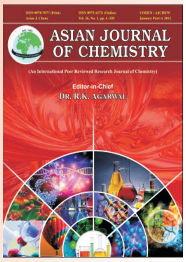
Estd. 1989
Asian Journal of Chemistry; Vol. 26, No. 22 (2014), 7544-7550
ASIAN JOURNAL OF CHEMISTRY
http://dx.doi.org/10.14233/ajchem.2014.16806



Determination of Cationic Degree for Cationic Polyacrylamide and Its Sludge Dewatering Properties

Yongjun Sun[1], Huaili Zheng[1,*], Houkai Teng[2], Qingqing Guan[1], Yili Wang[3], Wei Chen[1], Wei Fan[1] and Yong Liao[1]

[1]Key laboratory of the Three Gorges Reservoir Region's Eco-Environment, State Ministry of Education, Chongqing University, Chongqing 400045, P.R. China
[2]CNOOC Tianjin Chemical Research and Design Institute, Tianjin 300131, P.R. China
[3]College of environmental science and engineering, Beijing Forestry University, Beijing 100083, P.R. China

*Corresponding author: Tel./Fax: +86 23 65120827; E-mail: sunyongjun008@163.com; zhl@cqu.edu.cn

Received: 2 December 2013; *Accepted*: 4 April 2014; *Published online*: 6 November 2014; AJC-16181

P(AM-DAC-BA) was synthesized by ultraviolet initiation with acrylamide (AM), acryloyloxyethyl trimethyl ammonium chloride (DAC) and butyl acrylate (BA) as monomers and P(AM-DAC) was synthesized with acrylamide and acryloyloxyethyl trimethyl ammonium chloride. The polymer was characterized by Fourier transform infrared (FTIR) spectrum. Cationic degree of P(AM-DAC-BA) was determined by colloid titration and the optimum titration condition: the P(AM-DAC-BA) concentration of 1×10^{-5} - 5×10^{-5} g g^{-1}, pH 2-3, titration rate of 0.0653-0.0719 mL s^{-1}, addition of 2-3 drops of toluidine blue as indicator. The sludge dewatering performances of P(AM-DAC-BA) and P(AM-DAC) were also studied and both high solid content and low supernatant turbidity were achieved. The dewatering tests indicated that P(AM-DAC-BA) was better than P(AM-DAC) in sludge dewatering performance.

Keywords: Cationic polyacrylamide, Colloid titration, Cationic degree; Sludge dewatering.

INTRODUCTION

In the past two decades, a large number of municipal wastewater treatment plants were constructed to treat municipal wastewater to control water pollution in China. Activated sludge process was widely used for treating domestic wastewater[1]. But the activated sludge process produced a lot of sludge during the activated sludge process and sludge disposal had been the problem which could not be ignored. Especially requirements of environmental protection in the Three Gorges Reservoir Region had been increasingly demanded. To 2020, 1, 928, 000 m^3 d^{-1} of municipal wastewater were produced in Chongqing city, meanwhile 1542.8 m^3 d^{-1} of sludge volume were produced. However, the excess waste activated sludge from wastewater treatment with 95-99.5 % water was a significant drawback for this technology. Due to the huge production of waste sludge and its potential environmental pollution, the dewatering of sludge was necessary to obtain a dry product enough for further disposal[2].

To enhance the dewaterability of sludge, coagulation-flocculation process of activated sludge with flocculants was a cost-effective method before mechanic dewatering. The formation of large particles of sludge flocs and the properties of sludge settling were significantly improved by adding flocculant[3-5]. Since the surface of the sludge particles with a negative charge, cationic polyacrylamide flocculants were used widely in municipal wastewater treatment plants for sludge dewatering[6-7]. Cationic flocculants have several obvious advantages, such as a high positive charge with charge neutralization ability, good water solubility and a wide pH range for application[8]. With these advantages, cationic polyacrylamide flocculants could significantly improve sludge dewatering performance[9].

But it was necessary to determine cationic degree in the evaluation and application process of cationic polyacrylamide flocculants. So far there were no national standards for determination of cationic degree in China. However, there had several determination methods of cationic degree *i.e.*, elemental analysis method[10], $AgNO_3$ method[11], the streaming potential method[12], infrared spectroscopy method[13], colloid titration method[14], *etc*. These methods were usually expensive with complicated operation. But the colloid titration method was a simple, precise and accurate method thus drawing more and more attention[15].

In this paper, cationic polyacrylamide flocculant P(AM-DAC-BA) was synthesized through copolymerization of acrylamide (AM), acryloyloxyethyl trimethyl ammonium chloride (DAC) and butylacrylate (BA) under ultraviolet radiation by micellar polymerization method[16-17], while P(AM-DAC) was synthesized through copolymerization of acrylamide (AM), acryloyloxyethyl trimethyl ammonium chloride (DAC). Fourier Transform Infrared Spectroscopy (FTIR) was employed to study the structural characteristics. To optimize the measurement condition of cationic degree by colloid titration, the P(AM-DAC-BA) concentration, pH, titration rate and toluidine blue dosage, which may exert impact on the determination results of cationic degree, were investigated. At last, the dewatering abilities of waste activated sludge treated by P(AM-DAC-BA) and P(AM-DAC) were compared with each other. The effects of flocculant dosage, pH and cationic degree on the dewaterability of waste activated sludge were systematically investigated.

