

Preparation of Polyacrylamide Grafted onto Magnetic Cellulose as Flocculant in Wastewater Pre-treatment Application

Mohd Hizam and Norzita Ngadi

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia
81210, Johor, Malaysia

mhizam2@live.utm.my, norzita@cheme.utm.my

Abstract

Recently, many efforts has been made to improve the potency of natural polymer-based flocculants in wastewater treatment. Graft copolymerization of magnetic cellulose and polyacrylamide (PAM-g-MagCell) were synthesized through microwave assisted technique with the aid of ceric-ion-induced as catalyst. Through varying the monomer, polysaccharide and mass of catalyst, five grades of PAM-g-MagCell were synthesized. The influences of these factors toward grafting percentage were investigate. The flocculation performance of PAM-g-MagCell was also studied in treating anaerobically-treated palm oil mill effluent (AnPOME). The grafting ratio suggested that the optimum conditions for graft copolymerization were composed of 0.25 g catalyst ceric ammonium nitrate and 4:1 mass ratio of acrylamide monomer to magnetic cellulose. The results found that under such optimum conditions, flocculation performance had improved, whereby, sampled wastewater coloration and suspended solid were significantly reduced by 50% and 65%, respectively.

Keywords

Acrylamide, Cellulose, Flocculation, Microwave assisted, Jar test

1.0 Introduction

Palm oil thrives rapidly in regions with extensive tropical forest lands, spanning Asia, South Africa, and South America continents. Despite the recognition gained by the oil palm industry in driving the world economy, the industry's large-scale oil extraction activities have led to the generation of by-products in massive volumes, which have raised environmental concerns. Palm oil mill effluent (POME) is one of the largest non-fibrous by-products, released in the form of liquid discharge from oil palm processing plants, which contributed to water pollution. According to Madaki and Seng (2013), about 3.5 m³ or 2.5 tons of POME is yielded for every ton of processed crude palm oil (CPO).

In current practice, palm oil mill treat raw POME through utilizing traditional biological process, such as ponding system. Nonetheless, ponding system is considered as challenging as it requires a long retention time and large area (Abdurahman et al. 2013). Attributed to the challenges, scholars have explored various cost-effective and practical alternatives to treat POME. There is a compelling scholastic evidence that signifies the increase of interest in replacing inorganic material (i.e. alum or ferric chloride) in treating POME with environmentally friendly coagulants. Most recently, coagulation-flocculation has been used as an alternative to treat POME, owing to its nascent capability in destabilizing and aggregating colloids (Alhaji et al. 2016).

Among all natural sources, cellulose is one of the most abundant natural polysaccharide resources that has been subjected in many research efforts. Its application as coagulants or flocculants has been applied widely in many industries, such as in removing turbidity from drinking water (Sillanpää et al. 2018), municipal wastewater treatment (Suopajarvi et al. 2013) and various others. However, the natural polymer is vulnerable to biodegradation as the

content of its active components reduces the shelf life. In addition, the strength and stability of the flocs are also adversely affected as the result of natural biodegrading process.

Grafting copolymerization is a method used to modify the structure and properties of polymeric materials by improving its functional properties (Garcia-Valdez et al. 2018). Through grafting modification, the biodegradability of the natural polymer can be compensated. Grafted polysaccharide copolymer has been reported to show better performance in flocculation, attributed to the better approachability of the grafted chains to the colloidal particles. Different types of graft copolymers have been synthesized by the grafting of a synthetic polymer onto a natural polymer (i.e. starch, guar gum, amylopectin (AP), and sodium alginate) (Nayak et al. 2018). The graft copolymers that have been obtained are fairly shear-stable and have reduced biodegradability. Among all graft copolymers, an AP-based graft copolymer (AP-g-PAM) has shown a superior performance (Rath and Singh 1998). Despite this, the cost of AP is prohibitive and has poor water solubility. Therefore, in this study, cellulose was chosen as the backbone polysaccharide where PAM was grafted onto it.

