Full paper

Treatment of Textile Wastewater using Chitosan and Chitosan Grafted Acrylamide by Microwave Synthesis

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Graphical abstract
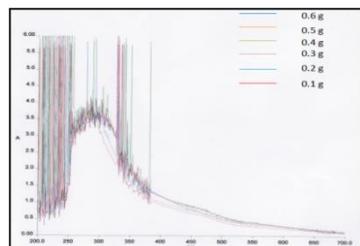
Abstract

Polymeric flocculants based on single chitosan and polyacrylamide grafted chitosan (Ch-g-PAM) have been successfully synthesized via microwave initiated method. Under optimal grafting conditions, 30.4% grafting has been observed in case of the microwave irradiation with exposed time, 76s and power, 640MW (80% from full power). The synthesized graft copolymers have been characterized by FTIR spectroscopy. Acidic medium was the best condition for flocculation with optimum pH of 3 and 4 using Ch-g-PAM and Chitosan, respectively. The longer the settling time, the better the flocculation performance as long as the flocs did not break. 60-90 minutes was the best settling time with optimum dosage of 0.1 g for both flocculants. Grafted chitosan with PAM showed the best result in removing the contaminants compared to single chitosan.

Keywords: Chitosan; PAM; flocculation; grafted flocculant

Abstrak

Kitosan dan gabungan kitosan dan Polyacrylamide (Ch-g-PAM) telah berjaya disintesis menggunakan kaedah gelombang digerakkan. Pada keadaan optimum bagi proses gabungan, 30.4% gabungan Ch-g-PAM telah diperolehi dalam masa 76 s dan 80% daripada kuasa penuh gelombang mikro iaitu 640 MW. Dalam keadaan berasid, proses penggumpalan berlaku dalam pada kadar yang optimum. pH 3 dan pH 4 merupakan pH yang optimum menggunakan chitosan dan Ch-g-PAM sebagai bahan penggumpal, masing-masing. Semakin lama waktu mendakan, semakin berkesan proses pemendakan berlaku selagi mendakan itu tidak pecah dan menghasilkan kekeruhan. 60-90 minit merupakan masa terbaik untuk proses ini berlaku dengan menggunakan 0.1 g dos bagi kedua-dua bahan penggumpal. Kitosan yang digabung bersama PAM merupakan bahan penggumpal yang lebih berkesan untuk digunakan dalam proses penggumpalan berbanding kitosan sahaja.

Kata kunci: Kitosan; PAM; penggumpalan; penggumpal tergabung

∎1.0 INTRODUCTION

Textile wastewater is known as difficult-to-treat pollutants due to the contents contained in the wastewater that difficult to be characterized. Textile wastewater is high in color, high in biochemical oxygen demand (BOD), high in chemical oxygen demand (COD) (or total oxygen demand, TOC), high in salt content and therefore need to be treated before discharging into the environment.

One example of toxic pollutant commonly found in textile wastewater is dyes. It exhibits a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups. It is also toxic to some organisms and may cause direct destruction of creatures in water. Azo dyes are the largest group of synthetic colorants (60–70%) and can be used to color the natural textile fibers, plastics, leather, paper, mineral oils, waxes, foodstuffs and cosmetics. It has become of concern in wastewater treatment because of its highly visible character in water (10-50 mg/l).

A number of processes have been tested for the decolorization of textile wastewaters, including sorption on activated carbon or biosorbents, oxidation and photo-oxidation, chemical treatment, and coagulation/flocculation.

Coagulation/flocculation treatments destabilize colloids and achieve their sedimentation. These actions are usually due to the action of chemical species and stirring. Defining each part, coagulation can be understood as the destabilization of the colloids due to the charges of the compensation on their surface that leads to the formation of the core. On the other hand, flocculation is the agglomeration of the destabilized particles to form micro floccules leading to the formation of bigger agglomerates called floccules that are able to sediment.[1]

The coagulation process can be enhanced by the additions of flocculants which assist the collection of dispersed particles, strengthen the flocs and agglomerate the flocs to larger sizes for improved effluent clarity [2]. As an example, polymers which contain adsorbing groups and can be negatively or positively charged or no charged can be used as a flocculants that help to form bridges between the flocs to increase the floc size.