EXPERIMENTAL

The acrylamide (AM) (Chongqing Lanjie Tap Water Company, Chongqing, China), butyl acrylate (BA) (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China), acryloyloxyethyltrimethyl ammonium chloride (DAC, 80 % in water) (Guangchuangjing IMP. EXP. Co., Ltd., Shanghai, China), toluidine blue (TB) as indicator (Shanghai blue technology development co., LTD, China), Poly-2-Acrylamide-2-Methylpropare -Sulfate Potasium (PAMPSK) and cetyl pyridine bromide (CPB) (Shanghai Constant treatment material Co., Ltd., Shanghai, China) as the titrant were purchased. All the reagents used in this experiment were without further purification.

Raw sludge was collected from the sludge thickener of Dadukou Drainage Co., Ltd (Chongqing, China). The samples were subsequently stored at 4 °C in the refrigerator and analyzed within 2 days. The characteristics of the sludge are listed in Table-1.

TABLE-1
CHARACTERISTICS OF WASTE SLUDGE

pH	Dry solids content (%)	TSS (%)	Mass density (mL g^{-1})
6.91 ± 0.12	1.40 ± 0.36	55 ± 9	0.89

Preparation of P(AM-DAC-BA) and P(AM-DAC): UV-initiated polymerization technique was used to synthesize P(AM-DAC-BA). P(AM-DAC-BA) was prepared by copolymerizing acrylamide, acryloyloxyethyl trimethyl ammonium chloride and butyl acrylate using V-50 as photo-initiator. First, Pre-determined mass of acrylamide, acryloyloxyethyl trimethyl ammonium chloride and butyl acrylate were added into a quartz reaction vessel. Deionized water was subsequently added to reach a monomer mass ratio of 30 %. Before adding the photo-initiator, pure N_2 was purged into an aqueous solution at room temperature for 15 min to remove oxygen. The reaction vessel was subjected to irradiation with a 500 W high pressure mercury lamp (Tianyuanhuiteng, China) for 80 min at ambient temperature. After irradiation, the copolymers were purified with acetone and ethanol and dried in a vacuum oven at 40 °C. The preparation procedure of P(AM-DAC) was the same as that described above except that no butyl acrylate was added.

FTIR spectra of P(AM-DAC-BA): Fourier Transform Infrared (FTIR) spectrums were recorded using KBr pellets on 550 Series II infrared spectrometer (BRUKER Company, Switzerland) with KBr as the pellet.

Determination of cationic degree

Determination of PAMPSK concentration: Standard solution of PAMPSK, containing 0.1000 g-0.4000 g L^{-1}, was prepared with deionized water. 0.1000 g toluidine blue (TB) 100 mL was dissolved in deionized water to prepare a 0.1 % toluidine blue (TB) solution as an indicator. Standard cation solution (CPB solution) was prepared by adding 0.0300 g CPB into 100 mL deionized water. Titration experiments were run by adding 10 mL CPB solution and 40 mL deionized water into conical flask with 2-3 drops of toluidine blue as indicator. When CPB solution in the conical flask was titrated by PAMPSK standard solution from blue to purple, it was the end point of titration. Meanwhile the blank experiment was done simultaneously[18].

$$c = \frac{10m \times 1000}{100M\,(V - V_0)} = 0.2485 \times \frac{m}{(V - V_0)}$$

where V (mL) and V_0 (mL) are PAMPSK solution titer of an investigated sample and blank one, respectively; *c* (mol L^{-1}) and M (g mol^{-1}) are the concentration of the PAMPSK solution and CPB relative molecular weight of CPB, respectively; *m* (g) is the weight of the CPB used for titration.

Determination of cationic degree: The cationic degree (CD) was calculated by the ratio of weight of cationic monomer to weight of total polymer. All the conversion of P(AM-DAC-BA)s were more than 99 % in the polymerization, so the measured cationic degree was relatively accurate and precise when the result was close to the theoretical cationic degree. Different concentrations of P(AM-DAC-BA) solution were prepared and injected into the conical flask with a pipette with addition of 2 to 3 drops indicator, the flask was titrated on a magnetic stirrer stirring gently, when the solution colour changed from blue to purple, that was the end point, while doing blank tests[19]. the cationic degree (CD) of the P(AM-DAC-BA) was calculated by the following equation:

$$CD(\%) = \frac{cM'(V' - V'_0)}{1000m}$$

where V′ (mL) and V'_0 (mL) are PAMPSK solution titer of an investigated sample and blank one, respectively; c (mol L^{-1}) and (g mol^{-1}) are the concentration of the PAMPSK solution and relative molecular weight of cationic monomer (DAC); m (g) is the weight of the dried sample used for titration.

