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MODIFICATION OF POLYETHYLENE GLYCOL AND CITRIC ACID ON PALM FIBER WASTE NANOFIBERS ON THE ADSORPTION OF VIOLET CRYSTAL DYES

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ABSTRACT

This study developed nanofibers derived from sugar palm fiber waste, incorporating citric acid and polyethylene glycol (PEG) modifications to adsorb crystal violet (CV) dye. The synthesis process involved alkalization-acid hydrolysis and bleaching techniques. Subsequent analyses of nanofiber characteristics were conducted using Fourier-Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX). The efficacy of these modified nanofibers in adsorbing CV was quantitatively measured using an Ultraviolet-Visible (UV-Vis) spectrophotometer. The study successfully synthesized nanofibers from sugar palm fiber waste with modifications: PEG-modified nanofibers (NP 2 and NP 24) and citric acid-modified nanofibers (NS 2 and NS 24). These modifications resulted in nanofibers with a smooth, white texture. FTIR analysis of the samples (N, NP 2, NP 24, NS 2, and NS 24) revealed the presence of functional groups essential for cellulose, specifically -OH, C-H, and C-O groups. The addition of citric acid introduced a new group, C=O, albeit with very weak intensity. PEG modifications were evident from the stretching observed in the -OH groups. SEM analysis confirmed the presence of a layer on the nanofibers, attributed to citric acid (NS 2 and NS 24) and PEG (NP 2 and NP 24). XRD results indicated that the pre-and post-modification nanofibers exhibited a semi-crystalline phase. Van der Waals electrostatic interactions between the absorbent material and the adsorbate predominantly guided the adsorption mechanism. Intriguingly, the citric acid and PEG modifications did not significantly alter the adsorption outcomes. The adsorption capacity remained stable over time, as evidenced by measurements of 0, 15, 30, 45, 60, 90, and 120 minutes.
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INTRODUCTION

Water, an important natural resource, is indispensable for various human activities, including domestic, industrial, and agricultural uses. In Indonesia, the demand for clean water is continually rising, yet the quality of this vital resource is diminishing, particularly due to the impact of industrial activities. A prime example is the batik industry, which generates significant volumes of hazardous liquid waste, accounting for nearly 85% of its clean water usage. This waste typically exhibits a dark coloration and a strong odor [1,2]. The batik industry predominantly employs synthetic dyes for their diverse color range, cost-effectiveness, and accessibility. However, the disposal of liquid batik waste poses serious threats to human health and aquatic ecosystems. It disrupts the ecological balance by impeding photosynthesis and diminishing oxygen levels in water bodies. Human exposure to this waste can lead to health issues like nausea, skin irritation, dermatitis, and headaches [3].

Crystal violet (CV), a common synthetic dye in batik processing, is particularly problematic due to its mutagenic and toxic properties. Its high stability renders it difficult to degrade in aquatic environments, and its presence diminishes light penetration into water bodies, further exacerbating ecological harm [4,5]. Consequently, there is an urgent need to process batik waste efficiently to prevent further pollution of water ecosystems [6]. Various physical and chemical waste treatment methods, such as photodegradation [7], electrolysis [8], and adsorption [9], have been explored to address this issue.

Among these methods, adsorption stands out for its simplicity, effectiveness, efficiency, and the potential for adsorbent regeneration [10]. It is an environmentally friendly approach, especially suitable for dye-containing waste due to its cost-effectiveness and non-production of harmful by-products [11,12]. Adsorption efficacy largely depends on the nature and type of adsorbent used. Ideal adsorbents possess characteristics such as a high adsorption rate and capacity, chemical stability, reusability, and eco-friendliness [13]. Various adsorbents have been investigated in previous studies, including activated charcoal [14], nano-silica [15], and nanofiber [16].

Nanofiber, in particular, holds significant potential as an adsorbent due to its high surface area, porous structure, and considerable elasticity. These properties make nanofibers highly effective in reducing environmental pollution [17]. The larger the surface area of the adsorbent, the greater the contact area, leading to more efficient absorption and, consequently, more effective adsorption [18]. Sugar palm fiber waste, a by-product of flour production from palm starch, is an exemplary material for nanofiber adsorbents. Despite being largely discarded and contributing to environmental pollution, sugar palm fiber waste contains about 43.88% cellulose [19], making it a promising candidate for dye adsorption in wastewater treatment.

