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Flocculation of Clay Suspensions Using Copolymers Based on Acrylamide and Biopolymer

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In this work, we synthesized new copolymers by modification of carboxymethylcellulose (CMC) with acrylamide and/or 4-vinylpyridine. These copolymers were characterized using Infra-Red Spectroscopy (FTIR), thermogravimetric analysis (ATG) and X-ray diffraction (XRD) methods. They were used as flocculants for treatment of water suspensions containing bentonite and kaolin particles. Moreover, the effects of several factors such as the pH, floculants concentration, suspensions concentration, and settling time were investigated. The obtained results showed that the presence of 4-vinylpyridine (4VP) in the copolymer had a positive effect on the efficiency of turbidity elimination. It is worth noting that for a settling time of 10 min, and for the CMC-AM-4VP copolymer, this efficiency reached the values of 89% and 75% for bentonite and Kaolin suspensions, respectively.

Keywords: Flocculant, CMC, Acrylamide, 4-Vinylpyridine, Bentonite, Kaolin

INTRODUCTION

Water is a renewable resource. There are two types of resources: surface water, which has a very rapid rate of renewal, and groundwater, which flows much more slowly. One of the major future challenges facing humanity is how to secure the supply of clean water to the world population. It is widely admitted that population growth and pollution have a strong impact on water quality [1]. Hence, there is an urgent need to remove the pollutants from water. The classical treatment steps to make water drinkable are pretreatment (screening, sieving...), pre-chlorination, clarification (coagulation-flocculation, settling, filtration), disinfection, and refining [2]. Today, coagulation-flocculation is one of the most used processes for the clarification treatment. It is widely applied as it is efficient and simple to operate [3,4]. However, the efficiency of this treatment step is related to several variables, such as the pH, type and dose of the flocculant, and the nature of the particles (mineral or organic matrices). Indeed, the coagulation-flocculation process highly depends on the nature of the charges in the medium. In neutral aqueous medium, these charges are carried by mineral particles. To destabilize the system, inorganic coagulants such as alum, poly (chloride aluminium), ferric chloride, ferrous sulphate, and magnesium chloride have been used for several decades [5]. However, due to their negative impact on human health and environment, some of these coagulants have been the subject of intensive scientific work to mitigate their effects [6,7].

To minimize the disadvantages of inorganic coagulants, flocculants based on synthetic polymers have been used as alternatives to neutralize the surface charge of colloidal particles, because they have a rapid settling and reduced sludge production [8]. Indeed, a large number of studies have reported the use of various polymers as flocculants to reduce the turbidity concentrations in aqueous solutions [9-11]. Polyacrylamides and their modified copolymers are the important inputs for the treatment of drinking water and

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wastewater following the coagulation/flocculation properties [12]. Therefore, biopolymers based flocculants have been attracting wide interest of researchers due to their advantages such as biodegradability and environmental friendly [13]. Carboxymethylcellulose (CMC) is a linear polymer of ether cellulose that is anionic and biodegradable. It has several important properties due to its solubility, rheology, and adsorption on surfaces [14]. Researchers have always used CMC to stabilize the mud based on water loaded with clay particles. Currently, the study of the interaction of the CMC with clays led to introduction of polymers poly cellulose anionic (or PAC) that is widely applied in water-based fluids. Several authors have successfully modified the biopolymer CMC using some unconventional modifiers [15,16] such as polyacrylamide for the wastewater remediation [17]. The obtained CMC/PAM composite hydrogel reveals a strong single ion affinity to copper (CuII), lead (PbII) and cadmium (CdII) ions. Thus, in order to combine the best properties of both, synthetic polymers PAM and P4VP are grafted onto the backbone of biopolymers to obtain tailor-made grafted flocculants. In the present work, we studied the possibility of modifying the CMC by acrylamide (AM) and/or 4-vinylpyridine (4VP) monomers to obtain CMC-AM and CMC-AM-4VP copolymers. Both copolymers were employed as a flocculants for the removal of two kinds of clay, bentonite and kaolin particles, from aqueous solutions. Optimization of the flocculation process was done by investigating the influence of different parameters.

