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TURBIDITY REMOVAL FROM BENTONITE SUSPENSION BY COAGULATION/FLOCCULATION USING MODIFIED p-PHENYLENEDIAMINE/POLY(ACRYLAMIDE)

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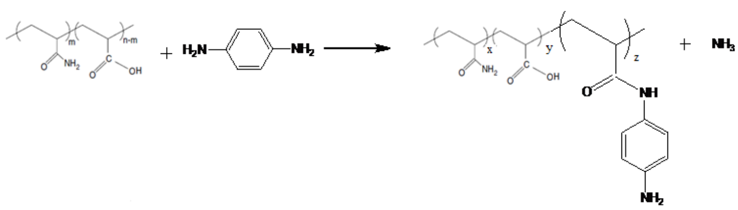

We were interested in this work by the modification of hydrolyzed poly (acrylamide) which allow us to obtain a new copolymer based on acrylamide and p-phenylenediamine (PPD). The properties of the obtained copolymer and its structure and composition were established by ^{1}H NMR, FTIR spectroscopy's and by TGA analysis. The prepared copolymer was used as a flocculent substance in the aim to remove turbidity from wastewater. Several experimental parameters such as pH of water, initial turbidity, flocculent concentration and dyes concentration, and their effects on the flocculation process were studied. The considered results show that the studied copolymer is good flocculent and efficient at a very low optimum concentration.

INTRODUCTION

Contamination of water resources, especially in terms of quality, is a serious problem today. It is the result of the massive use of organic and minerals products in agriculture, urban and industrial fields. Wastewater from textile industry including dyes represents an important source of pollution. This field is a major environmental and health problems. For this purpose, it is essential to treat these wastes to limit the amount of pollutants discharged into the environment. There are several conventional techniques for eliminating the excess of colored organic pollutants for example methylene blue.[1–4] Coagulation/flocculation is one of the chemical treatment processes commonly used for water and wastewater. It has a wide range of application in water and wastewater facilities due to its efficiency and simple operation.[5,6]

Polyacrylamides have a great technical and academic importance. Due to their properties, modified polyacrylamide, and its derivatives are an extremely important class of synthetic copolymers widely used in industrial and laboratory applications.[7–9] Derived poly (acrylamide), copolymers are the important inputs for the treatment of drinking water and wastewater following the coagulation/flocculation properties

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from the action of charge neutralization and adsorption in the solid-liquid separation practice.[10,11]

We were interested in this work by the modification of the hydrolyzed poly (acrylamide) (AD37) by p-phenylenediamine (PPD). We have obtained by this reaction of modification a new copolymer based on acrylamide and PPD as shown in Fig. 1. The obtained copolymer was used as a flocculent substance with the objective to remove turbidity from wastewater. The effect of several experimental parameters such as the pH of the aqueous medium, initial turbidity and flocculent concentration were investigated.

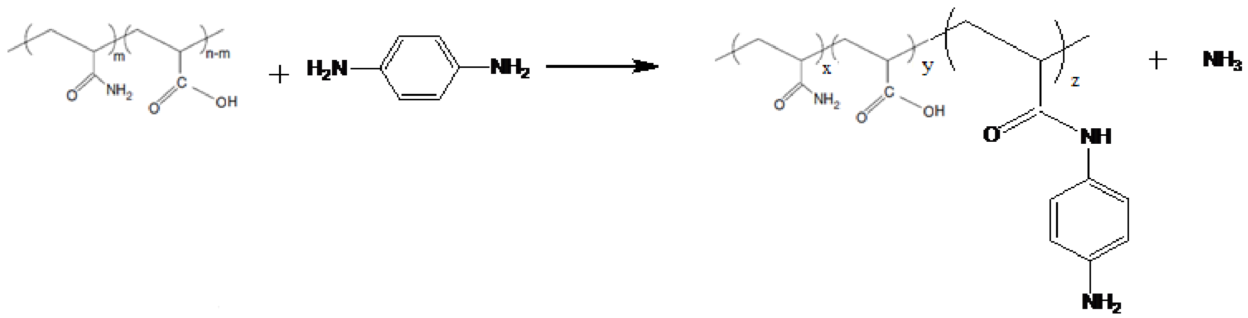

Fig. 1 – AD37-PPD copolymer obtained by modification of hydrolyzed poly(acrylamide) by p-phenylenediamine.

