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Development of 4-vinylbenzyl chloride (VBC) grafted onto branched polyethylenimine (PEI) onto bacterial cellulose sheet by gamma-induced irradiation technique for Cu^{2+} ion adsorption

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Abstract

Bacterial cellulose extracted and purified from Nata de coco was employed as a platform for Cu^{2+} ion adsorption. 4-vinylbenzyl chloride (VBC) was successfully grafted at the hydroxyl position by using gamma irradiation. The optimum was typically related to VBC concentration of 2% (v/v) and a radiation dose of 50 kGy. FTIR significantly reported the functional group of C-Cl related to VBC. No change of crystallinity and morphology was observed. The thermal decomposition was stable up to 200°C. The modification of branched polyethylenimine (PEI) was prepared in order to change the functionality to N–H stretching. This was expected to adsorb Cu^{2+} ion. It was evaluated under the variation of concentration, pH and time. Efficiency reported that concentration of 50 mg·L^{-1}, pH of 7, and adsorption time of 2 h were reported. The results exhibited that gamma ray–induced grafting, followed by PEI functionalization onto bacterial cellulose surface was considered as one of the most effective strategies for effective platform for Cu^{2+} ions in aqueous systems. It was remarkably noted that modified bacterial cellulose extremely provided the great promise as the eco-friendly platform for wastewater remediation.

1. Introduction

In recent years, with the rapid growth of worldwide population, the push towards to development of various technologies have been evident such as automotive vehicle, infrastructure as well as medical technology. Although various technologies offered the advantages due to facilitation of life, it also provided the limitation in terms of environmental pollution. It was remarkably noted that one of the most dangerous pollutions was referred to "water-based pollution". It can occur when harmful substances such as chemicals and microorganisms contaminate a stream, river, lake and ocean. It consequently degraded the water quality and rendered the toxicity to human and/or the environment [1-3].

In particular, copper ions (Cu^{2+}) are considered as one of the heavy metals. They can cause severe water pollution. Although copper is an essential trace element necessary for the survival of many living organisms, excessive accumulation of Cu^{2+} in aquatic can be extensively toxic to aquatic life. The contamination of Cu^{2+} may extremely lead to the change in the biological composition of ecosystems. Moreover, the role of copper ions can enter the human body through the consumption of contaminated seafood or aquatic organisms. These heavy metals tend to accumulate in the cells and tissues of living organisms. Continuous exposure to elevated levels of Cu^{2+} in humans may result in serious health issues. Therefore, the effective removal and control of copper ions from wastewater is of critical importance for both environmental protection and human health.

Up to the present time, numerous strategies have been extensively employed to remedy the quality of water. It typically involved to phase separation, sedimentation, biological and chemical process related to oxidation as well as polishing. These techniques significantly provided various benefits due to removal efficiency. However, in order to upgrade on impurities removal process from wastewater, one of the alternative approaches related to chemical adsorption was therefore considered. From the fundamental point of view, chemical adsorption, or called "chemisorption" was typically referred to adsorption which involved chemical reaction between surface and adsorbate by chemical bonding. It therefore resulted in a change in their electronic structure by sharing electron between adsorbate and adsorbent [4,5]. Recently, various categories of adsorbate have been extremely developed in order to effectively provide the superiority for wastewater remediation. Shirani *et al.* [6] evaluated the role of activated biochar for the treatment of artificial wastewater contamination. It can be employed in wastewater remediation of pharmaceutical products. Hashem *et al.* [7] investigated the performance of kitchen biowaste for treatment of tannery wastewater.

It was adhered with chromium ion as reported by EDS. The adsorption curve was well fitted with Freundlich kinetic model. Jiang *et al.* [8] evaluated the adsorption mechanism of rhodamine wastewater by metal organic framework. The mechanism of adsorption was strongly depended on specific surface area, type of metal center and organic ligand as well as molecular size of rhodamine.

With this regard, it can be suggested that one of the most important factors for adsorption mechanism was typically related to surface area. To design the adsorbate with additional feature of characteristic of specific surface was therefore considered as one of the most important aspects [9]. Recently, our research group has strongly developed bacterial cellulose-based composite [10]. It was structurally defined as a nano-porous network of cellulose, randomly distributed on its surface. It exhibited various hydroxyl groups onto network, offering the possibility to create the chemical bonding with adsorbent molecules. Ijaz *et al.* [11] studied the modification of bacterial cellulose by MoBTx MBene and 1,4-dithiothreitol for adsorption of indomethacin and losartan potassium. It presented remarkable ability to adsorb antibiotics and the excellence of regeneration ability. Liu *et al.* [12] investigated the adsorption mechanism of bacterial cellulose and locust bean gum composite for malachite green removal. It illustrated high adsorption rate of 95% and adsorption capacity of 2000 $mg \cdot g^{-1}$, along with good selectivity in multi-component system. It can be also presented good reusability after regeneration by hydrothermal treatment. Next to adsorption capacity of bacterial cellulose, it can be strongly noted that bacterial cellulose was considered as an eco-friendly material, non-toxicity as well as ease of fabrication. This was in agreement with "Green policy", which was related to sustainable usage of material. The use of product and process which related to hazardous chemical reagents should be preferably avoided.

