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ORIGINAL RESEARCH

KINETICS STUDY OF CELLULOSE NANOCRYSTALS MODIFICATION USING RARASAPONINS BY ELOVICH EQUATION

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Abstract

The modification of cellulose nanocrystals (CNCs) using rarasaponins (RSs) was carried out to enhancing the hydrophobicity of the CNCs. The RSs are a natural surfactant that has hydrophilic and hydrophobic sides. The linked RSs on the CNCs surface can be used to bond the hydrophobic drugs so that the modified CNCs can be applied as the hydrophobic drugs carrier in the medical field. The kinetics study was successfully carried out using the Elovich equation as the modeling equation. The Elovich equation fits the modification results well based on two parameters, i.e., the RSs/CNCs ratios and the times. The dispersion characteristics analysis was carried out to figure the enhancement of the hydrophobicity on the modified CNCs compared to the unmodified CNCs. According to the kinetics study and the dispersion characteristics analysis, the modification of CNCs using RSs could enhance CNCs utilization in the hydrophobic drug delivery system.

KEYWORDS:

cellulose Nanocrystals, Rarasaponins, Modification Process, Elovich Equation, Kinetics Study.

1 | INTRODUCTION

Cellulose nanocrystals (CNCs) are unique and very useful materials for various applications, such as pharmaceutical, food, and chemical industries. CNCs can be used for drug delivery systems, tissue engineering, composite material, other nanomaterial syntheses, protein and enzyme immobilization, and emulsion stabilizers [1–3]. Due to their fabulous physical and chemical characteristics, CNCs are suitable as a drug carrier in a drug delivery system. This utilization of CNCs is very advantageous for the medical field. CNCs have several characteristics, such as biodegradable, biocompatible, non-toxic, rich in reactive hydroxyl groups on the CNCs surface, good hydrophilicity, and easily modified material [4, 5].

Based on previous studies, CNCs have been isolated from various lignocellulose materials, such as pinewood, corncob [6], sugar palm fibers [7], discarded cigarette filters [8], sago seed shells [9, 10], and passion fruit peels [11]. Many lignocellulose materials can be used for CNCs production due to their high cellulose content. Besides that, several natural resources have been studied to produce CNCs for enhancing their economic value. In this study, bamboo shoots (BSs) were used as the raw material for CNCs production. Dendrocalamus asper is one of BSs kinds that is abundant in Southeast Asia, especially Indonesia. This kind of BSs is very popular among many people due to its large size and sweet taste. Because of that, these BSs are widely used in food applications. The utilization of BSs would increase the economic value in the form of CNCs. BSs have high cellulose content (22.8-34.8 wt%) and low lignin content (1.8-11 wt%)[12]. The high enough cellulose content is an important consideration in this BSs utilization. Another advantage of using BSs is the low lignin content that can facilitate the pretreatment process of BSs. The pretreatment process removes the hemicellulose and lignin contents and obtains the cellulose content as pure as possible. In obtaining pure cellulose, the pretreatment process is needed to break down the lignocellulose material's complex structure, where a strong lignin structure covers the cellulose. The pretreatment process can be done by physical, chemical, biological, and combined methods. The low lignin content can reduce the pretreatment process's cost, where the simple pretreatment process can be used to isolate the cellulose content. Based on these considerations, BSs are assessed as a potential raw material for producing CNCs.

In the drug delivery system, CNCs are easily used as a drug carrier for hydrophilic drugs but not hydrophobic drugs. The abundant hydroxyl groups on the CNCs surface make CNCs have hydrophilic characteristics. In the medical field, drug carriers are needed so that drugs injected into the human body can be taken orally. This makes it easier for the recipient to consume these drugs. The utilization of CNCs as a hydrophobic drug carrier is a challenge because CNCs have a low drug loading capacity for hydrophobic drugs. Although CNCs have a weakness as a hydrophobic drugs carrier, it is still worth to be used due to its safety for humans. The modification process of CNCs is needed to overcome this challenge. Previous studies have been carried out to enhance the hydrophobicity of CNCs. Several modification agents have been used such as castor oil [5], cyclodextrin[13], chitosan[14], hexadecyltrimethylammonium (HDTMA)[15], and cetyltrimethylammonium bromide (CTAB)[1, 16]. This study develops the modification of CNCs using rarasaponins (RSs). RSs are a natural surfactant with a hydrophobic side (aglycone chain) and a hydrophilic side (oligosaccharides chain). This characteristic is suitable for CNCs modification. The hydrophilic side of RSs is used to bind to CNCs, while the hydrophobic side can be used to bind the hydrophobic drugs. RSs is chosen because it is safe for human health and the environment. RSs can be isolated from Sapindus rarak De Candole that is abundant in Indonesia.

