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Synthesis and characterization of a new coagulant PA6/CMC for the removal of water turbidity

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Abstract

Turbidity adds an objectionable appearance to waters. The effectiveness of PA6/CMC composite in coagulation and flocculation to improve the quality of waters was investigated. Results of the "jar test" conducted indicated that by adding 0.01 gm of PA6/CMC at pH 5 and time of 30 min., turbidity of solution was reduced to about 95% at 50NTU and 98% at 100NTU respectively. The results of this study suggest that PA6/CMC copolymer is a potential coagulant for reducing turbidity during water treatment.

Keywords: Nylon6 waste, carboxy methyl cellulose, coagulation, Jar test, turbidity.

INTRODUCTION

Solid waste is defined as waste, sludge, and neglected solid deposits resulting from industrial and commercial operations, as well as community activities, as it not only poses a threat to the environment, but also poses an increasing threat to human health and lifestyle. Waste management includes waste collection, transportation, treatment, recovery and disposal[1]. In general, solid waste consists of fixed components (plastic, glass, metal, and others), where 19% is recycled and 11% is used for energy recovery, it is usually kitchen waste, paper, cardboard, and plastic waste. Recent research indicates that the amount of waste solid plastic generated annually in the world amounts to about 150 million tons, in addition to the amount of plastic waste accumulated in the sea[2]. The great global demand for polymers leads to the need for new sustainable ways to reproduce and recycle polymers from plastic waste[3], synthetic polymers are frequently applied in wastewater treatment to foster coagulation among the flocculants most employed in the laboratory[4].

A generic designation for a family of synthetic polymers composed of polyamides (repeating units linked by amide linkages). Nylon is a silky thermoplastic material that can be melted into fibers, films, or shapes, it can be mixed with a variety of additives to achieve many variations in different properties, it have found important commercial applications in textiles and fibers (clothing, flooring, rubber reinforcement), in shapes (molded parts for automobiles, electrical equipment, etc.) and in films (often for food packaging)[5], nylons are aliphatic polyamides group, that consist of polyethylene section $(CH_2)_n$ unattached by peptide units (NH-CO)[6]. Nylon-6 is the famous member of the family of nylons due to the verity that it is the low costly of its family, it is considered as fresh caprolactam, which is a ring-structured molecule, this ring is opened and the molecule polymerizes with itself as in Figure 1, it has close mechanical properties including the tensile strength and influence strength, however, from the economic terms, costs around 30% less [7], nylon used in the fiber and textile industries. [8].

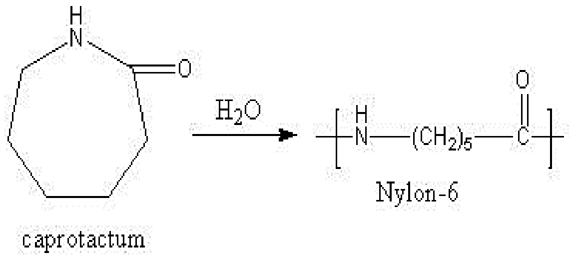


Fig. 1 Preparation of Nylon-6 from caprolactam

Carboxymethyl cellulose (CMC) is an anionic, water-soluble derivative of cellulose, a linear polysaccharide of anhydro-glucose, the repeating units are connected by β-1,4- glycosidic bonds. At the molecular level, the major difference between CMC and cellulose is only some anionic carboxymethyl groups (i.e. $–CH_2COOH$) in the CMC structure that replace the hydrogen atoms from some hydroxyl groups present in the pristine cellulose infrastructure[9]. The most important properties of CMC are viscosity building and flocculation, among all the poly- saccharides, CMC is easily available and it is also very cheap, it has high shear stability. The structure of CMC is shown in Figure 2. Polymeric flocculants are gradually being used more and more due to their low dose, ease in treatment, non-interference with pH of the suspensions and larger floc forming ability[10].

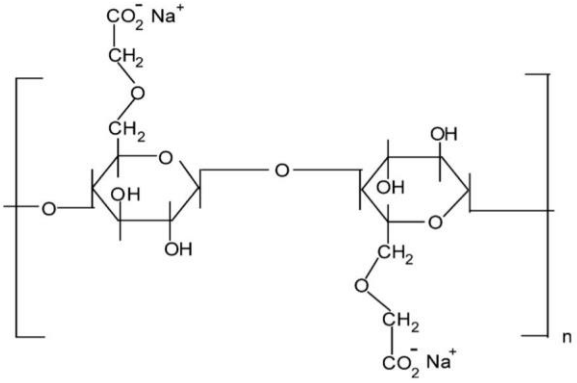


Fig. 2. Structure of CMC.

Turbidity is a basic process for testing water quality, it is commonly measured to determine the extent of water visibility by a turbidity meter. It is formed due to small particles that are often invisible to the naked eye and are similar to smoke in the air [11]. Although turbidity is resulted from various species of materials, such as colloids, particles, dissolved materials, and biomass. It is regulated to ≤1 NTU in most countries, a high turbidity level means a higher probability for people to injury gastrointestinal diseases and other health problems[12]. Different methods were proposed for turbidity removal by many researchers, for instance , Daverey et al used banana peels and Indian bean seeds aqueous extractants as natural coagulants to remove turbidity [13].

Coagulation is one of the most important chemical processes used to treat water and waste water [14], it is used to purify drinking water before filtration and sedimentation[15]. A coagulant is used that interacts strongly with water and forms hydroxide hydrophobic[16]. Inorganic polymers (natural or synthetic) are used in coagulation. Researchers used natural coagulants in wastewater treatment due to the advantages of these coagulants in terms of low toxicity, biodegradability, environmental friendliness, and safety for human health[17]. After coagulation comes flocculation, which is a chemical method of water treatment[18], which is slow or rapid stirring to encourage the particles formed from the coagulant to agglomerate into clumps large enough for sedimentation or filtration from the solution[19].

The aim of this study is to get rid of nylon 6 waste that causes environmental pollution and use it to prepare a composite polymer PA6/CMC and use the prepared polymer to remove turbidity of water by coagulation method and study the influencing factors such as pH, dose and time required for flocculation.

