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Evaluating the Coagulants of Polyaluminum Silicate Chlorides on Turbidity Removal

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Abstract: Polyaluminum silicate chloride (PASiC) is a new inorganic coagulant and has different characters from other cationic inorganic products used in water treatment. The optimal formulas and conditions to produce and use PASiC are not thoroughly well-known. PASiC can be formed by treating $AlCl_3$ solution with silicate compounds and the insoluble aluminum silicates are produced thereafter. It has been found that partially decreasing alum acidity with silicate would form a more stable solution than polyaluminum chloride (PAC). PASiC may enhance aggregation by the silicate in it to remove turbidity especially for the water of low turbidity and alkalinity. In this research, a series of PASiC coagulants were produced from the different basicities (B) and Al/Si molar ratios at the different aging temperatures and aging times. Accordingly, PASiCs prepared by the different basicities (B) and Si/Al molar ratios were added in a synthetic water with low turbidity and alkalinity to evaluate the efficiency of PASiC for colloids removal. Finally, the raw water from Min-Der water treatment plant (Miaoli, Taiwan) was used to evaluate the treatment efficiency of PASiC and Aluminum Sulfate $Al_2(SO_4)_3$. The results indicate that the PASiC with higher B value and lower Si/Al molar ratio has higher coagulation efficiency. We also found that under the aging temperature of 40°C will increase the

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aging rate, and the product of PASiC formed is more stable. PASiC evidently has higher turbidity removal efficiency than that of $Al_2(SO_4)_3$ when equivalent doses were used for Min-der reservoir water.

Keywords: Polyaluminum silicate chloride (PASiC), aging, coagulation, turbidity, basicity

INTRODUCTION

Coagulation/flocculation is widely used for particle removal in water and wastewater treatment. Polymeric and monomeric metal coagulants, including polyaluminum chloride (PAC) and aluminum sulfate, or polyferric sulfate (PFS) and ferric chloride are often adopted in the process. The hydrolysis of metal ions is an important reaction for the destabilization and the complexation of suspended particles and organic matter in coagulation. The hydrolysis of polymeric and monomeric coagulants are quite different (1). A series of complicated hydrolysis reactions take place as soon as the monomeric salt is added to water, which make the coagulation hard to control (2, 3). Usually, precipitates of metal hydroxide will be produced afterwards. The polymeric salt consists of metal hydroxyl complexes of various charges. The degree of hydrolysis of polymeric salts can be controlled during manufacture, therefore the complicated reactions caused by the hydrolysis of the metal salt in coagulation can be minimized. Consequently, the use of the polymeric salts provides a simpler and more precise way to control the reactions in coagulation (4–7). However, concerning that the main coagulation mechanism of polymeric metal for turbidity removal is by electronic neutralization, the polymeric metal coagulants will be unfavorable for low turbidity water treatment (8). Therefore, in the traditional treatment process, coagulation aids such as activated SiO_2 colloid are supplemented to improve the efficiency of turbidity removal. The combination of coagulation aids with aluminum or ferric salts to form a new type of liquid coagulant has been developed recently (9–12). The polyaluminum silicate chloride (PASiC) which is prepared from aluminum chloride and activated silica under certain conditions has been proved to promote the coagulating ability (13–16) and lower residual aluminum content than does polyaluminum chloride (PAC) (17). The stability of PASiC can be improved by adding polysilicate complexes during its synthesis. Not only can the hydrolysis of products during storage be minimized, but the molecular size is larger than without adding it (13). In addition, the polysilicate functioned as coagulant aid to form flocks in coagulation, which enabled avoiding from the disadvantages of the inorganic polymer use, such as PAC, which is not appropriate in low turbidity water treatment since the main mechanism of the coagulation is charge neutralization. The adding of negatively charged polysilicate in PASiC will neutralize its positive charge (14), and the overdose of base during PASiC preparation will result in the formation of solid particles from the hydrolysis of the coagulant, thus losing its ability to coagulate. Moreover, the aging process influenced the coagulation ability (18, 19). In the process, the inorganic coagulant performed under controlling temperature for a long period of time to lead to polymerization, so the coagulant can be stabilized and grows to have higher molecular size/weight. Therefore, this paper focuses on the ability of PASiC coagulants prepared from different Al/Si ratios, basicities (OH/Al molar ratios, denoted B), aging temperature and aging time to treat the synthesized water at low turbidity. Finally, the PASiC with the best turbidity removal efficiency was compared with other coagulants to understand the practicability, especially using in the low turbidity raw water taken from Min-der reservoir. $Al_2(SO_4)_3$ is the coagulant used in the water treatment plant now, and PAC will be used only in the condition of high turbidity.