For enhancement of flocculation efficiency and interest in nanotechnologies, particularly magnetic nanoparticles (MNPs) have attracted the attention of the scholastic community in the chemical, environmental and medical sectors. An instance of MNPs; iron content in magnetite (Fe_3O_4) is a potent reducing agent that increases the degradability of various organic and inorganic contaminants that are found in water bodies (Mohammed et al. 2017).

This study investigates the synthetic details of five graft copolymer grades based on magnetic cellulose (MagCell) and polyacrylamide (PAM) through varying the monomer, magnetic polysaccharide and catalyst concentrations to improve flocculant properties toward removal of total suspended solid (TSS) and color of anaerobically treated palm oil mill effluent (AnPOME).

2.0 Methodology

2.1 Materials

AnPOME was collected at Adela Palm Oil Mill, Johor with temperature ranging between 40 and 50°C. For preservation of sample purposes, the collected sample were kept in refrigerator at temperature about 4°C to help the sample to withstand biodegradation microbial action. Cellulose and magnetite powder were purchased from Qingdao Unionchem Co., Ltd. and Innoxia Ltd., respectively. Acrylamide ($\text{C}_3\text{H}_5\text{ON}$) with 98.5% purity was purchased from Bendosen Laboratory Chemicals, Malaysia. Hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$) with 99% purity was purchased from System ChemPur, Malaysia. CAN ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$) with 98% purity and acetone ($(\text{CH}_3)_2\text{CO}$) with $\geq 99.5\%$ purity was purchased from Sigma-Aldrich, Malaysia.

2.2 Preparation of Polyacrylamide grafted Magnetic cellulose (PAM-g-MagCell)

Firstly, magnetic cellulose (MagCell) were prepared using the crosslinking method as previously reported (Noor et al. 2018). However, graft copolymer flocculant were prepared by employing microwave assisted method. Briefly, pre-weighed MagCell were dissolved in 40 mL distilled water. 10 mL of water was used to dissolve desired amount of acrylamide and then mixed to the MagCell solution. All the desired amounts of magnetic cellulose and acrylamide are shown in Table 1. The solution was mixed gently until it becomes homogeneous and CAN was added. A microwave oven was employed to execute irradiation process. Microwave irradiation was performed at 800 W power. The irradiation of microwave was periodically paused alternately once the mixture started to boil ($\sim 65^\circ\text{C}$) during reaction and placed the vessel in cold water for cooling. The recurrence of microwave irradiation – cooling cycle continued until a gel-like mass was observed or up to 3 minutes of irradiation time (if no gelling took place). Once the process was complete, the grafting reaction occurred by prevailing the reaction vessel and its contents cooled and undisturbed for 24 hours. Later, a few drops of saturated hydroquinone solution were used to terminate the reaction. The gel-like mass left in the reaction vessel was poured into 250 mL of acetone. The precipitation formed resulting from graft copolymer was collected and dried in dry oven at temperature 60°C until constant weight was obtained. Subsequently, pulverizing, sieving, and purifying towards material were performed. Any impeded polyacrylamide (PAM) formed during striving homopolymer emergence reaction was separated from the complete graft copolymer synthesized as above, by solvent extraction whereby acetone was used.

Table 1: Impregnation ratio of PAM-g-MagCell

Grade	Weight of MagCell (g)	Weight of acrylamide (g)
PAM-g-MagCell 1	1	4
PAM-g- MagCell 2	1	2
PAM-g- MagCell 3	1	1
PAM-g- MagCell 4	2	1
PAM-g- MagCell 5	4	1

This study also includes the investigation of the effect of CAN amount to percentage grafting. In this part of study, the experiment was conducted by using the best magnetic cellulose and acrylamide ratio. Selected amounts of CAN were 0.25, 0.5, 1.5 g, and without CAN. The selected amounts of CAN were considered according to the previous grafting study by Yahya (2013). The grafting performance also was evaluated in term of percentage grafting (%G). The equation is as follows:

$$\%G = \frac{\text{Weight of graft copolymer} - \text{Weight of MagCell}}{\text{Weight of MagCell}} \times 100 \%$$