Materials and methods

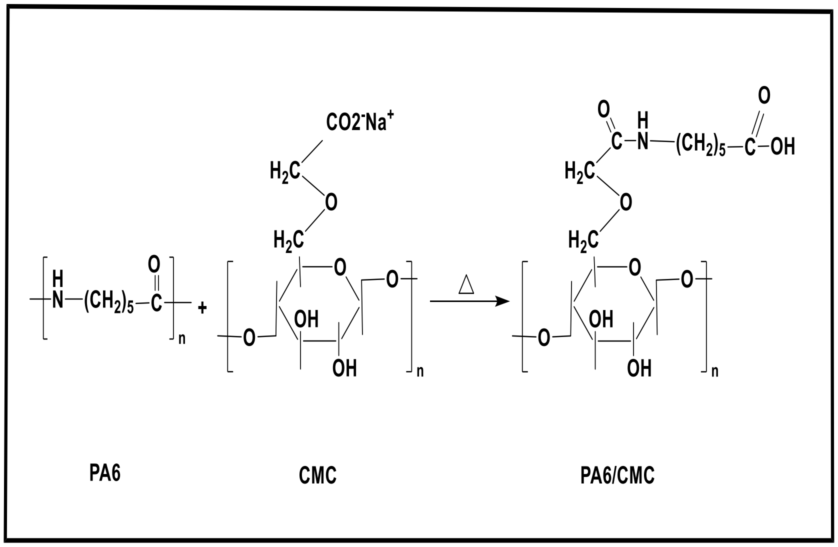
Materials

All materials in this work were of analytical grade and were used as received without further purification and then tested and prepared in order to be suitable for real experiments. Nylon-6 waste collected and cleaned, CMC, Formic acid, N, N Di methyl formamide, NaOH (0.1N), HCl (0.1N), ethanol, Stock solution of 500 NTU from bentonite, standard solutions for preparing 50, 100 NTU for the determination of turbidities using Turbidity meter.

Methods

Synthesis composite polymer PA6/CMC

PA6 (5 g) was dissolved in HCOOH (50 mL) by heating (60 C°) under stirring, 0.5 g of carboxy methyl cellulose was dispersed into 200 mL of HCOOH/DMF (1:4), sonicated for 1 hr. As (CMC) slurry was added to the PA6/HCOOH solution, a phase separation instantly occurred with most of the PA6 remaining in solution, while gray PA6-CMC nanohybrids which were found to float were easily collected, rinsed in water, coagulated in ethanol, ground into fine powder (100–150 µm) and finally dried in a vacuum-oven at 90 C° overnight. The amount of precipitate formed was found to be equal to 1.44 g.



Scheme 1. reactions between polyamide 6 (PA6) and carboxy methyl cellulose

Characterization techniques

The prepared polymer PA6/CMC was characterized by the following techniques:

Fourier Transformer Infrared Spectroscopy (FT-IR)

The active functional aggregates were determined using FTIR through the vibration frequencies in the PA6/CMC polymer, which is a spectrophotometer that determines the spectra between 500-4000 cm^{-1} after taking 0.1 gm of the polymer.

In Figure 3, the FTIR spectrum of PA 6 contains a band at frequency 3514.42 cm^{-1} that belongs to the amine group N-H and a distinct band at frequency 2924.18 cm^{-1} that belongs to the C-H aliphatic bond. There is also a clear band at frequency 1647.26 cm^{-1} that belongs to the carbonyl group C=O and a band at frequency 1550.82 cm^{-1} that belongs to the C-N bond, also observed bond at frequency1431.23 cm^{-1} belongs to the C-O.

In Figure 4, the FTIR spectrum of CMC. As this compound has absorption bands at the site 3510.56 cm^{-1} due to the presence of the hydroxyl group O-H, and the presence of an absorption band at the site 2877.89 cm^{-1} due to the presence of aliphatic C-H groups, as well as the presence of an absorption band at the site 1608.69 cm^{-1} refers to the carbonyl group C=O in the compound, while the absorption band at the site 1114.89 cm^{-1} is attributed to the presence of the C-O group, and the absorption band at the site 1060.88 cm^{-1} is due to the presence of aggregates C-C, and the presence of an absorption band at the site 895.00 cm^{-1} due to the presence of the -CH-bending group.

In Figure 5, the FTIR spectrum of PA6/CMC. Which contains two absorption bands at the 3487.42 and 3340.82 cm^{-1} sites attributed to the presence of the amine group N-H, and the presence of absorption bands at the 3078.49 cm^{-1} site attributed to the presence of the hydroxyl group (O-H), and the presence of two absorption bands at the two sites 2931.90, 2858.60 cm^{-1}, due to the presence of the aliphatic (C-H) group, as well as the appearance of a significant decrease in the intensity of the beam at the site 1658.84 cm^{-1}, which belongs to the C = O group. An increase in the intensity of the beam is also observed at the site 1539.25 cm^{-1} is due to the stretching frequency of the amine group N-H, which is attributed to the stability of the bonding of the carbonyl group in the CMC compound with the amine group in the compound PA6, as well as the presence of band at the site 1168.90 cm^{-1} due to the presence of a group C-N, and the presence of an absorption band at the 956.72 cm^{-1} site is attributed to the presence of the C-O group, while the two absorption bands at the 729.12 and 690.54 cm^{-1} sites are due to the presence of -CH- bending groups. Table. 1. Demonstrate the characteristic frequencies from the infrared spectra in PA6/CMC.

