The cellulose of *Boehmeria nivea* as natural flocculants: synthesis, modification, and flocculation analysis

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Abstract. Due to their non-toxicity and biodegradability, natural polymeric flocculants have gained popularity in water and wastewater treatment in recent years. Because of its broad availability, renewability, sustainability, and surface modification potential, cellulose, the most common polymer on the planet, is regarded as one of the foundation polymers for flocculant production and modification. The following article consists of a review of the latest developments regarding biopolymers, in particular, cellulose as a natural flocculant. One of the plants that can be developed in Indonesia is *Boehmeria nivea*, or what is known as Ramie, which contains cellulose that is still not utilized optimally. There is a method of isolation of alpha-cellulose derived from *Boehmeria nivea* and its application as a flocculant in synthetic wastewater presented in this paper. The alpha-cellulose of *Boehmeria nivea* was used as a flocculant in jar testing using kaolin suspension (5 g/L). The study shows that adding alpha-cellulose as an aid to PAC slightly increased the turbidity removal efficiency, and further modification of alpha-cellulose by cationic grafts into cationic cellulose is needed.

1. Introduction

Flocculants are usually polymers that have long chains and have solubility in water. Flocculants are used to separate solids that do not settle from suspended solutions [1]. At present, the use of polymer flocculants is more widely used than inorganic metal coagulants to enable and assist the process separation because of their high efficacy, so that synthetic and natural polymer flocculants are becoming prominent nowadays in their application in water and wastewater treatment due to their static nature in changing pH, high processing efficiency at low doses, and easy handling [2, 3, 4]. However, both synthetic polymer flocculants and natural flocculants have significant problems. The former is non-biodegradable and not environmentally friendly, whereas the latter has lower efficiency than the synthetic polymers [5, 6, 7]. So that recent studies regarding natural flocculant modification, also called bio-based flocculants, have been widely carried out to merge the properties of synthetic polymers and natural polymers [3, 8], which are presented in this paper. Another thing to be considered is that the sludge generated in the clarification process after coagulation-flocculation is expected to be biodegradable and ready to be disposed of after simple processing. It can reduce the overall maintenance cost [3, 9].
Indonesia has biomass potential that has not been processed effectively. One of the plants that can be developed is *Boehmeria nivea*, or what is known as Ramie, which is still not utilized optimally. Ramie is a textile raw material to replace cotton, with a productive period of 8 years which can be harvested in 90 days at the first harvest and an interval of 60 days at the second harvest and so on [10, 11]. Ramie stalks contain cellulose which can be extracted to be the basis of biomaterial composites. Ramie fiber has a high content of alpha-cellulose with low levels of pentosan and lignin. Ramie fiber which is used as the primary material for textiles is the bast fiber derived from the bark of plants. Meanwhile, unused Ramie stalks still contain cellulose and can be reused. For this reason, the use of cellulose derived from Ramie stem waste as a base material for coagulant-aid and environmentally friendly biodegradable flocculants has the potential to be carried out.

In order to make novel and innovative flocculants, a comprehensive characterization, also an assessment of flocculation performances is needed. Therefore, in this paper, there are explanations about the overview of flocculation, recent developments of natural flocculants, cellulose as natural flocculants, including isolation of alpha-cellulose of *Boehmeria nivea* and its application as a flocculant in synthetic wastewater.

### 2. Methodology

Cellulose is another potential contender for water and wastewater treatment because of its broad availability, renewability, durability, and surface modification capabilities. However, since cellulose is insoluble in water, the usage of unmodified cellulose is relatively limited. Many studies on the use of cellulose as a flocculant by changing its surface have concentrated on creating nano-cellulose, which has a wide surface area so that surface modification can be facilitated [1].

Cellulose is a homopolymer consisting of linear polysaccharide chains produced by repetitive connections of D-glucose and has biodegradability properties, making it promising with applications in different industries as a raw material for chemical processing. Cellulose may be derived from wood, plants, microorganisms, animals, seed fibers (cotton), wood fibers, tree bark fibers (flax, hemp, jute, and Ramie), grass, bamboo, and algae, and bacteria. Due to the abundance of free-OH groups on the chain, cellulose has a good water purification effect, allowing for the effective removal of metal ions and organic particles from water with a solid chelating impact [3].

