

Grafted flocculant based on the modified taro starch varied by length of polyacrylamide chain

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Abstract. The grafted flocculant was prepared from modified taro starch as a backbone. This flocculant was utilizing the combination properties of the synthetic and natural polymer. Taro starch was enzymatic modified using α amylase before grafting. Non terminated polyacrylamide (nt-PAM) with different chain length was grafted gently into the starch in a nitrogen (N_2) atmosphere. Further, this grafted flocculant was called starch-g-Pam. Mark Houwink equation was used to calculate the average molecular weight (M_v) of product that correlates directly with the intrinsic viscosity (η). Fourier Transform Infra-Red (FTIR) analysis was also carried out to depict its molecular structures. The flocculation performance test was evaluated to diminish the turbidity of the simulated wastewater (about 200 NTU). This artificial wastewater was created by dissolving kaolin in water (10 g of kaolin/1000 ml). The results explained that the grafted flocculant has good performance as well as some commercial organic flocculants. It can be highlighted that the longer chain of polyacrylamide, the better performance flocculation will be exhibited. Although fewer polyacrylamide is grafted into the backbone of the modified taro starch.

1. Introduction

The availability of clean water is now a hot issue due to many people lack access it in a sufficient amount of potable water, sanitation water, etc. To tackle this problem, a large amount of waste water should be processed in a treatment unit. This treatment is a terraced process to reduce or remove pollutants or contaminants from wastewater, such as minerals, organic matters, solids, nutrients, micro-organisms. The purpose of this treatment is to recover/improve the quality of water from wastewater sources to be utilized in particular need.

Flocculation is an efficient, eco-friendly and economical process in particular of wastewater treatment for disposal/reduction of suspended solid particles such as solid minerals, toxic heavy metals, etc. This process agglomerates colloidal particles, that difficult to be sedimented, into a bigger one. This agglomeration causes the easiness of further separation, such as filtration or sedimentation [1]. There are two types of flocculants that have been developed and available in the market, i.e. polymeric and non-polymeric flocculants. The polymeric flocculant exhibits the forming of large flocs and strongly bound to restrain the forces of shear degradation [2]. Thus, some researchers consistently devoted to developing this flocculant either from a synthetic polymer, natural polymer or combination both of them.

Many reports explained that the synthetic ones are showing better performance to tie up the colloidal particles than that of natural ones [2, 3]. However, the drawbacks of synthetic polymers are inadequate biodegradability and shear stability. In contrast, those weaknesses are not found in the natural polymers.



The natural ones have shear stable, highly biodegradable and non-toxic [4]. Thus, it is interesting to combine the excellences of properties both synthetic and natural polymer in a new flocculant. Grafting copolymerization is widely conducted to modify structure and properties of the polymer by inserting a certain functional group [5]. This method can be done through redox grafting [6], γ -ray irradiation [7], microwave irradiation [8], and electron beam irradiation [9].

Our previous work has successfully copolymerized the polyacrylamide and varied starches (i.e., taro starch, cassava starch and their modification) through redox grafting [10]. We grafted polyacrylamide in the form of free radicals into the starches. Free radicals were formed when the polymerization of acrylamide initiated by potassium persulfate was not terminated. The non-terminated polyacrylamide would substitute the hydroxyl groups in the starches. The modified starches both taro and cassava were easier to be replaced with non-terminated polyacrylamide than that of neat starches. Modified starch can be undertaken through chemical processes (esterification, oxidation, etc.), enzymatic process, or physical processes (pre-gelatinization and hydrothermal treatment). This process is to revamp the hydroxyl groups of starch. Generally, the flocculation performance of this flocculant is comparable to that of Tawas (alum). However, it still needs to enhance its effectivity.

There are some reports about the factors influencing the effectiveness of flocculant in the flocculation of colloidal particles, such as dosage of flocculant, type of suspended particles, etc. However, the characteristic effects of flocculant are found in few articles [11, 12]. In the present article, the polymerization time of non-terminated polyacrylamide before grafted into the starches was studied. This time represents the length of polyacrylamide chains. We used modified taro starch as a backbone. Taro starch was modified enzymatically by adding α -amylase. After grafted flocculants were obtained, we analyzed their molecular structure, average molecular weight and its flocculation performance in simulated wastewater.

2. Experimental details

Taro was available from the traditional market in Surakarta and made into taro starch. The taro starch was modified by enzyme α -amylase (from Sigma Aldrich). Some chemicals, i.e., Acrylamide, $K_2S_2O_8$, TMEDA, acetone, methanol and hydroquinone were also kindly ordered by Sigma Aldrich. Further, these chemicals were directly used without any specific treatment.

The formation of Starch-g-Pam was initiated with redox reaction to synthesize non terminated polyacrylamide (nt-PAM). This free radical polymer would be grafted into the modified taro starch by substituting the hydroxyl (-OH) groups. In this investigation, the polymerization time of acrylamide was varied at 0.5, 1 and 1.5 hours. Whereas, the other conditions of both synthesizing and grafting of nt-PAM were accorded to our previous work [10].