Sludge dewatering tests: The dewatering ability of the waste sludge was expressed in terms of residual turbidity of supernatant and dry solid content (DS). Dewatering tests for waste sludge were carried out at room temperature. Waste sludge of 500 mL volume was transferred into beakers before known dosage of flocculants were added. The initial pH of sludge was adjusted by adding NaOH (1 mol L^{-1}) or HCl (1 mol L^{-1}). The waste sludge was mixed by rapidly stirring at 120 rpm for 20 s in the presence of the flocculant, followed by a 10 min settling period. For turbidity measurement, the supernatant of the sample was extracted from the beaker at 1 cm below the supernatant surface (Turbidimeter supplied by HACH 2100Q, USA.). The conditioned sludge was poured into a Buchner funnel for filtration under a vacuum pressure of 0.06 MPa for 15 min or until the vacuum cannot be maintained (in < 15 min). Dry solid was determined by the following equation[20]:

$$DS = \frac{W_2}{W_1} \times 100\ \% \qquad (5)$$

where W_1 is the weight of wet filter cake after filtration and W_2 is the weight of filter cake after drying at 105 °C for 24 h.

RESULTS AND DISCUSSION

Principle of determination of cationic degree by colloidal titration: Colloid titration was based on the polyelectrolyte ionized in its aqueous solution with a positive or negative charge and polyelectrolytes with negative charge and positive charge combined between each other with the stoichiometric ratio by neutralization reaction. Polyelectrolyte with positive charge reacted rapidly with polyelectrolytes with negative charge and formatted stable polysalt precipitation. Toluidine blue (TB) as a titration indicator did not react with the cationic polymers and kept blue in tested samples. toluidine blue was very sensitive in discolouration from blue to purple, when PAMPSK dosage excessed equivalence point slightly and combined with toluidine blue.

With the addition of standard solution of PAMPSK, PAMPSK first reacted with the cationic flocculant P(AM-DAC-BA) and reached the equivalence point, slight excess of PAMPSK solution immediately combined with the toluidine blue and made the solution from blue to purple, thereby indicating the end of reaction quickly and accurately[21]. Scheme of colloid titration route for cationic degree of P(AM-DAC-BA) by PAMPSK was shown Fig. 1.

