Egyptian Journal of Chemistry

Flocculation Activity of Grafted Chitosan for Water Treatment

Raedah A.S. Alatawi[1], Abeer Abdulaziz H. Bukhari[1], Hanan M. A. Al-Sayed[2,3], Faridi U[4], S.A. Khali[5], Wael S. Mohamed[6]*

[1]*Department of Chemistry, Faculty of Science, University of Tabuk, Tabuk 71421, Saudi Arabia.*

[2]*Department of Nutrition and Food Science, Faculty of Home Economic, University of Tabuk, Tabuk, Saudi Arabia*

[3]*Food Science Department, Faculty of Agricultural, Ain Shams University, Cairo, Egypt.*

[4]*Biochemistry department, Faculty of Science, University of Tabuk, Tabuk 71421, Saudi Arabia*

[5]*Chemistry Department, Alwajh-College, University of Tabuk, Tabuk, Saudi Arabia.*

[6]*Polymers Department, National research Centre ,Cairo, Egypt.*

Abstract

Chitosan was grafted with 2-(dimethylamino) ethyl methacrylate monomer, or with 2-(dimethylamine) ethyl methacrylate-acrylic acid monomers. The obtained chitosan poly 2-(dimethylamine) ethyl methacrylate (I) as well as Chitosan poly- 2-(dimethylamine) ethyl methacrylate-acrylic acid (II) hybrids were evaluated in flocculation performance of kaolin suspension and also in the clarification behavior of treated tap water when combined with alum. The polymerization was carried out using potassium persulphate/sodium bisulphite redox initiation system at 60^OC for 3 hours. The obtained two grafted samples I and II were characterized using FTIR, thermal properties expressed as thermogravemetric analysis (TGA) and differential scanning calorimeter (DSC) as well as X-ray. The water clarification from kaolin suspension was evaluated for the two obtained hybrid polymers with respect to the pH, polymer dosage, and settling time. The combination between the prepared hybrid and alum was also investigated. The results showed that the grafted chitosan copolymers I & II exhibited thermal stability. The best flocculation for the two prepared hybrid I & II were observed at pH 6.5 and dosage concentration of 1 ppm with recorded turbidity of 3.01 & 2.66 NTU. The best flocculation was observed for native chitosan at pH 7.5 and 4.85 NTU. Combination between 25 ppm alum with 0.5 of each of I & II induced more water clarification with turbidity values of 1.84 & 1.65.

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

Organic flocculants are generally water-soluble polymeric materials or organic polyelectrolytes such as polyacrylamide (PAM) and its derivatives [1-2]. Many other water flocculating agents are now common such as different cationic gums represented by cationic starch, dextrin, guar. Chitosan is biopolymer having a characteristic structure in which there is a cationic amino group capable of introducing interaction with the negatively charged particles. In addition, chitosan is a polymer with a moderate to high molecular weight, so bridging mechanisms are possible. Also, chitosan exhibits solubility changes as a result of changes in pH or salt concentration. The solubility of chitosan increased in acidic media due to protonation of the amine groups, except in sulfuric acid solutions: although dissolving properties are dependent on other characteristics of chitosan such as molecular weight, degree of deacetylation and ionic composition of the solution. Chitosan dissolved in acidic media can precipitate when diluted into alkaline solutions [3-5]. Flocculation of kaolin suspensions in water using chitosan was studied in the pH range 5-9 and the turbidity ranging from 10 to 160 NTU. Chitosan, in presence of trace quantities of a substance present in aqueous soil extracts, effectively reduces turbidity due to kaolin by flocculation and settling. Flocculation efficiency is very sensitive to pH, and reaches a maximum at pH 7.5. The optimal chitosan concentration required to effect flocculation is independent of kaolin concentration within the range examined [6]. Chitosan samples - prepared with different molecular weights and degrees of deacetylation (DD) - were

---

_____

tested for coagulation with bentonite suspensions at pH 5 and 7 in demonetarized water and in tap water. It was found that coagulation was better in tap water than in demonetarized water, for every condition and lower doses of chitosan were required at pH 5 rather than at pH 7 [7]. The effects of chitosan characteristics - (i.e., degree of deacetylation and molecular weight) and environmental conditions (i.e., ionic strength and pH) on the flocculation of anaerobic sludge - were investigated. The results showed that chitosan enhanced the flocculation of sludge; the flocculation efficiency depended on both the degree of deacetylation and molecular weight. Chitosan with 85% degree of deacetylation was more effective than that with 70%, as the former required a lower dose to obtain 90% flocculation at all studied pH values [8]. Modification remains a viable tool to incorporate functional groups onto chitosan surface - which increase the attention due to their high specificity and good tolerance towards other functional groups being present. These properties could be achieved using suitable modifiers as dimethylamine ethyl methacrylate and acrylic acid [9-10]. The present work is aimed to prepare and characterize two flocculant agents based on chitosan namely, chitosan-g-poly DMAEMA and chitosan-g-poly2-(dimethylamino)ethylacrylate (DMAEMA) / acrylic acid (AA) hybrids. The characterization includes FTIR, thermal properties (thermogravimetric analysis and differential scanning calorimetric) and X-ray diffraction. Evaluation of the obtained two hybrid copolymers as flocculating agents for clarification of kaolin suspension was studied. The obtained results were compared with those obtained for chitosan blank. The effect of combination between alum and synthetic flocculating agents on the clarification behavior was also investigated. The work was further extended to include application of the optimum conditions in the treatment of tap water.

2. Experimental

2.1. Chemicals and materials

Chitosan powder was supplied by Fluka chemical with acetylation degree 14%. The viscosity average-molecular weight 70000 KDa. The Kaolin in this study was a commercial grade and having the following specification: particle size: 2 mm (83±2.0% w/w); particles larger than 300 mesh: 0.03% maximum; specific surface area: 16.5m2 g^{-1} (BET); bulk density of 0.35 kgdm^{-3}; moisture 2%

maximum; silica: 45%; alumina: 38%; ferric oxide 0.5%, titania: 0.45%; loss on ignition 15%. DMEMA and AA monomers were supplied with Fluka. Potassium persulphate (KPS) was supplied with Aldrich. Sodium bisulphite (SBS), acetic acid and other chemicals were of laboratory grade chemicals.

