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The Upcycle of Decorticated Waste of Boehmeria Nivea into Cationic Biopolymer Flocculant and Its Biodegradability

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Abstract

Boehmeria nivea, commonly known as ramie, has limited acceptance only for textile use, typically cultivated for fiber production obtained through decortication. Its decorticated waste still has remaining cellulose with untapped potential to be upcycled. This research employs cellulose extracted from discarded ramie stalks to create eco-friendly flocculants that are biodegradable. The upcycling method is the isolation of alpha-cellulose, alkalization, followed by cationization through a reaction with 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC). Experiments using raw surface water from the Cikapundung River, Bandung, West Java, Indonesia. The flocculant derived from the decorticated waste of Boehmeria nivea is utilized in two ways: first, in the coagulation-flocculation process to enhance the performance of the coagulant (Poly Aluminium Chloride), and second, in the direct flocculation process without the need for a coagulant. The application of cationic biopolymer, CBBn-dw, as a flocculant has been proven to be effective in clarifying raw surface water, with better results compared to the conventional coagulant PAC at its optimum dosage. It has been demonstrated that CBBn-dw provides turbidity removal efficiency up to 30% higher in a 5-minute settling time compared to PAC, with a dosage 50% lower than PAC. Meanwhile, the combination of PAC coagulant with CBBn-dw as a flocculant increases the percentage of removal of organic compounds (in COD) by up to 13% in a 15-minute settling time. The biopolymer and sludge produced from the coagulation-flocculation and direct flocculation processes using both biopolymers can biodegrade biologically, as tested according to the Standard Methods for Testing the Aerobic Biodegradation of Polymeric Materials, specifically the OECD 301 test method.

Keywords: *Boehmeria nivea, biodegradable flocculant, cationic biopolymer, cellulose, decorticated waste, flocculant, ramie, upcycling.*

Introduction

Boehmeria nivea is one of the biomass resources with the potential for development in Asia, particularly in Indonesia. Commonly known as ramie, it is a species typically cultivated for fiber production obtained through decortication, a manual or mechanical process in which the bast fibers attached are separated from the stalk and soaked in water, allowing the fibers to be scraped off. Ramie has limited acceptance only for textile use,

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hence it has been the focus of national research in recent years, representing an untapped biomass potential that has yet to be effectively processed and optimally utilized [1,2]. The shorter fibers and plant waste are used in papermaking. Moreover, since unused ramie stalks retain cellulose and can undergo upcycling, there exists a potential to utilize cellulose extracted from decorticated waste ramie stalks as a foundational component for eco-friendly biodegradable flocculants. Subsequently, this waste material from Boehmeria nivea is employed as a flocculant in water treatment processes.

Flocculants are water-soluble long-chain polymers used to separate solids or particles from suspended solutions [3]. Some inorganic flocculants in the form of synthetic polymers can cause secondary pollution and environmental problems, as they are not easily decomposed biologically, contain metals in the form of aluminum and iron hydroxides whose residues in drinking water can accumulate in the body's cells, and have a direct impact on human health when consumed [4–6]. Nowadays, the use of coagulants and flocculants from biopolymers has become important because it is expected to improve the quality of sludge generated in the sedimentation process, making it biodegradable [7,8]. Biopolymer-based coagulants and/or flocculants, due to their non-toxicity, biodegradability, and regenerative capability, can meet the increasing demand for environmentally friendly materials. These biopolymers have become the focus of research worldwide, such as starch-based flocculants, inulin-based flocculants, and cellulose-based flocculants [9].

The synthesis of flocculants using synthetic or commercial cellulose has been widely conducted [9–20]. In the meantime, various studies have been conducted on synthesizing flocculants utilizing natural cellulose. Liimatainen et al. (2012) and Suopajärvi (2013) utilized cellulose extracted from bleached birch (Betula verrucosa and Betula pendula), resulting in the production of anionic cellulose [21,22]. Zhu et al. (2016) modified cellulose from bamboo pulp of Phyllostachys heterocycle to create bamboo pulp cellulose-g-polyacrylamide, which was then utilized as a coagulant aid [23]. It can be concluded that the synthesis methods of biopolymers into polyelectrolytes, both cationic and anionic, have advantages. The use of cellulose as the base material for flocculants also shows promise. There is no biopolymer based on cellulose from Boehmeria nivea that has been applied as a flocculant, both in Indonesia and globally, despite its significant potential in the context of its application for clean water and waste treatment installations.

Experiments using raw surface water from the Cikapundung River, Bandung, West Java, Indonesia. The flocculant derived from the decorticated waste of Boehmeria nivea is utilized in two ways: first, in the coagulation-flocculation process to enhance the performance of the coagulant (Poly Aluminium Chloride), and second, in the direct flocculation process without the need for a separate coagulant. There has been an overview of various biodegradable polymers currently in use, along with their characterizations, and new developments in their synthesis and applications [24–27]. However, there is still limited research on biodegradable biopolymers based on cellulose. In this study, the degradability of the biopolymer has also been tested based on the Standard Methods for Testing the Aerobic Biodegradation of Polymeric Materials, specifically the OECD 301 test method [28,29]. The flocculant modified from the decorticated waste of Boehmeria nivea has biodegradability and the ability to regenerate as a natural polymer-based flocculant. It can meet the increasing demand for environmentally friendly materials.

Materials

The decorticated waste of Boehmeria nivea was sourced from Ramindo Berkah Persada Sejahtera, located in Wonosobo, Central Java, Indonesia. Sodium hydroxide compound and kaolinite powder were procured from Brataco Chemicals. The 96% analytical acetic acid solution and Urea GR for analysis were acquired from Merck. Additionally, the 60%

CHPTAC solution and 80% sodium chlorite were purchased from Sigma Aldrich. The water sample used is taken from raw surface water of Cikapundung River, Bandung, West Java Indonesia. The bacterial seeding for biodegradability test was taken from the activated sludge of the Bojong Soang Wastewater Treatment Plant in West Java, Indonesia.

Methods

The upcycle of decorticated waste of Boehmeria nivea into cationic biopolymer

First of all, the alpha-cellulose is isolated from the decorticated waste of Boehmeria nivea. The scheme for the experiment of isolating alpha-cellulose is adapted from previous studies [30–34] and involves a prehydrolysis, delignification, and bleaching process. The modification of alpha-cellulose (ACBn-dw) into a cationic biopolymer (CBBn-dw) entails reacting ramie ACBn-dw with 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTAC) [35].

