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APPLICATION OF CELLULOSE FROM PANDAN LEAVES AS GRAFTED FLOCCULANT FOR DYES TREATMENT

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Abstract

In this study, PAM chains were grafted onto the backbone of cellulose extracted from pandan leaves (*pandanus amaryllifolius* roxb.) via microwave assisted method. The performance of grafting between extracted cellulose and PAM was verified through the percentage of grafting (%G). The grafting of the PAM chains on the polysaccharide backbone was confirmed by SEM morphology analysis and FTIR spectroscopy. The efficiency of grafted copolymers was tested on removal of COD of synthetic dye, reactive black 5, conducted using a jar test experiment. The results obtained showed that the best achievement of the synthesized PAM-g-cellulose was in initial dye concentration of 0.025 g/l, with flocculant dosage of 0.06 g at pH 11.

Keywords: Grafted copolymers, Pandan leaves; Flocculant, COD, Reactive black 5.

1. Introduction

Flocculation is one of a technology which commonly used in wastewater treatment [1]. The demand of this technology among various wastewater treatment processes is because of its simplicity, low cost, effective role of suspended particles, dyes and heavy metals removal [2, 3]. The chemical used in flocculation is known as a flocculant. Flocculating materials are categoried by two; inorganic and polymeric. Whereas polymeric flocculants are further divided by natural, synthetic and grafted copolymers.

Considering both natural and synthetic polymeric flocculants, synthetic polymeric flocculants are widely used as alternative for inorganic flocculants. This is due to their rapid settling and can minimize the amount of sludge production [4]. The surface charge of the hydrated colloidal particles is neutralized

Nomenclatures

%G	Percentage of grafting
g	Grafted

Abbreviations

AM	Acrylamide
CAN	Ceric Ammonium Nitrate
COD	Chemical Oxygen Demand
EFB	Empty Fruit Bunch
FTIR	Fourier Transform Infrared
HCl	Hydrochloric acid
NaOH	Sodium Hydroxide
PAM	Polyacrylamide
RB5	Reactive Black 5
SEM	Scanning Electron Microscopy

by these flocculants. Therefore, the electric repulsion between the approaching particles can be reduced. Nevertheless, the flocculants also bridges the approaching particles through the polymer chains [5]. On the other hand, the disadvantages of synthetic flocculants are not biodegradable and considered as toxic because of the monomers release during the products degradation and leads to the health hazards [6]. Natural polymers are easy polymers toward availability and biodegradability [7]. This type of polymeric materials has been used during treatment for various types of wastewater [8, 9]. It is also an eco-friendly and non-hazardous materials. However, towards their most advantages character as biodegradable, the biodegradability has become the drawback since the shelf life can be reduced and the efficiency decreased due to the decreasing molecular weight [10].

Grafted copolymers are one of the available classes in polymeric flocculants [11]. Grafted copolymers are synthesized from natural and synthetic polymers for the purpose of obtaining the advantages from both types of polymers. Polyacrylamide has been used widely as a basis of many developed grafted copolymers flocculants [12]. This is because polyacrylamide can be easily synthesized to produce a very high molecular weight of graft copolymers flocculants [13]. In previous studies, there were a number of successful grafted copolymers flocculant have been synthesized [5, 10, 14, 15].

Microwave assisted method is most commonly used method in grafting. This method employs microwave in the presence of the free radical initiator [14]. This method was claimed as a promising method for synthesising grafted copolymers. Therefore, this study was proposed to synthesis a flocculant based on cellulose extracted from pandan leaves (pandan *amaryllifolius* roxb.) grafted with polyacrylamide (PAM). The potential of the flocculant was investigated for synthetic dyes in textile wastewater by using flocculation process.

2. Materials and Methods

2.1. Materials

Cellulose was extracted from fresh pandan leaves, collected in Segamat, (Johor, Malaysia) residential area. All the chemicals including acrylamide, ceric

ammonium nitrate (CAN), hydroquinone, acetone (analytical grade), and hydrochloric acid and reactive black 5 (RB5) powder were purchased from Sigma-Aldrich. Chemicals have been used as received without further purification.