We used an infrared spectrophotometry (Perkin-Elmer 630 IR) to determine the molecular structure of products. The wavenumber range of IR spectra was recorded at 4000-400 cm^{-1} . The preparation of IR samples was using a KBr pellet method in a solid state. The Mark Houwink equation as shown in equation (1) was involved in determining the average molecular weight (M_v) of the grafted flocculants where, the K and a constant are 6.31×10^{-3} g/ml and 0.8 for PAm in water, respectively [13].

$$\eta = KM_v^a \quad (1)$$

The performance of grafted flocculant was tested to agglomerate kaolin particles in colloidal size. The concentration of kaolin in this simulated wastewater is 10 g in 1 L of solution. The parent solution of flocculant was prepared by dissolving 10 mg grafted flocculant in 20 ml of water. The dosage of flocculant in this test is 4 ml of parent solution decanted into 500 ml of the artificial wastewater. The mixture was then shaken at 120 rpm (for 2 minutes) and 50 rpm (for 10 minutes), sequentially. Finally, the turbidity of mixture before and after adding the grafted flocculant was calculated by EUTECH TN100.

3. Results and discussion

The taro starch was modified enzymatically using α -Amylase prior to use as a backbone of grafted flocculant. The modified starch was visually clearer in water solution and had lower viscosity compared to the native one. However, the IR spectrum showed this modification was not changing the molecular structure taro starch [10]. The schematic representation of starch-g-polyacrylamide varied in polymerization time of acrylamide 0.5 h (A) and 1.5 h (C) is shown in figure 1.

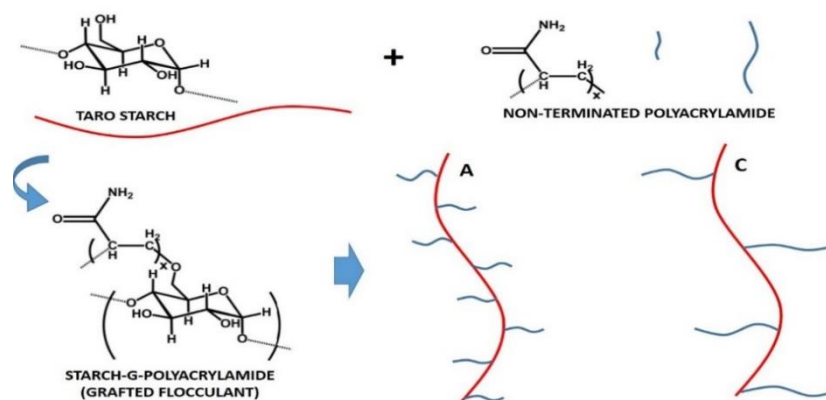


Figure 1. Schematic representation of starch-g-polyacrylamide varied in polymerization time of acrylamide: 0.5 h (A) and 1.5 h (C).

In this article, we study the effect of polymerization time of acrylamide toward flocculation performance of grafted flocculants. The same amount of acrylamide monomer was polymerized without any termination processes in the different time, i.e., 0.5 (A), 1 (B) and 1.5 hours (C). Further, we call the obtained flocculants as sample A, sample B and sample C representing those times, respectively. We proposed that it would produce the different length of radical chains. The amount of shorter chains was more than that of the longer chains. For 1.5 hours, it had enough time to propagation step and resulted in the longer chains of non-terminated polyacrylamide (nt-polyacrylamide). However, these chains were fewer formed due to the limited availability of acrylamide monomer. The IR spectrum of starch-g-polyacrylamide varied in polymerization time of acrylamide for sample A and sample C are shown in figure 2.

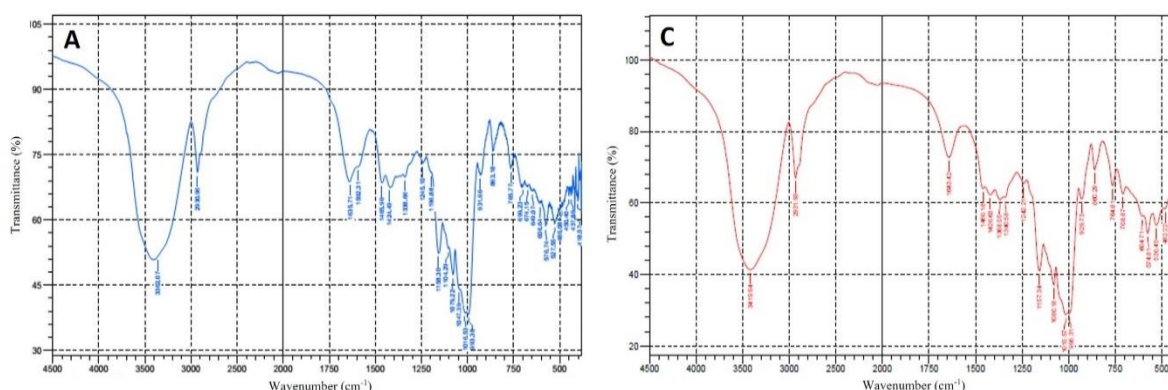


Figure 2. IR spectrum of starch-g-polyacrylamide varied in polymerization time of acrylamide: sample A and sample C.

