



# Optimization of Graft Polymerization and Performance of Carboxymethyl Chitosan / Polyacrylamide Flocculants

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Received date: 24 March 2014; Accepted date: 8 April 2014; Published date: 25 July 2014

Academic Editor: Sumit Mishra

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## Abstract

In this study, amphoteric graft copolymer-based flocculants were prepared by conventional peroxy graft copolymerization of acrylamide (AM) onto carboxymethyl chitosan (CMCH) using potassium persulphate (PPS) initiator. The optimization of grafting of AM onto CMCH was carried out by studying the influence of various process parameters including CMCH, acrylamide and PPS concentration, as well as reaction temperature and time on percent grafting. FTIR spectral and thermal analyses of polyacrylamide/carboxymethyl chitosan graft copolymer (CMCH-*g*-PAM) were studied to furnish evidence of grafting. By performing the grafting process via reacting carboxymethyl chitosan (2%), acrylamide (6%) in presence of PPS (0.1%), highest grafting percentage was found at reaction temperature of 55°C with reaction time of three hours. The flocculation of the kaolinite suspensions was investigated by studying the effect of CMCH-*g*-PAM dosage, treatment time and pH of suspensions. The graft co-polymer flocculants resultant in this study exhibited higher efficiency comparing with those obtained from homo-polymers of carboxymethyl chitosan or polyacrylamide. Furthermore, the flocculation efficiency of these grafted copolymers was significantly increased with increasing the grafting percentage, where the maximum efficiency (93%) was attained at the highest grafting percentage (146%).

**Keywords:** Carboxymethyl chitosan-*g*-polyacrylamide; Suspended kaolinite; Amphoteric flocculants.

## Introduction

Water pollution is owing to all human activities including domestic, industrial and agri-

cultural and thus, the causes of pollution in water can be considered endless. However,

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**Cite this Article as:** Emad Ali SOLIMAN, El-Sayed Mohamed El-Sayed MANSOUR, Hammed Ahmed Mohamed HASSAN and Noha Amaly Mohammed HASSAN (2014), "Optimization of Graft Polymerization and Performance of Carboxymethyl Chitosan / Polyacrylamide Flocculants", Journal of Research & Developments in Chemistry, Vol. 2014 (2014), Article ID 351498, DOI: 10.5171/2014. 351498

manufacturing plants is a major cause of water pollution that carries away their waste that can contain various dissolved or suspended harmful and toxic substances in fresh water bodies. Suspended substances, nutrients and organic load as chemical oxygen demand (COD) contribute major pollutants in these bodies. Therefore, the removal of these contaminants in waste water is one of the fundamental targets in waste treatment [1]. Further, stringent regulations are releasing in recent years to prevent discharge of these wastes into the municipal sewerage system without any treatment. Many technologies are developed to treat various types of wastes at adequate levels. However, the economic performance, including investment costs and operation of conventional waste treatment are prohibitive for a variety of industrial simulation, particularly small-scale sector. In this case, the physical-chemical coagulation-flocculation process is a most used key step in the primary purification of industrial wastewater and effluents and in some cases in secondary and tertiary treatment [2].

Generally, such solid-liquid separation processes are carried out by using inorganic or organic coagulating agents. The most common extensively used inorganic coagulants are alum and iron salts. The multivalent characteristics of these cations strongly attract to the colloidal particles rendering them insoluble. On the other hand, organic coagulating agents are also widely used such as polyelectrolyte (cationic or anionic), polyampholytes and nonionic polymers are more efficient agents than their inorganic counterparts and thus, they don't produce voluminous and gelatinous flocs [3]. Surface-adsorbed cationic and anionic polyelectrolytes or polyampholytes promote suspended particle coagulation rates by two distinct mechanisms: charge neutralization and/or polymer bridging [4-5].

Although the synthetic polymers can be tailored to the needs of a particular application and perform well in flocculation, they are often associated with environmental pollution. Natural polymers have the advantages

of low cost and biodegradability, but the biodegradability will affect the storage life and the flocculation performance. Therefore, several attempts have been made to combine the best properties of both by grafting synthetic polymers onto the backbone of natural polymers [6]. One of the advantages gained is the consequent reduced biodegradability because of a drastic change in the original regular structure of the natural polymer as well as the increased non-degradable synthetic polymer content within the product. However, the grafting of shear degradable polymers onto a rigid polysaccharide backbone was found to produce fairly shear-stable systems [8-9].

Chitosan is a cationic linear pseudo-natural polymer obtained from N-deacetylation of chitin in alkaline media. Chitosan has several intrinsic properties such as biocompatibility, biodegradability and its degradation products are non-toxic, as well as, its outstanding chelating behavior and thus it directed to numerous applications in waste water treatment, chemical industry, pharmacy, biotechnology and biomedicine [9-13]. Chitin and chitosan are widely used for waste water treatment for the removal both of dispersed particulates and dissolved pollutants. Further, water treated with these polymers experimentally showed a decrease in COD, total nitrogen and microbial population [14-15]. However, acidic solubility, low thermal and mechanical stability and flexible behavior of chitosan are the stumbling blocks in broadening its application in water treatment. Many physical and chemical modification approaches have been developed to jump over these blocks. Recently, a lot of attention has been paid to chemical modification. Though many researchers have shown that primary derivatization followed by graft copolymerization was one of the promising methods to improve tremendously chitosan properties, particularly, via amalgamation of synthetic polymers [16-21]. Grafting flexible polyacrylamide chains onto rigid polysaccharides such as chitosan has been suggested to have a potential to develop efficient, shear-stable, and controlled biodegradable flocculants for the treatment of industrial and mineral processing effluents [22]. In the

present study, carboxymethyl chitosan (CMCH) was chosen as polysaccharide backbone with polyacrylamide as a graft polymer for the preparation of amphoteric floccu-

lants. Whilst chitosan (CH) is a cationic polyelectrolyte, carboxyalkyl chitosan can be considered a polyampholyte which carry positive and negative charges [23]. Thus, the synthesis of graft copolymer was carried out using PPS-induced free radical polymerization. The effect of concentration of CMCH, AM and PPS as well as the reaction temperature and time on the graft copolymerization was studied by determining the grafting parameters. Moreover, the flocculation performance of the obtained grafted copolymers was investigated by studying the effects of pH values, flocculation time and dosage of the flocculants on treating kaolinite suspensions.