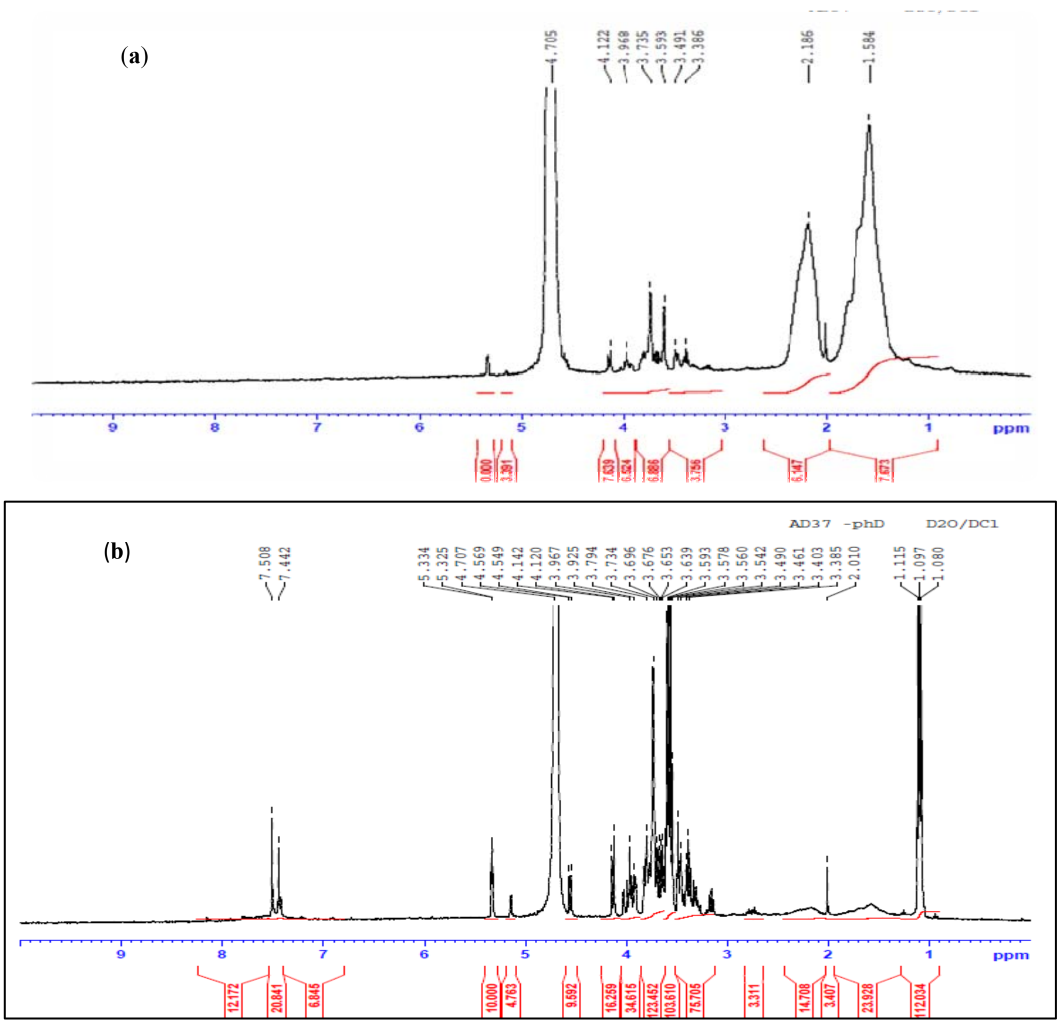

Fig. 2 – ^{1}H NMR Spectrum in D_2O / DCl mixture as solvent for AD37 copolymer; **b**) modified copolymer (AD37-PPD).

Table 1

Characteristics ^{1}HNMR of AD37 and AD37-PPD copolymers in D_2O/DCl [12,13]

AD37		AD37-PPD	
δ (ppm)	**Attributions**	**δ (ppm)**	**Attributions**
1.584	proton - CH_2- copolymer backbone	Between 1.080 – 1.115	proton - CH_2- copolymer backbone
2.186	proton - CH- copolymer backbone	Between 1.5 – 2.2	proton - CH- copolymer backbone
Between 3.386 – 4.122	protons - NH_2 function - $CONH_2$	Between 3.385 – 4.707	protons - NH_2 - of AD37 and PPD
4.705	protons of solvent D_2O/DCl	Between 4.769 – 4.707	protons of solvent D_2O/DCl
-	-	Between 5.325 – 5.334	proton - NH_2- of PPD
-	-	Between 6.8 – 7.442	H atom at meta position of protons in PPD phenyl ring
-	-	Between 7.5 – 8.2	H atom at ortho position of protons in PPD phenyl ring

RESULTS AND DISCUSSION

Characterization of the modified copolymer

^{1}H NMR characterization

The proton nuclear magnetic resonance (^{1}H NMR) spectrum of the modified copolymer (AD37-PPD) and hydrolyzed poly(acrylamide) were realized with a DMX-500 (Bruker Company, Germany) in D_2O/DCl mixture as solvent. Figure **2a** and **2b** shows the ^{1}H NMR spectrum of AD37-PPD copolymer compared with AD37 copolymer.