2.3 Flocculation Process

Characteristics of untreated AnPOME (initial turbidity, TSS and pH) were analyzed and then the average values were used for evaluation of flocculation performance. The coagulation-flocculation process was performed via jar test (Jar Tester SJ-10 Thrusoft). For each test sample, 1L of AnPOME was mixed with desired ratio of acrylamide and MagCell and also concentration of CAN in a 2L beaker. Then the mixture was stirred for 3 min at 200 rpm. During mixing, flocculant with ratios shown in Table 1 were added into each beaker. After that, the mixture were stirred for 15 min at 30 rpm. Finally, the system was left undisturbed for 30 min to permit the flocs settling. Supernatants were collected using syringe for subsequent analyses. The optimum grade of PAM-g-MagCell was obtained from the analyses result and the same procedure was repeated to study on the effect of CAN dosage as catalyst.

2.4 Analytical Analysis

The removal efficiencies of all pollutants were calculated using the following equation:

$$\text{Percent removal (\%)} = \frac{X_i - X_f}{X_i} \times 100\%$$

Where,

X_i = initial reading of parameters

X_f = final reading of parameters

To determine the TSS, a gravimetric analysis was used with the aid of vacuum filtration apparatus. The weight of solid retained on the filter paper was determined after drying for 1h at 103-105°C. Concentration of colour was measured by using HANNA COD Meter and Multiparameter Photometer (HI 83099) based on calorimetric method.

3.0 Results and discussion

3.1 Characteristic of Untreated AnPOME

Table 2 lists the values for the tested parameters of AnPOME sample prior to flocculation pre-treatment. The recorded values are the mean values before each jar test was performed.

Table 2: Selected initial characteristic of AnPOME

Parameters	Unit	Mean values
Initial pH	-	8.1
Total suspended solid (TSS)	mg/L	10,290
Color	PtCo	2,040

The raw POME is acidic and after undergoing a series of anaerobic digestion the wastewater become alkaline with pH range of 8.0 – 8.5 (Iskandar et al. 2018). The pH increment might be due to consumption of hydrogen ion (H^+) during methanogenic digestion by anaerobic bacteria in anaerobic pond (Zahrim et al. 2014). AnPOME also exhibits darker color compared to raw POME due to the presence of soluble tannin and lignin. These contents in AnPOME resulted from the digestion of lignocellulosic biomass present in raw POME by microorganism during the anaerobic digestion process (Taha and Ibrahim 2014).

3.2 Effect Ratio of MagCell to Acrylamide

The mass ratio of MagCell to acrylamide (AM) is one of factors that may affect the grafting percentage. Referring to Figure 1, for PAM-g-MagCell 1, the grafting percentage is optimum provided that the amount of Magcell is at the lowest dosage (1g). Reversely, the lowest grafting percentage was obtained when the dosage of MagCell was administered in excess while the mass of AM was limited to 1g.

