

Synthesis and application of cationic rice starch as a flocculants for water treatment

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Abstract:

A soluble cationic rice starch derivative having a quaternary amino group was synthesized by a technique based on dry method by the reaction of rice starch (isolated from broken rice as waste product) with 3-Chloro2-hydroxy Triethyl Ammonium Chloride (CTAC). The factors affecting the nitrogen content of the produced aminated starch mainly: reaction temperature, time and sodium hydroxide concentration besides the mL added of (CTAC) were studied and discussed briefly. It was concluded that higher nitrogen content of starch derivative is obtained at reaction temperature 60°C for 90 minute. Moreover increasing the liquor ratio of starch / (CTAC) was accompanied by an increase in nitrogen content till a certain ratio. Product obtained was characterized by FT-IR, Thermo gravimetric analysis TGA, elemental analysis (C,H,N,S) . The adsorption efficiency of metal ions as Zn, Cu, Ni, and Fe was determined using atomic absorption spectrometry (AAS). It was found that the quantity and the type of incorporated functional groups, as well as the type of metal ions, play an important role in the efficiency of cationic starch toward adsorption of metal ion in water. The flocculation performance of the obtained starch derivative was evaluated in terms of turbidity, organic matter.

Key word: *cationic starch , flocculants, water treatment.*

Introduction:

Flocculants are the materials, which are used in fast solid liquid separations by an aggregation process of colloidal particles; the process is termed as flocculation. Commercial forms of synthetic flocculants may contain toxic monomers from the synthesis and additives. In many countries, the disposal of flocculated sludge with polyacrylamide derivatives has been limited and will be strictly prohibited (**Semsar, Scholz, & Kulicke, 2007**). An important member of renewable primary products such as cellulose and chitosan, especially low-cost starch, are alternatives to synthetic flocculants. In recent years, considerable attention has been paid on starch derivatives used as flocculants and chelating agents to remove heavy metals. Starch is one of the most abundant natural polymers in the world. In its crude form, starch is a mixture of two

polymers of anhydroglucose units, amylose and amylopectin. Chemically modified starches are generally made by treating starch with agents that can react with hydroxyl groups or grafting with other polymers. Such starches have physicochemical properties that differ significantly from the parent starch, thus widening their usefulness in many applications in food manufacturing and other industrial processes (**Prakash, Solanki, & Prasad Rao, 2007; Rvanitoyannis, 1999**). Earlier in 1970, graft copolymers of starch and poly (2-hydroxy-3- methacryloyloxy propyltrimethyl-ammonium chloride) were prepared and were used as flocculating agents (**Fanta, Burr, Russell, & Rist, 1970**). It was also found that starch-g-polyacrylamide copolymer showed good flocculation ability because of synergistic characteristics in flocculation (**Karmakar & Singh, 1997**). Now many graft starch copolymers have been synthesized and flocculation were tested (**Hao/Chang, Duan, & Zhang, 2007; Khalil & Aly. 2001a, 2002b; Yao, 1992**). Cationic starch derivatives possessing positively charged groups were effective flocculants over a wide range of pH. They are non-toxic, easily biodegradable and can be used to treat organic and inorganic matter in waste water carrying negative charge (**Heinze, Haack, & Reusing, 2004; Jaernstroem, Lason, & Rigdahi, 1995; Nystrom, Backfolk, Rosenholm, & Nurmi, 2003; Pal, Mal, & Singh, 2005**). Conventionally cationic starch can be prepared by reaction of starch with N-3-Chloro--2-hydroxypropyl) trimethyl ammonium chloride in aqueous base or organic solvents.

In this paper, cationic rice starch quaternary ammonium salts was synthesized by a technique based on dry method.

2. EXPERIMENTAL:

2.1 Chemicals:

Egyptian broken rice as a natural waste product was obtained from local market, Egypt. Triethylamine LR (M.W 101.19) was supplied by s.d.fine-chem Ltd POICHA (R)391340. Epichlorohydrin (99%) was supplied by MERCK-Schuchardt. Sodium hydroxide was supplied by Spectrum, Hong Kong. Ethyl Alcohol was supplied by Adwic, German. The other chemicals used for analysis of water were of analytical grade.