There are a lot of flocculants used to treat textile wastewater in coagulation/flocculation process. Chitosan is among the well known flocculants that always being used as the neutral flocculant. Chitosan is known as a biopolymer that friendly environment due to the excellent properties especially its biodegradability since it can be degraded by soil microorganisms and water microorganisms. Although chitosan has found potential use in many areas, it is a brittle material and tends to absorb moisture. Besides, chitosan is a cellulose-like-poly-electrolyte biopolymer and a semi-crystalline polymer which is derived from the deacetylation of chitin. Chitin is a hard, inelastic nitrogenous polysaccharide extracted from crustacean shells, such as prawns, crabs, insects, and shrimps.

Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.89%) compared to synthetically substituted cellulose (1.25%). In the deacetylation process, some of the acetyl groups were removed from the molecular chain of chitin. This shortened the chain lengths of the chitin molecule, eventually leaving behind a polymer with a complete amino group called chitosan. This treatment produces 70% of deacetylated chitosan.

From Figures 1 and 2 of chitosan and chitin, respectively, it shows that chitosan has primary amine and two free hydroxyl groups for each monomer with a unit formula $C_6H_{11}O_4N$. This natural biopolymer is a glucosaminoglycan and is composed of two common sugars, glucosamine and N-acetylglucosamine, both of which are constituents of mammalian tissues.
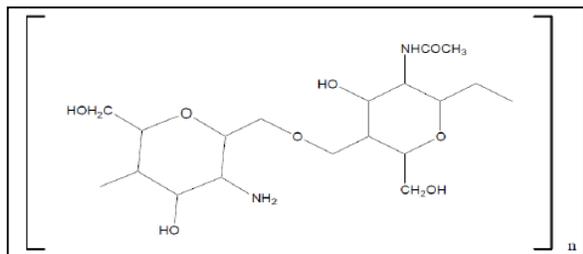
Figure 1 Molecular structure of chitosan
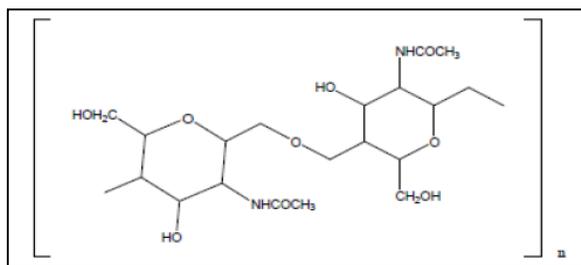
Figure 2 Molecular structure of chitin

Chitosan is the second abundant polysaccharide next to cellulose but it is the most abundant natural amino polysaccharide and is estimated to be produced annually almost as much as cellulose. Because of its excellent properties such as biodegradability, biocompatibility, non-toxicity and polyelectrolyte properties, chitosan is recommended as an effective coagulant for a wide variety of suspensions.[3-4]

Polymers have been established that it can flocculate particles via bridging, charge neutralization, electrostatic patch and depletion flocculation mechanisms. Meanwhile, polymer properties, such as molecular weight, charge density and charge types, can affect to flocculating and destabilizing actions.[5] Most of the polymers are known as synthetic flocculant. The example of synthetic polymer flocculants is polyacrylamide (PAM) and polyaluminium chloride (PAC)

PAM is a generic name for thousands of polymers (-$CH_2CHCONH_2$-) containing acrylamide as the major constituent. It is a crystalline and relatively stable monomer which has different charges (anionic, cationic or neutral), charge densities and molecular weights and they are amorphous and water soluble. PAM is a high molecular weight polymer, which could adsorb onto the surface of sludge particles with its long-chains where the tails and loops are extended far beyond its surface and can interact with other particles via bridging flocculation.

Flocculants with high molecular weights are usually long enough and contains a sufficient number of free functional groups, which can act as bridges, bringing many suspended solids together and building larger flocs. PAM is a high molecular weight polymer (molecular weight is 8-10 million Da). Thus, the bridging flocculation occurred with its long-chains where the tails and loops are extended far beyond its surface and can interact with other particles.

In reference to sludge settleability improvement by PAM, it is reported that the use of PAM improved the sludge settling characteristics.[6] In wastewater treatment plant, PAM is used as the flocculating agent and the acrylamide monomers are readily cross linked and bind with suspended solids in the wastewater

The advantage of polymeric flocculants is their ability to produce large, dense, compact and stronger flocs with good settling characteristic compared to those obtained by coagulation. It can also reduce the sludge volume. Furthermore, the polymer performance is less dependent on pH. In addition, it is possible to synthesize PAM with various functionalities which can be used to produce a good settling performance at relatively low cost. It is also an easy tailorability.[7]

However, PAM and its derivatives are not biodegradable and pose a number of environmental problems as the intermediate products of their degradation are hazardous as their monomer is highly toxic and carcinogenic. Therefore, hybridization of natural and synthetic polymers is the best way to increase coagulation/flocculation efficiency because of its application to biomedical and biodegradable materials. The chemical combination of natural and synthetic polymers yields new materials, which could have desirable properties including biodegradability.

