

Optimizing the coagulation/flocculation process for bentonite suspension with poly(acrylamide-co-(N-methyl-4-vinylpyridinium tosylate)) [AM7/VP10/0.1%/CTs]

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Abstract: In this work, we are interested in the quaternization of poly(acrylamide-co-4-vinylpyridine) [AM7/VP10/0.1%/] by the methyl-tosylate CH₃TS. The obtained copolymer poly(acrylamide-co-(N-methyl-4-vinylpyridinium tosylate)) [AM7/VP10/0.1%/CTs] has been characterized by ¹H NMR and UV-Vis spectroscopy. The macromolecular weight was determined by size exclusion chromatography as well as by viscosity. With the aim of removing turbidity by coagulation-flocculation from bentonite suspensions, the prepared copolymer was used as a flocculant. Several important parameters in the flocculation process, such as pH of water, initial turbidity, and flocculant concentration, were utilized for the optimization of wastewater treatment. Flocculation experiments were carried out in a conventional jar test where the turbidity removal was found about 90% at pH 3 with a low flocculant concentration range from 0.5 to 3 mg/L. In addition to obtaining good efficiency from using a semiindustrial pilot of flocculation, clear and clean water was produced during 2 h of treatment.

Key words: Acrylamide, 4-vinylpyridine, bentonite suspension, turbidity, flocculation

1. Introduction

Coagulation-flocculation is considered as the most important process in wastewater treatment. It could be used as a pretreatment, posttreatment, or main treatment.¹ In this process, the use of chemical coagulants and flocculant consists of combining insoluble particles (for example, bentonite and/or dissolved organic matter) into large aggregates. It has been proven that the resulting mixtures enhance the removal of different chemicals in subsequent sedimentation, floatation, and filtration stages.

The coagulation-flocculation process is strongly dependent on the nature of charges in the medium. In neutral aqueous medium, these charges are carried by inorganic particles. To destabilize the system, inorganic coagulants, such as alum, poly(aluminum chloride), ferric chloride, ferrous sulfate, and magnesium chloride have been used for decades.² However, because of their negative impact on human health as well as on the environment, some of these coagulants have been addressed in intensive scientific works to mitigate their effects.^{3,4} From this perspective, to minimize the drawbacks of inorganic coagulants, synthetic polymer-based

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flocculants have been used as alternatives to neutralize the surface charge of the colloidal particles, particularly because of their rapid settling and reduced sludge production.⁵ In addition to considerably reducing the electrical repulsion between the approaching particles, flocculants are capable of bridging the approaching particles with the polymer chains. For industrial purposes, water-soluble synthetic flocculants, mainly polyacrylamide-based flocculants, with different molecular weights and charge densities are being used widely because of their economic advantage, stable monomer source, matured synthesis technology, excellent flocculation effect, and easy tailorability.⁶

The performance of the coagulation-flocculation process depends on several parameters. In this paper, we focus on the coagulant and the flocculant type and dosage,⁷ the solution pH value and temperature,^{8,9} and the agitation speed and time.¹⁰ To improve this performance, the optimization of these parameters is of high significance.

The aim of the present study is to investigate the coagulation-flocculation properties of bentonite suspensions with a quaternized copolymer that is named poly(acrylamide-co-(N-methyl-4-vinylpyridinium tosylate)) [AM7/VP10/0.1%/CTs]. The influence of pH, copolymer dosage, initial bentonite dosage, and settling time on coagulation-flocculation efficiency are investigated with the objective of defining the best experimental conditions.

2. Results and discussion

2.1. Characterization of the quaternized copolymer

2.1.1. ¹H NMR characterization

The proton nuclear magnetic resonance (¹H NMR) spectrum of the quaternized copolymer (AM7/4VP10/0.1%/CTS) is realized with a DMX-500 (Bruker Company, Germany) in CH₃OD as solvent. The structure of the synthesized copolymer could be checked using NMR spectroscopy.