The decorticated waste of ramie plants (Boehmeria nivea) was finely chopped and ground to create fine fibers. These fibers were then filtered using a 300 μm mesh sieve to acquire a uniform fiber composition. Subsequently, the homogeneous fibers underwent pre-hydrolysis in a water bath at 105°C for 1 hour, employing a 1:20 (w/w) ratio of cellulose to 1 N 96% acetic acid. The fibers were further delignified in a water bath at 105°C for 1 hour, using 17.5% sodium hydroxide with distilled water as a solvent. The bleaching process is carried out by immersing α-cellulose in a 5% sodium chlorite ($NaClO_2$) solution using a Schott bottle for 15-20 minutes with a sample-to-solvent ratio of 1:8 (w/w). $NaClO_2$ is dissolved using distilled water from technical grade 80%. The addition of a few drops of 1N acetic acid solution is done to achieve an acidic pH range of 3-5. The resulting cellulose fiber residue was filtered through paper, rinsed with distilled water until reaching a neutral pH, and dried in an oven at 60°C for 24 hours, yielding ACBn-dw. ACBn-dw was then alkalinized at 4°C using a 12.5% (w/w) sodium hydroxide and 12% (w/w) urea solution. The mixture was stirred at room temperature with a magnetic stirrer at maximum speed for 3 minutes to create a cellulose solution. Following this, the cellulose solution was cationized with 20 mL 60% (w/w) CHPTAC while stirring at maximum speed for 3 hours with Lab Companion HP-3000 within the temperature range of 60-70°C. Finally, the cationic cellulose solution was dried in an oven at 60°C for 24 hours, resulting in the production of a CBBn-dw serving as a flocculant.

Flocculation test

Jar testing is conducted using the Velp Scientifica JLT6 Flocculation Tester. In the rapid mixing process (200 rpm, 3 minutes), a conventional coagulant, Poly Aluminium Chloride (PAC), is used. Meanwhile, in the slow mixing process (40 rpm, 7 minutes), the CBBn-dw synthesized in the previous stage will be added as a flocculant or coagulant-aid. Additionally, a comparison will be made with the conventional coagulant, namely PAC. The test parameter for this experiment was turbidity. The experiment was conducted at room temperature without any pH adjustment. Subsequently, the formed flocs were allowed to settle for 90 minutes, and supernatant samples were taken at 5, 15, 30, 45, 60, and 90 minutes.

A preliminary coagulation-flocculation experiment was conducted using a 5 g/L concentration solution of technical-grade kaolin. This process establishes the optimal dosage of coagulant and the required settling time. An artificial raw water solution of 5 g/L kaolin suspension was prepared in each of the five chemical beakers (5 pieces) with varying PAC dosages: 2 ppm, 5 ppm, 10 ppm, 15 ppm, and 20 ppm.

The next experiment of coagulation-flocculation and direct flocculation was conducted using raw surface water. The water sample was taken from the Cikapundung River. In the

coagulation-flocculation experiment, PAC was used in three different doses: 10, 20, and 30 mg/L. The optimum dose of PAC was then used for the comparison with CBBn-dw (10, 25, and 50 mg/L). The experiment was conducted without adjusting pH and temperature. Supernatants were taken at a specified minutes of sampling time. Parameters tested are turbidity (NTU) and organics in COD (mg/L).

Statistical analysis

The data analysis was conducted using statistical tests, including the Homogeneity of Variance test, One-Way ANOVA (Analysis of Variance), and Duncan's Multiple Range Test (DMRT) for post-analysis, using IBM SPSS Statistics version 26.0.0. If the obtained data is homogeneous (with a significant p-value above 0.05), the One-Way ANOVA test can be performed. The hypotheses for the ANOVA test are as follows:

- If the p-value > 0.05, there is no significant difference between data groups.
- If the p-value < 0.05, there is a significant difference between data groups.

DMRT is used to determine the significant differences between data groups, guiding the selecting of the best experimental treatment, such as coagulant and flocculant dosages, as well as settling time. Additionally, a two-sample T-test is conducted to assess the significance of differences between two variations: samples of waste ramie plant α-cellulose with and without bleaching. If the p-value < 0.05, it indicates that the bleaching process significantly influences turbidity removal in the water sample. The data used includes the removal efficiency after settling at specific time intervals.

Characterization of cationic biopolymer of decorticated waste of Boehmeria nivea (CBBn-dw)

We utilized appropriate analytical techniques to characterize the CBBn-dw. The sample preparations were completed at room temperature (25°C). The Nano Particle Analyzer Horiba SZ-100 Zeta Potential Analyzer and Particle Size Analyzer were used to assess the zeta potential, charge density, and particle size respectively. Nuclear magnetic resonance (NMR) was used to determine the degree of substitution (DS) and get structural information. The ^{1}H and ^{13}C NMR spectra were acquired on an Agilent DD2 spectrometer at 500 MHz for ^{1}H and 125 MHz for ^{13}C, with residual and deuterated solvent peaks serving as reference standards. NMR samples were produced by dissolving the materials in D2O. To investigate the functional groups present in the material, Fourier transform infrared spectroscopy (FTIR) was performed using a Bruker Alpha II Platinum ATR. The Scanning Electron Microscope (SEM) is used to visualize surface details of a sample in high resolution. Energy Dispersive X-Ray Spectroscopy (EDS) analysis also be performed with SEM using Hitachi SU3500. For SEM-EDS observation, the sample cannot contain liquids or be in a liquid phase. The samples used for FTIR and SEM-EDS analysis underwent 24 hours of drying at 60°C in an oven.

Biodegradability test

Biodegradability testing of the biomaterial is required to determine its potential degradability, as well as the degradability of the treatment sludge if discharged into water bodies. As a result, the test conditions are liquid, specifically when the biomaterial is utilized as a flocculant and settles as sludge. The biomaterial's biodegradability is tested using the Standard Methods for Testing the Aerobic Biodegradation of Polymeric Materials [28]. The OECD 301 Ready Biodegradability test method is employed for the liquid condition [29].

In essence, aerobic fermentation is used in the biodegradability test of the biomaterial, which is in the form of a biopolymer in liquid circumstances. The batch reactor is employed in a static mode of operation. The inoculum, which acts as a source of microorganisms, is made by seeding 200 mL of sludge with 1 L of water and 1 g of glucose as a carbon source over three days. This mixture is aerated for three days before

being fed at 5% of the water sample to the experimental batch reactor. The CBBn-dw under test is the medium's sole source of organic carbon. The experiment lasted 6 days, with microbes introduced on the second day. Organic chemicals in COD and BOD, as well as Mixed Liquor Suspended Solids (MLSS) to evaluate biomass growth in the liquid media, are among the metrics measured. The test usually lasts 28 days. However, testing can be stopped before 28 days if the biodegradation curve for at least three observed parameters achieves a generally stable value. The response order in the coagulation-flocculation process, which normally occurs within hours, is also used to calculate measurements for 5 days.

Results and Discussion

The upcycle of decorticated waste of Boehmeria nivea into CBBn-dw

The objective of this study is to upcycle the decorticated waste of Boehmeria nivea into a cationic biopolymer that can act as a flocculant in the treatment of raw surface water, capable of neutralizing the negative charge of colloid particles. The Zeta Potential value on the surface of α-cellulose helps determine the efficacy of flocculant destabilization during the flocculation process [3,22,36]. The flocculation process has two major mechanisms: bridging and charge neutralisation. Both rely on the size of the polymer and the surface properties of particles in the solution [3,36,37].

