Carbamated Corncobs as a natural coagulant for water treatment

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Abstract:

This work deals with synthesis of carbamated corncobs via reaction with urea. The factors affecting the nitrogen content of the produced carbamated corncobs such as urea concentration, the liquor/corncob ratio, reaction time and temperature were studied. The nitrogen content of the produced carbamated corncobs was increased by increasing urea concentrations and decreasing liquor/corncob ratio at the same reaction temperature and time. The product obtained was characterized by FT-IR, HNMR and elemental analysis (C, H, N, and S). The clarification efficiency of corncobs derivative for metal ions in raw water such as Fe^{3+} , Ca^{2+} and Mg^{2+} was determined. Also both of total organic carbon (TOC) and dissolved solid (TDS), turbidity and conductivity were measured. It was concluded that using the produced carbamated corncobs in mixture with FeCl_3 enhanced the water clarity and decrease the required dose of FeCl_3 to its half value in the same time enhancing the clarification efficiency of the water.

Keywords: Carbamated corncobs, water treatment, coagulation, flocculation, clarification.

1-INTRODUCTION:

Flocculation is a process of collecting smaller particles to form larger particles, and settling of colloidal particles from stable suspensions. This process is caused by the addition of chemicals known as flocculants in minute quantities. It is well known that the use of organic and inorganic flocculants improves the efficiency of solid/liquid separation in a wide range of papermaking, wastewater treatment and mineral processing industries [1-4]. The inorganic flocculants, which are mainly based on hydrolyzable salts of aluminum, cannot be removed easily during treatment, and the residue in water can cause some health problems [5]. Inorganic coagulants such as aluminum sulfate, ferric chloride, calcium carbonate and synthetic inorganic polymer (polyaluminium chloride (PACl) are common coagulants used for such treatment, which is generally at a high cost. However, the sludge obtained from treatments using aluminum salts leads to disposal problems such as aluminum accumulation in the environment. Moreover, some studies have reported that residual aluminum sulfate (alum) and polyaluminium chloride may induce Alzheimer's disease. On the other hand, synthetic organic polymers, such as poly acrylamide, have neurotoxic and carcinogenic effects. One possible solution to these problems may be natural coagulants which must be safe for human health and biodegradable [6].

Natural and synthetic polymeric flocculants, which are able to destabilize colloidal suspensions, had wide application as flocculating agents in the past decade. Water-soluble synthetic polymers [7-9] have a disadvantage of non-biodegradability and cost-effective. Thus, the demand for effective, cheap and environmentally friendly natural flocculants for wastewater treatment is increasing. With the characteristics of nontoxic and biodegradable, the so-called “green flocculants” such as starch [10, 11], amylopectin [12], alginic acid [13], guar gum [14], and so forth, have been paid much attention.

Corncoobs is an agricultural waste containing polysaccharide composed of cellulose, hemicellulose and lignin. [15]. Hemicellulose contains hydroxyl and carbonyl functional groups which can be used as chelating agent for metal ions to form an insoluble complex in the form of a flock [16].

The present work dealt with the conversion of agriculture waste corncoobs to economically valuable products which can be used as coagulant in water treatment.

2-EXPERIMENTAL

2-1 – Material and Chemicals:

- Corncoobs were obtained from local farms in Egypt.
- Raw water was collected from river Nile at west delta (Alamia canal in Eltabia, Alex) Egypt.
- Dimethylformamide (DMF) was supplied by S.D. fine-chem Ltd (SDFCL), Urea (99%) was supplied by ADWIC, ethanol (95%) was supplied by Gateway Co., and other chemicals of laboratory grade were used.

2- 2-Preparation of carbamated corncoobs:

Corncoobs have been grind into a fine powder then sieved in 200µm sieve. 10 g of corncob powder were mixed with different weights of urea (5, 10, 15 and 20 g) and certain volumes of DMF with different liquor/corncob ratio. The reaction mixture was heated at (160 °C) for (30 minutes), then after cooling the reaction products were washed with ethyl alcohol (70%) to get ride of unreacted materials, then finally washed with absolute alcohol and dried.