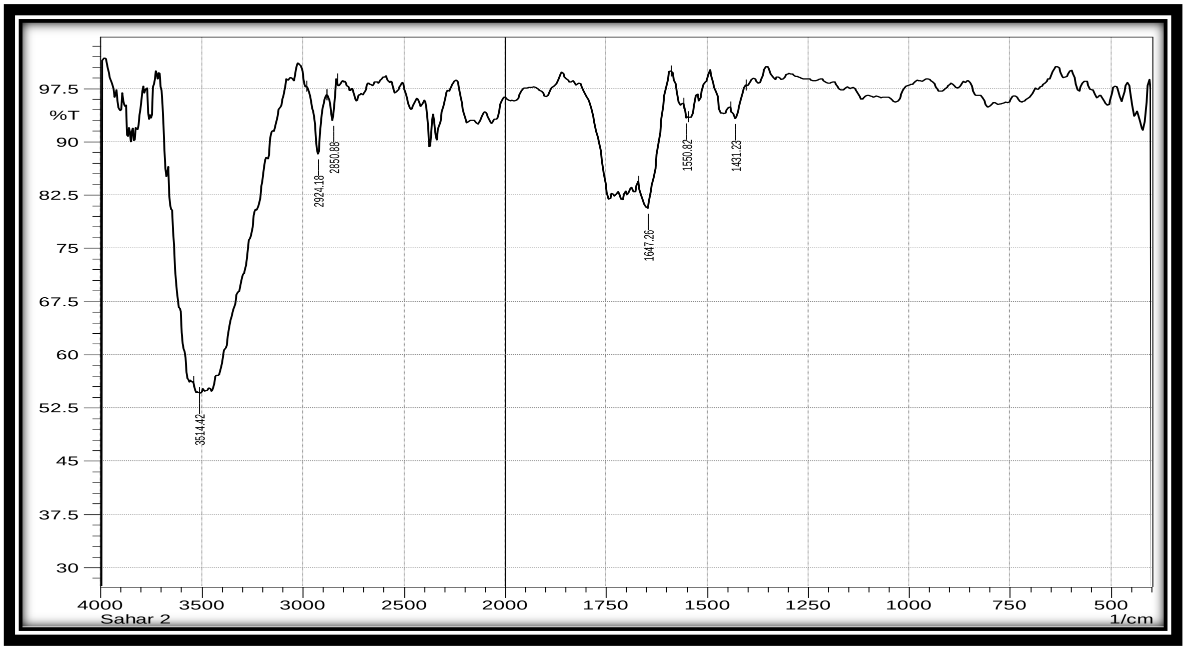


Figure. 3. FTIR spectrum of Nylon-6

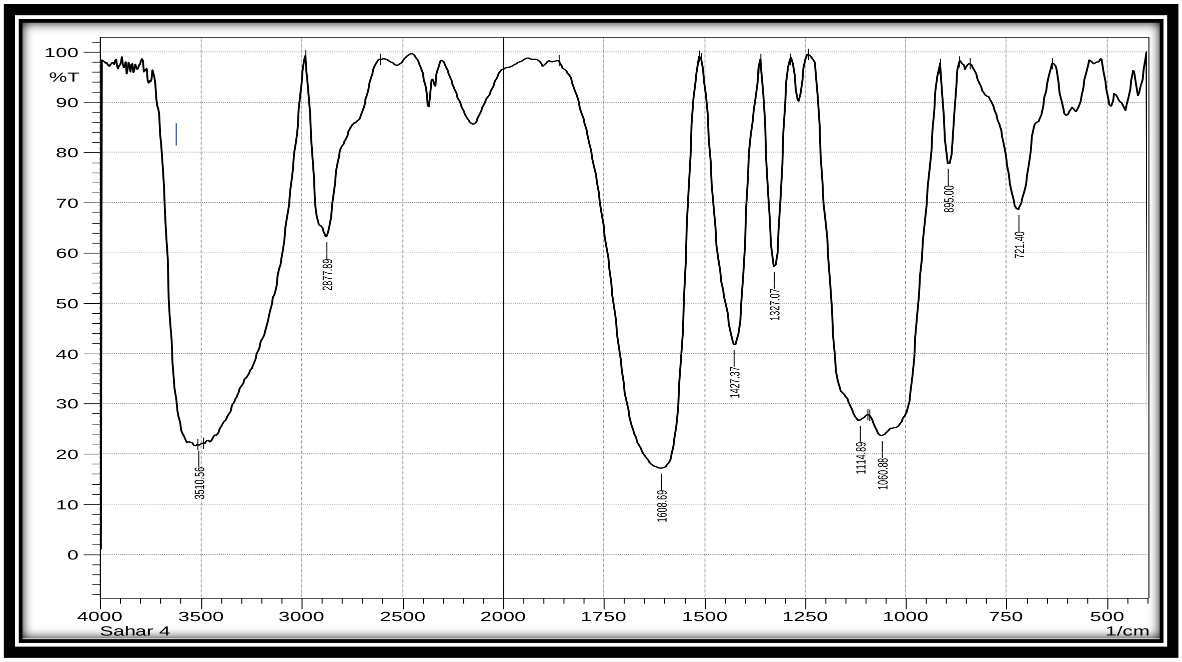


Figure. 4. FTIR spectrum of Carboxy methyl cellulose

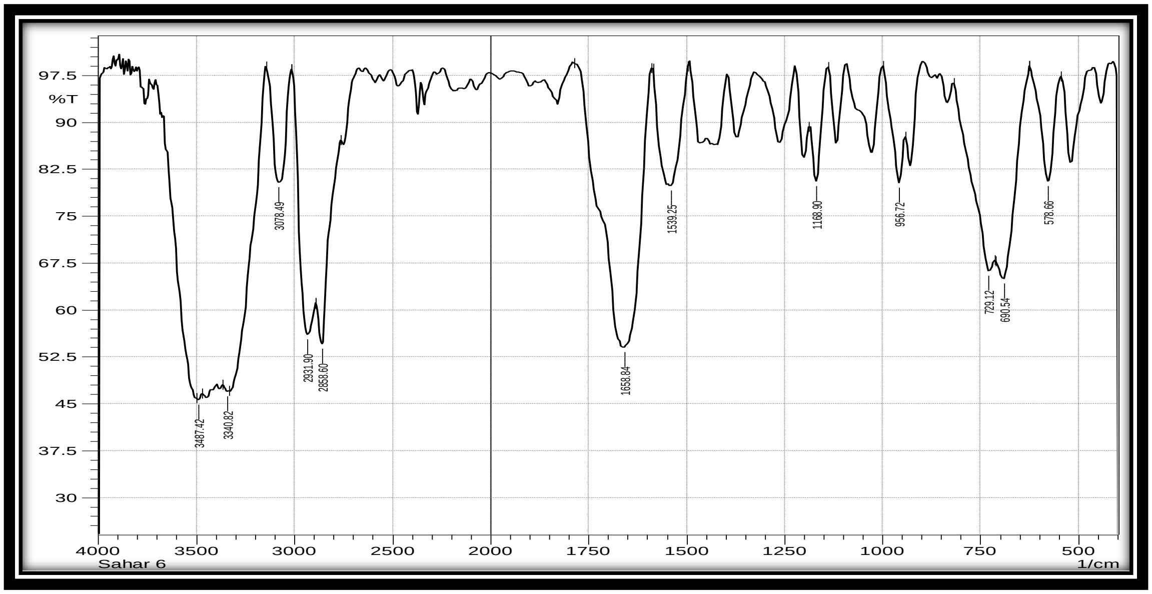


Figure. 5. FTIR spectrum of PA6/CMC

Table. 1. characteristic frequencies from the infrared spectra in PA6/CMC

Frequency (cm^{-1})	Assignment
3514.42	N-H in PA6
3487.42	N-H in PA6/CMC
1539.25	N-H stretching in PA6/CMC
3078.49	O-H hydroxyl group in CMC
3510.56	O-H hydroxyl group in PA6/CMC
1647.26	C=O carbonyl group in PA6
1608.69	C=O carbonyl group in CMC
1658.84	C=O carbonyl group in PA6/CMC
1550.00	C-N bond in PA6
1168.90	C-N bond in PA6/CMC
2924.18	C-H aliphatic in PA6
2877.89	C-H aliphatic in CMC
2931.90	C-H aliphatic in PA6/CMC
1431.23	C-O stretching in PA6
1114.89	C-O stretching in CMC
956.72	C-O stretching in PA6/CMC

