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Synthesis of Novel Polyacrylamide with 4-Arm and Flocculation Behaviour in Treating Wastewater

CUIQIN LI[1], WEIWEI KANG[1], WEIGUANG SHI[1], HONGZHI SHANG[2] and JUN WANG[1,*]

[1]Provincial Key Laboratory of Oil and Gas Chemical Technology, College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, Heilongjiang Province, P.R. China
[2]Institute of Oil Production Engineering, Daqing Oilfield Company, Daqing 163458, Heilongjian Province, P.R. China

*Corresponding author: Tel./Fax: +86 459 6504224; E-mail: wangjun1965@yeah.net

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A novel non-ionic star polyacrylamide was prepared using ceric ammonium nitrate and pentaerythritol as redox initiation system at 47 °C in aqueous medium. The non-ionic star polyacrylamide has been characterized by FT-IR spectroscopy, ^{1}H NMR spectroscopy, gel permeation chromatography (GPC), thermal analysis (DTG) and intrinsic viscosity measurement. The weight-average molecular weight of the star polyacrylamide with 4-arm was 4.67×10^6 and the star polyacrylamide has better heat-resistant performance than linear polyacrylimde. The star polyacrylamide was applied as flocculation systems. The results indicated that the dual-component system was superior to the single one. In conjunction with an inorganic polymeric aluminum (PA), effective flocculation was achieved by the star polyacrylamide. Meanwhile, the amount of star polyarylamide required was significantly lowered, compared with the single system of star polyacrylamide. Temperature, shear and pH effects were investigated to identify optimum application conditions for the flocculation.

Keywords: Star polyacrylamide, Flocculation, Organic polymeric flocculants, Wastewater.

INTRODUCTION

With the rapid development of industrial technology and the continual expansion in the production scale, large amounts of untreated effluent have been drained into rivers directly which has made more and more water polluted and lead to a series of social, economic and environmental problems[1]. Flocculation phenomena occur commonly in those processes, such as the removal of oils, heavy metals, ink and other contaminants from wastewater. Flocculation is often brought by the addition of small amounts of polymer flocculants. The polymers are chosen depending on the nature of the particles and the pH of the suspension. Various flocculants have been developed, such as polymeric aluminum, polyacrylic acid, polyacrylamide and their derivatives, in order to achieve desirable flocculation efficiency[2,3]. Compared with the organic flocculants, inorganic flocculants, such as salts of multivalent metals like aluminum or iron have several disadvantages such as greater dosage, larger volume of sludge and pH sensitivity[4,5]. Among the organic polymer flocculants, polyacrylamide and its derivatives are the most common and extensively used flocculants for kaolin in aqueous media. This is mainly because amides of polyacrylamide can form hydrogen bonds with much substance[6].

High molecular weight polyacrylamide bridge among adsorbed particles, then dozens of particles linked together as a floc and sink accelerated, which makes polyacrylamide an ideal flocculant. However, the flocculation ability of the linear polyacrylamide to form bridges is deteriorated, if the loops or tails of polymer chains are not sufficiently long. With the development of star polymer, a kind of polymer with more compact steric structure, it becomes possible to form a much more firm "active" bridging between particles[7,8]. Meanwhile, the solution viscosities of star polymers are strongly influenced by arm molecular weight rather than the entire molecular weight of the star polymers. Based on these properties of star polymers, star polyacrylamides with arms were developed and were applied as flocculants in treating wastewater[9]. Moreover, the flocculation of organic polymeric flocculant is critically dependent on many physicochemical factors, including the particle size and distribution, the solid concentration, the pH and the ionic strength of the suspending medium, the molecular weight and charge density of the flocculants and the adsorption density and conformation of the adsorbed flocculants[10]. Researches were found that the flocculation mechanism of high molecular weight polyacrylamide is closely related to its structure[11]. As star flocculants have more extended conformation, it's possible for them to obtain flocculation effect which linear polymers don't have.

In this paper, a novel star non-ionic polyacrylamide was synthesized using ceric ammonium nitrate and multi-hydroxyl reducer (pentaerythritol) as redox initiator system to induce the radical polymerization of acrylamide. The performance of the star polyacrylamide as flocculants was evaluated. Star polyacrylamide with different molecular weight were used in both single and dual-component flocculation systerms. Temperature, shear and pH effects were probed to determine the optimum conditions for the effective flocculation.