In Figure 1, we depict the ¹H NMR spectrum of this copolymer as follows:

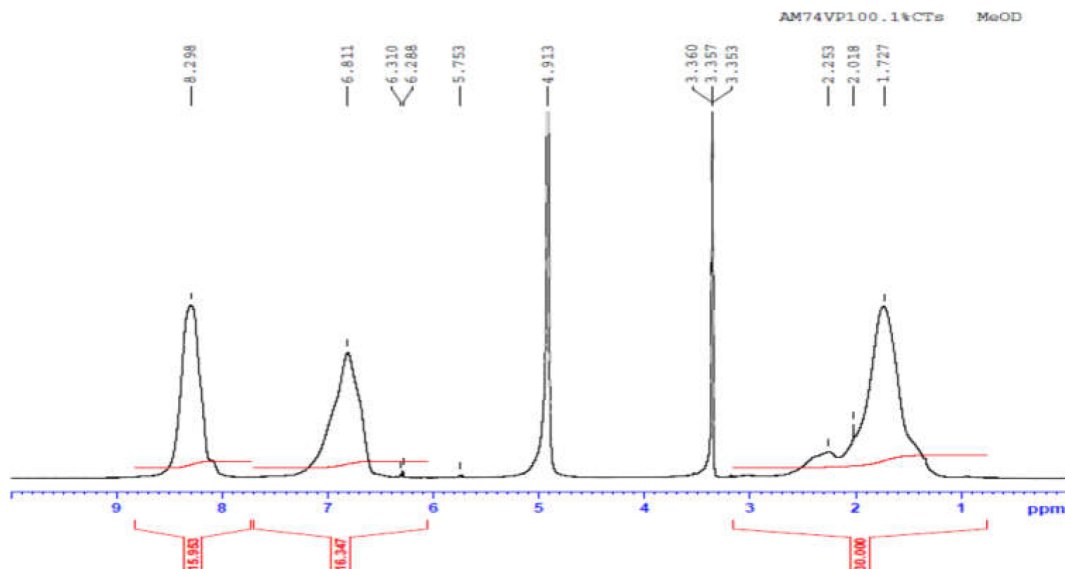


Figure 1. ¹H NMR spectrum of the quaternized copolymer (AM7/4VP10/0.1%/CTS) in CH₃OD.

- A large peak between 1.3 and 2.1 ppm with a maximum at 1.73 ppm, which corresponds to ($-\text{CH}_2-$) and ($-\text{CH}-$) of the linear chains of the copolymer.^{11,12}
- At 2.25 ppm, we observed a peak assigned to ($-\text{CH}_2-$) protons of the quaternized 4VP.¹¹
- A thin peak at 3.36 ppm is assigned to (CH_3-) of tosylate (TS).¹³
- 4.9 ppm was assigned to the solvent protons.
- For the aromatic protons, we distinguish four types of proton. There are quaternized and nonquaternized cycles of 4-vinylpyridine (4VP) and tosylate (TS). The protons of quaternized cycles are deblinded.^{11,14,15}
- A large peak between 6.6 and 7.2 ppm with a maximum at 6.8 ppm corresponds to the H atom at the ortho position of aromatic cycles of the copolymer.
- A large peak between 8.0 and 8.5 ppm with a maximum at 8.3 ppm was assigned to the H atom at the meta position of aromatic cycles of the copolymer.

2.1.2. UV-Vis spectra

The UV-Vis absorption spectra were recorded on an OPTIZEN 2120 UV-Spectrometer in the Laboratory for the Application of Organic Electrolytes and Polyelectrolytes (LAEPO), University of Tlemcen, Algeria. Figure 2 shows the UV-Vis spectra of (AM7/4VP10/A0.1%) copolymer compared with the quaternized copolymer (AM7/4VP10/A0.1%/CTS) in bidistilled water.