In general, the Elovich equation has been usually used for describing the adsorption kinetic that indicates a chemical reaction. The Elovich equation can figure out the type of chemical interaction in the adsorption phenomenon. Here, the Elovich equation was tried to be used as models for this modification process's kinetics study. This work aimed to study the modification process of CNCs kinetically using RSs. To prove the hydrophobicity enhancement, the characteristic dispersion analysis was carried out towards the modification product.

2 | MATERIAL AND METHOD

2.1 | Isolation of Cellulose Nanocrystals

BSs were dried using an oven at 50°C and powdered into small size. In the pretreatment process, BSs were refluxed using sodium hydroxide solution (20 wt%) at 100°C for four h. The solid residues were dried and continued for the next steps. The solid residues were mixed with sodium hydroxide solution (2 M) and hydrogen peroxide solution (50%) with a ratio of 1:1. The solid residues contained high cellulose content.

Pretreated bamboo shoots (PBS) were hydrolyzed using a sulfuric acid solution (55 wt%) at 45°C. 10-folded cold distilled water was added to the suspension to stop the acid hydrolysis process. The acid solution was separated, and then the solid residues were washed until neutral. The supernatant was obtained and dried using a freeze dryer at a pressure of 0.08 mbar and a temperature of -42°C.

2.2 | Extraction of RSs

The extraction of the powdered and dried Sapindus rarak De Candole was conducted using 150 mL of distilled water at 80°C for 60 min with a solid/solvent ratio of 1:10 g/mL. After the process, the solids residue was separated, and the liquid extract was dried using a freeze dryer at a pressure of 0.08 mbar and a temperature of -42°C. This process was carried out by following the previous method[17].

2.3 | Modification of Cellulose Nanocrystals

RS solution was added CNCs suspension with RS/CNC mass ratios of 0.5, 1.0, and 1.5. The mixture was stirred for a certain time (kinetics study). The time parameter was varied from 10 to 600 min (for 10 data). The combined parameters were used to study the kinetics behavior of this modification process.

2.4 | Analyses

There are two analysis method were carried out in this study, i.e. determination of linked RSs on the CNCs and dispersion characteristic analysis. In determination first analysis, the total saponins content analyzed the RS solution's residual concentration to calculate the linked RSs on the CNCs. The calibration curve was figured out using diosgenin as the standard solution. The diosgenin solutions were varied by 100-700 mg/L in methanol-water solvent (a ratio of 4:1). 0.5 mL of the diosgenin solution was added by 0.5 mL vanillin reagent (8% in ethanol) and 5 mL of sulfuric acid solution 72% volume. It was heated at 60°C until the color changed, and then it was cooled. The absorbance measurement was done at 544 nm using UV/Vis Spectrophotometer. In the residual RSs solution, the concentration was measured in the same way by replacing the diosgenin solution with the residual RSs solution. The amount of linked RSs on the CNCs surface (q) in mg/g was calculated using the following equation:

$$q = \frac{(C_o - C_r)V}{m} \tag{1}$$

where C_o and C_r are the initial and residual RSs concentration in mg/L. V is the volume of the modification process in Liter, and m is the mass of CNCs in gram.

In the second analysis, i.e. dispersion characteristic analysis, the unmodified and modified CNCs samples were dispersed in two kinds of solvents, such as water and ethanol solvents (0.1 wt%). The mixtures were sonicated for one hour. The investigation was done after three weeks of resting at room temperature.