The HORIBA SZ-100 was used to detect zeta potential at room temperature (25°C) with water as the dispersing medium. The tests were done for two samples, the isolated ACBn-dw and its modification into cationic biopolymer, CBBn-dw. ACBn-dw from Boehmeria nivea decorticated waste has a negative zeta potential, according to the analysis. Most colloidal systems are also negatively charged. Using an effective flocculant can bring the zeta potential near to zero, which reduces suspension stability [3,21], further modification of ACBn-dw into CBBn-dw is required to increase the zeta potential to a positive value [36]. After alkalization and cationization process, the measurement of zeta potential analysis is also done in triplicate, with a mean value of 22.0 mV. This proves that the modification of the CBBn-dw has been successfully carried out.

The CBBn-dw ^{1}H NMR spectrum in a solution of deuterium oxide (4.79 ppm) are displayed in Figure 3. The protons on the cellulose backbone are responsible for the chemical shift at 3.0 ppm (a). The methyl protons linked to the alkyl-ammonium moieties (b) from CHPTAC are detected as the intense peak seen at 3.2 ppm. This indicates that it has been integrated into the backbone, forming cationic biopolymer [38–40].

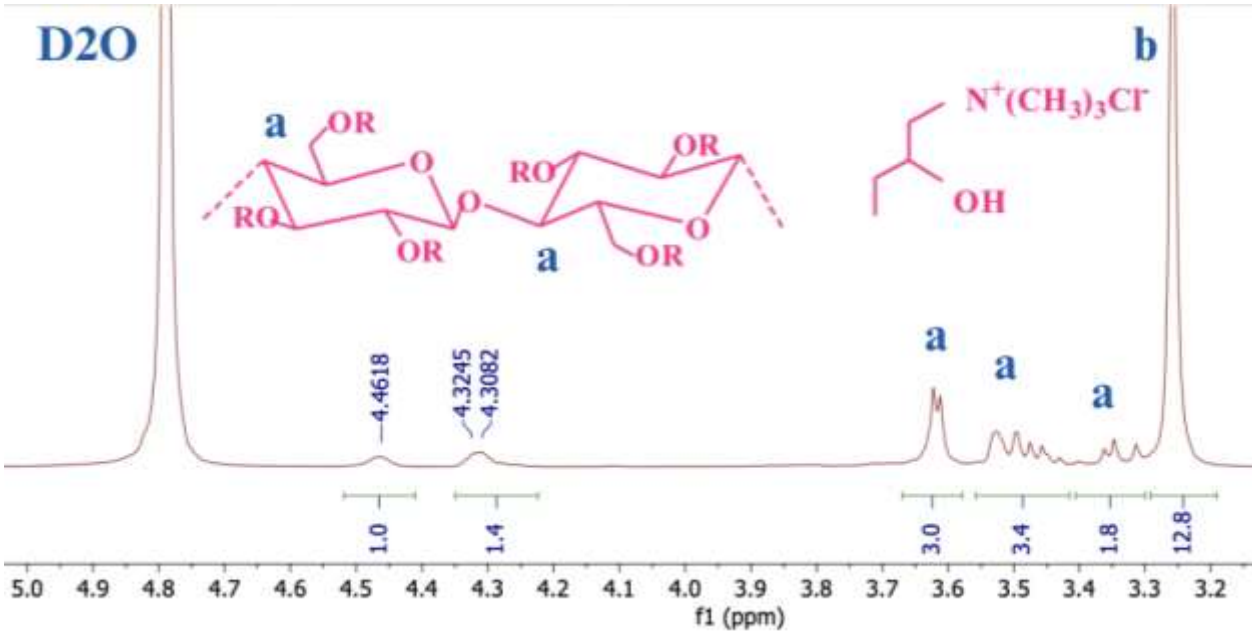

Fig. 1 The ^{1}H NMR spectrum of CBBn-dw.

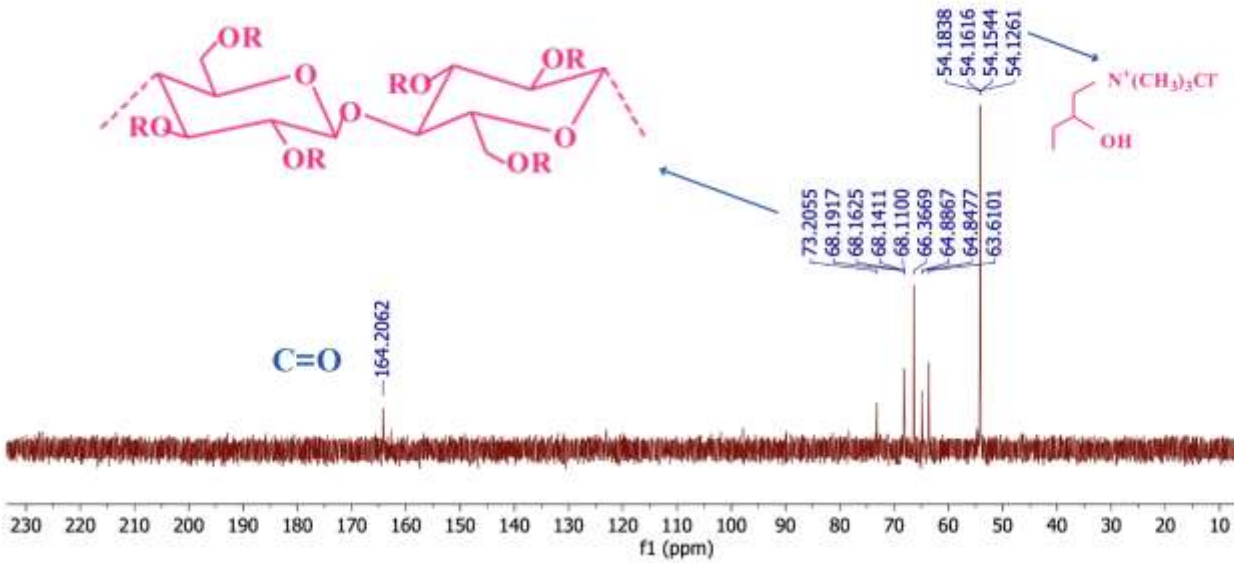

Fig. 2 The ^{13}C NMR spectrum of CBBn-dw.

The ^{13}C NMR spectrum dissolving in deuterium oxide are displayed in Figure 4. N-bound methyl (b) can be linked to the vibrational peak at 54 ppm, while carbon atoms can be linked to the peak range of 63-73 ppm. At 164 ppm, carbonyls (C=O) are ascribed as the functional group. Figures 3 and 4 demonstrate that the ammonium salt group was effectively integrated into cellulose, with R denoting $N^{+}(CH_3)\ Cl^{-}$.

The application of CBBn-dw as flocculant

The objective of this invention can be achieved by providing a process to produce biomaterial as a flocculant in the treatment of raw surface water, consisting of the following stages: a preliminary experiment using an artificial raw water sample and a main experiment using raw surface water. One advantage of this biomaterial over other/conventional flocculants is its use in direct flocculation processes without the need for a coagulant. The biomaterial in this invention is a polyelectrolyte and can act as a dual agent in direct flocculation processes.