2-3- Analyses:

2-3-1. Elemental analysis:

Carbon, hydrogen, sulphur and nitrogen contents of the produced cationic corncoobs specimens were determined using VARIO CHNS CUBES Elemental Analyzer.

2-3 -2. FT-IR measurements:

The spectra of corncoobs and cationic corncoobs samples in the form of (KBr) disks were recorded using an IR Instrument (JASCO FTIR 4110, Japan) in the frequency range of (4000-400 cm⁻¹).

2-3-3. Determination of the Turbidity:

The turbidity of the examined water was measured in nephelometric turbidity units (NTU) using Orbeco-Hellige turbidimeter series 965.

2-3-4. Determination of Organic matter:

Organic matter of water expressed as total organic carbon (TOC) was determined using Shimadzu total organic carbon analyzer model TOC-V CSN.

2-3-5. Determination of conductivity and total dissolved solid (TDS):

Conductivity and (TDS) measurements of water were performed using Orion conductivity meter model 150Aplus that was calibrated with conductivity standard Jenway 1413 $\mu\text{S}/\text{cm}$ at 25 °C certified Traceable to N.I.S.T solution according to EPA 9050 A standard method.

2-3-6. Determination of metal ions:

The metal ions of the examined water were quantified using:

- Perkin Elmer 2100 DV Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).
- Atomic Absorption Spectrometer, Perkin Elmer model A Analyst 400.

2-3-7. Removal efficiency:

% Removal of metal ions, organic matter and turbidity were calculated from the following equation:

$$\% \text{Removal} = C_0 - C / C_0 \times 100$$

Where, C_0 and C represent the metal ion concentration or organic matter or turbidity of raw water before and after coagulation treatment by corncobs derivatives, respectively.

3- RESULTS AND DISCUSSION:

Recently, significant consideration had been dedicated searching new water treatment innovations utilizing natural materials. These natural materials are generally nontoxic, biodegradable and of affordable cost which are considered as agricultural waste.

The grinded native corncob was analyzed by using energy dispersive x-ray (EDX) and elemental analysis analyzer it has the following specifications:

Figure (1) Energy dispersive X-ray (EDX) of native corn cobs

Figure (1) showed the X-ray analysis chart, which show that the native corn cobs contains each of C, Si, K and Ca elements.

It is also seen that the elemental analysis of native corncobs are:

Element	C	H	N	S
Percentage	24.54	4.00	0.17	1.42

Continuation of our previous work on water treatment [17-19], carbamated corncobs were prepared in alkaline media by reacting corncobs with urea in the presence of dimethylformamide (DMF) as an aprotic solvent to give corncobs carbamate. The extent of the reaction expressed as percentage of the nitrogen content varied by varying different factors including the concentration of the reactants and the liquor ratio at constant temperature and time.

The enhancement of nitrogen content as the urea concentration increases, within the range studied, when the temperature was 160 °C for 1 hour and different liquor ratio is depend on the immobility of corncobs hydroxyl groups. Their reaction with urea would essentially depend upon availability of urea molecules in the proximity of the hydroxyl groups in corncobs molecules.

The reaction processed as follows:

Firstly, urea molecule decomposes to isocyanic acid and ammonia [20] as shown in equation (1).

The significant enhancement of the reaction efficiency expressed as product nitrogen percent could be associated with:

- (i) Increasing the swellability of corncobs granules.
- (ii) Common ion effect for increasing the ionization power of isocyanic acid formed through decomposition of urea to increase the reaction with corncobs as shown in equation (2):

Making the medium slightly alkaline, which decreases liberation of ammonia, preventing the probability of reaction between two corncob carbamate molecules under the influence of high reaction temperature as shown in equation (3):

3-1. Carbamated corncobs investigation:

3-1-1. Parameters affecting the production of carbamated corncobs:

The parameters influencing the reaction of corncobs including urea concentration, liquor/corncob ratio at constant time and temperature were studied to decide the optimum conditions for the reaction yield expressed as nitrogen content.