2.5 | Elovich Equation

Elovich equation is widely used for modeling the chemical adsorption kinetics. This equation can model the kinetics interaction in this modification process with similar behavior with the chemical adsorption. In this modification, the CNCs and RSs would act as the adsorbent and the adsorbate based on their phases during the process. This equation's basic assumption is the heterogenous adsorbing surfaces where it figures out the CNCs surface as the heterogeneous surface. The mildly rising kinetics behavior of the process fits this equation well[18]. The basic equation of the Elovich equation is given Aharoni and Tompkins[19] by Eq. 2.

$$\frac{d_g}{d_t} = a\ e^{-bg} \tag{2}$$

A and b are the initial rate constant (mg/g min) and the Elovich constant (g/mg). Using the boundaries of $q = 0$ at $t = 0$ and $q = q$ at $t = t$ the integrated form of Eq. 2 becomes:

$$q = \frac{1}{b} ln(t + t_o) - \frac{1}{b} ln(t_o) \tag{3}$$

where $t_o = \frac{1}{ab}$. If the assumption of $t \gg t_o$ is applied, Eq. 3 becomes:

$$q = \frac{1}{b} ln(ab) + \frac{1}{b} ln(t) \tag{4}$$

Eq. 4 is the final Elovich equation for investigating the constants.

TABLE 1 The classification of the equilibrium factor of the Elovich equation.

Zone	RE	Behavior
I	RE > 0.3	Slow interaction
II	0.3 > RE > 0.1	Mild interaction
III	0.1 > RE > 0.02	Rapid interaction
IV	RE < 0.02	Instant interaction

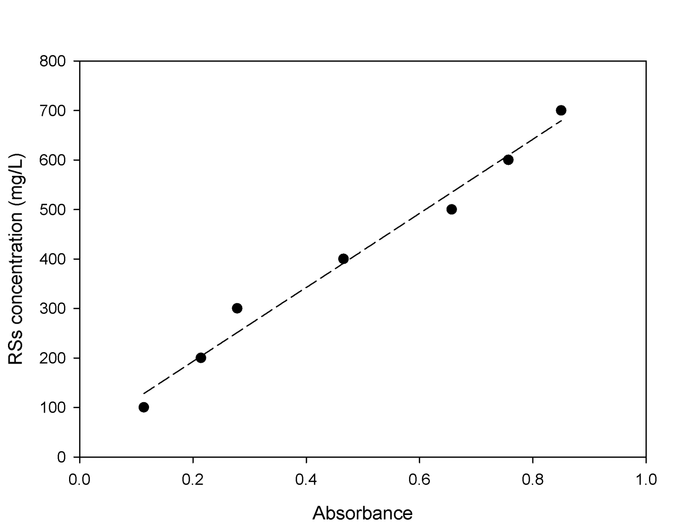

FIGURE 1 The calibration curve of RSs concentration.

For approaching the equilibrium factor of the Elovich equation, the dimensionless Elovich equation (Eq. 7) is developed by determining t_ref as the longest time in the process and q_ref as the concentration in the solid phase at $t = t_{ref}$. Thus, Eq. 4 is rewritten as:

$$q_{ref} = \frac{1}{b} ln(ab) + \frac{1}{b} ln(t_{ref}) \tag{5}$$

$$q - q_{ref} = \frac{1}{b} ln(\frac{t}{t_{ref}}) \tag{6}$$

$$\begin{aligned} \frac{q}{q_{ref}} &= \frac{1}{q_{ref} b} ln(\frac{t}{t_{ref}}) + 1 \\ \frac{q}{q_{ref}} &= R_q ln(\frac{t}{t_{ref}}) + 1 \end{aligned} \tag{7}$$

where RE indicates the equilibrium factor of the Elovich equation. The RE value is divided into four zones (I – IV) that vary from sloping to steep curves of $\frac{t}{t_{ref}}$ versus $\frac{q}{q_{ref}}$. The classification of these zones is given in Table 1 [18]. The third column, i.e. The Behavior, is the behavior of approaching the equilibrium condition.

3 | RESULTS AND DISCUSSION

Figure 1 shows the calibration curve for determining the total saponins content or RSs concentration. The diosgenin was used as the standard solution because it represents the hydrolysate of the saponins content in the RSs solution. The hydrolysate is the

TABLE 2 The results of the modification process of CNCs using RSs.