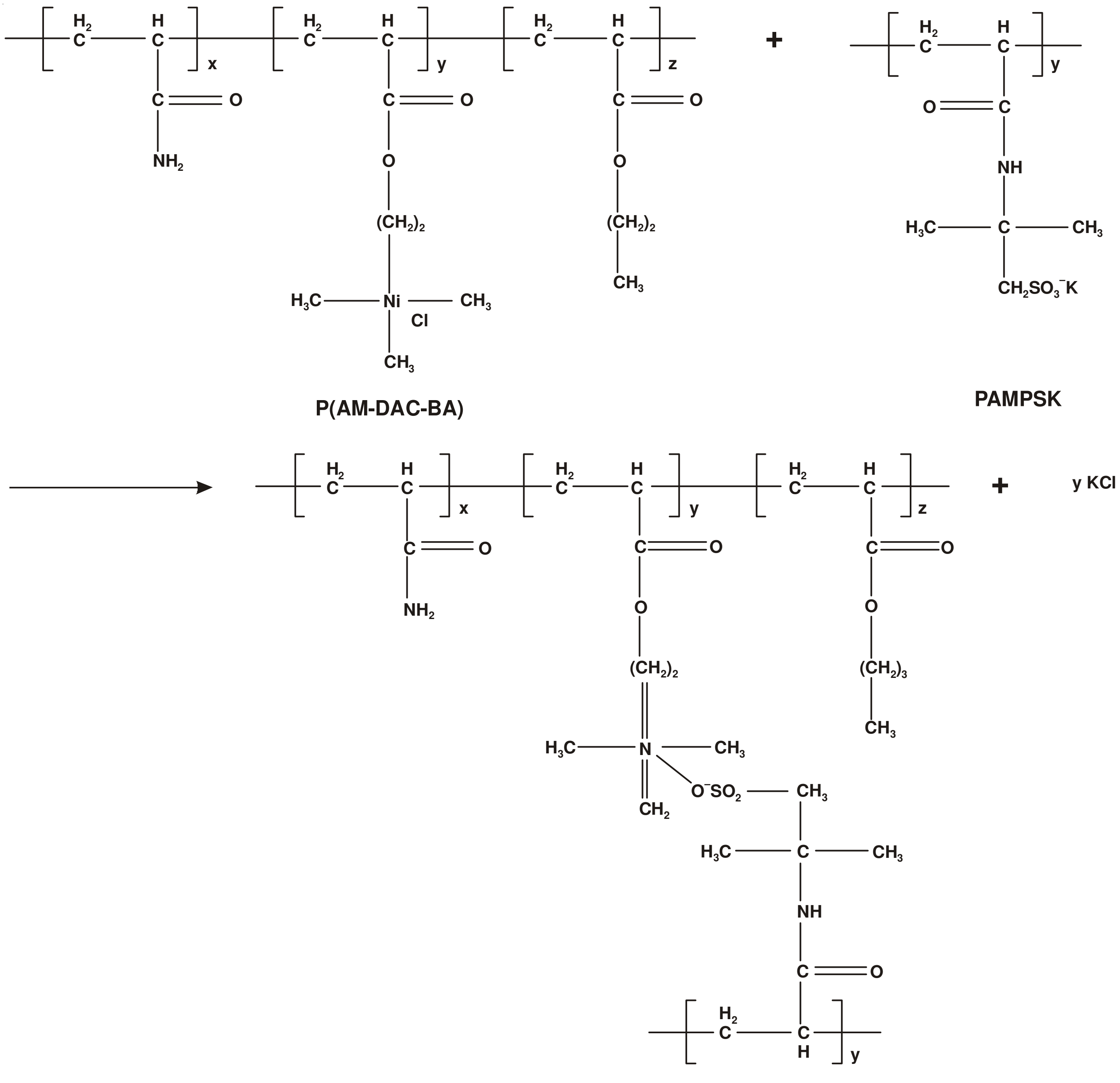


Fig. 1. Colloid titration route for cationic degree of P(AM-DAC-BA) by PAMPSK

FTIR spectrum of P(AM-DAC-BA) and P(AM-DAC): Fig. 2 shows the FTIR spectrum of P(AM-DAC-BA). The absorption band observed at 3423 and 1167 cm^{-1} originated from strong stretching vibration of an amino group and a carbonyl group of amide in the acrylamide chain, respectively. Bending vibration absorption peaks of $-CH_2-N^+(CH_3)_3$ group of acryloyloxyethyl trimethyl ammonium chloride appeared at 1452 cm^{-1}. The stretching vibration absorption peak at 1654 cm^{-1} was attributed to the -C=O group in the acrylamide and butyl acrylate. The stretching vibration peak at 953 cm^{-1} represented the -CO-O group in the butyl acrylate unit. Comparing with that of Fig. 3, the peaks in Fig. 2 are similar to those in Fig. 3, except for a small chemical shift. The results of the FTIR spectrum demonstrated that P(AM-DAC-BA) and P(AM-DAC) were successfully synthesized[22].

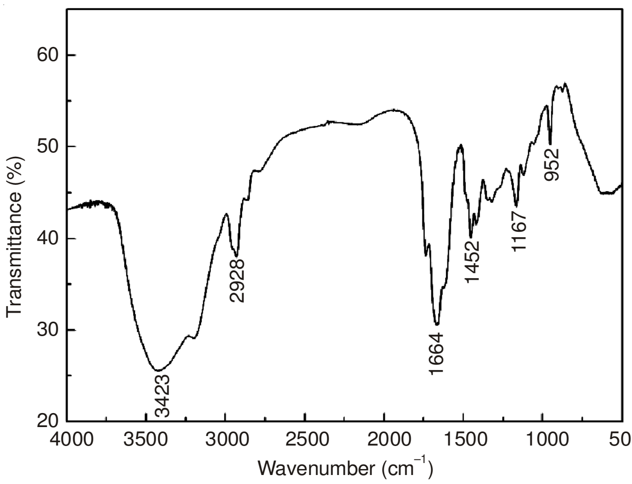


Fig. 2. FTIR spectrum of P(AM-DAC-BA)

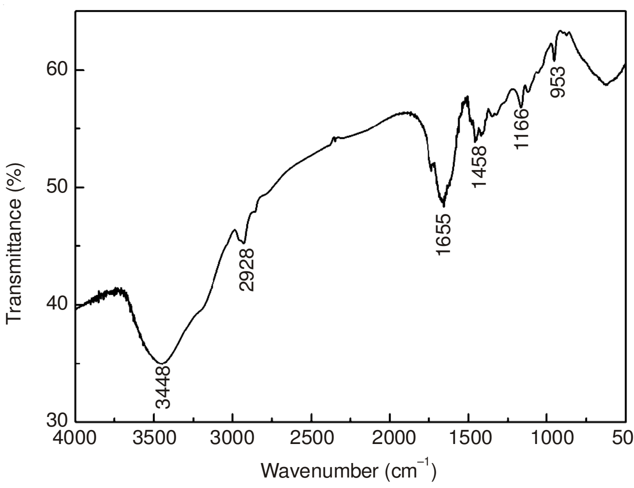


Fig. 3. FTIR spectrum of P(AM-DAC)

Determination of cationic degree of P(AM-DAC-BA)