2.2. Preparation of chitosan-g-poly (DMAEMA) and chitosan-g-poly (DMAEMA/AA) hybrids [11]:

2 gm of dry chitosan was dissolved in 2% acetic acid in a 250 ml stoppard flask, followed by the addition of 1gm of acidified DMAEMA solution (pH 4.1 ±0.2 with nitric acid) or admixture of 1g acidified DMAEMA and 0.5 g acrylic acid monomers. 10 mmol/20 mmol of the potassium persulphate / sodium bisulphite (KPS/SBS) redox initiation system was slowly added to the flask during stirring at room temperature. The flask was placed in Shaker water bath using the following sequence: 50°C for 30min; 60°C for 30 min and finally 70°C for one h. The solid contents of the obtained copolymers were determined gravimetrically. Scheme 1 illustrates the proposed mechanism of the grafting of DMAEMA is the same with that previously reported for AEMA.

2.3. Separation of chitosan–g-poly DMAEMA and chitosan–g-poly DMAEMA /AA:

For some chemical characterization such as FTIR, thermal analysis (TGA and DSC) and X-ray diffraction, the grafted chitosan copolymers were separated in acetone, filtered and washed several times with distilled water until pH 7 was reached. The obtained copolymers were dried at ambient conditions.

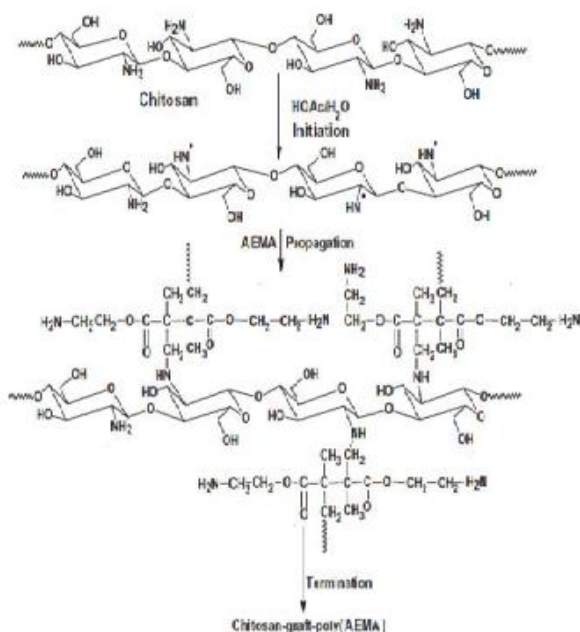### 2.4. Preparation of kaolin solutions and flocculation procedure

Kaolin suspensions were prepared by the addition of 2 g of the kaolin powder thoroughly mixed with 1L of tap water and allowed to settle undisturbed for about 30min. The turbid supernatant was withdrawn and diluted to obtain 30 and 170 NTU for the experiments. The hybrid copolymers were diluted with distilled water to give a 0.5 wt-% solution. Chitosan-g-poly (DMAEMA) and chitosan-g-poly (DMAEMA/AA) hybrids with concentration 10% were independently added to 500 ml of the kaolin suspension, stirred for 10 mins. At the following different stirring speed 210, 90, 30 rpm using jar tester JLT4 -VELP Scintifica. The turbidity of the supernatant was measured directly or after

_____

different studied settling time (Table 1 and figures 5:12).

2.5. Testing and analysis

2.5.1. Polymer Characterization

X-ray diffraction for chitosan, chitosan–poly DMAEMA and chitosan-poly DMAEMA-AA have been investigated by X-ray diffraction using Philips analytical X-ray B.V. The IR spectra of the prepared samples were recorded using Nicolet 380, Thermo FTIR spectrophotometer. Thermogravimetric analysis (TGA) was carried out at a temperature range starting from the room temperature up to 600OC under inert nitrogen atmosphere with heating rate of 10OC/min using Shimadzu TGA-50, Japan. Samples were also analyzed by derivative thermo-gravimetry (DTG) to assist in the identity of the decomposition behavior of the investigated samples. Differential Scanning Calorimeter (DSC) was carried out at the same condition of the TGA using Shimadzu DSC-50, Japan.

Scheme 1: Mechanism of grafting of DMAEMA onto chitosan [11]

2.5.1.1. Water Evaluation

The turbidity measurement of the supernatant solution in Nephelometric Turbidity Units (NTU) using HANNA, HI 98703 Turbidity meter. The instrument was calibrated using standard solutions according to the standard method before use. The data values of the measurement were an average of five sequence values. The conductivity was measured in micro siemens (µs) using Conductivity Meter Model FE 287, Micro Conductivity meter, EDT Instruments. PH was determined by pH meter model HANNA Instruments. The organic matter expressed [7] was determined by consumption of KMnO4 in acidic solution. All other water chemical analysis was performed in accordance to the standard methods [8].

3. Results and Discussion

3.1. Characterization of chitosan-g-poly (DMAEMA) and chitosan-g-poly (DMAEMA/AA)

Both of chitosan-g-poly (DMAEMA) and chitosan-g-poly (DMAEMA/AA) copolymers were characterized using Infra red spectroscopy (FTIR), (X-ray) Diffraction analysis and Thermal gravimetric analysis (TGA and DSC).

