NaOH-EDTA pulping and the experimental responses.

Run	Coded Variables		Decoded Variables		Responses		
	X_1	X_2	NaOH (%)[a]	EDTA (%)[b]	Y_P (%)	Y_L (%)	Y_C (%)
1	-1	-1	14.0	5.0	55.5	51.8	78.9
2	-1	+1	20.0	5.0	49.1	59.8	84.9
3	+1	-1	14.0	10.0	66.2	53.2	82.9
4	+1	+1	20.0	10.0	58.1	61.5	89.9
5	-1.4	0	12.8	7.5	60.0	49.2	81.0
6	+1.4	0	21.2	7.5	50.4	61.0	89.8
7	0	-1.4	17.0	4.0	52.9	55.4	80.1
8	0	+1.4	17.0	11.0	65.8	61.0	86.3
9	0	0	17.0	7.5	62.8	59.7	85.8
10	0	0	17.0	7.5	62.8	60.1	86.0
11	0	0	17.0	7.5	63.2	59.3	85.9
12	0	0	17.0	7.5	63.3	60.2	85.8
13	0	0	17.0	7.5	63.4	58.9	85.8

[a] NaOH charge, calculated on the mass of solute per volume of solvent.
[b] EDTA charge, calculated on dry-mass of banana stem.

3.3. Statistical analysis

The simultaneous effects of NaOH (X_1) and EDTA (X_2) charges were further investigated using response surface methodology with central composite design as in Table 3. This design was greatly used for the evaluation of pulping process at a reduced number of experimental runs (Berhanu et al., 2018; Brahim et al., 2017; Hassan et al., 2020). Responses values as in pulp yield (Y_P), lignin removal (Y_L), and cellulose yield (Y_C) are also rendered in the last three columns. The highest lignin removal of 61.5% and cellulose content of 89.9% was obtained after pulping using 20% NaOH and 10% EDTA (run 4), while the highest pulp yield of 66.2% was obtained after pulping using 14% NaOH and 10% EDTA (run 3). This finding highlighted that manipulation of NaOH charge will determine whether the extraction would favour for high lignin removal or high pulp yield. Nevertheless, a high EDTA charge was favorable for both responses. The protective action of EDTA against cellulose degradation was observed with increasing pulp yield and cellulose content as the EDTA charge increases (runs 7–9).

Table 4 summarizes the statistical significance of the models and verifies for adequacy based on the values of R^2, adjusted R^2, predicted R^2, p-value, and lack-of-fit. Only second-order polynomial model was considered since it produces quadratic curve as required for surface plot. A local minimum or maximum could be observed from surface plot for a significant second-order polynomial model which indicates the optimum point. Here the values of R^2 are higher than the confidence level, thus indicate a good fit of the model to the experimental data. The significance of each term was then evaluated at 0.05 based on null hypothesis (Ott, 1988). Lower p-values were observed for all terms except for interaction term (X_1X_2) on lignin removal (Y_L). However, the value for adjusted R^2 is close enough to R^2 suggesting that the insignificant term does not have much effect on the fitted model (Mathews, 2005). Also, the insignificant lack-of-fit further uphold the adequacy of the fitted model as agreed by Wutisatwongkul et al. (2016).

Table 4. Statistical analysis of quadratic models for NaOH-EDTA pulping.

Terms	p-values		
	Y_P (%)	Y_L (%)	Y_C (%)
Constant	0.000	0.000	0.000
X_1	0.000	0.000	0.000
X_2	0.000	0.002	0.000
X_1^2	0.000	0.000	0.000
X_2^2	0.000	0.039	0.000
X_1X_2	0.018	0.899	0.002
Lack-of-fit	0.45	0.127	0.238
R^2	0.999	0.978	0.999
Adjusted R^2	0.998	0.962	0.999
Predicted R^2	0.994	0.877	0.997

The second-order polynomial equation was then fitted to each response and the reduced models are given in **Eq. 11–13**. The predicted R^2 values are good enough for these equations to be use for new observation.

$$Y_P = -84.62 + 14.45X_1 + 7.42X_2 - 0.45X_1^2 - 0.3X_2^2 - 0.058X_1X_2 \quad (11)$$

$$Y_L = -48.6 + 10.11X_1 + 2.26X_2 - 0.26X_1^2 - 0.12X_2^2 \quad (12)$$

$$Y_C = 44.2 + 1.83X_1 + 3.65X_2 - 0.03X_1^2 - 0.22X_2^2 - 0.03X_1X_2 \quad (13)$$