EXPERIMENTAL

Materials

4-Vinylpyridine (4VP, 98%) and the acrylamide (AM) compound were supplied by Aldrich (France) and by Merck (France), respectively. The carboxymethylcellulose (CMC) used was provided by PROLABO; it's soluble in water and its substitution degree is about 0.82-0.95. Other reagents including ammonium persulfate (APS), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were used without further purification and were provided by Aldrich. In addition, absolute ethanol was purchased from Aldrich and was used as non-solvent for the copolymers while the bi distilled water was used as solvent for the synthesized copolymers. The raw bentonite sample, 97% montmorillonite, was donated by a local company issued from the fields of Hammam Boughrara-Maghnia, Algeria. Kaolin contained kaolinite minerals and was obtained from Sigma-Aldrich (France).

Methods

Kaolin and bentonite suspensions were prepared in 5 l of distilled water as synthetic wastewater. Flocculation experiments were carried out in a conventional Jar-Test apparatus according to the procedure described in our earlier works [10,18,19]. For assessing flocculant efficiency, we used a turbidy meter to measure the initial turbidity (T_0) and the turbidity of the suspension after adding different amounts of the flocculant (T_f). The turbidity removal percent was calculated from the formula [10,18,19]:

$$Turbidity\ removal\% = \frac{(T_0 - T_f)}{T_0}$$

Synthesis of the Copolymers

Flocculants CMC-AM and CMC-AM-4VP were obtained by modification of carboxymethylcellulose (CMC) by acrylamide monomers (AM) and/or 4-vinylpyridine (4VP) according to the following procedure: in a flask, an amount of CMC was totally dissolved in bi-distilled water. The solution was heated under stirring for 30 min. In a beaker an amount of acrylamide monomer (AM) and/or 4-vinylpyridine (4VP) were dissolved in 25 ml of bi-distilled water. The solutions were mixed in a flask and the mixture was stirred with a magnetic stirrer until complete mixing was obtained. In addition, we prepared an aqueous solution of ammonium persulfate (APS) as initiator, and then the APS solution was added to the mixture under pure nitrogen. After 20 min, the mixture refluxed until a gel was obtained. The resulted product precipitated in a corresponding volume of ethanol. The obtained product was filtered and dried at 70 °C for 24 h. Thereafter, the flocculants CMC-AM and CMC-AM-4VP were obtained and used for further flocculation experiments.

Characterization Apparatus

The XRD patterns of the samples were obtained with

X-ray diffractometer ULTIMA IV (Rigaku, Tokyo, Japan), operating with Copper Kα radiation (λ = 1.54 Å) at 40 kV and 30 mA. All experiments were carried out at room temperature with 2θ varying from 2 to 40° with a scan speed of 2°/min sweep and 0.02° pitch. Infrared (IR) spectra of the samples were realized using an Agilent Cary 600 Series FTIR Spectrometer coupled to a Digital computer allowing the drawing of spectra between 4000 and 400 cm^{-1}. Thermogravimetric analyses of our copolymers were obtained using High-resolution TGA (TA Instruments SDT Q600) over the temperature range 50~800 °C with heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Characterization of the Modified Copolymer Infra-Red Spectroscopy (FTIR)

The Infrared Spectrum of CMC, CMC-AM, and CMC-AM-4VP are shown in Fig. 1, indicating that the modification of CMC was successfully achieved. It should be noted that the FTIR spectra were characterized by the appearance of new important absorption band reduction indicating the existence of AM (C-N, Amide I...), and an aromatic ring of 4VP (C=C, C=N) in CMC-AM, and CMC-AM-4VP, respectively. Table 1 shows the attributions of the bands of the carboxymethylcellulose (CMC) and the modified copolymers (CMC-AM and CMC-AM-4VP) [17,20,21].

