ISSN 1001-0742
CN11—2629/X

Article ID: 1001-0742(2004)03-0443-04 **CLC number**: X703 **Document code**: A

Flocculation performance of a novel synthesized flocculant with low ecological risk

ZHANG Kai-song, ZHOU Qi-xing*, XIAO Hong

(Key Laboratory of Terrestrial Ecological Process, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China. E-mail: Zhouqixing2003@yahoo.com)

Abstract: Combined flocculants with low ecological risk are urgently required in water supply and wastewater treatment in China. A novel flocculant was thus developed under the condition of low ecological risk(noted as CAS). The experiments to examine wastewater treatment performance of the new product showed that there was favourable performance in the flocculation process in contrast to commercial flocculants in treating kaolin suspensions, municipal effluent and domestic wastewater. Flocculation performance included the turbidity removal rate, sediment character and a decrease in COD(chemical oxygen demand). The sediment time of flocculation is short and the removal rate of turbidity treated by CAS is high compared with PAC(polyaluminum-chloride), PAM(polyacrylamide) and the combined addition of PAC and PAM. The optimal concentration required to affect flocculation processes is dependent on kaolin concentration and the character of the wastewater within the range examined. It also showed that CAS is effective to treat wastewater with high turbidity.

Keywords: combined flocculation; turbidity; sediment velocity; COD; ecological risk

Introduction

Flocculation is a process that involves the formation of aggregates and the setting of colloidal particles form stable suspensions caused by the addition of soluble chemicals known as flocculants in minute quantities (Bratby, 1980). The application of flocculants is a very important way to reduce or remove suspended solids (Divakaran, 2001), nutrients such as nitrogen and phosphorus (Aguilar, 2002), organic matter (Armand, 2000), and pollutants such as heavy metals and hydrocarbons (Morlay, 2000) in wastewater. Commercial flocculants are generally categorized into three major groups: inorganic flocculants, organic synthetic polymer flocculants and naturally bio-polymer flocculants. These flocculating agents have been widely used to purify drinking water, to treat municipal effluent and industrial wastewater and to remove deleterious ingredients in range of industrial water reused processes (Zhang, 2003; Zhou, 2000).

There has been growingly interesting in adverse environmental effects and ecological risk of present commercial flocculants. The toxicity of inorganic flocculants has been raised great attention (Zhang, 2000). Previous research confirmed that aluminum is toxic to plants, animal and microorganisms (Lee, 2001; Poléo, 1997; Reider, 1995; He, 1998). Aluminium coagulation has come under scrutiny in recent years due to concerns about metal residuals in the public water supply. In response, various regulations have been promulgated including a World Health Organization suggestion for 0.2 mg/L maximum Al (World Health Organization, 1998). The sludge obtained from such treatment poses disposal problems and tends to accumulate in environment (Kvech, 2002). Although not conclusively proved, increasing concern about the residual aluminium which may be presented in water as a result of alum treatment is being expressed by the public in connection with the Alzheimer's disease (Reider, 1995). The synthetic polymer flocculants also have ecological and healthy risk in the producing process and in sludge treatment (Dearfield, 1988; Vanhorick, 1983).

At present, the development of safe biodegradable flocculants that will minimize ecological risk is urgently required (Ji, 2002; Sun, 2001). A tendency comes into being in the area of flocculants research: combining different kinds of materials into a compound (Divakaran, 2001; Kurenkov, 2001; Tripathy, 2001). These combined flocculants may be used in large range of pH value, the dose of flocculants is reduced and a higher degree of water clarification is achieved, in particular, the healthy and ecological risk has largely reduced. Under such a condition, we synthesized a novel graft copolymer which is named as CAS with low ecological risk by substituting cationic Al^{3+} to the fullest extent. The flocculation performance of CAS was examined in order to push the new product into markets.

1 Materials and methods

1.1 Comparative flocculants used in the study

Commercial flocculants such as polyaluminum chloride (PAC) and polyacylamide (PAM) were used and the structure was totally classified by its manufactures. The rate of Al_2O_3 in PAC is 30%, and the comparative molecular weight of PAM is 8×10^6.

1.2 Tested wastewater

Kaolin suspensions include three kinds of suspensions with different kaolin concentration of 100 mg/L, 400 mg/L and 2000 mg/L. Municipal wastewater was taken from the Shenyang municipal wastewater pilot mixed by domestic wastewater, commercial waste and some industrial effluent, and its turbidity was measured as 160 NTU. Domestic wastewater was taken from a septic pool in the Jingsheng

Foundation item: The National Science Fund for Distinguished Young Scholars (No. 20225722) supported by the National Natural Science Foundation of China and the Knowledge Innovation Project (No. KZCX2-SW-416) of Chinese Academy of Sciences; * Corresponding author

Community in Shenyang, and its raw turbidity was nearly 100 NTU.