2-2- Testing and analysis:

All series of water examination and chemical analysis were carried out according to the standard method of (**ASTM Book of Standards,I, II 2001**).

2-2.1 Infrared Analyses:

A Fourier transform infrared system (FTIR), JASCO FTIR 4110 spectrometer Japan, was used.

Samples were prepared using the KBr disc technique. The infra, red absorption spectra were recorded in the region of 4000-400 cm^{-1} .

2-2-2 -Atomic absorption for Determination of heavy metal in water:

The heavy metals were determined by using atomic absorption spectrometer Solaar S-4 S- Series Thermo Electron Corporation UK.

2-2-3 Thermogravimetric Analysis (TGA).

Thermogravimetric analysis of native and modified starches was performed with Thermogravimetric determinator Leco: Mac-500.ST. Joseph. Michigan-USA. This apparatus provides a continuous measurement of sample weight at a range of temperatures between ambient and 600 °C. The samples were heated in an alumina cell to 600°C at heating rate of 10 °C/mm with nitrogen as the circulating gas.

2-2-4 Elemental analysis (C,H,N,and S):

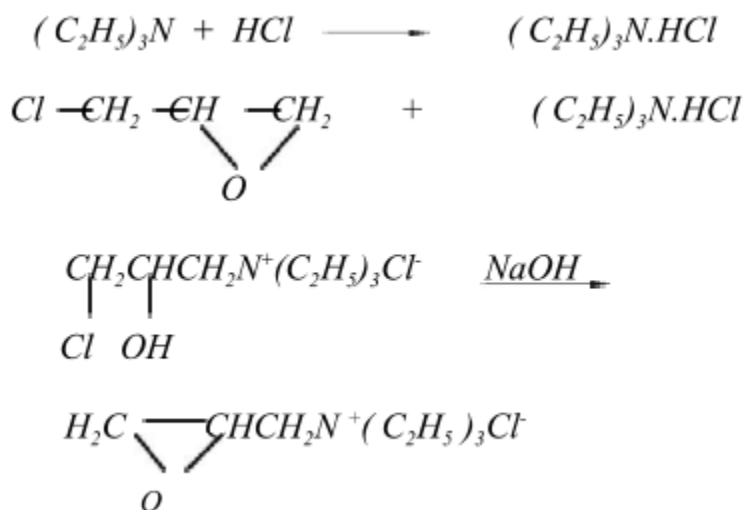
The elemental analysis for (C, H, N,and S) were determined by Leco Truspect (CHN) Analyzer,Leco Corporation 3000 LAKE View AVE.ST. Joseph , MI- USA.

2-3 Rice starch isolation by the NaOH method:

The NaOH method of (Yamamoto *et al.*,1973). was used, except the ratio of rice flour to dilute NaOH solution was increased, and the starch was neutralized with acid prior to washing. The broken rice (20 g) was mixed for 3 h at 25°C with (0.5 M) aq. NaOH (50 mL) and the slurry filtered. The filtrate was centrifuged for 20 min, the supernatant was discarded, and the sediment was washed twice with distilled water (50 mL) and centrifuged. The residue was suspended in water and adjusted to pH 7 by adding (1M) hydrochloric acid, and the slurry was centrifuged. The supernatant was discarded, and the dark tailings layer top of the starch was carefully scraped away and discarded. The starch was washed three times with water (50 ml) until the tailings fraction became negligible after centrifuging. The starch was dried in a convection oven at 40 °C for 48 h.

2-4-Preparation of quaternary ammonium salt:

According to previous work present elsewhere (Guo. Naini *et.al*, 2000). Quaternary ammonium salt was prepared by using triethyle amine , HCl and epichlorohydrine, at optimum condition as illustrated in the following reaction:



2- 5- Preparation of starch derivatives:

Starch has been grinding into a fine powder then sieved in 200µm sieve. 2 gram of starch powder was suspended in 200 ml demineralized water and stirred at room temperature for one hour. Then 5 portions of 10 ml from the suspended starch were separated. The previously prepared (CTAC) was added in different amount (1 to 5 ml) to the starch suspensions drop by drop with continuous stirring in stoppered flasks. The mixture poured into (10 ml) dilute aqueous NaOH solution with different concentration then heated at different temperature, time under water bath heating. Next, after cooling the reaction mixture to room temperature, the solutions pH was adjusted to 7 using conc. HCl. The produced starch derivative was precipitated by ethyl alcohol. The precipitated products were then filtered twice, washed with an excess of alcohol. The products were dried at 60°C in vacuum oven for 24h.