The application of nanofibers in environmental remediation can be significantly enhanced through chemical modifications, such as incorporating polyethylene glycol (PEG) and citric acid. These modifications are designed to augment the adsorption capabilities of nanofibers. The integration of PEG plays a pivotal role in encapsulating particles, preventing the formation of aggregates, and aiding in particle size control [20]. On the other hand, citric acid's contribution lies in its ability to react with the hydroxyl groups in cellulose and lignin, forming ester bonds [21]. This chemical alteration is particularly beneficial as it introduces ester groups into the nanofiber structure. Ester groups, characterized by their electron-rich nature, enhance the nanofiber's ion-binding capacity, surpassing the adsorption capabilities of unmodified nanofibers [22].

The primary objective of this research is to examine the effectiveness of nanofibers modified with PEG and citric acid in adsorbing the crystal violet (CV) dye. This investigation is vital for its potential to mitigate environmental contamination stemming from batik industry waste and its implications in enhancing water quality. By focusing on this innovative approach, the study aims to offer a viable solution to address the pressing environmental concerns posed by the discharge of synthetic dyes into aquatic ecosystems.

METHODS

1. Material

The materials used in this research were palm fiber waste, distilled water, Sodium Hydroxide (NaOH) 5% made in Germany CAS-No: 1310-73-2, Hydrochloric Acid (HCl) made in Malinckrods (USA) CAS-No: 7647- 01-0 3.5 M, HCl 5 M, Sodium chlorite made in Germany CAS-No: 7647-14-5, glacial acetic acid made in Germany CAS-No: 64-19-7, deionized water, crystal violet made in China CAS-No: 548-62-9, Polyethylene glycol 400 (PEG) made in Germany, and citric acid made in Austria CAS-No: 5949-29-1.

2. Procedure

a. Preparation of Cellulose Nanofiber

Dried palm fiber was washed with distilled water until clean, clear, and dried. Once it was dry, then cut it approximately 0.1-1 cm. Most of the lignin and hemicellulose were removed by treatment with 5% NaOH solution at 50◦C for 4 hours. Then, they neutralized using distilled water and soaked with 3.5 M HCl to break down and separate the microfibrils. After that, it was lined with distilled water to remove the acid. Then, it was ground into pulp form and treated again with alkali to remove the remaining non-cellulosic constituents, followed by acid hydrolysis with 5 M HCl. Delignification was then carried out by a bleaching process with a solvent-to-fiber weight ratio of 25:1 using a 4:1 mixture of sodium chlorite ($NaClO_2$) and glacial acetic acid for 2 hours at 60◦C. After the delignification, the fibers were washed with deionized water to pH 7 to obtain cellulose nanofibers.

b. Preparation of PEG Modified Nanofiber

This was done by weighing 14g of PEG and 1g of nanofiber (14:1) and soaking the nanofiber with PEG with time variations of 2 hours and 24 hours, after being mentioned as NP 2 and NP 24.

c. Preparation of Citric Acid Modified Nanofiber

This was done by weighing 1g of citric acid, dissolving it in 20 mL of distilled water, and soaking 1g of nanofiber in a citric acid solution prepared for varying times of 2 hours and 24 hours. Here are mentioned NS 2 and NS 24, respectively.

d. Characterization

Nanofiber characterization aims to determine the success of nanofiber modification by PEG and citric acid. PEG and citric acid-modified nanofibers were characterized using FTIR (Fourier Transform Independent) from Shimadzu to determine surface functional groups, XRD (X-Ray Diffraction), X'pert PRO PANanalytical to determine crystal phase and crystal size, and SEM-EDX (Scanning Electron Microscopy-

Energy Dispersive X-Ray), Joel JCM 7000, to determine the morphology on the surface.

e. Adsorption

Adsorption was done by preparing 100 ml of 10 ppm and 50 ppm crystal violet dye each. Then, the modified nanofiber was contacted with 0.1g of citric acid and PEG for 2 hours, sampling every 15, 30, 45, 60, 90, and 120 minutes. The variation of contact time aims to determine the effect of time on adsorption capacity. Next, it was filtered using Whatman Qualitative paper No. 3. After that, the filtrate was analyzed using a UV-Vis spectrophotometer with a wavelength of 590 nm to determine the absorbance of crystalline violet [23].