Effect of P(AM-DAC-BA) concentration on determination of cationic degree: Fig. 4 shows the influence of P(AM-DAC-BA) concentrations on the cationic degree. In order to investigate the titratable range of P(AM-DAC-BA) concentration, different concentrations of P(AM-DAC-BA) were titrated by PAMPSK standard solution. As shown in Fig. 4, when the P(AM-DAC-BA) concentration was higher than 0.5×10^{-4} g g^{-1}, the calculated value of the cationic degree began to decrease. When the concentration was lower than 0.5×10^{-4} g g^{-1}, the titration value was close to the theoretical cationic degree, but when the concentration higher than 0.5×10^{-4} g g^{-1} would produce more large error[22]. P(AM-DAC-BA) with high concentration would increase the precipitation of the reaction and flocs produced in the solution by flocculation effect, leading to titration system turbid and toluidine blue adsorption by flocs[19]. Thus discolouration of toluidine blue was not sharp and sensitive at the end point of the titration and the end point of titration was not easy to judge. Therefore, the P(AM-DAC-BA) concentration of 1×10^{-5} - 5×10^{-5} g g^{-1} was appropriate for determination of cationic degree by colloidal titration.

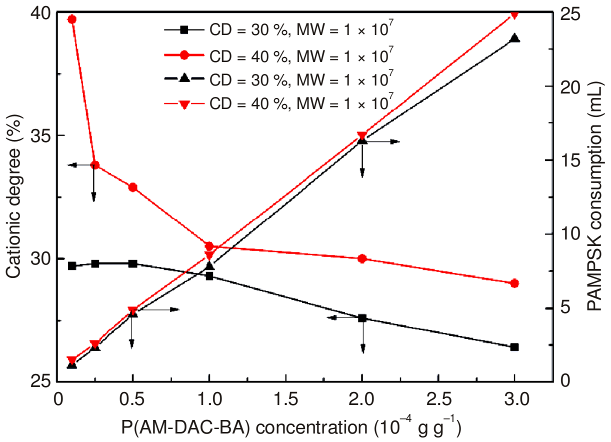


Fig. 4. Effects of P(AM-DAC-BA) concentrations on determination of cationic degree

Effect of pH on determination of cationic degree: Fig. 5 shows the effects of pH on determination of cationic degree, (a) different cationic degree in theory and (b) different molecular weight (MW). 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH was used to adjust the pH of the P(AM-DAC-BA) solution before titration. As shown in Fig. 5, the volume of PAMPSK consumption and the measured cationic degree were both stable in pH range 3 to 5 and 11 to 12. However, the measured values of the cationic degree were rather changeable in the pH range 5 to 11. The possible reason for the instability of the measured cationic degree was mainly attributed to the insufficient dissociation. In the range of pH 3-5, P(AM-DAC-BA) chain was extended into solution sufficiently and therefore the P(AM-DAC-BA) was favored to the dissociation in acidic condition. In this study, the optimum pH for determination of the cationic degree of the P(AM-DAC-BA) by colloid titration[13] was 3 to 5.

Effect of titration rate on determination of cationic degree: Because of the complex structure of P(AM-DAC-BA), titration rate had a greater impact on the determination of cationic degree. Table-2 shows the relationship between the cationic degree and the titration rate. When the titration was faster, the measured cationic degree was larger than the theoretical cationic degree. If the titration rate was decreased, the measured cationic degree was close to the theoretical

TABLE-2
EFFECT OF TITRATION RATE ON DETERMINATION OF CATIONIC DEGREE

Samples	Cationic degree in theory	Titration rate (mL s^{-1})					
		0.1075	0.0719	0.0653	0.0546	0.0343	0.0224
1#	20	22.1	19.4	19.3	18.1	18.0	18.2
2#	30	30.6	29.7	29.12	28.2	25.5	27.9

