



**SYNTHESIS OF FLOCCULANTS BASED ON RESPONSIVE POLYMERS AND ITS USE IN SOLIDS REMOVAL FROM RIVER WATER AND WASTEWATER**  
**SÍNTESIS DE FLOCULANTES A BASE DE POLÍMEROS SENSIBLES Y SU USO EN LA REMOCIÓN DE SÓLIDOS EN AGUA DE RÍO Y AGUAS RESIDUALES**

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**Abstract**

Flocculants based on responsive polymers were synthesized by means of free radical polymerization in aqueous environment at 25 °C. Poly(*N*-isopropylacrylamide) (PNIPAAm), statistical copolymers from NIPAAm and either acrylamide (AAm) or acrylic acid (AAc), and a copolymer composed of the three different monomers were prepared. These materials were characterized by Dynamic Light Scattering (DLS), Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA). The polymer diameters in water were in the range from 22 to 42 nm. Copolymers containing acid units exhibit a sharp T/pH-responsive behavior. Polymeric flocculants were evaluated in the turbidity removal from high-turbidity river water and wastewater (urban and agricultural). Temperature and time of flocculation, as well as composition and dosage of polymer were tested. The most effective temperature and time of flocculation were found to be 40 °C and 15-25 min, respectively. Polymer dosage of 0.1 mg mL<sup>-1</sup> is sufficient for a high percentage of turbidity removal (~80%). At 1 mg mL<sup>-1</sup> of flocculant, turbidity removal from 23.9 to 99.2% depending on the polymer composition and water quality were reached.

*Keywords:* water treatment, flocculation, turbidity removal, responsive polymers, PNIPAAm.

**Resumen**

Se sintetizaron floculantes, compuestos de polímeros sensibles, vía polimerización por radicales libres en medio acuoso a 25 °C. Se prepararon poli(*N*-isopropilacrilamida) (PNIPAAm), copolímeros estadísticos de NIPAAm con acrilamida (AAm) o ácido acrílico (AAc), y un copolímero compuesto de los tres diferentes monómeros. Estos materiales se caracterizaron por Dispersión de Luz Dinámica (DLS), Espectroscopia de Infrarrojo con Transformadas de Fourier (FT-IR) y Análisis Termogravimétrico (TGA). Los diámetros de los polímeros en agua estuvieron en un intervalo de 22 a 42 nm. Los copolímeros con unidades ácidas exhiben un comportamiento de respuesta a cambios de temperatura y pH. Los floculantes poliméricos fueron evaluados en la remoción de turbidez del agua de río con turbidez elevada y agua residual (urbana y agrícola). Se probaron la temperatura y el tiempo de floculación, así como la composición y dosis de polímero. La temperatura y el tiempo de floculación más efectivos fueron 40 °C y 15-25 min, respectivamente. La dosis de polímero de 0.1 mg mL<sup>-1</sup> es suficiente para lograr un porcentaje de remoción de turbidez elevado (~80%). A 1 mg mL<sup>-1</sup> de floculante, se alcanza una remoción de turbidez de 23.9 a 99.2%, dependiendo de la composición de polímero y la calidad del agua.

*Palabras clave:* tratamiento de aguas, floculación, remoción de turbidez, polímeros sensibles, PNIPAAm.

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## 1 Introduction

Water is an essential requirement for the survival of living beings. River water needs to be treated before domestic use. Alike wastewater must be treated before it is released back to the environment (Deblonde *et al.*, 2011; Tomar and Suthar, 2011; Divakaran and Pillai, 2002; Ipek *et al.*, 2004). The removal of contaminants from these effluents involves the flocculation process. Flocculation is the solid-liquid separation achieved by binding and precipitation of substances present in water (Alexander *et al.*, 2012; López-Vidal *et al.*, 2014). In most cases, organic polymeric flocculants are employed to induce attractive forces between fine particles, driving to the formation of large aggregates that precipitate (Wang *et al.*, 2013; Gregory and Barany, 2011; Pal and Pal, 2012; Schwarz *et al.*, 2007). In comparison with alum, some of the advantages flowing from the use of organic polyelectrolytes in water treatment are: lower coagulant dose requirements, a smaller volume of sludge, a smaller increase in the ionic load of the treated water, reduced level of aluminium in treated water, cost savings of up to 25-30% (Bolto and Gregory, 2007). Some polymers are able to remove above 95% of solids contained in water (Ebeling *et al.*, 2005). The flocculation by means of organic polymers depends strongly on several characteristics related to particles (charge, concentration and size), polymers (the chemical structure, the molar mass, the charge density and the polymer chain hydrophobicity) and medium (the ionic strength, pH and temperature) (Ghimici and Constantin, 2011). The conventional polymeric flocculants (e.g. polyaluminium chloride) form low density flocs having large amount of water trapped. This results in an adverse effect during the stage of sediment consolidation (Li *et al.*, 2009). Therefore, the preparation of new flocculants, which overcome the drawbacks of conventional hydrophilic flocculants, is a scientific challenge that opens the possibility for technological development.