2.2. Synthesis of polyacrylamide grafted cellulose

An amount of cellulose was dissolved in 40 ml of distilled water. Next, a desired amount of acrylamide was dissolved in 10 ml of water. Both solutions were mixed homogeneously. This step was then followed by addition of 0.5 g of ceric ammonium nitrate (CAN) as a free radical initiator. The content was placed in a turntable microwave oven with 800 W of irradiation power. The microwave irradiation was periodically pause for every 1 minute (until three minutes cycle reached) and cools the contents in cold water to minimize the competing homopolymer formation reaction. Lastly, the contents was allowed to cool and left undisturbed for 24 hours.

After that, a few drop of saturated solution of hydroquinone was used to terminate the reaction. The gel like mass obtain was poured into 250 ml of acetone [6]. The precipitate was collected and dried in dry oven at 60^0C for 6 hours. Table 1 shows the synthesis details of various grades of PAM graft cellulose. The grafting performance was shown through the percentage grafting (%G). The equation is as follow:

$$\%G = \frac{(Weight\ of\ Grafted\ Copolymers - Weight\ of\ Polysaccharide)}{Weight\ of\ Polysaccharide} \times 100 \quad (1)$$

Table 1. Synthesis details of PAM-g-cellulose.

Grade	Weight of cellulose (g)	Weight of acrylamide (g)
PAM-g-cellulose 1	1	7
PAM-g-cellulose 2	1	5
PAM-g-cellulose 3	1	3
PAM-g-cellulose 4	1	1
PAM-g-cellulose 5	3	1
PAM-g-cellulose 6	5	1
PAM-g-cellulose 7	7	1

2.3. Characterization of polyacrylamide grafted cellulose

a) Scanning electron microscopy (SEM) analysis

The morphology of the structure of cellulose and PAM-g-cellulose analysis were examined using scanning electron microscopy (SEM) JEOL JSM-6390LV model. An accelerating voltage of 3 kV was used to conduct the analysis. Both cellulose and PAM-g-cellulose have been coated with gold before the analysis to avoid electron charging during the analysis.

b) Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of cellulose and PAM-g-cellulose were recorded in a Fourier Transform Infrared (FTIR) spectrophotometer with a wavelength fixed at 600 to 4000 cm^{-1}. Each sample was mixed with several amount of KBr pellet. Then, the mixture was pressed into thin transparent films. Finally, the mixture was analysed.

2.4. Application of polyacrylamide grafted cellulose as flocculant

Jar Text Experiment

Jar test experiments was used to conduct the flocculation process. Reactive black 5 was used as synthetic dye which stimulated textile wastewater sample. Firstly, a flocculant was added to the one litter of dye sample and stirred with rapid and slow mixing rate. The rapid mixing rate used for this experiment was 200 rpm for 3 minutes. While for slow mixing rate, 30 rpm was operated for 15 minutes. Then, the suspension was allowed to settle for 30 minutes. After that, the supernatant was withdrawn from the top layer of the suspension. The supernatant then was examined its COD level. The experiment was conducted at different initial dye concentration (0.025 to 0.10 g/l), dosage of the flocculant (0.02 to 0.12 g) and pH of the dye solution (3 to 11). The pH of the dye solution was adjusted using 0.1M of sodium hydroxide (NaOH) and 0.01M of hydrochloric acid (HCl). The experimental ranges of all the independent variables were obtained from the screening results of this study. The previous studies were taken as references in selecting the levels and range of the independent variables. Then, a set of preliminary study (screening) was conducted to confirm the level and range of the independent variables that suitable in this study.

3. Results and Discussion

3.1. Synthesis of polyacrylamide grafted cellulose

In this study, PAM-g-cellulose was synthesized by microwave assisted method. A chemical free radical initiator, ceric ammonium nitrate (CAN) was used to generate a free radical sites on the cellulose backbone. The formation of free radical sites on the polymer backbone is important so that the monomer can get added up through the chain propagation step [15]. The PAM-g-cellulose was synthesized by varying the ratio between polysaccharide (cellulose) and monomer (acrylamide (AM)) concentration. In this study, it is important to identify the amount of the monomer used since it is given the performance of the polysaccharide with and without the addition of the monomer. All the respected results of the synthesis are tabulated in Table 2. The best grade of PAM-g-cellulose was identified through the higher percentage of grafting (%G). From the results, it is clearly shown that, the best grade of the grafted copolymers is when the amount ratio of cellulose and acrylamide was 1: 7.