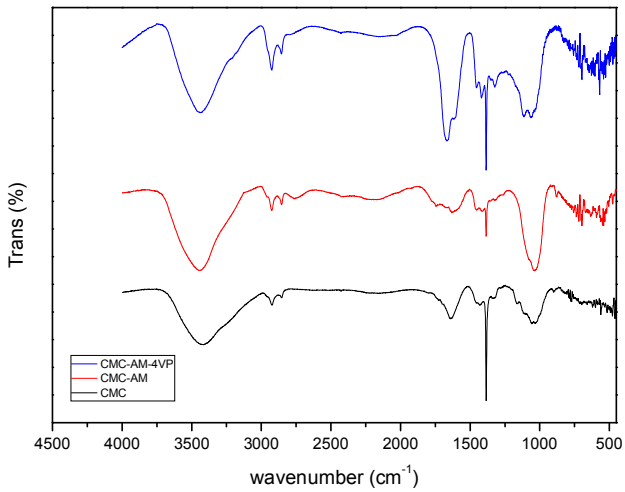

Fig. 1. IR spectra (FTIR) of CMC, CMC-AM, CMC-AM-4VP polymers.

Table 1. Vibration Bands of the Carboxymethylcellulose (CMC) and the Modified Copolymers (CMC-AM and CMC-AM-4VP) [17,20,21]

Frequency ν (cm^{-1})			Attribution	Nature
CMC	CMC-AM	CMC-AM-4VP		
3440			O-H (CMC)	Stretching
	3407	3600-3000	O-H (CMC)	Stretching
			N-H (AM)	
		2935	C-H	Stretching of 4VP units
2920	2930		C-H	Stretching
	1664		Amide I (C=O)	Stretching
		1640	C=N	Stretching
1601			COO^-	Stretching
	1453		CH_2	Stretching
1424			CH_2	Stretching
		1415	C=C	Stretching
	1394		C-N	Bending
1320			O-H	Bending
	1120		CH-O-CH_2	

Thermogravimetric Analysis (TGA)

The thermal decomposition behaviors of CMC, PAM, CMC-AM, and CMC-AM-4VP copolymers are illustrated in Fig. 2.

The black curve in Fig. 2 represents the thermogram of CMC; we distinguished two areas of mass loss. The first loss of mass between 50 and 200 °C is due to the presence of a small amount of moisture in the sample. The second one between 200 to 400 °C is due to the loss of CO_2 from the polysaccharide. As there is a COO-group in the case of CMC, it is decarboxylated in this temperature range [20]. The thermogram of CMC-AM depicted in red curve shows that the polymer degradation occurred in three steps. The first loss of mass from 50 to 200 °C is due to evaporation of the water containing in the copolymer, while the second decomposition at a temperature range from 200 to 350 °C indicates the degradation of CMC and PAM. The third degradation at a temperature range from 350 to 800 °C is due to the decomposition of the cyclized product [20]. Indeed, the decomposition of the CMC-AM-4VP copolymer (curve blue) occurred at approximately 220 °C up to 500 °C with a weight loss of 65.63%. The decomposition of the copolymer was at a temperature about 800 °C. From the TGA curves, it was evident that the CMC-PAM-4VP was thermally more stable compared to CMC and CMC-AM. Thus, based on the TGA results we concluded that grafting the chains onto the polysaccharide backbone improved the thermal stability of the polysaccharides.

X-Ray Diffractometry (XRD)

The XRD analysis was performed to further investigate the structure of the prepared copolymers and prove the modification of carboxymethylcellulose by grafting AM and/or 4-VP chains onto their polysaccharide backbone. The XRD patterns of the CMC, CMC-AM and CMC-AM-4VP are presented in Fig. 3. As can be seen from this figure, a large peak around 21° was observed which corresponds to the low crystallinity of the structure of these polymers [22,23]. The broad peak at 2θ = 21° (or known as the amorphous bump) confirmed the amorphous nature of