Thermal gravimetric Analysis (TGA)

(TGA) is a useful technique for examining thermal stability to an information field of its composition, or the temperature at which weight loss occurs in the idea of survival of a material under standard conditions [20]. The advantages of the thermogravimetric analysis technique is a sufficiently small sample that allows for quantitative or qualitative analysis, low cost and the analysis is not completely accurate due to the presence of volatile components in the sample[21].

The Figure 6, represents the thermogravimetric analysis curve of the prepared polymer PA6/CMC. We note from the figure that this polymer decomposes in one stage at the temperature of 446 C° with a weight loss of 65%. The weight loss in the initial stages could be related to the loss of the water part of the polymer main chain. As at the temperature of 418 C° it lost 25% of its weight, and at the temperature of 438 C° the compound lost 50% of its weight, and at the temperature of 452 C° the compound lost 75%, while at the temperature of 500 C° a significant loss of weight occurred by 98.17 % of the weight of the compound attributed to the cleavage of the polymer and gaseous products at this temperature, which leaves a charring content (carbon residue) at 600 C°, as the remaining weight was 2% of the weight of the polymer, and when calculating the thermal functions of the dissociation curve, we note that the prepared polymer PA6/CMC loses half of its weight as T50% at 438C°, and the total dissociation velocity of the polymer is 8.111%/min.

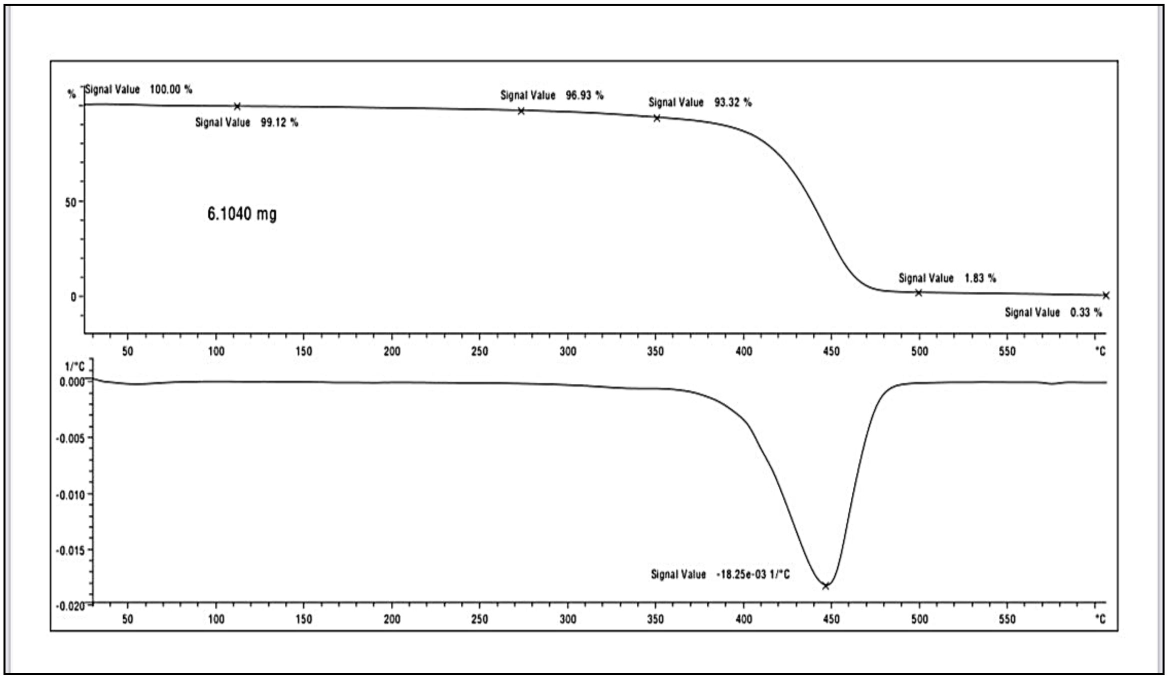


Fig. 6. Thermogravimetric diagram of PA6/CMC

X-ray Diffractometry

(XRD) It is an analytical technique used to distinguish the crystalline phases of a number of materials, is strong and non-destructive to describe crystalline materials, as it provides structural information such as crystallinity, separation, grain size and crystal defects, peaks are produced for X-ray diffraction by constructive interference of a group of monochromatic beams of X-rays scattered at specific angles[22].

The crystallinity index (CI) can be calculated using the following formula on the basis of X-ray diffractograms:

$$CI\ (\%) = [(Im - Iam)/Im] \times 100$$

where Im is the crystalline peak's maximum intensity in arbitrary units, about 2θ, and Iam is the amorphous diffraction [23].

It was observed that the X-ray diffractogram Figure 7. of PA6/CMC. It shows the presence of a sharp band at = 21.6° (2θ), and this indicates the presence of a strong reflection at this angle of the compound. The crystallization rate reached (75%). This is due to the fact that the polymeric chains formed hydrogen bonds between H-N and C=O, which made them in the form of parallel to the axis.