The purpose of this characterization by ^{1}H NMR is to confirm the structure of the modified copolymer. We notice the presence of several peaks corresponding to all the protons H in the copolymers. They are assigned to different protons, which confirm the presence of PPD molecules in the modified copolymer (AD37-PPD). (Table 1) gives the attributions of the peaks of AD37 and AD37-PPD copolymers. [12,13]

Infra-red spectroscopy (FTIR)

The IR spectra were recorded on an FTIR Cary 600 spectrophotometer used in Laboratory of Application of Electrolytes and Polyelectrolytes Organics (LAEPO), at University of Tlemcen, Algeria. Figure 3 shows the AD37-PPD spectrum (below) and the AD37 spectrum (above).

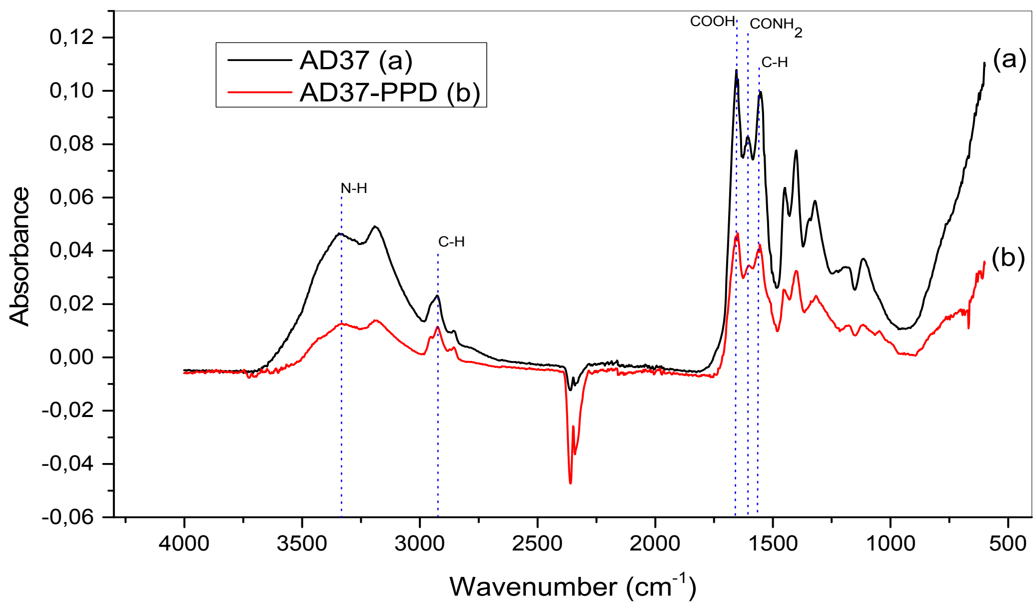

Fig. 3 – IR spectra (FTIR): **a)** AD37-PPD copolymer; **b)** AD37 copolymer.

Table 2

Vibration bands of the partially hydrolyzed polyacrylamide (AD37) and the modified copolymer (AD37-PPD)[14]

Frequency ν (cm^{-1})		Attribution	Nature
AD37	**AD37- PPD**		
3334	3332	N-H	Stretching
2926	2924	C-H	Stretching
1654	1655	C=O (COOH)	Stretching
-	1602	C=O ($CONH_2$)	Stretching
1552	1555	C-H	Bending
1384	1384	C-N	Stretching

