

Synthetic Polyelectrolytes Based on Acrylamide and Their Application as a Flocculent in the Treatment of Palm Oil Mill Effluent

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Abstract: Five cationic polyacrylamides of varying molecular weights but similar charge density were synthesized using free radical polymerization and Mannich reaction, characterized by different methods (infra red (IR) spectroscopy, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), viscosity measurements and conductometric titration) and applied as flocculants to palm oil mill effluents (POME). Flocculent performance was assessed by determining the polyelectrolyte dosage and the removal efficiency of the resulting supernatants using turbidity, suspended solids (SS) and chemical oxygen demand (COD) as indicators. It was found that varying in the molecular weight of the cationic polyacrylamide from 20×10^3 to 1.5×10^6 g mol⁻¹ affects flocculent performance significantly. Polyelectrolyte adsorption increased as the molecular weight of the polyelectrolyte increased. High molecular weight cationic polyacrylamide (1.5×10^6 g mol⁻¹) is the most effective polymer as it obtains a high removal efficiency (%) with a dosage as low as 60 mg L⁻¹ at pH 3 of POME. The very high molecular weight cationic polyacrylamide (over 5 million g mol⁻¹) produced very poor floc formation this is because polyelectrolytes having very high molecular weights do not dissolve readily but tend to form gel lumps.

Key words: Cationic polyacrylamide, molecular weight, palm oil mill effluent

INTRODUCTION

Palm oil mill effluent (POME) is a major agro-industrial waste in the Southeast Asian region. In Malaysia, which is essentially an agricultural country, her major polluting industrial effluents have been from agro-based industries of which palm oil and rubber industries together contribute 80% of industrial pollution. The palm oil industry faces a serious problem of dealing with this waste, as this large volume of liquid waste would create serious pollution problems to receiving watercourses if they are discharged untreated. The effluents from these sources are mainly organic in nature. Its direct discharge into the receiving streams and rivers poses a serious danger to the environment.

Several treatment systems have been developed by the palm oil industry in Malaysia. The most common treatment technologies of POME consisting of anaerobic and aerobic or facultative processes and the most popular being the ponding system.

Sinnappa treated POME by anaerobic digestion resulting in methane as a value added product^[1].

Agamuthu *et al.*^[2] have shown that aerobic digestion of POME decreases carbon content and inorganic nitrogen but increases the organic nitrogen and pH and changes pH from the acidic range to an alkaline one.

Chin *et al.*^[3] have treated POME using a pond system; he evaluates the treatment efficiency of a pond system consisting of 8 ponds in series treating 600 cu m/day of POME. The effluent was not able to meet the discharge standard^[3].

Zuhairi^[4] studied the combined use of alum, polyaluminium chloride (PAC), FeCl₃ or FeSO₄ and anionic polyacrylamide on POME treatment by using modified jar test where their effectiveness were gauged on the basis of the (BOD)₅, COD and SS removal. Results showed that the optimisation of coagulation and flocculation processes on settleable solid-free POME was generally reached at between 150-200 mg L⁻¹ of FeCl₃ and FeSO₄ and 300-350 mg L⁻¹ of alum and PAC. The optimum coagulant dosages were found to be dependent on the strength of the wastewater^[4].

Synthetic polyelectrolyte flocculants with high molecular weight has been widely used in industrial and

municipal water treatment, papermaking and mineral processing industries^[5-8]. They have largely replaced the traditional inorganic flocculants such as aluminum sulphate, ferric sulphate and ferric chloride.

The use of synthetic polyelectrolyte flocculants in the water treatment field began in the late 1950's. There are a few characteristics of polyelectrolytes that make them more suitable for a certain specific water treatment application. The most important characteristics are the molecular weight, the varying charge density, the nature of the monomer units that make up the polyelectrolytes and the type of charged group.