## Materials and Methods

### Materials

Chitosan (DD=85%), potassium persulphate (PPS), chloroacetic acid, acetic acid (99%), acrylamide (monomer), and glutaraldehyde (60%) were obtained from Sigma-Aldrich chemical LTD (Germany). Acetone (99.9%), sodium hydroxide, was purchased from El-Nasr pharmaceutical company for chemicals (Egypt). Kaolinite (Egyptian highly refined ball clay powder with very fine size) used mainly for manufacturing refractory bricks and mortar, was kindly donated from Alexandria Company for Refractories.

### Preparation of carboxymethyl chitosan (CMCH)

Carboxymethyl chitosan was prepared according to the method reported by Chen and Park [24]. Briefly 10 g of chitosan were dispersed in 100 ml of aqueous isopropyl alcohol (50 %) with stirring at room temperature for 30 min. Aliquot portions of 15 ml sodium hydroxide (10 M) were added at an interval of 5 min under agitation at room temperature. The reaction mixture was stirred for an additional 45 min. Then, 30 g of chloroacetic acid was dissolved in this

mixture portion wise at interval of 5 min under warming at 55-60 °C with stirring for 1 h. The resultant solution was filtered. The filtrate was washed with aqueous solution of ethanol (80 % v/v), then dried in a vac-

uum oven at 50 °C for 24 hrs.

### Preparation of carboxymethyl chitosan polyacrylamide graft copolymers (CMCH-g-PAM)

Definite amounts (0.3 -24 gm) of CMCH were dissolved in 45 ml distilled water, then (0.05 - 1 gm) PPS dissolved in 10 ml distilled water then slowly added to the three necked flask to initiate graft copolymerization. In a constant temperature, water bath was maintained at a constant temperature in the range of 25 - 60 °C. Nitrogen gas was bubbled for 30 min to remove the dissolved oxygen under stirring. After 10 min, a predetermined amount (1 - 6 gm) of acrylamide dissolved in 45 ml distilled water was charged into a three necked round bottom flask. After grafting time (1-5 hrs), CMCH-g-PAM was precipitated by the addition of an excess of acetone (80 %), filtered, and then the precipitate was washed by aqueous ethanol solution (90% v/v) to eliminate all of CMCH, AM and its homopolymer. Afterwards, graft copolymers were dried under vacuum at 50 °C. The grafting percentage was calculated using the following equation;

$$\% G = [W_{\text{CMCH-g-PAM}} / W_{\text{CMCH}}] \times 100 \% \quad [25]$$

### FTIR spectroscopic analysis

FTIR spectra were obtained by a Shimadzu AIM8400 FTIR spectrometer equipped with ATR-8400M objective (Shimadzu Co, Ltd, Tokyo, Japan). This objective adopted a germanium prism tip. The spectra were recorded over a range of 500-4000 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> and averaged over 32 scans.

### ***Thermogravimetric analysis (TGA)***

Thermal analysis was performed by using Shimadzu TGA-50 Analyzer (Shimadzu Co. Ltd., Kyoto, Japan). Specimen (10 mg) were thermally scanned from 25 to 900°C in the open corundum crucibles under nitrogen with a flow rate of  $\approx 200$  ml/min) at a scanning rate 10°C/min.

### ***Scanning Electron Microscopy (SEM)***

Microstructure and topography of CMCH and CMCH-g-PAM films were characterized by a JEOL JSM-6360 LA scanning electron microscope (JEOL Ltd., Rigaku, Tokyo, Japan). Examination was performed at an acceleration voltage of 15 kV with a magnification power of 1000-3000X. Film samples were first coated with gold using JFC-1100E sputtering coater.

### ***Swelling measurement***

Definite weights (2 gm) of CH, CMCH or CMCH-g-PAM were put onto sintered glass funnel, immersed in 1000 ml beaker filled with distilled water and then covered with Para-film. Afterwards, water was withdrawn by water pump throughout constant time of 15 min, and then weight the swollen samples. Weight values were taken at equilibrium, which was determined by three consecutive measurements having the same weight. The swelling ratio of the specimens was calculated according to the following equation:

$$S_R = \frac{W_s - W_d}{W_d} \quad [26]$$

Where  $W_s$  and  $W_d$  represented the weights of the swollen and dry state samples, respectively. The dynamic weight gain was determined versus time to illustrate the swelling behavior of these polymers.

### ***Flocculants performance assessment (Jar Test)***

To prepare the clay suspension (turbid water), accurate weighed amounts (5 - 20 gm) of kaolinite powder were dispersed in distilled water with stirring using mixer at 500 rpm for 2 min. Adjusting pH value (4-9) during stirring was achieved using 0.1N NaOH or HCL. Then stirring continues for another 2 min at a rate of 100 rpm. Temperature keeps in water bath at constant degree, with adding NaCl to obtain solution with ionic strength ranging from 0.1 to 0.6 M. Afterwards, allow the dispersed solutions to settle for 1 - 20 min., before sampling using automatic pipette from a height of 2 cm below the surface in each beaker for turbidity measurement. For assessing flocculants' efficiency, control (without flocculants) was first used to measure the initial turbidity ( $T_0$ ), and so, the turbidity of the clay suspension after adding different amounts of the flocculants (1 - 10 ppm) ( $T_1$ ) was measured using the same sampling method. The turbidity removal percent was calculated by the following equation;