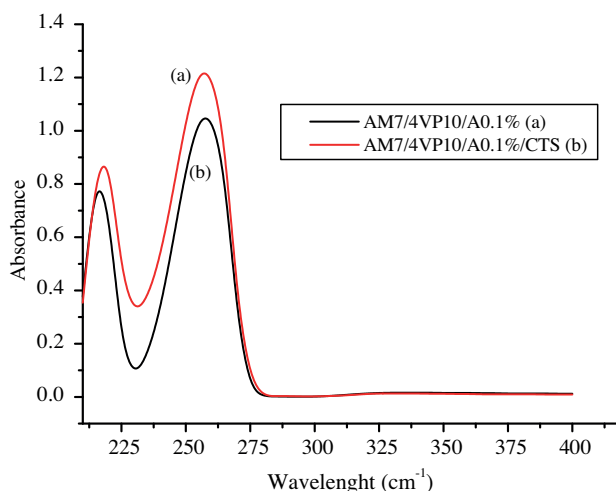


Figure 2. UV-Vis spectra in aqueous solution at ambient temperature: a) (AM7/4VP10/A0.1%) copolymer; b) (AM7/4VP10/A0.1%/CTS) copolymer.

The presence of 4-vinylpyridine (4VP) monomer in the (AM7/4VP10/A0.1%) copolymer is confirmed by the UV-Vis spectrum. The 4VP monomer showed an intense absorption at 256 nm connected to a $\pi \rightarrow \pi^*$ band, which is in accordance with the results reported in the literature.^{11,16} However, the acrylamide (AM) monomer did not have any absorption in this area. From the UV-Vis spectra, we could calculate the percentage (%) of 4VP and AM monomers in the (AM7/4VP10/A0.1%) copolymer chains.¹¹ Table 1 gives the values of weight ratios of acrylamide (AM) and 4-vinylpyridine (4VP) monomers in the (AM7/4VP10/A0.1%) copolymer.

Table 1. Experimental conditions and composition of the (AM7/4VP10/A0.1%) copolymer.

Copolymer	Precipitation (solvent / not solvent)	Conversion percentage %	w/w% of AM/4VP by ¹ H NMR	w/w% of AM/4VP by UV-visible	M _w (g/mol)	M _v (g/mol)
AM7/4VP10	Ethanol / ether	75	52.8/47.2	53.5/46.5	2.3 × 10 ⁵	1.2 × 10 ⁵

We could also deduce the quaternization percentage of the (AM7/4VP10/A0.1%/CTS) copolymer from the previous spectra in Figure 2. When the nitrogen atoms were quaternized in the copolymer, we observed the disappearance of the $\pi \rightarrow \pi^*$ band, which caused a decrease in absorbance values corresponding to this band. We remarked, however, that the initial (AM7/4VP10/A0.1%) copolymer and the (AM7/4VP10/A0.1%/CTS) quaternized copolymer concentrations remained identical. Thus, we could say that the difference between the two absorbance values was related to the quaternization percentage.

$$\Delta A = A_{\text{copolymer}} - A_{\text{quaternized copolymer}}$$

$$\text{The quaternization percentage} = \frac{\Delta A}{A_{\text{copolymer}}}$$

$$\text{The quaternization percentage} = \frac{1.229 - 1.051}{1.229}$$

$$\text{The quaternization percentage} = 14\%$$

2.2. Natural settling of bentonite suspensions

Before the study of turbidity elimination from bentonite suspensions by flocculation, we studied the natural settling of bentonite for various initial concentrations. To this end, concentrations of 30, 100, and 500 mg/L having initial turbidity values of 9, 25, and 127 NTU, respectively, were prepared in 1-L beakers by rapid dispersion of the relative amount of bentonite in bidistilled water. The resulting suspensions were allowed to settle in the open air without any agitation. The residual turbidity was measured as a function of time for 48 h and its elimination percentage was estimated. The obtained results are represented in Figure 3.

We are reporting the turbidity removal from the bentonite suspensions under natural settlement as a function of time. From the obtained results, it could be said that the natural settling of bentonite is a very slow process. A maximum elimination percentage of 34% was recorded with the 500 mg/L suspension after 48 h of settling. We consider this bentonite concentration to be of high turbidity level. Furthermore, weak turbidity elimination percentages were recorded with the two other concentrations, namely 13% for the suspension of 30 mg/L and 15% for the suspension of 100 mg/L. It could, therefore, be concluded that the low turbidity level's water was the most difficult to be naturally settled. The settling of bentonite particles lasted for a long time and the velocity of settling was much slower in the investigated initial concentration range. Even at 500 mg/L, the bentonite suspension showed good stability, and the turbidity removal did not decrease below 34% even after 48 h of settling. The low natural settling percentage of bentonite suspensions can be the result of several parameters related to the nature of bentonite, such as the crystal structure and the surface charge of bentonite particles. It is well documented that bentonite mainly consists of montmorillonite, which is made of clay layers. The stability behavior of colloidal particles is directly related to the nature of the surface charges, and these surface charges are a function of the pH. At low pH, the surface of bentonite particles is positively charged through the