To modify bacterial cellulose with higher efficiency, the grafting reaction inducing by gamma irradiation was considered as one of the most effective routes. It was typically related to the penetrating form of gamma radiation of electromagnetic radiation onto surface of bacterial cellulose [13]. The advantage of this technique is being free of catalyst, solvent and any chemical reaction. The process was conducted within a controllable time. It was consequently therefore easy to be scaling up for mass production process. The role of gamma ray can be activated to form free electron onto cellulose chain and then it was chemically grafted with other active molecules to form a reactive cellulose fibrous network [14]. Recently, Khiewsawai *et al.* [15] employed gamma irradiation technique to fabricate cellulose based hydrogel composite. 25 kGy of gamma ray was employed to form hydrogel between cellulose, polyethylene glycol and branched polyethylenimine composite. It was therefore employed as a platform for mercury (II) adsorption in seafood. This was in agreement with previous work of Kanbua *et al.* [16]. Gamma ray can be employed to fabricate composite for selective membrane of battery application.

To date, the objective of this research work is to employ gamma irradiation technique for bacterial cellulose surface modification. It was fabricated the composite membrane by 4-vinylbenzyl chloride (VBC) grafted onto branched polyethylenimine (PEI). Physico-chemical properties were then determined. After that Cu^{2+} adsorption test was performed.

2. Experimental

2.1 Chemical reagents and materials

Nata de coco, a dessert produced in Southeast Asia, was purchased from a local market, Thailand. It was stored in refrigerator. It was employed as a starting material for bacterial cellulose production. Sodium hydroxide (NaOH) and sodium bicarbonate ($NaHCO_3$) were purchased from Merck, Co., Ltd. (Germany). These chemical reagents were employed to extract and purify bacterial cellulose. 4-vinylbenzyl chloride (VBC) and branched polyethylenimine (bPEI) were purchased from Sigma-Aldrich, Co., Ltd. (USA). Both chemical reagents were used to structurally modify bacterial cellulose. Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) was purchased VWR Chemicals BDH, VWR International Ltd. (UK). Hydrochloric acid (HCl, 37%) was purchased from KEMAU, Co., Ltd. (Australia). All chemical reagents were used as received without further purification.

2.2 Methodology

2.2.1 Extraction and purification of bacterial cellulose

Bacterial cellulose, nano-cellulose, based fiber was chemically extracted from nata de coco. It is a product derived from the fermentation by the bacterium Acetobacter xylinum (or A. xylinum). This bacterium synthesizes pure cellulose in the form of a gel-like pellicle that floats on the surface of the liquid during the fermentation process. It was rinsed with distilled water in order to remove the excess sugar and syrup. After that, it was blended with a laboratory blender in order to obtained pellicles. Then, they were treated with 0.1 M of NaOH at 80°C for 1 h for removal of any remaining microorganism, medium components, and soluble polysaccharides. The extraction process was prepared by connecting to suction flask equipped with vacuum pump in order to filtrate solvent. The purified bacterial cellulose pellicles were then thoroughly washed with distilled water until a neutral pH was achieved. Additional information related to bacterial extraction has been reported in many previous articles [17-19].

2.2.2 Grafting of 4-vinylbenzyl chloride onto bacterial cellulose surface, followed by substitution with branched polyethylenimine

At the initial stage, the bacterial cellulose sheet was prepared from suspension. It was connected to a suction flask connected to vacuum pump to remove the solvent. Then, it was dried for a week. After that, it was employed as a platform for 4-vinylbenzyl chloride (VBC) grafted onto branched polyethylenimine (PEI). Briefly, 1% to 5% (v/v) of VBC dissolved in deionized (DI) water was used for the grafting process with a radiation dose ranging from 10 kGy to 50 kGy. Then, the chloride group was substituted by amine groups (NH_2) as PEI attacked the carbon atom in the benzyl chloride group, causing the chlorine (Cl) to leave as a leaving group. The experiment was conducted at ambient atmosphere. The composite membrane was characterized by FTIR, XRD, TGA, SEM and contact angle measurement.

Degree of grafting was calculated by using the following Equation

$$\text{Degree of grafting} = \frac{(W_f - W_i)}{W_i} \times 100$$

where W_i and W_f are the weights of bacterial cellulose sheet before and after grafting process, respectively.

2.2.3 Cu^{2+} adsorption test

To test the ability of Cu^{2+} adsorption, 10 mg·L^{-1} to 90 mg·L^{-1} of $CuCl_2$ was dissolved into distilled water. It was continuously stirred for 1 h in order to ensure the uniformity. After that, modified bacterial cellulose with the size of 0.75 cm × 0.75 cm was immersed into the solution. The temperature was set at 25°C. The mixture was then stirred at 160 rpm for 4 h. Then, it was investigated by UV-vis spectroscopy. In case of pH, the concentration was fixed at 50 mg·L^{-1}. The pH range was set to 4 to 8, while in case of time, the range of time was set from 0.5 h to 4 h.

The adsorption capacity was calculated by using the following Equation

$$\text{Adsorption capacity} = \frac{(C_0 - C_e)V}{m}$$

$$\text{Efficiency of adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100$$

where C_0 is the initial concentration of Cu^{2+} solution before the immersion of the adsorbent, C_e is the concentration of the Cu^{2+} solution after the immersion of the adsorbent, V is the volume of solution containing Cu^{2+}, and m is the dry mass of adsorbent.