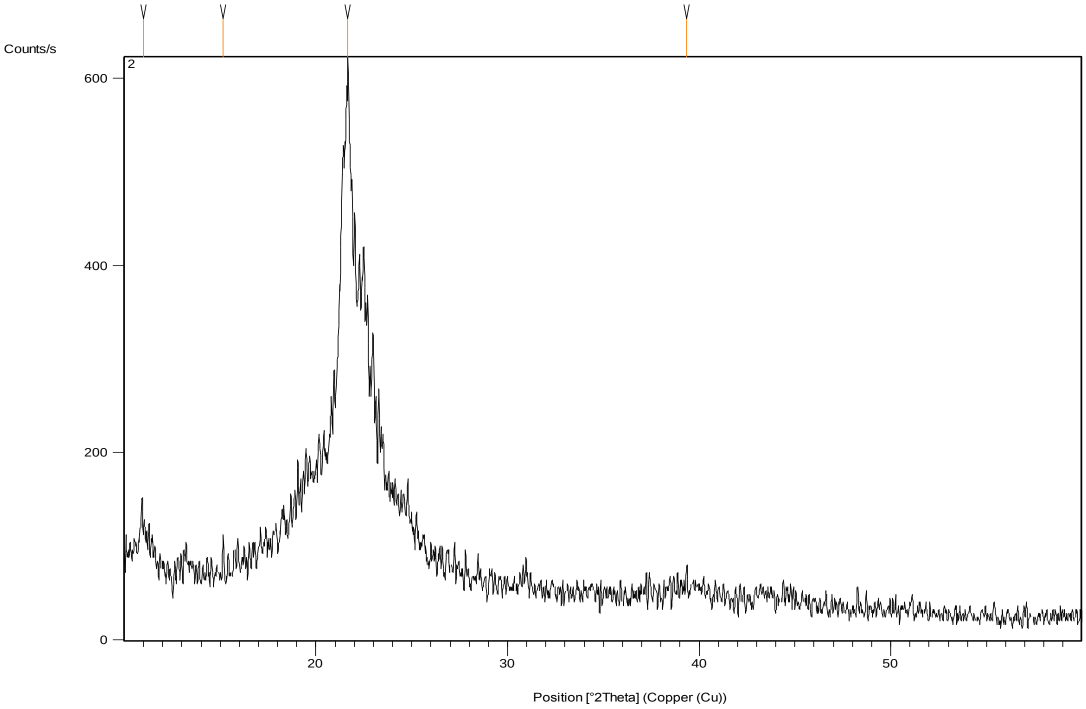


Fig. 7. X-Ray Diffractometry of PA6/CMC

Field Emission Scanning Electron Microscopy (FESEM)

FESEM is an advanced microscope that provides superior magnification and very accurate observation with less effort than the SEM found in most laboratories[24]. FESEM is the ideal choice for maximum sample flexibility for high-performance, high-resolution imaging, and excellent analysis of synthetic materials. This technique can be used in a wide range of applications such as metallurgy, ceramics, polymer, physics, chemistry, life sciences, and nano research[25].

The FESEM micrographs of PA6/CMC showed in Figure 8, as small sized particles with small nanoparticles with long nanoparticles containing cracks and long voids at 1µm, 10 µm, 200 nm where it was observed cavities and pores of different sizes and shapes that developed during the process of heat treatment and chemical activation, these pores will work to increase the spaces surface of compounds, so these holes and pores play an important role.

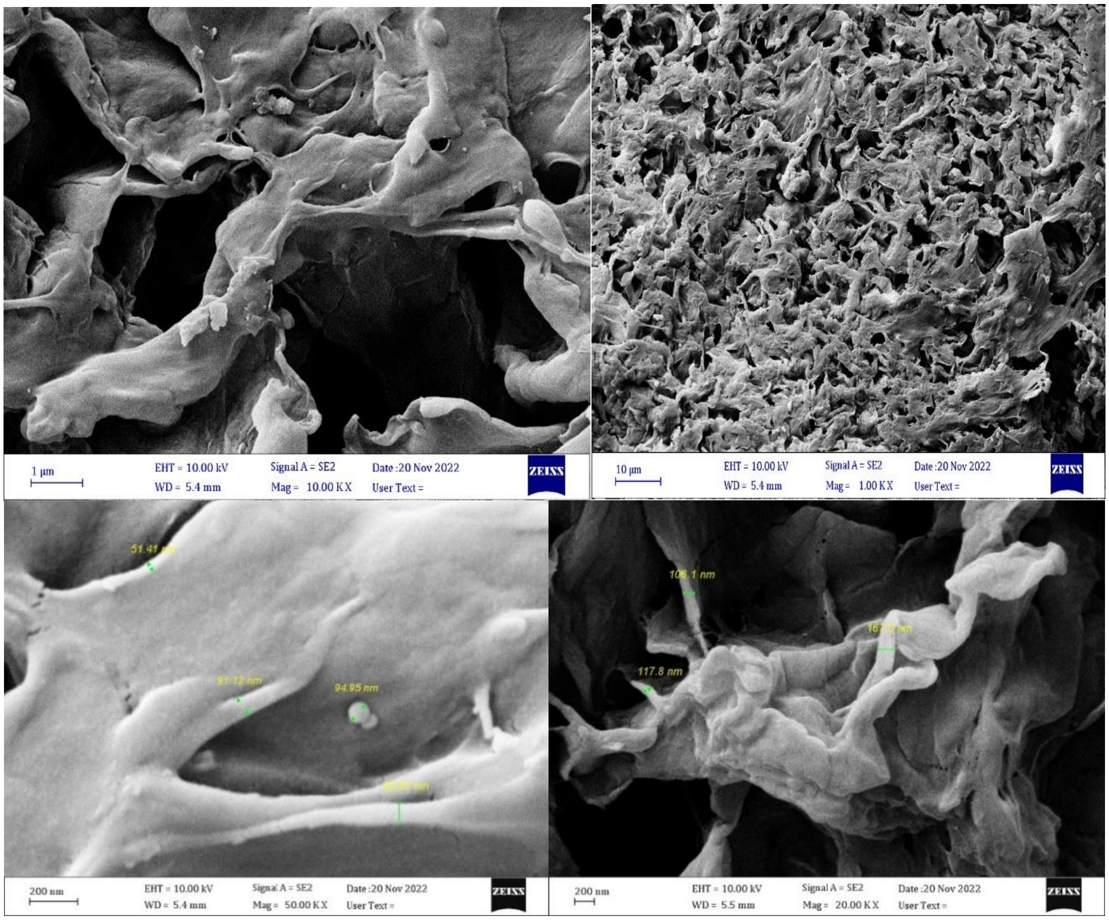


Figure. 8. FESEM micrograph for PA6/CMC

Energy -dispersive X-ray (EDX)

Energy Dispersive X-ray (EDX) is an analytical chemical technique used to analyze the elements associated with the electron microscope based on the generation of distinct X-rays that reveal the presence of the elements in the samples, as it contains On both quantitative and quantitative information, each element has its own distinct atomic structure, and thus it has a group of distinct peaks in the X-ray spectrum [26].