Graft copolymers with a maximum percentage of grafting will have highest intrinsic viscosity because a higher percentage of grafting and also instantly increase the hydrodynamic volume of the polymer molecule in solution. The graft copolymers show better performance when compared to the base polysaccharides, because the presence of the dangling longer branches of PAM (as an example) onto rigid polysaccharide backbone which leads to better approachability toward the contaminants as per Singh's Easy Approachability Model.[8]

The flocculation characteristics of the graft copolymers are caused by polymer bridging. For effective bridging to occur, the length of the grafted chains should be longer so as to adsorb on a particle surface to another particle surface. Hence, the polymer with longer grafted chains would be more effective than that with shorter chains.

Microwave heating method exhibit the most potential to synthesize the grafted polymer because in microwave irradiation based synthesis, the percentage grafting depends on monomer concentration, power and exposure time of the irradiation where these factors are electronically controlled. Moreover, microwave irradiation as efficient thermal energy constitutes a very original method of heating materials, different from the classical ones. Main advantage is that, it results in almost instantaneous homogeneous heating of materials in a selective manner.

The reasons for the large diffusion of microwave technology relate to its clear advantages over more traditional technologies which are shorter acid digestion time, a supposed better recovery of volatile elements and compounds, lower contamination levels, minimal volumes of reagents are required, more reproducible procedures and a better working environment.

■2.0 MATERIALS AND METHODOLOGY

2.1 Materials

Wastewater was collected from American and Efird (Malaysia) Sdn. Bhd. which is situated in Kulai, Johor Bahru. The wastewater was stored in refrigerator in order to minimize the change in characteristic of wastewater sample. Chitosan (10 g) and PAM (10 g) was obtained from the pollution laboratory, faculty of Chemical Engineering, UTM. Chitosan solution was prepared by dissolving in 1% acetic acid solution for about one hour due to the characteristic of chitosan which is only dissolved in acidic medium. The pH was adjusted using the sodium hydroxide (NaOH) and acid hydrochloric (HCl). Chitosan is only efficient over limited pH range and when present in excess. Hydroquinone (20mg) was used to stop the grafted polymer. Distilled water was used to dilute the PAM powder.

2.2 Method

The procedures for this experiment are basically divided in two parts which are the preparation of the flocculants solutions and also the jar test in order to treat the wastewater.

2.2.1 Flocculant Preparation

3g of chitosan was prepared by dissolving in 1% acetic acid solution (25mL) for about one hour. The pH was adjusted using the sodium hydroxide (NaOH) and acid hydrochloric (HCl) . At lower pH value, the amount of chitosan needed is lower than at higher pH. For grafting process,3.0 g of chitosan was diluted in 1% acetic acid solution (25 ml) whereas the PAM was dissolved in distilled water in small amount. These two solutions were mixed before added in the 150 ml open necked flask and placed in the microwave (MW7 IE). After screening process, the microwave power was set to 80% from full power (640 W) due to maximum temperature (70ºC) and the best exposed time is 76 s. Grafted chitosan was precipitated in methanol-water in ratio 7:3 in order to separate grafted chitosan from PAM. Then, the grafted produced was extracted with

methanol–water solvent using soxhlet apparatus for 4 hours to dissolve all the homopolymer and the solid was dried in vacuum at temperature 50ºC for 24 hours . The colorless product was dried until get constant weight of Ch-g-PAM. This is matter in order to get the pure coagulant. The grafting was reacted with 20 mg of hydroquinone overnight to terminate further reaction of grafting. The percent of grafting (G) was calculated by using Equation 1:

% G = (weight of graft copolymer – weight of polysaccharide)/weight of polysaccharide x 100   (1)

2.2.2 Jar Test

The jar test is a method used for evaluating and optimizing the flocculation processes. This study consists of batch experiments involving rapid mixing, slow mixing and sedimentation. The apparatus allowed six beakers to be agitated simultaneously. 500 ml of flocculants-wastewater solutions were agitated in at 200 rpm for 3 min and then 40 rpm was quickly established for 15 min.