2.3 Characterization techniques

2.3.1 ATR-FTIR (Attenuated total reflectance fourier transform infrared)

The structure and functional groups were analyzed using an Attenuated total fourier transform infrared spectrometer (ATR-FTIR), BRUKER model INVENIO R, in the wavelength range of 4000 cm^{-1} to 400 cm^{-1}. The sample was prepared as a thin sheet. Prior to investigation, sample was heated at 100°C in order to avoid moisture adsorption.

2.3.2 X-ray diffraction

The crystallinity was conducted using an X-ray diffractometer (XRD), Bruker model D8 ADVANCE, with the testing performed over an angular range from 10° to 60°. The sample prepared as a sheet was attached onto sample holder. Prior to test, sample was stored in desiccator for a night before investigation.

2.3.3 Thermogravimetric analysis

The thermal behavior was analyzed using a Thermogravimetric Analysis (TGA) instrument (Mettler Toledo, model TGA2). The measurements were carried out in an aluminum oxide crucible under a N_2 atmosphere. The temperature was increased from room temperature to 600° at a heating rate of 10°C·min^{-1}, with a N_2 flow rate of 20 mL·min^{-1}.

2.3.4 Scanning electron microscope

The morphological properties were then examined using a field emission scanning electron microscope (FE-SEM; JEOL, model JSM-7800F) at magnifications of 100×, with an accelerating voltage of 2 kV. Before analysis, the samples were then Au-sputtered in order to enhance the electrical conductivity onto surface.

2.3.5 Contact angle measurement

The wettability of the material was evaluated by measuring the contact angle of a liquid droplet on its surface. They were conducted by using a Theta Lite Optical Tensiometer (Biolin Scientific, model 100) based on the analysis of the liquid–solid interfacial tension along a reference plane.

2.3.6 UV-vis spectroscopy

The absorption properties were analyzed using UV-vis spectrophotometry. Absorbance was measured at a wavelength of 203 nm using a UV-vis spectrophotometer (PEAK, C-7100 series). The wavelength region was set ranging from 400 nm to 900 nm. It was tested at ambient temperature.

3. Results and discussion

3.1 Characterization of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface

4-vinylbenzyl chloride (VBC) was successfully grafted onto bacterial cellulose sheet. It adhered through covalent bond formation with the hydroxyl groups of bacterial cellulose throughout the network. The vinyl group at the end group of VBC molecule facilitates easy grafting. The process of grafting did not provide any change onto physico-chemical properties of bacterial cellulose.

Figure 1 illustrates the correlation between degree of grafting (%) and gamma irradiation dose. The amount of 4-vinylbenzyl chloride (VBC) was ranged from 1% to 5% (v/v) with the variation of dose range. It was observed that degree of grafting was significantly increased with respect to amount of 4-vinylbenzyl chloride (VBC). This was probably due to the fact that with the existence of VBC content, it offered the possibility to be adhered at the hydroxyl group position of bacterial cellulose chain by activation of gamma irradiation. The role of gamma ray may activate the bacterial cellulose chain by forming free radical to form the reaction with VBC. It was also observed that with the increment of dose, the degree of grafting was relatively high. However, it was controversial that with higher dose, bacterial cellulose was changed to brittleness. It may crack when high load was applied. The optimal dose was estimated to be 50 kGy for VBC grafted onto bacterial cellulose chain. It exhibited as a thin-sheet along with high flexibility.

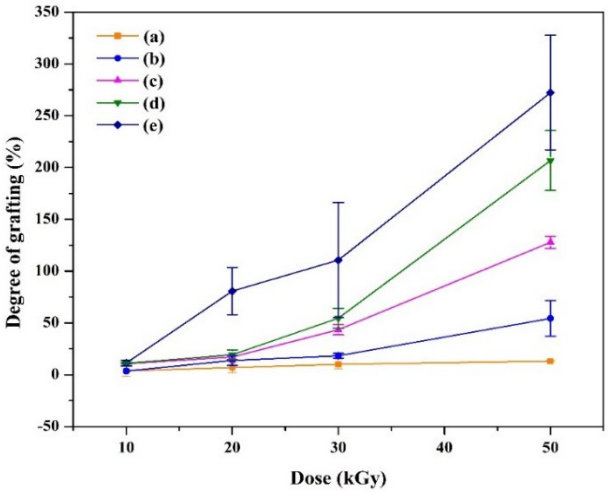

Figure 1. Degree of grafting and dose of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface (a-e) 1, 2, 3, 4, and 5% (v/v) of VBC.