3.4. Response optimization

The three-dimensional response surface plots in Figure 5 derived from Eq. 11–13 illustrate the effects of each pulping variable on the respective responses. A quadratic effect of NaOH charge was observed for pulp yield and lignin removal, while a linear effect was observed for cellulose content. In all cases, a weak quadratic effect of EDTA charge was observed in which high EDTA charge was favorable to achieve maximum pulp yield, lignin removal, and cellulose yield. It was also noteworthy that the significant interaction between NaOH and EDTA charge has produced a downward curve for pulp yield and cellulose content whereas an upward curve was obtained from OFAT design (refer to Figures 3 and 4). At low EDTA charge, a strong increase in lignin removal and cellulose content was observed as the NaOH charge increased but a minimal NaOH charge was required to achieve high pulp yield. Surface plots for pulp yield and lignin removal show that the maximum point laid within the intermediate range of NaOH charge. Therefore, numerical optimization was performed and the desired goal was defined to give maximum values for all responses.

The optimum condition was achieved at 17.7% NaOH and 10.0% EDTA with a desirability of 1. The corresponding predicted values for pulp yield, lignin removal, and cellulose content were 64.8%, 61.1%, and 87.5%, respectively. Verification of the predicted values has resulted in 62.7 ± 1.2% pulp yield, 58.1 ± 1.5% lignin removal, and 86.3 ± 1.1% cellulose content. Since the experimental values were in good agreement with the predicted ones, therefore the optimum conditions and the effectiveness of the models were confirmed.

3.5. Pulp analyses

To evaluate the efficiency of this optimized pulping process, the pulp yield and compositions of pulp extracted with EDTA (NaOH/EDTA pulp) were analyzed and compared with a control extracted without EDTA (NaOH pulp). The recorded pulp yield is 62.7 ± 1.2% for NaOH/EDTA pulp and 44.2 ± 0.9% for NaOH pulp. The increase in cellulose yield was higher than the previous report by Bicu and Mustata (2013). Figure 6 shows that both NaOH and NaOH/EDTA pulps has higher cellulose content as compared to the initial cellulose content in the banana stem due to the removal of soluble fractions during pulping process. The addition of 10% EDTA has improved the cellulose content around 0.6% and concurrently reduced the lignin content around 1.1%.

The significant role of EDTA in minimizing cellulose degradation was further evaluated through FTIR analysis. Figure 7 shows the spectra for banana stem, NaOH pulp, and NaOH/EDTA pulp. The appearance of pronounced peaks around 3298–3311 cm^{-1}, 2900–2913 cm^{-1}, and 1024–1028 cm^{-1} are typical characteristic of cellulose backbone ascribed to –OH, C–H, and C–O–C stretching bands, respectively