After mixing, the beakers were carefully removed from the flocculator and allowed to settle for approximately 30 min. The portion of the supernatant solution was taken and analyzed. The experiment was repeated for different flocculant dosage (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g), different pH (3,4,5,7,9 and 11) and different settling time (15, 30, 45, 60, 90 min) by keeping the other parameter constant in order to study their effect in flocculation and to obtain the optimum condition for each parameter. The treated sample was tested for its COD, turbidity, color and concentration removal.

■3.0 RESULTS AND DISCUSSION

3.1 Characterization of The Chitosan Based Flocculants

Ch-g-PAM was designed and synthesized as described in methodology. The FTIR of chitosan and Ch-g-PAM are shown in Figures 3a and 3b, respectively. The FTIR spectrum of Figure. 3a illustrated characteristic peaks of chitosan: 3486 cm^{-1} (O–H stretch), 1659 cm^{-1} (carbonyl stretch in amides), 1151 cm^{-1} (bridge–O– stretch) and 1025 cm^{-1} (primary C–OH stretch). In Figure 3b, a sharper peak than (a) appeared at 1659cm^{-1} indicated the additional of amide group from PAM. Thus, it is confirmed that the PAM was successfully grafted onto chitosan backbone.
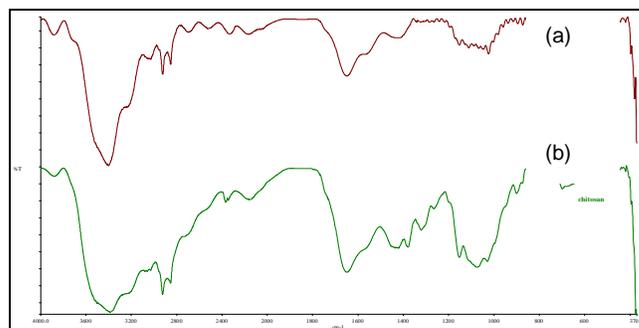
Figure 3 FTIR for a) chitosan; b) Ch-g-PAM

3.2 Effect of Dosage

Before each of the parameters was measured, the initial characteristic of textile wastewater has been determined. Using this value, the characteristic before and after the treatment was determined and compared. The initial characteristic of textile wastewater is listed in Table 1.

Table 1 Initial characteristic of textile wastewater

Parameter	Value
pH	12.15
COD	1245
Turbidity	231
Color	Dark Red

Dosage is one of the most important parameters that affect to the performance of chitosan and Ch-g-PAM in coagulation/flocculation. Basically, insufficient dosage or overdosing would result in the poor performance in flocculation. The effect of dosage was analyzed at pH 4, 200 rpm of mixing rate for 3 minutes and 40 rpm for 15 minutes and 30 minutes of settling time for a range of chitosan and Ch-g-PAM dosage which varied from 0.1 to 0.6 g.

The pH of wastewater was adjusted to pH 4 according to the characteristic of chitosan that only soluble in acidic aqueous phase. The pH was controlled by adding either weak acid (HCl) or strong base (NaOH). Tables 2 and 3 show the results obtained for effect of flocculant dosage towards color removal for chitosan and Ch-g-PAM, respectively.

Table 2 Data for effect of flocculant dosage for chitosan on color removal

Chitosan, g	Value
0.1	<0.5
0.2	<0.5
0.3	<0.5
0.4	<0.5
0.5	<0.5
0.6	<0.5

Table 3 Data for effect of flocculant dosage for Ch-g-PAM on color removal

Chitosan, g	Value
0.1	<0.5
0.2	<0.5
0.3	<1.5
0.4	<1.5
0.5	<1.5
0.6	<1.5

As can be seen, the optimum dosage where the removal of color was the lowest is 0.2 g. The color of wastewater changes from dark to transparent according to the code resulted (<0.5). Chitosan was acknowledged as a very efficient coagulant to remove color thus the different between the dosages were not obvious.

Ch-g-PAM was not as effective as single chitosan in removing the color where the optimum dosage used was 0.2 g in order to get the clearest. However, the result between 0.1 g and 0.2 g were closely determined but the optimum was selected based on the naked eye observation of the color. At highest

dosage (0.4-0.6 g), the efficiency decreased where the color degradation was not obvious.