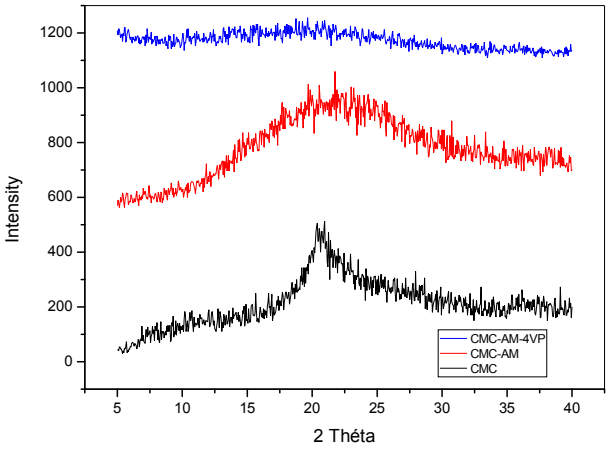

Fig. 3. XRD patterns of CMC, CMC-AM, and CMC-AM-4VP polymers.

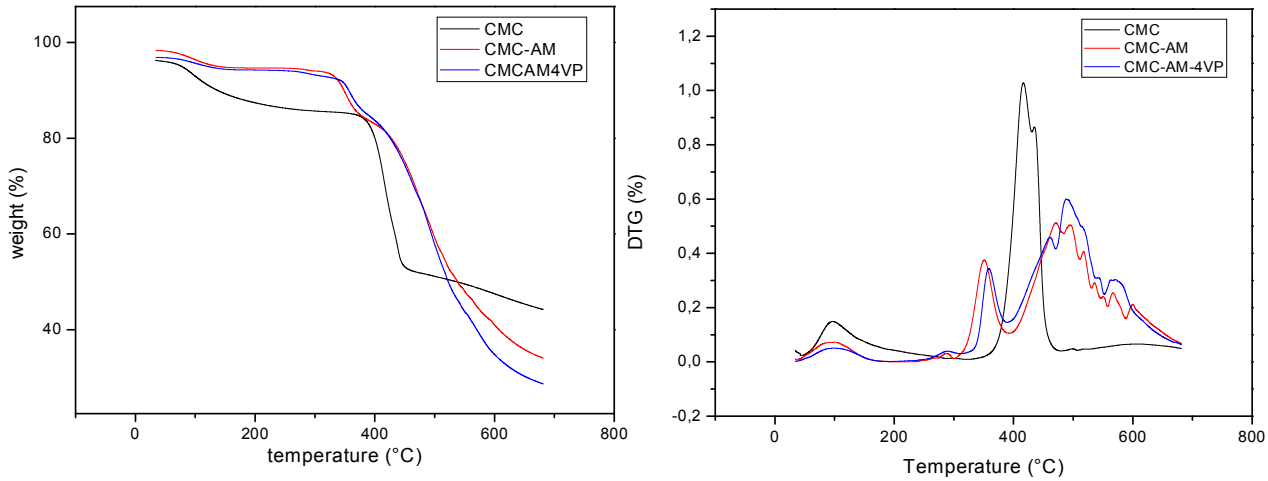

Fig. 2. Thermogravimetric analysis of CMC, CMC-AM and CMC-AM-4VP polymers.

these polymers. The relative intensity of the large peak between 15° and 30° of the CMC, CMC-AM polymers was reduced by the addition of 4VP. The width of the peak indicated the increased amorphous nature of these copolymers.

Study of the Natural Settling of Bentonite and Kaolin Suspensions

In order to investigate the turbidity elimination from both bentonite and kaolin suspensions by the coagulation-flocculation process, we first studied the natural settling of bentonite and kaolin with different initial concentrations. For this reason, suspensions of 50, 100 and 150 mg l^{-1} were carefully prepared in 1 l beakers by rapid dispersion of the relative amount of bentonite or kaolin in distilled water. Residual turbidity was measured as a function of time during one week of settling and its elimination percentage was estimated. The obtained results are depicted in Fig. 4a and Fig. 4b.