Time (min)	q (mg/g) (Ratio 0.5)	Ratio 1.0	Ratio 1.5
20	61.91	86.79	79.49
40	75.84	106.77	97.10
60	85.04	119.08	108.34
90	93.42	130.29	117.21
120	99.87	139.13	126.02
180	108.72	151.69	135.67
240	114.81	160.18	142.71
360	123.73	171.99	152.39
480	129.55	180.87	159.72
600	134.19	187.00	165.12

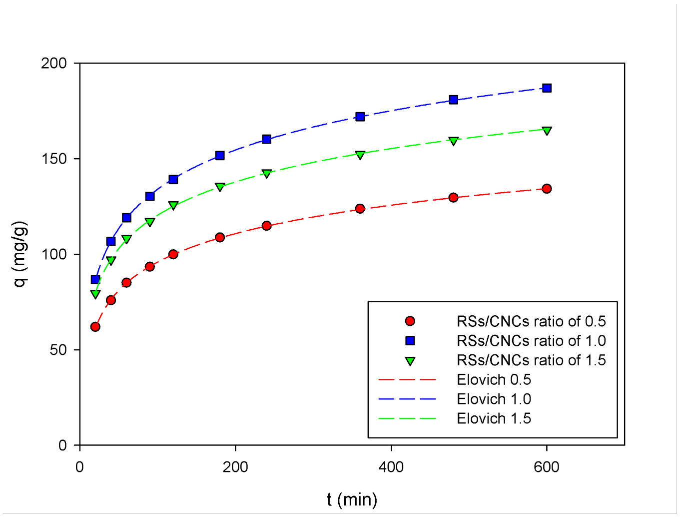

FIGURE 2 The nonlinear regression of the modification results using the Elovich equation.

aglycone region only that the oligosaccharides region has been hydrolyzed using a sulfuric acid solution. The RSs concentration can be determined using Eq. 8.

$$[RSs] = 722.18Abs + 60.03 \tag{8}$$

where $[RSs]$ and Abs are the RSs concentration and the measured absorbance, respectively.

The RSs extraction was carried out from the Sapindus rarak De Candole. The RSs concentration of the RSs extract was 68.48 ± 2.05% through the total saponins content determination.

The modification of CNCs using RSs was carried out, where the results are shown in Table 2. The combined parameters (both initial RSs concentrations and times) were used to investigate this process's kinetics behavior.

Table 2 shows that the RSs/CNCs ratio of 1.0 gives the highest amount of linked RSs on the CNCs surface. From the RSs/CNCs ratio of 0.5 to 1.0, the q values show the enhancement every time. The increase of the driving force causes it. This process's driving force is the RSs concentration difference between the liquids and solids phases' concentration. The increase of ratio would increase the RSs concentration difference so that the mass transfer of RSs compounds from the liquids phase to the CNCs surface would enhance. However, from the RSs/CNCs ratio of 1.0 to 1.5, the q values show the reduction values. The overmuch RSs compounds in the process make the interaction of RSs compounds and the CNCs decrease due to the reduced free space in the solution. So, the RSs/CNCs ratio of 1.0 is the best ratio among the used ratios.