Figures 4 and 5 show the results of COD and turbidity removal level at different dosage for both coagulant chitosan and Ch-g-Pam, respectively.
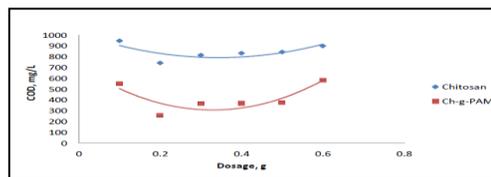
Figure 4 Graph of COD (mg/L) against dosage (g) for chitosan and Ch-g-PAM
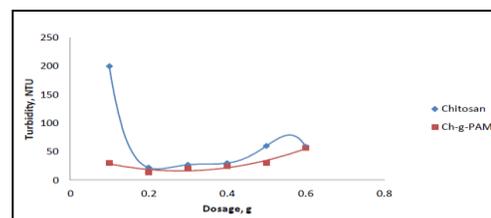
Figure 5 Graph of turbidity (NTU) against dosage (g) for chitosan and Ch-g-PAM

For dosage ranged from 0.1 g to 0.6 g, the COD and turbidity removal level using chitosan and Ch-g-PAM flocculant varies as shown in Figures 4 and 5 respectively and have similar trend. It shows that Ch-g-PAM was more effective compared to single chitosan in removing COD and turbidity.

Both COD and turbidity of wastewater treated using chitosan was high at the lowest dosage (0.1 g) and decreased before increasing back at higher dosage (0.4, 0.5 and 0.6 g). The optimum was occurred at 0.2 g where the turbidity and COD removal was the lowest (22.2 NTU and 743 mg/L respectively). The optimum value dosage of Ch-g-PAM was 0.2 g with COD removal 256 mg/L and turbidity level 38.3 NTU.

Higher dosage of chitosan (0.4-0.6 g) increased the COD level and turbidity due to the poor performance of chitosan where the excess polymer is adsorbed on the colloidal surfaces and producing re-stabilized colloids. Thus, there were no sites available on the particle surfaces for the formation of interparticle bridges. The re-stabilized colloidal particles become positively charged and cause the electrostatic repulsion among the suspended solids.

The graft copolymer (Ch-g-PAM) showed better performance when was compared to the base polysaccharides, because the presence of the dangling longer branches of PAM onto rigid polysaccharide backbone which leads to better approachability toward the contaminants. The flocculation characteristics of the graft copolymers were caused by polymer bridging. For effective bridging, the length of the grafted chains should be longer as to adsorb on a particle surface to another particle surface.

Figure 6 shows the absorbance spectra of chitosan at different dosage. The absorbance of each dosage decreased indicating that it removed the contaminant. However, at 0.2 g, the absorbance tended to be the lowest which means that the optimum removal of contaminant was achieved at 0.2 g of chitosan.
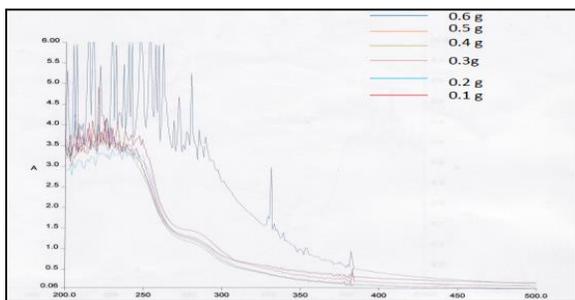
Figure 6 Absorption spectra of single chitosan towards dosage

Figure 7 shows the absorption spectra of Ch-g-PAM at different dosage. The result was slightly different compared to the effect towards COD removal and turbidity. Previously, 0.2 g was the optimum dosage to treat the wastewater using grafted flocculant. However, in UV-vis spechtrophometer analysis, 0.5 g was the selected one. This can be said that during the analysis, the sample of wastewater to be tested was mixed unconditionally with the flocs that formed during the settling time. The second optimum dosage was 0.2 g where the difference between the two absorbance was not obviously seen. Taking 550 nm as a reference, the value of absorbance at dosage 0.5 g and 0.2 g were 0.4 and 0.5 respectively, thus the optimum dosage chosen was 0.2 g Ch-g-PAM. The other value of dosages (0.1, 0.3, 0.4 and 0.6 g) shows the un-obviously pattern of decreasing absorbance.
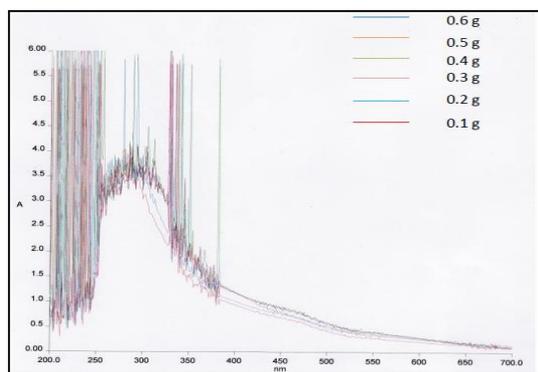
Figure 7 Absorption spectra of Ch-g-PAM towards dosage