Figure 9 shows the PA6/CMC x-ray energy dispersion spectroscopy, as we note the presence of 80.1% carbon, oxygen by 11.2%, and nitrogen 8.7% This indicates the interaction between PA6 and CMC, as well as the appearance of a peak of energy at 0.2 KEV, which is attributed to the element carbon, as well as the appearance of a peak of energy at 0.3 Kev, which is attributed to the presence of an element. nitrogen, a peak of energy at 0.52 Kev attributable to the presence of oxygen.

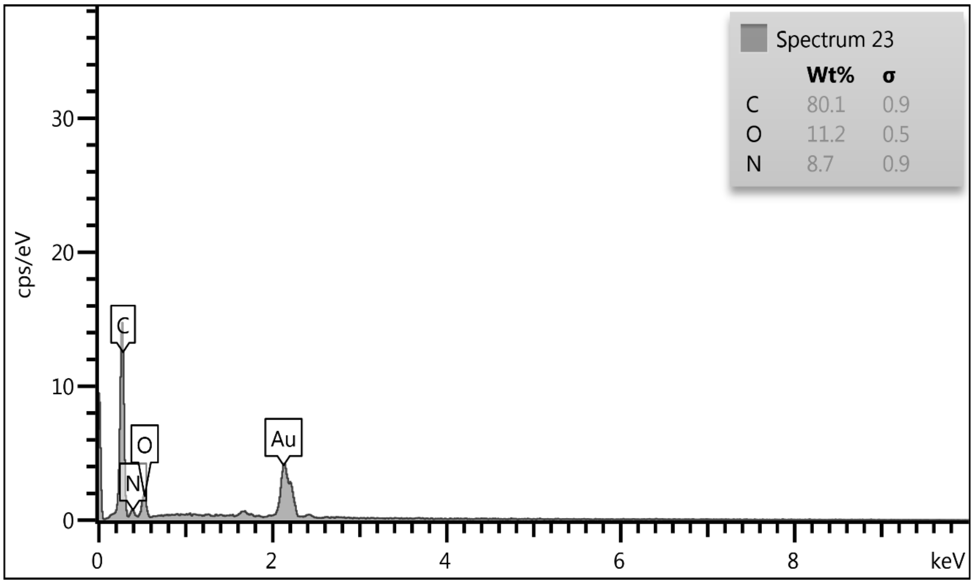


Figure. 9. X-ray energy dispersive spectroscopy for PA6/CMC

Coagulation study

Characterization of bentonite

Bentonite was grounded by mill and then sieved. The sieve portion was kept below 200 µm for all tests [27].

Preparation of Synthetic Turbid Water

To prepare water with a turbidity of 50, 100 (NTU), 20 g of ground bentonite was added to 500 ml of distilled water (DW) and mixed at 500 rpm for 5 minutes. Left the suspension to settle for 20 min, after which the supernatant was filtered to remove large unsuspended particles. The prepared suspension was used as a stock to prepare water samples with different turbidity concentrations for coagulation tests. and a test jar was used for coagulation experiments[28].

Coagulation experiment

A batch test for coagulation and flocculation was performed using jar test equipment that consist of six-beakers as in Figure 10. All studies were conducted at (25 C°), and each beaker contained 250 mL of bentonite water at turbidities of 50, 100 NTU. The coagulant and turbid water mixture was stirred at high speed 200 rpm for 1 min, followed by slow speed at 15 rpm for 15 minutes. The flocs were allowed to settle for 20 minutes. Samples were drawn with a volumetric pipette at 3 cm below the surface of the mixture, final turbidity was determined using a turbidity meter. The instrument's sensitivity allows it to detect turbidity as low as 0.02 NTU. (Nephelometric Turbidity Units), and the effect of several parameters, including pH, coagulant dose, initial turbidity[29].

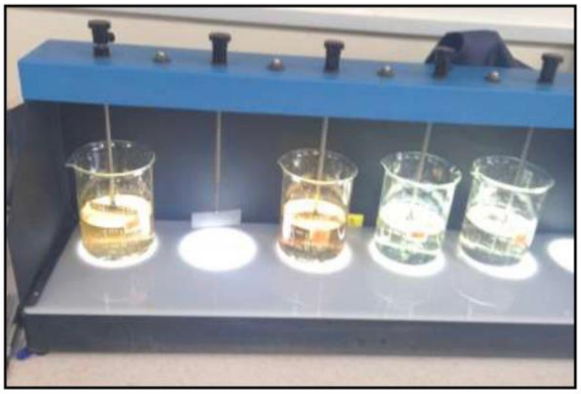


Fig. 10 Instrument Jar test

Treatment turbidity with prepared compound PA6/CMC as coagulants

After the prepared compound were added to the jars, which contained turbid water, one minute of vigorous mixing at 200 rpm and 15 minutes of gradual stirring at 15 rpm were completed. The agglomerates were allowed to settle for 20 minutes. Using a turbidity meter, the supernatant's turbidity was assessed after being pipette-withdrawn from a 3 cm depth. The removal efficiency of the studied parameters in these experiments was calculated by direct equation [30].

$$\text{Removal Efficiency} = \frac{(To - Ti)}{To} \times 100$$

Where, To , Ti represent the initial and final turbidity, respectively.

Effect of pH on residual turbidity

` In order to inspected the coagulation efficiency, a number of jar test experiments were performed. The prepared compound PA6/CMC with solutions of turbidity 50, 100 (NTU) under various pH conditions. The suspension's pH was changed by adding either (0.1 N) NaOH or (0.1) N HCl. By using pH values for each turbidity value: 2, 3, 4, 5, 6, 7, 8, 9 and 10. chosen pH that gives the highest turbidity removal efficiency. The results shown in Figure 11 showed the effect of pH on the turbidity removal efficiency using PA6/CMC polymer, which shows that the optimal pH is 5, as it was observed that the turbidity removal efficiency increased to 91% and 95% at 50 and 100 (NTU).)

respectively, while the turbidity removal efficiency decreases at pH 10 to reach 65% and 70% at 50 and 100 (NTU), respectively, which indicates that the turbidity removal efficiency is better in the acidic medium than the basic one, as it is at PH 5 the sedimentation of the masses was more and better, and this indicates the ionization of the prepared polymer PA6/CMC added to water at this pH, as the concentration of hydrogen ions H^+ and hydroxide OH^- is almost neutral, allowing positive ions to adsorb with organic materials and solids, causing charge neutralization at this. The acidic pH which facilitates the sedimentation process, and thus flocculate in the form of large particles forming bridges between the organic and colloidal materials during the mixing process with the composite polymer, which leads to their agglomeration and sedimentation from the water by the action of gravity.