3.1.1. FTIR spectroscopy

Figures 1 (A, B, C) show the FTIR spectra of chitosan blank, chitosan-g-poly (DMAEMA) and chitosan-g-poly (DMAEMA/AA) respectively. In the IR spectrum of un-grafted chitosan (Figure 1A) the absorption bands at 1600cm^{-1} is due to characteristic N-H bending vibration for chitosan [9]. On the other hand, the FIIR spectra of both chitosan-g-poly (DMAEMA) and chitosan-g-poly (DMAEMA/ AA) show disappearance of N-H band with presence of new other characteristic bands. This manifests the proceeding of the graft copolymerization reactions on the primary amino groups of chitosan. Also, the presence of medium band - that appeared at 1383 cm^{-1}, in figure 1B and 1C - could be attributed to symmetric stretching for C-N group which confirm the presence of DMAEMA polymer in the two studied copolymers [10].
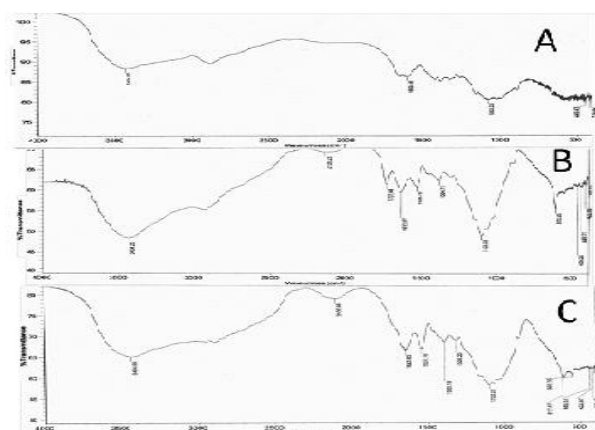

Figure (1): FTIR spectrum of **A)** ungrfted chitosan, B)chitosan -g- poly (DMAEMA), C) chitosan -g- poly (DMAEMA / AA)

The presence of characteristic bands at 1660-1700 could be related to the C=O groups of each of acrylate and carboxylic acid groups of the two studied copolymers. The broad band at 3340 cm^{-1} is due to stretching of –OH groups and 1109 cm^{-1} for C-O stretching of primary alcohols of abundant chitosan [11].

3.1.2. X-ray diffraction

The results represented in Figures 2 (A, B, C) show the results of Wide-Angle X-Ray (WAXS) diffractograms of the un-grafted chitosan as well as chitosan-g-DMAEMA and chitosan-g-DMAEMA-AA copolymers. It is evident that chitosan (figure 2A) is characterized by a remarkable crystalline peak at 2θ=20° [12]. This beak disappears when chitosan is grafted either with DMAEMA or DMAEMA/AA which confirms inclusion of the crystalline region in grafting after depletion of all amorphous regions (figure 2 B & C). Moreover, the presence of new remarkable crystalline peaks at 2θ =30 ^{o} and 2θ=31° for chitosan-g-DMAEMA/AA is attributed to the characteristic acrylic acid band at this region (figure 2 C).

3.1.3. Thermal Analysis:
3.1.3.1. Thermo gravimetric analysis

TG is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure 3 shows the thermo-gravimetric analysis (TG) and derivative thermo-gravimetry (DTG) for chitosan (blank), chitosan-g-DMAEMA (graft yield 47%), and chitosan-g-DMAEMA/AA (graft yield 68 %), respectively. As it is evident, the spectrum for chitosan shows three characteristic stages for decomposition. The first stage starts at 46°C and ends at 91°C with a weight loss of 5.3 %. This could be recognized due to the moisture content for chitosan. This observation is in accordance with other related work [13]. The second stage related to the main decomposition of chitosan macromolecules occurs in one step of decomposition starting at 246°C and ends at 307°C with maximum decomposition temperature of 283°C and weight loss of 45%. Similar work was also reported for chitosan [14]. The third stage of decomposition is related to the carbonization process which occurs up to 600°C with a weight residue of 17.5%. For the two studied chitosan derivatives (chitosan-g-DMAEMA and chitosan-g-DMAEMA/AA), the first stage starts at

45°C & 46°C and ends at 100°C & 88°C with weight loss of 15%&13% respectively. The second stage of decomposition, representing the main decomposition, proceeds in two steps. The first step starts at 200°C and ends at 245°C with maximum decomposition temperature of 224°C. The weight loss in this step for the two studied samples was 16% & 19% respectively. This step, most probably, could be related to the degradation of the grafted chains of either poly-DMAEMA or poly-DMAEMA/AA [15]. Moreover, the second step of degradation for the two studied samples starts at 248°C and ends at 304°C with maximum decomposition temperature of 285°C. The weight loss for the two samples was 33% & 28 % respectively. This step of degradation simulates and corresponds to main degradation process recorded for chitosan. The third stage of degradation occurs up to 600°C with weight loss of 0.9 % & 16 % for the two samples.
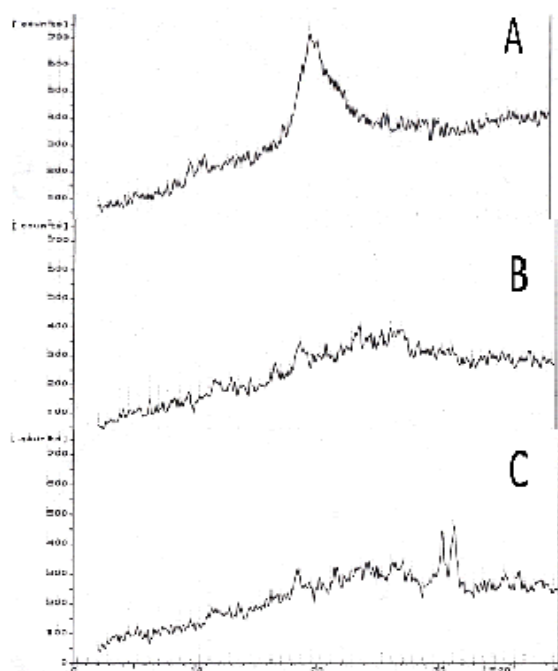