MATERIALS AND METHODS

Preparation of PASiC

The Al/Si ratio and B values of PASiC are the important index of coagulation efficiency. Generally, low Al/Si and high B will increase the degree of polymerization, and the molecules of PASiC formed having a higher molecular weight. The charge effectiveness in coagulation process might be smaller and the stability of the coagulant was reduced. When it was stored longer, a large amount of precipitate was produced and the function of the coagulant was lost (5). To thoroughly understand these phenomena, 20 different PASiC solutions were prepared with B values of 0.5, 1.0, 1.5, 2.0, 2.3 and Al/Si ratios of 5, 10, 15, and 20 according to the method developed by Gao et al. (13). 23.5 ml of 1.5 M HCl was added into a quick stirred 50 ml of 0.5 M SiO_2 solution, then a solution of 0.329 M polysilicate (PSi) formed and the solution was adjusted to pH 2 using HCl. 0.25 M $AlCl_3$ solution was diluted with pure water, and various amounts of PSi solutions ($1.57 \sim 6.28$ ml) were added according to the proposed Al/Si ratios. The B value was then adjusted using 0.5 M NaOH (20–50 ml, titration rate is 0.05 ml/min) to have the gathering interaction between the aluminum and the silica, and the final volume of solution is 100 ml. Final pH was measured first and the experiment of coagulation was performed to understand the effects of aging and the temperature on the stability of PASiC. The aging temperature of PASiC was conducted at 20, 40, 60, and 80°C in a thermo stated bath.

Coagulation Experiment

The low turbidity synthesized water was prepared from the following steps. First, the high turbidity synthesized raw water was prepared by adding 1 g of kaolin into 1 L of deionized water and settled for 30 min after four hours of rapid mixing. Second, the 600 ml supernatant from the high turbidity synthesized raw water then diluted into about 10 L deionized water to obtained the 20 NTU low turbidity water. Third, 0.072 g/L $NaHCO_3$ and 12.244 g/L $NaClO_4$ were added to the diluted solution to control the basicity and ionic strength at 50 mg/L as CaCO3 and 10^{-2} M, respectively. The jar test procedure (20) involved rapid mixing at 100 rpm for 30 sec, followed by slow mixing at 20 rpm for 30 min, and 30 min settling in 1 L beakers. The same Jar-test procedure was followed to test the real water sample taken from Min-Der reservoir (pH 7.91, turbidity 8.5 NTU, alkalinity 68 mg/L as $CaCO_3$). The maximum dosage was determined under the condition that the solution pH following coagulation will not be less than 6.3.

Analysis

Samples were taken from 3 cm below the surface of the coagulated–flocculated–sedimented water. The pH values of the samples were determined by a digital pH meter. Turbidity was determined by using an HACH model 2100 turbidity meter. The residual of dissolved aluminum in filtrates after 0.45 μm membrane were determined by the absorption at 535 nm using the ERC (Eriochrome Cyanide R) method (only for the coagulation samples of Min-Der reservoir water) (21).

RESULTS AND DISCUSSION

The relationship between the turbidity removal efficiencies and the PASiC dosages with the different B values and the Al/Si ratios are shown in Fig. 1. It was found that under the condition without controlling solution pH (minimum pH is 6.3) and at Al/Si 5, the turbidity removal was influenced greatly by the value of B. Increasing of B from 0.5 to 2.0 increased the suitable dosage range for effective turbidity removal, but there was no removal efficiency when B reached 2.3. This result showed that increasing the B will increase the degree of polymerization, but reduce the positive charge on PASiC (13). Therefore, the dosage of PASiC needed to reverse the electrical charge increased. When the value of B was high, the size of molecule formed increased, and the particles were removed through the mechanism of bridging, so the effective dosage range was enlarged. But when B value was too high, such as 2.3, it made the coagulant unstable and the precipitate occurred during the preparation of the coagulant, and resulted in no turbidity removal. Another evidence was observed in Fig. 1 that comparing the turbidity removal efficiencies of different Al/Si ratios but with the same basicity, the turbidity removal was not efficient when using PASiC with Al/Si 20 than that of other Al/Si ratios, especially when B equals to 2.0. This