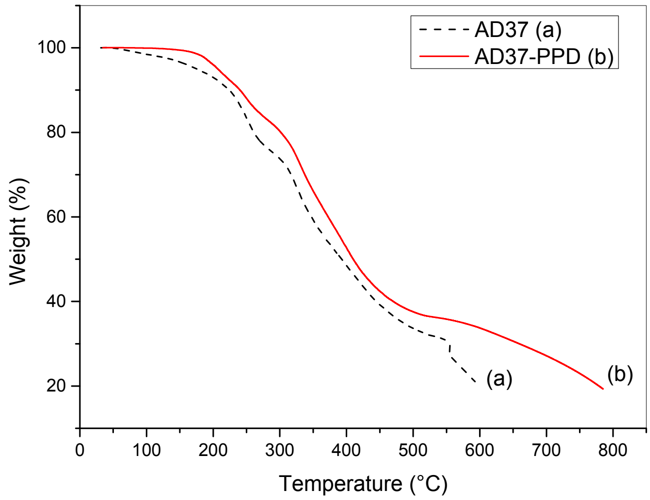

Fig. 4 – Temperature dependence of weight loss (TGA) for:
(a) Hydrolyzed polyacrylamide (AD37); **(b)** Modified copolymer (AD37-PPD).

The FTIR analysis was used to confirm the PPD adsorption onto the AD37 copolymer (Table 2) gives the attributions of bands of AD37 and AD37-PPD copolymers. [14]

Thermogravimetric analysis (TGA)

The thermogravimetric analysis is an important method for the study of the thermal stability of this copolymer. Thermogravimetry experiment was carried out on a TA Instruments Q600 (LAEPO-Laboratory). Measurements were performed under the air atmosphere. The same conditions were used for tests, with heating rate of 10 °C/min in the range of temperature between 50 and 800 °C under the air flow. The thermal decomposition behavior of AD37-PPD compared to the AD37 copolymers was shown in (Figure 4).

Thermogram of AD37 copolymer is depicted in curve **4a**. We note that an initial weight loss between 50 and 200 °C is observed due to the residual water and solvent. The decomposition of this copolymer is between 250 and 500 °C with a weight loss at approximately 60%. It is ascribed to carbonization and imines reactions of the amide groups. The copolymer is completely decomposed at approximately 600 °C. While the decomposition of the AD37-PPD copolymer begins at approximately 210 °C up to 500 °C with a weight loss of 52%. The decomposition of the AD37-PPD copolymer is at a higher temperature compared to the AD37 copolymer. As well, the modified copolymer has a good thermal stability. This result confirms the modification of the AD37 by the PDD.

Study of the Natural Settling of Bentonite Suspensions

Bentonite settlement kinetics have been studied with different initial concentrations of Bentonite (50, 100 and 150 mg/L) with the following turbidities 10, 28 and 35 NTU. For this, we used beaker (1000 mL) which contains 300 mL of each Bentonite concentrations. Samples are taken to measure the residual turbidity. Figure 5 represents the kinetics of the natural settling of bentonite suspensions for the different Initial concentrations.

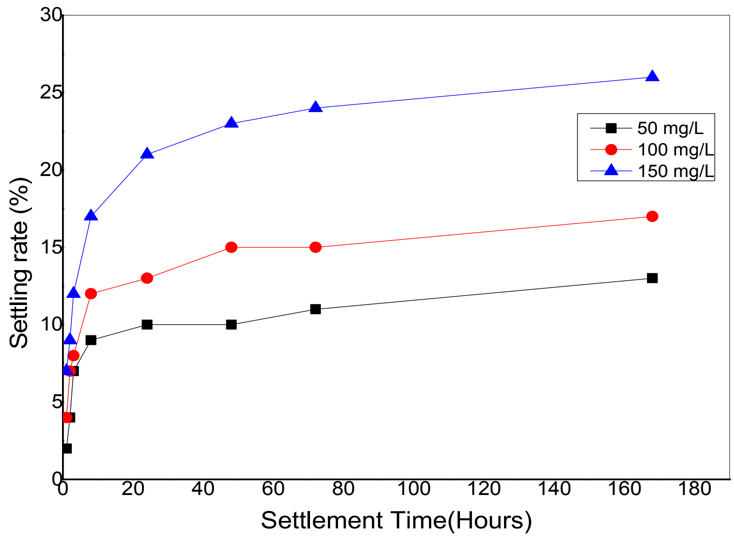

Fig. 5 – Settling rate of natural Bentonite suspension as a function of time at 25 °C.