$$\text{Turbidity removal \%} = \frac{T_0 - T_1}{T_0} \quad [27]$$

## **Results and Discussion**

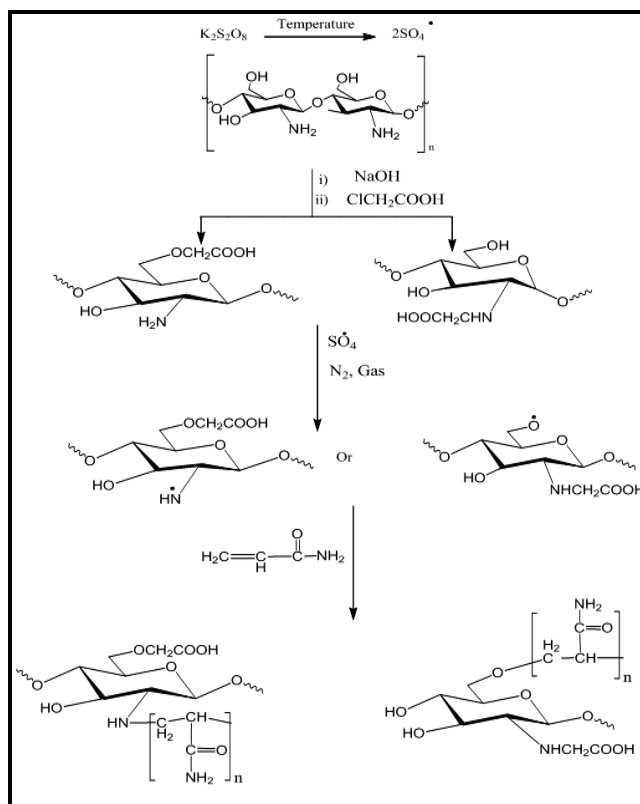
### ***Factors affecting grafting percentage***

#### ***CMCH concentration***

Generally, grafting percentage (%G) was found to increase significantly with increasing CMCH concentration as shown in Figure 1, where %G was 66 at CMCH concentration of 0.3 %, however it reached its maximum (146 %) at CMCH concentration of 2 %. Whereas, further increase in CMCH concentration led to a significant decrease in grafting percentage which reached to 18% at CMCH concentration of 24 %. The initial increase in the grafting percentage associated with the increase of carboxymethyl chitosan concentration can be attributed to the increase in the number of active sites (amine and hydroxyl groups) on carboxymethyl chitosan molecules leading to accommodate

higher amounts of acrylamide monomer (AM) and consequently increase the produced grafted PAM (scheme 1). Whereas, further increase in CMCH concentration may increase the viscosity of the reaction medium that can cause hindrance of the reactants'

collision and thus reducing their reactivity, in addition to a decrease of AM / CMCH ratio. These findings were in agreement with those obtained in the study of Ranjbar-Mohammadi with his colleagues on grafting chitosan onto wool fabric [26].



**Scheme 1: CMCH grafting mechanism**

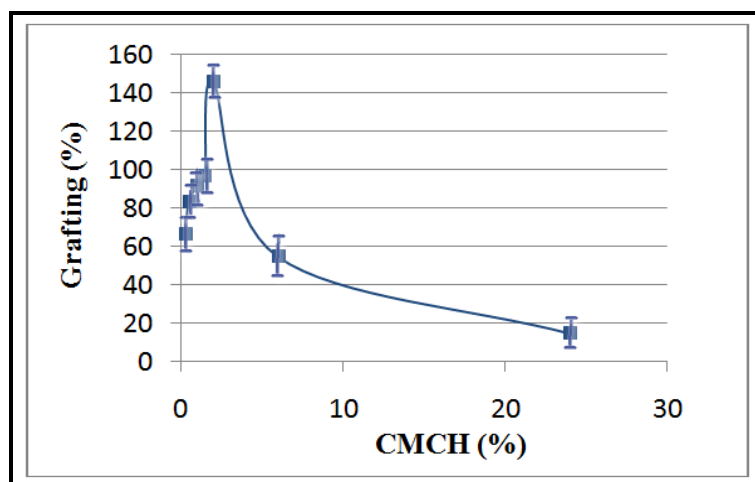


Figure 1: Effect of CMCH concentration on grafting percentage

#### Monomer concentration

The grafting percentage grew dramatically with increasing AM concentration reaching its maximum value at AM concentration of 6 % (Figure 2). However, higher increase in AM concentration led to a noticeable decrease of the grafting percentage. These results were not in agreement with the results reported by Ávila with his workers [7]. This

behavior could be explained by the fact that an increase of AM concentration leads to the accumulation of monomer molecules in close to the CMCH backbone. Hence, increasing

monomer concentrations over saturation could be in favor of free radical-induced polymerization of AM monomer on expense of its reaction with CMCH polymer backbone.

i.e., homopolymerization overlies on grafting copolymerization. Furthermore, the formation of homopolymer in the presence of an excess of monomer can shield the polymer backbone and consequently stands as a hurdle towards graft copolymerization. Such assumptions can be associated with diffusion limitations, which can be governed by the dilution [26].

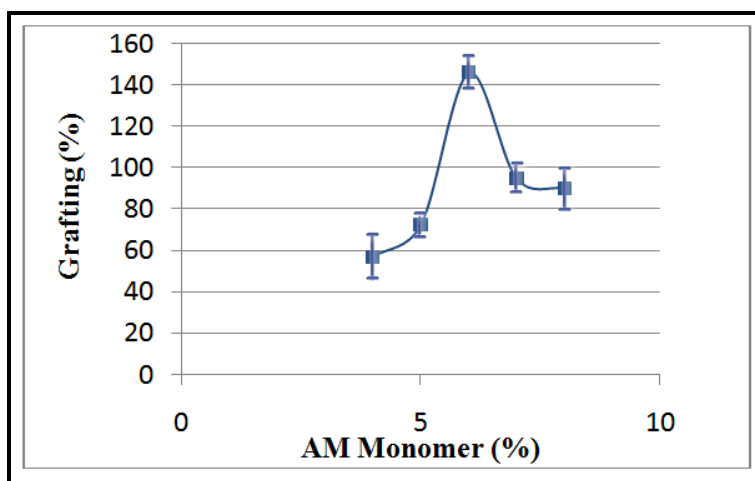


Figure 2: Effect of monomer concentration on grafting percentage

### Initiator concentration

Indeed, initiator concentration is well known to have a crucial impact on polymerization. Therefore, determining the optimum concentration of PPS in view of the enhancement of grafting was achieved by using concentrations in the range of 0.05 – 1 % at constant concentrations for both CMCH and AM. The obtained results were presented in Figure 3. These results indicated that the grafting percentage increased with increasing the initiator concentration up to 0.1 %, thereafter it decreased gradually with the further increase in PPS concentration. The increase of grafting percentage can be attributed to the increase of active grafting sites on the CMCH backbone chains (free radicals) with the increase of initiator concentration which