In order to identify the chemical structure of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface, FTIR was employed. Figure 2 shows the FTIR spectra of modified bacterial cellulose surface. The pristine bacterial cellulose was also provided for comparison. All of characteristic peaks were similar. It was observed that with the grafting of 4-vinylbenzyl chloride, no significant change related to functional group was therefore observed. This was probably due to the fact that only small amount (1% to 5% (v/v)) of VBC was grafted. The characteristic peaks at the wavenumber of 3345 cm^{-1} and 1057 cm^{-1} were existed. These peaks were relatively referred to the vibration of O–H stretching and C–O stretching. They were belonged to hydroxyl group and carbonyl group, respectively. The position of O–H group was located into glucose unit, whereas the position of C–O was related to glycosidic bond. It was important to note that with these functional groups onto modified bacterial cellulose, it was facile to adhere with water molecule by H-bond linkage formation throughout network. Modified bacterial cellulose was suggested to store in desiccator in order to avoid the adsorption of water molecule [20,21]. On the other hand, the peaks at the wavenumber of 2917 cm^{-1} and 671 cm^{-1} were presented. These peaks were related to the vibration of C–H stretching and C–Cl stretching. The existence of C–H stretching was related to glucose unit, while the presence of C–Cl stretching was referred to chloromethyl group. It can be employed to identify the successful graft reaction of VBC onto bacterial cellulose sheet [20,22,23].

Next to functional group determination of modified bacterial cellulose, the crystallinity was also observed. Figure 3 reports the XRD pattern of modified bacterial cellulose by grafting with VBC. It was observed that with the small amount of VBC content (only 1% to 2% (v/v)), the crystallinity of modified bacterial cellulose was still similar to pristine. It was observed that the diffraction angle (2θ) values of 14.50° and 22.57° were presented, with an additional minor peak at 2θ = 16.76°. These peaks correspond to the (1-10), (110), and (200) crystallographic planes, respectively, confirming the crystalline structure of bacterial cellulose. This agreement with previous work of Gomes *et al.* [21]. However, when the amount of VBC was relatively high, the trend of crystallinity was less. The crystallinity of modified bacterial cellulose was changed to amorphous phase. Therefore, grafting of VBC affected the internal structure of bacterial cellulose. This result was in agreement with Table 1.

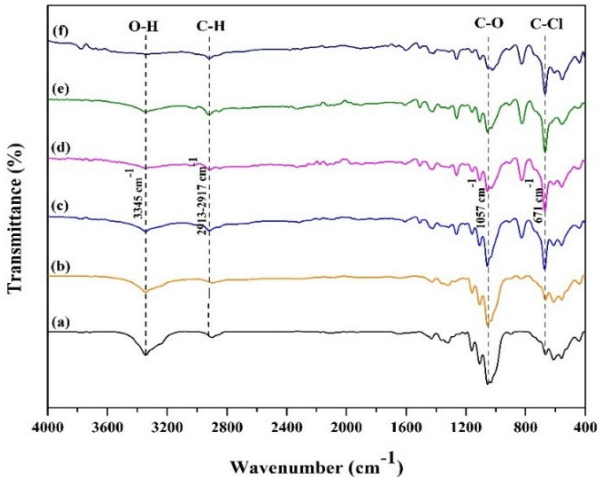

Figure 2. FTIR spectra of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface (a) Bacterial cellulose (BC), and (b-f) 1, 2, 3, 4, and 5% (v/v) of VBC.

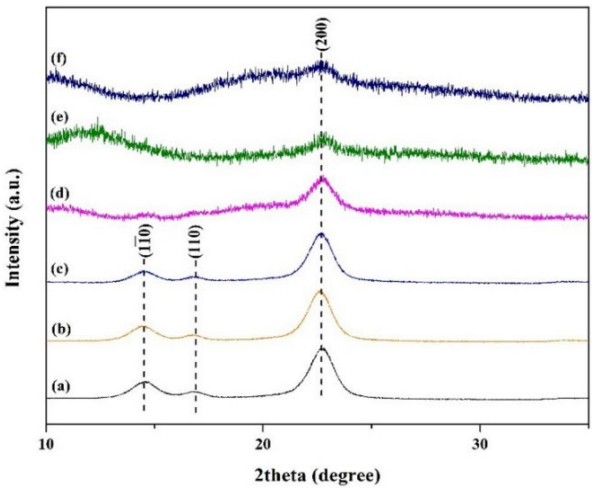

Figure 3. XRD pattern of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface (a) Bacterial cellulose (BC), and (b-f) 1, 2, 3, 4, and 5% (v/v) of VBC.

Table 1. Crystallinity conditions for 4-vinylbenzyl chloride grafting.

Simple	Crystallinity [%]	Amorphous [%]
Bacterial cellulose	75.9	24.1
BC-g-1%VBC	74.5	25.5
BC-g-2%VBC	65.2	34.8
BC-g-3%VBC	41.2	58.8
BC-g-4%VBC	45.4	54.6
BC-g-5%VBC	43.6	56.4

Figure 4 illustrates the thermal decomposition behavior of 4-vinylbenzyl chloride (VBC) grafted onto the surface of bacterial cellulose. The experiment shows that the presence of 4-vinylbenzyl chloride (VBC) significantly enhances the thermal properties compared to pristine bacterial cellulose. The temperature range can be divided into three distinct regions. From room temperature to 300°C, only 5% (v/v) weight loss was observed, which generally corresponds to the evaporation of water from the surface of the modified bacterial cellulose. This is consistent with the previous work of Bai *et al.* [24]. Subsequently, in the temperature range of 300°C to 400°C, a broad region of weight loss was observed. It is typically related to the pyrolysis process of the modified bacterial cellulose. When the temperature exceeded 400°C, the percentage of weight loss was still considerable, but it depended on the amount of VBC used in the test. It is possible that the 4-vinybenzyl chloride (VBC) grafted onto the surface of bacterial cellulose contributes to improved heat resistance of the material.