2-5 Water samples preparation:

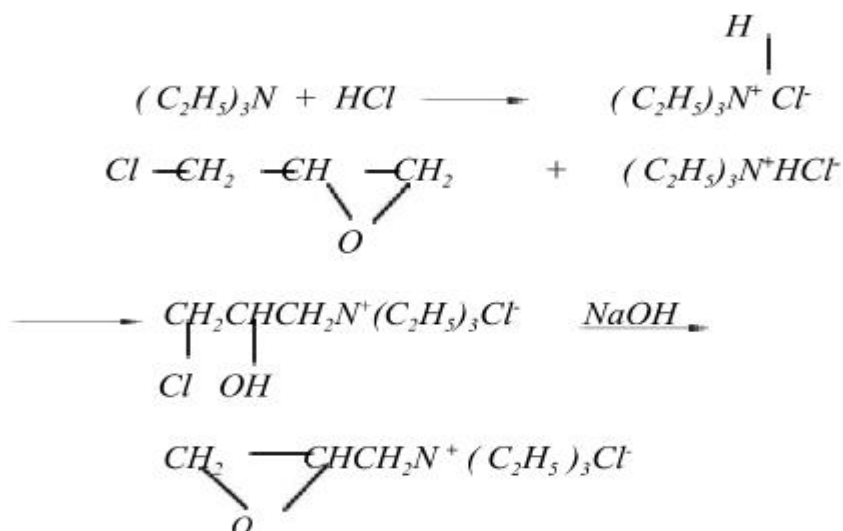
Jar test method is the best way to simulate clarification and permits the comparison of various chemicals combination for determining the optimum chemical program to establish the correct order of addition. The most critical measurements in jar test are coagulation and/or flocculants dosages, floc size, settling characteristics, floc forming time, and finished water clarity. The flocculator in the aforementioned jar test method contains six (1 liter) beakers in conjugation with multiple stirrers. Each beaker was filled with one liter of raw water and stirred at 100 rpm. The different doses of coagulant were added rapidly and stirred for 3 minutes. The stirring rate was then reduced to 50 and 20 rpm for a period of 5 and 10 minutes respectively to allow complete floc formation, then stirring was stopped. The relative settling rate, floc size and supernatant clarity were recorded. After a settling period of 15 minutes, 250 ml of supernatant water were siphoned-off for further analysis.

3-Results and discussion:

In the last few decades, considerable attention had been devoted to find new water treatment technologies using natural materials. These natural materials are usually nontoxic, environmentally friendly and of low cost. This investigation represents a contribution in this trend. Starch is abundant, naturally occurring and eco-friendly materials.

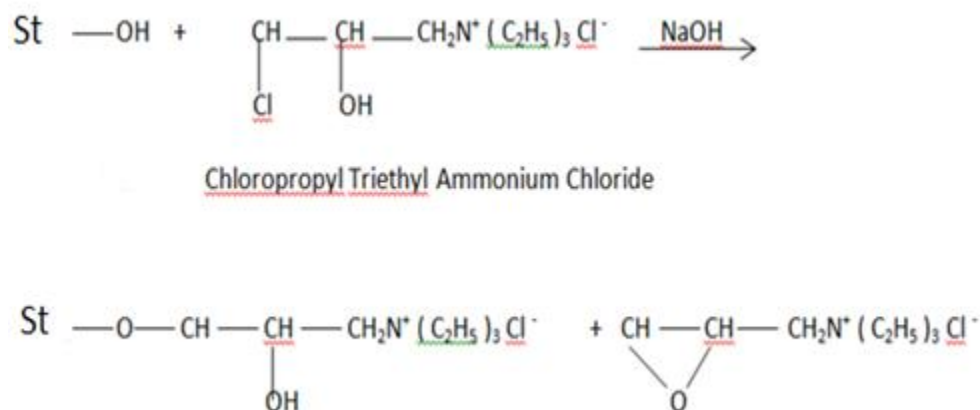
Thus, a cationic starch was prepared by new technique by reacting 3-chloro-2-hydroxy triethylammonium chloride (CTAC) with starch. The product was prepared as soluble starch and its efficiency as a coagulant for water clarification and as adsorbent for some heavy metal ions was studied.