Synthetic polyelectrolytes are known to be as much as 80 times more efficient (weight for weight) in the removal of suspended colloidal particles than the traditional water treatment agents^[9]. The typical molecular weight of the polymers ranges from 10,000 g mol⁻¹ to 10 million g mol⁻¹. Their effectiveness as flocculants increases with increasing molecular size.

The objective of this research was to synthesize cationic polyacrylamides (C-PAM) based on acrylamide monomer of the same charge density, but differing in molecular weights and to assess the effectiveness of the cationic polyacrylamides in flocculating POME at pH 3. The efficiency of the polymer as a flocculent was assessed by measuring turbidity, suspended solids (SS) and chemical oxygen demand (COD) of the supernatant before and after treatment with polymer. These parameters were used to obtain information about the suitability of a particular polyacrylamide as a flocculent for POME.

MATERIALS AND METHODS

Acrylamide (Fluka, 99%), potassium persulfate (Fluka, 98%) and N,N,N',N'- tetramethylethylenediamine (TMEDA), (Fluka, 98%). Formaldehyde (HCHO) and dimethylamine (CH₃)₂NH, were purchased from Merck, Germany as laboratory grade. Anionic exchange resin Duolite 113, a quaternary ammonium type in the Cl⁻ form was purchased from BDH Germany as laboratory grade.

Equipment and instrumentation: The polymerization reaction was carried out on a Memmert water bath (thermostatically controlled, heated up to 100°C). One liter five necked Pyrex glass reactor was suitably placed into the Memmert water bath. The reactor was equipped with a mechanical stirrer, condenser equipped with water collector, thermometer and nitrogen gas (OFN) inlet tube. Six position stirring apparatus for "Jar Tests" with variable speed control and light base. 2100 Hach Turbidimeter and DR/2100 Hach spectrophotometer.

Recrystallization of chemicals: Acrylamide (AM) and potassium persulfate were recrystallized twice from acetone and distilled water respectively and dried in vacuum for 24 h at 60°C. The rest of the chemicals were used without further purifications.

Synthesis of polyacrylamide: A mixture of acrylamide and different types of initiators were used to synthesize different molecular weights polyacrylamide. Thioglycolic acid, hydrogen peroxide and potassium persulfate were used as initiators for low, medium and high molecular weight, respectively. The mixture was dissolved in 500 ml distilled water. The reaction was performed in a three-neck flask equipped with a mechanical stirrer and a reflux condenser. Polymerization was carried out at 40°C in Nitrogen atmosphere for 3 h under stirring.

Mannich reaction products from polyacrylamide: Positively charged (cationic) derivatives are obtained by reacting the amide group with formaldehyde and a secondary amine, to produce so-called 'Mannich bases'. Reactions are carried out in aqueous solution at moderate temperatures (40-60°C) and the derivative is a tertiary amine which is positively charged only under acidic pH (2-5) conditions.

Polyacrylamide characterization

Fourier transform infrared (FTIR) spectra analysis: In this study, Nicolet FTIR machine, Model: Avator 360 FTIR spectrometer, manufactured by Nicolet analytical instrument USA Inc. was used. Analysis was conducted by identification of monomer and synthesized products. Potassium bromide (KBr) pellet was prepared by using a sampling device. KBr pellet was placed into FTIR window and then scanned by taking blank spectrum. After completion of the spectrum of the blank, KBr pellet was taken off from the window and KBr pellet thinly coated with test sample was placed again in the FTIR window to measure the spectrum of the sample. On average, 10 scans were used for the synthesized sample.

Glass transition temperature (T_g) measurement: The glass transition temperature (T_g) of all synthesized polyacrylamides were measured using Perkin-Elmer, DSC thermal analyzer. It is equipped with a DSC cell programmed at a heating rate of 10°C min⁻¹, measuring temperature range was 20 to 250°C. Samples were prepared for DSC measurement by weighting between 5.0 mg to 10.0 mg of dry polymer into an aluminum pan. The pan was then sealed with an aluminum cap.