Figure (2): XRD Patterns of **A)** ungrfted chitosan, B)chitosan -g- poly (DMAEMA) C) chitosan -g- poly (DMAEMA / AA).
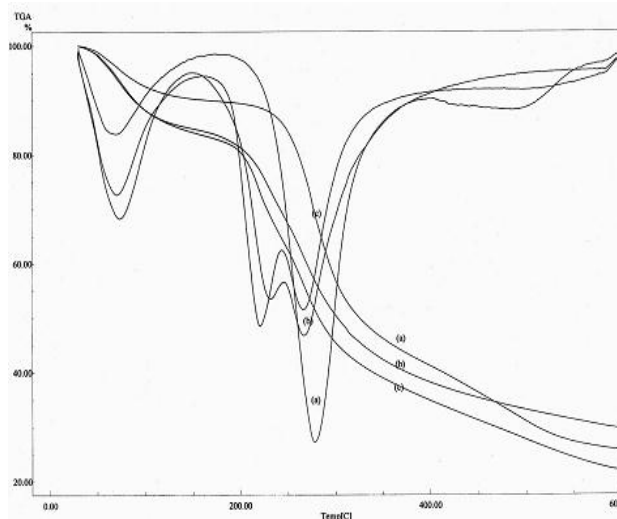
Figure (3): The thermogravimetric analysis of (a) un-grafted chitosan, (b) chitosan-g - poly (DMAEMA) and (c) chitosan - g - poly (DMAEMA /AA).

3.1.3.2. Differential scanning calorimetry

Figure 4 shows the DSC of chitosan, chitosan-g-DMAEMA, and chitosan-g- DMAEMA/AA, respectively. It is evident that the DSC of chitosan shows an endothermic ranging between $45^{o}C$ and $105^{o}C$ with a peak at $61^{o}C$ which due to the loss of water. Moreover, there is an exothermic transition at $298^{o}C$ may correspond to the decomposition of the main macromolecular structure of chitosan. The DSC of chitosan grafted samples shows an endothermic peak at $70^{o}C$ and related to the loss of bonded water. Also, there is one exothermic peak at $262^{o}C$ and $250^{o}C$ and two endothermic peaks at $238^{o}C$ and $281^{o}C$ for chitosan-g-DMAEMA also at $222^{o}C$ and $279^{o}C$ for chitosan-g-DMAEMA/AA.
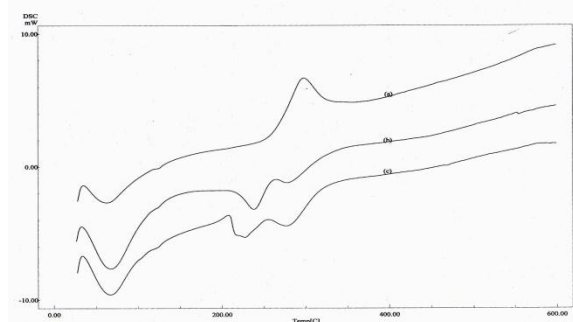

Figure (4): The differential scanning calorimeter of (a) ungrafted chitosan, (b) chitosan-g - poly (DMAEMA) and (c) chitosan - g - poly (DMAEMA / AA).

3.2. Evaluation of the prepared grafted chitosan hybrids as flocculants

The prepared copolymer hybrids namely, chitosan -g- poly (DMAEMA) and chitosan-g-poly (DMAEMA/AA) were evaluated as flocculating agents for suspended kaolin solutions having two different turbidity valued (30 and 170 NTU); and the data obtained is compared with that obtained by using un-grafted chitosan. The best conditions for flocculation were studied in terms of pH; polymer dosage; settling time and combination of different alum concentration with the polymer.

3.2.1. Effect of different pH

The data obtained in Figure 5 shows the effect of different pH of the kaolin solution on the flocculation performance (expressed as turbidity value, NTU) for chitosan-g-poly (DMAEMA) hybrid (I) and chitosan-g-poly (DMAEMA/AA) hybrid (II) and un-grafted chitosan. The dosage of three examined flocculants was adjusted at 1ppm. The flocculation performance was measured as a function of the turbidity (NTU) of the kaolin suspended solution after 30 min. settling time. It is evident, irrespective of the turbidity values of the suspended solution that the best flocculation for chitosan-g-poly (DMAEMA) hybrid (hybrid I) and chitosan-g-poly (DMAEMA/AA) hybrid (hybrid II) was at pH 6.5. Meanwhile, the best flocculation for un-grafted chitosan was at pH 7.5.
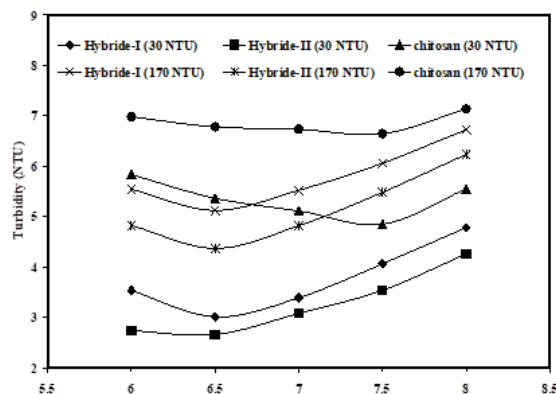

Figure (5): Effect of pH on turbidity removal of kaolin. Flocculant agents dosage: 1ppm, settling time 30 min.

It is well known that the best flocculation occurs when the net charge at the surface of the polymer and colloidal silica of kaolin is approximately zero [16]. Also, chitosan is known as cationic substrate with its abundant amino groups. Colloidal silica with its negative charge will be

absorbed at the surface of chitosan and best flocculation with highly magnitude of negatively charged colloidal particles was obtained at pH 6.5. This finding in accordance with other articles demonstrated that the best flocculation for chitosan was obtained at pH 7.5 [17]. For the two hybrids I & II, the chitosan structure was changed by adding either tertiary amino groups of DMAEMA monomer alone (I) or in conjunction with acrylic acid (II). So, variation will occur to the hybrids I and II with respect to the molecular weight, charge density as well as the branching effect. This variation greatly influences the mechanism of flocculation and the optimum pH suitable for flocculation. The data also reveal that the flocculation efficiency for the studied compounds in the following sequence hybrid II > hybrid I > chitosan. This was observed regardless of the magnitude of turbidity value of the suspended solution.