The formation of the quaternary ammonium salt and its reaction with starch are represented by the following schemes:



It is believed that the reaction of CTAC with starch might occur as the following:

Under alkaline condition, (CTAC) readily generates starch amino ether can be obtained



3-2. Factors affecting reaction of starch with (CTAC):

The factors affecting reaction of starch with (CTAC) such as: temperature, duration time, sodium hydroxide concentration, as well as, Starch / (CTAC) ratio have been studied in order to discover the optimum conditions for reaction yield as nitrogen content.

3.2.1. Effect of temperature:

Table (1), show the effect of temperature on the nitrogen content of the starch derivatives at 1ml (CTCA), 20min and 10% NaOH. It is clear that the nitrogen content increases as the temperature is raised up to 60°C. This may be attributed to the fact that, by raising the temperature more than 60°C the swelling of starch granules increases, so that the penetration of the amine through the starch granules will be difficult.

(C°) Temperature	C	H	N	S	C/N
20	43.65	9.6	1.13	0.36	38.62
40	43.65	9.2	1.42	0.36	30.7
60	43.65	9.11	1.47	0.36	29.69
80	43.65	9.14	1.35	0.36	32.33

Table (1): Effect of the temperature on the Nitrogen Content (%) of Starch derivative

3.2.2 Effect of Reaction time:

The results represented in Table(2) show the effect of the reaction time on the efficiency of the reacting products as nitrogen content at 1ml (CTCA), and 10% NaOH. It is found that, at the chosen temperature (60 °C), the increase of the reaction time from 20 to 120 min is accompanied by an increment in the reaction rate, and that, after 80 min, the increase is so small. It may be concluded that longer reaction time leads to an increase of the reactivity of the ions and molecules in the reacting medium; hence, the activation reaction power is increased leading to greater nitrogen contents in the aminated starch obtained.

(minute)Time	C	H	N	S	C/N
20	43.65	9.6	1.13	0.36	38.62
40	43.65	9.2	1.17	0.36	39.68
60	43.65	9.1	1.2	0.36	37.3
80	43.65	9.9	1.25	0.36	37.3
100	43.65	9.9	1.26	0.36	37.3
120	43.65	9.9	1.26	0.36	37.3

Table (2) Effect of the Time on the Nitrogen Content (%) of starch derivatives.

3.2.3 Effect of sodium hydroxide concentration:

Table (3) represents the effect of NaOH concentration on nitrogen content in the product. For the best working conditions of temperature (60°C) , reaction time (100 min) and 1ml (CTCA), different concentrations of NaOH ranging from 10-60% were examined. It is clear that, by increasing the NaOH concentration till 40%, the nitrogen content increases to a maximum value indicating that this concentration is sufficient for complete neutralization of starch and amine hydrochloride and swelling of the starch granules. Further increase of NaOH concentration caused no increase in the nitrogen content. This may be attributed to the fact that excess of the alkali in the reacting medium caused formation of a gelatinized layer around the starch granules, hence, preventing the penetration of the amine to react with it.

(%) NaOH Concentration	C	H	N	S	C/N
10	43.65	9.6	1.17	0.36	38.62
20	43.65	9.02	1.21	0.36	39.68
30	43.65	9.0	1.24	0.36	37.3
40	43.65	9.6	1.28	0.36	37.3
50	43.65	9.8	1.26	0.36	37.3
60	43.65	9.8	1.26	0.36	37.3

Table (3)- Effect of the NaOH on the nitrogen content (%) of starch derivatives.

3.2.4 Effect of (CTAC) mL added:

Different milliliters of (CTAC) namely (1, 2, 3, 4, and 5 ml) were examined at the aforementioned chosen conditions. The obtained results are represented in Table (4) which indicates that by increasing the amount of (CTAC), the reaction product increases till 5 ml.