The intrinsic viscosities and the molecular weights of the polyacrylamides:

The intrinsic viscosities of the polyacrylamides were measured using Ubbelohde viscometer, no. 4809 ASTM at 25±0.1°C. The polyacrylamide solutions were prepared in distilled water. The intrinsic viscosity calculations were made for dry polymer after filtration through 250-micron sieve to remove any undissolved 'gel' lumps. Viscosity average molecular weight was determined using Mark-Houwink equation relates the intrinsic viscosity $[\eta]$ of the polymer to its viscosity average molecular weight $[M_v]$ from the relation:

$$[\eta] = 68 \times 10^{-5} \cdot [M_v]^{0.66}$$

Determination of the cationic content of the cationic polyacrylamides:

The charge density and percentage cationic charge density of each polymer was determined by displacement of chloride from the anionic exchange resin Duolite 113. The chloride was determined by conductometric titration.

Efficiency of POME treatment: Under stirring, a certain amount of C-PAM was added into POME taken from MAL POME industry at Jawi in Penang. The characteristics of POME are shown in Table 1.

Table 1: Characteristics of POME

Parameter	Range	Mean
pH	3.4-5.2	4.2
Biological oxygen demand (BOD)	10250-43750	25000
Chemical oxygen demand (COD)	15000-100000	50000
Total volatile solids (TVS)	9000-72000	34000
Suspended solids (SS)	5000-54000	18000
Total volatile solids (TVS)	9000-72000	34000
Oil and grease (O&G)	150-18000	6000
Ammonical nitrogen (AN)	4-80	35
Total nitrogen (TN)	180-1400	750

All in mg L⁻¹ except pH.^[14]

The transmittance of the upper liquid in the container was measured at different dosage and pH of POME by a 2100 Hach spectrophotometer and Hach turbidimeter. The effect of C-PAM dosage on removal of turbidity (NTU), SS (mg L⁻¹) and COD (mg L⁻¹) were examined^[10].

RESULTS AND DISCUSSION

The effect of molecular weight has been studied using five cationic polyacrylamides of varying molecular weights but similar charge densities. (Cationic polyacrylamides A, B, C, D and E as shown in Table 2).

The results presented in Fig. 1 show that the very low molecular weight cationic polyacrylamide A (20X10³ g mol⁻¹) is a less effective flocculent as it required a high dose i.e. 260 mg L⁻¹ to obtain 98% turbidity removal, 96%

Table 2: Different molecular weights but same charge densities and %cationic character of cationic polyacrylamides

Cationic polyacrylamide	Viscosity average molecular weight (g mol ⁻¹)	Charge density (C/g)	%Cationic character
(A)	20X10 ³	373.0	74.6
(B)	170X10 ³	364.0	72.8
(C)	550X10 ³	363.0	72.6
(D)	1.5X10 ⁶	356.0	71.2
(E)	Over 5 million	352.5	70.4