3.2.2. Effect of different dosage concentration

Figure 6 shows the variation of dosage concentration (0.1 – 1.5 ppm) on the flocculation performance of the three studied flocculating agents using two different kaolin suspended solution having 30 and 170 NTU. The pH was adjusted at 6.5 for each of hybrid I & II and 7.5 for chitosan. It is evident, regardless of the type of flocculating agents and turbidity values that the best flocculation increases by increasing the dosage concentration up to 1 ppm after which level off occurs. Overdosing higher than 1 ppm results in the reversal of particle charge (from negative to positive) due to the adsorption of excess hybrid I, hybrid II or chitosan molecules, and it is difficult for the particles to form flocs because of electronic repulsion of the adsorbed flocculating agents. It is also evident that the hybrid II gives higher flocculation performance than the other two studied flocculating agents. For instance, the obtained turbidity values for hybrid II were 2.66 & 4.37 for the two kaolin suspended solutions (30 &170NTU). This is against 3.01 & 5.12 as well as 4.85 & 6.64 were obtained for each of hybrid I and chitosan for the two-kaolin suspension solution [18].

3.2.3. Effect of different settling time

The settling time is the time needed for the sedimentation of very smaller particles of colloidal silica. The data obtained in Figure 7 represent the effect of the settling time on the flocculation performance expressed as turbidity value (NTU) for

the examined hybrids I & II as well as chitosan. The dosage concentrations and pH were adjusted as previous optimum conditions. It is evident that by increasing the settling time the turbidity values of two kaolin suspended solutions (30&170) decrease, i.e., more flocculation performance is mentioned by increasing the settling time from 5 min to 45 min.
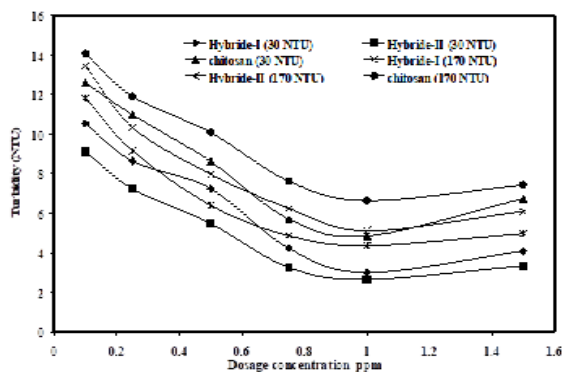

Figure (6): Effect of flocculants agent dosage on turbidity removal of kaolin. pH 6.5 for each hybrid I & hybrid I and 7.5 for chitosan, settling time 30 min.

More logically, increasing the contact time between the flocculating agents in the solution is accompanied by more accumulation of the fine and smaller particles. Another probable explanation states that the finer particle needs more time for sedimentation in a colloidal particle. A particle of diameter 0.1mm needs 38 sec for sedimentation. Meanwhile, a particle of diameter 1×10^{-5}mm needs 6.3 year for sedimentation [5]. More interesting feature is that the turbidity value (NTU) of the chitosan flocculating agent is about twice the value obtained by hybrid II. In other words, hybrid II has more effective action for flocculation than chitosan.
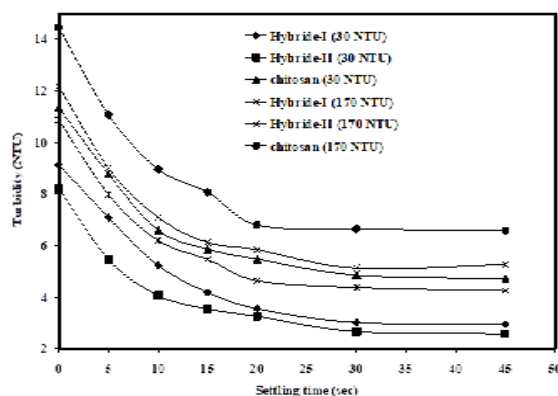

Figure (7): Effect of settling time on the turbidity removal of kaolin. Flocculant agent dosage 1ppm, pH 6.5 for each hybrid I & hybrid II and 7.5 for chitosan.

3.3. Effect of combination between alum and synthetic flocculating agents

It is well known that a trace amount of alum in water after clarification is harmful for human health and causes serious diseases. On the other hand, utilization of synthetic flocculating alone for water flocculation may be not effective for recommended turbidity value (NTU) to be used according to the standard value of WHO. So, successful study was made for combination between the synthetic flocculating agents and alum to reduce the magnitude of Al ion in clarified water in one side and also to obtain most optimum water turbidity clarification on the other.

The data represented in Figures 8-10 show the effect of different alum (20-40ppm) / synthetic flocculating agents' concentrations on the turbidity values of kaolin suspended solution having 30 NTU. The flocculation was performed at optimum conditions of 45min settling time and pH 6.5 for hybrids I & II and 7.5 for chitosan.

The obtained results clarify the following aspect: a) regardless of the synthetic flocculating agent type, increasing alum concentration is accompanied by gradual increase of the flocculation performance of the treated suspended water up to 25ppm after which level off occur, reflecting the advantage of alum as a flocculating agent for negatively charged silica, b) regardless of the alum concentration, increasing synthetic flocculating agent or chitosan concentrations were accompanied by observed increment of the flocculation performance of the treated suspended water up to 0.5 ppm after which level off occur.
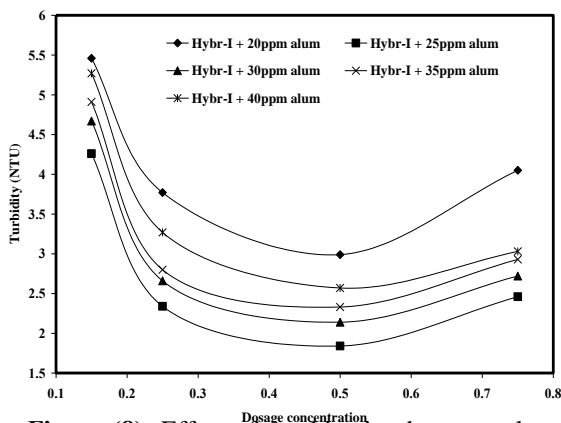