in turn led to higher grafting. While, its decrease at PPS concentration over 0.1 % can be explained on the basis that excessive free radicals produced simultaneously at these high concentrations could activate multiple free radicals coupling that led to the formation of AM homopolymer or cross-linking CMCH since free radicals formed onto CMCH chains can be terminated prior to AM addition [28]. Hence, the formation of homopolymers can be expected due to the non-availability of active sites on CMCH. On the other hand, at higher initiator concentration, PPS can decompose to  $\text{HSO}_4^\bullet$  and  $\text{O}_2$  whilst  $\text{O}_2$  act as scavenger for free radical formed on polymer backbone chains and thus decreasing the grafting polymerization [29].

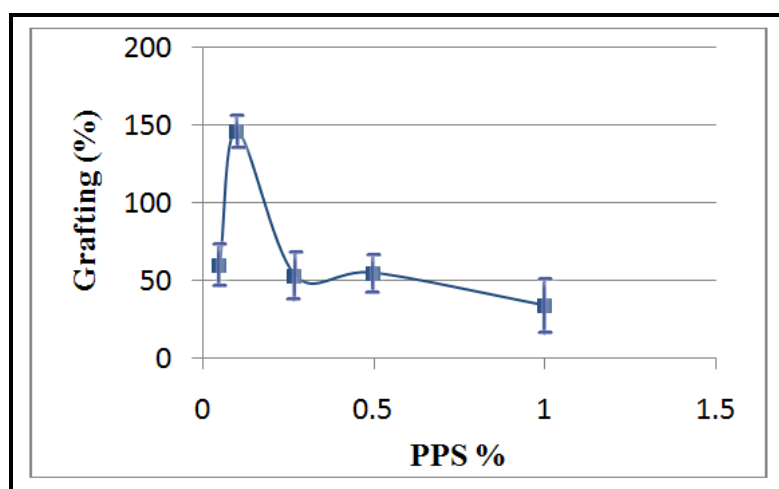


Figure 3: Effect of initiator concentration on grafting percentage

### Grafting temperature

As shown from Figure 4 when grafting copolymerization was accomplished at varying temperature in the range of 45 - 65°C, highest grafting percentage was attained at 55°C, while it was decreased at lesser or upper optimum temperature. These findings can be explained in view of the fact that the low temperatures are insufficient to activate free radicals' formation. However, obtaining the highest grafting percentage at optimum temperature can be ascribed to its ability to

promote formation of free radicals and swelling of CMCH leading to enhance diffusion of AM monomer. The further increase in temperature can be in favor of the combination of macro-radicals to be dominant reactions leading to the formation of AM homopolymer which increases the viscosity of the reaction medium and thereby hinders for the diffusion of monomer and inhibits graft copolymerization [30]. Based on the aforementioned, the optimum temperature meets the halfway between both tendencies, since it facilitates the diffusion of AM mono-

mer into CMCH phase and activates the formation of free radicals via increasing the

dissociation rate of initiator to be in the active form [29].

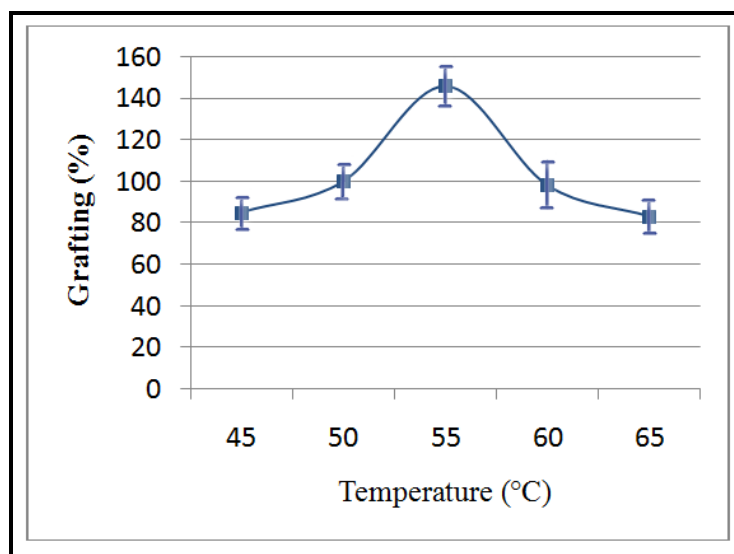


Figure 4: Effect of temperature on grafting percentage

#### Grafting time

The effect of the reaction time on the grafting percentage was presented in Figure 5. The grafting percentage was gradually increased with extending the reaction time from 1 to 3 hrs. Nevertheless, it decreased with the prolongation of the reaction time over 3 hrs. These findings are in agreement with those of Joshi and Sinha that reported that there is a slight decrease in the grafting percentage with the increasing time of polymerization, and thereafter it becomes constant [22]. The increase of the grafting percentage with the prolonging time of the reaction can be attributed to give a break to produce more free

radicals onto polymer backbone and open up its structure. Forasmuch, the bulky groups, such as carboxymethyl ( $-\text{CH}_2\text{COOH}$ ) in the CMCH can promote the swelling and thereby diffusion of PPS and AM into CMCH [30]. However, the observed decrease in the grafting percentage with the long time of reaction can be explained on the basis of depleting acrylamide monomer with the progression of the grafting process. Furthermore, this decrease may be also attributed to enhance the viscosity of the reaction medium by growing the yield of graft copolymers and subsequently slow down reactants' collision and lower grafting ratios [29].