In order to evaluate the morphological properties of modified bacterial cellulose, scanning electron microscope was employed. This technique permits to analyze the microstructure of modified bacterial cellulose surface. Figure 5 demonstrates the microstructure of modified bacterial cellulose. It typically presented as a nano-fiber form. The length and diameter of modified bacterial cellulose fiber was estimated to be 100 and 10 nm with randomly distributed throughout network. This is in agreement with previous work of Koromilas *et al.* [22]. At higher magnification, the interconnected nanofiber structure is clearly visible, indicating that the surface modification does not disrupt the nanoscale arrangement. However, at lower magnification, individual nanofibers cannot be distinguished due to the larger scale. At this magnification, the surface appears densely packed and smooth with no visible porosity, as the nanoscale features are beyond the resolution of these images. The interface between fiber chain was presented due to the repulsive force of OH group located as a pendent group alongside bacterial cellulose chain. With the presence of interface, the position was free for VBC grafting. The location of VBC can be inserted alongside of bacterial cellulose chain throughout network and on-top of bacterial cellulose surface, suggesting that modified bacterial cellulose presented the uniformity of distribution when composite will be prepared.

Wettability was considered as one of the most important properties of modified bacterial cellulose surface. It typically related to contact angle measurement. Figure 6 reports the contact angle measurement of modified bacterial cellulose. It demonstrated that the contact angle was significantly increased with respect to the VBC content. The characteristic feature was changed from hydrophilicity to hydrophobicity. This was probably due to the fact that the presence of VBC contained a non-polar aromatic ring. Upon grafting onto bacterial cellulose, these groups were replaced by the benzene ring, thereby hindering hydrogen bonding and reducing water wettability. As a result, the contact angle significantly increased.

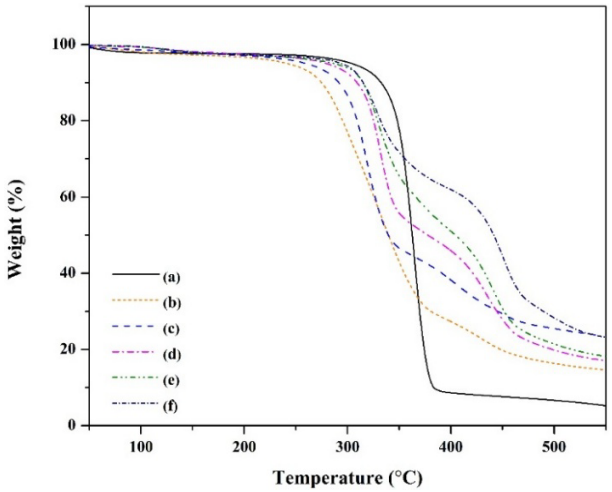

Figure 4. Thermal decomposition behavior of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface (a) Bacterial cellulose (BC), and (b-f) 1, 2, 3, 4, and 5% (v/v) of VBC.

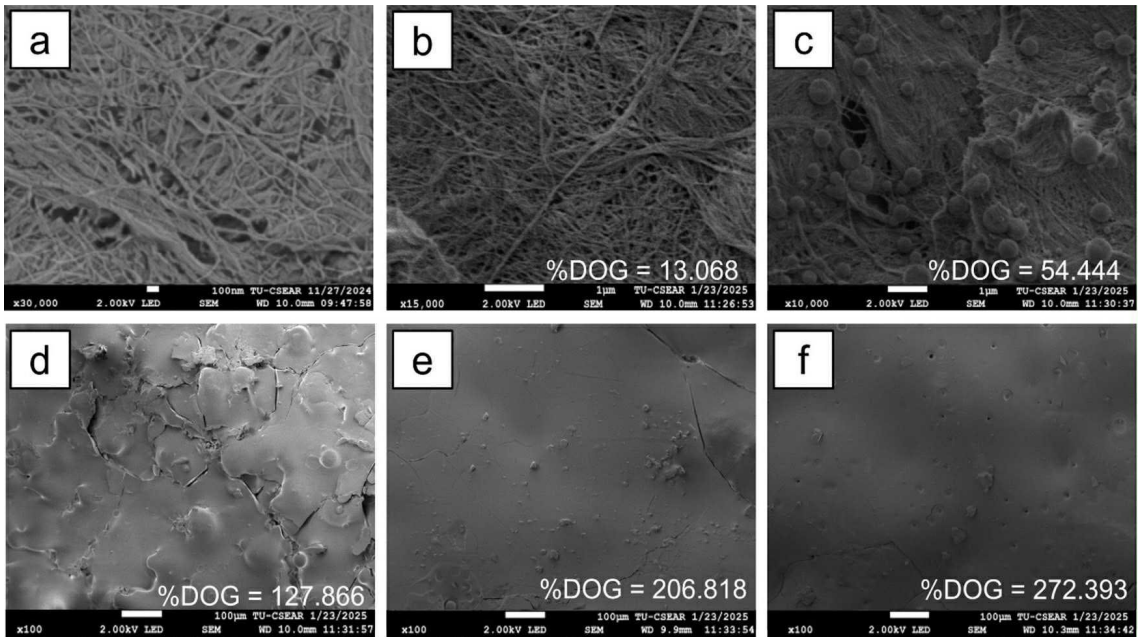

Figure 5. SEM microstructure of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface (a) Bacterial cellulose (BC), and (b-f) 1, 2, 3, 4, and 5% (v/v) of VBC.