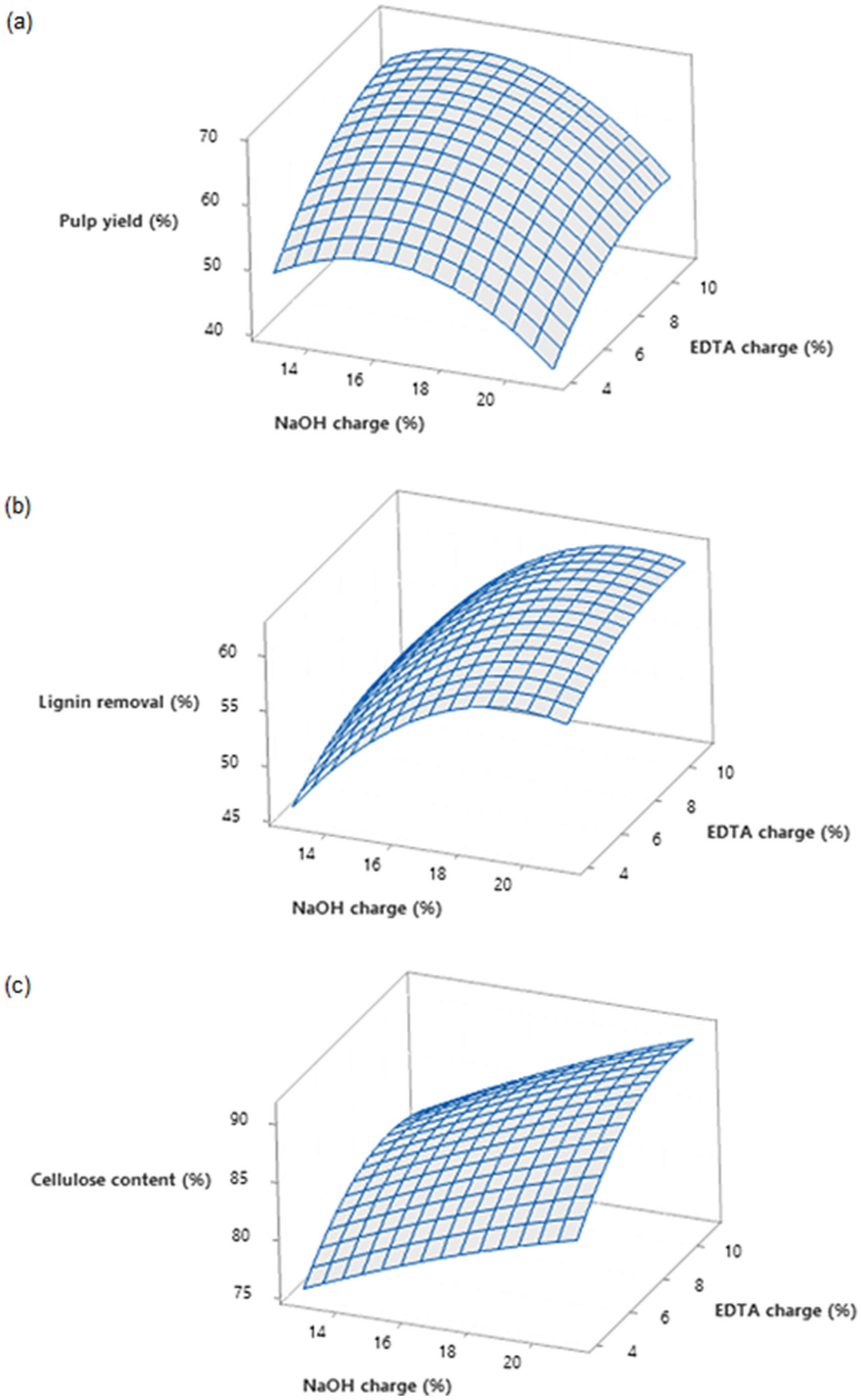

Figure 5. Three-dimensional response surface plots showing the interaction effects between NaOH and EDTA charges on (a) pulp yield, (b) lignin removal, and (c) cellulose content.

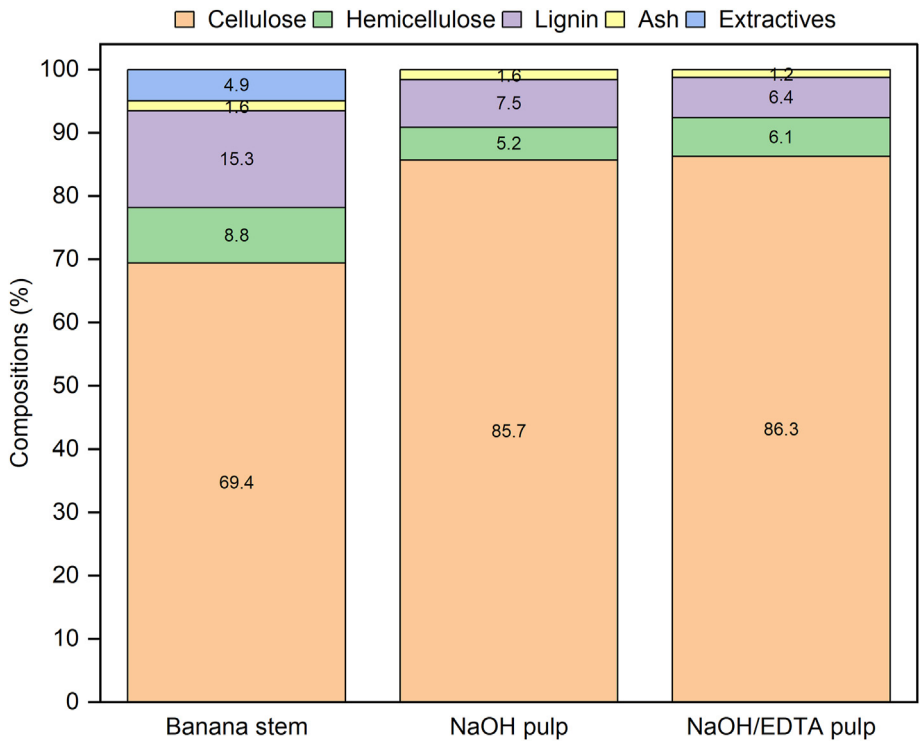

Figure 6. Composition of banana stem, NaOH pulp and NaOH/EDTA pulp.