Responsive water-soluble polymers have been proposed as flocculants that can significantly improve the solids dewatering and sediment consolidation (Franks, 2005; O'Shea *et al.*, 2010; Tokuyama *et al.*, 2010). Stimuli-responsive polymers exhibit a reversible phase transition induced by changes in pH or temperature (Salgado-Rodríguez *et al.*, 2004; Ponce-Vargas *et al.*, 2013). The transition of thermosensitive polymers takes place when the lower critical solution temperature (LCST) is reached. The event is accompanied by an

endothermic process of water release from the polymer chains (Kubota *et al.*, 1990). This unique physicochemical property of "smart" polymers makes them candidates for their application as ideal flocculants (O'Shea *et al.*, 2010; Tokuyama *et al.*, 2010). Poly(*N*-isopropylacrylamide) (PNIPAAm) has been the most studied thermosensitive polymer. In water, PNIPAAm undergoes a sharp coil to globule transition turning the chain insoluble, followed by hydrophobic aggregation and phase separation above 32 °C. This behavior is possible because of the good balance between hydrophilic and hydrophobic interactions in the polymer (Schild, 1992). The LCST of PNIPAAm can be adjusted by copolymerization with hydrophilic monomers, containing carboxylic acids, amines or hydroxyls as substituents (Picos-Corrales *et al.*, 2012a; Licea-Claverie *et al.*, 2009). Thus, the interactions among polymer-polymer or polymer-aqueous environment are controlled (Salgado-Rodríguez *et al.*, 2004). Additionally, PNIPAAm has been shown to be noncytotoxic at low concentrations (0.1-10.0 mg mL<sup>-1</sup>) (Malonne *et al.*, 2005).

Responsive flocculants based on PNIPAAm have been comprehensively tested in solids removal from aqueous samples. It has been demonstrated that at temperatures above the LCST, PNIPAAm is able to act as both a flocculant and a flotation collector (Tokuyama *et al.*, 2010; Franks *et al.*, 2009). PNIPAAm with higher molecular weight produces faster settling rates and clearer supernatants at 50 °C (Li *et al.*, 2009). Using this thermosensitive polymer, alumina flocculation is enhanced with increasing solution temperature (Burdukova *et al.*, 2011). Charged PNIPAAm increases both the particle/bubble attachment as well as the floatability of coarse alumina and quartz particles respectively (Forbes *et al.*, 2011). PNIPAAm allows the successful coadsorption of undesirable metal ions (Cu (II) or Cr (III)) and humic substances in water (Tokuyama *et al.*, 2010).

Experimental studies on turbidity removal from river water and wastewater using flocculants based on PNIPAAm were not found in the literature. It is known that solids flocculation from high-turbidity river water is a problem faced by potabilization plants during the rainy season, as an example the potabilization plants in Culiacan, Mexico. In this work, it was the goal to prepare "smart" flocculants that lead to overcome the problem in the reduction of high turbidity levels. For the flocculants design, the thermosensitivity of PNIPAAm (Li *et al.*, 2009),

the ability of poly(acrylamide) (PAAm) to bind to particle surfaces and act as a thickener (Erciyas *et al.*, 1992), and the adsorption property of poly(acrylic acid) (PAAc) onto particles surface depending on the pH (Liufu *et al.*, 2005) were exploited. These materials may allow a high removal of solids from high-turbidity river water and wastewater.

## 2 Experimental

### 2.1 Materials

N-isopropylacrylamide (NIPAAm) was purified by recrystallization in hexane. Acrylic acid (AAc) was purified by passing through an inhibitor remover column. Acrylamide (AAm) was used as received. N,N,N',N'-Tetramethylethylenediamine (TEMED) was used as an accelerator, and ammonium persulfate (APS) was used as an initiator. All these chemicals were obtained from Sigma-Aldrich-Mexico. Deionized water (Golden Bell) was locally purchased.

### 2.2 Preparation of responsive polymers

Responsive polymers were prepared by free radical polymerization (Feng *et al.*, 1988; Tokuyama and Iwama, 2009). For the NIPAAm polymer, the total monomer concentration used in the aqueous solution was 0.22 mmol mL<sup>-1</sup>. For the redox pair initiation system, TEMED and APS were added at 1 mol% and 0.5 mol%, respectively, with respect to the monomer concentration. NIPAAm copolymers were synthesized varying the comonomer content on the feed from 5 to 10 mol% (from 3.2 to 6.6 wt.%) with respect to NIPAAm. Notations are assigned to the type and composition of each polymer: poly(N-isopropylacrylamide) (PNIPAAm), poly(N-isopropylacrylamide-co-acrylamide<sub>5%</sub>) (PNIPAAm-AAm4), poly(N-isopropylacrylamide-co-acrylamide<sub>10%</sub>) (PNIPAAm-AAm7), poly(N-isopropylacrylamide-co-acrylic acid<sub>5%</sub>) (PNIPAAm-AAc11), poly(N-isopropylacrylamide-co-acrylic acid<sub>10%</sub>) (PNIPAAm-AAc18) and poly(N-isopropylacrylamide-co-acrylamide<sub>5%</sub>-co-acrylic acid<sub>5%</sub>) (PNIPAAm-AAm-AAc17). The percentages are given in moles. The polymerization was performed in a Schlenk flask under continuous stirring and nitrogen atmosphere at 25°C. The reaction time was 2 h (polymerizations without acrylic acid) and 20 h (polymerizations with acrylic acid). The resulting polymers were precipitated by heating the solution to

a temperature above the LCST and then extensively washed with deionized water in order to remove the unreacted monomers. Cellulose tubular membrane with a molecular weight cut off of 12000-14000 was used. The polymers were then dried in an oven at 60 °C.

As an example, the preparation of poly(N-isopropylacrylamide-co-acrylamide<sub>5%</sub>) is described in detail: N-isopropylacrylamide (0.950 g, 8.395 mmol), acrylamide (0.032 g, 0.450 mmol) and deionized water (38 mL) were added to a Schlenk flask. The aqueous solution was bubbled with nitrogen for the removal of dissolved oxygen. After 20 min, APS (0.010 g, 0.044 mmol) dissolved in 2 mL of oxygen-free deionized water was added dropwise, and then TEMED (14 µL, 0.093 mmol) added very slowly using a micropipette. The polymerization was followed by stirring at 25°C for designated times.