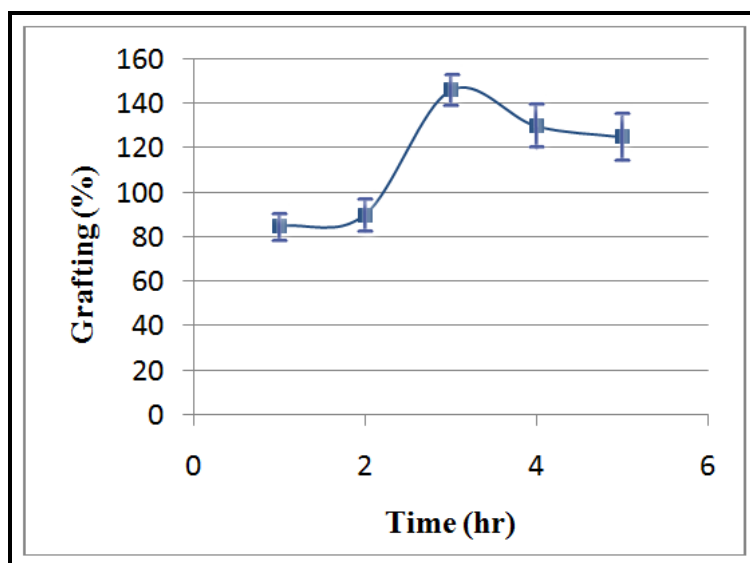


Figure 5: Effect of grafting time on grafting percentage

#### ***Physico-chemical properties characterization***

##### ***Compositional properties***

The spectra of CH and grafted polymer (CMCH-*g*-PAM) were shown in Figure 6. FTIR spectrum of chitosan exhibited two strong characteristic absorptions peaks; one  $\sim 1575\text{ cm}^{-1}$  due to N-H bending and other peak assigned to N-H and O-H stretching at  $\sim 3369\text{ cm}^{-1}$ . Furthermore, adsorption peak appeared at  $1321\text{ cm}^{-1}$  due to C-N bending, in addition to a small band at  $1649\text{ cm}^{-1}$  which refers to (C=O) of acetamide group (-CONH-) belonging to acetylated unites of chitosan. However, FTIR spectrum of CMCH-*g*-PAM exhibited an absorption band

at  $\sim 1662\text{ cm}^{-1}$  due to C=O (amide) stretching vibrations, peak at  $\sim 1423\text{ cm}^{-1}$  of  $\text{COO}^-$  stretching vibrations and peak at  $\sim 2945\text{ cm}^{-1}$  due to the C-H of  $\text{CH}_2$  stretching vibrations. Such graft copolymer spectrum also showed more intense broad adsorption peak appeared at  $\sim 3390\text{ cm}^{-1}$  due to the overlapping of O-H and N-H stretching of CMCH and PAM.

The slight shifting and more intensity of the latter absorption peak confirm grafting reac

tion between carboxymethyl chitosan and polyacrylamide.

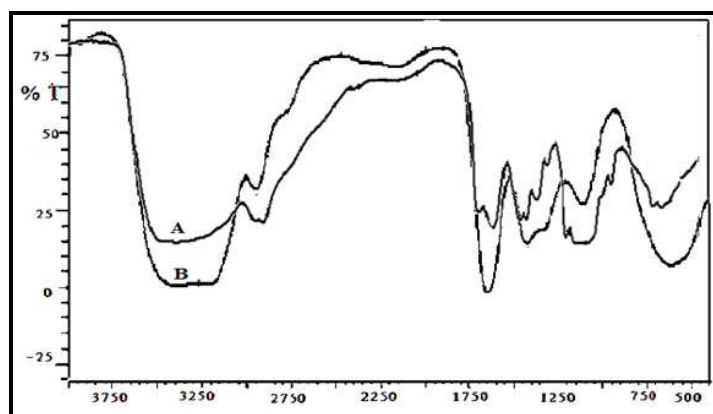


Figure 6: FTIR spectra of Chitosan (A) and CMCH-g-PAM copolymer (B)

### Thermal stability

Thermal stability of CH and CMCH-*g*-PAM were assessed by thermogravimetric analysis. Figure 7 presented the thermograms of chitosan and graft copolymer. The thermogram of chitosan exhibited four distinct stages of thermal degradation; weight loss 13.8 % in the range of 27 – 152 °C was corresponding to the loss of adsorbed and bound water. Since chitosan contains (NH<sub>2</sub>) and (OH) functional groups, the hydrogen bonding force is strongly formed among molecules [31]. The second stage of the thermal degradation occurred at 220 - 455 °C with weight loss was ~ 21 %. This weight loss can be attributed to degradation and deacetylation of chitosan [32]. Further weight loss by ~ 20 % occurred at temperature range 455 – 800 °C due to the dehydration of glycoside unit and decomposition of

the acetylated and deacetylated units of chitosan. On the other side, CMCH-*g*-PAM exhibited also four subsequent distinct degradation (weight loss) stages (25 – 799 °C) ; first stage was from 25 – 168 °C with weight loss ~ 16 % due to the loss of adsorbed and bound water, second stage 228 – 352 °C during which ~ 17 % weight loss was assigned to decarboxylation of CMCH and subsequent loss of CO<sub>2</sub>. Afterwards, ~26 % weight loss between 354 – 472 °C that contributes to the degradation of both the CMCH backbone and the grafted polyacrylamide chains amalgamated onto CMCH-*g*-PAM. Finally ~22 % weight loss up to 799 °C due to the decomposition of the glycosidic units of CMCH. These findings revealed that grafting slightly increased the initial decomposition temperature of CMCH-*g*-PAM compared with that for chitosan.