Preliminary experiments

Firstly, a preliminary coagulation-flocculation experiment was conducted with an artificial water sample. In this experiment, the application of the flocculant, namely CBBn-dw, was carried out for turbidity removal with pH adjustment. The water sample used was a kaolin suspension (5 g/L) with an initial turbidity of 7349 NTU. The pH of the water sample was adjusted using NaOH (0.1 M) and HCl (0.1 M), and no temperature adjustment was made during the experiment. The experiment was conducted at room temperature (25 °C), with the sample temperature ranging from 22.3 to 23.0 °C. The direct flocculation process was performed by adding CBBn-dw in the rapid mix process at a stirring speed of 500 rpm for 3 minutes, followed by the slow mix process at a stirring speed of 150 rpm for 7 minutes. Supernatant collection from the sample was done at settling times of 5, 15, and 30 minutes.

Two controls were used in this experiment: A) untreated water sample and B) treated water sample without pH adjustment. Both controls had an initial pH of 8.18. After the settling process, control sample A had a pH of 8.1 with turbidity ranging from 4188 to 4944 NTU. Meanwhile, control sample B showed an increase in pH to 9.0 with turbidity ranging from 15.03 to 18.20 NTU. The post hoc analysis results using Duncan's Multiple Range Test can be seen in Appendix 1, indicating the best removal in column 10, with a settling time of 15 minutes and initial pH adjustments of 9 and 10.5. Control sample B is in column 2, showing a significant statistical difference. However, the turbidity removal percentage of 99.6% indicates excellent efficiency, making it more prudent to conduct turbidity treatment using the direct flocculation process without pH adjustment to minimize the use of chemicals.

The subsequent application of CBBn-dw in the coagulation-flocculation process is carried out for color removal. Artificial raw water is used as the water sample, using Reactive Orange 16 (RO16) dye at a dosage of 10 ppm, resembling peat water, which is a natural water source. Additionally, RO16 has a negative zeta potential, ranging around -20 mV. The concentration of RO16 is measured using a UV-vis spectrophotometer with a wavelength of 494 nm [41,42].

Table 1 Homogeneity of variance for RO16

		Levene Statistic	df1	df2	Sig.
Removal_RO16	Based on Mean	7.61	4	10	.00
	Based on Median	2.05	4	10	.16
	Based on Median and with adjusted df	2.05	4	2.14	.34
	Based on trimmed mean	7.02	4	10	.01

Table 2 Results of One-way ANOVA for RO16

Removal_RO16

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2650.94	4	662.76	40.47	.00
Within Groups	163.75	10	16.38		
Total	2814.69	14			

Table 3 Duncan's Multiple Range Test for RO16 removal (%)

Duncan				
Cationic Cellulose	N	Subset for alpha = 0.05		
		1	2	3
40 mg/L	3	27.47		
80 mg/L	3		56.41	
120 mg/L	3		57.02	
160 mg/L	3		61.05	61.05
200 mg/L	3			64.84
Sig.		1.00	.21	.28

Means for groups in homogeneous subsets are displayed.

Jar testing was conducted using CBBn-dw with dosage variations of 40, 80, 120, 160, and 200 mg/L. This experiment was adapted from previous studies [41–44]. Rapid mixing at 300 rpm was performed for 5 minutes, followed by slow mixing at 50 rpm for 10 minutes. For settling time, the water samples were left undisturbed for 30 minutes before measuring using a spectrophotometer. Each treatment was repeated three times, and the reported values are the averages of these three measurements, with pH and conductivity measurements taken at the end [43]. The results of RO16 color removal using CBBn-dw can be seen in Table 3. In another study, the removal efficiency of methylene blue and RO16 reached 90% using CMC-g-PAM [45].

Statistical analysis was performed similarly to before, including the homogeneity test, One-way ANOVA, followed by Duncan's Multiple Range Test as post hoc analysis. In Table 1, the homogeneity test results indicate that two variables, concentration, and absorbance, have p-values > 0.05, meaning that the data obtained are homogeneous and can be tested using One-way ANOVA. Meanwhile, the One-way ANOVA results (Table 2) have a Sig. value < 0.05, indicating statistically significant differences in the data, and Duncan's Multiple Range Test can be conducted to determine the range of significance between data groups (Table 3).

The post hoc analysis results using Duncan's Multiple Range Test can be seen in Table 3. The color removal mechanism from the solution can be investigated through the physicochemical properties of supernatant, floc, and sludge. Changes in conductivity and pH indicate interactions between the dye and CBBn-dw. By examining the chemical structure, precipitation, and microstructure of the sludge, insights into sludge formation during the color removal process can be obtained [44]. It can be concluded that the higher the dosage of CBBn-dw given, the higher the removal of RO16 color, with the best removal efficiency of 64.84% achieved by CBBn-dw at a dosage of 200 mg/L (Table 3).

Application in flocculation of raw surface water

In this phase, coagulation-flocculation and direct flocculation experiments were conducted using surface water. The water sample was taken from the Cikapundung River, with the characteristics of surface water around the Balai Besar Wilayah Sungai Citarum, Babakan Siliwangi, as shown in Table 4. Subsequently, tests for the biodegradability of cationic along with an analysis of the sedimented sludge after the treatment process using biopolymers. Finally, a biopolymer recovery experiment was conducted to assess the regenerative capabilities of the biopolymer.

Table 4 Characteristics of raw surface water

pH	Temperature (°C)	Turbidity (NTU)	Color (Pt/Co)	TSS (mg/L)	Organics in mg/L COD
6.44	23.8	93.33	25	374.12	479.368

In this experiment, the jar test was conducted in two stages: optimization of coagulant dosage (PAC) and a comparison between PAC and CBBn-dw as a flocculant in the coagulation-flocculation and direct flocculation processes. At the sampling location, the measured pH of surface water was 6.44, with a temperature of 23.8 °C. The turbidity value of the sample was 93.33 NTU, with a Total Suspended Solids (TSS) value of 374.12 mg/L, visual color of 25 PtCo, and Chemical Oxygen Demand (COD) of 479.368 mgO_2/L. In the coagulation-flocculation experiment, PAC was used at three different doses: 10, 20, and 30 mg/L. The experiment was conducted without adjusting pH and temperature, although there was an increase in the sample's pH to 7.65. The experiment took place at room temperature (25 °C), with the sample temperature ranging from 22.7 °C at the beginning of the experiment to 24.5 °C at the end of the experiment.