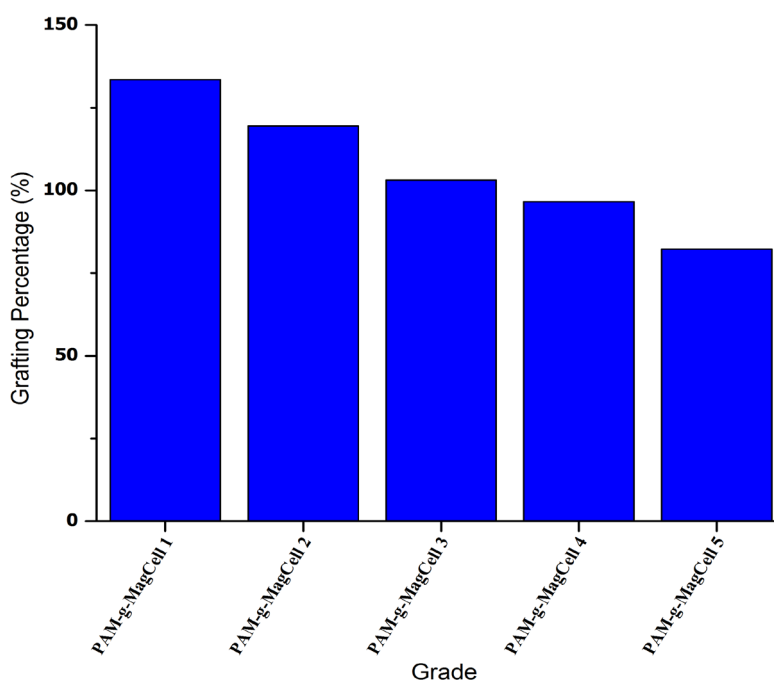


Figure 1: Effect ratio of MagCell to AM on grafting percentage

This can be explained by the fact that, initially, more radicals reach into the MagCell polymer backbone resulting in an increase in grafting percentage; at the least number of MagCell while fixed concentration of CAN (Thakur et al. 2013). A higher concentration of AM facilitates the contact of MagCell with monomer much easily, which speeds up graft copolymerization leading to an improved grafting percentage. In contrast, increasing the amount of MagCell while limiting the amount of AM produces the least grafting percentage. This could possibly be explained as the following: A lesser amount of monomer is grafted by free radicals that are provided by a large amount of MagCell backbone.

The effect of grafting percentage on the flocculation performance in removing TSS and colour is shown in Figure 2. Experimental results indicate that the removal efficiency of AM/MagCell ratio copolymer increases remarkably high as the grafting percentage increases. At 133.47% grafting percentage, the removal of TSS and reduction of colour by PAM-g-Magcell 1 reached 79.47% and 51.47%, respectively.

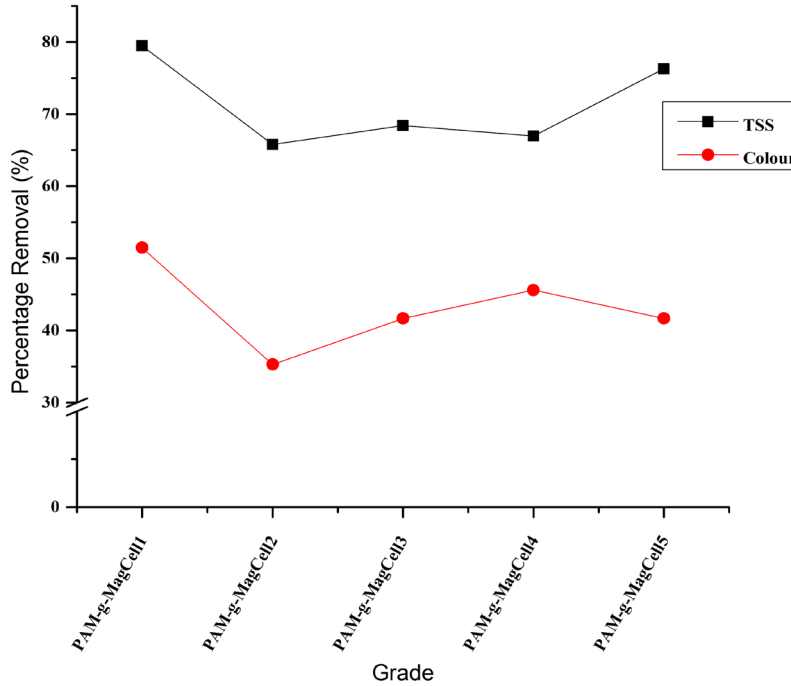


Figure 2: Effect ratio of MagCell to AM on TSS and color removal

Based on the results, when acrylamide concentration was increased while the MagCell and CAN concentrations were fixed, graft polymers with longer PAM chains were obtained. Consequently, this had raised the approachability of the polymers to attract pollutants resulting in an increase in the percentage of removal, owing to the entrapment of a higher quantity suspended solid particles by longer polymer chains.