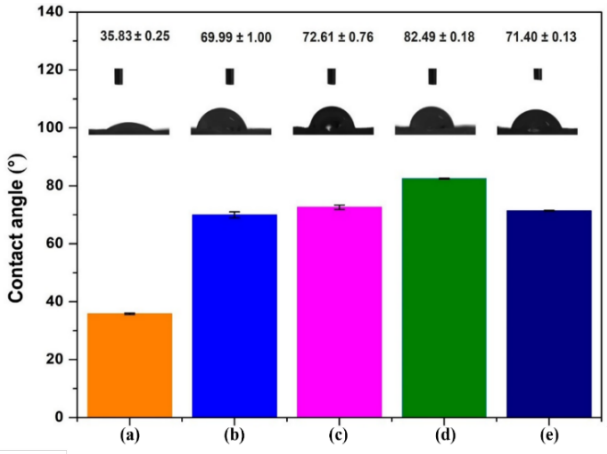

Figure 6. Contact angle of 4-vinylbenzyl chloride (VBC) grafted onto bacterial cellulose surface (a-e) 1, 2, 3, 4, and 5% (v/v) of VBC.

3.2 Modified PEI onto bacterial cellulose sheet and investigation as a platform for Cu^{2+} ion determination

In order to design bacterial cellulose-based platform for Cu^{2+} ion adsorption, the modification of VBC by polyethylenimine (PEI) was performed to introduce N–H functional groups. These functional groups enabled the adsorption of Cu^{2+} ions. According to Lewis theory, PEI contains amine groups with lone pairs of electrons, which act as Lewis bases by donating electron pairs to Cu^{2+} ions, which act as Lewis acids. This interaction leads to the formation of coordinate bonds between PEI and Cu^{2+} ions. However, only 2% (v/v) of VBC grafted onto the bacterial cellulose at 50 kGy was selected for investigation. Therefore, no significant change was observed upon PEI modification.

Figure 7 reports the physico-chemical properties of PEI modified on VBC grafted onto bacterial cellulose sheet. The variation of time was investigated based on comparison with pristine bacterial cellulose and VBC-grafted bacterial cellulose. Figure 7(a) illustrates the FTIR spectra of PEI modified onto VBC-bacterial cellulose surface. The characteristic peaks at the wavenumber of 1560 cm^{-1} and 1426 cm^{-1} were therefore observed. These peaks were relatively referred to C–N stretching and N–H stretching, respectively. The amine group was then occurred due to the presence of PEI. The presence of N–H stretching was permit to adhere with Cu^{2+} ion onto modified surface of bacterial cellulose. In addition, the characteristic peak at the wavenumber of 671 cm^{-1} was presented. It was corresponded to C–Cl stretching. The intensity of this peak was strongly observed in case of VBC-grafted onto bacterial cellulose. In case of PEI modification, the intensity of peak was slightly less due to the substation with N-H group. Furthermore, the characteristic peaks at the wavenumber of 3345 cm^{-1} and 1057 cm^{-1} were observed due to the presence of O–H stretching and C–O stretching. These peaks were typically referred to hydroxyl group and carbonyl group, respectively. They related to functional group of glucose unit and glycosidic bond. It can be suggested that modified bacterial cellulose was facile to adhere with water molecule by H-bond linkage. It should be stored in desiccator. The peak at the wavenumber of 2819 cm^{-1} was observed due to C–H stretching. It involved the main chain structure of bacterial cellulose.

Figure 7(b) presents the XRD pattern of PEI modified onto VBC-bacterial cellulose surface. All of characteristic peaks were identical with pristine bacterial cellulose sheet, suggesting that no change due to crystallinity was observed when PEI and VBC were used to modified the structure of bacterial cellulose. This was probably due to small amount. It was observed that the diffraction angle (2θ) values of 14.50°, 16.76° and 22.57° were presented. These peaks correspond to the (1–10), (110), and (200) crystallographic planes, respectively, confirming the crystalline structure of bacterial cellulose. This is in agreement with Figure 3. In order to define the thermal decomposition behavior, thermogravimetric analysis was employed to evaluate. Figure 7(c) exhibits the thermal decomposition behavior of PEI modified onto VBC-bacterial cellulose surface. It was observed that with the presence of PEI and VBC modification, the thermal resistance of 200°C was observed. The data was slightly less compared to pristine bacterial cellulose, which was thermally resisted up to 300°C. However, the use of platform at ambient temperature was still possible. Figure 7(d) also reports the contact angle measurement of PEI modified onto VBC-bacterial cellulose surface. With modification with PEI, the characteristic of water molecule observed by contact angle measurement was changed from hydrophobicity to hydrophilicity. It was changed from 72° to 20° when PEI was employed to modify. The hydrophilicity of PEI modified onto VBC-bacterial cellulose surface may allow the platform to adhere with Cu2+ ions in water-based solution.