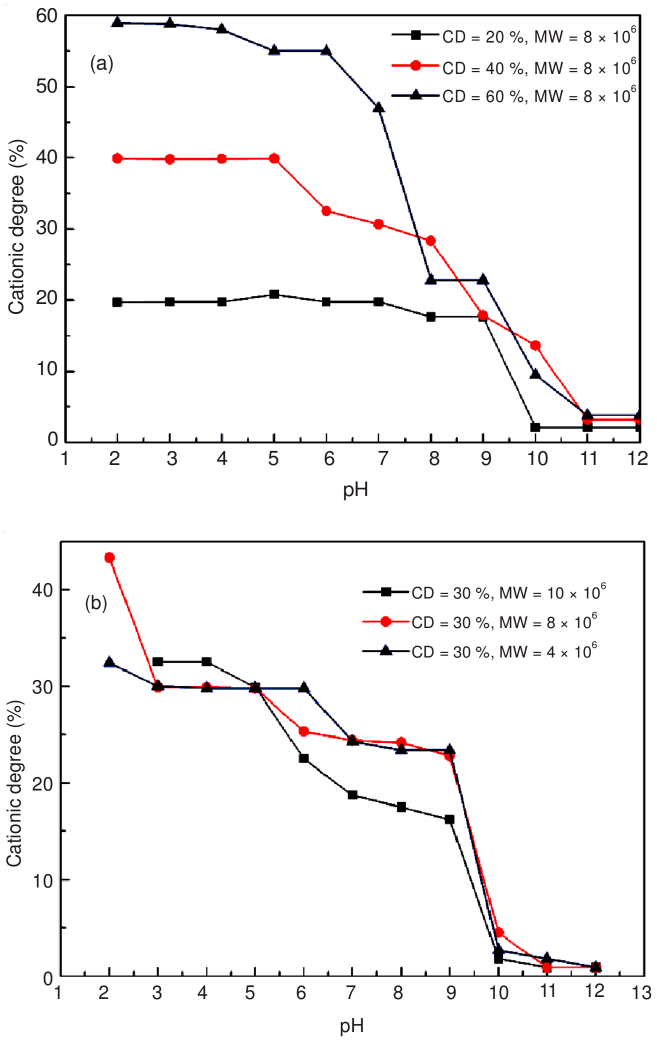


Fig. 5. Effects of pH on determination of cationic degree, (a) different cationic degree in theory, (b) different molecular weight (MW)

cationic degree but further reducing the titration rate would decrease the measured value. Due to the complex structure, high viscosity and dispersion properties of P(AM-DAC-BA) and P(AM-DAC-BA) of complex aggregation state could make polymer chain curled thus affecting the accuracy of titration results[14,19]. Faster titrate rate could cause the unobvious discolouration and a larger measured cationic degree by the increased consumption of PAMPSK. Therefore, the titration rate of 0.0546 0.0719 mL s^{-1} was adopted as the optimal condition.

Effect of residual surfactant on determination of cationic degree: P(AM-DAC-BA) was synthesized by micellar polymerization method using cationic surfactant CTAB as additives forming the micelle. If purification process of P(AM-DAC-BA) was incomplete and insufficient, the residual surfactant would have a great influence on determination of cationic degree. Table-3 illustrates effect of residual surfactant on determination of cationic degree. Since the CTAB was added in the polymerization process to form the micelle to dissolve hydrophobic monomer butyl acrylate, CTAB was not involved in bonding or reactions. CTAB was cationic and had a ability to neutralize and react with the anionic PAMPSK, making volume consumption of PAMPSK larger and the measured cationic degree greater. After purification, the measured cationic degree was close to the theoretical cationic degree, which was more accurate and precise.

Effect of dosage of toluidine blue on determination of cationic degree: In order to make the discolouration sensitive and easy to judge at the end point of titration process, an appropriate dosage of indicator toluidine blue was required. Too much dosage of indicator toluidine blue would cause discolouration delayed; otherwise the discolouration of the solution was not obvious. Whether increasing or decreasing the dosage of indicator toluidine blue would change PAMPSK consumption affecting the accuracy of the titration results. The indicator should be added at an amount in an appropriate range and usually 2-3 drops of indicator toluidine blue[19]. P(AM-DAC-BA) was titrated by PAMPSK indicating the end of reaction in acidic condition. During the titration, toluidine blue had no effect on P(AM-DAC-BA) in acidic condition and the solution was blue. When the end point was obtained, P(AM-DAC-BA) reacted with PAMPSK completely, meanwhile excess PAMPSK functioned with toluidine blue making toluidine blue become purple, which was the end point of titration. Therefore, 2-3 drops of toluidine blue was adopted as the optimum addition of indicator.

Sludge dewatering tests

Effect of flocculant dosage on dewatering performance: As shown in Fig. 6, the maximum dry solid content 27.9 % and minimum supernatant turbidity 34.8 NTU were

TABLE-3
EFFECT OF RESIDUAL SURFACTANT ON DETERMINATION OF CATIONIC DEGREE

Sample number	Theoretical cationic degree	Measured cationic degree before purification	Measured cationic degree after purification
1	10	14.0	9.2
2	20	24.6	18.5
3	30	36.1	29.8
4	40	54.6	36.6

obtained by P(AM-DAC-BA) at dosage of 40 mg L^{-1}, while maximum dry solid content 25.9 % and minimum supernatant turbidity 56.1NTU was obtained by P(AM-DAC) at dosage of 120 mg L^{-1}. With the dosage increased, dry solid contents increased firstly and then decreased slightly. The supernatant turbidity decreased rapidly and then increased slowly as the dosage increased. High cake solid content and low supernatant turbidity were obtained at the P(AM-DAC-BA) dosage of 40 mg L^{-1}, but high solid content and low turbidity of the supernatant were obtained by P(AM-DAC) at dosage of 120 and 40 mg L^{-1}, respectively. When the flocculant dosage was low, sludge flocs formed were small and sludge-liquid separation was ineffective, resulting in low dry solid content and high supernatant turbidity. With excess dosage, the dewatering efficiency decreased. The main reason for the decrease was overdosing effect of the flocculant and restabilization of charged sludge particles. Meanwhile overdosage of flocculant would increase the residual flocculant in the liquid phase in sludge sample and liquid viscosity and specific resistance of sludge increased, resulting in increasing the difficulty of filtering and low dry solid[2,17]. Therefore, 40 and 120 mg L^{-1} was adopted as the optimum dosage of P(AM-DAC-BA) and P(AM-DAC), respectively.