Composition	C	H	N	S	C/N
Starch	41.52	8.17	0.265	0.32	156.6
Starch/1ml (CTAC)	43.65	9.6	1.42	0.35	30.7
Starch/2ml (CTAC)	46.72	9.81	1.85	0.36	25.25
Starch/3ml (CTAC)	48.64	9.91	1.92	0.37	25.33
Starch/4ml (CTAC)	49.44	9.98	1.97	0.38	25.09
(CTAC)ml 5/Starch	49.89	10.12	1.87	0.38	26.67

Table (4)- Effect of the CTAC concentration on the nitrogen content of starch/(CTAC).

3-1 .Infrared of cationic rice starch:

Figures (1) show the FTIR spectra of isolated rice starch (blank) and cationic rice starch products (St/1m CTAC to St/5ml CTAC) respectively from up to down. In IR spectra of isolated rice starch the absorption bands at 1600cm^{-1} is due to characteristic (O-H) bending bands for rice starch. On the other hand, the IR spectra for cationic starch show reduction of (O-H) band with presence of new other characteristic bands increased by increasing CTAC. This manifest the proceeding of cationic starch .Also, the presence of medium band appeared at 1371cm^{-1} , could be attributed to symmetric stretching for (C-N) group witch confirm the presence of tertiary amine in the cationic starch.