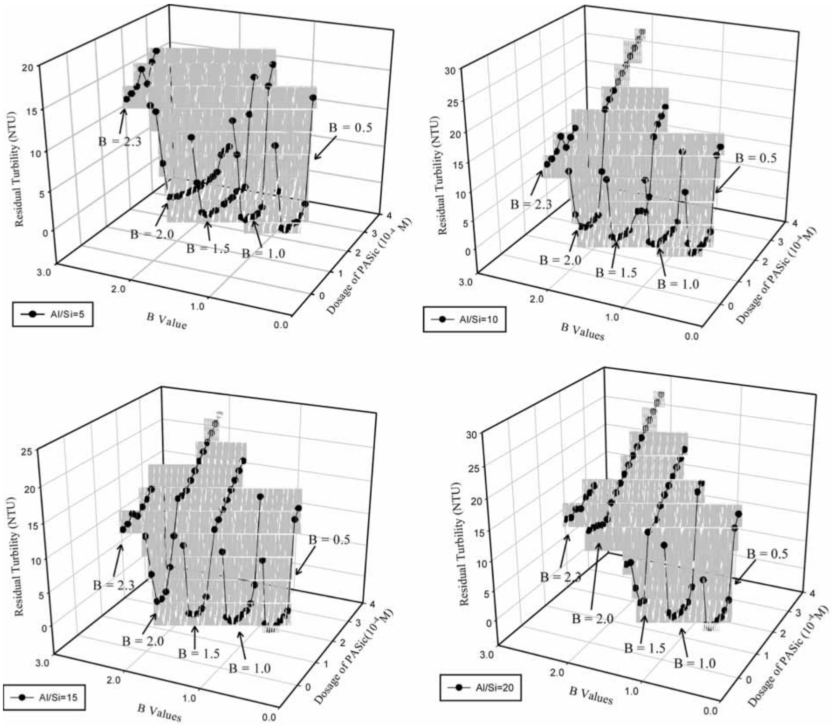

Figure 1. Comparison of turbidity removal efficiencies of different Al/Si ratios and B values.

might be due to the fact that the reduction of the proportion of activated silicon reduced the degree of polymerization of PASiC (in the same B value), and produced the high positive charged PASiC, which has similar characteristics with PAC (22). This result is similar to the study of Gao (13, 14), where it was noted that if Al/Si ratio is too high, the coagulation ability for particle removal will be relatively small. However, generally it is expected that the PASiC with higher molecular weight would have better coagulation efficiency. As shown in Fig. 1, the coagulant with low Al/Si ratio and high B value has wider application range of effective dosage. This result corresponds with the study of Gao (13, 14). However, if the B value is too high, it will reduce the stability of the coagulant. This study showed that PASiC coagulant with Al/Si 5 and B values from 1.5 to 2.0 would prove better coagulation efficiency.

The new formed PASiC needs the process of aging to accelerate the polymerization, so the coagulant can be stabilized and grows to have higher molecular size/weight (22, 23). Aging is usually performed under room temperature for a long period of time. Some research found that the aging of polymerized coagulant is greatly influenced by temperature (18, 19). Increasing temperature appropriately can accelerate the aging rate, but if the temperature is too high, it will make the coagulant unstable. The PASiCs (B = 1.5, Al/Si = 5) with four different aging temperatures and different aging times were tested in the experiments of coagulation. The turbidity removal efficiencies of the raw water with turbidity 20 NTU and low basicity were compared in the PASiC dosage of 1×10^{-4} M (Al + Si). If the PASiC was aged at 40°C (B = 1.5, Al/Si = 5) less than 2 hours, it showed a stable turbidity removal (Fig. 2a), if it was aged at 60°C, it needed 4 hours of aging time to reach the same removal efficiency. If it was aged at 80°C, the residual turbidity fluctuated, indicating that it is a very unstable coagulant. When the aging was done at 25°C for 8 hours, it did not show a good coagulation efficiency. It can be concluded from the above data that PASiC can be aged at 40°C within 2 hours to be a stable coagulant. In order to understand clearly the influence of aging time, the PASiC with different ratios of Al/Si and the same value of B (1.5) were prepared and tested in the same coagulation experiment. As the ratio of Al/Si increased, the aging time for reaching stability increased (Fig. 2). For instance, the aging time needed is 6 hours at below 40°C for PASiC with Al/Si 15 to have effective coagulation. Similar results were found for the PASiCs aged at 60°C and 80°C with Al/Si in the range of 5 to 15. However, if the ratio of Al/Si was 20, the coagulant produced had no coagulation efficiency, in other words, when the activated Si proportion in PASiC too small, the coagulant for the low turbidity and basicity water used in this study lost its function (Fig. 2). In conclusion, if the aging was done at 40°C in any Al/Si ratio studied in this research, it evidently showed better coagulation efficiencies than that of other temperatures.