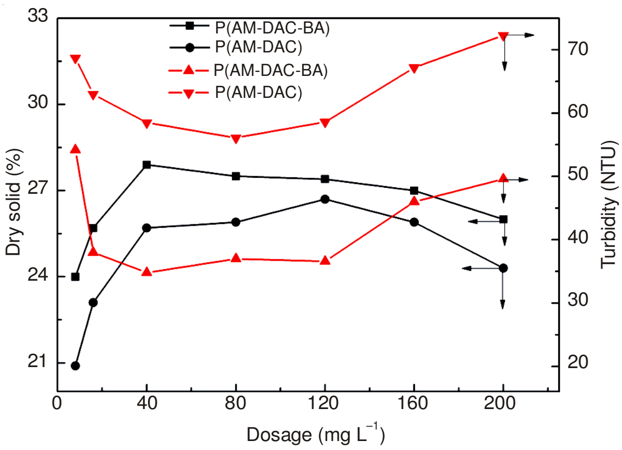


Fig. 6. Effect of flocculant dosage on dewatering performance

Effect of pH on dewatering performance: The surface charge of sludge particles was affected by pH and was one of the key factors controlling flocculation and sludge dewatering effect. As the pH increased, the dry solid content gradually decreased. The extracellular polymeric substance was dissolved under acidic condition of the sludge, thereby increasing the sludge dewatering performance. The negative charge of sludge particles increased in alkaline conditions, increasing the repulsion between sludge particles and specific resistance of sludge[23]. But for P(AM-DAC), as the pH increased, the dry solid content first increased fast and then decreased suddenly. Because the use of P(AM-DAC) as a flocculant at low pH, the electrostatic repulsion effect of hydrogen ion (H$^+$) was much larger than the dissolution effect of extracellular polymeric substance on sludge particles, so that dry solid content obtained by P(AM-DAC) was low in the acidic conditions[17]. As shown in Fig. 7, larger flocs and better sludge dewatering performance were obtained at pH 6-8. Therefore, pH 6-8 was adopted as the optimal condition.

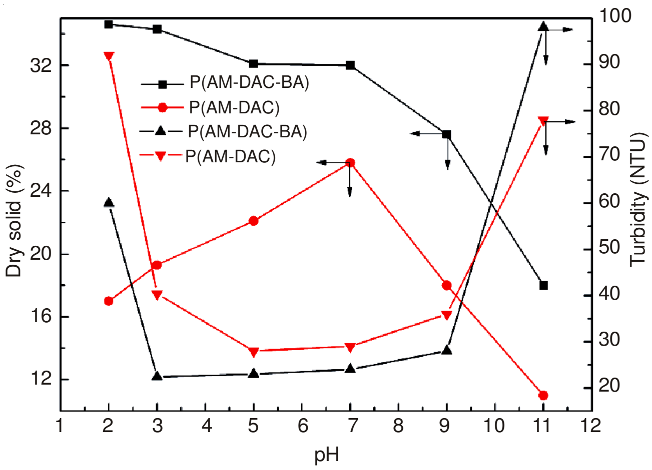


Fig.7 Effect of pH on dewatering performance

Effect of cationic degree on dewatering performance: Fig. 8 shows the effect of cationic degree on dewatering performance, dry solid content increased first and then decreased with increase of cationic degree, while the supernatant turbidity decreased first and then increased dramatically. When the cationic degree was low, the flocculant could not neutralize negative sludge particles effectively, leading small flocs. Sludge particles flocculated by flocculant with high cationic degree were easy to attain opposite charge on flocs surface before the aggregation of colloidal particles into large flocs. The electrostatic repulsion effect would deteriorate flocculation process and dewatering performance. As shown in Fig. 8, the dry solid content 32 % and the supernatant turbidity 24 NTU were obtained by P(AM-DAC-BA) at cationic degree 30 %, while the dry solid content 27.4 % and the supernatant turbidity 31.2NTU were obtained by P(AM-DAC) at cationic degree 40 %. Therefore, the cationic degree 30 % for P(AM-DAC-BA) and the cationic degree 40 % for P(AM-DAC) were adopted as the optimal condition for sludge dewatering process.