Table 2. Percentage of grafting (%G) of PAM-g-cellulose.

Grade	Weight of cellulose (g)	Weight of acrylamide (g)	%G
PAM-g-cellulose 1	1	7	170.0 ± 0.02
PAM-g-cellulose 2	1	5	147.50 ± 0.02
PAM-g- cellulose 3	1	3	131.47 ± 0.02
PAM-g- cellulose 4	1	1	109.50 ± 0.02
PAM-g- cellulose 5	3	1	103.01 ± 0.02
PAM-g- cellulose 6	5	1	101.17 ± 0.02
PAM-g- cellulose 7	7	1	98.90 ± 0.02

3.2. Characterization of polyacrylamide grafted cellulose

3.2.1. Scanning electron microscopy (SEM) analysis

The SEM analysis micrographs of extracted and PAM-g-cellulose are shown in Fig. 1. This figure shows that there is a change in the morphology of cellulose. Originally, cellulose morphology was in form of flaky structure. However, after cellulose has been grafted with polyacrylamide (PAM), the morphology was change to porous spongy structured. PAM chains was believed been grafted on the cellulose. From the findings, it can justify that the grafting process was successfully done using microwave assisted synthesis method.

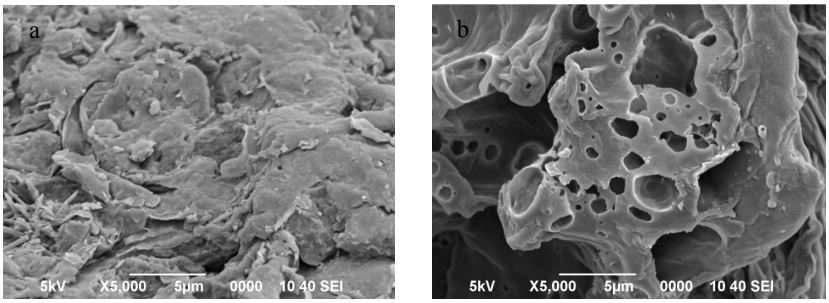

Fig. 1. SEM micrograph of (a) cellulose (extracted from Pandan leaves) (b) PAM-g-cellulose.

3.2.2. Fourier transform infrared (FTIR) spectroscopy analysis

Figure 2 shows the FTIR spectroscopy of cellulose and PAM-g-cellulose copolymers (PAM-g-cellulose 1). From the spectrum of cellulose, it is clearly shows a broad peak at 3434.06 cm^{-1}. The arising of this peak is due to stretching vibration of O-H group. Arising of two peaks at 2900 cm^{-1} corresponds to C-H stretching vibrations [16]. The absorption peak at wavelength 1429.38 cm^{-1} is attributed to the CH_2 bending [17]. In addition, the prominent band at 1053.53 cm^{-1} is referred to the C-O-C pyranose ring skeletal vibration [18].

The same reason also indicates to PAM-g-cellulose spectrum at which a broad peak at 3410.26 cm^{-1} was arising. The peak also assigned for O-H stretching band for hydroxyl group of cellulose. C-H stretching vibration for PAM-g-cellulose was aroused at peak 2906.51 cm^{-1}. On the other, the absorption peak at 1646.26 cm^{-1} in PAM-g-cellulose spectrum assigned for C=O stretching vibration.

The additional peaks were observed in the copolymer spectrum. Those additional peaks are well explained by the presence of grafted PAM chains and confirming the successful of grafting. A narrow shoulder was observed in the copolymer spectrum at absorption peak 3694.05 cm^{-1}. The absorption peak indicates the N-H starching band of amide group of PAM. The extra peak was also observed at 1383.09 cm^{-1}. This assigned for C-N stretching. For C-O-C stretching vibration, the peak was observed at absorption peak 1063.31 cm^{-1}.

