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Study on Coagulation Characteristics of Drinking Water Sources in Upper Yangtze River

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A series of coagulants such as polyaluminum chloride (PAC), polymeric ferric sulfate (PFS), aluminum sulfate (AS) and ferric chloride (FC), as well as the composite coagulants which composed with polydimethyldiallylammonium chloride (PDADMAC) were used to treat drinking water sources in the upper Yangtze river at Chongqing. pH and temperature as the two significant factors were tested. The results showed that the coagulation effect by coagulants composed with PDADMAC was improved greatly. The work of turbidity removal was good, and the effect of organics removal was poor when pH in the raw water was stable. By modifying the pH to 5, the better organics removal ratio was achieved when aluminum-based coagulants were used. Analogously when the pH ranged from 4 to 6, the better organics removal ratio was also achieved by using iron-based coagulants. When the pH was beyond 11, the organics removal ratio improved remarkably. In different seasons, the feature of raw water quality played a more important role than temperature in coagulation effects. Optimization of coagulant would be the suitable enhanced coagulation technology for current water treatment process in Chonqing.

Keywords: Coagulation, Polydimethyldiallylammonium chloride, Polyaluminum chloride, Composite coagulant.

INTRODUCTION

Coagulation is a central part of water treatment process, which plays a main role in removing colloidal particles and particulates. After coagulation, other impurities such as natural organic matter (NOM) in raw water can be removed with supressing turbidity. But remaining natural organic matter in water after treatment can lead to many potential hazards, such as producing color or smell in drinking water, encourage the growth of bacteria in water distribution system, producing disinfection by-products, increasing disinfectant dosage, *etc.*[1-3], Previous research has shown that enhanced coagulation technology such as increasing coagulant dosing quantity or controlling reaction conditions of pH can improve the removal rate of natural organic matter in water, which is also the recommended method of controlling disinfection by-products precursor by the United States environmental protection agency (USEPA) and the world health organization.

The Yangtze river is the main drinking water source of Chongqing, which is located in the three gorges reservoir area of upper reaches of Yangtze river and it has particularity of natural landscape, water quality and economic development state. On the base of other countries and regions studies[4,5,6], it is necessary to do researches on characteristics of coagulation of Yangtze river and inquire suitable enhanced coagulation technology for Chongqing area. This study reports the effect of different coagulants types, different dosing quantity, pH value and temperature on coagulating effect of raw water in the Yangtze river in Chongqing systematically, for purpose of reducing turbidity, removing of organic matter and eliminating the dangers of disinfection by-products economically, effectively and for the most part.

EXPERIMENTAL

Main instrument: ZR4-6 six jars of jar test apparatus, ZBX-4 portable turbidity meter, DR5000 ultraviolet and visible spectrophotometer, Liquid TOC II total organic carbon analyzer, SenSion3 pH meter

Polyaluminium chloride (PAC): Active ingredient Al_2O_3 content is 29.4 %, basicity is 88.3 %; Polydimethyldiallylammonium chloride (PDADMAC): solid content is 38 %, characteristic viscosity is 80-140 mL/g; Polymeric ferric sulfate (PFS), full iron content is 11 %, basicity is 8-16 %, the above three kinds of medicine are merchant industrial products. Chlorinated high iron (FC), molecular weight was 270.29; aluminum sulfate (AS), molecular weight is 666.42, the above two kinds of chemicals are analytically pure.

The configuration of composite coagulants: polydimethyldiallylammonium chloride (PDADMAC) is made into mother liquor with mass concentration of 10g/L and then compound it respectively with polyaluminum chloride, polymeric ferric sulfate, ferric chloride and aluminum sulfate four kind of coagulant to form compound coagulants. In the test, compound proportion is quality ratio of polydimethyldiallylammonium chloride and other four kind of coagulant, this test using a compound ratio of 1 %.

Experimental method: Add 1 L water samples in the six jars of jar test apparatus, respectively. Each sample was rapidly mixed at 200 revolutions per minute (rpm) for 3 min, slowly mixed at 50 rpm for 13 min and then settled (0 rpm) for 40 min. At the end of each jar test, the supernatant sample was withdrawn by syringe from about 2 cm below the water surface for testing turbidity, UV_{254}, DOC separately.

Raw water quality: The experiment with the test water obtained from the Yangtze river in Chongqing city in spring cold season and summer high temperature season in 2011, respectively and the average water quality indicators are shown in Table-1.