3-1-1-1. Urea concentration:

The effect of urea concentration based on the weight of corncobs on the nitrogen content of the produced carbamated corncobs is represented in Table (1). It is clear that the nitrogen percent increases by increasing the urea concentration within the range studied, when using

10 g of corncobs, at temperature of 160 °C for 30 minutes. The enhancement of the nitrogen percent may be due to the immobile of hydroxyl groups of corncobs, and their reaction with the urea that essentially depend upon availability of urea molecules. The results obtained showed that the highest nitrogen content was for 10g corncobs, 15g urea at 160 °C for 30 minutes.

Table (1): Variation of Nitrogen Content (%) of corncobs derivative with increasing urea concentration..

Urea weights (g)	C (%)	H (%)	N (%)	S (%)
0.0	43.94	6.24	0.23	1.42
5.0 g	38.45	6.12	6.46	1.28
10.0 g	36.72	6.10	8.45	1.21
15.0 g	35.26	6.09	10.29	0.95
20.0 g	33.64	6.07	10.28	1.18

The reaction condition: 10 gm. corncobs. 160 °C. 30 min.

3-1-1-2. liquor/corncobs ratio:

Table (2) shows the dependence of nitrogen content of the carbamated corncobs on the liquor/corncobs ratio, which is the amount of (ml liter) of DMF to the weight of corncobs in (grams). It is clear that the extent of carbamation of corncobs decreases considerably by increasing the liquor/corncobs ratio. This is evident by the considerable decrement in nitrogen percent upon increasing the liquor/corncobs ratio. This can be attributed to that, increasing the liquor ratio leads to increasing the dilution of the reactants, as a result decreasing the collision probability between the reactant molecules thereby the magnitude of carbamation decreases.

Table (2): Effect of the liquor/corncobs ratio on the nitrogen Content of corncobs derivative.

Liquor ratio	C (%)	H (%)	N (%)	S (%)
1/2	38.45	6.12	6.46	1.28
1/1	39.98	6.02	4.90	0.88
3/2	40.82	5.96	4.08	0.68
2/1	41.61	5.90	3.26	0.47

The reaction condition: 10 gm. corncobs., 15 gm. urea., 160 °C., 30 min.

The results obtained showed that the optimum reaction condition for highest nitrogen content was 10g corncobs, 15g urea at 160 °C for 30 minutes and liquor/ corncobs ratio 1/2.

3-1-2. FT-IR of the corncobs and its carbamated derivatives:

The FT-IR spectra of the native corncobs and carbamated one at the chosen optimum reaction conditions were studied.

FT-IR is helpful for the evaluation of the outer-sphere and inner-sphere carbamated corncobs. The obtained results of figures (1, 2) indicate that the FT-IR spectrum of native corncobs contains 6 clear bands, while the spectra of carbamated corncobs shows 12 clear bands. In addition, it is evident that the stretching frequency of the (OH) groups was shifted from 3487.68 cm⁻¹ in the spectra of the native corncobs to 3456.78 cm⁻¹ in carbamated corncobs. More over the intensities of the (OH) bands in carbamated corncob sample at

3456.78 cm^{-1} is lower than the (OH) band at 3487.68 cm^{-1} in the native corncobs. This indicates that, there are external hydroxyl groups in the corncobs that are responsible for the interactions with urea. Nevertheless, it was shown that a stretching (C-H) band appeared at 2857.02 cm^{-1} in the carbamated corncob sample. Also new bands appeared in the range 1659.42-1670.11 for (C=O) stretching in the spectrum of carbamated corncob samples. Also there is amid group apared at 1750 cm^{-1} which indicate that carbamated corn cobs is formed.