In the aging process, the polymer of the coagulant will grow from the monomeric and the dimeric, and the release of H^+ will lower solution pH. As shown in Fig. 3, the PASiC aged at 40°C due to pH changes in 2 hours and reaching the period of stabilizing. On the other hand, if the aging was done at 60 or 80°C, the aging temperature has a negative effect on the stability of the pH. In addition, if there is no aging process performed, the phenomenon of pH decreasing after 8 hours was not distinguishable. Therefore, the aging in high temperature can really enhance the polymerization of PASiC; however, if the temperature is too high, the product will become unstable. In order to thoroughly understand the effect of aging time, three different conditions were chosen for the coagulation experiments with pH 7, B 1.5, and Al/Si 5 (Fig. 4). There was an obvious difference between the results of one month aged and one day aged coagulants at room temperature. It should be noted that the result produced by the coagulant of aged under the optimal temperature of 40°C for 8 hours is similar to that of one month aged at room temperature; therefore, increasing the aging temperature can really enhance PASiC to approach stability.

The optimal values of B (1.5), Al/Si ratio (5), aging temperature (40°C) and time (8 hours) concluded according to above data were based in the

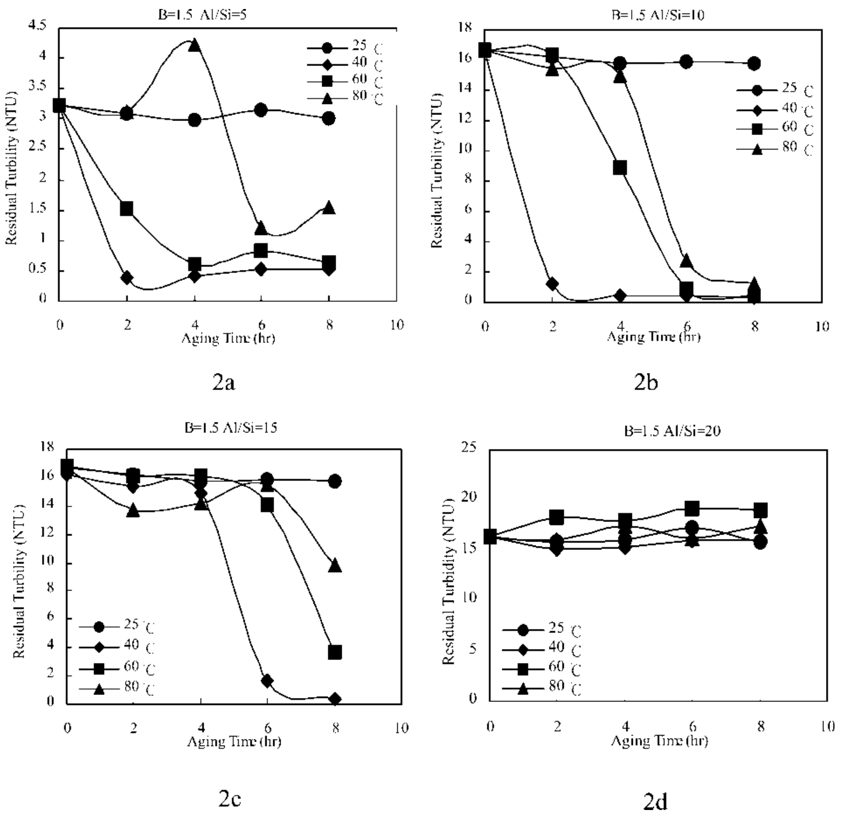

Figure 2. The effect of different aging temperatures and times on the residual turbidity after coagulation. (Al + Si dosage = 1×10^{-4} M).

following study to compare the efficiencies of coagulation by PASiC, PAC (produced in the same condition but without adding Si), and $Al_2(SO_4)_3$. The effective efficiency could be reached with a low dosage of PASiC at pH 7 (Fig. 5) compared to that of PAC. Generally, polymerized coagulant such as PAC is more suitable to use in high turbidity solution, and due to its high surface charge, charge neutralization will be concluded as the predominant mechanism. In low turbidity solution, coagulation aids such as activated SiO_2 can be added to increase the turbidity to promote coagulation. As for PASiC, it does not have only the high charge, but the hydrolysis of polysilicate which could produce SiO_2 to increase turbidity. However, its coagulation efficiency was even better than that of $Al_2(SO_4)_3$ (Fig 5). Additionally, the optimal pH range for each coagulant is important the point to be considered. Experiments were performed in the dosage of 1×10^{-4} M (Al + Si) at different pH values as shown in Fig. 6. The results show the suitable pH range of PASiC is around neutral, which is different from that of $Al_2(SO_4)_3$ in more acidic range (from 6 to 8).