Because of its low water solubility and chemical reactivity, cellulose has traditionally had limited use as a flocculant. Cellulose modification was performed to address cellulose's weak water solubility and low chemical reactivity, and carboxymethylation is a traditional and effective chemical modification technique. Related studies regarding the modification of cellulose for use as a flocculant can be seen in Table 1.

| Base Polymer | Modification | Result | Ref. |
|--------------|--------------|--------|-----|
| *Eucalyptus* Kraft bleached pulp | Synthesis of cationic cellulose using CHPTAC reagent and synthesis of anionic cellulose using sodium metabisulfite as a reagent. | The results showed that the percentage of color removal by CC (cationic cellulose) and ADAC (anionic dialdehyde cellulose) gave more than 90% processing efficiency. | 3 |
| *Date palm rachis* | Anionic polyelectrolyte: sodium carboxymethylcellulose (CMC). | Comparison of modified flocculants with PAM shows that CMCNa produces 10% better flocculation performance than PAM. | 16 |
| Base Polymer | Modification | Result | Ref. |
|--------------|--------------|--------|------|
| Bleached birch (Betula verrucosa and Betula pendula) | Combined alum coagulation-flocculation treatment and soluble/nanoparticle anionic dialdehyde cellulose derivatives (ADAC). | The coagulation-flocculation treatment combination is only effective in acidic conditions (pH < 5) due to the presence of alum in the coagulation process. ADAC is stable at pH 3-9 and temperature 30-60°C. | 17 |
| Bleached birch (Betula pendula) chemical kraft wood pulp | Synthesis of bioflocculants: cationic nanocelluloses, dicarboxyl acid nanocellulose (DCC), sulphonated nanocellulose from kraft pulp (ADAC), and cationic nanocellulose (CDAC). | In the coagulation-flocculation process with ferric as a coagulant, anionic nanocelluloses (DCC and ADAC) demonstrated good efficiency in urban wastewater treatment. Meanwhile, CDAC is successful over an extensive range of pH and temperature in flocculating kaolin suspension. | 18 |
| Microcrystalline cellulose | Cationic cellulose (CC) is synthesized by a CHPTAC cellulose reaction. Polycrylamide is then grafted into cationic cellulose-grafted-polyacrylamide (CC-g-PAM). | Under acidic and neutral conditions, CC-g-PAM is efficient as a flocculant for kaolin suspension, while CC demonstrates improved results under alkaline or alkaline conditions. | 19 |
| Bamboo pulp cellulose from Phyllostachys heterocycla | Synthesis of cellulose-g-polyacrylamide bamboo pulp | The best coagulation-flocculation efficiency is given by the combination of Fe³⁺ with BPC-g-PAM. | 20 |
| Hydrophilic natural cotton | Synthesis of biodegradable natural-based flocculants by sulfonating cotton to produce cellulose sulphate (CS). | Direct flocculation using CS is possible and can reduce the use of chemicals (alum or alum) for the coagulation process. | 21 |
| Powdered α-Cellulose | A novel biodegradable flocculant: 2,3,6-tricarboxylate cellulose (TCC) | For kaolin suspension, TCC shows outstanding flocculation performance. | 8 |
| Powdered Cellulose | Synthesis of water-soluble quaternized celluloses. | With a maximum degradation of 48 percent within 48 hours using cellulase, quaternized cellulose shows good biodegradability and enables biopolymer recovery and reuse. | 22 |

Water-soluble modified cellulose serves an essential role as a potential replacement for oil-based flocculants. Several cellulose derivatives have been studied and shown to be effective at eliminating suspended particles. There is also growing interest in developing low-cost biomass (cellulose) absorbers for the treatment of dyestuff-contaminated (decolorized) wastewater from various wastewater sources. Anionic sodium carboxymethyl-cellulose (CMCNa) produced from agricultural palm oil waste, for
example, has been studied as an environmentally safe flocculant coupled with aluminum sulphate as a coagulant to reduce turbidity in the treatment of drinking water [16].