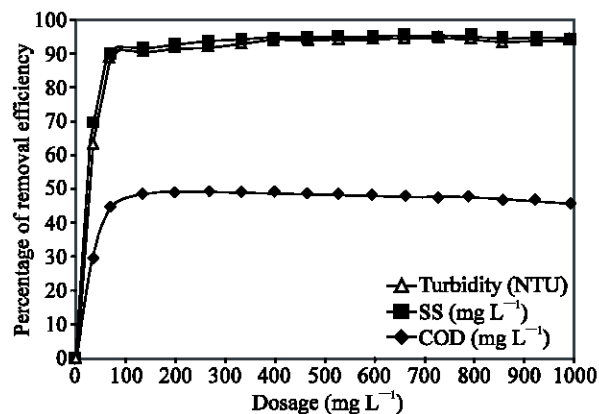


Fig. 1: Effect of cationic polyacrylamide (A) dosage on removal efficiency

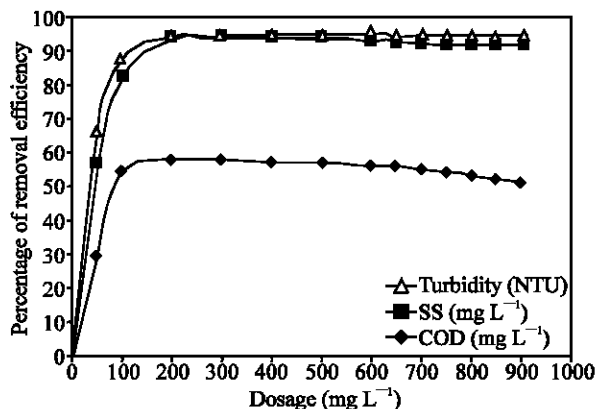


Fig. 2: Effect of cationic polyacrylamide (B) dosage on removal efficiency %

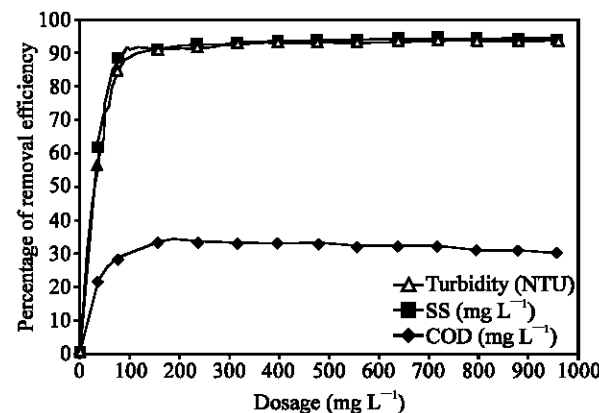


Fig. 3: Effect of cationic polyacrylamide © dosage on removal efficiency

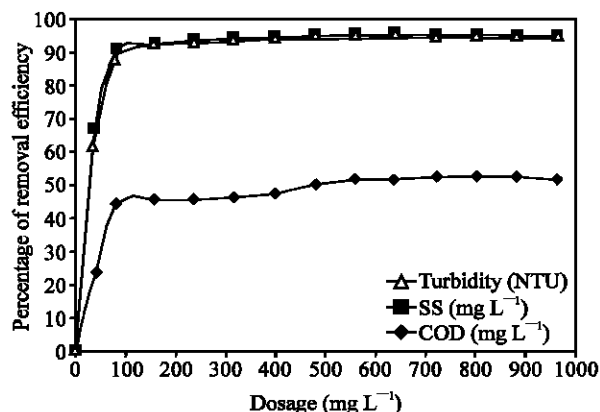


Fig. 4: Effect of cationic polyacrylamide (D) dosage on removal efficiency

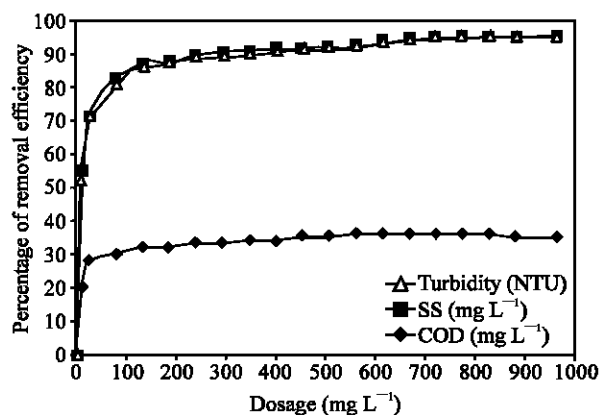


Fig. 5: Effect of cationic polyacrylamide (E) dosage on removal efficiency

SS removal and 51% COD removal. A large number of cationic polyacrylamide A molecules is needed to acquire high removal efficiency. The results in Fig. 2 show that the cationic polyacrylamide B ($170 \times 10^3 \text{ g mol}^{-1}$) with low molecular weight is also a less effective flocculent, as it required 200 mg L^{-1} to obtain 99% turbidity removal, 98% SS removal and 60% COD removal. It can be observed from Fig. 1 and 2 that increasing the molecular weight of polyacrylamide from a very low molecular weight ($20 \times 10^3 \text{ g mol}^{-1}$) to low molecular weight ($170 \times 10^3 \text{ g mol}^{-1}$) will increase the removal efficiency % using the same dosage.