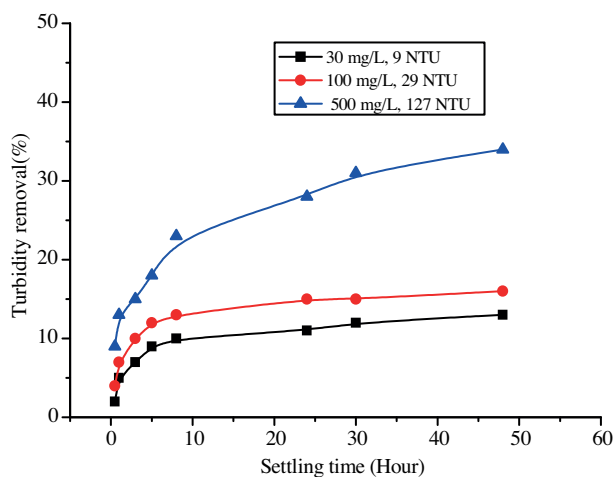


Figure 3. Turbidity removal as a function of time of natural settlement at 25 °C.

protonation of surface hydroxyl groups (Al-OH, Si-OH) and can interact with either permanently negatively charged to form a bridge.¹⁷ When the pH increases, the hydroxyl groups in the surface of particles successively undergo deprotonation and reversing of the positive charges to negative on the surface. In the present work, the initial pH of bentonite suspensions is between 6 and 9, which means that the surface of bentonite particles is mainly negatively charged and leads to a stronger repulsion interaction between the suspended particles,^{18,19} resulting in a slower aggregation kinetics and low settling percentage, which corresponds to the registered data of natural settling in our work. Based on this conclusion, we propose in what follows to study the elimination of turbidity from bentonite suspensions by flocculation using (AM7/4VP10/A0.1%/CTS) as the flocculant.

2.3. Application of turbidity removal by flocculation

2.3.1. Effect of the initial turbidity level on the flocculation performance

Flocculation experiments were carried out using a jar test as described in Section 3.5. Initially, bentonite suspensions of 9, 25, and 150 NTU were prepared in several beakers. Different amounts from the original solution of copolymer [AM7/4VP10/A0.1%/CTS] at 10³ mg/L were added to each beaker. The turbidity removal was estimated after 5 min of settling. All experiments were carried out at the initial pH of each suspension. The obtained results are reported in Figure 4.

In Figure 4, we show the following:

1. The flocculation performance of bentonite suspensions remains weak at the natural initial pH of treated water, where the surface charge of bentonite particles is almost completely negative. We are talking about the copolymer charge density (+) (14%), which is insufficient to neutralize all the bentonite particles.
2. A maximum turbidity removal of 42% is reached with the highly turbid water (500 mg/L).
3. Turbidity removals of 37% and 31% were recorded, respectively, with the intermediate and weakly turbid aqueous media (100 and 30 mg/L).
4. The optimum dosage of copolymer increases according to the initial bentonite concentration. This can be explained by a critical amount of polymer chains required to assure the best electrostatic interaction

between the ammonium groups of 4VP units and negatively charged particles of bentonite. Beyond the optimum concentration, because of the high quantity of the polymer, an important intrachains hydrogen interaction will take place and the charged sites on the polymer chain will be inaccessible to the bentonite particles. As a result, the absorbed polymer particles' amount will decrease. Flocculation experiments were carried out at different pH values of [AM7/4VP10/A0.1%/CTS] solution.