As it is clear from Fig. 4a, the natural settling of bentonite is a very slow process. The results thus are in good agreement with our earlier studies [18,19]. The figures shown above indicate that a maximum removal percentage of 27% was reached at the concentration of 150 mg l^{-1} during one week of settling. Interestingly, for the kaolin suspension an increase in settling rates as a function of time was observed (Fig. 4b). A maximum of 92% was reached for the same concentration of bentonite suspension (150 mg l^{-1}) and for the same time (one week) of settling. This can be explained by the existence of a large number of suspended particles in kaolin suspension. High turbidity's can be recorded with kaolin and bentonite at the same concentration. This phenomenon promotes the accumulation of these particles and their rapid decantation. The results show that water with high turbidity levels was the easiest to sediment naturally [24].

Application of Synthesized Copolymers to Turbidity Removal by Flocculation

Effects of pH and concentration of CMC-AM copolymer on bentonite and Kaolin turbidity removal. In order to understand the pH effect on coagulation-flocculation efficiency and to determine the optimal pH, we performed the coagulation-flocculation phenomena of bentonite and kaolin suspension at the low concentration of 50 mg l^{-1} with the addition of different concentrations of the copolymer at different pH values (2.6; 4.1; 7.3 and 10). However, Flocculation experiments were carried out using Jar-test described previously. Initial turbidity was measured using a turbidity meter, considering that the initial turbidity solutions were left to settle and the residual turbidity of the supernatant was measured after 10 min. The obtained results are shownd in Fig. 5a and Fig. 5b, which plots the percentage of the turbidity removal against the of bentonite and kaolin suspension are T_0 = 10 NTU and T_0 = 30 NTU, respectively. At the end of the operation, the

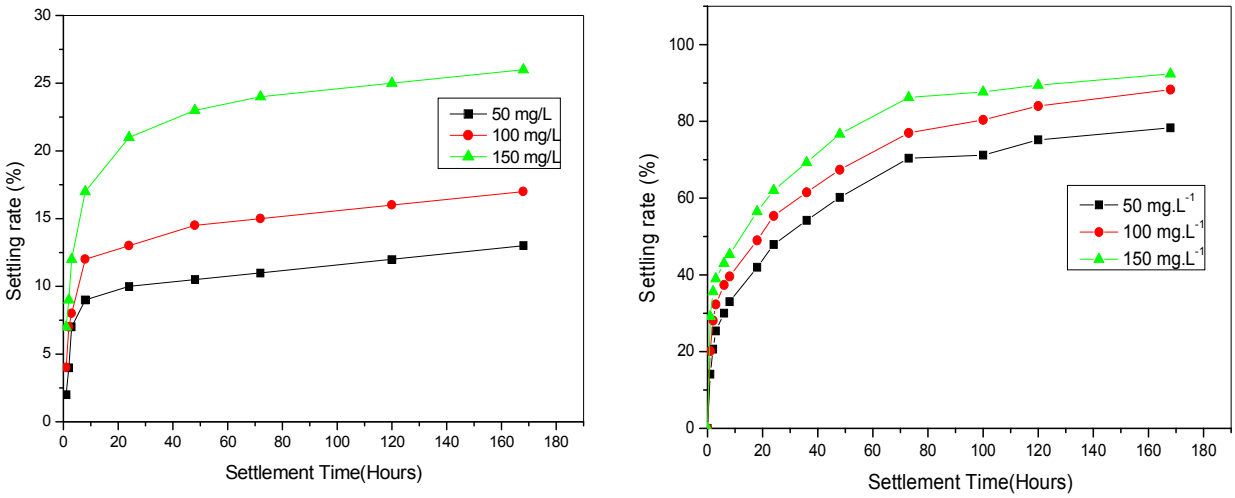

Fig. 4. Settling rate of suspension as a function of time at 25 °C a) Natural Bentonite; b) Kaolin.

concentration of the CMC-AM copolymer at different pH values.