EXPERIMENTAL

Acrylamide, pentaerythritol, hydroquinone, sodium hydroxide, acetone and ceric ammonium nitrate were analytical reagents purchased from Tianjin Cherme Chemical Reagent Development Center (China). Polymeric aluminum (PA) were provided by Beijing Yili Fine Chemicals (China). One kind of linear polyacrylamides (PAM) with the weight-average molecular weight of 5×10^6 was obtained from Daqing Refining and Chemical Company (China). Wastewater was provided by Daqing Oil Field (China).

Synthesis of star polyacrylamide: Pentraerythritol (0.0208 g, 0.153 mmol) was dissolved in 100 mL of distilled water with constant stirring and bubbling of a slow stream of nitrogen for about 0.5 h and desired quantity of acrylamide was dissolved in 50 mL of distilled water and added drop by drop to pentraerythritol solution. Then oxygen free nitrogen gas was purged through the solution mixture for 0.5 h. At the stage, ceric ammonium nitrate solution (10 mL) of desired concentration was added and accordingly nitrogen gas purging was continued for another 15 min. The reaction lasted for 24 h at 45 °C, after which it was terminated by adding saturated solution of hydroquinone. The star polyacrylamide gels formed was dissolved in distilled water and was extracted with excess of acetone to remove acrylamide. The graft copolymers were treated with a mixture of N,N-dimethylformamide and acetic acid (1:1 by volume) to remove the homopolymers. The star polyacrylamide was dried in a vacuum oven to constant weight at 60 °C (**Scheme-I**).

The sample of star polyacrylamides as KBr pellets were subjected to IR spectral analysis by infrared spectrophotometry (VECTOR22, Bruker, Germany). ^{1}H NMR was recorded on a Varian NOVA 400 MHz NMR spectrometer using the solvent (D_2O) signal as an internal standard.

Gel permeation chromatography: Weight-average molecular weight of the star polyacrylamide was recorded on a Waters 515-2414 Gel permeation chromatography using the phenylethylene as standard sample. The test conditions were as following: Carrier solvent was chloroform at 25 °C, the flow rate of the mobile phase was about 1 mL/min.

Intrinsic viscosity: The intrinsic viscosity $[\eta]$ of star polyacrylamides in water was measured by viscometry. The measurements were carried out using an Ubbelohde viscometer at 30 ± 0.05 °C. The flux-times were recorded with an accuracy of ± 0.05s. Extrapolation from data obtained for five concentrations of solutions was used to evaluate $[\eta]$ from the Huggins equation, $\eta_{sp}/c = [\eta] + k_h[\eta]^2c$.

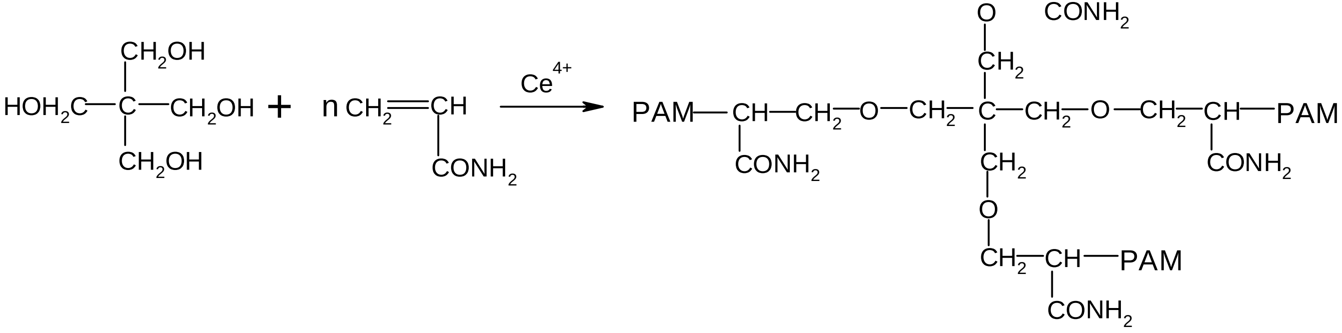
Flocculation tests: The wastewater was put into a breaker and the flocculant was added in an amount concentration aqueous solution. Immediately after the addition of the flocculant, the suspension was stirred at a fast speed of 200 rpm for 10 min. After the floc was settled down for 2 h, the transmittancy of the supernatant liquid was measured with spectrophotometer 722 (λ_{max} = 400 nm, 1 cm colorimetric ware).

Dewatering tests: Polymer solution of 1 g/L was added in a 500 mL cylinder with wastewater. They were mixed by moving a perforated plunger up and down eight times to ensure the suspension was well dispersed by visual inspection. The settling rate of flocculated suspension was determined by recording the time taken for the 'mud-line' to pass between the 450 and 350 mL marks[12]. After the suspension was settled down for 24 h, the supernatant liquid was carefully sucked out of the cylinder. Surface and free moisture in flocs was removed by TGL-16C centrifuge at the speed of 4000 rpm for 0.5 h. Then the weight of the slurry was recorded. The result was the average value of three repeated test.