Figure (8): Effect of combination between alum and hybrid I at different concentration on the turbidity removal of kaolin. Kaolin suspended solution (30 NTU), pH 6.5, and settling 45min.
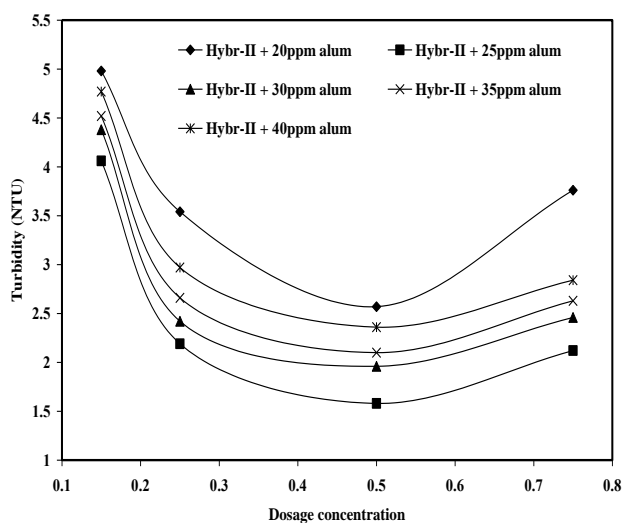

Figure (9): Effect of combination between alum and hybrid II at different concentration on the turbidity removal of kaolin. Kaolin suspended solution (30 NTU), pH 6.5, settling 45min.
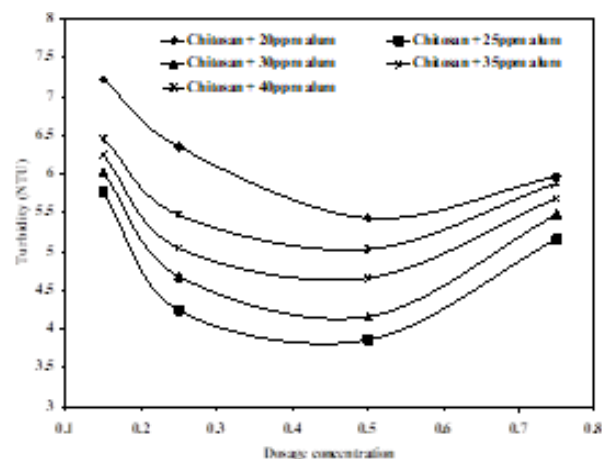

Figure (10): Effect of combination between alum and chitosan at different concentration on the turbidity removal of kaolin. Kaolin suspended solution (30 NTU), pH 6.5, settling 45min.

The previous finding manifests the postulation of the increase in the located sites available for more accumulation and aggregation of negatively charged colloidal silica particles [19]. A point of interest is that alum used in best water flocculation with a concentration of 35-40 ppm. Also, from our previous data best flocculation for our studied compounds was 1 ppm. Combination between alum and the studied three flocculating agents is associated by pronounced decrease of its concentration to 25 ppm for alum and 0.5 ppm for the studied three flocculating agents.

_____

Moreover, the quality of clarification is more improved than that obtained for each component alone [20]. For instance, the turbidity value (NTU) for 1ppm dosage hybrid I was 3.01(NTU) was inconsistent with turbidity the value of 1.84 (NTU) for 0.5ppm with 25ppm alum. The data plotted in figure 8-10 shows that at constant alum concentration (25ppm), the variation of flocculation performance follows the following sequence: Hybrid II +25ppm alum > Hybrid I +25ppm alum> chitosan. The all-pervious data conclude that imparting each of cationic monomer such as DMAEMA and anionic monomer such as AA onto chitosan macromolecule gives highest flocculation performance than obtained by imparting only cationic monomer onto chitosan or untreated chitosan (blank).

3.4. Clarification of raw water using previously obtained optimum conditions

For practical application of our previously obtained optimum conditions for colloidal water clarification, samples of tap water have been treated with the optimum dosage of the three flocculating agents at different settling time conditions. This was done as an extension of our study to include the feedback of this study in purification of real contaminated water with different pollutants such as colloidal silica, organic mater, heavy metal and other trace pollutants [21-23].

The dosage concentrations of the three studied flocculating agents are adjusted at 1 ppm in case of using them alone or 0.5 ppm in case of using them in combination with 25ppm alum. The data obtained are summarized in Figures 11-12. As it is evident, the clarification behavior represented as turbidity value as NTU improved by using hybrid II more than hybrid I and lowest clarification was observed by using chitosan blank. Also, using a combination between the suggested three flocculating agent (0.5ppm) with 25ppm alum have a pronounced effect on the clarification characterization.

For instance, using 0.5 ppm dosage of hybrid I in combination with 25ppm of alum gives clarified water with turbidity value of 1.56 NTU. This is against turbidity value of 2.6 NTU obtained using 1 ppm dosage of hybrid I alone. Moreover, the turbidity of the water much more clarified to reach 0.96 NTU using 0.5 ppm dosage of hybrid II in combination with 25ppm of alum. The turbidity of the treated

water using 1ppm dosage of chitosan was 3.8 NTU and using 0.5 ppm dosage in combination with 25 ppm of alum reach to a value of 2.3 NTU.
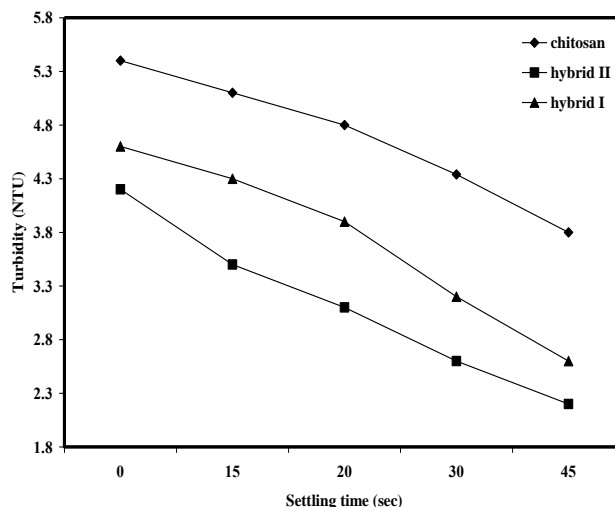