Figure (1) FT-IR spectra for native corncobs

Figure (2) FT-IR spectra for cationic corncobs at chosen optimum reaction condition
3-1-3. HNMR of the corncobs and its carbamated derivatives:

The native corncobs and product obtained were mainly characterized using $^1\text{HNMR}$ spectroscopy. A representative $^1\text{HNMR}$ spectrum of native corncobs and its carbamated derivative is given in Figure (3, 4). The spectrum in Figure (3) is the native corncobs and in figure (4) is the carbamated derivative of corncobs. The spectra represented in Figure 4 show signals due to the carbonyl and amide groups of urea in the carbamated sample.

Figure (3) HNMR spectra for native corncobs

Figure (4) HNMR spectra for carbamated corncobs at chosen optimum reaction condition

3-4.Application of the produced carbamated corncobs in water treatment:

Corncoobs can build complexes with certain ions such as calcium and magnesium. Amino sites are the main reactive groups for organic matter and colloidal silica removal from water.

A comparison was made between cationic corncoobs and ferric chloride as traditional coagulant. For this purpose, a simulation of clarification applying Jar test method which is considered the most applicable way to permit the comparison of various chemicals combination for determining the optimum chemical program was applied. The most important measurements in jar test are coagulation and/or flocculent dosages, flock size, settling characteristics, flock forming time, and finished water clarity. The flocculation in the aforementioned jar test method is composed of a set of four beakers (1 liter) in conjugation with multiple stirrers. Each beaker was filled with one liter of raw water and stirred at 100 rpm. The different doses of coagulants were added rapidly and stirred for 5 minutes. The stirring rate was then reduced to 50 and 20 rpm for a time period of 10 and 20 minutes respectively to allow complete flock formation, and then stirring was stopped. The comparative settling rate, flock size and supernatant clarity were recorded. After a settling time of 20 minutes, 250 ml of supernatant water were siphoned-off for further analysis.

3-4.1 Organic matter turbidity and other pollutants removal from water by corncoobs derivatives using jar test:

Table (3) shows the effect of using carbamated corn coobs on the specification of treated water. The results revealed that the using of 30 ppm of carbamated corn coobs have the lowest values of the examined parameters.

Comparing the uses of carbamated corncobs derivatives in different doses with ferric chloride and ferric chloride only, the examined parameters revealed that corncobs derivatives are able to remove turbidity, and reduce total hardness and total carbon and gives better water clarity.

Parameters	Raw water	Carbamated corncobs concentration (ppm)					
		10	15	20	25	30	35
Turbidity (NTU)	8.0	1.8	1.8	1.8	1.8	1.5	1.5
Conductivity (μ S)	567	550	557	556	556	554	556
Fe (ppm)	1.4	0.32	0.26	0.26	0.24	0.18	0.21
Mg (ppm)	22.0	22.0	19.8	17.2	16.8	14.2	14.1
Ca (ppm)	21.44	24.5	21.8	19.7	18.7	17.6	17.12
TC (total carbon) ppm	45.41	42.54	41.63	40.97	40.54	39.89	39.91
IC (inorganic carbon) ppm	40.17	36.32	34.99	34.22	34.02	34.52	34.65
TOC (total organic carbon) ppm	5.42	6.21	5.63	5.99	6.52	5.24	5.25

Table (4) shows that the optimum dose that gave best result was (25-30 ppm of carbamated corncobs with 35 ppm of ferric chloride). The efficiency of carbamated corncobs is due to protonation of its amino groups in water which makes corncobs positively charged, and thereby very attractive for flocculation and different kinds of binding applications. Since most natural colloidal particles, including organic matter, bacteria and macromolecules, are negatively charged attractive electrostatic interactions may lead to flocculation. Besides, corncobs derivatives possess positively charged groups due to the creative primary amino group. Therefore, the corncobs derivative can remove organic matter, and some inorganic elements from water.

Table (4): The effect of adding combination of ferric chloride and carbamated corncob to the raw water with concentration of 35 ppm of ferric chloride and a range of modified corncobs injection from 10 to 35 ppm.