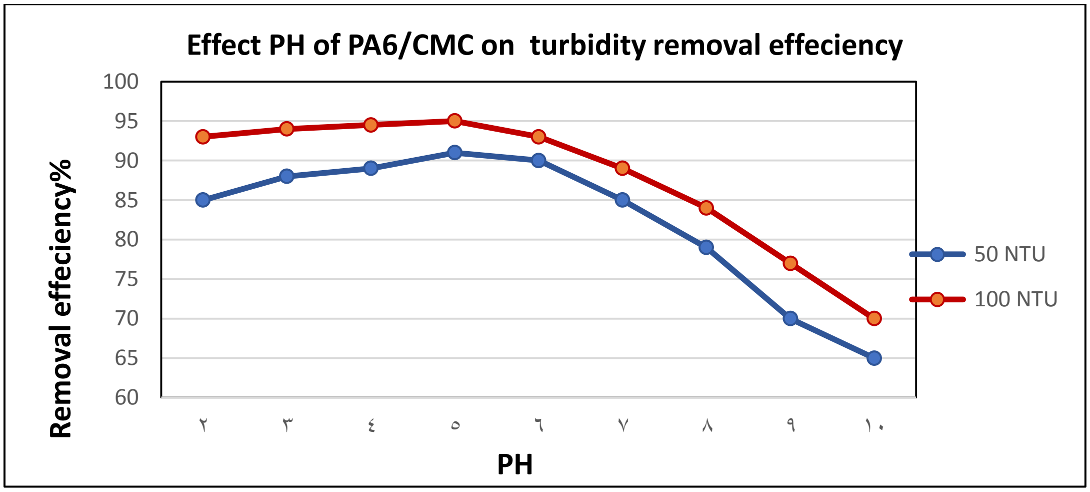


Fig. 11. Turbidity removal efficiency of PA6/CMC as function of pH

Effect of the prepared polymer dosage on residual turbidity

Dosage is one of the most important factors to consider in order to determine the optimal performance of any coagulant to remove contaminants because the coagulant alters or destabilizes negatively charged particles, dissolved and colloidal contaminants[31]. In this study, the water removal efficiency was studied at different doses of polymer PA6/CMC, as it used different weights ranging from 0.01 gm to 0.4 gm to destabilize the bentonite suspension at 50, 100 (NTU), better coagulation and turbidity in water can be achieved with the help of coagulation. The results shown in the Figure 12 show a decrease in the turbidity removal efficiency with increasing the dose, and thus the optimal dose of the prepared polymer PA6/CMC was obtained at 0.01 gm at both 50 and 100 (NTU), as the turbidity removal efficiency was 92% and 95% at 50 and

100 (NTU) respectively. The main reason for increasing the dose for turbidity 100 (NTU) is that the lower dose could not remove the increased turbidity.

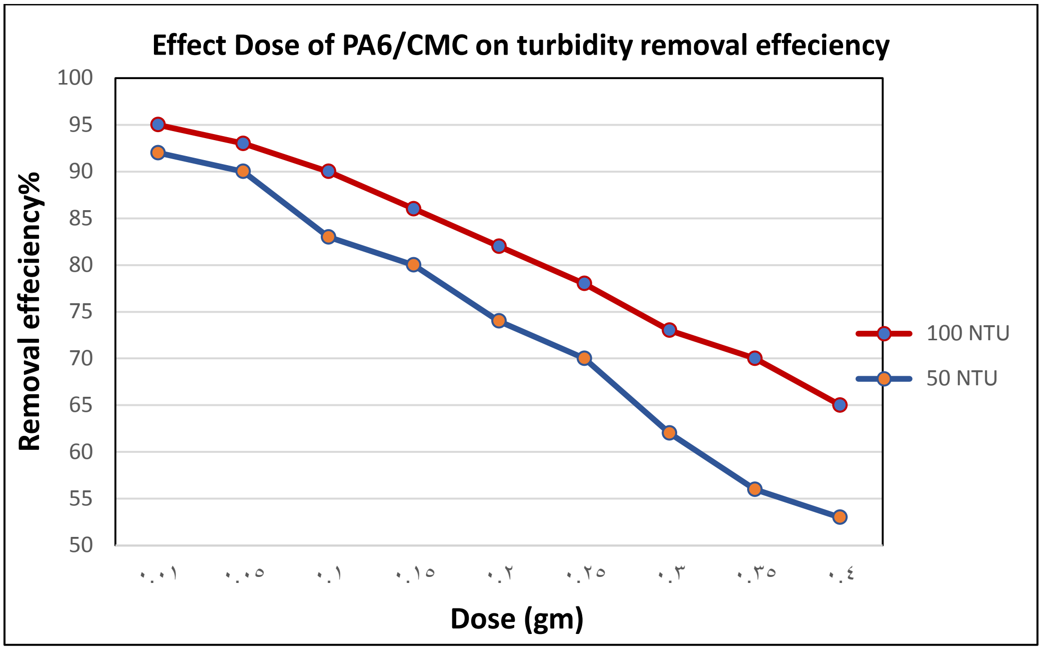


Fig. 12. Turbidity removal efficiency of PA6/CMC as function of Dose

Effect of flocculation timing on remaining turbidity

The effect of time is an important factor, as it is important to determine the optimal time for the state of equilibrium to predict the performance and quality of the adsorbent material for the adsorption process [32]. The treatment time was studied on the efficiency of water turbidity removal by the prepared polymer PA6/CMC (fig.13) to destabilize the bentonite suspension at 50, 100 (NTU) and for different time periods from 10 min to 60 min, and the time that achieves the highest turbidity removal efficiency by the prepared polymer PA6/CMC was chosen. It can be seen that the percentage of dissolved solids removal increases with increasing settling time, in the prepared polymer PA6/CMC the removal efficiency was low at time between (10-20) min, while the percentage of turbidity removal efficiency increased at 30 min, to be the removal efficiency of turbidity 95% at 50 NTU and 98% at 100 NTU, as there was an increase in the removal of dissolved solids after the equilibrium stabilized, we note that the turbidity removal efficiency rates increase significantly at the beginning until the time 30 min, after which the increase is constant until reaching saturation, this it indicates that an increase in the settling time is required to achieve the highest turbidity removal efficiency. Table. 2. Show Turbidity removal efficiency of the prepared polymer PA6/CMC under ideal conditions