RESULTS AND DISCUSSION

Synthesis of star polyacrylamide: Star polyacrylamide was synthesized by conventional method using cetic ammonium nitrate as a free radical initiator in an inert atmosphere of nitrogen. The effects of the monomer and the free radical initiator concentration on the properties of the star polyacrylamide are shown in Figs. 1 and 2. The optimized properties were determined by its higher intrinsic viscosity by varying the monomer and initiator concentration.

With increase in concentration of monomer, intrinsic viscosity increased continuously and achieved the maximum.



Scheme-I: Conceptual scheme for the synthesis of star polyacrylamide

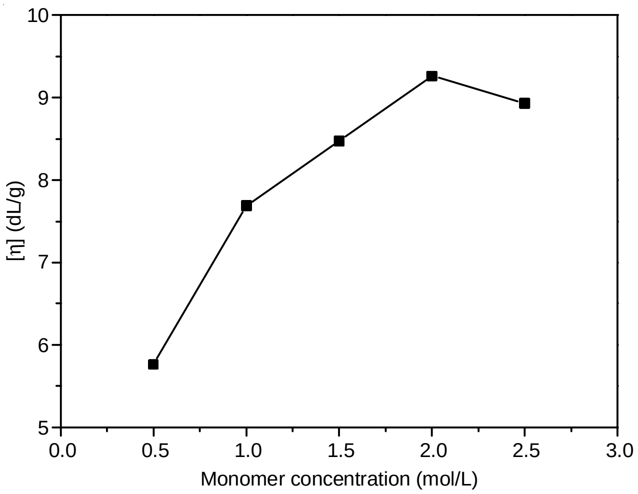


Fig. 1. Effect of monomer concentration on the intrinstic viscosity

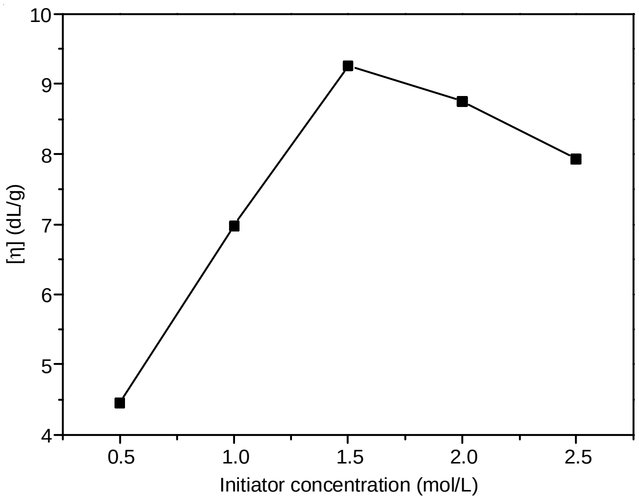


Fig. 2. Effect of initiator concentration on the intrinstic viscosity

When the concentration of monomer was 2 mol/L, the intrinsic viscosity decreased. This behaviour could be explained by the fact that an increase in monomer concentration led to the accumulation of monomer molecules in close proximity to the pentaerythritol molecules. The decrease in the intrinsic viscosity after optimization could be accounted that once the graft polymer radical had formed, the excess monomer would shield the star polymer, which might cause to decrease the rate of polymerization. In addition to this, the completing homopolymer formation reaction became significant with excess monomer concentration and might lead to depletion of viscosity. When the initiator concentration was lower, the polyacrylamide chain was shorter and the grafting rate was smaller. With increase in initiator concentration, the polyacrylamide chain grafted to the pentaerythritol molecules was longer and this leads to higher intrinsic viscosity. When the initiator concentration was more than 1.5 mol/L, the intrinsic viscosity of star polyacrylamide decreased. This accorded with the common rule of polymerization. When the ratio of the molar concentration of monomer and initiator was nearly 1:1, the intrinsic viscosity achieved the maximum.

FT-IR: The IR spectra (Fig. 3) of star polyacrylamide indicated that the star polyacrylamide were fully substituted as the strong alcoholic hydroxyl peak at 3630 cm^{-1} had disappeared and the ether bond (-C-O-C-) asymmetric vibration and symmetric stretching vibration peak had appeared at 1170, 1140 and 969 cm^{-1}, respectively. The absorption peak at 1730 cm^{-1} is due to the C=O stretching vibration.