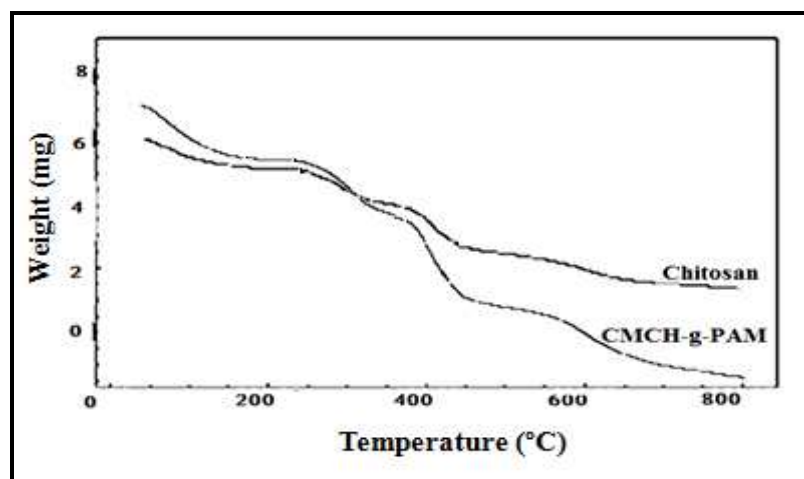


Figure 7: Thermograms of Chitosan and CMCH-*g*-PAM copolymer

#### ***Morphological and micro-structure properties***

Scanning electron micrographs of carboxymethyl chitosan and its graft copolymer with PAM were shown in Figure 8. Figure 8A exhibited cohesive and dense structure of CMCH via appearing relatively smooth and continuous surface with no distinct perturbations. Whereas, SEM micrograph of CMCH-*g*-PAM (Figure 8B) showed

that the graft copolymerization of chitosan with polyacrylamide dramatically changed the conformation of CMCH polymer chains, since the heterogonous structure was observed because the interruption of the chain packing occurs by conformational defects leading to major disruption in the perfection of the chain packing. These conformational defects in CMCH chains can be attributed to the grafted PAM chains and consequently confirms graft polymerization.

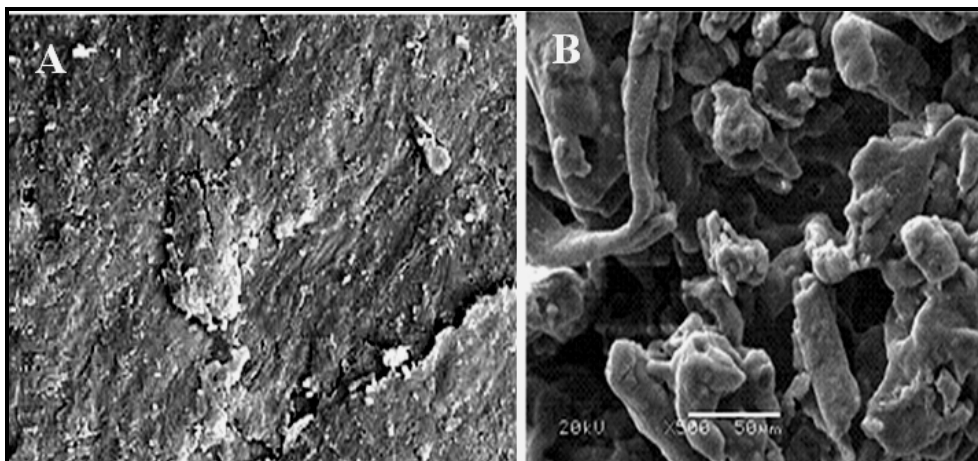


Figure 8: Scanning electron micrographs (SEM) of CMCH (A) and CMCH-*g*-PAM copolymer (B)

### Swelling behavior

Swelling of CH, CMCH and CMCH-g-PAM was gravimetrically determined by measuring the weight gain with time when they were placed in distilled water at room temperature. Measurements were taken at equilibrium, which was determined by three consecutive measurements having the same weight. Chitosan and CMCH gave swelling by 40 and ~50 %, respectively at 15 min, after which these polymers were going to dissolve.

However, swelling of grafted copolymer reached to ~55% at 30 min. (Figure 9). Change swelling behavior of chitosan may be attributed to the introduction of carboxymethyl groups that improve remarkably the solubility of CMCH in aqueous solution [33]. However, hydrogen bonding is responsible for enhancing moisture retention ability of graft copolymer, where, the hydrophilic groups such as carboxylic and amino groups is known to form H-bonds with water molecules.