Figure 8 was conducted based on the hypothesis of Cu^{2+} ion adsorption onto PEI modified onto VBC-bacterial cellulose surface. The experiment was reported based on adsorption capacity and efficiency. The adsorption results were conducted based on the variation of concentration, pH range and time in order to find the optimal condition. Figure 8(a) remarkably notes that the optimal concentration for Cu^{2+} adsorption was presented at 50 $mg{\cdot}L^{-1}$. The optimal initial concentration obtained from the adsorption efficiency curve indicates the concentration at which the adsorption process achieves the highest performance. The adsorption efficiency reached a maximum of 32.89%, which was notably higher than the values obtained at both lower and higher concentrations. This optimal concentration reflects both the adsorption capacity and the efficiency of adsorption, as both parameters exhibit a similar trend at this concentration. Moreover, Figure 8(b) reports effect of pH range for Cu^{2+} adsorption. It was observed that the adsorption efficiency was slightly high at neutral region. At acidic region, there was high amount of H^+ ions into solution. This ion was interfered with Cu^{2+} adsorption onto functional group of platforms. Meanwhile, in the basic region, Cu^{2+} ions precipitated as $Cu(OH)_2$, which prevented further adsorption of Cu^{2+}. The adsorption efficiency decreased. This is in agreement with previous work of Qin *et al.* [25]. Figure 8(c) reports the effect of time onto Cu^{2+} adsorption onto modified bacterial cellulose surface. It was observed that the adsorption behavior was slightly high at the initial stage (with 2 h). After that, it was stable. It can be implied that the efficiency of usage was rapid within initial stage, suggesting that functional group of modified bacterial cellulose provided the superiority for Cu^{2+} adsorption. The Cu^{2+} adsorption mechanism was presented in Figure 9. Although the maximum adsorption capacity obtained in this study was not very high, this may be attributed to partial pore blockage caused by surface modification. Nevertheless, the PEI-modified bacterial cellulose offers significant advantages, including environmental friendliness and high selectivity toward Cu^{2+} ions, making it a promising material for practical applications in sustainable wastewater treatment.

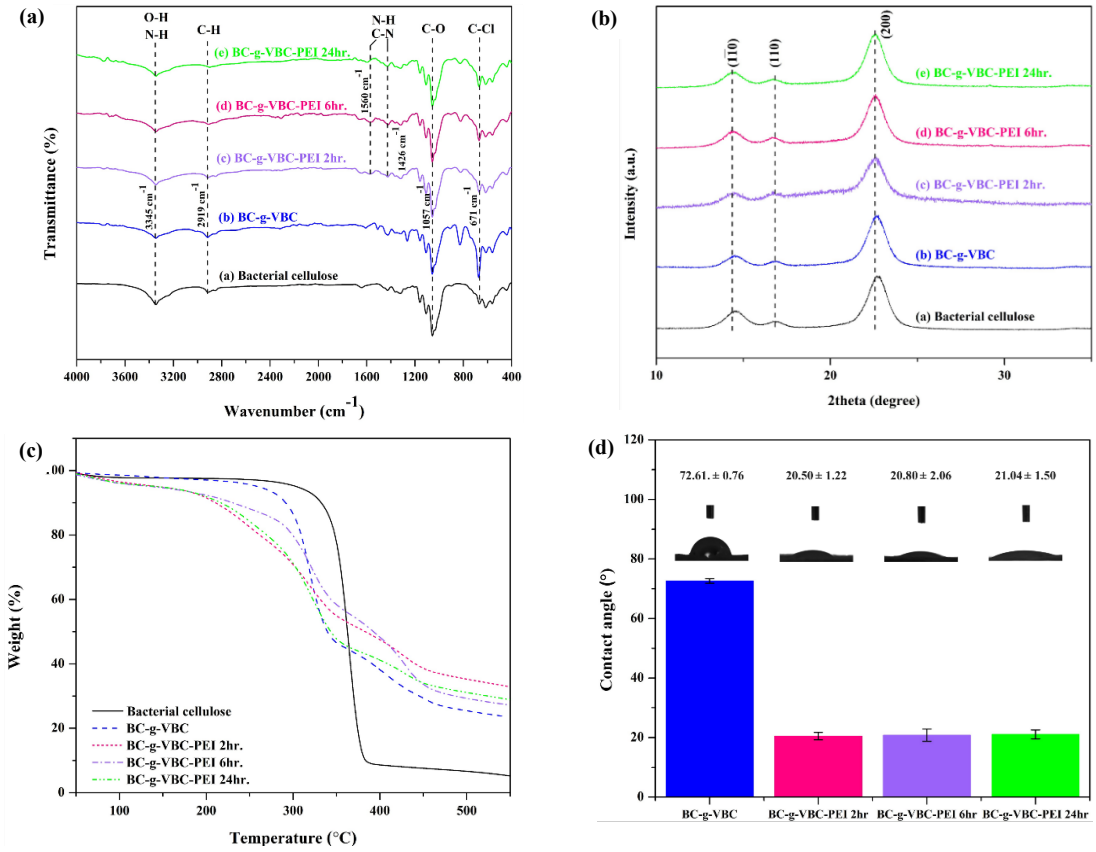

Figure 7. Characterization of PEI modified onto VBC-bacterial cellulose surface (a) FTIR spectra, (b) XRD pattern, (c) Thermal decomposition behavior, and (d) Contact angle measurement.