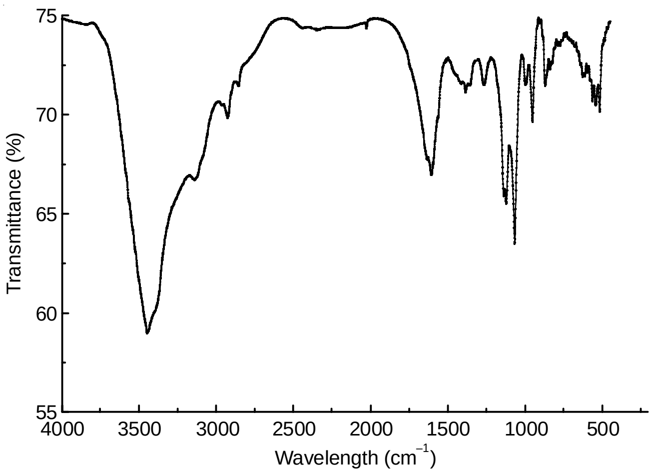


Fig. 3. Infrared spectra of star polyacrylamide

^{1}H NMR: It is obvious from the ^{1}H NMR spectra (Fig. 4) of the star polyacrylamide that had four distinct peaks. The absorption peak at $\delta = 3.45$ ppm was for the hydrogen proton of $-CH_2-O-C-C-CON-$ group. The absorption peaks at $\delta = 2.18$ ppm and 1.57 ppm were for α and β hydrogen proton of $-C-O-CH_2-CH-CON-$ group respectively. The absorption peak of the hydrogen proton of -C-OH had disappeared.

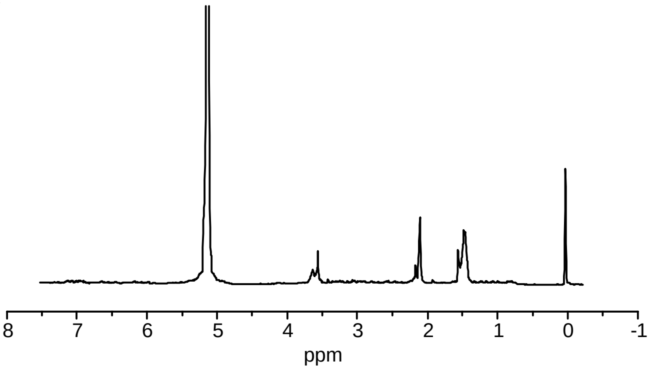


Fig. 4. ^{1}H NMR spetra of the star polyacrylamide (solvent: D_2O)

Thermal analysis of star polyacrylamide: The thermal stability of the star polyacrylamide was investigated by the thermal gravimetric analysis (TGA). TGA is the most favored technique for rapid evaluation in the thermal stability and degradation behaviours of various polymers. As shown in Fig. 5, the TGA diagram of the star polyacrylamide shows four steps for the weight loss. The star polyacrylamide was non-volatile and stable thermally under 200 °C. The star began to degrade in the range of 200-400 °C, corresponding to the degradation of $-CONH_2$ branched of polymer. The second one occurs in the range of 400-443 °C, which may attribute to the thermal decomposition of the polyacrylamides branched of polymer. When the temperature exceeds 520 °C, the thermal gravimetric curve goes to mild and is almost unchanged.

Gel permeation chromatography chromatograms of star polyacrylamide: As logically expected, star polyacrylamide has high molecular weight and higher the molecular