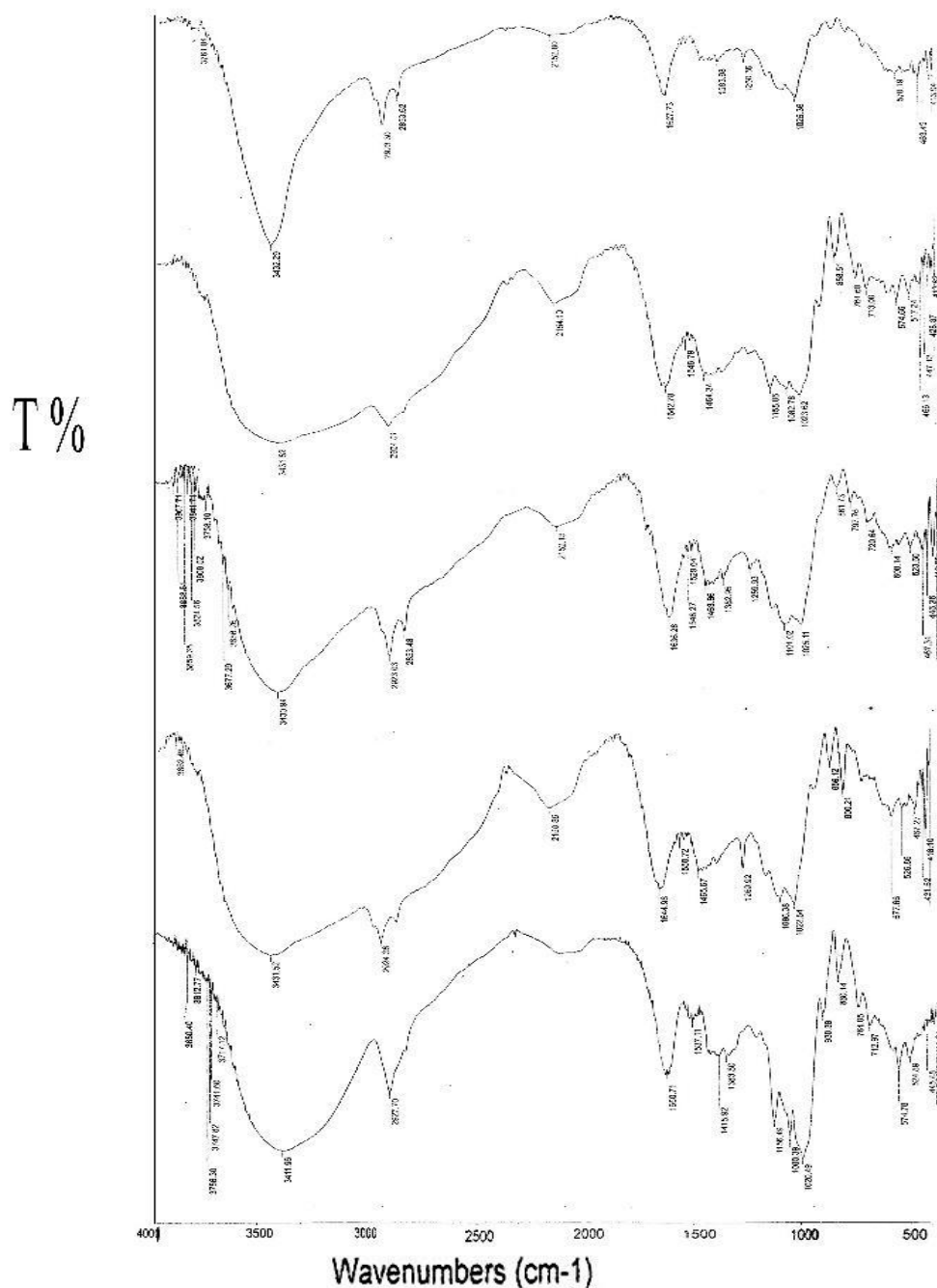


Figure (1): FT-IR of starch and their derivatives.

From the above mentioned the best working conditions for maximum nitrogen content is temperature (60°C), reaction time (100 min) at 40% NaOH and liquor ratio starch/4ml(CTCA).

3.2. Thermo gravimetric analysis (TGA):

TGA is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure (2) show the thermo- gravimetric analysis (TGA) for starch (blank), and cationic starch, respectively. As it evident, the spectra for starch show three characteristic stages for decomposition. The first stage starts at 45 °C and end at 95 °C with a weight loss of 6.4 %. This could be recognized due to the moisture content for starch. The second stage which related to the main decomposition of starch macromolecules occurs in one step of decomposition start at 246 °C and end at 307, °C with maximum decomposition temperature of 283 °C and weight loss of 45%. The third stage of decomposition is related to the carbonization process which occurs up to 600 °C with a weight loss of 17.5%.

For the cationic starch sample at the best working conditions the first stage starts at 46 °C and end at 100 °C with weight loss of 15%. The second stage of decomposition, representing the main decomposition, proceeds in two steps. The first step starts at 200 °C and end at 245 °C with maximum decomposition temperature of 224 °C. The weight loss in this step for the studied sample was 19% .This step, most probably, could be related to the degradation of cationic starch. Moreover, the second step of degradation for the studied sample starts at 248 °C and end at 304 °C with maximum decomposition temperature of 285 °C The weight loss for the sample was 33%. This step of degradation simulates and corresponds to main degradation process recorded for starch. The third stage of degradation occurs up to 600 °C with weight loss of 16 % for cationic starch.

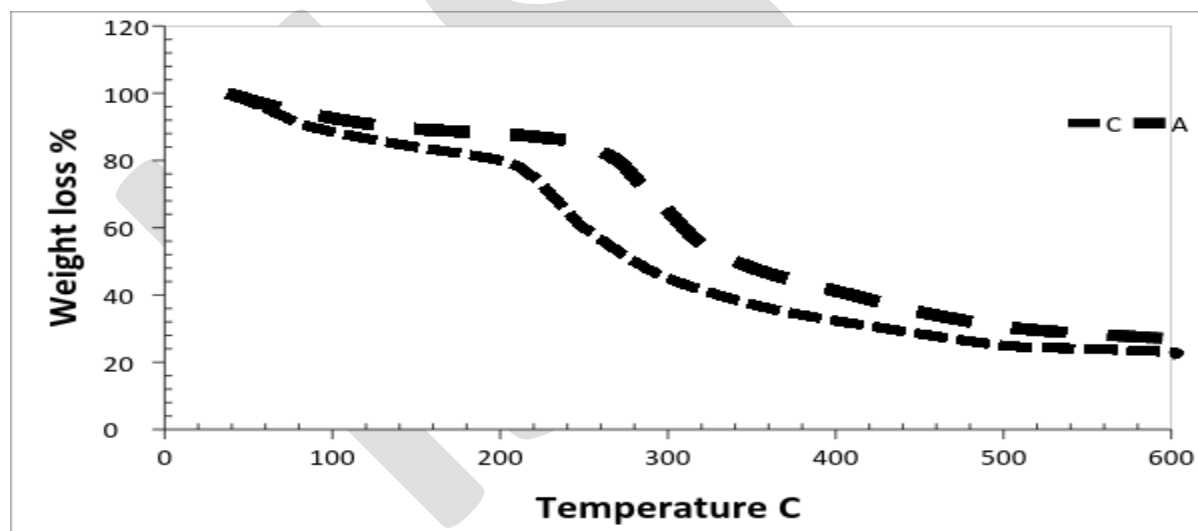


Figure (2) TGA of starch (A) and cationic starch at the best working conditions (C)