RESULTS AND DISCUSSION

Comparison of coagulants treatment effects: In the spring cold season of 2011, the raw water of Yangtze river was used for testing treatment effects of different coagulants. Fig. 1 showed that the different coagulants have large differences in treatment effects and when use a single coagulant polyaluminum chloride has good turbidity removal effects while polymeric ferric sulfate does well in removing organic matter.

When using polyaluminum chloride (PAC) and aluminum sulfate (AS), the dosage of 0.03 mmol/l could achieve the low turbidity of settled water, the dosage of 0.04 mmol/L could reach the deep UV_{254} value of settled water; When using ferric chloride and polymeric ferric sulfate, the dosage of 0.04 mmol/L could achieve the low turbidity of settled water, the dosage of 0.04 mmol/L could reach the deep UV_{254} value of settled water.

Therefore, the same coagulating agent, the optimal doses for treatment of organic matter are higher than the treatment of turbidity and by adding more coagulant dosage to improve the removal rate of organic matter, this is also the USEPA recommends one of the enhanced coagulation way. Fig. 2 shows that when using a small amount of the organic polymer flocculants of polydimethyldiallylammonium chloride (PDADMAC) compound with polyaluminum chloride to achieve optimal UV_{254} value, the dosage is lower than those of dosage consumption alone and the dosage on organic removal effect has been improved remarkably. So compounding with a small amount of organic polymer flocculants can give full play to its high positive charge and large surface area features, can improve the ability of electric neutralization and adsorption and can strengthen its processing efficiency[7,8].