1.3 Flocculation tests

In 1000 ml flocculation jars, 1000 ml of the flocculating suspension was taken. The jars were placed on the mixer by stirring blades in the suspension. Diluted CAS and commercial agent solution was added to each jar under stirring. The suspensions were stirred at a constant high speed of 140 r/min for 1 min so as to let the flocculants mixed in the suspension absolutely, then, followed by the speed of 40 r/min for 5 min. The flocs developed during slow stirring (20 r/min) for 10 min. Later, the suspensions were settled down. Clean supernatant liquid 3 cm under the horizon was drawn and its turbidity was measured at the time of 5, 10, 20, 30, 60, 120 min. Turbidity, COD were measured.

2 Results

2.1 Removal of turbidity

Contamination of municipal wastewater by suspended materials such as mud, dirt, turbidity, organic matter and decaying vegetation can be a serious operational problem besides reducing its aesthetic quality. The most important role of flocculants in wastewater treatment is to reduce suspension solids. Turbidity reflects the concentration of waste suspension solids. The turbidity is one of the most important characteristics of wastewater. The lower the turbidity is, the lower pollution concentration in waste is. Moreover, the measurement of turbidity is simple feasible and fast. So the turbidity was selected as a criterion parameter to identify the flocculating performance of the flocculants. In all the case, the performance of a particular flocculants was expressed in terms of turbidity after settling down for 30 min.

Kaolin suspensions were taken to identify the performance of flocculants, when treating kaolin suspensions with concentration 100 mg/L. The remained turbidity treated by CAS was less than 2.0 NTU with the dose 3.0 mg/L. This tiny member was not reached by the comparative flocculants. The turbidity of the supernatant liquid treated by CAS was lower than those treated by the same dose of commercial flocculants such as PAC and PAM, respectively. Moreover, it was also lower than the combinative addition of PAC and PAM(the dose of PAM is 1.0 mg/L). The optimized dose of CAS and PAC is 4.5 mg/L with the minimization of turbidity is 1.6 and 5.3 NTU, respectively. The optimized dose in treating 400 mg/L of suspensions was 3.0 mg/L of CAS, 6.0 mg/L of PAC and the residual turbidity of the treated wastewater was 0.2 and 3.7 NTU, respectively. The tiny turbidity is 8.9 NTU with the optimized dose of 2.0 mg/L when treating the higher concentration(2000 mg/L) of kaolin sewage, with the comparison to 20.0 NTU of PAC with the dose of 2.5 mg/L. The optimal concentration required to affect flocculation is independent of kaolin concentration within the range examined. The results of different kaolin suspensions showed that CAS is more effective to treat wastewater with high turbidity(Fig.1).

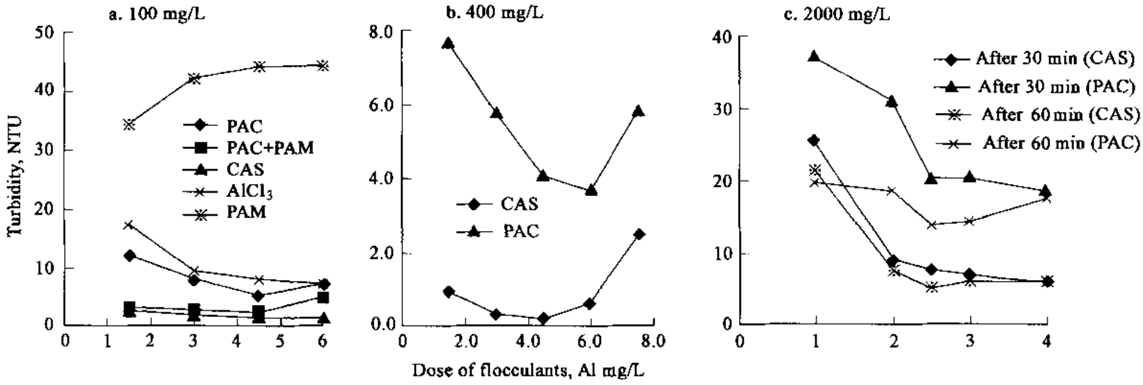

Fig.1 Different performance in treating kaolin suspensions by various flocculants(dose of a flocculant vs turbidity)

With the comparison to PAC, the data from Fig.2 indicated that CAS showed better performance in treating domestic wastewater and municipal effluent. When the dose of CAS used is more than 4.5 mg/L, the efficiency of removal turbidity done by CAS is better than that done by PAC. The municipal effluent is mixed by domestic wastewater, commercial waste and industrial waste. The turbidity of the mixed effluent is higher than that of single domestic waste. The optimal dose of the flocculant required to affect wastewater is independent on the characteristic of the wastewater. The optimal dose by CAS is 9 mg/L in the treatment of domestic wastewater while 4.0 mg/L in municipal effluent was tested. With the same dose of flocculants, the residual turbidity of supernatant liquid in municipal effluent is lower than which in domestic wastewater. It was also showed that CAS is more effective in treating domestic wastewater with high turbidity.