From the mentioned figures, it can be concluded that CMC-AM copolymer had a slight low performance for the removal of turbidity from the bentonite and kaolin suspensions at different pH. At pH = 2.6, the removal of turbidity reached a maximum of 33% and 50% for the concentrations of 1 mg l^{-1} and 10 mg l^{-1} in bentonite and kaolin, respectively. This result can be explained by the lack of positive charges (+) on the copolymer, which were insufficient to neutralize the bentonite and kaolin particles and led to a low adsorption result [24,25].

Effect of pH and concentration of CMC-AM-4VP copolymer on bentonite and Kaolin turbidity removal. As shown in Fig. 6, the pH was critical index to investigate the flocculation performance. Fig. 6a shows the turbidity removal from bentonite suspension as a function of copolymer (CMC-AM-4VP) dosage for different values of pH at 25 °C, when Fig. 6b represents the same study but for the kaolin suspension. In both cases, we observed that our copolymer had low efficiency for turbidity removal in the basic medium. Indeed, in acid medium, our copolymer

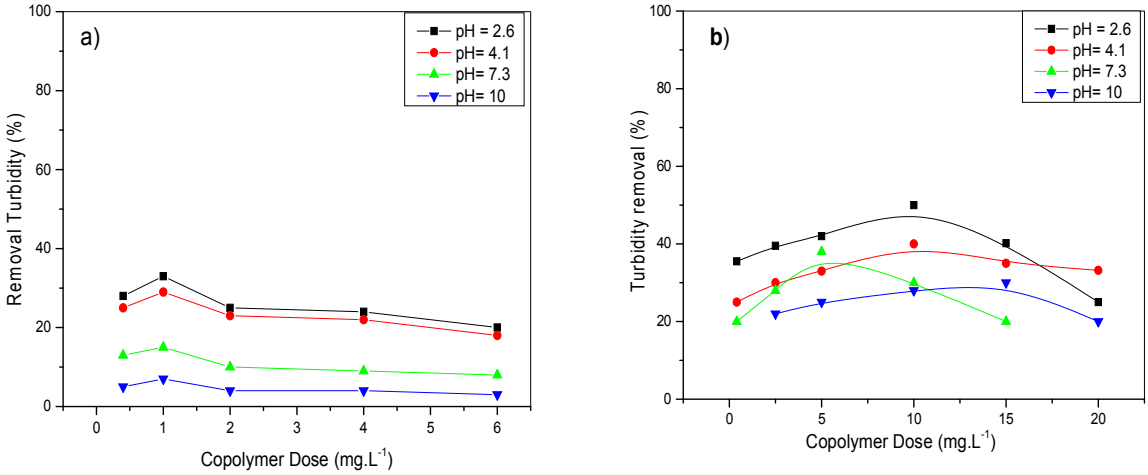

Fig. 5. Turbidity removal as a function of CMC-AM concentration for different values of pH at 25 °C and t = 10 min a) from bentonite suspension; b) from Kaolin suspension.