### 2.3 Flocculation using responsive polymers

River water, urban wastewater and agricultural wastewater were collected in the municipality of Culiacan (Sinaloa, Mexico). Raw water was treated using PNIPAAm, PNIPAAm-AAm4 and PNIPAAm-AAm7. Water samples were acidified (pH<5) prior to the treatment by polymer containing acid groups in order to control the hydrophilicity of the flocculant. The flocculation technique using the thermosensitive polymers was implemented as follows (Fig. 1). First, the polymer was added to river water or wastewater samples containing dissolved and dispersed solids below the LCST (e.g., 30 °C). Next, the temperature was increased over the LCST under constant stirring, inducing phase separation. Thus, the hydrophobic macromolecule led to flocculation. Solids were sequestered by the phase-separated polymer due to hydrophobic interaction. After the flocculation, flotation of the aggregates was observed. Floccs and aqueous phase were separated by decantation. In this study, temperature and time of flocculation, as well as composition and concentration of flocculant were tested.

### 2.4 Characterization methods

Dynamic light scattering (DLS) was used to determine the hydrodynamic diameter ( $D_h$ ). Measurements were carried out at room temperature (25 °C) using a Zeta-sizer "nano-ZS" from Malvern Instruments (ZEN3500) equipped with a green laser operating at  $\lambda = 532$  nm.

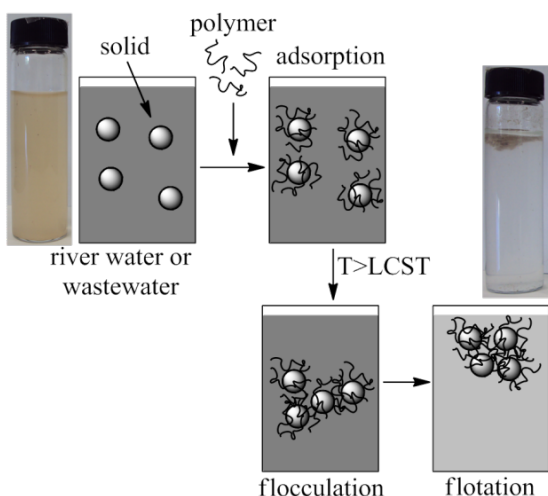


Fig. 1. Diagram of the separation technique using thermosensitive polymers.

The angle of measurement is  $173^\circ$  (backscattering) and the size analysis was performed by CONTIN. The polymer concentration used was  $1 \text{ mg mL}^{-1}$ . Before measurement, samples were filtered off using a 0.45 micron syringe filter for eliminating dust. The chemical structure of the polymers was analyzed by Fourier transform infrared spectroscopy (FT-IR). The analyses were performed on a Spectrum 400, FT-IR/FT-NIR, Spectrometer from Perkin Elmer. The comonomer content was determined by thermogravimetric analysis (TGA) using a SDT2960 simultaneous DSC-TGA, TA Instruments. The temperature range was from 30 to  $700^\circ\text{C}$ , using a heating rate of  $10^\circ\text{C min}^{-1}$  in a nitrogen flow ( $45 \text{ mL min}^{-1}$ ). The transmittance as a function of temperature was used for determining the LCST of the prepared polymeric materials in aqueous solution. For this, UV-VIS analyses were recorded using a JENWAY 6705 UV-VIS spectrophotometer (Xenon lamp) at a wavelength of 600 nm. The polymer concentration was  $1 \text{ mg mL}^{-1}$ . The solutions were prepared, shaken for 15 h and stored overnight in refrigerator. The temperature range was from 24 to  $45^\circ\text{C}$ , using 10 min of equilibration time at each temperature in the heating cycle. The LCST value was taken as the temperature before a sharp decrease in transmittance was observed. Turbidity analyses were performed with a Hach 2100N Turbidimeter equipped with a stable halogen-filled Tungsten filament lamp. Water conductivity was measured on a Orion STAR A2125 Conductivity Meters, Thermo Scientific. Conductivity and turbidity measurements after the treatment were carried out at  $25^\circ\text{C}$ .

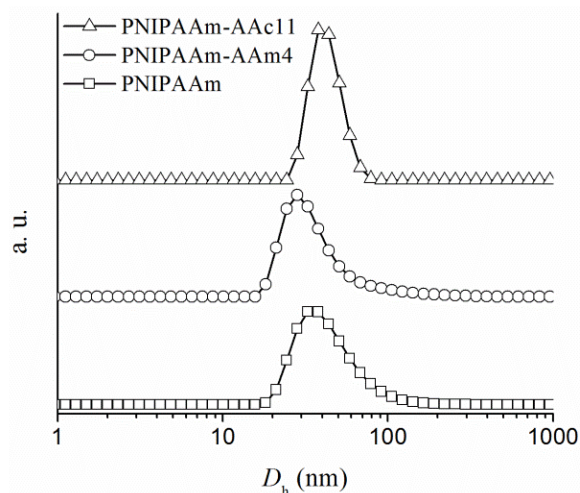


Fig. 2. Hydrodynamic diameter distributions in deionized water at  $25^\circ\text{C}$ .

Parameters of raw water and treated water were determined to evaluate the efficiency of flocculation.

### 3 Results and discussion

#### 3.1 Synthesis and characterization of responsive polymers

The aqueous one-pot synthesis strategy allowed the preparation of five different polymeric flocculants: PNIPAAm, PNIPAAm-AAm4, PNIPAAm-AAm7, PNIPAAm-AAc11, PNIPAA-AAc18 and PNIPAAm-AAm-AAc17. Reactions were carried out for 2 h (polymerizations without acrylic acid) and 20 h (polymerization with acrylic acid). Despite the inhibitor removal, AAc slows down the processes of polymerization significantly compared to AAm, which may be caused either by an additional interaction between AAc and TEMED or by the difference in comonomers reactivity and higher incorporation of AAc on the copolymer as will be demonstrated below. Polymer yields were determined gravimetrically, resulting in values  $>80\%$ . Fig. 2 shows the distributions of hydrodynamic diameter ( $D_h$ ) by intensity for three responsive polymers.  $D_h$  was estimated from the diffusivity coefficient determined by DLS. Unimodal size distributions are related to samples with single diffusivity and demonstrate homogeneity of the nanometric macromolecules in aqueous solution (Picos-Corrales *et al.*, 2014). PNIPAAm-AAc11 exhibits the narrower distribution, indicating a better chain length control when the comonomer acrylic acid is used.