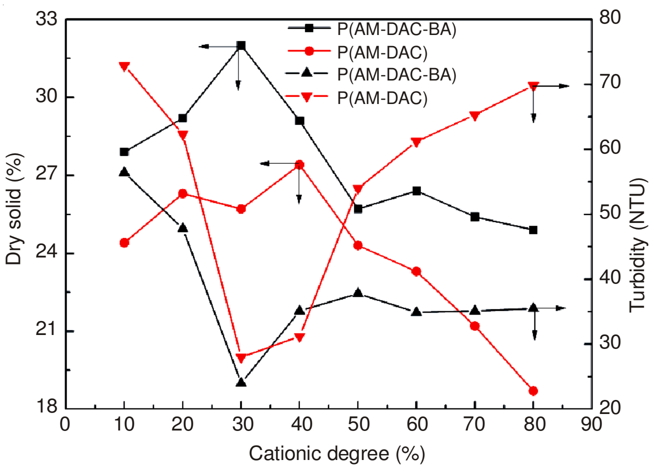


Fig. 8. Effect of cationic degree (CD) on dewatering performance

Conclusion

In this study, P(AM-DAC-BA) and P(AM-DAC) were synthesized by UV induced polymerization. The IR analysis shows the presence of functional groups in ternary copolymers, proving that the copolymer was synthesized with acrylamide, acryloyloxyethyl trimethyl ammonium chloride and butyl acrylate. The optimization results showed the optimum conditions of determination of cationic degree by colloid titration for P(AM-DAC-BA) concentration, pH value and titration rate were 1×10^{-5} to 5×10^{-5} g g^{-1}, 2-3 and 0.0653-0.0719 mL s^{-1}, respectively. A series of sludge dewatering results showed that P(AM-DAC-BA) had a better flocculation performance on sludge dewatering than P(AM-DAC). The maximum dry solid content and the supernatant turbidity of 32 % and 24 NTU were achieved at the dosage of 40 mg L^{-1} with the initial sludge pH of 5.

ACKNOWLEDGEMENTS

This research was supported by the National Natural Science Foundation of China (Project Nos. 21177164 and 51078366)

REFERENCES

1. W. Wang, Y.X. Luo and W. Qiao, *Front. Environ. Sci. Eng*., **4**, 102 (2010).
2. H.L. Zheng, Y.Y. Sun, C.J. Zhu, J.S. Guo, C. Zhao, Y. Liao and Q.Q. Guan, *Chem. Eng. J*., **234**, 318 (2013).
3. G.C. Zhu, H.L. Zheng, Z. Zhang, T. Tshukudu, P. Zhang and X.Y. Xiang, *Chem. Eng. J*., **178**, 50 (2011).
4. G.C. Zhu, H.L. Zheng, W.Y. Chen, W. Fan, P. Zhang and T. Tshukudu, *Desalination*, **285**, 315 (2012).
5. G.C. Zhu, H.L. Zheng, P. Zhang, Z.J. Jiao and J. Yin, *Environ. Technol*., **34**, 91 (2013).
6. H. Saveyn, D. Curvers, O. Thas and P. Van der Meeren, *Water Res*., **42**, 1061 (2008).
7. Y. Qi, K.B. Thapa and A.F.A. Hoadley, *Chem. Eng. J*., **171**, 373 (2011).
8. E. Neyens and J. Baeyens, *J. Hazard. Mater*., **B98**, 51 (2003).
9. H.L. Zheng, Y.X. Pan and X.Y. Xiang, *J. Hazard. Mater*., **141**, 457 (2007).
10. H.Z. Zhao, Q.Y. Yue, B.Y. Gao, H. Yu and Z.K. Luan, *Fine Chem*., **18**, 645 (2001).
11. H.Z. Shang, Y.B. Zheng and J.P. Liu, *J. Appl. Polym. Sci*., **119**, 1602 (2011).
12. Z.H. Wu, S.P. Chen and Z.H.X. Tian, *J. Anal. Sci*., **17**, 207 (2001).
13. H.L. Zheng, P. Zhang, Y.Z. Chen, M.Z. Tang, S.J. Jiang, C.J. Zhu, G.C. Zhu, J.Y. Ma and Z.Q. Zhang, *Spectroso. Spectr. Anal*., **32**, 334 (2012).
14. S. Kam and J. Gregory, *Colloids Surf. A*, **159**, 165 (1999).
15. X.H. Feng, M. Leduc and R. Pelton, *Colloids Surf. A*, **317**, 535 (2008).
16. J.Y. Ma, H.L. Zheng, M.Z. Tan, L.W. Liu, W. Chen, Q.Q. Guan and X.K. Zheng, *J. Appl. Polym. Sci*., **129**, 1984 (2013).
17. J.R. Zhu, H.L. Zheng, Z.Z. Jiang, Z. Zhang, L.W. Liu, Y.J. Sun and T. Tshukudu, *Desalin. Water. Treat*., **51**, 2791 (2013).
18. H. Terayama, *J. Polym. Sci*., **8**, 243 (1952).
19. E. Kokufuta, *Macromolecules*, **12**, 350 (1979).
20. H.Z. Shang, J.P. Liu, Y.B. Zheng and L.G. Wang, *J. Appl. Polym. Sci*., **111**, 1594 (2009).
21. X.F. Gu, F. Tian and Y.J. Zhang, *Speci. Petrochem*., **6**, 15 (2003).
22. Z.H. Yang, Y. Feng, S.B. Sang and Y.H. Zhou, *J. Cent. South Univ*., **37**, 516 (2006).
23. E. Neyens, J. Baeyens and R. Dewil, *J. Hazard. Mater*., **106B**, 83 (2004).