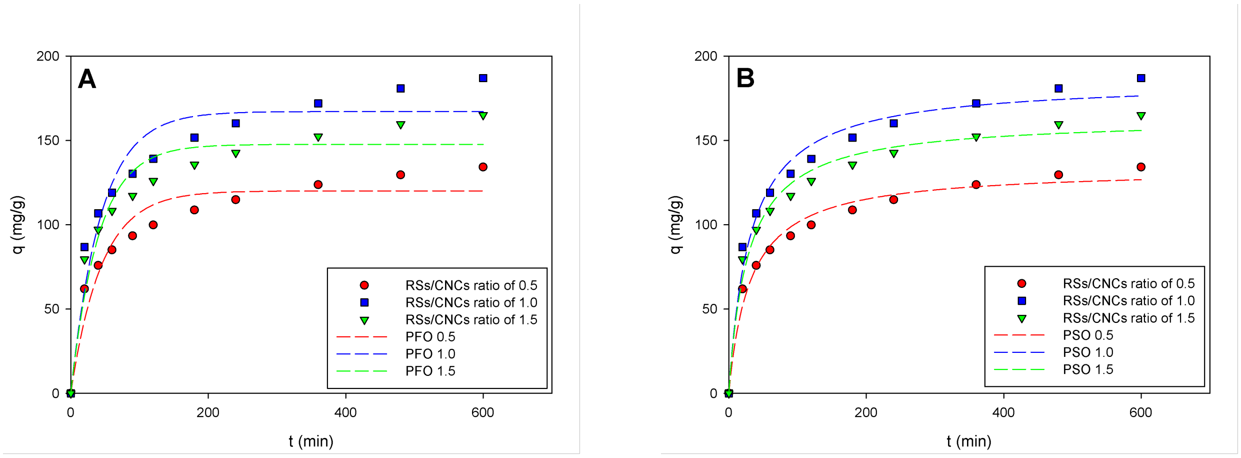

FIGURE 3 The nonlinear regressions of the modification results using (A) the Pseudo-first order (PFO) and (B) the Pseudo-second order (PSO).

TABLE 3 The constants of the Elovich, Pseudo1st order, and Pseudo-2nd order equations for modeling the modification results.

RSs/CNCs ratio	Elovic Equation		
	a (mg/g min)	b (g/mg)	R^2
0.5	18.8830	0.0467	0.9999
1.0	27.3683	0.0338	0.9999
1.5	30.2595	0.0398	0.9996
RSs/CNCs ratio	**Pseudo-1st Order Equation**		
	k_1 (min-1)	g_e (g/mg)	R^2
0.5	0.0223	120.0962	0.9287
1.0	0.0227	167.1512	0.9274
1.5	0.0247	147.6692	0.9302
RSs/CNCs ratio	**Pseudo-2nd Order Equation**		
	k_2 (min-1)	g_e (g/mg)	R^2
0.5	0.000237	133.5823	0.9809
1.0	0.000174	185.3282	0.9804
1.5	0.000218	163.1966	0.9822

Based on the Elovich equation, the nonlinear regression was carried out as shown in Figure 2, where the constants are written in Table 3. The Elovich question fits the data of modification results well. It is proven by the values of R^2 that show a value of more than 0.99. The values indicate the initial attachment rate of RSs to CNCs. It demonstrates the increased mass transfer statement and the RSs/CNCs ratio (RSs concentration difference). The values increase along with the increase of the RSs/CNCs ratio.

Furthermore, the b values indicate the Elovich constant. The RSs/CNCs ratio of 1.0 shows the lowest b value among the others. It is due to the highest linked RSs on the CNCs surface. The b values also indicate the number of linked components in the opposite way, where the decrease of b values means the increase of the amount of linked RSs on the CNCs surface. This Elovich equation's good fitness to the data can describe the behavior of the modification process where the chemical reaction happened on the heterogeneous solid's surface. Here, the chemical reaction is between the RSs and CNCs by hydrogen bonds due to the rich hydroxyl groups on the CNCs surface. It also proves the heterogeneous characteristics of the CNCs surface.

For supporting the modeling result of the Elovich equation, the modeling using the Pseudo-first order (PFO) and Pseudo-second order (PSO) equations were also carried out, as shown in Figure 3. The PFO equation has good fitness toward the data due to the R^2 values of more than 0.92. However, the R^2 values of the PFO equation are still lower than the R^2 values of the PSO equation that are more than 0.98. It proves that the modification process does not follow physical behavior but chemical behavior where there is chemical interaction. The q_e values of both PFO and PSO equations indicate the same meaning, i.e., the amount of linked RSs on the CNCs surface. Both modelings show the highest q_e at the same point (RSs/CNCs ratio of 1.0). The k_1 values represent the rate constant that is linear with the initial concentrations[20]. The k_1 values increase along with the increase of the RSs/CNCs ratios (initial RSs concentrations), as shown in Table 3. The k_2 values represent the rate constant, but these have a complex function towards the initial concentration[20]. The k_2 values are affected by the initial RSs concentrations and the affinity between the RSs and CNCs.