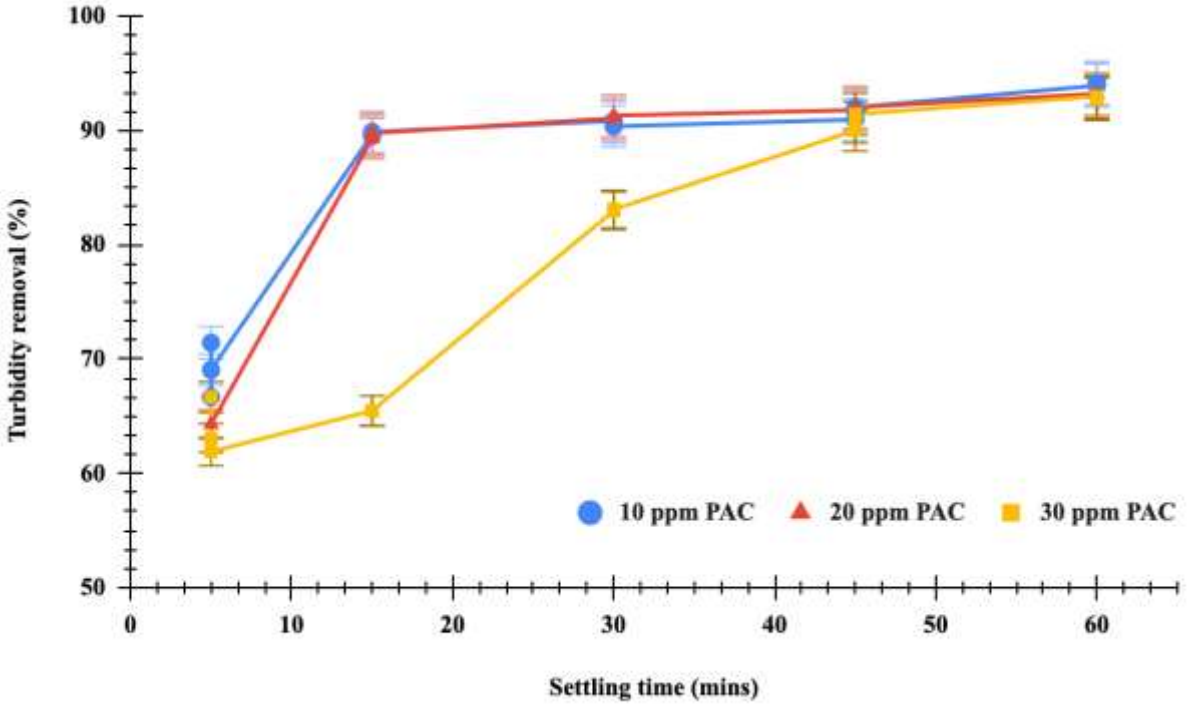

Fig. 3 Optimization of PAC dosage for turbidity removal

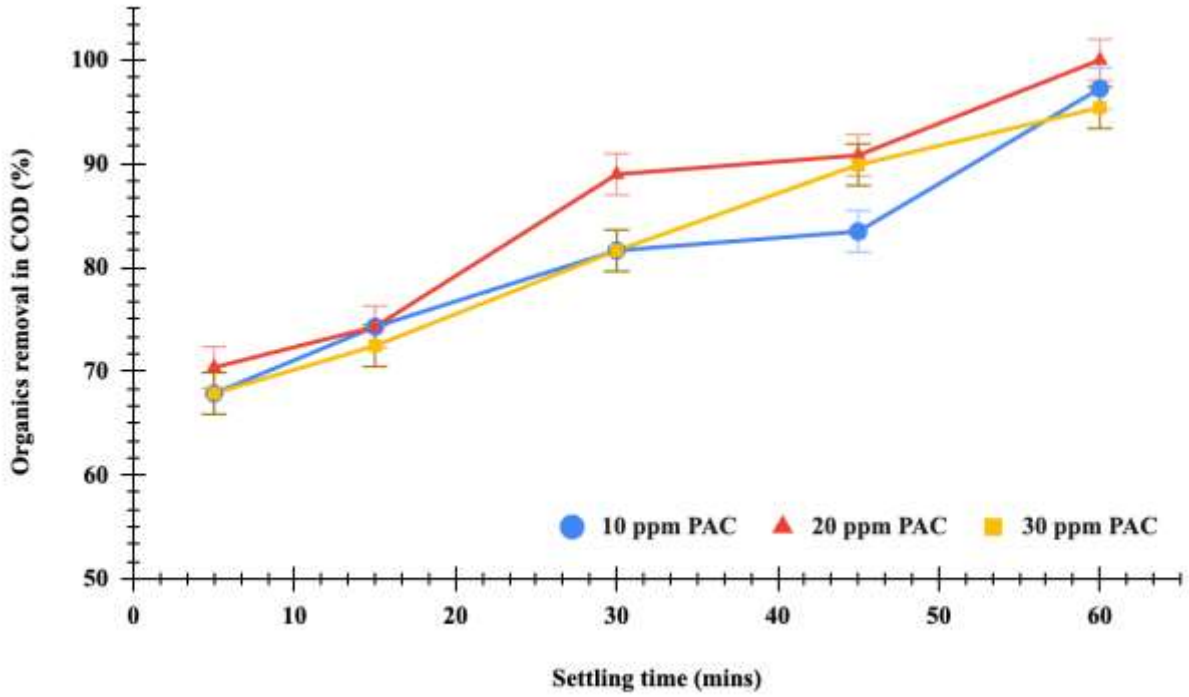

Fig. 4 Optimization of PAC dosage for organics removal (in COD)

Figures 3 and 4 depict the results of turbidity (NTU) and organics (COD) removal. In turbidity removal, doses of 10 and 20 mg/L of PAC yielded relatively similar results, while for organics removal, the highest removal was achieved with a PAC dose of 20 mg/L. Based on the experiments, a PAC dose of 20 mg/L with a settling time of 30 minutes after the mixing process provided the best results, with a turbidity of 7.4 NTU at the 30 minutes. Therefore, a concentration of 20 mg/L PAC was used in the subsequent experiments using CBBn-dw as a flocculant.

In the next experiment, a comparison was made between the optimum dose of PAC and a flocculant using CBBn-dw derived from the decorticated waste of ramie (Table 5). The water sample used was the same as in the previous experiment. The rapid mix and slow mix speeds were set at 200 rpm and 40 rpm for 3 minutes and 7 minutes, respectively. The treated water was then left to settle for half an hour. At 5, 15, and 30 minutes, the supernatant was collected. The parameters tested in this experiment were turbidity and organic compounds in COD.

Table 5 Experiment matrix

Sample	Coagulant PAC (mg/L)	Flocculant CBBn-dw (mg/L)
1.	20	-
2.	20	10
3.	-	10
4.	-	25
5.	-	50
6.	-	-

In samples 1 and 2, PAC was added during the rapid mix, followed by the addition of CBBn-dw flocculant during the slow mix. Meanwhile, the direct flocculation process was carried out by adding CBBn-dw flocculant during the rapid mix (samples 3-5). Sample 6 was control without the addition of coagulant and flocculant. Figure 5 and 6 show the results of turbidity and organics removal. It is evident that the biopolymer provides the best removal results for turbidity, and the combination of PAC coagulant with CBBn-dw as a flocculant provides the best removal of organics (in COD).