Figure (11): Effect of synthetic flocculant agent types on the turbidity removal of tap water. Flocculants dosage concentration (1ppm), settling time 45min.
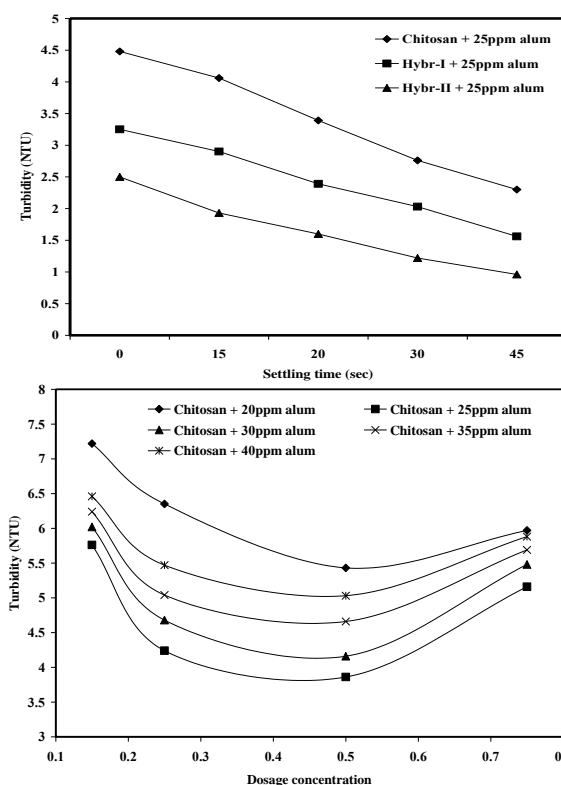

Figure (12): Effect of combination between alum and synthetic flocculant agents on the turbidity removal of tap water. Flocculants dosages concentration (0.5ppm) settling time 45min.

_____

3.4.1. Characteristic of treated raw water

To explain clearly the importance of this study a collective table was made to compare the characteristics of tap water taken as a control, with that after independently treated with 44ppm of alum, 1ppm of synthetic flocculating agents and mixture of 25ppm & 0.5ppm of alum & synthetic flocculating agents. The obtained results are given in Table 1. As it can be seen for the conductivity, the use of alum caused an increment of its value 375 than that of the raw water 357 while, synthetic flocculating agents showed a slight increase when a mixture of both of them was used [24]. The turbidity of the treated water was considerably decreased by using mixture of alum and synthetic flocculating and reached to lowest turbidity values of 0.9 NTU against a value of 2.3 NTU for that obtained using combination of alum with untreated chitosan [25]. The total alkalinity was affected by treatment with alum, synthetic flocculating agents or their admixture and the recorded values were 109, 118, 111, 122, 114,121 and 110 respectively, while that of tap water was 152.

With respect to the total hardness, it was slightly affected with the treatment by alum, and /or synthetic flocculating agents or their mixtures.The obtained results in Table 1 assured the fact that using alum (44ppm) or synthetic flocculating agents (1ppm) caused about similar reduction of organic matter expressed as $KMnO_4$ and equal to 14.6, 13.9, 13.6 and 13.4 respectively, while the aforementioned mixture caused a decrease up to 13.1.

Conclusions

Two types of chemically modified chitosan namely; chitosan-g-poly DMAEMA (as hybrid I) and chitosan-g-poly DMAEMA/AA (as hybrid II) were prepared, characterized via FTIR, X-ray and thermal characterization. The two prepared polymeric hybrids were used to flocculate kaolin solution having two turbidity values (30 and 170 NTU) as well as remove some pollutants from the raw water and their efficiency compared with un-grafted chitosan. The optimum condition for flocculation of hybrid I and hybrid II were obtained at pH 6.5 and at pH 7.5 for pure Chitosan. The combination of different alum concentrations with the grafted copolymer hybrids showed that the obtained turbidity values were markedly decreased for the hybrid I, hybrid II and un-grafted chitosan. The characteristics of tap water after independent treatment with pure synthetic flocculating agents or its mixture with alum were measured and demonstrated that using combination between alum and hybrid I or II gives the most clarification characterization.

Acknowledgment

Table(1) : Variation of water constituents at the optimum dosage of aluminum sulfate and different synthetic flocculating agents concentration using 20 ml tap water for 30 min.

Parameters	tap water	alum (44ppm)	Chitosan (1ppm)	Chitosan (0.5ppm) – Alum (25ppm)	Hybrid I (1ppm)	Hybrid I (0.5ppm) – Alum 25ppm	Hybrid II (1ppm)	Hybrid II (0.5ppm) + Alum 25ppm
pH	7.9	6.8	7.8	7.0	7.8	7.3	7.8	7.2
Conductivity	357	375	366	371	360	372	361	373
Partial alkalinity as caco3	0	0	0	0	0	0	0	0
Total alkalinity as caco3	152	109	118	111	122	114	121	110
Total hardness as caco3	102	100	91	90	90	89	90	89
Calcium hardness as caco3	67	58	57	56	55	56	56	55
Magnesium hardness as caco3	46	39	39	40	39	39	39	40
Sulphate as so4	14	33	12	23	11	22	12	22
Organic matter as KMno4	27	14.6	13.9	13.7	13.8	13.6	13.4	13.1
Turbidity (NTU)	13.4	2.9	3.8	2.3	2.6	1.5	2.2	0.9

References

1. Hasan, H.A.; Muhammad, M.H.; Ismail, N.I. A review of biological drinking water treatment technologies for contaminants removal from polluted water resources. J. Water Process Eng. 2020, 33, 101035.

2. Musarurwa, H.; Tavengwa, N.T. Application of carboxymethyl polysaccharides as bio-sorbents for the sequestration of heavy metals in aquatic environments. Carbohyd. Polym. 2020, 237, 116142.