Another research developed and analyzed the anionization of flocculant dicarboxyl acid nanocellulose (DCC) in municipal wastewater for its iron sulfate coagulant flocculation properties [18]. Zhang [19] and Pellizzer [3] reported the synthesis and homogenous characterization of polyacrylamide-grafted cationic cellulose flocculants with CHPTAC or 3-chloro-2-hydroxypropyl-trimethylammonium chloride as a reagent (2016). Meanwhile, Khiari et al. [16] and Chen et al. [8] produced anionic biodegradable flocculants with a carboxymethylation process. Graft copolymerization has been demonstrated to be a valuable method for improving flocculation ability [6, 8, 18, 23].

2.1. Materials
Boehmeria nivea were obtained from Padasuka Street, Cimenyan District, Bandung, West Java, Indonesia. The sample taken was a 6-month-old Ramie plant stem, which resulted from the first harvest on the plantation. The stalks were ground and then sieved through 300 μm mesh. Sodium chlorite solution (5%) was purchased from Sopyan Jaya Chemicals. Sodium hydroxide and Kaolinite used were technical grade powder from Brataco Chemicals. Acetic acid solution for analysis (96%) was from Merck. Polyaluminium chloride (PAC) was provided from the Water Quality Laboratory, Environmental Engineering ITB.

2.2. Isolation of alpha-cellulose from Boehmeria nivea
The isolation of alpha-cellulose from Boehmeria nivea is adapted from previous studies [24, 25, 26, 27, 28]. First of all, a pre-hydrolysis process was carried out with acetic acid as a solvent. The ratio of powder and solvent is 1:20 (w/w)—pre-hydrolysis by boiling in a water bath at a temperature of 105°C for 1 hour. The sample was filtered with filter paper and rinsed using distilled water until the pH was neutral.

In the delignification process, the alkaline solution used was sodium hydroxide (NaOH) with various concentrations of 5%, 10%, 15%, 17.5%, 20%, 25% (w/v) with distilled water as the solvent. Delignification was also carried out by heating over a water bath at 105°C for 1 hour. The sample was then filtered through filter paper and rinsed using distilled water until the pH was neutral. The filtrate contained in the solution is beta-cellulose and gamma-cellulose, while the residue left on the filter paper is alpha-cellulose which will be used in this study.

The bleaching process or pulp bleaching was carried out by immersing alpha-cellulose into 5% sodium chlorite (NaClO2) solution using a Schott bottle for 15-20 minutes with a ratio of sample and solvent 1:8. The addition of a few drops of acetic acid 1N (CH3COOH) solution was carried out to obtain an acidic pH (3-5) [29]. The bleaching process was carried out twice to ensure color removal [30]. Then, the solution was filtered, and the residue was rinsed repeatedly until the pH was neutral [25, 26, 27].

2.3. Coagulation-flocculation experiments
The alpha-cellulose of Boehmeria nivea was used as a flocculant in jar testing using kaolin suspension (5 g/L). The coagulant used in the experiment was PAC (1 mL = 10 mg).

The first jar testing was carried out to determine the optimum coagulant dose and settling time. Synthetic water in the form of kaolin suspension (5 g/L) was prepared as much as 1 L in each beaker (5 glasses) with variations in PAC doses, namely 2 mL, 4 mL, 6 mL, 8 mL, and 10 mL. Stirring was carried out using a magnetic stirrer at 200 rpm (rapid mixing) for 3 minutes, followed by stirring at 40 rpm (slow mixing) for 7 minutes. After that, the formed floc was allowed to settle for 120 minutes, and supernatant sampling was carried out at 5, 30, 60, and 120 minutes.

The second jar testing was carried out to determine the performance of α-cellulose as a flocculant or coagulant-aid against PAC. There were six types of alpha-cellulose produced because, in the delignification process, NaOH was used with various concentrations of 5%, 10%, 15%, 17.5%, 20%, 25% (w/v) with distilled water as the solvent. Synthetic water in kaolin suspension (5 g/L) was prepared as much as 1 L in each beaker (6 glasses) with a dose of optimum PAC as a coagulant from the first jar.
testing. Mixing was carried out using a magnetic stirrer at 200 rpm (rapid mixing) for 3 minutes, then added the six types of alpha-cellulose in a beaker and stirred at 40 rpm (slow mixing) for 7 minutes. After that, the floc formed was allowed to settle for 60 minutes.

3. Results and discussion

3.1. Optimization of coagulant dosage and clarifying time

As stated before, the first jar test was done to know the optimum dosage of PAC as the coagulant. The kaolin suspension used for this experiment had a turbidity of 931 NTU. Variations in coagulant dose and settling time affect turbidity removal efficiency, which can be seen in Figure 1.