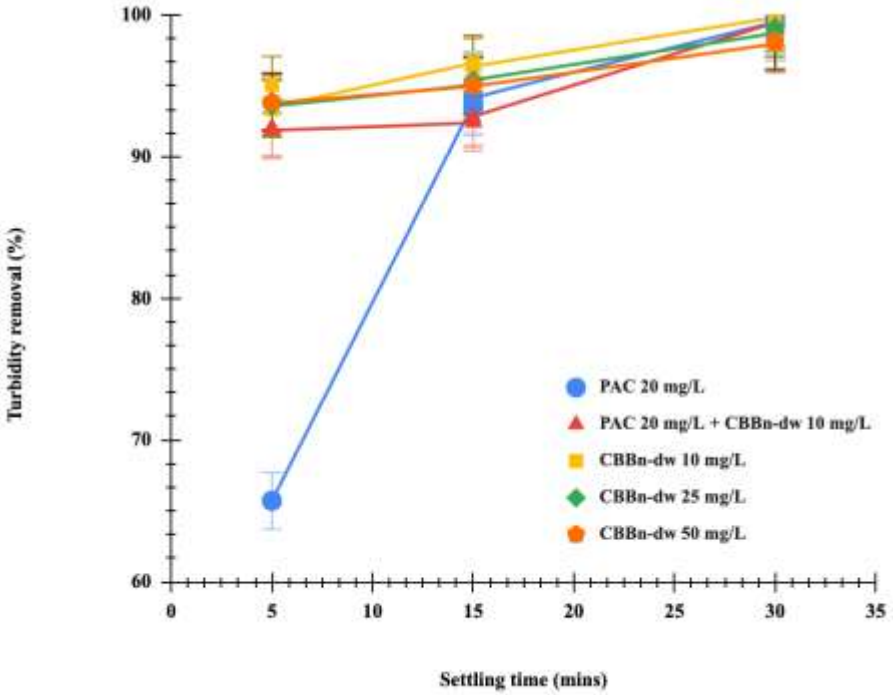

Fig. 5 Comparison of PAC and CBBn-dw (CB) for turbidity removal

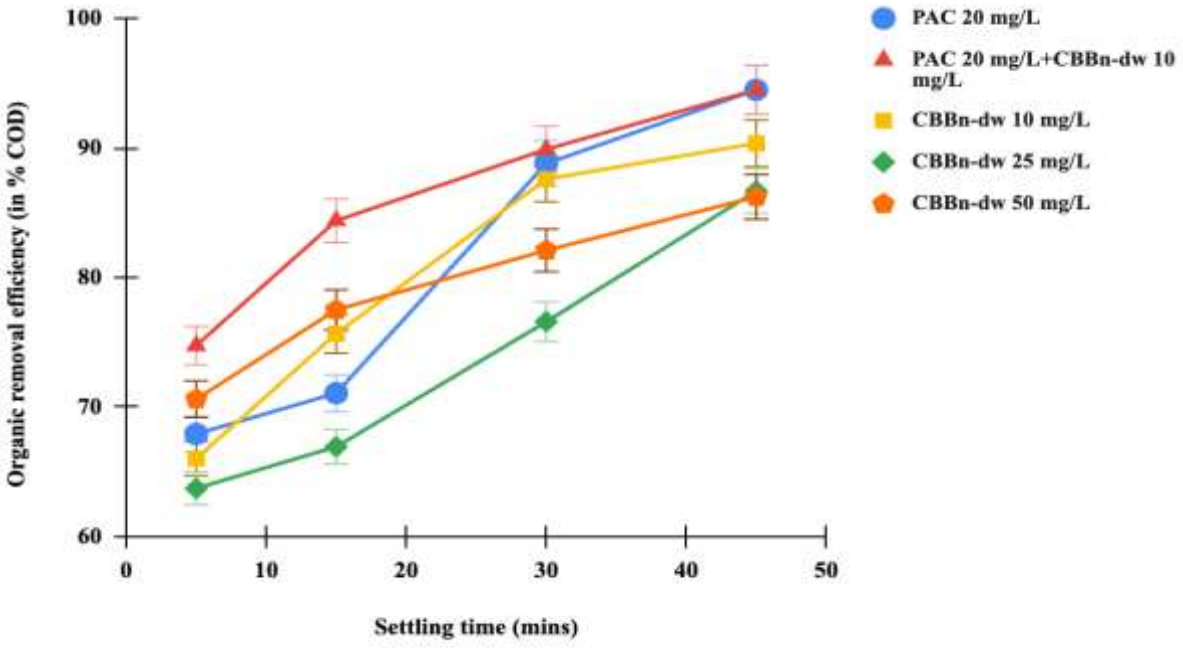

Fig. 6 Comparison of PAC and CBBn-dw for removal of organics in COD

During the experiment, noticeable differences were observed between water samples using the optimum dose of PAC and CBBn-dw flocculant. The flocs formed in the sample using CBBN-DW as a flocculant appeared larger, and the treated water was relatively clearer. This can be seen at the five-minute settling mark (Figure 5). The lowest turbidity in the water sample was achieved by the combination of PAC and CBBN-DW, reaching 0.4 NTU after 30 minutes of settling time.

Fig. 7 Figure VI.5 Jar Test Comparison of PAC and CBBn-dw (Left-Right: 1-6)

To determine whether the addition of CBBN-DW has the potential to increase organic compounds in water samples, especially in the supernatant or the produced water, measurements of organic compounds in COD were conducted. The same river water sample was used as a control, with the initial concentration of organic compounds in the COD value being 160 mg O_2/L. The values of organic compound content differed from the initial sample due to fluctuations in concentration on different measurement days. Shortly after the addition of biopolymer during rapid mixing, the organic compound value slightly decreased to 149.3 mg O_2/L (in COD). The amount of organic compounds in COD decreased to 42.7 mg O_2/L after processing through the direct flocculation process and settling for 30 minutes. This indicates that the use of CBBN-DW at a relatively low dose does not increase the organic content in the treated water.

The modified decorticated waste of ramie cellulose can be used to create biopolymers, which could be employed as flocculants in the treatment of drinking water. These biopolymers have the advantage of having two functions: they neutralize the negative charge of colloidal particles and stabilize unstable particle aggregates by using a bridging mechanism to create flocs, which can operate as both coagulants and flocculants. This offers the possibility of fully replacing inorganic coagulants, such as Poly Aluminium Chloride (PAC). The role of a coagulant is to destabilize colloids and remove particles in the colloid system. Biopolymers can achieve this as they can be manipulated to carry both positive and negative charges. The use of biopolymers as coagulants and flocculants provides an alternative option with fewer chemical requirements. Not only is the dosage of biopolymer needed less than that of conventional PAC coagulants, but biopolymers also do not require pH conditioning in their processing. The settling time required by biopolymers is relatively shorter. Furthermore, biopolymer-based treatment has proven to produce less sludge, easing sludge handling.

The comparison of coagulant and flocculant pathways can be observed in Figure 8. The long-chain biopolymer used in this study carries both positive and negative charges and is referred to as a polyelectrolyte. In the first pathway, the polymer acts as a flocculant in a colloidal system destabilized earlier by inorganic coagulants. In the second pathway, the

polymer can effectively serve as a primary coagulant [46,47], reducing processing and settling times, as well as the amount of chemicals used.