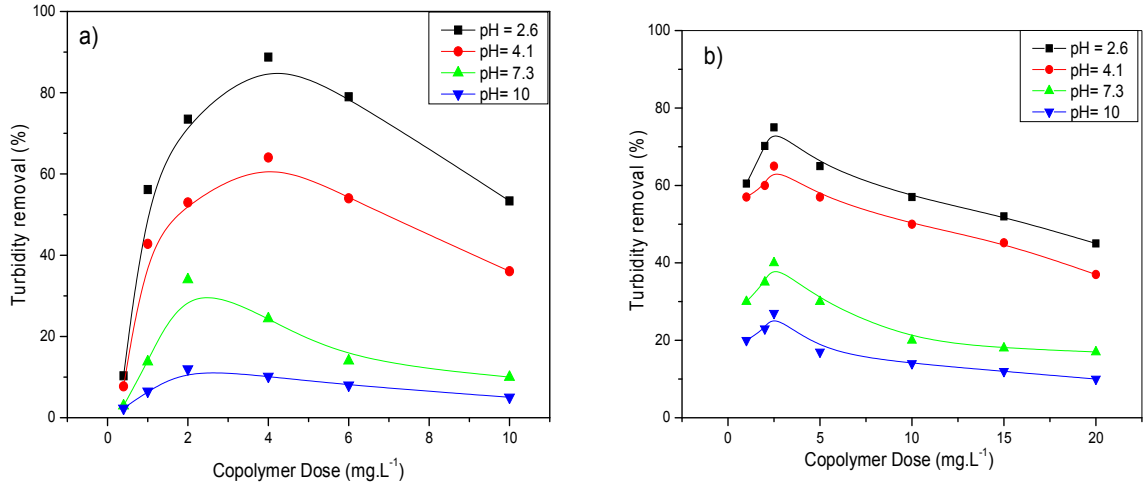

Fig. 6. Turbidity removal as a function of CMC-AM-4VP concentration for different values of pH at 25 °C and t = 10 min a) from bentonite suspension; b) from Kaolin suspension.

showed a good flocculant behavior. In bentonite suspension, the turbidity removal efficiency achieved a percentage of 89% with a copolymer concentration of 4 mg l^{-1} at pH = 2.6. In fact, in the kaolin suspension, the turbidity removal efficiency was also significantly increased with a decrease in pH values. The value of 75% for a copolymer concentration of 2 mg l^{-1} at pH = 2.6 was obtained. In both cases, the cationic sites on the copolymer chains increased. Consequently, the possibility of adsorption of bentonite and kaolin particles increased as the charge density rose. This phenomenon may be attributed to electrostatic interaction between cationic copolymer sites and negatively charged clay particles (bentonite and kaolin). It is considered a flocculation mechanism, although the bridging mechanism plays an important role [26,27].

Study of Kinetic Flocculation of Clay (Bentonite and Kaolin) Suspensions

In order to study the evolution flocculation process, supernatant turbidity was measured at different settling time after the end of the flocculation process. The turbidity removal values from both bentonite and kaolin suspensions using CMC-AM and CMC-AM-4VP were plotted against time, shown in Fig. 7 and Fig. 8.

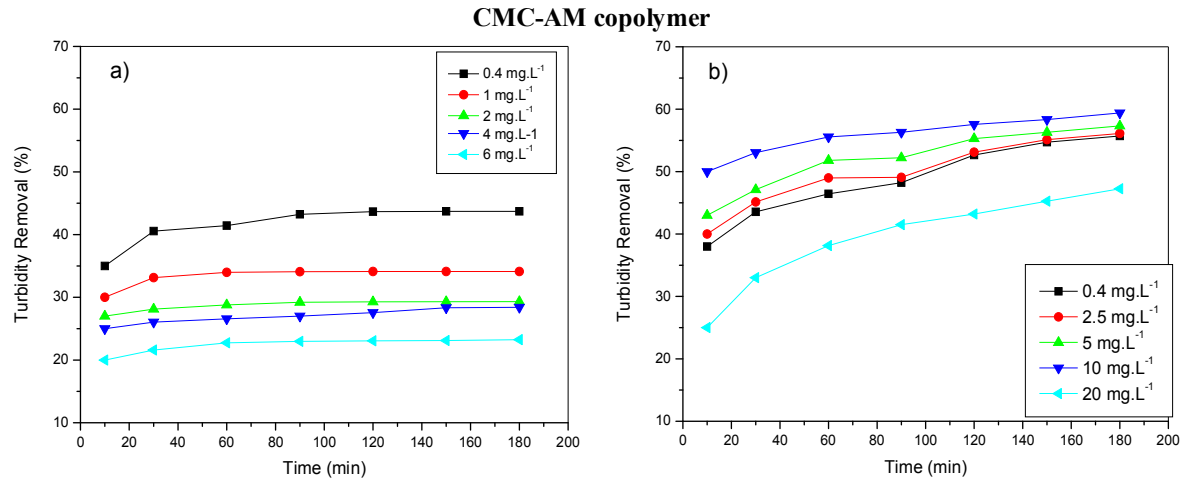

Fig. 7. Kinetics of the settling pollutants in the presence of different concentrations of the CMC-AM copolymer at pH = 2.6a) bentonite suspension; b) Kaolin suspension.