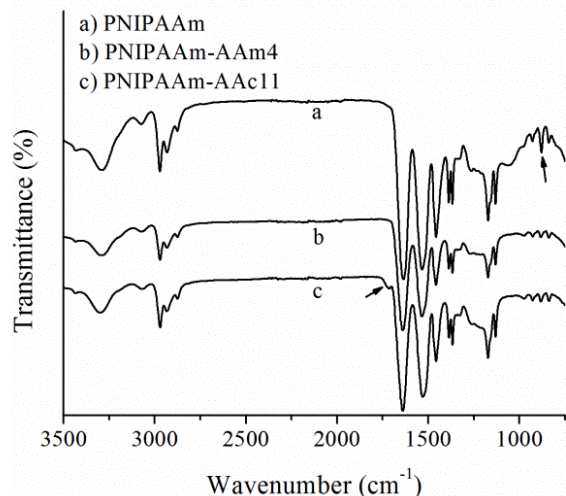


Fig. 3. Fourier transform infrared spectra (FTIR) of polymers.

It can be seen, that the polymer sizes are in a closed range irrespective of the comonomer type.

Fig. 3 shows the FTIR spectra of PNIPAAm, PNIPAAm-AAm4 and PNIPAAm-AAc11. All spectra contain the typical absorption bands of amide groups at  $1640\text{ cm}^{-1}$  (C=O stretching); at  $1530\text{ cm}^{-1}$ , N-H in-plane bending vibration; at  $3290\text{ cm}^{-1}$ , N-H stretching band. The double band at  $1387$  and  $1367\text{ cm}^{-1}$  formed by symmetrical bending vibration and coupling split originating from bimethyl of isopropyl group is also observed. For the PNIPAAm-AAc11, an absorption band appeared at  $1715\text{ cm}^{-1}$ , belonging to the C=O stretching of acrylic acid units (Zhang *et al.*, 2009). The intensity of this signal is low because the percentage of acid comonomer is low. PNIPAAm and PNIPAAm-AAm4 spectra are very similar, only an intensity difference in the absorption band at  $878\text{ cm}^{-1}$  is observed. This is attributed to the comonomers chemical similarity and the very low AAm content in the copolymer.

TGA thermograms of different polymers are shown in Fig. 4. In comparison with the homopolymer, the comonomers show an effect on the thermal stability of copolymers which can be easily observed. In all the cases, an initial mass loss between 5 wt.% and 7 wt.% are observed up to a temperature of  $150\text{ }^{\circ}\text{C}$ , which is attributed to water present as adsorbed moisture. In the second phase, degradation of copolymers containing AAm and AAC starting at  $225$  and  $325\text{ }^{\circ}\text{C}$ , respectively, is observed. It can be seen that AAC units exhibit a stepwise thermal decomposition (Dubinsky *et al.*, 2005). The TGA curves show the major decomposition for all samples

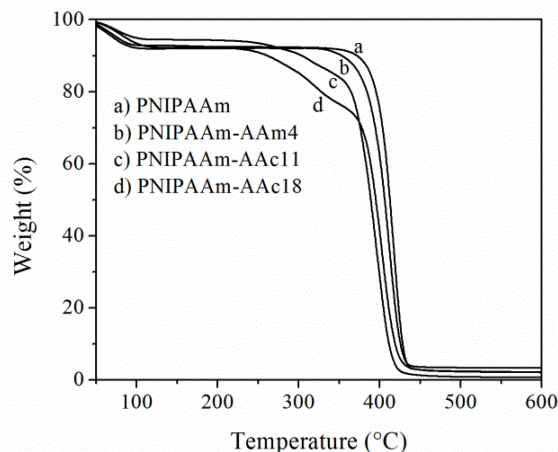


Fig. 4. Thermogravimetric analysis (TGA) of polymers.

in the temperature range from  $360$  to  $450\text{ }^{\circ}\text{C}$ , which should be attributed to the thermal degradation of NIPAAm units when the thermograms of PNIPAAm and copolymers are compared. The copolymers composition was calculated from the derivative of the weight percent curve based on the thermogravimetric procedure previously reported (Picos-Corrales *et al.*, 2012b).

Table 1 shows a series of synthesized polymers produced with the aim to get different chemical compositions. Sizes ( $D_h$ ) in water of most polymers were in the range from  $32$  to  $42\text{ nm}$ . PNIPAAm-AAm-AAc17 shows the lowest size due to the use of three comonomers with different reactivities. As can be seen in the third column, AAm content in the respective copolymers was very close as in the feed. For copolymers containing AAC, the wt.% was higher than expected from the comonomer mixture. This is an indication that the incorporation of the comonomer does not follow the rules for ideal copolymerization as observed in a previous report for others acid comonomers (Picos-Corrales *et al.*, 2012a). The comonomer type and composition play an important role in the LCST behavior of statistical copolymers. The last two columns in Table 1 summarize the LCST values measured in deionized water (pH $\sim$ 7) and in a buffer solution at pH 4 for the polymers prepared. The thermosensitive behavior at pH 4 is shown in Fig. 5. For PNIPAAm-AAm4, PNIPAAm-AAm7 and PNIPAAm-AAc11 in water (pH $\sim$ 7), an LCST close to  $37\text{ }^{\circ}\text{C}$  was obtained, which proves the effect of AAC and AAm in the solubility of their respective copolymers.