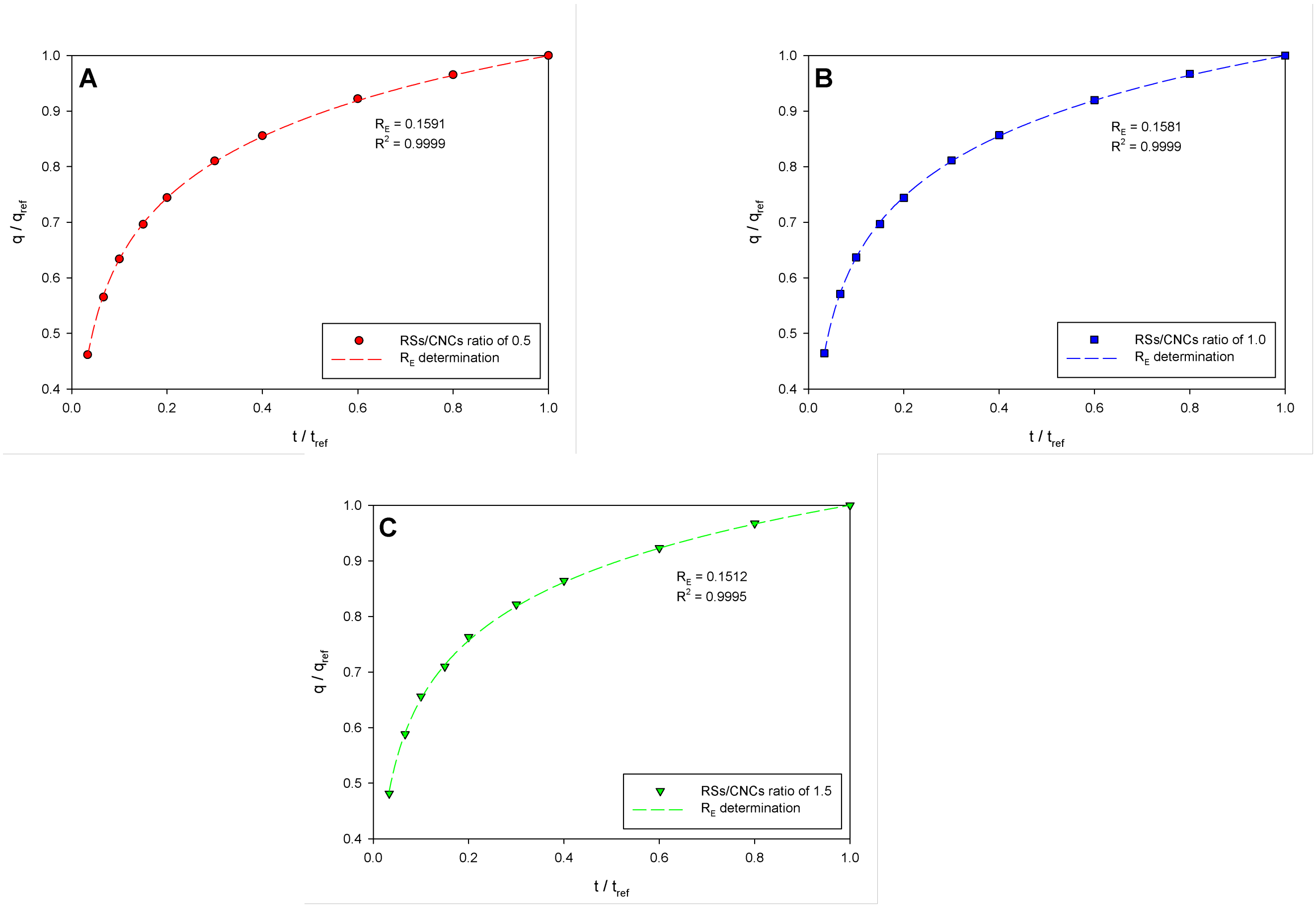

FIGURE 4 The nonlinear regression of the equilibrium factor of the Elovich equation for RSs/CNCs ratios of (A) 0.5 (B) 1.0 and (C) 1.5.