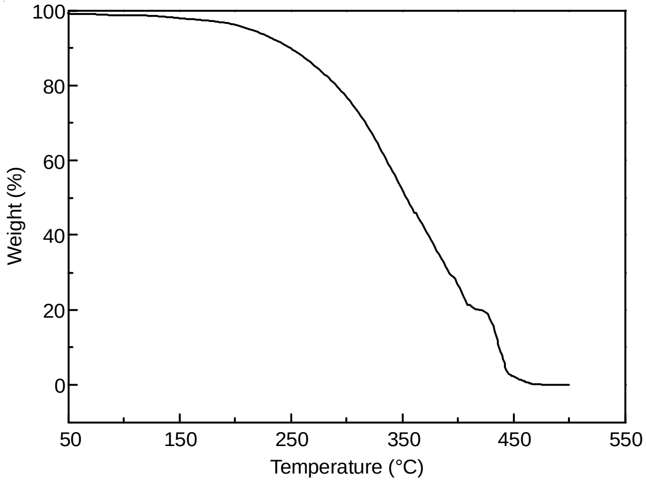


Fig. 5. TG curves of the star polyacrylamide

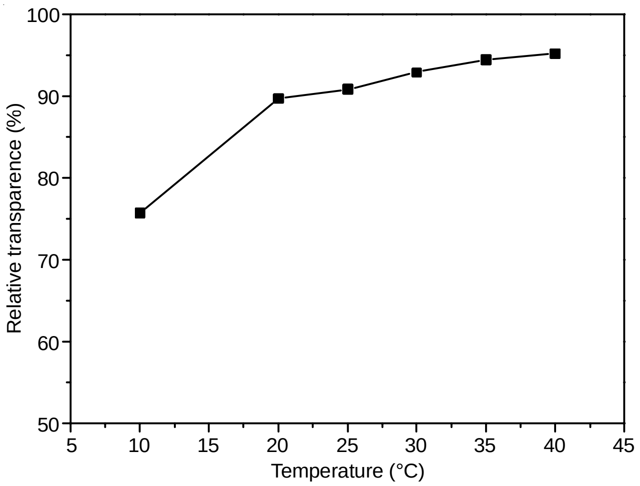


Fig. 6. Influence of agitation temperature

weight is, the viscosity will be higher. The desired correlation between the viscosity and the average molecular weight is shown in Table-1. The average molecular weight increased with the increase of the monomer concentration. When the monomer concentration was 2 mol/L, the average molecular weight was largest and the largest average molecular weight was 4.67 × 10^6.

Effect on relative transmittance

Effect of test parameters: Agitation temperature has been evaluated as a factor in the flocculation process. The wastewater has to do with seasonal variation and agitation temperature of effluents may be rather different in summer than in winter. So agitation temperature is important in the treatment plant with different conditions. The relative transmittance of the wastewater was over 90 % above 25 °C and the relative transmittance increased slightly with the agitation temperature increasing (Fig. 6). This probably was because the polymer can be dissolved at high temperature, so that the long polymer molecular chains could adsorbed on the surface of the clay particles to form a net structure. This accelerated the flocculation effect and improved the relative transmittance of wastewater treated by the novel polyacrylamides. But the higher agitation temperature could cause higher treatment cost, so 30 °C was selected as optimum one.

The pH solution is an important factor in the flocculation process and the use of flocculants at its optimum pH displayed maximum removal of pollutant. To optimize the pH of the flocculation process, a known amount of star polyacrylamide solution was added to an amount of wastewater at different pH values adjusted with concentrated H_2SO_4 and NaOH. It could be noticed that the relative transmittance increased with pH values of the flocculation process. The flocculation was more effective and the relative transmittance was above 90 % at a pH range between 7 and 10 (Fig. 7).

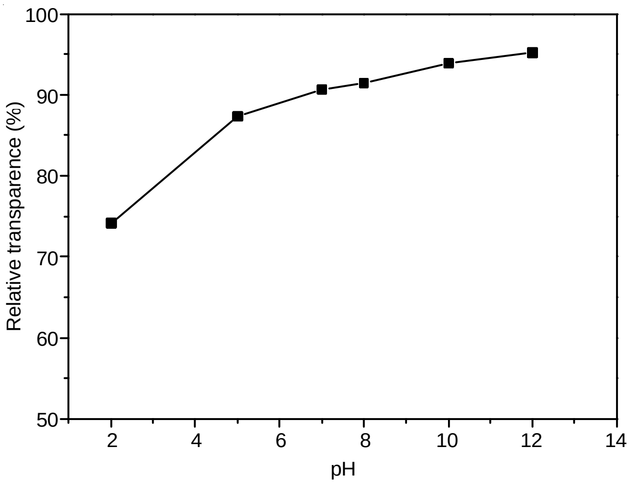


Fig. 7. Influence of pH

Generally, agitation time is not so important for the flocculation. However, the polymer molecular chains can not extent at a shorter agitation time and the long molecular chains can not be adsorbed on the clay particles. Fig. 8 showed the flocculation of the wastewater by the synthetic flocculant at different agitation time. The relative transmittance of the wastewater treated by the star polyacrylamide was above 90 % at 20 min of agitation time. 0.5 h was selected as an average value in order to complete the test procedure that would be used in the whole investigation.