2.3.2. Effect of the initial pH on the flocculation performance

It is well documented in the literature that polymer-induced flocculation of particulate suspensions involves many steps, namely the mixing of polymer molecules among the particles, adsorption of polymer chains on the particles, rearrangement of the adsorbed chains, collisions between polymer-adsorbed particles, flock formations, and break-up of flocks.²⁰ The [AM7/4VP10/A0.1%/CTS] has the possibility to be positively more charged by acid additions. An initial pH adjustment is done using 1 M HCl and NaOH. The flocculation experiments were carried out according to the same process described in Section 3.5, while maintaining the optimum dose of the copolymer with every turbidity level. The obtained results are represented in Figure 5.

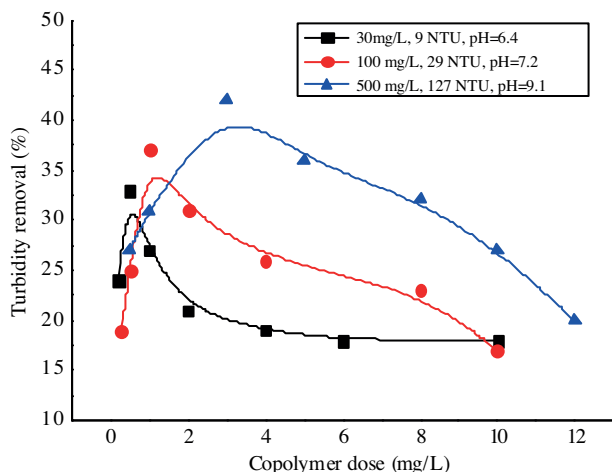


Figure 4. Turbidity removal as function of the copolymer dose [AM7/4VP10/A0.1%/CTS] at 25 °C.

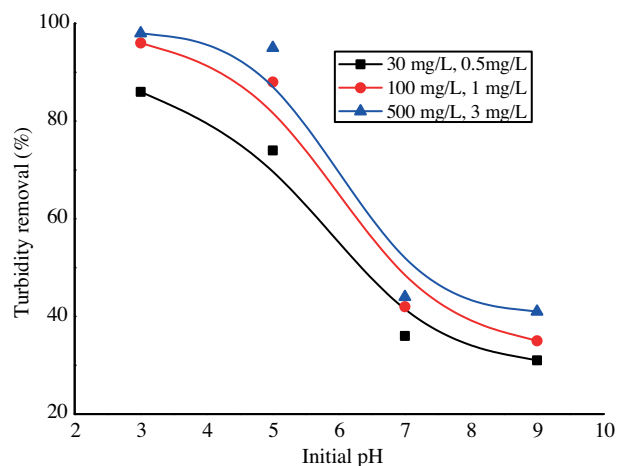


Figure 5. Effect of the initial pH on the turbidity removal with the optimum copolymer concentration [AM7/4VP10/A0.1%/CTS] at 25 °C.

In Figure 5, we depict the turbidity removal efficiency (8%) as a function of pH at 0.5, 1, and 3 mg/L polymer concentrations for 30, 100, and 500 mg/L bentonite dosages, respectively. The highest efficiency (about 90%) was obtained with [AM7/4VP10/A0.1%/CTS] at 1 and 3 mg/L, respectively, when the pH of the polymer solution was 3.

In a previous study,²¹ the authors described the natural sedimentation of bentonite suspensions in tap and demineralized water. They showed that the stability behavior of colloidal particles is closely related to the surface charges. They also showed that these surface charges were functions of the pH. At low pH, the edge was positively charged through the protonation of surface hydroxyl groups and could interact with the negatively charged basal surface to form “edge-to-face” bridging. With an increasing pH, the surface hydroxyl groups successively undergo deprotonation, decreasing the positive charge and eventually reversing the positive charge to negative on the edge.²¹ In an acidic medium, at pH 3, the contribution of positive charges present in the [AM7/4VP10/A0.1%/CTS] copolymer is demonstrated by a net improvement of turbidity removal percentage.