RESULTS AND DISCUSSION

1. Synthesis

Figures 1a and 1b depict the physical characteristics of palm fiber pre- and post-synthesis and modification. Initially, as shown in Figure 1a, the unprocessed palm fiber exhibited a brown hue, characteristic of its natural state, with noticeable irregularities in its fibrous structure. However, post-synthesis modifications led to notable changes in texture and color, as evidenced in Figure 1b. The samples labeled N, NS 2, and NS 24 displayed a smoother surface with a subtle yellowish tint. Conversely, the samples NP 2 and NP 24 exhibited a smoother texture and were distinctly white.

1a. **1b**

Figure 1a. Raw palm fiber (before synthesis); **1b.** Synthesis results of (a) N, (b) NP 2, (c) NP 24, (d) NS 2, (e) NS 24

These observations align with existing research indicating that nanofibers derived from palm fiber waste typically have a smooth texture and white appearance [14]. The whitening effect is attributed to bleaching before modifying the nanofiber [16]. The slight yellowish hue observed in the N, NS 2, and NS 24 samples could be a result of residual impurities within the nanofiber structure, not eliminated during the processing stages

2. Characterization

a. *Fourier Transformed Infrared* (FTIR)

The results of FTIR characterization were used to determine functional groups and describe the bonds in a molecule—palm fiber waste nanofiber contained cellulose. The functional groups of cellulose were OH, C-O, and C-H [16]. The OH group produced a wide signal at a wavenumber of 3400-3000 cm-1 with stretching vibrations. The C-H group had a medium and weak signal at a wave number of 2800-3000 cm^{-1}, and the C-O stretching vibration was 1280-1030 cm^{-1}.

Figure 2 indicated that all nanofibers before and after modification showed cellulose-forming functional groups, namely OH, C-O, and C-H [16]. The OH groups within nanofibers modified by citric acid underwent a reaction with citric acid molecules, creating a minimum of 2 carboxylate groups and 1 ester group. [21]. The ester group (C=O) was at the wave number of 1735-1750 cm^{-1} [24]. In sample NS 2, the C=O wave appeared with a very weak intensity at a wave number of, while in 24, it appeared at a wave number of 1747 cm^{-1} with a weaker intensity than NS 2. This was also shown in the OH groups on the NS 2 , which had a wider intensity, where the hydroxyl groups successfully reacted with citric acid, which had a carboxylic group to form an ester group. Meanwhile, in the NS 24, the OH intensity was sharp, and the C=O group intensity was weaker. The presence of ester groups could increase the adsorption ability of nanofibers because ester groups had more electrons, which could have more ions than nanofibers that were not modified by citric acid.