From the reported results we can conclude that the natural settling of bentonite suspensions is a very slow process. Indeed, for a Bentonite concentration of 150 mg/L, 26% of elimination is achieved after one week of settling. We note that the natural sedimentation of high concentration of bentonite is very slow processes which agree with the results of literature.[15,16]

Application of AD37-PPD copolymer to the removal of turbidity from Bentonite suspensions by coagulation / flocculation

pH and concentration of AD37- PPD effect on bentonite settling

The AD37-PPD copolymer is used as a flocculent, in order to eliminate the turbidity of bentonite suspensions. However, the procedure of JAR-TEST described previously is respected throughout the experimental section. To evaluate the pH effect on the coagulation /flocculation efficiency and to determine the optimal pH, coagulation / flocculation of bentonite suspension (100 mg/L) is achieved by adding various concentrations of AD37-PPD for different values of pH. The initial turbidity of bentonite suspension is T_0 = 28 NTU. At the end of the operation the solutions are left to settle, and the final turbidity of the supernatant is measured after 10 min. The obtained results are represented in (Figure 6), the percentage of the removed turbidity is plotted according to the concentration of the AD37-PPD copolymer at different pH values. The AD37-PPD copolymer shows low efficiency of turbidity removal in the basic medium (pH > 6.15). It reaches a maximum of 32.15% at a concentration of 2 mg/L.

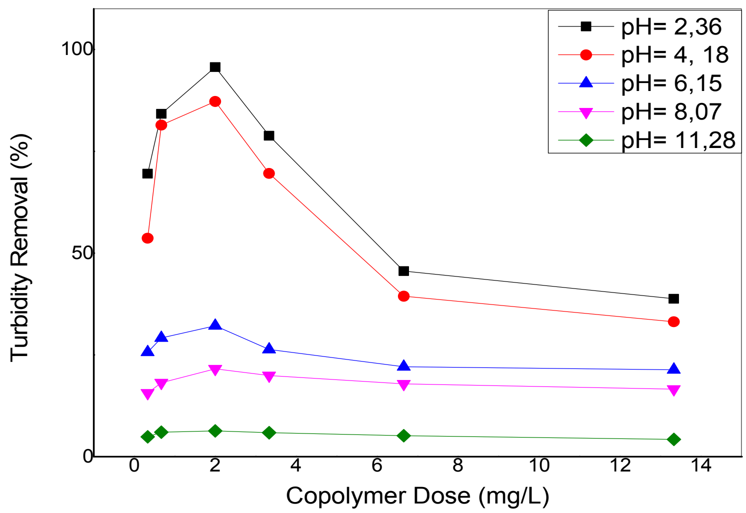

Fig. 6 – Turbidity removal from bentonite suspension as a function of AD37-PPD concentration for different values of pH at 25 °C and t = 10 min.

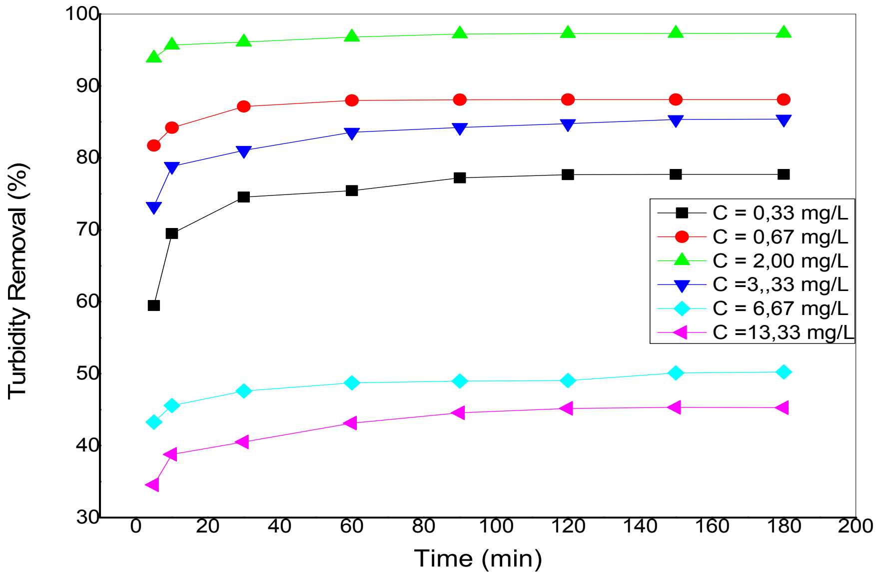

Fig. 7 – Kinetics of the settling bentonite in the presence of different concentrations of the AD37-PPD copolymer at pH = 2.36.