3.3 Effect of Catalyst (CAN) dosage on Graft copolymerization

The effect of catalyst dosage on graft copolymerization was evaluated by considering the grafting percentage, in addition to flocculation performance, in terms of TSS and colour reduction of AnPOME. Figure 3 and 4 represent the results. It was found that the grafting percentage increased as the CAN dosage increased, at first. However, as the catalyst dosage exceeded 0.25g, the grafting percentage reduced significantly.

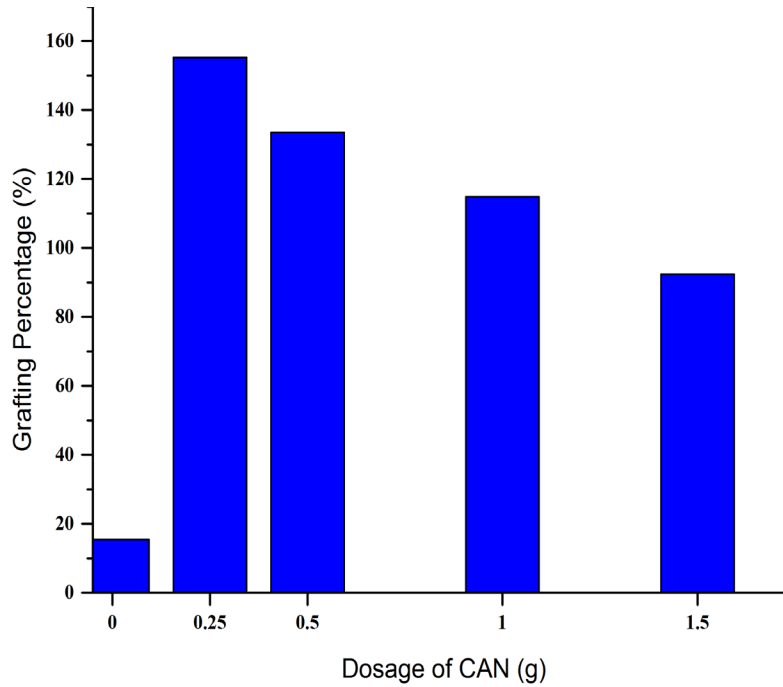


Figure 3: Effect of CAN's dosage on grafting percentage

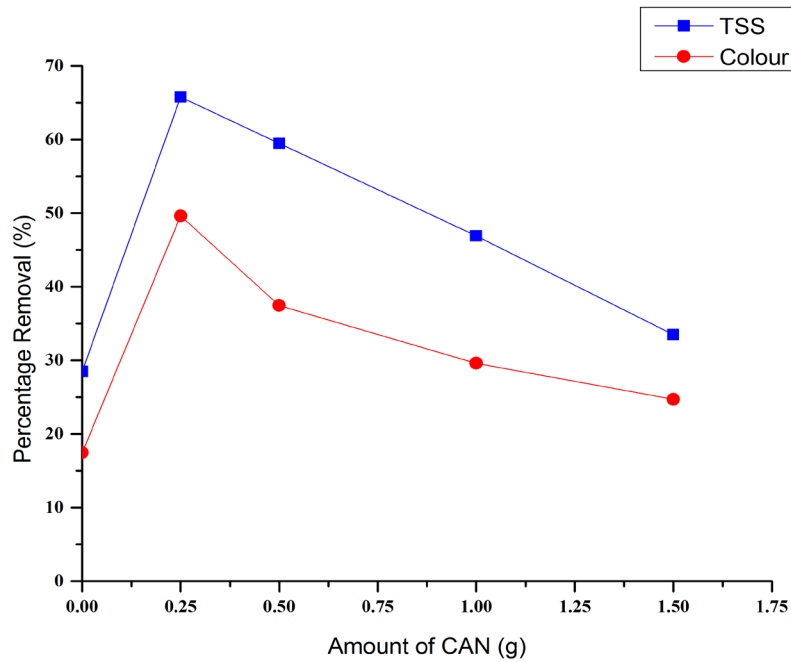


Figure 4: Effect of CAN's dosage on TSS and color removal.