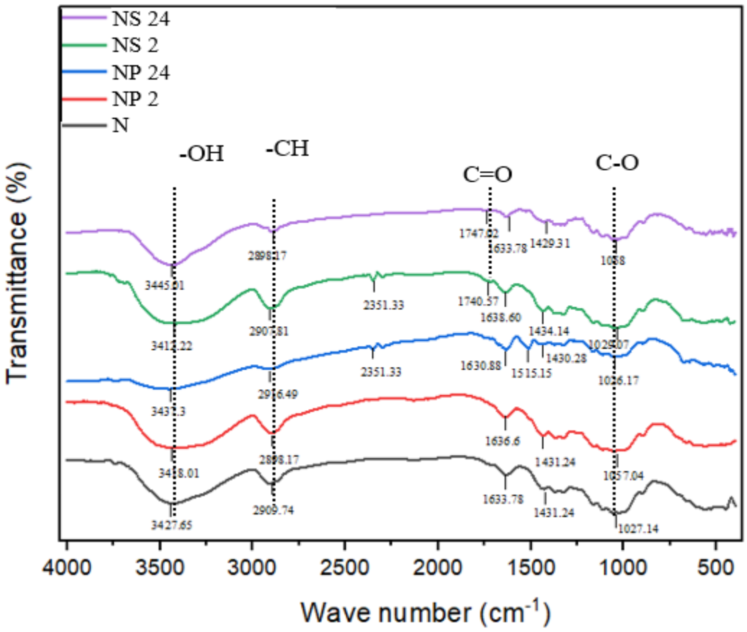


Figure 2. FTIR Spectra of Nanofiber based on the modification variations

The presence of a PEG group was indicated by the presence of hydroxyl (OH), aliphatic -CH, and C-O groups [25]. On the PEG-modified nanofiber, the OH spectrum appeared at wave numbers 3418 cm^{-1} (NP 2) and 3418 cm^{-1} (NP 24), -CH groups at wave numbers 2909 cm^{-1} (NP 2) and 2898 cm^{-1} (NP 24), as well as the C-O group at wave numbers 1057 cm^{-1} (NP 2) and 1026 cm^{-1} (NP 24). The OH PEG group bound hydrogen to the cellulose nanofiber. The longer the soaking time, the wider the OH vibrations [26]. The broadening of the OH group's vibration indicated a decrease in the OH group after modification with PEG. The- OH group decreased due to PEG's hydrophilic nature, which caused increased interactions between hydrogen bonds [25]. The FTIR spectra results of the PEG-modified nanofibers did not show a shift in the wave number. This was because the groups on the nanofiber had the same groups as PEG.

b. X-ray diffraction (XRD)

The results of XRD characterization were carried out to determine the material's type and size. Figure 3 shows the results of XRD nanofiber before and after modification. The amorphous structure did not have peaks indicating the presence of a particular phase [27]. The nanofibers before and after modification with PEG or citric acid had an amorphous peak at 2θ = 15^o-16^o and a crystalline peak at 2θ = 22^o. Cellulose usually peaked at 2θ = 14.82^o, 16.44°, and 22.79^o [28].

In the nanofiber, before and after modification, each had 2 highest peaks at angles 15^o and 22^o with the same crystal plane, namely at 001. This indicated that the nanofiber had a semi-crystalline structure [29].

The nanofiber size was calculated using the Debye-Scherrer equation as in equation 1.

$$D = \frac{0{,}9\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots (1)$$

Where D is the crystalline size (nm), 0.9 is Scherrer's constant, λ is the X-ray wavelength (1.5406 Å) β is the FWHM (Full Widht at Half Maximum), and θ is the diffraction angle [16]. The results of the XRD diffractogram on sample N showed peaks at 14.7^o and 22.482^o. Sample N had a high intensity at peak 2 theta = 22.4822^o with an FWHM value of 0.5353°. Based on the results of calculations using the Debye-Scherrer equation, the nanofiber size was 15.131 nm.

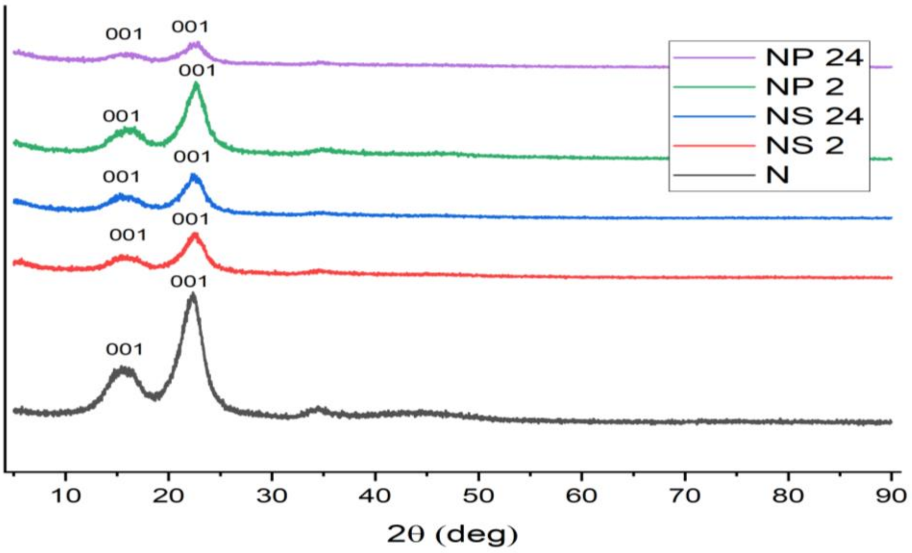


Figure 3. XRD results Synthesis results of (a) N, (b) NS 2, (c) NS 24, (d) NP 2, and (e) NP 24

In the NS 2 sample, the peaks obtained were at peak 2 theta = 15.905^o and 22.390^o. The highest peak was at 22.390° with an FWHM value of 0.3346°. Based on the results of calculations using the Debye-Scherrer equation, the nanofiber size was 24.203 nm. Meanwhile, at NS 24 the peaks obtained were at peak 2 theta = 15.533^o and 22.455^o with an FWHM value of 0.4684°. Based on the results of calculations using the Debye-Scherrer equation, the nanofiber size was 17.291 nm. This showed that the addition of citric acid could increase the fiber diameter. The increase in fiber diameter was caused by citric acid molecules diffusing into the nanofiber and forming a cross-linking network between macromolecules, resulting in a denser buildup [30].