![Figure 1. Variation of PAC (mL) and clarifying time.](image)

It is seen that, in general, efficiency increases with increasing deposition time. The turbidity of the sample decreased significantly up to a settling time of 60 minutes, from 931 NTU to the range of 20-36 NTU (removal efficiency ranged from 96-97%), depending on the dose of PAC administered. After that, the lowest turbidity reached 11.35 NTU (98.78%) during 120 minutes of settling time in the first glass, adding 2 ml of coagulant. Therefore, the dose of PAC as a coagulant will be used in the second jar testing experiment, with the addition of alpha-cellulose as a flocculant.

3.2. Application of alpha-cellulose as a flocculant

The second jar testing was carried out to determine the performance of α-cellulose as a flocculant or coagulant-aid against 2 ml PAC that was selected from the first jar test. There were 6 types of alpha-cellulose used, depending on the delignification process, NaOH was used with various concentrations of 5%, 10%, 15%, 17.5%, 20%, 25% (w/v). The water sample used in this experiment was synthetic wastewater, 5 mg/L kaolin suspension, with a turbidity of 5520 NTU. Figure 2 shows that the addition of alpha-cellulose as a coagulant-aid application to PAC increased the turbidity removal efficiency after 60 minutes of settling time, which reached 99%. However, it can be seen that there was no significant difference between the 6 types of α-cellulose.

The addition of PAC as coagulant facilitates the destabilization of colloid, then enables the agglomeration of suspended and dispersed particles into flocs. Agglomeration is a contact and adhesion process in which dispersed particles are united together by weak physical interaction, leading to solid-liquid separation and particles formation that are larger than colloid size [12]. The help of alpha-cellulose
then assists this as flocculant, a biopolymer with high molecular weight, through a bridging mechanism [1]. These large particles or clumps will settle and produce clarified supernatants [3, 13, 14].

![Figure 2](image)

**Figure 2.** Removal efficiency with application of alpha-cellulose as a flocculant.

3.3. *Zeta potential of alpha-cellulose*

Since there was no significant difference between the six alpha-cellulose samples, a NaOH concentration of 17.5% in the delignification process was selected for the zeta potential measurement of alpha-cellulose. It is because alpha-cellulose is insoluble at the NaOH concentration limit of 17.5% [31]. Zeta potential determines the potential at the surface of alpha-cellulose [18] and is a helpful tool for determining the flocculant's destabilizing efficiency and proposing a flocculation process [1].

Bridging mechanism and charge neutralization are the two main mechanisms in the flocculation process. They usually depend on the polymer size and surface properties of particles in the solution [1, 3]. It can be shown by the measurement of zeta potential of both alpha-cellulose as the biopolymer and kaolin suspension as the solution. In the next study, it is proposed to know the various zeta potential of kaolin suspension to indicate the charge neutralization phenomenon that occurs.

Zeta potential was measured using HORIBA SZ-100 with water as the dispersion medium at room temperature (25°C). Sample of alpha-cellulose (NaOH 17.5%) was done in triplicate, and the average calculation result was -51.47 mV. Zeta potential determines the potential at the surface of alpha-cellulose [18], which means the alpha-cellulose of *Boehmeria nivea* is negatively charged. Most colloidal systems are also negatively charged. As the stability of suspensions is reduced by using an effective flocculant that can bring their zeta potential near zero [1], further modification of alpha-cellulose by cationic grafts is required to increase the positive zeta potential.

4. **Conclusion**

The alpha-cellulose isolated from the stalk of *Boehmeria nivea* waste was used as a flocculant in jar testing using kaolin suspension (5 g/L) as the synthetic wastewater, with turbidity as the research parameter. The first jar testing showed that an addition of 2 mL PAC as coagulant had the highest turbidity removal efficiency, whereas the second jar testing did not give a clear result in which alpha-cellulose had the best result. The study shows that adding alpha-cellulose as an aid to PAC slightly increased the turbidity removal efficiency. Cellulose is a good candidate of biomaterial for natural flocculants for turbidity removal. However, further modification of alpha-cellulose by cationic grafts into cationic cellulose is needed.
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