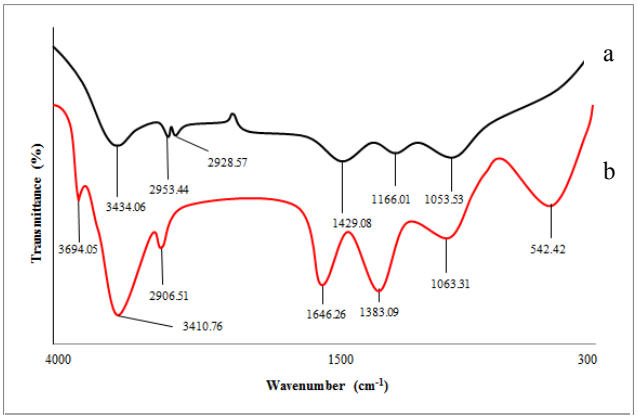

Fig. 2. FTIR spectrum of (a) cellulose (extracted from pandan leaves) and (b) PAM-g-cellulose.

3.3. Application of polyacrylamide grafted cellulose as flocculant

3.3.1. Effect of initial dye concentration

Figs. 3 to 6 show the level of COD before and after treatment with different flocculant dosage in different initial dye concentration. There are different variations in the trend of COD level as were varied. However, as can be seen in all figures, the reduction of COD level was occurred after the flocculant was being added to the suspension. The COD level was reduced until the flocculant dosage achieved the maximum performance. Generally, the less amount of initial dye concentration has less level of COD. The statement was met with the explanation by de Souza et al. [19]. It is clearly can be claimed that, all the initial dye concentration have shown their own optimum performance in reducing the COD level.

3.3.2. Effect of flocculant dosage

The effect of flocculant dosage was investigated by varying the dosage of the flocculant but keeping other conditions constant (in this case the initial dye concentration and pH of suspension). Figures 3 to 6again show the COD level with the effect of flocculant dosage in different initial dye concentration. Observing all the flocculant dosage performance from 0.02 to 0.12 g, the best performance is at flocculant dosage range from 0.02 to 0.10 g. For this maximum amount of flocculant dosage, about 30% to 50% reduction in COD level was achieved at pH 3, 7 and 11 in all four different initial dye concentrations.

The addition of flocculant to the suspension has promoted to an adsorption of the particle in suspension to the flocculant in which they become attached to two or more particles thus bridging them together. However, interestingly this phenomenon is observed up to a particular optimum flocculant dosage beyond which the flocculation will diminish. The reason lies on the explanation that, in every polymer flocculants, there are an optimal dosage at which the flocculation efficacy is maximum (i.e. the COD level of the supernatant is minimum). Beyond this dosage, the flocculation efficacy will decrease (i.e. the COD level of the supernatant increases). This was due to the destabilization of the flocs formed by the excess polymers (flocculant) [20]. This behaviour of the flocculation curve finely confirms the interparticle bridging mechanism involved behind the phenomenon [21].

3.3.3. Effect of pH

The effect of pH toward flocculation efficiency was also studied. Das and Somasundaran [22] claimed that pH is one of the significant parameter need to be investigated during flocculation studies. Abu Hassan et al. [21] claimed that, the effect of pH is important as it shows the stabilization of the suspension. The effect of pH in this study focused on the reduction of COD level. Figures 3 to 6 show the effect of pH on the flocculation process for the grafted copolymer (PAM-g-cellulose) flocculant. The pH was analysed at pH 3, 7 and 11. As can be seen, pH 11 has the best reduction value of COD level. At the pH, the best percentage reduction of 50% was achieved in initial dye concentration of 0.025 g/l with flocculant dosage of 0.06 g. However, at different initial dye concentration, the best pH was different. Therefore, the pH range of 3 to 11 was suitable for this study since the optimum pH performance on COD level reduction lies from that range.