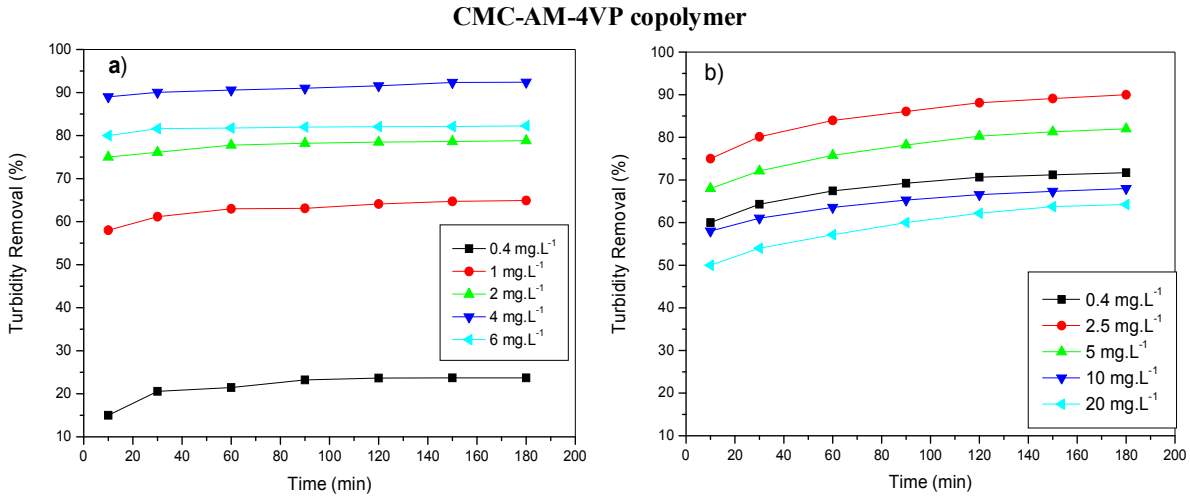

Fig. 8. Kinetics of the settling pollutants in the presence of different concentrations of the CMC-AM-4VP copolymer at pH = 2.6 a) bentonite suspension; b) Kaolin suspension.

From the figures, we noticed a stability of the turbidity removal from bentonite suspension in the case of both CMC-AM and CMC-AM-4VP. A slight improvement of the turbidity removal was obtained. From these results, it can be concluded that the flocculation process using prepared copolymers was a very fast process as described in the previous section. The formed flocs showed a good stability without any further release of the flocculated particles.

CONCLUSIONS

In this study, the CMC-AM and CMC-AM-4VP copolymers were prepared by the modification of carboxymethylcellulose (CMC) with the acrylamide (AM) and/or 4-vinylpyridine (4VP) monomers. The resulting copolymers were characterized by infrared spectroscopy (FTIR), thermal analysis (ATG), and X-ray diffraction (XRD). The adsorption of clay (bentonite and kaolin) particles onto CMC-AM and CMC-AM-4VP copolymers were studied using a Jar-Test conducted under different experimental conditions while varying parameters such as the contact time, pH of turbid solution, flocculant dosage, and initial clay concentrations. The results showed that the efficiency of the removal of suspended particles from bentonite and kaolin depended on the type of copolymer and the pH of the medium. The first copolymer (CMC-AM) showed low efficiency in removing bentonite and kaolin turbidity. However, using copolymer (CMC-AM-4VP), a good flocculant behavior was obtained in acid medium for bentonite and kaolin suspensions; a percentage of 89% and 75% were achieved with copolymer concentrations of 4 mg l^{-1} and 2 mg l^{-1} at pH = 2.6, respectively. This result provided by the adsorption of negatively charged clay (bentonite and kaolin) particles on the copolymer by the addition of HCl acid.

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