Table 1. Data of size, composition and LCST for different polymers

Polymer	Comonomer feed (wt.%)	$D_h^a$ (nm)	Comonomer content <sup>b</sup> (wt.%)	LCST <sub>water</sub> (°C)	LCST <sub>pH 4</sub> (°C)
PNIPAAm	0	37	0	32	-
PNIPAAm-AAm4	3.2	32	4	36	30
PNIPAAm-AAm7	6.6	38	7	38	36
PNIPAAm-AAc11	3.2	42	11	36	28
PNIPAA-AAc18	6.6	40	18	-	28
PNIPAAm-AAm-AAc17	6.6	22	17	-	32

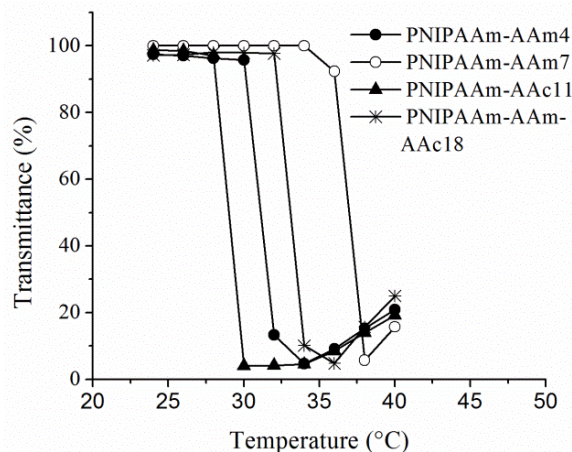


Fig. 5. LCST behavior of different flocculants at pH 4.

The LCST value is increased or is not detectable with increasing comonomer content because of the higher incorporation of hydrophilic units, indicating that the interaction among the polymer segments and the solvent molecule are getting more preferred to the interactions within the polymer segments (Picos-Corrales *et al.*, 2014). Furthermore, the LCST value decreases with decreasing pH value. This means that by adding the comonomer to PNIPAAm the LCST is pH dependent. For copolymers containing AAc, the LCST difference comparing water at pH 7 and pH 4 is dramatic. In this case, the AAc degree of ionization in the copolymer can be considered as the principal effect. The pKa value of PAAc is 4.7 (Lee *et al.*, 1999), then the degree of ionization can be calculated using the Henderson-Hasselbach equation (Conio *et al.*, 1976). At a pH value of 7, close to 100% of acid units are expected to be ionized; however, at pH 4 only 17% of the AAc units are ionized. At low pH, the carboxylic acid groups form hydrogen-bonds with the amide group in the NIPAAm structure. This would lead to additional polymer-polymer interactions making phase separation by heating (LCST) a less endothermic process than in

pure PNIPAAm, since fewer sites are available for the water-NIPAAm hydrogen bonds (Salgado-Rodríguez *et al.*, 2004). Therefore, the LCST of PNIPAAm-AAc11 and PNIPAA-AAc18 at pH 4 is 28 °C. In the case of copolymers containing AAm, the LCST is lower at pH 4 (amino groups tend to be protonated in acidic environment), which can be attributed to the decrease in polymer-solvent interactions due to the protonation and the loss of the hydrogen bond with water molecules (Fang *et al.*, 2011). PNIPAAm-AAm-AAc17 is subject to the influence of both AAm and AAc units.

### 3.2 Flocculation studies in river water

The study assessed the effectiveness of flocculants, based on responsive copolymers, in removing solids from river water. For these experiments, highly turbid water was collected from Culiacan River (Sinaloa, Mexico) during rainy season in August. Samples with different turbidity, depending on the weekly precipitation, were analyzed with minimal delay after collection. The average values of some parameters, sampling in the same point at two different weather conditions, were the following: weather condition A (pH 6.8, turbidity 758 NTU, and conductivity 246  $\mu\text{S cm}^{-1}$ ) and weather condition B (pH 7.5, turbidity 92 NTU, and conductivity 250  $\mu\text{S cm}^{-1}$ ). In this case, the area around the river is a clay rich soil which increases considerably the turbidity with the rainfall intensity.

In turbid water samples, the interaction between particles may be repulsive or attractive. When there are attractive forces, the flocculation occurs rapidly. The attractive forces between particles can be controlled by external factors (Franks, 2005). Therefore, temperature and time of flocculation, as well as convenient polymer dosage were tested to optimize the flocculation process. All experiments were carried out in duplicate. Data are reported to have an estimated error between 5 and 7%.

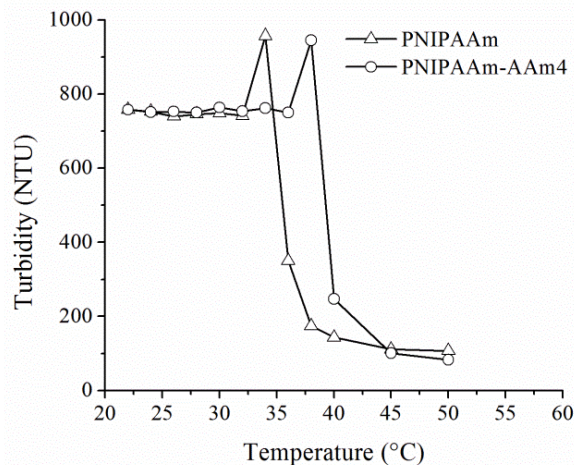


Fig. 6. Determination of the flocculation temperature.