2.2 Flocculation sediment velocity

Flocculating sediment performance is a key factor in the treatment of wastewater. Rapid flocculation in the short time means low construction and operation fees. When treating 100 mg/L of kaolin suspension, CAS showed a rapid sediment in the optimized dose (3.0 mg/L) than not only separately adding of PAC, PAM with the dose of 4.5 mg/L but also combinatively adding of them(the dose of PAC and PAM is 4.5 mg/L and 1.0 mg/L) in the early flocculation period(0—30 min). According to Fig.2, when the dose of CAS was 4.5 mg/L, the efficiency of removing turbidity by CAS was nearly equal to that of PAC. However, CAS showed a rapid flocculating performance, especially in the early

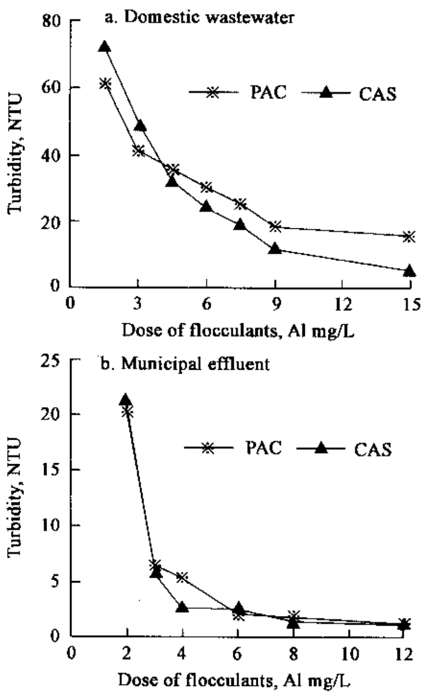

Fig.2 Different performance in treating domestic wastewater and municipal effluent by CAS and PAC (dose of a flocculant vs turbidity)

period of flocculation processes (0—10 min) (Fig.3). Fig. 3b, the sediment time suited to CAS should be 30 min, the turbidity after setting 30 min and 120 min is not very large. It was also confirmed that the flocs formed by CAS in the flocculating process is more suitable to sediment than which formed by PAC.

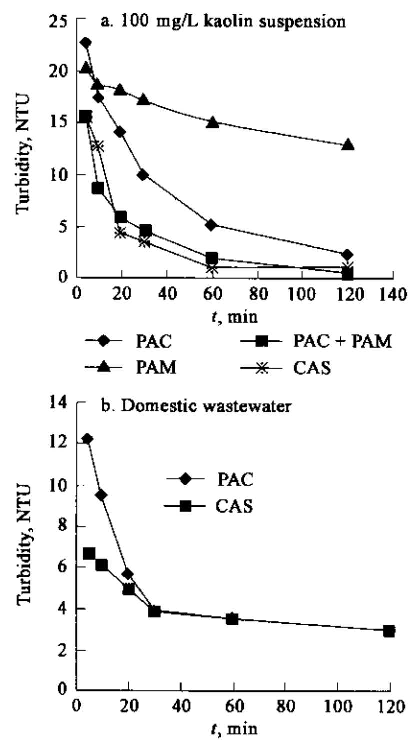

Fig.3 Flocculation velocity of kaolin suspension and domestic wastewater by various flocculants

When the turbidity suspension concentration was high, the turbidity after setting 30 min and 60 min was low (Fig. 1c). It indicated that the optimal settling time is 30 min in high turbidity wastewater, with the comparisons to more than 60 min in PAC. The optimal sediment time of CAS is 30 min in lower concentration sewage with the comparison to 30 min of PAC. The reason is that the flocs formed by CAS may be more suitable to sediment in high turbidity wastewater.

2.3 A decrease in COD

COD of domestic wastewater and municipal effluent was measured with 198 mg/L and 240 mg/L, the raw turbidity was 100 NTU and 160 NTU. Table 1 indicates that CAS showed higher efficiency at removing COD than PAC in either samples, and the result also indicated that CAS showed higher efficiency in higher turbidity samples.