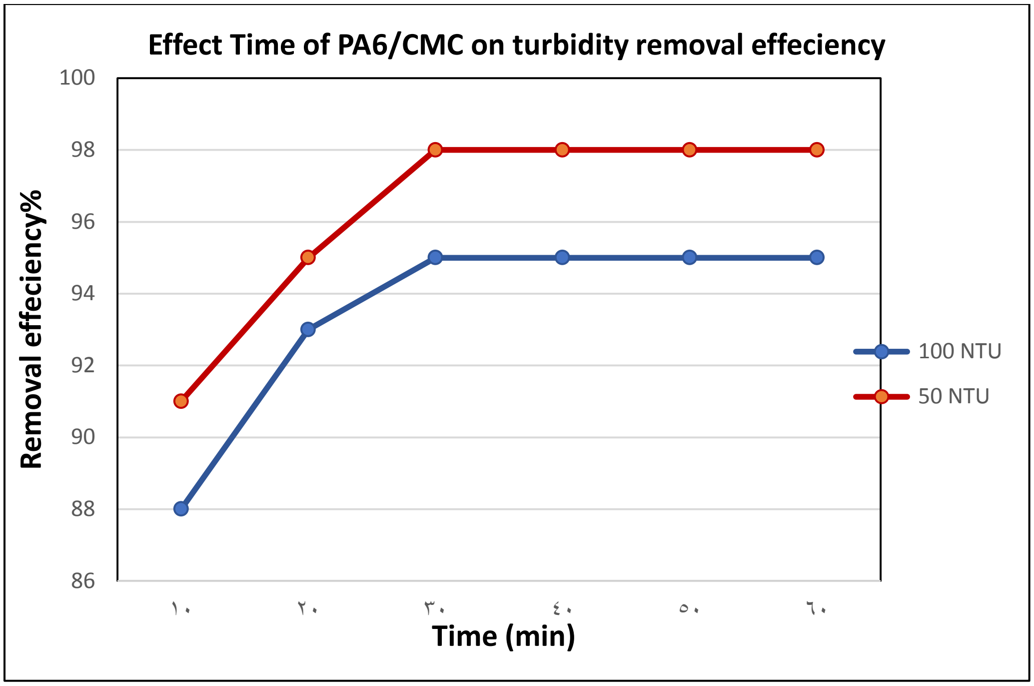


Fig. 13 Turbidity removal efficiency of PA6/CMC as function of Time

Table. 2. Turbidity removal efficiency of the prepared polymer PA6/CMC under ideal conditions

polymer	PH		Dose		Time	
	50 NTU	100 NTU	50 NTU	100 NTU	50 NTU	100 NTU
PA6/CMC	91	95	92	95	95	98

Treatment of raw water samples with modified polymers

To find out the efficiency of the prepared polymer PA6/CMC to reduce the turbidity of the raw water, a jar test is conducted on a sample taken from the Shatt Al-Arab water in Basra with a turbidity of 128 NTU. 50 ml of the water sample is taken and its pH is adjusted at 5, then 0.01 gm of PA6/CMC is added to it, shaken with an electric vibrator, and left for 30 minutes, then the turbidity was measured with a turbidity meter. The polymer achieved a high removal efficiency of water turbidity, as the turbidity decreased to 8.5, so that the turbidity removal efficiency was 93% as in Figure 14.

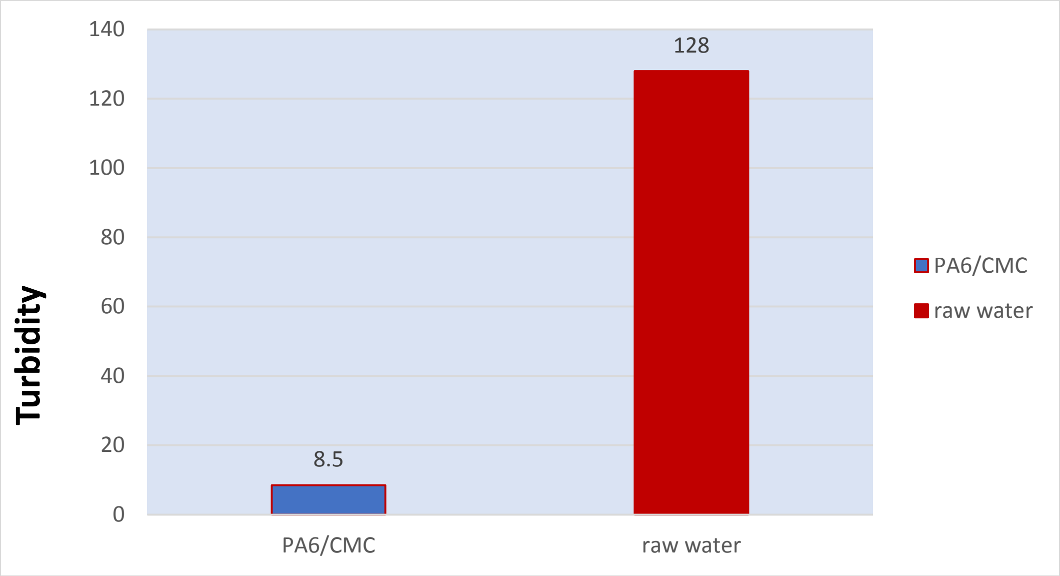


Fig. 14. Effect of prepared polymer PA6/CMC on raw water

Conclusions

This study has successfully examined the capability of PA6/CMC composite to be used as excellent coagulant in replacing the use of the current chemical coagulants. This low-cost coagulant shows promising coagulation performance with turbidity removal exceeding 95%. PA6/CMC composite is comprised of high polysaccharide content, making it the main active coagulant agent. The study also showed that PA6/CMC composite with high polysaccharide content requires a lower coagulant dosage. The coagulation mechanism is interparticle bridging and charge neutralization.

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