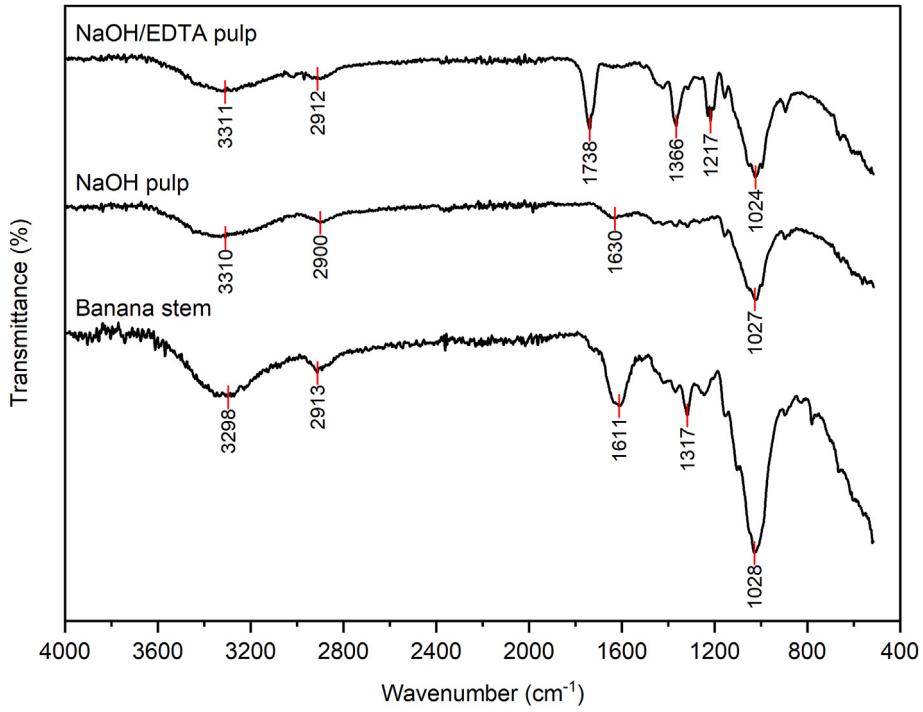

Figure 7. FTIR spectra of banana stem, NaOH pulp and NaOH/EDTA.

(d'Halluin et al., 2017; Tibolla et al., 2018). The sharp bands around 1611 cm^{-1} and 1317 cm^{-1} observed from the spectrum of banana stem was ascribed to C=C stretching in aromatic ring of lignin and C–O stretching in the syringyl unit, respectively (Shi et al., 2019; Tibolla et al., 2018). The significant reduction for these bands from the spectrum of both NaOH and NaOH/EDTA pulps attested for the efficient lignin removal during the pulping process. The new bands observed from the spectrum of NaOH/EDTA pulp near 1738 cm^{-1} and 1366 cm^{-1} was ascribed to C=O stretching of ester linkages between cellulose and EDTA and C–N stretching of EDTA, respectively. The similar bands were previously observed during cellulose modification also using EDTA (d'Halluin et al., 2017; Daochalermwong et al., 2020). Another common band for modified cellulose was also previously observed near 1217 cm^{-1} ascribed to C–O stretching of the ester linkages (El Nemr et al., 2015).

Appearance of these three new bands proved that esterification of EDTA on cellulose was a success.

Degree of polymerization is a relative indication for the number of glucose units in a single cellulose polymer chain. During peeling-off reaction, glucose units at cellulose reducing ends were continuously eliminated forming soluble degradation products. Cleavage of glycosidic bonds produced new reducing ends that also possible to initiate new peeling-off reaction (Van Loon and Glaus, 1997). Here in this study, the degree of polymerization calculated from viscosity measurement is 2140 (16.3 ± 0.7 mPa.s) for NaOH/EDTA pulp and 1907 (13.5 ± 1.2 mPa.s) for NaOH pulp. The higher degree of polymerization for NaOH/EDTA pulp is therefore ascertained that esterification of EDTA on cellulose structure has indeed protected the cellulose against successive hydrolysis by NaOH. Previously Cordeiro et al. (2004) reported that alkaline extraction of banana stem in presence of anthraquinone for 30 min produced pulp with degree of polymerization of 1254. Although the value was a bit lower, the evaluated kappa number attested that greater amount of lignin was removed with addition of anthraquinone. This finding suggested that EDTA is a better cellulose-protective agent, but it is less efficient for lignin removal as compared to anthraquinone.

4. Conclusions

A modelling for pulping of the banana stem using NaOH and EDTA is provided. Efficient lignin removal of approximately half of the initial lignin content was achieved after a short pulping of 30 min and low temperature of 100 ± 5 °C. The addition of EDTA has significantly improved the pulp yield with better lignin removal and sequential increase in the cellulose content. The optimum 62.7 ± 1.2% pulp yield, 58.1 ± 1.5% lignin removal, and 86.3 ± 1.1% cellulose content was achieved after pulping using a mixture of 17.7% NaOH and 10% EDTA at a liquid-to-solid ratio of 10 ml/g. Further analysis on the cellulose structure is crucial to understand the interaction between NaOH, EDTA, and cellulose during the pulping process. Eventually, banana stem is a rich source of cellulose which was extractable at high yield using NaOH and EDTA.

Declarations

Author contribution statement

Nurul Amal Nadhirah Mohamad: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Junaidah Jai: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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