In the process of copolymerization, the initiating system of CAN generated free radicals to initiate polymerization of PAM and graft copolymerization of Magcell, with AM or PAM chains. The high grafting percentage with Ce^{4+} ions was attributed to the preferential creation of active radicals by CAN initiator on the Magcell backbone rather than on the monomer (Mino and Kaizerman 1958; Gupta and Khandekar 2006). Further increment in the amount of CAN due to hydrolysis had led to a decrease in grafting percentage. The hydrolysis product deactivated the creation of active

sites at a fixed quantity of polymers. In addition, reduction of grafting percentage beyond the optimum amount of CAN may be attributed to the formation of more Fe^{3+} ions at a higher molar ratio, which resulted in the termination of polyacrylamide chain's growth (Thakur et al. 2013).

The presence of CAN not only affected the grafting percentage but also affected the percentage of pollutant removal. Figure 4 indicates that increasing the dosage of catalyst had increased the percentage of removal of TSS and reduction of color, prior to decreasing after reaching a certain limit. Percentage of removal was at peak when the CAN dosage was set at 0.25g. Under such dosage, more free radicals were released from the polymerization of AM. As a result, more PAM chains were produced to entrap the TSS and color molecules, which consequently increased the percentage of removal. Beyond this optimum point, the performance fell significantly due to the hydrolysis of CAN. The hydrolysis had lessened the formation of active sites, which were required for the polymerization of PAM to occur. As a consequence, less chains were available for the removal of colloidal solids and color pigments.

4.0 Conclusion

PAM-g-MagCell 1 yielded the highest grafting percentage and good flocculation performance in removing TSS and color presence in AnPOME. The study on catalyst concentration also observed that minimal amount of CAN (0.25g) had managed to produce the highest grafting and removal percentages. Among the grafted grades, copolymers having fewer but longer PAM chains showed better flocculation performance than those with shorter PAM chains, owing to easy approachability of the dangling grafted chains to attach to contaminants. Microwave assisted are proven to be the best option to enhance the grafting process between monomer and natural polymer as backbone. In overall, the results support the objectives in this study.

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Biographies

Mohamed Hizam Mohamed Noor currently is a PhD student at Universiti Teknologi Malaysia, Malaysia. He earned M.Sc in Environmental Engineering at the same institution in 2018. He also earned BEng in Process and Chemical Engineering at the Universiti Teknologi MARA, Malaysia in 2017. He has published journal and conference papers. His research interests include wastewater treatment technologies, magnetic nanoparticle and optimization.

Norzita Ngadi is an Associate Professor and senior lecturer in the Department of Chemical and Energy Engineering at Universiti Teknologi Malaysia, Malaysia. She earned B.S in Chemical Engineering in 1999 at Universiti Sains Malaysia, Penang. Then further her study at Universiti Teknologi Malaysia and obtained MEng in 2002 under same field. In 2009, she completed her PhD at University of Canterbury, New Zealand in the field of bionanotechnology and protein fouling. Apart being a lecturer, she also was appointed as program coordinator, committee member for many events such as RCCHE2016, POISChE2016, UTMost Imagination 2012 etc. Moreover, she also one of the board advisor for research and development of palm kernel shell activated carbon's project in 2016 and technical editor for ACTA Materialia Turcica from 2017 until now. She also has become reviewer, judge, and editor for many conferences, journals and proceeding. She has published journal and conference papers. Her research interests include wastewater treatment technologies, protein fouling, surface coating, catalytic reaction and renewable fuel.