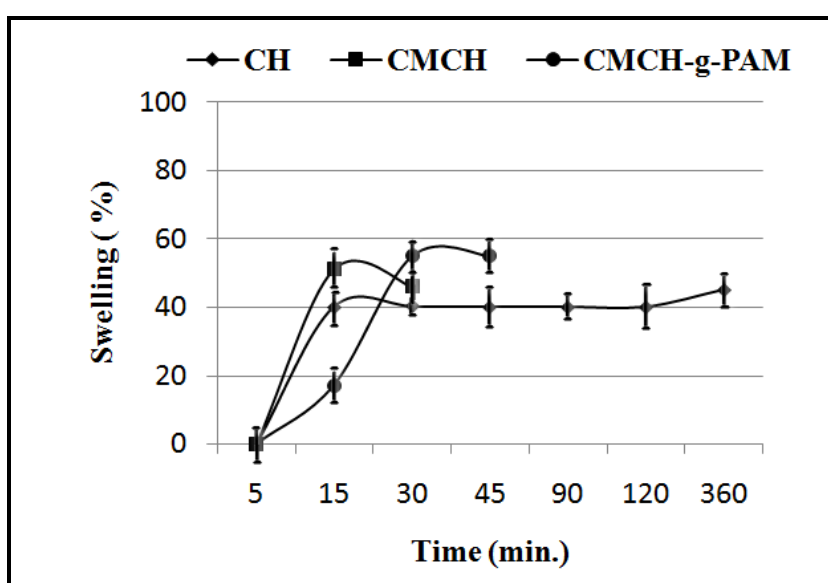


Figure 9: Swelling percentages of chitosan, CMCH and CMCH-g-PAM vs. time

### Factors affecting flocculation (turbidity removal of clay suspensions)

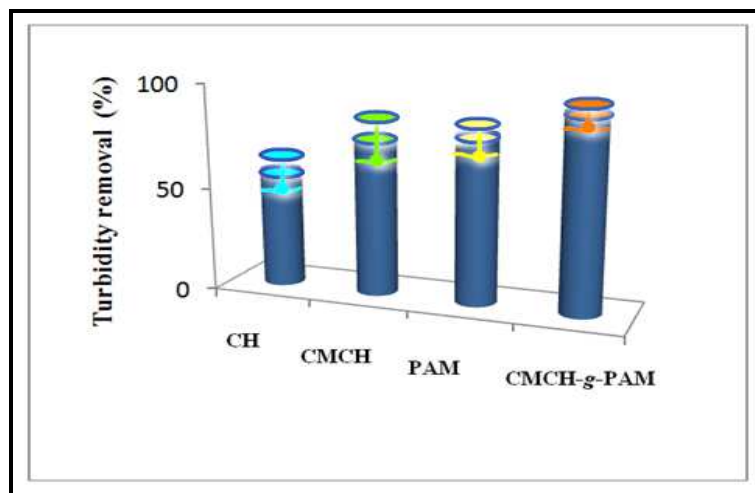
#### Polymer type

The compositional characteristics of the polymer-based flocculants including both type and content of functional groups, branching, and molecular weight of the polymer are considered to be among the main factors affecting the flocculation efficiency. Therefore, the flocculation performance of CH, CMCH, PAM, and CMCH-g-PAM was investigated by measuring the turbidity of kao-

linite suspensions after flocculation (Figure 10). From these results, it was observed that CMCH-g-PAM grafted copolymer has the highest flocculation efficiency. On the other hand, chitosan revealed the lowest efficiency. However, the efficiency of CMCH was comparable to that of PAM. High flocculation performance of graft copolymer can be due to their loose and branched structures giving potential flexible behavior that enhances the bridging effect of these flocculants. Additionally, charge density arising from various charged functional groups ( $-\text{COO}^-$ ,  $-\text{NH}_2^+$ ) on these flocculants provides flocculation power

towards fine dispersed kaolinite particulates. This was on contrary of CH, CMCH, and PAM

which are considered linear polymers.



**Figure 10: Turbidity removal of clay suspension using chitosan, CMCH, PAM and CMCH-g-PAM**

### ***pH***

In the present study, the initial turbidity of kaolinite suspensions (turbid water) was measured at different pH values. These measurements indicated that the initial turbidity was increased by increasing pH as presented in Figure 11. This can be due to the increase of – ve charge density on kaolinite particulates in alkaline media (at basic pH 9) that increase repulsion between clay particles together and with –ve hydroxyl groups of basic medium which prevent aggregation of the particles. On the contrary, the highest percentages of turbidity removal from clay suspensions using CH, CMCH and CMCH-g-PAM were observed in acidic medium (pH = 6) (Figure 12). This result can be attributed to increasing + ve charge density on CH, PAM, CMCH and CMCH-g-PAM as a result to protonation of amine groups that form + ve charge centres on these polymer molecules, whereas, kaolinite particles have – ve zeta potential in this acidic medium and consecutively so strong electrostatic attraction has been achieved between oppositely charged macromolecular flocculants and clay particles (Charge neutralization) . However,

the superior flocculating efficiency of CMCH-g-PAM and CMCH compared with CH can refer to higher charge density arising from many of amine groups carrying a positive charge at the acidic pH and thus the hydrophilicity and wettability of these polymer molecules were increased. Furthermore, high molecular weight and branching of graft copolymer enhance the flocculation performance since the extended chain tends to be adsorbed onto the particle in a flat configuration, whereas the negative charges on the bare parts of surface of one particulate easily attach to the excess net residual positive charges of the polymer absorbed on another one [34, 35]. On the other side, CMCH-g-PAM accomplished only about 75 % of turbidity removal at neutral pH as shown in Figure 12. Such lower efficiency of turbidity removal occurring at pH 7 compared with that occurring at acidic pH can be attributed to that at this neutral pH, kaolinite zeta potential becomes more – ve, whilst less protonation of amine groups leads to lower + ve zeta potential of flocculants than that occurring in acidic medium and consequently attraction force between clay particulates and polymer can be reduced. In alkaline medium (pH = 9), the

turbidity removal percentage of grafted copolymer decreased to about 37 %. This can be due to - ve zeta potentials for both carboxylate groups of graft copolymers and ka-

olinite particulates and simultaneously less protonation of amine groups, therefore the resultant electrostatic repulsion can reduce the flocculating performance [6,36].

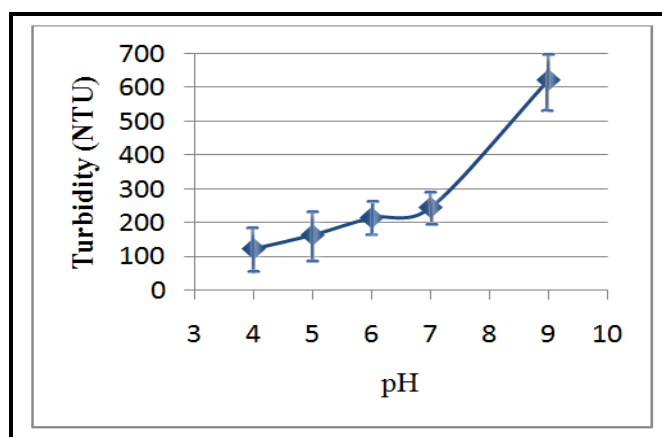


Figure 11: Effect of pH on the initial turbidity of clay suspension (10 gm/L)