3.2 Effect of Settling Time

The coagulation/flocculation process consisted of three distinct steps which helped the process flow. First, the flocculant was added and a rapid and high-intensity stirring was initiated. The purpose here was to obtain a complete mixing and homogenous dispersion of the flocculant in the wastewater, and to maximize the effectiveness of the biopolymer for the destabilization of colloidal particles as well as for the initiation of the coagulation. Critical parameters for this step are the duration and the velocity of stirring as too long duration could break up the aggregated flocs. For this reason, the suspension was slowly stirred in order to increase the contact between the flocculated particles and to facilitate the development of large flocs. The mixing was brought to an end and the flocs were allowed to settle at different duration (15, 30, 45, 60, 90 and 120 min).

Tables 4 and 5 show the results obtained from differentiating the settling time towards color removal of both coagulant chitosan and Ch-g-PAM respectively.

Table 4 Data for effect of coagulant dosage for chitosan on color removal

Chitosan, g	Value
15	<0.5
30	<0.5
45	<0.5
60	<0.5
90	<0.5
120	<0.5

Table 5 Data for effect of coagulant dosage for Ch-g-PAM on color removal

Chitosan, g	Value
15	<1.5
30	<1.5
45	<1.5
60	<1.5
90	<1.5

From Table 4, it showed that using chitosan as flocculant can degrade the color of wastewater from initially dark to almost clear color. The system used which was coding number showed the treated wastewater has a value of <0.5 for each of settling time. Compared to the initial value, the removal was quite high and proved that chitosan was efficient in removing the color of wastewater at any settling time.

Referring to Table 5, the efficiency using Ch-g-PAM in removing the color was not as good as chitosan. The code obtained from the analysis was higher which means that the color removed was not clear as much as chitosan.

Figures 8 and 9 show the comparison of COD removal and turbidity level using chitosan and Ch-g-PAM at various settling time respectively.
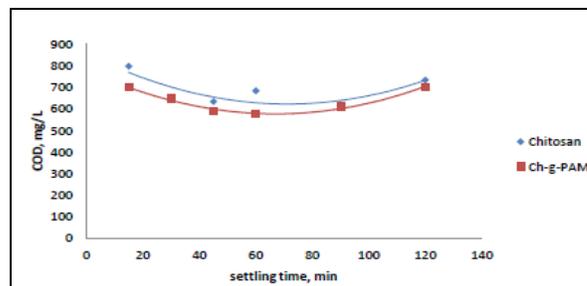
Figure 8 Graph of COD (mg/L) against settling time (min) for chitosan and Ch-g-PAM
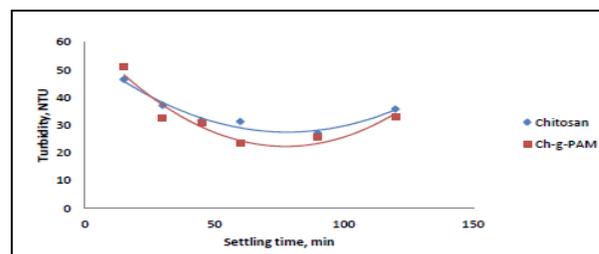
Figure 9 Graph of turbidity (NTU) against settling time (min) for chitosan and Ch-g-PAM

Looking at the results closely, regardless the 15 minutes settling time, the level of turbidity and COD removal was not obviously changes from 30 minutes to 90 minutes. It means that the settling can be done within 30 minutes without taking a longer time because the result was quite similar. Using a chitosan, the optimum settling time was at 90 minutes due to the lowest COD removal and turbidity which were 621 mg/L and 27.0 NTU respectively. For Ch-g-PAM, 60 minutes was enough for settling with turbidity 23.6 NTU and COD removal 639 mg/L. Based on Figures 7 and 8, the level of turbidity and COD removal was high initially and decreased as the settling time increased and after some times, the level was going down again. Longer time in settling tends the flocs produced to break again and mixed with the supernatant of the wastewater thus affected the turbidity of the wastewater.

The performance of grafted Ch-g-PAM was inferior to the un-grafted chitosan. This is because of the presence of the amino group into the backbone of chitosan. Chitosan makes smaller but stronger flocs, which settle slowly with time. On the other hand, grafted chitosan forms larger but relatively loose flocs with its long PAM side chains, which settle rapidly. During rapid settling, some portion of the floc breaks. These small flocs remain suspended for long time in the aqueous and increase the turbidity value of supernatant liquid. That was the reason why at longer settling time (90 min) as shown in Figure 9, the turbidity increased.