In the NP 2 sample, the peak obtained was at peak 2 theta = 15.022°, 16.668°, and 22.761°. The highest peak was at 2 theta 22.761° with an FWHM value of 0.535°. Based on the results of calculations using the Debye-Scherrer equation, the nanofiber crystal size was 15.138 nm. At NP 24, the peaks obtained were at peak 2 theta = 14.314° and 22.150° with an FWHM value of 0.2007°. Based on the results of calculations using the Debye-Scherrer equation, the nanofiber crystal size was 20.173 nm. The size of the nanofibers before and after PEG modification showed that the size of the PEG-modified nanofibers is larger than the non-modified nanofibers. This was because PEG functioned as a capping agent or as a wrapper so that the nanofiber size became larger.

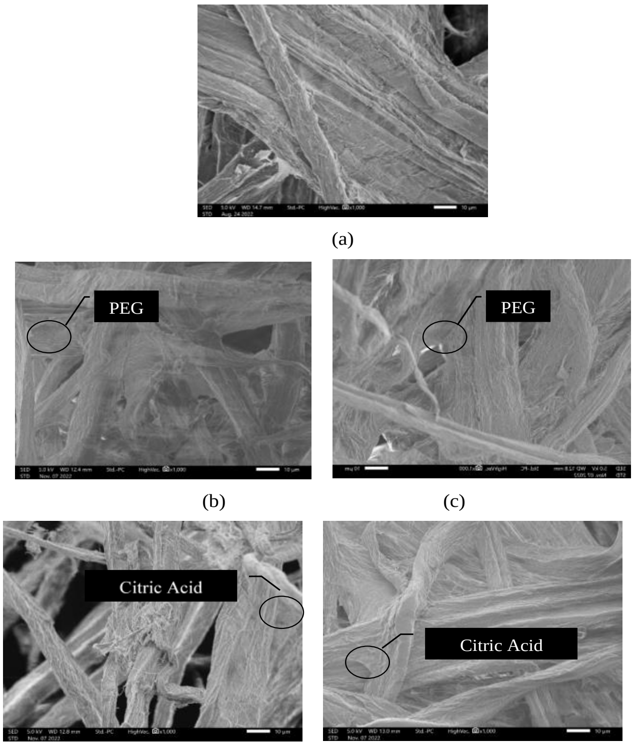
c. SEM – EDX

Characterization by SEM-EDX was used to determine the morphological appearance and elemental content of the nanofiber before and after modification. The results of SEM-EDX are presented in Figure 4. The surface morphology of the adsorbent could be observed using SEM (5.0 kv; 100 μm). In Figure 4, changes in nanofiber morphology could be seen before and after modification. The N sample looked homogeneous and there was no visible membrane covering it. After being modified with PEG, the adsorbent's surface showed the fibers sticking together. The addition of a PEG capping agent functioned as a template and wrapped particles so that aggregates were not formed. The SEM results of nanofibers modified with citric acid showed that the fibers and the presence of connective tissue and the nanofiber surface appeared heterogeneous. This was due to a carboxyl group from citric acid [31]. This carboxy group was suggested to enhance the electrostatic interaction between nanofibers and adsorbent [34].

Table 1. Chemical Composition

Samples	Elements	Mass (%)	Atom (%)
N	C	38.49	45.46
	O	61.51	54.54
NP 2	C	41.49	48.58
	O	58.51	51.42
NP 24	C	39.65	46.67
	O	60.35	53.33
NS 2	C	39.31	46.32
	O	60.69	53.68
NS 24	C	38.00	44.95
	O	62.00	55.05

The results in Table 1 show that before and after the modification, nanofiber contained the elements O (Oxygen) and C (Carbon). Elements O and C were the cellulose matrix. NP 2 and NP 24 showed a decrease in the O element component. This was also in line with the FTIR results in Figure 2, which indicated that vibrations in the OH group were increasingly widening. In NS 2, the C element increased. This was also in line with the C=C group, which appeared in NS 2, where this group was considered an impurity in NS 2. In NS 24, the C and O groups tended to be stable. This was also in line with the FTIR results in Figure 2, which did not show the addition of C=C groups as in sample NS 2.