Table 1 Different capability of COD removal by CAS and PAC

Wastewater type	Dosage, Al mg/L	COD, mg/L treated by CAS	COD, mg/L treated by PAC
Domestic wastewater	3.0	111	134
	4.5	93	125
	9.0	75	98
Municipal effluent	3.0	98	138
	4.0	93	100
	6.0	85	87

When treating the domestic wastewater, the dosage of CAS was less than 4.5 mg/L, the residual COD was under 100 mg/L, PAC needed nearly 9.0 mg/L to reach this level, and the dose was 3.0 mg/L of CAS in treating the municipal effluent with comparison to 4.0 mg/L of PAC. In the low concentration, the priority of CAS in removal COD is more, either in domestic or municipal effluent. With the same dose (3.0 mg/L), CAS showed more effective in the municipal effluent, the removal rate of COD was 44%, 60% with comparison to PAC, the removal rate of COD was 32% and 30%.

3 Discussion

According to the bridging mode of flocculation (Gregory, 1996), major mechanisms of flocculation of polyelectrolytes are surface-charge neutralization and bridging. Surface-charge neutralization occurs if the charge of flocculants is opposite in sign to that of suspended particles. Addition of such a flocculant to suspensions will result in aggregation caused by specific ion absorption. For neutral flocculants, such as single PAM, the most important mechanism of flocculation is the polymer bridging. Essentially polymer bridging occurs because segments of a polymer chain get absorbed on various particles, thus linking the particles together. For effective bridging to occur, there must be sufficient polymeric chain lengths, which extend far enough from the particle surface to attach to other particles (Tripathy, 2001).

In the flocculation of CAS, in the early period of flocculation, surface-charge neutralization will take place, and play the main role, although charge of the particle and / or polymer cannot play a major role in the whole flocculation. To the whole course of flocculation, copolymer bridging plays decisive role. The single PAM had no effect in treating the kaolin suspension sewage because there is litter charge on its polymer to aggregate the suspension solid during the process of flocculation. When combinative adding with PAC, it shows better performance than the single PAM and single PAC. But it showed poor function when contracted with CAS. CAS is combined with inorganic salt and organic polymer, cornstarch, a kind of polysaccharides. The polysaccharides backbone intensely touched with aluminum (might be polyaluminum and other sorts of aluminum compound) in the combinational reaction. It prolonged the length of polymer chain and the formula of compound, the cationic aluminum salt was grafted on the backbone. When the aluminum salt has hydration in the solution, surface-charge neutralization would take place in the same time. In the coming process the polymer bridging would happen, most starch-modified backbone on the combination copolymer play a role in forming loop or bridge and the flocculating body intensively.

The component of starch of corn is some graft polymer and some linear chain of polysaccharides. In case of linear polymers, the polymer segments attached to the surface in trains, projected into the solution as tails, or formed a part of loops, which linked the train together. This type of intense bridging is not possible in the case of single linear polymers. Single linear polymers of starch showed poor flocculation ability. After modified by aluminum salt, polyaluminum or other sorts of aluminum compound, CAS might be linked with linear polymers of starch at the end of a linear polymer or in the middle of polymers. The graft copolymers were formed. So it is very easy for the graft copolymer of CAS to contact with, and attach to other particles (including the particles in the wastewater and those of the copolymers) in aqueous phase, bridging between these particles can easily be formed. The graft copolymer CAS, due to the better approachability of the dangling grafted chains onto the starch-modified backbone, can easily bind the colloidal particles through bridging to form flocculating body.

In the previously research, aluminum salt is a latent contaminated resources in water and wastewater treatment. The optimized dose of CAS is lower than PAC in treating municipal effluent, domestic wastewater and kaolin suspension. The most important role is that the active aluminum contained in CAS is rarely because of the combinative reaction, active aluminum is thoroughly reacted with modified starches. When flocculation is happened the aluminum is sedimentated with the flocs. The dose of aluminum is lower than that in PAC. CAS has a biodegradable polysaccharide backbone, starch is decomposed completely by environmental microorganisms and these degraded monomers are resources of carbohydrate to environmental creature. There is no toxicity monomer such as acrylamide in PAM. The ecological risk of CAS is greatly decreased as well as the flocculation performance enhanced significantly.