Figure 10 shows the absorbance spectra of chitosan at different settling time. It showed that as the settling time increased, the absorbance decreased and increased back at 120 minutes. The lowest absorbance occurred at 90 minutes settling time which was the perfect performance of flocculation compared to other time. 15 minutes was the least because no sufficient time to remove dye. The value of absorbance was the highest at 15 minutes of settling time.
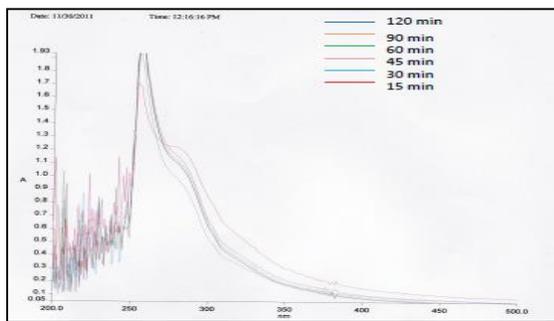
Figure 10 Absorption spectra of single chitosan towards settling time

Figure 11 shows the absorbance spectra of Ch-g-PAM at different settling time. As can be seen, the absorbance was closely packed and the changes were small and not obvious. However, the optimum settling time in removing contaminant was 60 minutes based on the lowest absorbance shown which is 0.7 (taking wavelength at 550 nm as a reference). One simple conclusion can be made by observing this absorbance pattern which is the tester does not need to wait for a longer time to settle the flocs because the contaminant removal level was close.
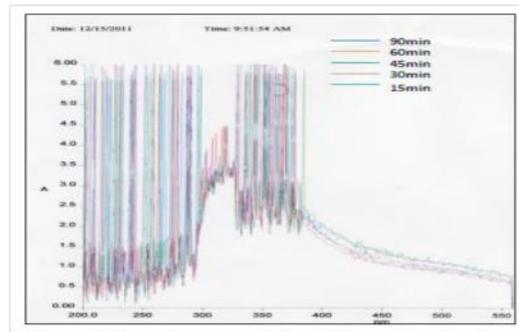
Figure 11 Absorption spectra of Ch-g-PAM towards settling time

4.3 Effect of Ph

Tables 6 and 7 show results of color removal using chitosan and Ch-g-PAM respectively at variety of pH starting with pH of 4 to 11. This experiment was run at dosage 0.2 g and settling time 60 minutes.

Table 6 Data for effect of pH for chitosan

Chitosan, g	Value
3	<0.5
4	<0.5
5	<0.5
7	<1.5
9	<1.5
11	<1.5

Table 7 Data for effect of pH for Ch-g-PAM

Ch-g-PAM, g	Value
3	<0.5
4	<0.5
5	<1.5
7	<1.5
9	<1.5
11	<1.5

From Table 6, chitosan efficiency to remove color was acknowledged. It was very dependent on pH and in this case, it was 4. Although the result shown was similar, from the observation, the clearest color was at pH 4. These results are explainable by some phenomena. Once chitosan gets dissolved in water, it becomes a charged molecule. The repulsion between these molecules keeps chitosan at a uniform dispersion. At lower pH, better dispersion cause better interaction effect that consequently improved the elimination. Thus, the best acidity level for chitosan to de-color wastewater was at pH 4.

At pH above than 4, improvement of color removal was observed. However, greater amounts of chitosan were required. In this case, the dosage of chitosan used was 0.2 g according to the optimum obtained from the previous experiment. Thus, the color removal of wastewater for pH greater than 4 was not fully clear (<1.5).

As shown in Table 7, the best results were performed at lower pH (acidic medium) compared to basic medium. At pH 3 and 4, the degradation of color was higher where the result yield was <0.5 respectively. However, by observation during the experiment, the clearer was at pH 4 which was the optimum. At higher pH (5-11), the Ch-g-PAM was not much effective to