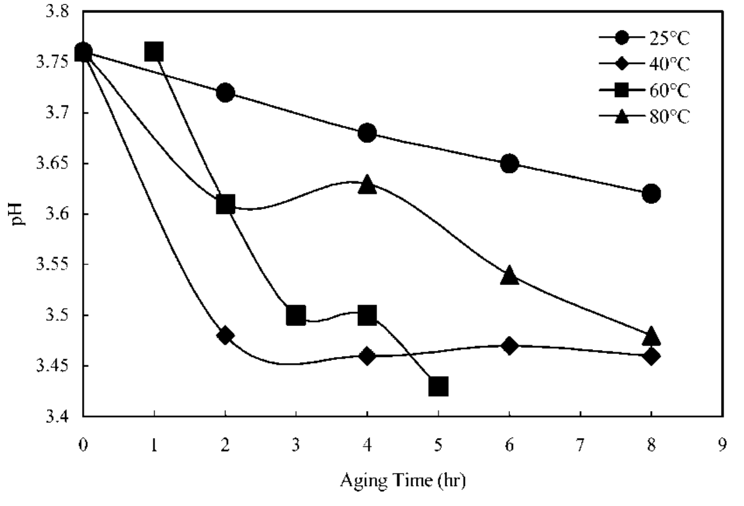

Figure 3. The effect of different aging temperatures and times on the pH of PASiC.

The practicability of PASiC was tested using the water of low turbidity and alkalinity from Min-Der reservoir. Results in Fig. 7 show that PASiC proved compatible coagulation efficiency with $Al_2(SO_4)_3$. On the other hand, a higher dosage of $Al_2(SO_4)_3$ was needed to remove the turbidity effectively. This result indicated that big molecular polymers formed after the hydrolysis of both polysicilate and aluminum, and the concentrations of monomeric and dimeric decreased. The effects of bridging and sorption enhance the coagulation and decrease the dosage of coagulant needed. Besides, the formation of polymers after the hydrolysis of aluminum produced the particles of silicate to complement the deficiency of turbidity,

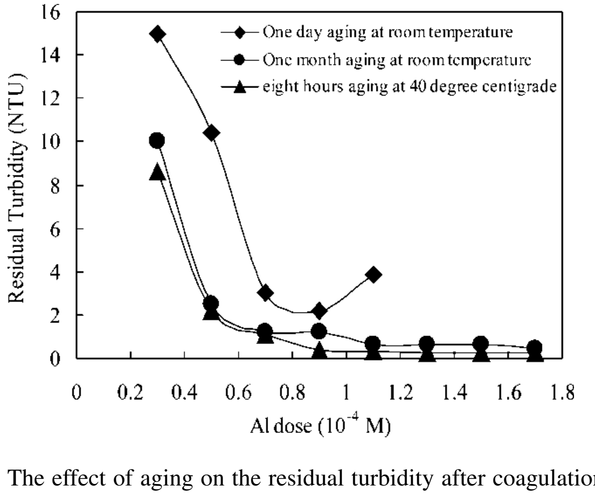

Figure 4. The effect of aging on the residual turbidity after coagulation at pH 7.

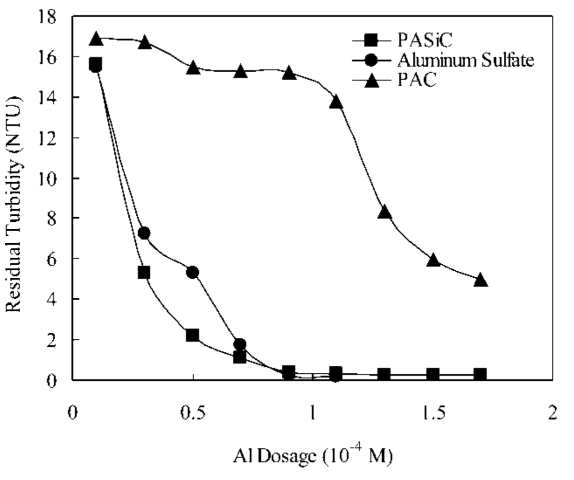

Figure 5. The relations between residual turbidities and coagulants at pH 7.