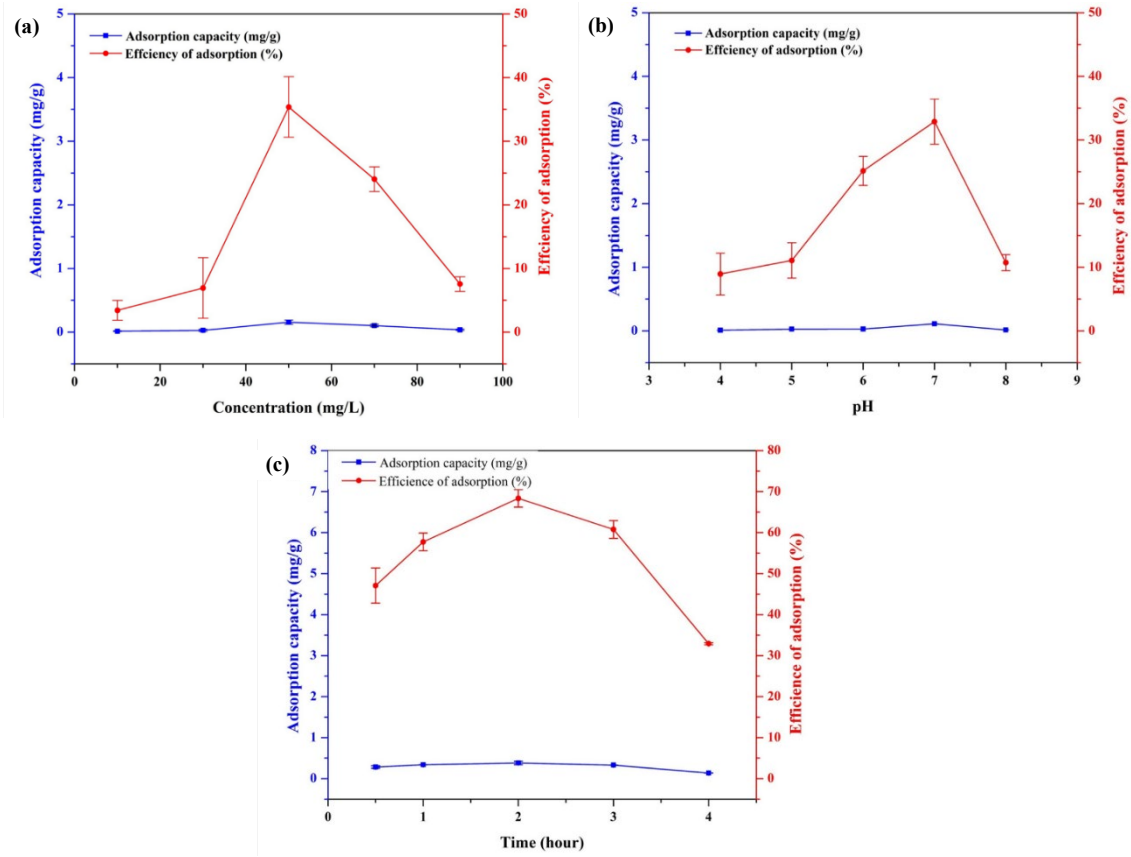

Figure 8. Cu^{2+} adsorption experiment onto PEI modified onto VBC-bacterial cellulose surface (a) Effect of concentration, (b) Effect of pH, and (c) Effect of time.

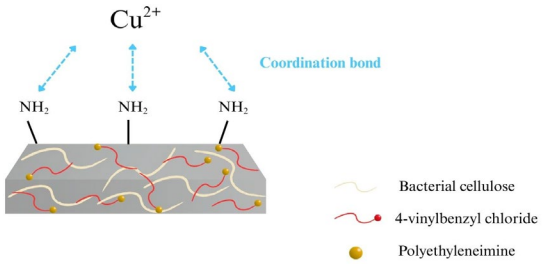

Figure 9. Cu^{2+} adsorption mechanism.

4. Conclusion

4-vinylbenzyl chloride (VBC) was successfully grafted onto hydroxyl group of bacterial cellulose (BC) by gamma irradiation. The bacterial cellulose, extracted and purified from Nata de coco, served as a base material for Cu^{2+} ion adsorption. Branched polyethyleneimine (PEI) was used to introduce amine (N-H) functional groups onto the modified bacterial cellulose. The optimal conditions were a radiation dose of 50 kGy and a VBC concentration of 2% (v/v). No changes in the crystalline structure were observed, and the material exhibited thermal stability up to 200°C. The microstructure revealed a randomly distributed bacterial cellulose network. The optimal Cu^{2+} adsorption performance was achieved at an initial concentration of 50 $mg{\cdot}L^{-1}$, pH 7, and adsorption time of 2 h. The results demonstrate that gamma irradiation-induced grafting, followed by amine (N–H) functionalization using PEI, can effectively transform bacterial cellulose into a sustainable and efficient adsorbent for the removal of Cu^{2+} ions from aqueous systems. This work primarily focused on the grafting process, with Cu^{2+} adsorption serving as a preliminary evaluation of the modified material. Future studies will investigate the adsorption capability toward other heavy metal ions to assess the broader applicability of the developed adsorbent.

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