For example, by adding only 0.5 mg/L of copolymer in 30 mg/L bentonite suspension, the turbidity removal percentage varied from 32% at pH 6.4 to 86% at pH 3. When the pH of the solution exceeded a value 6, the copolymer was less protonated and the positive charges disappeared gradually. This effect caused the turbidity removal percentage to decrease. In our previous work,²² we showed that the use of a similar copolymer structure without charges in the flocculation process at pH values above 7 could decrease the turbidity removal percentage to very low values. For pH values above 7, the chains were less expanded. This phenomenon could explain the low turbidity removal percentage values. The same results were observed by Anleu et al. in a study of flocculation properties of N-oxide polymers and the effect of pH on the expansion of the polymer's chain and their ability to flocculate suspended particles.²³

2.3.3. Pilot flocculation experiments

With the aim of optimizing the flocculation performance of [AM7/4VP10/A0.1%/CTS] in a continuous water treatment process, we used a semiindustrial pilot of coagulation flocculation²⁴ as shown in Figure 6.

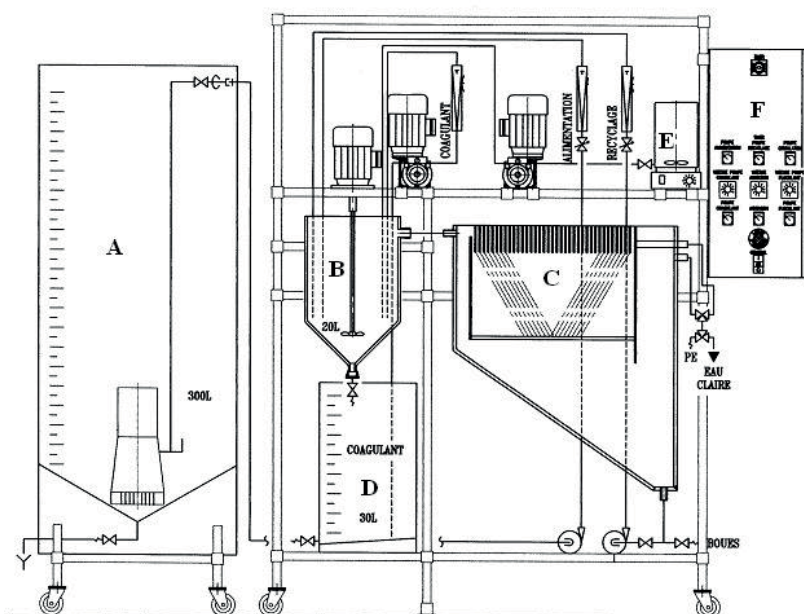


Figure 6. Representation of semiindustrial pilot of coagulation/flocculation: A- tank of 300 L, B- reactor, C- decanter, D- coagulant tank, E- flocculant tank, F- control.

A copolymer solution with the concentration of 0.5×10^3 mg/L was added to the reactor at a flow rate of 210 mL/h. The alimentation flows were adjusted to get the optimum concentration of the flocculant in the reactor. During the flocculation process the mixture in the reactor was stirred at a speed of 100 rpm. When the reactor was completely filled, the treated suspension flowed to the decanter previously filled with clear water ($Tu = 0$ NTU). At the decanter outlet, the treated water's turbidity was measured every 10 min for 2 h. The same experiments were done with and without lamella in the decanter in order to deduce the effect on the quality of the treated water. The flocculation process showed no significant effect on the value of initial pH 7. The turbidity removal results using [AM7/4VP10/A0.1%/CTS] are plotted in Figure 7.

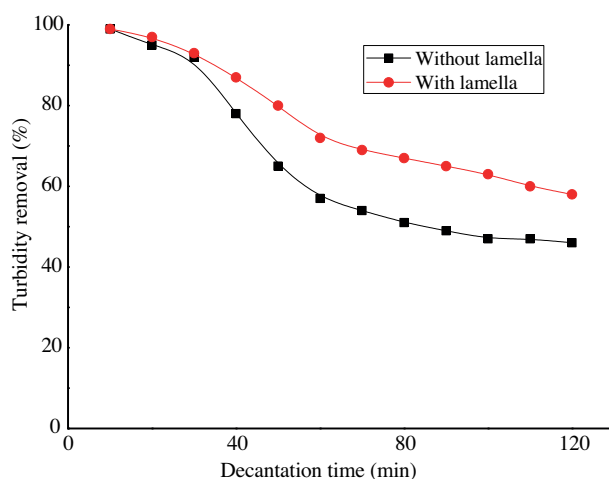


Figure 7. Flocculation performance of pilot as a function of decantation time, [AM7/4VP10/A0.1%/CTS] 1 mg/L, pH 3, T = 25 °C.