and its low electricity could adsorb the particles in the water to form precipitable floc and then lowered the turbidity (22). On the other hand, because the uptake and discharge of aluminum by living tissues are hard to regulate, toxic levels of aluminum accumulation can lead to maladies such as Alzheimer's syndrome, osteoporosis, anemia, and anorexia (7). Therefore, large residual aluminum in drinking water should be avoided. As shown in Fig. 7, all results indicate that the coagulation by PASiC has lower dissolved Al residual than by $Al_2(SO_4)_3$ and the concentration is also lower than the suggestion level of World Health Organization (0.2 mg/L or less is a practicable level for aluminium in finished water). Thus, the use of PASiC can really

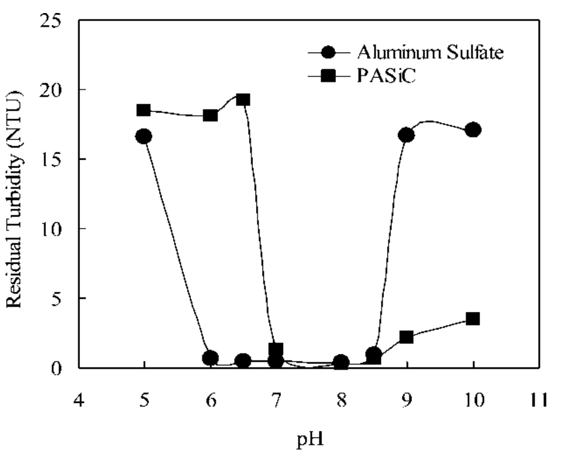

Figure 6. Comparison of the residual turbidities in different pH values (Al Dosage = 1×10^{-4} M).

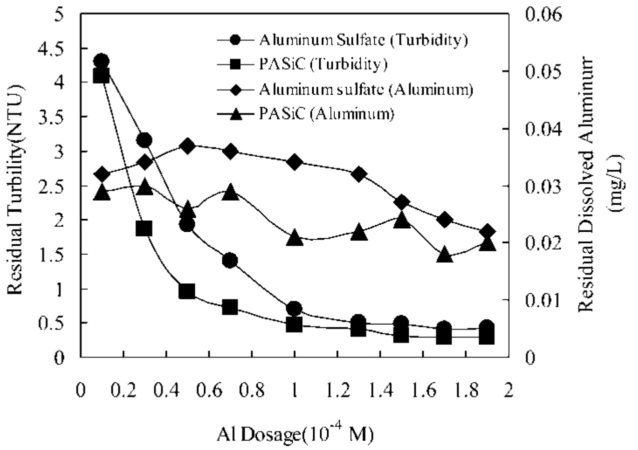

Figure 7. The changes of residual turbidities and dissolved aluminium by different coagulants.

change the concept that inorganic polymer coagulant can only be used in high turbidity water.

CONCLUSION

PASiC is a new inorganic coagulant formed by polysilicate and aluminium salt through copolymerization. The Al/Si ratio and basicity (B) should be considered in the preparation of PASiC. If the value of B is too high, the PASiC coagulant formed will be unstable, and a high amount of precipitate will be produced after the synthesis, whereas the efficiency drops down. Lowering the ratio of Al/Si can increase the polymerization of PASiC and big size of molecules will be formed, however, if it is too low, the precipitate will occur soon in PASiC preparation. The optimal values of Al/Si and B to form PASiC are 5 and 1.5 $\sim$ 2.0, respectively. The process of aging should be followed after the production of PASiC, which can increase the stability of the polymer. When aging was performed under room temperature, the time needed was longer; high temperature can enhance the aging. The aging done at 40°C shortened the time to approach stability; however, if the temperature was too high (80°C), the PASiC produced was unstable. Moreover, the comparison of three different coagulants (PASiC, PAC and $Al_2(SO_4)_3$) tested on the turbidity removal of the low turbidity synthesized water showed that PASiC has better removal efficiency and a wider pH application range (7 $\sim$ 10) than that of $Al_2(SO_4)_3$. On the other hand, if $Al_2(SO_4)_3$ is replaced by PASiC to treat the raw water of Min-Der reservoir, the coagulant dose will be less and not only will there be a higher turbidity removal, but also lower dissolved Al residual than $Al_2(SO_4)_3$ will be obtained. In conclusion, because PASiC is a promising new coagulant, much more attention should be paid to the treatment efficiency of different quality water to provide more useful information for further development of PASiC.

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