Agitation speed was varied between 10 and 60 rpm for a fixed period of 10 min. The effect of the agitation speed on the flocculation was shown in Fig. 9. As it can be appreciated, no high differences are found affecting this parameter. The relative transmittance reached the maximum value at agitation speed of 40 rpm. This is because higher agitation speed could accelerate polymer chains extending faster in flocculation process and this

TABLE-1
AVERAGE MOLECULAR WEIGHT UNDER THE DIFFERENT MONOMER CONCENTRATION

Star polyacrylamide	Monomer concentration (mol/L)	Intrinsic viscosity (dL/g)	Weight average molecular
Star-PAM(I)	0.5	5.76	2.94 × 10^6
Star-PAM(II)	1.0	7.69	8.17 × 10^5
Star-PAM(III)	1.5	8.48	1.89 × 10^6
Star-PAM(IV)	2.0	9.26	4.67 × 10^6

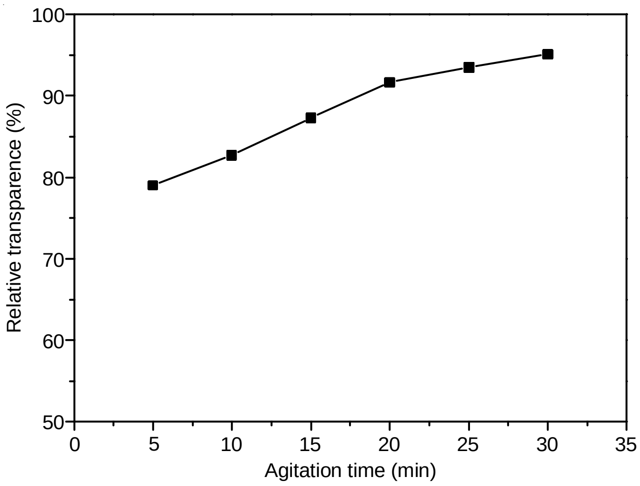


Fig. 8. Influence of agitation time

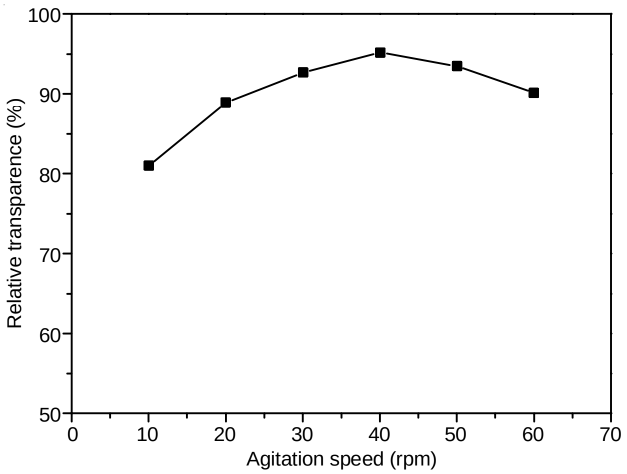


Fig. 9. Influence of agitation speed

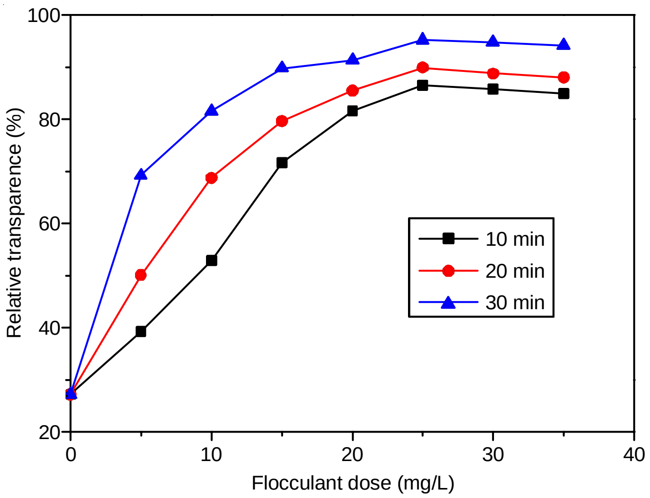


Fig. 10. Effect of the flocculant dosage on the relative transmittance of the wastewater

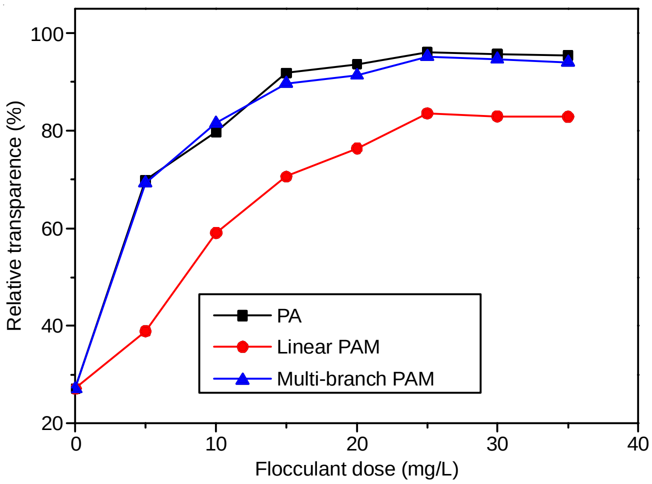


Fig. 11. Effect of the flocculant dosage on the relative transmittance of the wastewater under sedimentation time of 0.5 h

improved the flocculation efficiency by adsorption bridging. However, the agitation speed was too high to induce the polymer molecular chains to break and the flocculation lowered. Agitation speed was important from the point of view of helping flocs to be formed so 40 rpm value was selected as optimum one.