Figure 4 shows the nonlinear regression for determining the equilibrium factors of the Elovich equation. These nonlinear regressions fit the data well, as shown by the R^2 values of more than 0.99. The fitness of these three plots is also proven by experimental data points in the regression line. Figure 4 (A, B, and C) show the nonlinear regression of the experimental data from the use of RSs/CNCs ratios of 0.5, 1.0, and 1.5, respectively. The results show that these three RSs/CNCs ratios give a similar RE value (around 0.15-0.16), as shown in Figure 4. It is in the range of RE value between 0.1-0.3 (zone II). These RE values indicate the behavior of the mild interaction rate between the RSs and CNCs (zone II). The behavior of zone II represents the fitness of the Elovich equation to the modification process. Zone, I, and IV behavior would give unsatisfied modeling due to their prolonged and instant interaction. The mild behavior indicates the chemical interaction in this modification process occurs naturally.

This Elovich equation is successfully used to describe the interaction between the RSs and CNCs in the modification process. Due to the R^2 values, this equation showed the most satisfying modeling compared to the Pseudo-first order and Pseudo-second order equations. The Elovich equation can describe the chemical interaction well in the modification process where the RSs are attached to the heterogeneous CNCs surface by hydrogen bonds.

Figure 5 shows the result of the dispersion characteristic analysis of unmodified and modified CNCs. Water and ethanol were used as the solvents of this analysis. The water was used as the polar solvent, while the ethanol can disperse both polar and

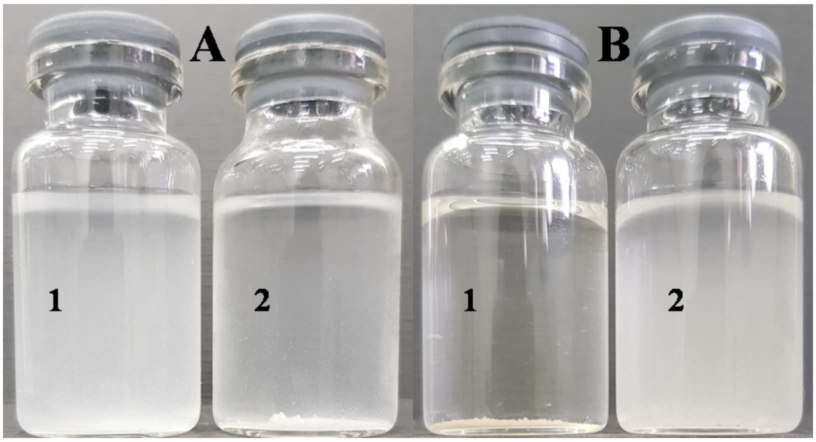

FIGURE 5 The characteristic dispersion analysis of (A) the unmodified CNCs and (B) the modified CNCs in (1) water and (2) ethanol as the solvents.

nonpolar materials. The unmodified CNCs could be dispersed in water but not in ethanol. It means that the unmodified CNCs have very high hydrophilicity. After the modification process, the RSs were linked on the CNCs surface, making the hydrophobicity increase due to the surface's hydrophobic side. It was proven by the good dispersion of the modified CNCs in ethanol.

Moreover, the modified CNCs could not be dispersed in water. This indicates that the modification process changes the hydrophilic characteristics to the hydrophobic characteristics. This characteristic dispersion analysis was successfully carried out to figure out the hydrophilic-hydrophobic characteristics of the CNCs.

4 | CONCLUSION

The kinetics study has been carried out to the modification results by using the Elovich equation. This equation gave more satisfactory modeling results toward the Pseudo-first order and Pseudo-second order equations. In this modification process, the RSs/CNCs ratios affected the mass transfer rate of the RSs from the liquid phase onto the CNCs surface. However, the highest amount of linked RSs on the CNCs surface was obtained at a RSs/CNCs ratio of 1.0. From the dimensionless Elovich equation, RE's values also showed satisfying results ($R^2 > 0.99$). The importance of RE indicates the mild interaction rate behavior. It confirmed the results of the direct nonlinear regression towards the modification data.

5 | ACKNOWLEDGMENT

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