LCST values obtained in deionized water suggest that flocculation temperature is greater than 30 °C. The flocculation temperature in weather condition A was investigated using PNIPAAm and PNIPAAm-AAm4 (Fig. 6). Equilibration time at each temperature was fixed at 15 min. Before the LCST, the turbidity of the solution does not register significant variation. With PNIPAAm, the phase separation of dissolved polymer takes place at 34 °C, which is observed as a turbidity increase close to 950 NTU; at this temperature, the polymer turns hydrophobic and the interaction between polymer and dispersed solids is favored. However, flocculation-flocculation stage begins at 36 °C and is improved at 38 °C (turbidity lower than 200 NTU); turbidity decreases slightly for further temperature increase (40, 45, 50 °C). Thus, temperature of 38 °C is the lowest one where the polymer becomes very hydrophobic and allows a good solid-liquid separation. The plot of flocculation temperature for PNIPAAm-AAc11 was quite similar to the PNIPAAm-AAm4 one. With PNIPAAm-AAm4, the polymer phase separation occurs at 38 °C (turbidity close to 940 NTU); the flocculation-flocculation starts at 40 °C and is better at 45 °C (turbidity ~100 NTU). PNIPAAm-AAm4 shows higher phase separation temperature because the AAm units enhance the polymer-water interaction. In all cases, flocculation-flocculation was observed. This is attributed to the adhesion of air bubbles on the aggregate (Tokuyama *et al.*, 2010).

The evaluation of flocculation time was performed in the weather condition A testing PNIPAAm, PNIPAAm-AAm4 and PNIPAAm-AAc11 (Fig. 7). Fig. 7a shows a graph of turbidity versus time using PNIPAAm; at 35 °C, despite time increase,

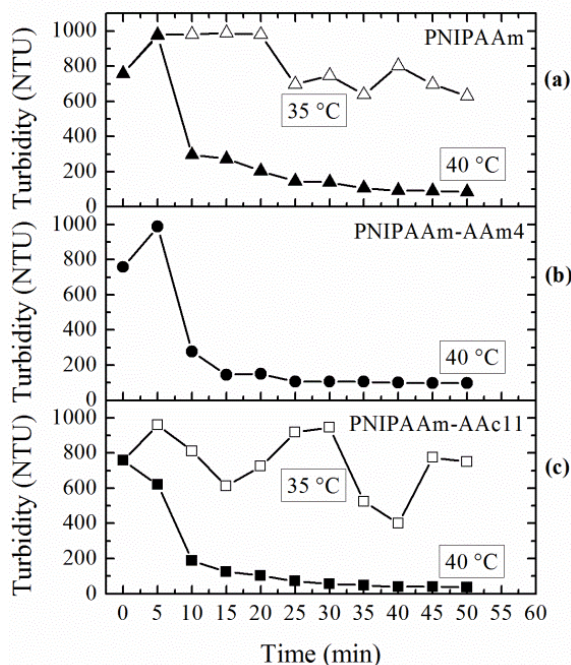


Fig. 7. Determination of the flocculation time at 35 and 40 °C, using polymer dosage of 1 mg mL<sup>-1</sup>.

the hydrophobic interaction between polymer and water pollutants is weak, then the flocculation was not achieved; at 40 °C, 5 min are sufficient to break the polymer-water interaction and induce the hydrophobic interactions, cutting down the optimal flocculation time to 10 min; turbidity decreases continuously with further time increase; nevertheless, 25 min was considered enough time for an effective flocculation process. For weather condition A and using PNIPAAm-AAm4 at 40 °C (Fig. 7b), phase separation and flocculation behavior with time are similar to that obtained using PNIPAAm as flocculant, but turbidity in 15 min is about 125 NTU' slower than when using PNIPAAm. From the Fig. 7c, it is seen that PNIPAAm-AAc11 is not a good flocculant when the solution temperature is 35 °C, while at 40 °C this copolymer exhibits a phase transition already at 5 min, where the turbidity was found to be 130 NTU lower than the initial value; however after 5 min at 40 °C, the flocculation behavior is similar than for PNIPAAm-AAm4. Time of 15 min is adequate for flocculation by using any of the studied copolymers. This experiment shows that copolymers improve the flocculation efficiency in river water at lower time than PNIPAAm. However, for longer times (~50 min), the achieved turbidity removal by flocculation is similar for all temperature sensitive polymers studied. Amino and acid groups of the comonomers, within the



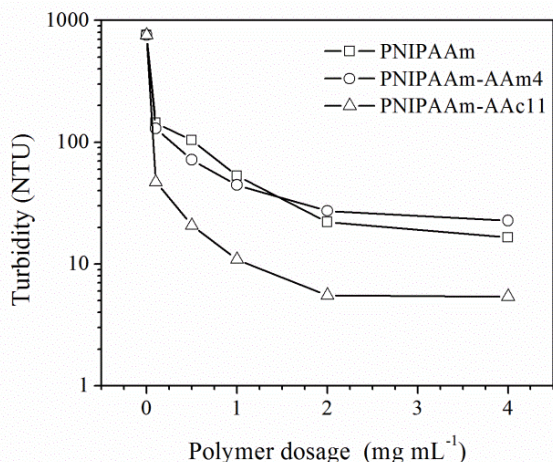


Fig. 8. Elimination of water turbidity studied at different polymer dosage at 40 °C for 30 min.

respective copolymer, provide a higher binding force among the macromolecule and the dispersed solids present in high-turbidity river water.