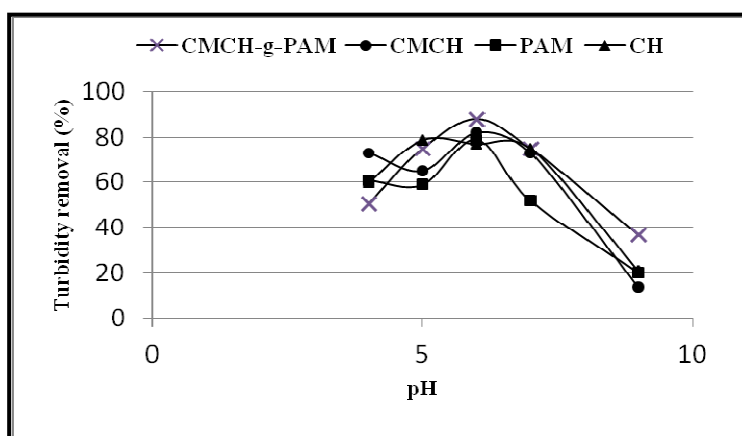


Figure 12: Effect of pH of clay suspension (10 gm/L) on turbidity removal using flocculants at dosage of 5 ppm

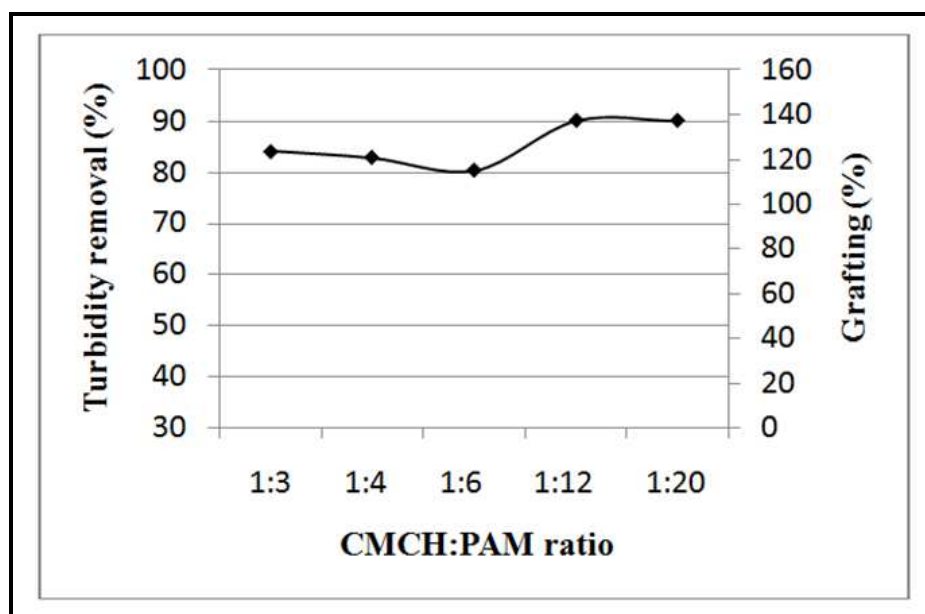
### Grafting percentage

The grafting percentage of CMCH-*g*-PAM exhibited a noticeable effect on the flocculation efficiency (Figure 13). In general, turbidity removal percentage for clay suspension using graft copolymer was noticeably increased with increasing the grafting percentage, so the graft copolymer having the highest grafting percentage (146%) exhibited effi-

ciency of the turbidity removal that reached ~ 90 % with a noticeable mechanical stability for the resultant flocs (Figure 14). Since these expanded polymer chains play an axial role in bridging mechanisms that are highly responsible for flocculation performance. These results can be explained on the basis that increasing grafting ratio was associated with increasing the molecular weight of polymers and the length of the grafted poly-

mer chains that led to enhancing flocculating performance via bridging mechanism. On the other hand, positive charges of protonated amine groups ( $\text{NH}_3^+$ ) mounted onto PAM long branched chains linked to the CMCH backbone, whilst these CMCH backbone chains carry negative charge on anionic carboxylate groups ( $-\text{COO}^-$ ) when dissociate at pH 6 enhancing the flocculation performance via charge neutralization mechanism. Hence, the adjacent charged groups that repel each other will lead to expanding the polymer

chains. Therefore, the bridging by high molecular weight polymer chains can be considered the main mechanism in the flocculation of kaolinite particulates with the contribution of role of ionic functional groups in charge of neutralization, because increasing the degree of ionicity (charge density) of the more expanded form of polymer chains leads to enhancing flocculating power with increasing the rate of settling, i.e., increasing of the floc size [37].



**Figure 13: Effect of grafting percentage on turbidity removal from clay suspension (10 gm/L) at pH 6 using CMCH-g-PAM at dosage of 5 ppm**





**Figure 14: Photograph indicating turbidity removal from kaolinite suspension (10 g/L) using chitosan and CMCH-g-PAM (% G = 146), at dosage of 2.5 ppm and pH 6**

## Conclusion

In the present study, carboxymethyl chitosan was successfully grafted with acrylamide using potassium persulphate as an initiator. Graft copolymers with high grafting percentages reached to 146% were obtained. The optimization of the parameters reaction were studied. The finding of these experi-

ments indicated that performing grafting copolymerization using carboxymethyl chitosan and acrylamide at the concentration of 2 and 6%, respectively in the presence of 0.1% of initiator at 55°C for 3 hrs resulted in graft copolymer having the highest grafting percentage. The graft copolymers were structurally characterized using FTIR, and SEM. Moreover, the thermal stability of the graft copolymer was assessed using TGA. These analyses confirmed the formation of graft copolymer having higher initial thermal decomposition temperature. The flocculation performance of the obtained graft copolymer was tested using kaolinite suspensions, where the effect of grafting percentage and dosages of graft copolymer and pH on flocculation performance were studied with comparison to chitosan, CMCH and PAM.

Under the same conditions, CMCH-g-PAM was found to be more efficient than chitosan, carboxymethyl chitosan and polyacrylamide.

## Acknowledgements

The authors highly appreciate that this work has been funded by Egyptian Academy of Scientific Research and Technology (ASRT).

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