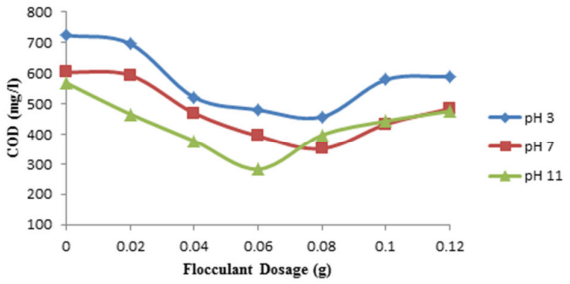

Fig. 3. COD versus flocculant dosage plot for PAM-g-cellulose at pH 3, 7 and 11 in initial dye concentration of 0.025g/l.

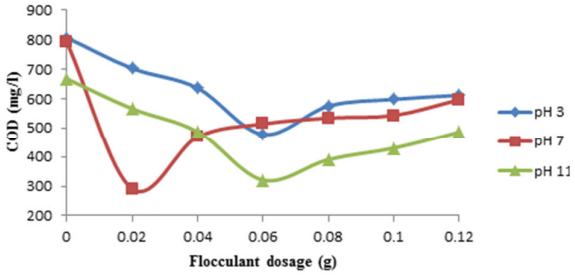

Fig. 4. COD versus flocculant dosage plot for PAM-g-cellulose at pH 3, 7 and 11 in initial dye concentration of 0.05g/l.

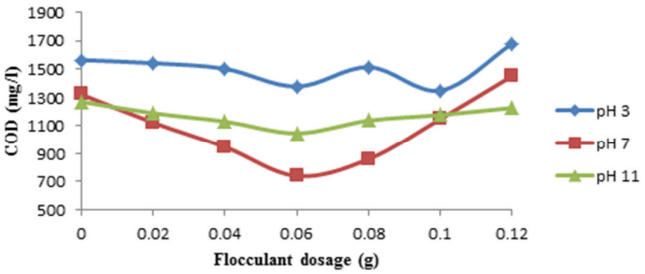

Fig. 5. COD versus flocculant dosage plot for PAM-g-cellulose at pH 3, 7 and 11 in initial dye concentration of 0.075g/l.

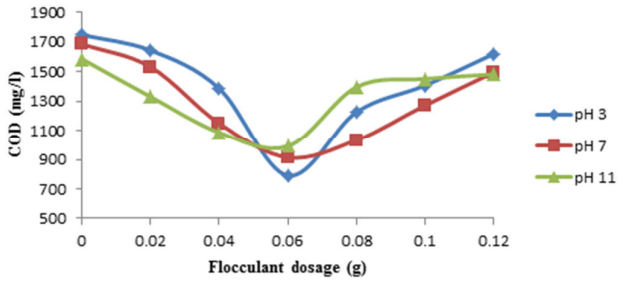

Fig 6. COD versus flocculant dosage plot for PAM-g-cellulose at pH 3, 7 and 11 in initial dye concentration of 0.10g/l.

4. Conclusions

PAM-g-cellulose copolymers was successfully been synthesized through microwave assisted synthesis method. There were seven selected ratio involved in the study which have been analysed through their performance in the percentage of grafting (%G). Some concluding observations from the study are given below.

- Ratio of 1:7 (i.e., cellulose to PAM) was the best ratio to synthesis graft copolymers. The best ratio of grating that have the higher %G characterized through SEM analysis and FTIR spectroscopy have proven that grafting was occurred between and PAM and cellulose.
- From the flocculation studied, the maximum achievement of the synthesized PAM-g-cellulose was in initial dye concentration of 0.025 g/l, with flocculant dosage of 0.06 g at pH 11.
- The develop copolymers was found to has an ability to reduce the COD level in alkaline suspension of reactive black 5 dye.

5. Future Study

In flocculant preparation part, optimization study should be included as well. Besides that, other parameters on flocculation study are recommended to explore in order to understand more about the flocculation efficiency. Further, other characteristics can be studied such as the turbidity, pH and colour

reduction of textile wastewater containing dyes. The other types of dyes can also broadly be investigated.

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