It is well known that effective flocculation requires that the adsorbed polymer extends far enough from the particle surface to attach to other particles and that there is sufficient free surface available for adsorption of these extended chains. If excess polymer is adsorbed, the particles become restabilized because of surface saturation or by steric stabilization (Erciyes *et al.*, 1992). For this reason, the effect of polymer dosage on the turbidity elimination was evaluated in the weather condition A using the polymers PNIPAAm, PNIPAAm-AAm4 and PNIPAAm-AAc11 at 40 °C for 30 min. As can be seen in Fig. 8, the effectiveness of polymers in turbidity removal from river water is highly dependent on flocculant concentration. Sample turbidity decreases markedly with increasing the polymer dosage in the range from 0.1 to 2 mg mL<sup>-1</sup>. At the dosage of 0.1 mg mL<sup>-1</sup>, turbidity falls from 758 to less than 150 NTU, indicating that this dosage is sufficient to generate a good polymer-contaminant interaction and leads to a high turbidity removal. The dosage of 2 mg mL<sup>-1</sup> improves significantly the flocculation in water with the characteristics mentioned above. Apparently, higher polymer dosage does not break the equilibrium of a small amount of dispersed particles. PNIPAAm and PNIPAAm-AAm4 show a comparable efficiency in turbidity elimination as a function of concentration, suggesting a similar interaction of both polymers with the suspended solids, so AAm units do not contribute significantly. The system of weather condition A and PNIPAAm-AAc11 exhibits the best results due to a

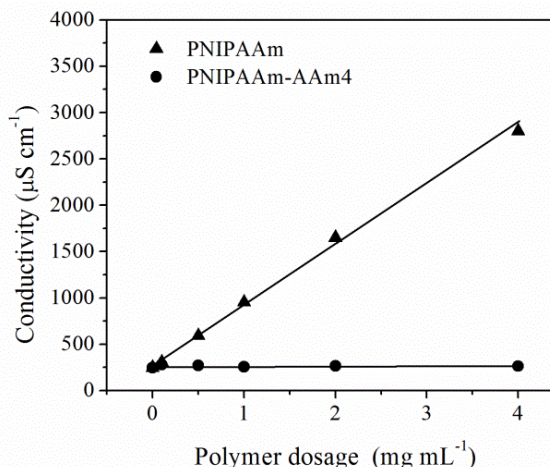


Fig. 9. Water conductivity at different polymer dosage and 25 °C.

better interaction between polymer-solids driven by the pendant acid groups of the flocculant. It can be considered that flocculant concentration of 1 mg mL<sup>-1</sup> allows a convenient turbidity removal prior to other stages of the treatment, when highly turbid water is fed.

Water conductivity (weather condition A) was measured at 25 °C prior and after the treatment with PNIPAAm or PNIPAAm-AAm4. Through this analysis, the ability of both polymers to trap species was evaluated, considering a direct relationship between conductivity and dissolved solids (Atekwana *et al.*, 2004). Results shown in Fig. 9 indicate that the water conductivity increases linearly with increasing PNIPAAm concentration. However, the water conductivity is independent on the PNIPAAm-AAm4 dosage. To interpret this trend, the effect of residual polymer and dispersed solids was assessed. It was found experimentally that the conductivity of deionized water increases around 5 μS cm<sup>-1</sup> when polymer at 1 mg mL<sup>-1</sup> is dissolved; therefore, the higher conductivity is not attributable to residual PNIPAAm. On the other side, from the literature we learned that various heavy metal ions can be adsorbed onto humic substances present in natural waters (Tokuyama *et al.*, 2010). Thus, it is proposed that PNIPAAm displaces adsorbed ions and removes mainly dispersed solids, so conductivity is greater at higher dosage because adsorbed ions become dissolved ions (Fig. 10). On the other hand, PNIPAAm-AAm4 may interact with dispersed solids and adsorbed ions due to protonation and chelation (Fang *et al.*, 2011; El-Hamshary *et al.*, 2003; Orozco-Guareño *et al.*, 2010), leading to the



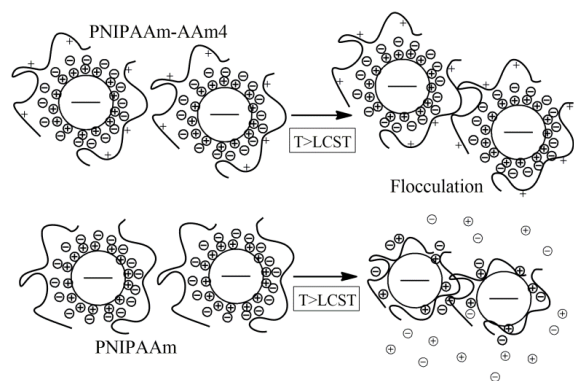


Fig. 10. Flocculation mechanism using PNIPAAm and PNIPAAm-AAm4.

flocculation of both species. For this reason, the concentration of dissolved ions remains practically constant and the solution conductivity is independent on the PNIPAAm-AAm4 concentration. This study was not performed with the system with PNIPAAm-AAm11, because of the HCl used in the acidification. Nevertheless, it is known that copolymers containing AAc exhibit the ability to remove metal ions from aqueous solutions (Orozco-Guareño *et al.*, 2010; El-Hag Ali *et al.*, 2003). In all cases, hydrophobic interactions among polymer chains induce floc formation (Lee *et al.*, 2009).

The percentages of turbidity removed were evaluated as a function of the polymer composition using river water with different solids concentration. Turbidity removal (%) was calculated as  $TR(\%) = [(T_0 - T_f)/T_0](100)$  with  $T_0$  and  $T_f$ , being the turbidity of raw water and treated water, respectively. According to Table 2, flocculants based on copolymers allow a greater turbidity reduction, excluding PNIPAAm-AAm7. It can be seen that the higher

the AAm content, the lower the turbidity removal, then the polymer-water interaction increases with the AAm units in the macromolecule. The systems using copolymers from PNIPAAm-AAc show the best results in turbidity elimination because of a good polymer-solids interaction. Comparing data obtained from the treatment of weather conditions A and B, it is observed that the turbidity reduction depends strongly on the water turbidity, when PNIPAAm is used. The copolymers effectiveness may be considered independent on the water turbidity. Results of color reduction were consistent with the data obtained for turbidity. The behavior of water conductivity in the weather condition B was the same as observed in weather condition A. The conductivity of sample B increases from 250 to 855  $\mu\text{S cm}^{-1}$  after the treatment with PNIPAAm, and remains close to 250  $\mu\text{S cm}^{-1}$  when PNIPAAm-AAm4 is the flocculant. This trend is attributed to a difference in the polymer-solids interaction, as previously explained.