It could be concluded that the use of the lamella improves the quality of the treated water along the process time. The elimination efficiency goes from 46% to 58% after 2 h of continuous treatment. Synthesized copolymers showed results in good agreement with the results of Mansri et al., where a charged poly(acrylamide) polymer was used for the turbidity removal by flocculation.²⁴

2.4. Conclusions

Through adiabatic copolymerization, the copolymer (AM7/4VP10/A0.1%) has been prepared. Its macromolecular weight, determined by size exclusion chromatography method, was equal to $M_W = 2.3 \times 10^5$ g/mol. The copolymer quaternization by CH₃TS has led to 14% cationic charge from 4VP units without affecting the hydrophobic balance of the copolymer chains.

The copolymer (AM7/4VP10/A0.1%/CTS) is very efficient for the coagulation-flocculation of bentonite suspensions. The copolymer solution could be applied as a flocculant in a wide range of pH between 3 and 9. It is very important to optimize the selection of conditions, such as the quaternization percentage, flocculant dosage, and pH, which can influence the coagulation-flocculation efficiency. The best yield of turbidity removal of about 90% was recorded at pH 3 where the cationic charge density increased and the electrostatic interaction through charge neutralization is considered as a mechanism of flocculation, although the bridging mechanism plays a contributory role regarding the important macromolecular weight of the copolymer. The water treated using the (AM7/4VP10/A0.1%/CTS) copolymer as a flocculant is clear and clean, in which the residual turbidity conforms to the national emission standard (Official Journal of the Algerian Republic no. 26 of 23 April 2006, Executive Decree no. 06-141 of 19 April 2006 defining the limit values ??for discharges of industrial liquid effluents, MES 35-40 mg/L).

3. Experimental

3.1. Products and reagents

4-Vinylpyridine (4VP, 98%) was provided by Aldrich (France). It was dried over calcium chloride overnight and fractionally distilled under reduced pressure of 15 mmHg and 68 °C, having removed the first and last

10% of the monomer. The acrylamide compound was provided by Merck (France). Bidistilled water was used. Ammonium persulfate (APS, Aldrich) was used as an initiator without further purification.

Bentonite has particular water adsorption properties, but modified bentonite could absorb various substances.²⁵ Bentonite powder came from the fields of Hammam Boughrara, Algeria. It is composed essentially of montmorillonite.²⁶ The different chemical elements of this bentonite are given in Table 2.²⁷

Table 2. Chemical composition of the bentonite.

Species	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI
% (w/w)	65.19	17.26	2.11	1.21	3.08	2.13	0.58	0.19	8.23

3.2. Copolymerization of acrylamide (AM) and 4VP

Copolymerization was realized in a reactor. AM and 4VP were dissolved in bidistilled water. The mixture was stirred and purged with nitrogen for 15 min. Aqueous ammonium persulfate (NH₄)₂S₂O₈ was added as an initiator. We started the reaction by rapid heating of the mixture. Then the obtained copolymer was dissolved in ethanol and precipitated in diethyl ether repeatedly. The product was then dried under vacuum at room temperature to a constant weight and stored in desiccators.¹¹ The molecular weight (Mw) and the viscosity molar mass (Mv) were determined using size exclusion chromatography and a capillary standard Ubbelohde viscometer, respectively.

3.3. Quaternization preparation

Tosyl chloride reagent (Ts-Cl) (0.12 mol, 22.86 g) in pyridine as solvent (20 mL) was added to a cooled solution (0 °C) of methanol (CH₃OH) (1.2 mol, 22.86 g) in anhydrous toluene (140 mL). The mixture, at 0 °C, was stirred for 24 h to separate the two phases. The organic phase was dissolved in chloroform (100 mL) and then washed three times with 100 mL of water containing sodium bicarbonate. It was then dried over sodium sulfate and filtered and then the solvent was removed.¹³

3.4. Quaternization of the copolymer

A quantity of poly(acrylamide-co-(4-vinylpyridine)) was dissolved in 50 mL of absolute ethanol and then introduced into a 100-mL flask. A known amount of CH₃TS was added. The mixture was stirred over a period of 48 h at 70 °C. After evaporation of the solvent excess, the resulting product was dissolved and then precipitated in a large amount of diethyl ether. The product was dried at 70 °C for 24 h. The obtained copolymer, poly(acrylamide-co-(N-methyl-4-vinylpyridinium tosylate)), was characterized by ¹H NMR and UV-Vis spectra as described below (Figure 8).