(a)

(b) (c)

(d) (e)

Figure 4. SEM results (5.0 kv; 100 μm; 1000x) (a). N (b) NP 2, (c). NP 24, (d). NS 2, (e). NS 24

3. Adsorption

a. Reaction Mechanism

In solution, pH played a role in the protonation of the active site of the adsorbent molecule so that it would affect the surface charge of the adsorbent. pH_{PCZ} was one of the parameters that played a role in determining the optimal pH on the nanofiber surface to absorb the absorbate. The pH_{PCZ} of nanofibers was about 7.4 [32]. At neutral pH, the positive (H^+) and negative (OH^-) sites had the same number. Hence, the adsorbent could absorb cationic dyes well because no competitors inhibited the interaction between CV and the active site of the adsorbent [33]. If the pH was below 7, H^+ ions increased and would try to interact with the negative partial of cellulose. As a result, there would be interaction competition between CV cations and H^+ ions so that the adsorption capacity would decrease. If the pH were more than 7, adsorption capacity would decrease because OH would attack the positive partial of CV^- so CV could not interact with the negative partial on the nanofiber.

Positive CV (N+) sites at neutral pH would interact with negative sites on functional nanofibers, such as OH groups. This was also in line with the research explaining that functional groups in the form of ketones, aldehydes, phenols, and ethers could undergo electrostatic interactions with a cationic molecule so that they could undergo chemical adsorption [34]. The interaction between CV and nanofiber was Van der Waals electrostatic interaction,n, as in Figure 5. Van der Waals' electrostatic interaction was the intermolecular attractive force between solid molecules and the adsorbed solute. It was greater than the attractive force between the solute itself in the solution and was concentrated at the solid surface [35].

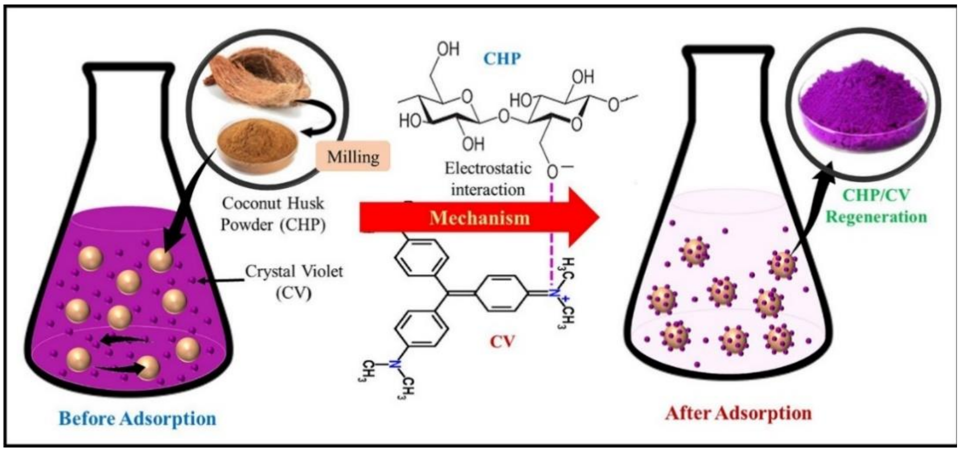


Figure 5. Adsorption of CV by Nanofiber [36]

b. CV Adsorption Capacity

Based on the adsorption results on CV with 7 sampling times at 0, 15, 30, 45, 60, 90, and 120 minutes, data were obtained as in Table 3. In Table 2, the highest percentage of substances adsorbed on N were obtained from NS 2, NS 24, NP 2, and NP 24 re, respectively, 95.743, 95.822, 95.760, and 95.051%. The results of the adsorption process on CV 10 ppm by nanofiber before and after modification tended to be stable, and the addition of citric acid and PEG had no effect on the adsorption results. These differences in contact time between the adsorbent and the adsorbate did not significantly influence the adsorption results. The results of the adsorption process on CV 10 ppm by nanofiber before and after modification with citric acid tended to be stable after 15 minutes, whereas NP 2 and NP 24 had a stable adsorption capacity from the start of contact. It is worth noting that the adsorption stability meant the adsorption process could be conducted efficiently, for example, for up to 30 minutes.