This can be explained by the absence of positively charged sites which play the leading role in the removal mechanism of negatively charged bentonite particle by charge neutralization.[17] A good flocculent behavior is shown by the AD37-PPD copolymer in acid medium. At pH = 2.36, the turbidity removal efficiency achieved a percentage of 95.67% with a copolymer concentration of 2 mg/L. This result is related to the adsorption of the negatively charged bentonite particles on the surface of the copolymer on the ammonium ($-NH_3^+$) sites created by the addition of HCl acid.

Study of kinetic flocculation of bentonite suspensions

To study the evolution of coagulation / flocculation process in the removal of turbidity, supernatant turbidity is measured at different settling time. The obtained results are illustrated in Fig. 7.

This figure represents the variation of the turbidity removal percentage as a function of decantation time in the presence of different AD37-PPD copolymer concentration at pH = 2.36. These results show a slight improvement with all copolymer concentration as a function of time. We can say that the flocs formed are stable and do not destroy themselves.

MATERIALS AND METHODS

Materials

The hydrolyzed polyacrylamide (AD37) was provided from Rhône-Poulenc (France). Its rate carboxylate function is $\tau = 0.27$, as determined by ^{13}C NMR and potentiometry. Its weight-average molar mass is 5×10^6 g/mol which is estimated by light scattering.[18–20]

The p-phenylenediamine (NH_2-φ-NH_2) (PPD) was provided by Aldrich. It is poorly soluble in water and soluble in ethanol. Its molecular mass is 108 g/mol. Absolute ethanol was from Aldrich and was used as a non-solvent for the copolymer. The bi-distilled water was used as solvent for the copolymer; its pH value is about 6. Bentonite has particular water adsorption properties; however modified Bentonite can adsorb various substances.[21] A sample of Bentonite (BC) was supplied by a local company issued from the fields of Hammam Boughrara–Maghnia, Algeria. It is composed essentially of montmorillonite.[16] The different chemical elements and proprieties of the Bentonite are mentioned in a previous work of Mansri *et al.*[22]

Methods

At 25 ± 1 °C, flocculation experiments were carried out in a conventional Jar-Test apparatus. It consisted of six paddles on a bench. The paddles were connected to each other by a gear mechanism, and all these paddles were simultaneously rotated by the same motor at a controlled speed and time. Wastewater samples of 1000 mL each were transferred to the jars and then pH adjusted using HCl (1 M) or NaOH (1 M) solutions. The required dose of modified copolymer (AD37-PPD) was added to each beaker. Directly after the addition of the copolymer dosage, the wastewater sample in the jar was stirred rapidly at a paddle speed of 120 rpm for 2 min then stirred slowly at a paddle speed of 50 rpm for 10 min. Finally, the treated wastewater could settle for 5 min. [23]

For assessing flocculent efficiency, we use a turbidimeter to measure the initial turbidity (T_0) and so the turbidity of the suspension after adding different amounts of the flocculent (0.1 – 5 ppm) (T_f). The turbidity removal percent was calculated from the formula: [17,24]

$$\text{Turbidity removal }\% = \frac{\left(T_0 - T_f\right)}{T_0} \times 100$$

Synthesis of the modified poly(acrylamide) (AD37-PPD)

The synthesis of our copolymer was carried out by modification of hydrolyzed polyacrylamide (AD37) by the p-phenylenediamine (PPD) according to the following procedure: in a 100 mL beaker, we introduce 2.5 g of hydrolyzed polyacrylamide (AD37) containing 30 mL of bi-distilled water, then we leave under stirring for 24 hours. In a 25 mL flask, we prepare an aqueous solution of p-phenylenediamine (NH_2-φ-NH_2) (PPD) acidulated with HCl. We added 10 mL of the aqueous solution of PPD to the aqueous solution of AD37 in the beaker. Stirring and heating were maintained for 2 hours. The resulting product was dissolved and then precipitated in a large amount of ethanol. The product was dried at 70 °C for 24 hours.

CONCLUSIONS

The flocculation of turbid water using jar test is performed in different low, medium and high turbidity level. The flocculation experiments using modified Poly(acrylamide) AD37-PPD solutions indicated that flocculation process effectively removed turbidity from water. The AD37-PPD copolymer shows low efficiency of turbidity removal in the basic medium (pH > 6.15) with a maximum of 32.15% with a concentration of 2 mg/L. A good flocculent behavior is shown by this copolymer in acidifying the starting medium. A percentage of 95.67% is achieved with a concentration of 2 mg/L at pH = 2.36. This result provided by the adsorption of bentonite particle negatively charged on the copolymer by the addition of HCl acid.

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