The scheme that summarizes the preparation of the quaternizing and the quaternized copolymer is given in Figure 9.

3.5. Flocculant performance assessment by jar test

At room temperature of about 25 ± 1 °C, flocculation experiments were carried out in a conventional jar test apparatus equipped with flat paddle impellers and cylindrical jars containing 500-mL samples of bentonite suspension. Under rapid agitation of 120 rpm, a predetermined amount of copolymer flocculant was dosed into

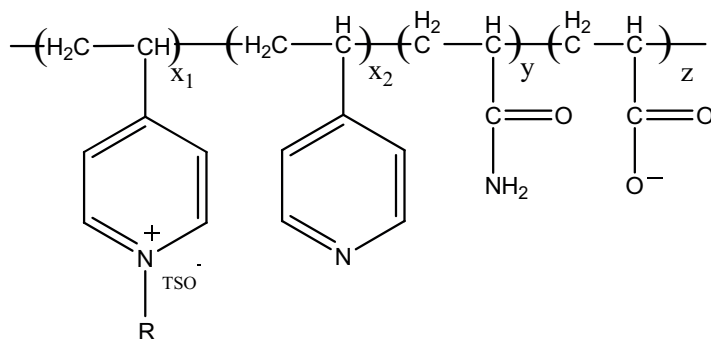


Figure 8. [AM7/4VP10/A0.1%/CTS] copolymer obtained by quaternization of poly(acrylamide-co-(4-vinylpyridine)) using CH_3TS at 70°C .

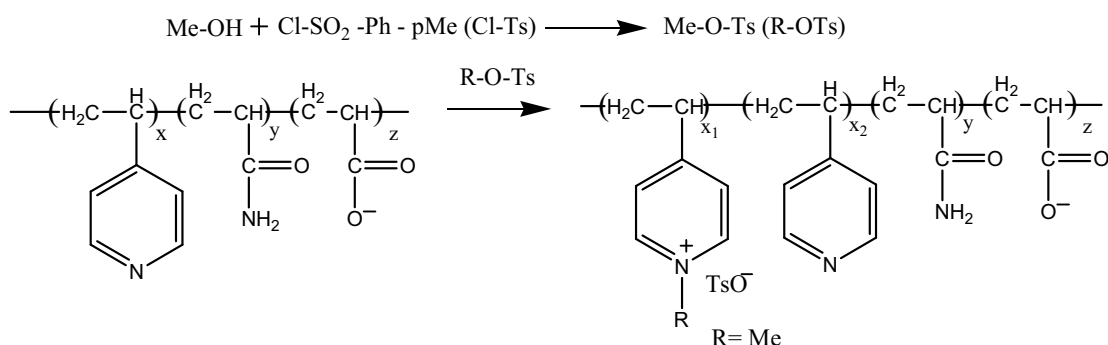


Figure 9. Scheme for the preparation of the quaternizing compound (CH_3TS) and the quaternized copolymer [AM7/4VP10/A0.1%/CTS].

the bentonite suspension to flocculate particles for 1 min. The stirring speed was then reduced to 50 rpm for 4 min to allow flocks' growth and the suspension was finally allowed to settle for 5 min.^{24,28}

In order to assess flocculant efficiency, we used a calibrated turbidimeter (Hanna HI-93703C) to measure the initial turbidity (T_0). The turbidity of the bentonite suspension after adding different amounts of the flocculant (0.2–12 mg/L) is (T_f). The turbidity removal percentage was calculated by the following equation:²⁹

$$\text{Turbidity removal \%} = (T_0 - T_f)/T_0 \quad (1)$$

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