Based on the results of Table 3, the highest percentage of adsorbed substances in N, NS 2, NS 24, NP 2, and NP 24 were, respectively, 98.479, 97.007, 97.336, 98.421, and 98.621%. The results of the adsorption process on CV 50 ppm by nanofiber before and after modification tended to be stable and the addition of citric acid and PEG did not affect the adsorption results. In addition, the difference in contact time between the adsorbent and the adsorbate did not significantly influence the adsorption results. The adsorption process usually happens rapidly in the first 15 minutes, is steady for a certain time, and sometimes decreases afterward. This is because molecules of the dyes bind the vacant active sites of the nanofiber fast until saturation point is achieved to the point where no more active sites can be occupied. This was shown by the results of the adsorption capacity at each additional time which tended to be stable.

The CV adsorption capacity of 10 ppm had the highest value for N, NS 2, NS 24, NP 2, and NP 24, respectively 9.540, 9.574, 9.582, 9.576, and 9.505 mg/g. Meanwhile, the CV adsorption capacity of 50 ppm had the highest value for N, NS 2, NS 24, NP 2, and NP 24, respectively, 49.239, 48.503, 48.668, 49.210, and 49.311 mg/g.

These results show that all the samples had excellent adsorption performance since the dye was almost completely adsorbed for 10 and

50 ppm. The performance may be due to the oxygen content of the samples, which were relatively the same (Table 1). The more the oxygen, the more the dye interacted because of electrostatic force [36]. Several factors, such as number of oxygen content, surface area, and surface negative charge, were considered to affect the adsorbent's performance [37].

Table 2. Results of 10 ppm CV Adsorption

Time	Samples									
	N		NS 2		NS 24		NP 2		NP 24	
	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)
0	0	0	0	0	0	0	0	0	0	0
15	92.242	9.224	93.220	9.322	94.447	9.445	95.760	9.576	94.814	9.481
30	95.395	9.540	95.711	9.571	95.692	9.569	95.469	9.547	94.362	9.436
45	94.335	9.443	95.560	9.556	95.822	9.582	95.279	9.528	95.051	9.505
60	94.443	9.443	95.587	9.559	95.225	9.522	94.337	9.434	94.726	9.473
90	94.870	9.487	95.408	9.541	95.565	9.556	95.005	9.500	94.421	9.442
120	95.323	9.532	95.743	9.574	95.511	9.551	95.002	9.502	94.166	9.417

Table 3. Results of 50 ppm CV Adsorption

Time	Samples									
	N		NS 2		NS 24		NP 2		NP 24	
	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)	% absorbed	Qe (mg/g)
0	0	0	0	0	0	0	0	0	0	0
15	97.458	48.729	96.996	48.498	96.565	48.283	98.421	49.210	97.780	48.890
30	98.202	49.101	96.504	48.252	97.031	48.515	98.039	49.020	98.503	49.252
45	98.224	49.112	96.885	48.442	97.174	48.587	98.418	49.209	98.357	49.178
60	98.259	49.129	95.587	48.503	97.336	48.668	98.188	49.094	98.621	49.311
90	97.239	48.620	96.493	48.246	96.825	48.413	97.895	48.947	98.140	49.070
120	98.479	49.239	97.004	48.502	96.457	48.229	98.069	49.034	98.346	49.173

CONCLUSION

Based on the research results, it can be concluded that the nanofiber before and after modification has a smooth texture and is white. FTIR results on nanofibers before and after modification show that the functional groups that form cellulose are -OH, C-H, and C-O. Adding citric acid produces a new group, namely the C=O group, with a very weak intensity. Meanwhile, the FTIR results on nanofibers modified with PEG show stretching of the -OH groups. The nanofiber's SEM results show a layer on the nanofiber that shows citric acid and PEG. The XRD results show that there are 2 peaks which indicate that the nanofiber before and after modification has a semi-crystalline phase. Van der Walls electrostatic interactions occur in the adsorption mechanism that occurs betweennt and the absorbate experiences. The adsorption results on CV have a stable adsorption capacity as the contact time increases. In addition, it also shows that modification with citric acid and PEG does not affect the adsorption results.

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