### 3.3 Turbidity removal from wastewater

The flocculants capacity in removing solids from wastewater was evaluated by sampling wastewater of two sources: domestic wastewater and agricultural wastewater. High-turbidity wastewaters were collected in the municipality of Culiacan (Sinaloa, Mexico) in November 2013. The average characteristic parameter values of wastewater are the following: urban wastewater (pH 7.35, turbidity 446 NTU, and conductivity 1315  $\mu\text{S cm}^{-1}$ ) and agricultural wastewater (pH 7.82, turbidity 184 NTU, and conductivity 3150  $\mu\text{S cm}^{-1}$ ). The high conductivity of agricultural wastewater may be related to the wide variety of ions from residual fertilizers.

Table 2. Turbidity removal from river water by different polymers using a concentration of 1 mg mL<sup>-1</sup> at 40 °C for 30 min

Polymer used	Weather condition A (758 NTU)		Weather condition B (92 NTU)	
	Turbidity (NTU)	Turbidity removal (%)	Turbidity (NTU)	Turbidity removal (%)
PNIPAAm	53	93.0	21	77.2
PNIPAAm-AAm4	44	94.2	16	82.6
PNIPAAm-AAm7	183	75.8	-	-
PNIPAAm-AAc11	11	98.5	2	97.8
PNIPAAm-AAc18	6	99.2	-	-
PNIPAAm-AAm-AAc17	46	94.0	3	96.7

Table 3. Turbidity removal from wastewater by different polymers at 1 mg mL<sup>-1</sup> and 40 °C for 30 min

Polymer used	Urban (446 NTU)		Agricultural (184 NTU)	
	Turbidity (NTU)	Turbidity removal (%)	Turbidity (NTU)	Turbidity removal (%)
PNIPAAm	61	86.3	6	96.7
PNIPAAm-AAm4	45	89.9	5	97.3
PNIPAAm-AAc11	19	95.7	2	98.9

Table 3 summarizes the water parameters after the flocculation using responsive polymers. Data are reported having an estimated error between 5 and 7%. The Percentages of turbidity removal are higher than 85%. Copolymers improve slightly the flocculation efficiency as compared with PNIPAAm, which shows that the incorporated comonomers play an important role in the polymer-solids interaction, as explained above. The performance in turbidity elimination is better in agricultural wastewater because the PNIPAAm aggregation is favored by the high salt concentration (Du *et al.*, 2010). Results of conductivity were consistent with the data obtained using river water. As example, the conductivity of urban wastewater increases from 1315 to 1821  $\mu\text{s cm}^{-1}$  after the treatment with PNIPAAm, and remains close to 1300  $\mu\text{s cm}^{-1}$  when PNIPAAm-AAm4 is the flocculant. PNIPAAm-AAm4 exhibits a different interaction with the contaminants, as explained before.

## Conclusions

Responsive polymers based on NIPAAm, NIPAAm and AAm, and NIPAAm and AAc were obtained by free-radical aqueous polymerization at room temperature. Polymers LCST increases with increasing comonomer content. Copolymers exhibit lower LCST in water at pH 4 as compared with deionized water (pH~7), which is driven by the presence of ionizable groups. These polymers are efficient in removing solids from high-turbidity river water and wastewater. The effective flocculation temperature was 40 °C. Flocculation using statistical copolymers, with low comonomer content, is faster than with PNIPAAm. Turbidity elimination is enhanced with increasing the polymer dosage in the range from 0.1 to 2 mg mL<sup>-1</sup>. PNIPAAm-AAm4 is efficient in the removal of dispersed solids and adsorbed ions. Turbidity removal higher than 85% can be reached when responsive flocculants are used for the solid-liquid separation in river water and wastewater (urban and agricultural). The best performance in turbidity elimination was

observed in systems using PNIPAAm-AAc11 as flocculant. The synthesized polymers can be used as efficient flocculants in tropical regions where ambient temperature is close to 40 °C during summer, for example the states of Sonora, Sinaloa, and Veracruz in Mexico.

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## Nomenclature

AAC	acrylic acid
AAm	acrylamide
APS	ammonium persulfate
$D_h$	hydrodynamic diameter
DLS	dynamic light scattering
FT-IR	Fourier Transform Infrared Spectroscopy
LCST	Lower Critical Solution Temperature
NIPAAm	N-isopropylacrylamide
NTU	Nephelometric Turbidity Unit
PNIPAAm	Poly(N-isopropylacrylamide)
PNIPAAm-AAm4	Poly(N-isopropylacrylamide-co-acrylamide4%), wt. %
PNIPAAm-AAm7	Poly(N-isopropylacrylamide-co-acrylamide7%), wt. %
PNIPAAm-AAc11	Poly(N-isopropylacrylamide-co-acrylic acid <sub>11</sub> %), wt. %
PNIPAAm-AAc18	Poly(N-isopropylacrylamide-co-acrylic acid <sub>18</sub> %), wt. %
PNIPAAm-AAm-AAc17	poly[N-isopropylacrylamide-co-(acrylamide-co-acrylic acid) <sub>17</sub> %], wt. %
TGA	Thermogravimetric Analysis
TEMED	N,N,N',N'-Tetramethylethylenediamine

TR (%)	Turbidity Removal (%)
$T_0$	Turbidity of Raw Water, NTU
$T_f$	Turbidity of Treated Water, NTU

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