remove color due to the solubility characteristic of one of the polymer grafted which is chitosan that insoluble in basic medium. Figures 12 and 13 showed the comparison of COD removal and turbidity level using chitosan and Ch-g-PAM at different pH respectively.
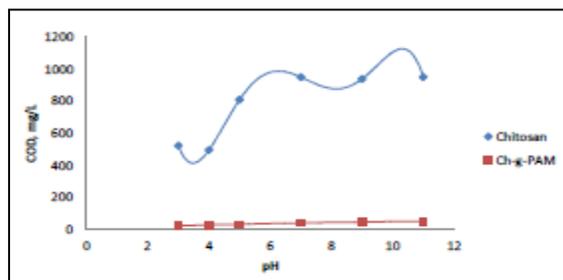
Figure 12 Graph of COD (mg/L) against pH for chitosan and Ch-g-PAM
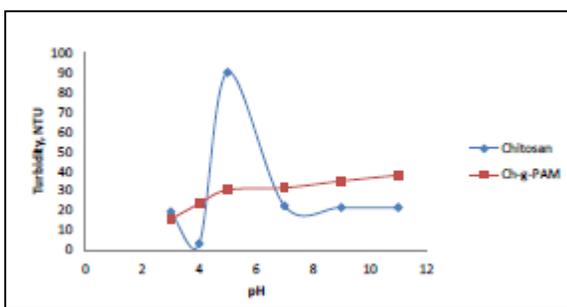
Figure 13 Graph of turbidity (NTU) against pH for chitosan and Ch-g-PAM

In Figure 12 the removal of COD result obtained proves that grafted Ch-g-PAM was more effective compared to chitosan. However, from Figure 13, it shows the vice versa. At pH 4 by using chitosan, the COD removal level and turbidity was 496 mg/L and 3.3 NTU respectively, pH 3 was the most effective condition in reducing the level of COD and turbidity using a Ch-g-PAM. The COD removal and turbidity at pH 3 was 27.8 mg/L and 15.6 NTU, respectively.

There were high percentage of the functional group of NH_2 on chitosan surface has been protonated at pH 4 and gradually reduced as pH increased. As pH increased the contribution by the charge neutralization of the chitosan to destabilize the particles become less important. Based on observation, the floc produced by chitosan appears rapidly at pH 4 and form a large size, which can be easily settled.

Comparing chitosan and Ch-g-PAM, chitosan was found pH dependent whereas Ch-g-PAM was efficient over the wide range of pH. In Figure 13, the results obtained shows that chitosan was more effective than Ch-g-PAM and this might because the flocs produced mix with the supernatant and thus affected the turbidity measurement.

Figure 14 shows the absorbance pattern of wastewater towards variety of pH starting at acidic medium, pH 3 to basic medium, pH 11 for chitosan. The most effective of pH used was at pH 4 where the absorbance was the lowest and the least effective was at pH 11. This was due to the solubility characteristic of chitosan which soluble in acidic medium and insoluble in basic medium.
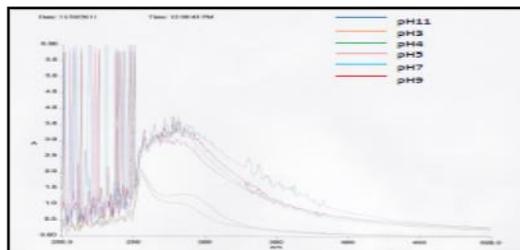
Figure 14 Absorption spectra of single chitosan towards pH

Figure 15 shows the spectra of sample after being treated with Ch-g-PAM. The results obtained were consistent with the previous result where the optimum pH in removing the contaminant was 3. At pH 3, the value of absorbance was the lowest which is 0.3 (taking 550 nm as reference) compared to other pH. Thus it shows that this flocculant showing a better performance at acidic medium.
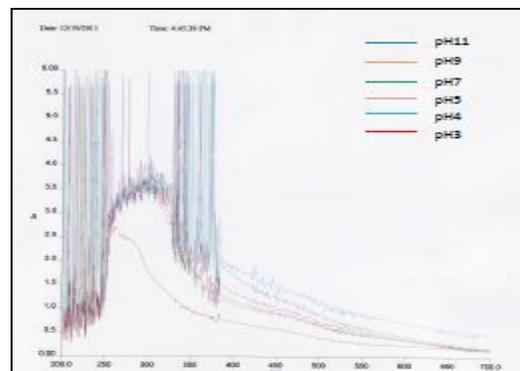
Figure 15 Absorption spectra of Ch-g-PAM towards pH

■4.0 CONCLUSION

The grafted flocculant was successfully synthesized using microwave initiated method. Flocculant dosage, settling time and pH affect the performance of the flocculation process. Under the range used in this study, the optimum condition to treat textile wastewater was achieved at 0.2 g, pH of 4 and settling time of 90 minutes for chitosan while for Ch-g-PAM was at 0.2 g, pH of 3 and settling time of 60 minutes. It also appeared that Ch-g-PAM perform better to treat textile wastewater compared to chitosan.

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