By increasing the molecular weight to medium cationic polyacrylamide C ($550 \times 10^3 \text{ g mol}^{-1}$) level the removal efficiency also increased as shown in Fig. 3. Figure 4 shows that the high molecular weight cationic polyacrylamide D ($1.5 \times 10^6 \text{ g mol}^{-1}$) is the most effective flocculent, giving the highest removal efficiency with lowest dosage at $\approx 60 \text{ mg L}^{-1}$. The larger molecular size cationic polyacrylamide is able to bring about a greater bridging effect or a stronger electrostatic attraction.

The very high molecular weight polyacrylamide (over $5 \text{ million g mol}^{-1}$) resultant in poor floc formation and yielded reduced removal efficiency (Fig. 5) because polyelectrolytes with very high molecular weights do not dissolve readily but tend to form gel lumps known as "fish eyes". This cationic polyacrylamide with very high molecular weight will be unsuitable because it can no longer be dispersed in the medium.

The molecular weight of a polymer can affect polymer adsorption and particle flocculation. The size of the polymer can affect the rate of collisions. It is imaginable that the length of the loops and tails of adsorbed polymer molecules may be longer for the larger molecules and this will enhance the capture of particles. The formation of more loops of sufficient length to bridge the "gap" between the colliding particles may also lead to a stronger bridging effect between aggregating particles. The length of the loops and tails are particularly important in the flocculation of suspended particles. Another consideration is the size of the adsorbed polymer patches. The patches are larger for the polymer of higher molecular weight, giving a more patchy adsorption. As a result, the electrostatic attraction between positive and negative surface regions on different particles is stronger^[11].

Graham has also pointed out that increasing the molecular weight of a polyelectrolyte of a given charge density would increase the unevenness of the surface charge distribution which would give rise to a greater "electrostatic patch" attraction and the number of polymer loops of adequate length to allow interparticle bridging^[12].

For cationic polyacrylamide of high molecular weight bridging is the dominant mechanism for flocculation but for polymers of low molecular weight charge neutralization play a major role.

Stabilization with cationic polyacrylamides involves a combined coagulation-flocculation reaction. The cationic polyacrylamide molecules first act as a coagulant by reducing the forces of repulsion between the particles and then a flocculent in bridging^[13].

Based on the above results, the following conclusions can be drawn:

- Very low molecular weight ($20 \times 10^3 \text{ g mol}^{-1}$) cationic polyacrylamide is effective only at very high dosages up to 260 mg L^{-1} .
- The cationic polyacrylamide with a molecular weight ($170 \times 10^3 \text{ g mol}^{-1}$) is also effective flocculent only at high dosage as it is required 200 mg L^{-1} to obtain 99% turbidity removal, 98% SS removal and 60% COD removal.
- By increasing the molecular weight of cationic polyacrylamide to ($550 \times 10^3 \text{ g mol}^{-1}$) the removal efficiency % will also increased.

- High molecular weight cationic polyacrylamide ($1.5 \times 10^6 \text{ g mol}^{-1}$) is the most effective polymer as it obtains a high removal efficiency % with a dosage as low as 64 mg L^{-1} .
- Very high molecular weight cationic polyacrylamide (over 5 million g mol^{-1}) produced poor floc formation this is because polymers having very high molecular weights do not dissolve readily but tend to form gel lumps known as "fish eyes".

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