Fig. 10 showed the flocculation of the wastewater by the synthetic star polyacrylamide flocculant for three sedimentation time (10, 20 and 30 min). With the increase of the dosage and the sedimentation time, the relative transmittance of the wastewater increased. The optimum relative transmittance at 0.5 h sedimentation time was achieved with 25 mg/L. At the optimum dose, the relative transmittance was 95.2 %.

Effect of flocculant dosage: To evaluate the efficiency of the novel synthetic polyacrylamide, it was compared with the commercial organic flocculation linear-polycarylamide and the inorganic flocculation polymeric aluminum. The performances of the samples in the relative transmittance of the synthetic wastewater were studied under the above optimum conditions. The results were listed in Fig. 11. With the increase of the dosage, those three samples had similar trend on flocculation. The relative transmittance increased rapidly first with increasing flocculants concentration and then reached the maximum value at a dosage of 25 mg/L. Increasing the flocculants concentration beyond this value does not improve the relative transmittance any further and instead it leads to a decrease in relative transmittance. The flocculation of the novel polyacrylamides was superior to linear-polyacrylamides. This might be attributed to the many long molecular chains of the synthetic polyacrylamides, which made it easier for them to touch each other and get incorporated to form a net structure. This behaviour made it easier for flocculant to bridge more particles. However, the principle of the inorganic flocculant polymeric aluminum was using its cationic charge to neutralize part of the anionic surface charge of clay and provide association points for bridge. Since the inorganic flocculant polymeric aluminum has more cationic charge to provide more effective points for bridging flocculation, the flocculation was superior to the linear-polyacrylamides and the synthetic.

In order to achieve desirable flocculation efficiency, the novel organic polyacrylamide combined with the inorganic polymeric aluminum has higher flocculation behaviour. Fig. 12 shows the flocculation behaviour of the wastewater by the novel polyacrylamides dosage ranging from 1 to 20 mg/L for 0.5 h and sedimentation time at 20 mg/L coagulant polymeric aluminum. The results indicated that the relative transmittance increased rapidly with increasing the flocculant dosage and reached the maximum value of 99.3 % at a dosage of 20 mg/L. But when the dosage of synthetic polyacrylamides was 10 mg/L,

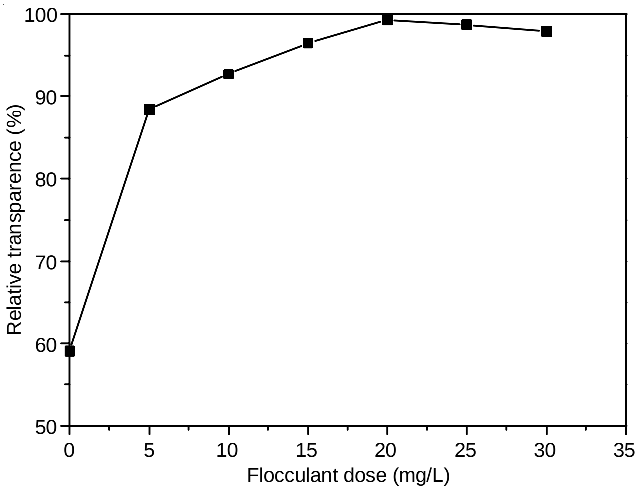


Fig. 12. Effect of novel polyacrylamides on the transparence of wastewater with the dosage of 20 mg/L polymeric aluminum

the relative transmittance of synthetic wastewater was above 90 %. The flocculation of composite flocculant was superior to that obtained with either of the two separate flocculants. One could reasonably assume that the flocculation efficiency of the synthetic wastewater by composite flocculant occurred not only by charge neutralization but also by adsorption bridging as well at the low concentration of novel polyacrylamides. When some surface charges of clay were partially neutralized on adsorption of counter-ions of polymeric aluminum, the repulsive force and double layer gap between the particles were considerably reduced. The bridging mechanism became more significant compared with charge neutralization as the long chain polymer molecules could span the reduced gap between the particles at high concentration of novel polyacrylamides.