Parameters	Raw water	Carbamated corncobs (ppm)						
		0	10	15	20	25	30	35
Turbidity	8.0	1.5	1.4	1.5	1.5	1.4	1.3	1.5
Conductivity	567	590	583	581	584	576	575	570
TC (total carbon) ppm	45.41	46.65	42.65	41.32	39.9	38.42	42.79	41.72
IC (inorganic carbon) ppm	40.17	33.71	32.11	31.32	30.98	32.94	32.7	32.62
TOC (total organic carbon) ppm	5.42	12.95	10.62	9.79	8.78	5.28	9.45	9.11

3-4-2. Effect of mixture of ferric chloride and produced carbamated corncobs to produce the best water clarity.

The results obtained reveal that reducing the dose of ferric chloride from 35 ppm to 20 ppm with using the carbamated corncobs gave a best water clarity and Table (5) shows that the

optimum dose that gave best result was (35 ppm of carbamated corncobs with 20 ppm of ferric chloride).

Table (5): shows the effect of adding combination of ferric chloride and carbamated corncob to the raw water with concentration of 20 ppm of ferric chloride and a range of carbamated corncobs injection from 10 to 40 ppm.

Parameters	Raw water	Carbamated corncobs (ppm)						
		10	15	20	25	30	35	40
Turbidity (NTU)	8.0	1.8	1.8	1.8	1.8	1.5	1.2	1.3
Conductivity (μ S)	567	550	557	556	556	558	556	567
Fe (ppm)	1.4	0.32	0.26	0.26	0.24	0.18	0.21	0.36
Mg (ppm)	22.0	22.0	19.8	17.2	16.8	16.2	15.1	15.4
Ca (ppm)	21.44	24.5	21.8	19.7	18.7	19.6	19.12	19.5
TC (total carbon) ppm	45.41	42.54	41.63	40.97	40.54	39.99	39.91	42.62
IC (inorganic carbon) ppm	40.17	36.32	34.99	34.22	34.02	34.92	34.65	36.76
TOC (total organic carbon) ppm	5.42	6.21	5.63	5.99	6.52	5.44	5.25	5.98

Also Figures (5) show the water clarity of raw water and floc forming due to flocculation by using ferric chloride and the carbamated corncobs. It is clearly seen that adding the prepared carbamated corncobs to ferric chloride enhanced the flocculation process and water clarity where the size of flocs when using carbamated corncobs is much higher than that formed when using ferric chloride only and the size of flocs increased with increasing the amount of the carbamated corncobs. Also, the time of floc formation and settling time is better when using carbamated corncob with ferric chloride and the time decreased with increasing the amount of prepared carbamated corncobs.

Figure (5) show the floc forming at the end of flocculation processes Where the dosing amount of (A) 20 ppm FeCl_3 , (B) 20 ppm FeCl_3 + 30 ppm carbamated corncobs, and (C) 20 ppm FeCl_3 + 35 ppm carbamated corncobs.

3-4-3. Removal efficiency at optimum conditions:

The effects of using carbamated corncobs and ferric chloride mixture at the optimum conditions on each of turbidity, TDS (Total dissolved solids), TC (total carbon), IC (inorganic carbon), TOC (total organic carbon), Mg^{2+} , and Ca^{2+} was calculated as percentage removal are listed in Table (6).

Table (6) Effect of adding ferric chloride and carbamated corncobs at the optimum condition on the percentage removal of turbidity, TDS, TC, IC, TOC, Mg^{2+} and Ca^{2+} from tested water

Items	Removal efficiency
Turbidity	81.2%
TDS	1.9 %
TC (total carbon)	16.1%
IC (inorganic carbon)	12.2%
TOC (total organic carbon)	3.9%
Mg^{2+}	26.8%
Ca^{2+}	27.1%

4-Conclusion:

The protonation of amino groups in water makes carbamated corncobs positively charged, and thereby very effective for flocculation. Since most natural colloidal particles in water, including organic matter, bacteria and macromolecules, are negatively charged particles. The attractive electrostatic interactions between natural colloidal particles and carbamated corncobs may lead to flocculation. Therefore, the carbamated corncobs can remove organic and inorganic matters carrying negative charges from water, and hence enhancing the water clarity when used with a half dose of ferric chloride.

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