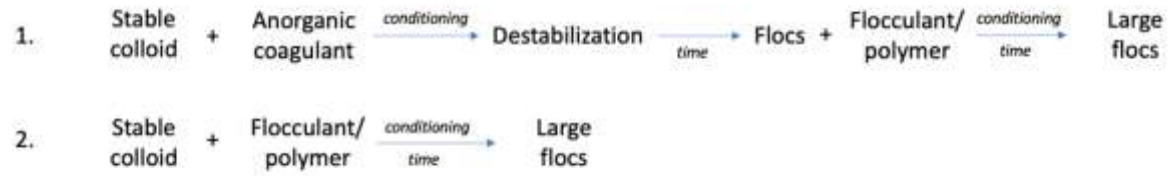

Fig. 8 Pathways of coagulant and flocculant [46,47]

According to the analysis of flocculation performance and flocculation kinetics, the assumed mechanism of CBBn-dw flocculation for colloidal system are a combination of charge neutralization and bridging mechanism. The stable colloid is destabilized by the addition of CBBn-dw. After the charge neutralization process, numerous small aggregates are produced. These aggregates collide and further agglomerate with the electrostatic attraction force of the CBBn-dw through the bridging mechanism. These larger aggregates then form heavier and denser flocs, which ultimately settle.

Regeneration of CBBn-dw

After coagulation-flocculation and direct flocculation experiments, a biopolymer regeneration trial from processed sludge was conducted. The settled sludge was rinsed with methanol and dried in an oven at 60°C for 24 hours. To determine the presence of biopolymer, chemical characterization was performed using FTIR. After drying, the flocculation ability of the regenerated biopolymer was determined based on coagulation-flocculation and direct flocculation experiments. Important functional groups present in the CBBn-dw include peaks at 3300, 2900, 1600, 1400, and 1050, indicating hydroxyl groups (-OH), C–H (stretching), amine groups (N–H bending), C–N (stretching), and ether (R–O–R) [10,30,38,48]. These functional groups exhibit strong peaks compared to the previous CBBn-dw as described below (Figure 9). Further research on regenerated biopolymer ability in coagulation-flocculation and direct flocculation experiments has the potential to be done.

The FTIR spectra of cationic cellulose and ACBn-dw exhibit different functional group absorptions. Figure 9 compares the FTIR spectra of CBBn-dw, regenerated CBBn-dw, and ACBn-dw. The highest intensity band at 3300 cm^{-1} is connected with O-H stretching vibrations. Cellulose's hydroxyl (-OH) groups on the chain give it a high water-purification function, allowing efficient removal of metal ions and organic substances from water. The presence of these hydroxyl groups eliminates the need for a hydroxylation process in cellulose-based flocculant synthesis, minimizing sludge volume in the sedimentation process. The bands that appear at 2800 and 1400 cm^{-1} correspond to C–H strain and $–CH_2$ buckling, respectively. The H–O–H stretching vibrations of water absorbed in carbohydrates and the C–H deformation vibrations of cellulose are represented by the peaks at 1600 and 900 cm^{-1}, respectively [30,49]. The ester bond of the carboxylic groups is represented by the peak at 1700 cm^{-1}, which is absent from the peak intensity at 1500 cm^{-1}, which was linked to C=C stretching vibrations. The range of spectra that corresponds to the functional groups of lipid, protein, and nucleic acid concentration is 3400-3000 cm^{-1} and 1800-1050 cm^{-1} indicating the removal of hemicellulose and lignin in the chemical process. This preservation ensures the retention of the cellulose's original molecular structure [30,49–51].

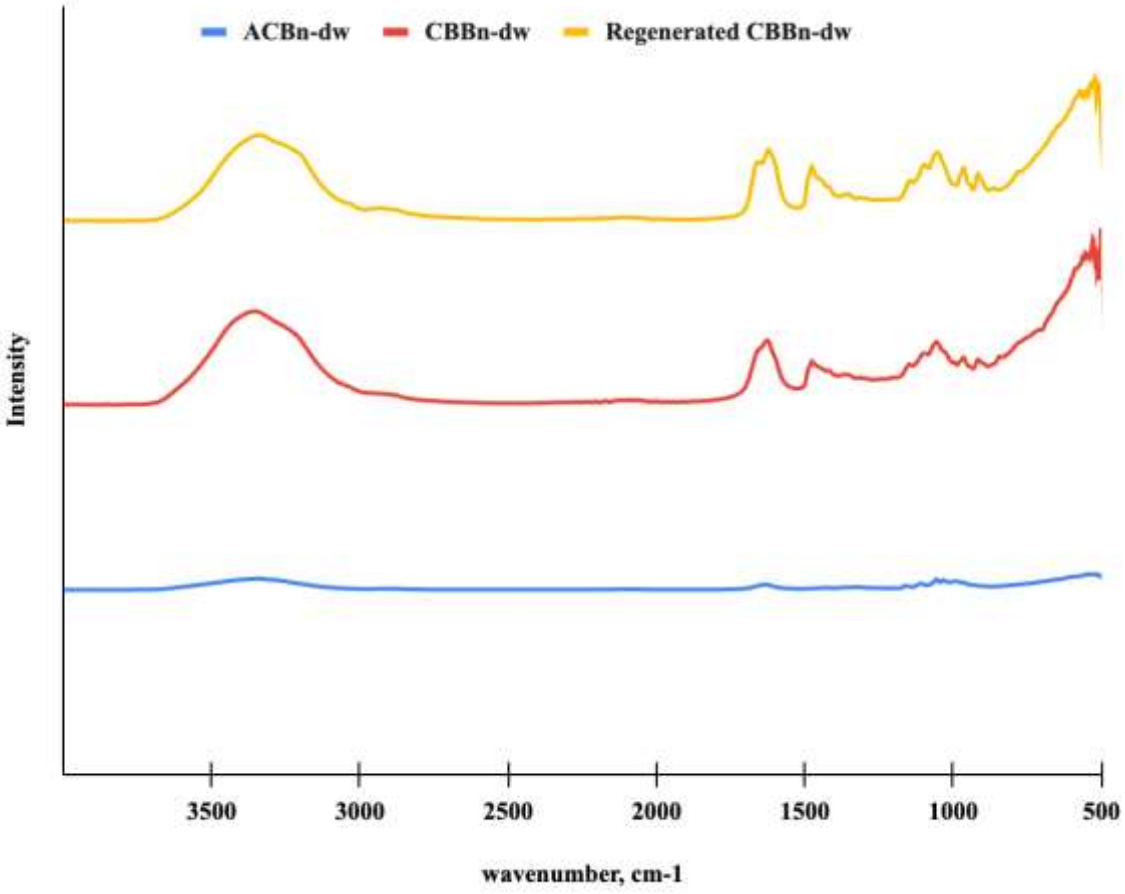

Fig. 9FTIR spectra of ACBn-dw , CBBn-dw, and regenerated CBBn-dw from the decorticated waste of Boehmeria nivea

Biodegradability of CBBn-dw

The degradability of the biopolymer has also been tested based on the OECD 301 test method. The parameters measured are organic compounds in COD and BOD, as well as Mixed Liquor Suspended Solids (MLSS) to determine the biomass growth in the liquid medium. The increase in biomass in the MLSS value and the decrease in the number of organic compounds in COD and BOD in the water samples over 5 days prove that the biopolymer is biodegradable.