3. Luo, J.; Fan, C.; Xiao, Z.; Sun, T.; Zhou, X. Novel graphene oxide/carboxymethyl chitosan aerogels via vacuum-assisted self-assembly for heavy metal adsorption capacity. Colloids Surf. A Physicochem. Eng. Asp. 2019, 578, 123584.

4. Ramazani, A.; Oveisi, M.; Sheiki, M.; Gouranlou, F. Natural polymers as environmental friendly

adsorbent for organic pollutants such as dyes removal from colored waste water. Curr. Org. Chem. 2018, 22, 1297–1306.

5- Qi, X.; Liu, J.; Wang, C.; Li, S.; Li, X.; Liang, Y.; Sarfaraz, K. Synthesis of the Hydrophobic cationic Polyacrylamide (PADD) initiated by ultrasonic and its flocculation and treatment of coal mine wastewater. Processes 2020, 8, 62.

6- Mohammadi, E.; Daraei, H.; Ghanbari, R.; Athar, S.D.; Zandsalimi, Y.; Ziaee, A.; Maleki, A.; Yetilmezsoy, K. Synthesis of carboxylated chitosan modified with ferromagnetic nanoparticles for adsorptive removal of fluoride, nitrate, and phosphate anions from aqueous solutions. J. Mol. Liq. 2019, 273, 116–124

7- Feng, L.; Li, X.; Lu, W.; Liu, Z.; Xu, C.; Chen, Y.; Zheng, H. Preparation of a graft modified flocculant based on chitosan by ultrasonic initiation and its synergistic effect with kaolin for the improvement of acid blue 83 (AB 83) removal. Int. J. Biol. Macromol. 2020, 150, 617–630

8- Ziegler-Borowska, M.; Węgrzynowska-Drzymalska, K.; Chełminiak-Dudkiewicz, D.; Kowalonek, J.; Kaczmarek, H. Photochemical Reactions in Dialdehyde Starch. Molecules 2018, 23, 3358.

9- Węgrzynowska-Drzymalska, K.; Grębicka, P.; Młynarczyk, D.T.; ChełminiakDudkiewicz, D.; Kaczmarek, H.; Gośliński, T.; Ziegler-Borowska, M. Crosslinking of chitosan with dialdehydechitosan as a new approach for biomedical applications. Materials 2020, 13, 3413.

10- Charhouf, I.; Bennamara, A.; Abourriche, A.; Chenite, A.; Zhu, J.; Berrada, M. Characterization of a dialdehyde chitosan generated by periodate oxidation. Int. J. Sci. Basic Appl. Res. 2014, 16, 336–348.

11. Mauricio-Sanchez, R.A.; Salazar, R.; Luna-Barcenas, J.G.; Mendoza-Galvan, A. FTIR spectroscopy studies on the spontaneous neutralization of chitosan acetate films by moisture conditioning. Vib. Spectrosc. 2018, 94, 16.

12- Lee, J.; Park, S.; Roh, H.; Oh, S.; Kim, S.; Kim, M.; Kim, D.; Park, J. Preparation and Characterization of Superabsorbent Polymers Based on Starch Aldehydes and Carboxymethyl Cellulose. Polymers 2018, 10, 605.

13- Sirviö, J.; Honka, A.; Liimatainen, H.; Niinimäki, J.; Hormi, O. Synthesis of highly cationic water-soluble cellulose derivative and its potential as novel biopolymeric flocculation agent. Carbohyd. Polym. 2011, 86, 266–270.

14- Kleim, S.; Kreutzbruck, M.; Bonten, C. Review on the biological degradation of polymers in various environments. Materials 2020,13, 4586.

15- Li, M.; Witt, T.; Xie, F.; Warren, F.J.; Halley, P.J.; Gilbert, R.G. biodegradation of starch films: The roles of molecular and crystalline structure. Carbohyd. Polym. 2015, 122, 115–122.

16- Silva, W.C.; Souza, I.; Benasii, V.M.; Roa Bretas, J.P.; Grazziotti, P.H.; Nelson Lee, D.; dos Reis, A.B. Determination of the biodegradability of chitosan utilizing the most probable number technique. Acta Sci. Biol. Sci. 2020, 42, 52956.

17- Matica, A.; Menghiu, G.; Ostafe, V. Biodegradability of chitosan based products. New Front. Chem. 2017, 26, 75–86.

18- Bolto, B.; Gregory, J. Organic polyelectrolytes in water treatment. Water Res. 2007, 41, 2301–2324

19- Dao, V.H.; Cameron, N.R.; Saito, K. Synthesis, properties and performance of organic polymers employed in flocculation application. Polym. Chem. 2016, 7, 11–25.

20- Zhang, L.; Liu, P.; Wang, Y.; Gao, W. Study on physic-chemical properties of dialdehyde yam starch with different aldehyde group contents. Thermochim. Acta 2011, 512, 196–201.

21- Warren, F.J.; Gidley, M.J.; Flanagan, B.M. Infrared spectroscopy as a tool to characterize starch ordered structure. A joint FTIR-ATR, NMR, XRD and DSC study. Carbohyd. Polym. 2016, 139, 35–42.

22- Charhouf, I.; Bennamara, A.; Abourriche, A.; Chenite, A.; Zhu, J.; Berrada, M. Characterization of a dialdehyde chitosan generated by periodate oxidation. Int. J. Sci. Basic Appl. Res. 2014, 16, 336–348.

23- Wang, B.; Zhang, Y.; Miao, C. Preparation of cationic chitosan-polyacrylamide flocculant and its properties in wastewater treatment. J. Ocean Univ. China 2011, 10, 42–46.

24- Rinuado, M. Chitin and chitosan: Properties and applications. Prog. Polym. Sci. 2006, 31, 603–632.

25- Sharma, B.R.; Dhuldhoya, N.C.; Merchant, U.C.
Flocculants. An Ecofriendly Approach. J. Polym.
Environ. 2006, 14, 195–202.