Effect on settling behaviour: The effectiveness of the synthetic wastewater flocculation by the three flocculants measured in terms of settling rate is presented in Fig. 13. The untreated synthetic wastewater exhibits extremely slow settling rate of 0.5 mm/min. The settling rate increased gradually with the increasing synthetic polyacrylamides concentration and reached a value of about 12.6 mm/min at a dosage of 30 mg/L. Increasing the synthetic polyacrylamides concentration beyond this value couldn't improve rapidly settling rate any further. The settling rate of the flocs of the synthetic wastewater treated by the commercial flocculants were lower than the synthetic polyacrylamides under the same condition. This might be attributed to the many long molecular chains of the novel polyacrylamides, which promotes the association among polymer molecules and hydrophobic kaolin particles to form a big flocs.

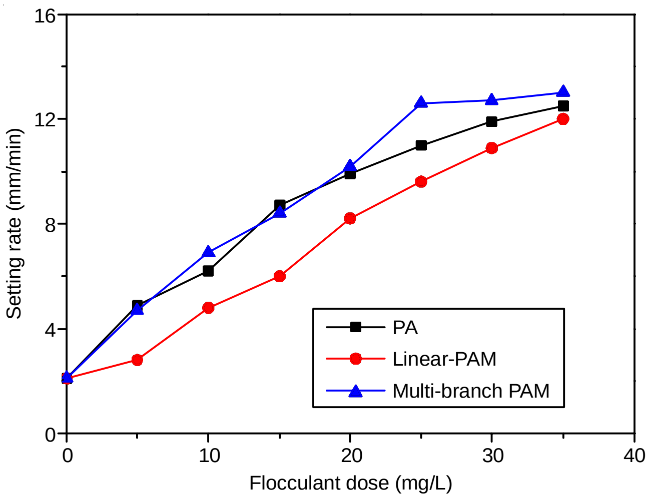


Fig. 13. Effect of flocculant on the settling rate of wastewater

Fig. 14. displayed the settling rate of the wastewater by the synthetic polyacrylamides dosage ranging from 0 to 30 mg/L at the concentration of 20 mg/L the coagulant polymeric aluminum. The settling rate increased first and then decreased with the concentration of the synthetic polyacrylamides increased. The settling rate was 15 mm/min at the concentration of 20 mg/L. The concentration agreed with that of the optimum relative transmittance.

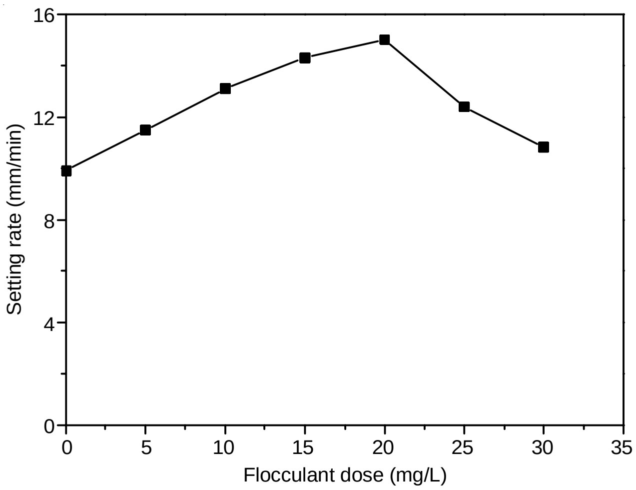


Fig. 14. Effect of star polyacrylamides on the settling rate of wastewater with the dosage of 20 mg/L polymeric aluminum

Conclusion

The novel non-ionic star polyacrylamide was prepared using ceric ammonium nitrate and pentaerythritol as redox initiation system and used to treat the wastewater from oil recovery plant. The flocculation performances and the dewatering efficiencies were evaluated by the relative transmittance and the setting rate of the floc. The synthesis was successful with high graft degree which was confirmed by IR, ^{1}H NMR TGA and gel permeation chromatography. As a novel kind of organic polymer flocculant, the star polyacrylamide showed better flocculation effeciency due to its star chains and high molecular weight and could bridge among adsorbed particles to form big flocs and sink accelerated. Moreover, the star polyacrylamide combined with inorganic flocculant polymeric aluminum had improvement of flocculation properties in wastewater from oil recovery plant. The water treated with the synthetic star polyacrylamide reached the sewage discharge standard. The synthetic polyacrylamide was used to treat wastewater from oil recovery plant as a novel organic polymer flocculatant.

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