The obtained nt-polyacrylamide with different length of chains was then grafted into the modified taro starch as the backbone. The schematic representation of the obtained flocculants was depicted clearly in figure 1. It can be seen that the backbone of sample A was more grafted by the shorter chains

of nt-polyacrylamide. It means that the hydroxyl groups in this sample were more substituted. Compared to the sample C, the hydroxyl groups were fewer substituted by the longer chains of nt-polyacrylamide. This statement will be confirmed by Fourier-transform infrared spectroscopy (FTIR) analysis.

The similar IR spectra of grafted flocculants varied their length of polyacrylamide chains were shown in figure 2. The absorption band data of samples was recapitulated in table 1. It can be underlined at wavenumber around 3419.94 cm^{-1} and 3392.89 cm^{-1} that indicating the hydroxyl (-OH) groups. The different intensity is clearly appearance which the stronger intensity is seen for sample C. It was confirming our previous statement that the hydroxyl groups in modified taro starch of sample C were still more exist and unsubstituted with nt-polyacrylamide.

Table 1. Comparison infrared spectra of Sample A and Sample C.

Wavenumbers		Chemical Bonding	Mode	Notification
Sample A	Sample C			
3419.94	3418.92	-OH	Stretching	stronger intensity for sample C
1643.42	1643.40	-C-O	Stretching	
1340.58	1340.58	-CH-	Deformation	asymmetric, symmetric
1368.55	1368.55			
1420.63	1420.60			
1460.18	1460.15			
1193.99	1190.49	C-N	Bending	Similar intensity for sample A and C
1240.32	1241.02			
1242.21	1268.21	-C-OH	Bending	
890.00	921.10	-C-C-	Stretching	

Figure 2 also shows two similar peaks around 1193.99 cm^{-1} and 1240.32 cm^{-1} indicating the existence of C-N bond. This bond refers to the appearance of chemical bonds between starch and polyacrylamide in the obtained products as illustrated in figure 1. This result was confirming that starch-g-polyacrylamide has been successfully formed through “grafting to” method.

Table 2. Tabulation of intrinsic viscosity $[\eta]$ and average molecular weight (Mv).

Grafted Flocculant	Backbone, gram	Acrylamide, M (4 ml)	Polymerization time, h	$[\eta]$, ml/g	Mv. 10^3
Sample A	2.5	0.1	0.5	7.4 ± 0.2	6.862
Sample B	2.5	0.1	1.0	7.6 ± 0.1	7.095
Sample C	2.5	0.1	1.5	7.7 ± 0.2	7.212

Table 2 summarizes the measurement of intrinsic viscosity and the calculation of molecular weight of starch-g-PAm. As seen in this table, the molecular weight of grafted flocculants has almost the same. In agreement, their intrinsic viscosity was also on the same trend. It may be explained that the utilization of the same starch gives the same opportunity of free radical to substitute the hydroxyl groups of the starch. Whereas, the free radical was added in the same amount of monomer although resulting in the different of nt-polyacrylamide chains.

Table 3 recapitulates flocculation test in the simulated wastewater containing a kaolin suspension. It shows that sample C is more efficient to reduce the water turbidity, although the average molecular weight is almost same. It might be concluded that this phenomenon was related to the length of

polyacrylamide grafted in the backbone. The longer chains may be easier to get hold of colloidal kaolin particles becoming agglomerates. However, it needs further analysis to verify this explanation.

Table 3 also shows the performance of the grafted flocculants may be compared to the synthetic commercial flocculant (Alum/ $\text{Al}_2(\text{SO}_4)_3$). The percentage residual turbidity of sample C was almost the same value with the synthetic one, i.e., 12.46 NTU and 6.23 NTU, respectively. The acidity of the simulated wastewater after flocculation tended to decrease. However, the larger drop in acidity occurred when alum was used. This phenomenon showed the advantages of the grafted flocculant.

Table 3. Flocculation test of grafted flocculant for 1 hour.

Criteria	Sample			
	A	B	C	Alum
Colloidal particle	Kaolin	Kaolin	Kaolin	Kaolin
Temperature, °C	30	30	30	30
pH before/after flocculation	7.1/6.6	7.1/6.5	7.1/6.6	7.1/6
Volume of the simulated wastewater, L	0.5	0.5	0.5	0.5
Dosage of flocculant, mg/L	2.67	2.67	2.67	2.67
Initial Turbidity, NTU	200	200	200	200
Residual Turbidity, NTU	19.83	16.51	12.46	6.23
Removal, %	90.08	91.74	93.77	96.88

4. Conclusion

The different length of non-terminated polyacrylamide can be obtained by varying the polymerization time. The obtained nt-polyacrylamide was successfully grafted into the modified taro starch. The average molecular weight related to the intrinsic viscosity was observed in the similar value. However, the longer of polyacrylamide chains grafted in the starch the more effective of its performance to decrease turbidity of kaolin suspension in water. It means that the agglomeration of colloidal particles was easily achieved when the length of polyacrylamide chains was getting longer. Although, the number of chains is fewer. Generally, the grafted flocculant consisting of modified taro starch and polyacrylamide is potential to be applied in a part of wastewater treatments.

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