Figure 10 shows the results of testing the biodegradability of CBBn-dws in liquid media. The addition of CBBn-dws does not potentially increase organic compounds in treated water. Meanwhile, an increase in biomass is observed from the rise in MLSS values and a decrease in the number of organic compounds in COD and BOD in water samples, with biodegradability reaching 81.25%.

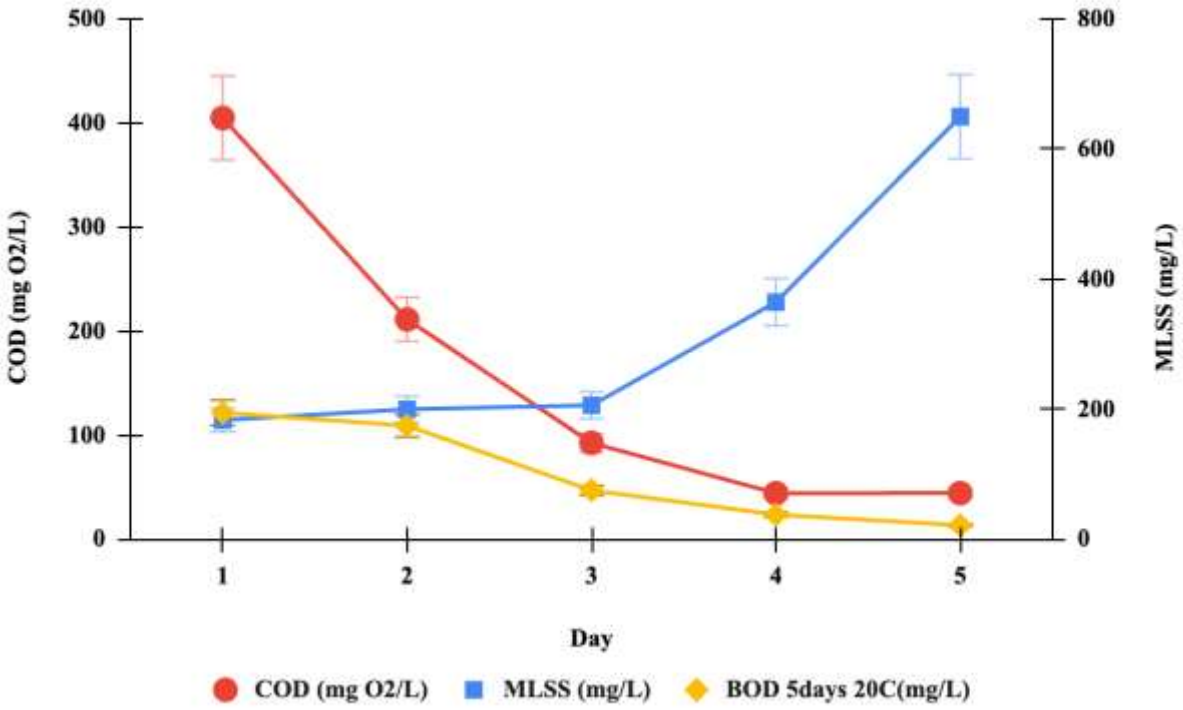

Fig. 10 The biodegradability test of CBBn-dw in liquid condition

The carbon is converted into biomass, carbon dioxide, polymer or oligomer leftovers, and inorganic dissolved carbon by microbes and oxygen. Carbon dioxide generation or oxygen consumption are typically used to measure biodegradation. More specifically, given the amount of carbon in the biopolymer, the criterion is the fraction of oxygen or carbon dioxide eaten or produced by microorganisms divided by the theoretical maximum amount of either gas. Microorganisms use the carbon from the biopolymer in metabolic processes to create biomass and new oligomers in addition to CO_2. Therefore, the amount of polymer converted cannot be determined from a single measurement of CO_2 or O_2 consumed. Therefore, MLSS measurements are necessary to determine biomass production in the media [28,29].

The BOD/COD ratio of the settled sludge ranges from 0.30-0.53. which can identify the biodegradability and non-toxicity of the biopolymer-settled sludge. According to Samudro and Mangkoedihardjo (2010), the biodegradable zone in sludge can be identified by the ratio of BOD/COD, which is between 0.1 and 1. In the results of biodegradability testing of biopolymers, the BOD/COD ratio ranges from 0.30 to 0.53 (Table 6). It can be concluded that the tested CBBn-dws can biodegrade. Based on this ratio, it can also be inferred that CBBn-dws have non-toxic properties, as their BOD/COD ratio is less than 0.1, which is the toxic zone in sludge [52–54].

Table 6 BOD/COD ratio of biodegradability test

Day	COD (mg O_2/L)	MLSS (mg/L)	BOD 5days 20°C (mg/L)	BOD/COD ratio
1	404.930	183	121.5	0.30
2	211.270	200	109.0	0.52
3	92.43	206	46.8	0.51
4	44.10	365	23.5	0.53

5	44.14	650	13.2	0.30

Conclusions

This study upcycles of decorticated waste of Boehmeria nivea into cationic biopolymer, CBBn-dw. The flocculant derived from the decorticated waste of Boehmeria nivea is utilized in two ways: first, in the coagulation-flocculation process to enhance the performance of the coagulant (Poly Aluminium Chloride), and second, in the direct flocculation process without the need for a coagulant. Experiments using raw surface water from the Cikapundung River, Bandung, West Java, Indonesia, showed that the CBBn-dw provides a turbidity removal efficiency up to 30% higher in 5 minutes of sedimentation compared to PAC, with a dosage 50% lower than PAC.

CBBn-dw and sludge resulting from coagulation-flocculation processes and direct flocculation are biodegradable, regenerative, and reusable. CBBn-dw from ramie has prospects for use as an alternative to flocculants which can also function as coagulants because of the main characteristics of biomaterials with positive charge and long polymer chains. The use of decorticated waste of Boehmeria nivea biopolymer as a flocculant that can be engineered as a cationic flocculant has been shown to remove suspended solids, turbidity, and organic compounds better than conventional metal-based coagulants (PAC) as a comparative coagulant. In conclusion, cellulose's hydroxyl (-OH) groups on the chain give it a high water-purification function, allowing efficient removal of metal ions and organic substances from water. The presence of these hydroxyl groups eliminates the need for a hydroxylation process in cellulose-based flocculant synthesis, minimizing sludge volume in the sedimentation process. This study also has successfully addressed the characteristics of biopolymer degradability and proven the hypothesis that the CBBn-dw can biologically degrade in a liquid medium.

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