3-2 Evaluation of cationic rice starch as flocculant:

The cationic starch derivative possessing positively charged groups (amino groups) which acts like ion exchanger. They can remove organic and inorganic matter carrying negative charge from water. By using cationic rice starch for the clarification of raw water in a dose from (2-10 mg/l), the examined parameters revealed that cationic rice

starch is able to remove turbidity, organic matter, colloidal silica, and sulfate gives better water clarity. Table (5) showed that the optimum dose that gave best result was (6 mg/l). It can be noticed that it have coagulation properties as those mentioned by many authors (Heinze, Haack, & Reusing, 2004; Jaernstroem , *etal*, 1995; Nystrom,*etal*, 2003; Pal, *et al.*, 2005).

Parameter	Raw Water	Cationic starch dose (mg/l)				
		2	4	6	8	10
Turbidity (NTU)	3.7	1.905	1.04	0.85	0.89	0.9
Sulphates (mg/l)	36	34	30	24	123	22
Organic matter (mg/l as KMnO ₄)	19	14.29	12.23	8.19	8.29	9.29
Colloidal silica(mg/l as SiO ₂)	9.5	8.26	7.2	5.4	6.1	6.3

Table (5): Effect of cationic dose on the quality of treated water.

3-4 Metal ions removal from water by cationic rice starch:

Industrial effluents may contain a mixture of heavy metal ions, and therefore, testing of chelation is recommended for the obtained cationic rice starch as ion chelating agent. The adsorption of the metal ions Zn, Pb, Fe, Ni, and Cr by the cationic rice starch was studied. For this purpose a sample of water was injected by (2 mg/l) from each of (Fe, Cu, Cd, Ni, Co, Mn, and Zn). The effect of different cationic starch concentrations (2, 4, 6, 8 mg/l) on the removal of such elements from water was studied. Figure (3) show that the cationic starch has high efficiency for removal of elements. For instance, as much as 95% of (Ni, Zn, Co, Cd, Mn) were removed by using (8 ppm) of cationic starch, and 100% removal of (Fe and Cu). Also it's clearly seen from Figure (3), that the increment of cationic starch accompanied by decrement of metal' ions in water to be examine reaching to complete removal of metals ions at (8 mg/l).

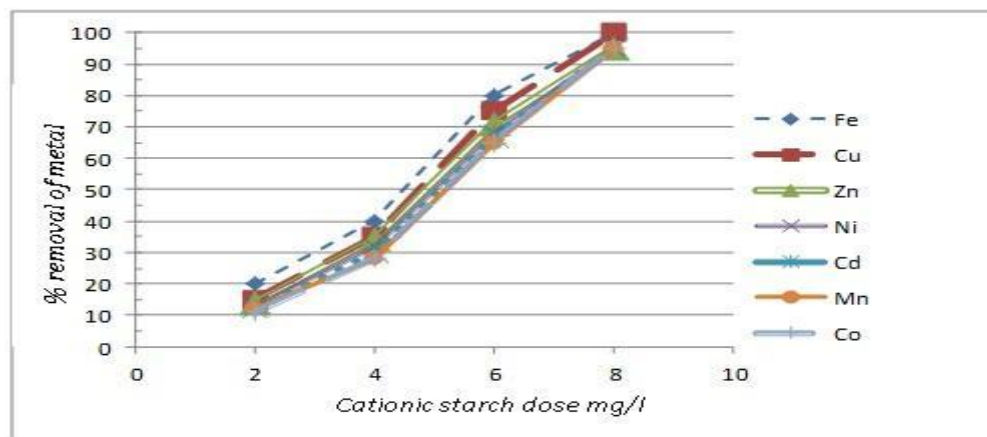


Figure (3): Effect of cationic starch dose on heavy metal removal.

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