4 Conclusions

There is favorable performance in flocculation processes in contrast to commercial flocculants in treating kaolin suspensions, municipal effluent and domestic wastewater. The removal rate of turbidity treated by CAS is high compared with PAC, PAM and the combined addition of PAC and PAM. The optimal sediment time of CAS is 30 min in the test samples with comparison to more than 60 min of PAC. The optimal concentration required to affect flocculation is dependent on kaolin concentration and the character of the wastewater within the range examined. Combination reaction might prolong the chain of copolymers, change the charger on the backbone of starches thus significantly enhance the flocculation performance.

References:

Aguilar M I, Sáez J, Lloréns M *et al*., 2002. Nutrient removal and sludge production in the coagulation-flocculation process[J]. Wat Res, 36: 2910—2919.

Armand M, Vilge-Ritter A, Rose J *et al*., 2000. Coagulation-flocculation of natural organic matter with Al salts: speciation and structure of the aggregates [J]. Environ Sci Technol, 34: 3242—3246.

Bratby J, 1980. Coagulation and flocculation[M]. Croydon (UK): Uplands Press.

Dearfield K L, Abernathy C O, 1988. Acrylamide: its metabolism, developmental and reproductive effects, genotoxicity and carcinogenicity[J]. Mutant Res, 195: 45—77.

Divakaran R, Pillai V N S, 2001. Flocculation of kaolinite suspensions in water by chitosan[J]. Wat Res, 35: 3904—3908.

Gregory J, 1996. Industrial water soluble polymers[M]. Cambridge: The Royal Society of Chemistry.

He Z L, Zhou Q X, Xie Z M, 1998. Soil-chemical equilibria of beneficial and harmful elements[M]. Beijing: China Environmental Science Press. 35—44.

Ji G D, Sun T H, Zhou Q X *et al*., 2002. Constructed subsurface flow wetland for treating heavy oil-produced water of the Liaohe Oilfield in China[J]. Ecological Engineering, 18: 459—465.

Kurenkov V F, Snigirev S V, Churikov F I *et al*., 2001. Preparation of anionic flocculant by alkaline hydrolysis of polyacrylamide(Praestol 2500) in aqueous solutions and its use for water treatment purposes[J]. Russian Journal of Applied Chemistry, 74: 445—448.

Kvech S, Edwards M, 2002. Solubility controls on aluminum in drinking water at relatively low and high pH[J]. Wat Res, 36: 4356—4368.

Lee J C, Kim J S, Kang I J *et al*., 2001. Potention and limitation of alum or zeolite addition to improve the permormance of a submerged menbrane bioreactor[J]. Wat Sci Technol, 43: 59—66.

Morlay C, Cromer M, Vittori O *et al*., 2000. The removal of copper(Ⅱ) and nickel (Ⅱ) from dilute aqueous solution by a synthetic flocculant: a polarographic study of the complexation with a high molecular weight poly (acrylic acid) for different pH values[J]. Wat Res, 34: 455—462.

Poléo A B S, Østbye K, Øxnevad S A *et al*., 1997. Toxicity of acid aluminium-rich water to seven freshwater fish species: a comparative laboratory study [J]. Environ Pollut, 96: 129—139.

Reider S, Kukull W, Standish-Lee P. 1995. Drinking water aluminum and bioavailability[J]. J AWWA, 87: 86—100.

Sun T H, Zhou Q X, Li P J, 2000. An innovative land treatment system for urban wastewater and practice in China[C]. In: Local government and water session. The Second World Water Form, The Hauge. 8—22.

Sun T H, Zhou Q X, Li P J, 2001. Pollution ecology[M]. Beijing: Science Press.

Tripathy T, Karmakar N C, Singh R P, 2001. Development of novel polymeric flocculant based on grafted sodium alginate for the treatment of coal mine wastewater[J]. Journal of Applied Polymer Science, 82: 375—382.

Vanhorick M, Moms W, 1983. Carcinogen of acylamide[J]. Carcinogenesis, 4: 1459—1463.

World Health Organization, 1998. Guidelines for drinking-water quality[S]. 2nd ed. Addendum to Vol. 2. Health criteria and other supporting information, Geneva, Switzerland. 3—13.

Zhang G, Wang Z, 2000. Mechanism study of the coagulant impact on mutagenic activity in water[J]. Wat Res, 34: 1781—1790.

Zhang K S, Zhou Q X, Sun T H, 2003. Advances and applications of treatment technology for sewage harmlessness and resourcefulness in small cities and towns[J]. Engineering Sciences, 5: 88—92.

Zhou Q X, 2000. Application of biotechniques to water purification: Principles and methods[M]. In: Water management, purification, and conservation in arid climates (Goosen F. A. and Shayya W. H. ed.). Lancaster: Technomic Publishing Co., Inc. 31—44.

(Received for review May 12, 2003. Accepted July 3, 2003)