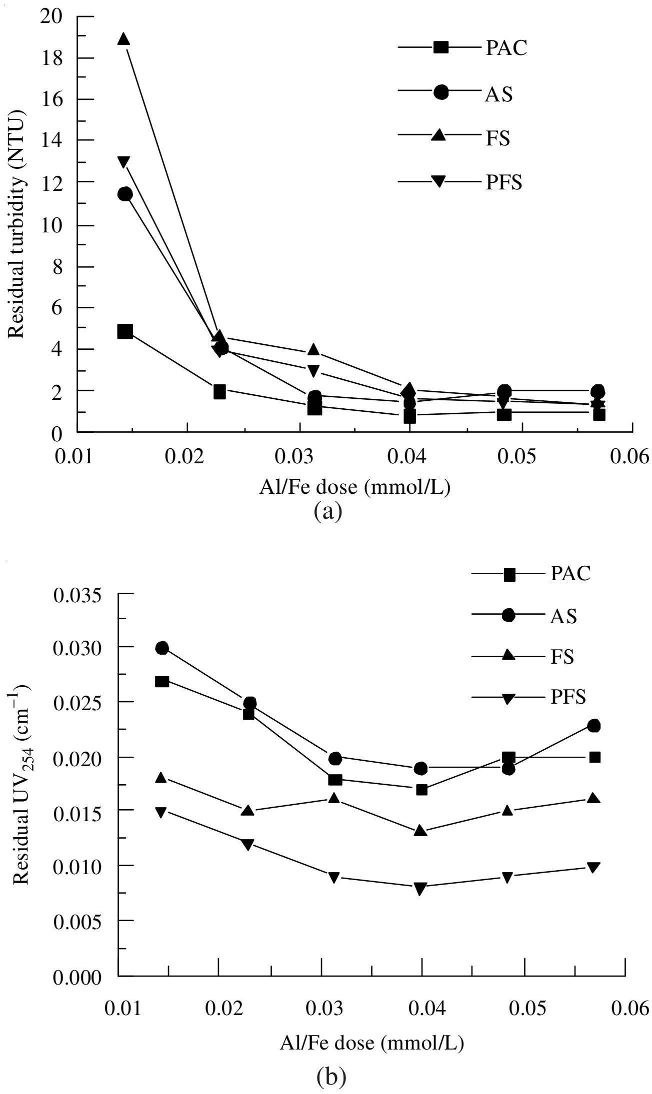

Fig. 1. Effects of single coagulants for turbidity and UV_{254} removal

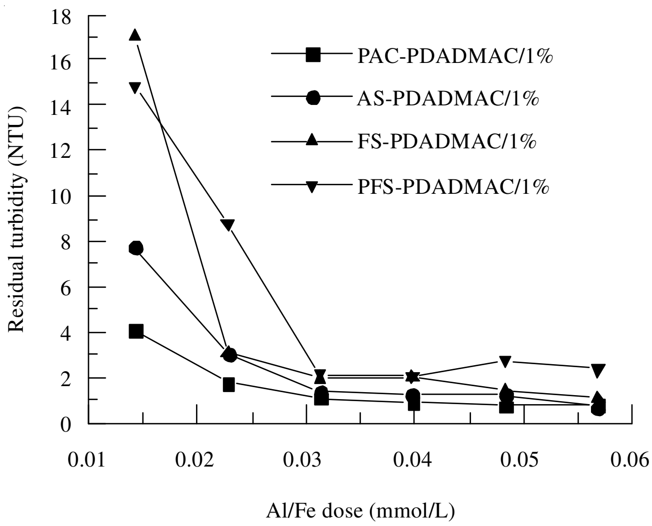

TABLE-1
TEST RAW WATER QUALITY INDICATORS

	Turbidity (NTU)	Permanganate index (COD_{Mn}) (mg/L)	Ultraviolet absorbance (UV_{254})	Temperature (°C)	pH
Low temperature seasons	35.6	1.76	0.091	10.6	7.85
High temperature seasons	678	5.12	0.054	29.6	7.98

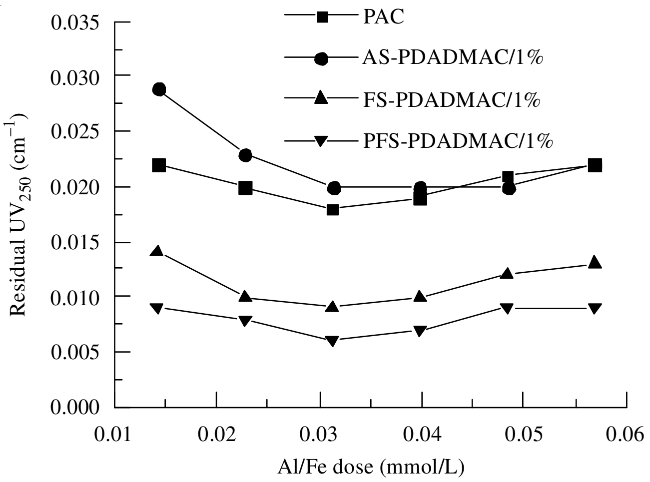

Fig. 2. Effects of composite coagulants for turbidity and UV_{254} removal

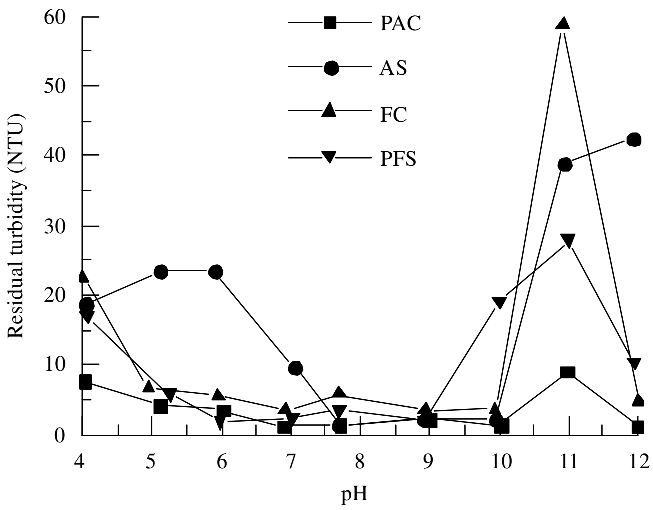

Fig. 3. Effects of pH for turbidity removal

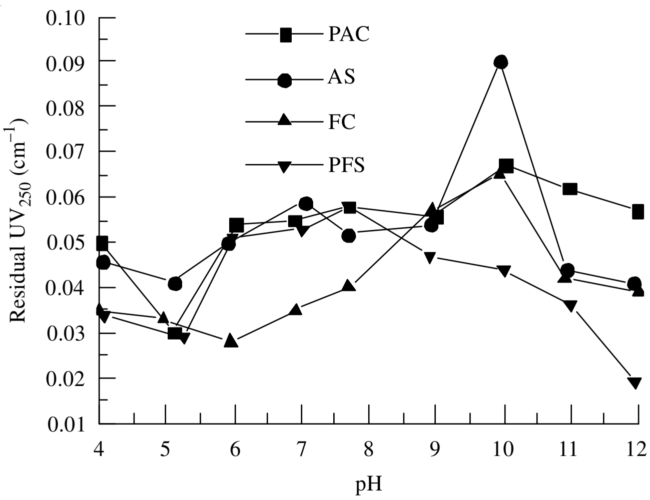

Fig. 4. Effects of pH for UV_{254} removal

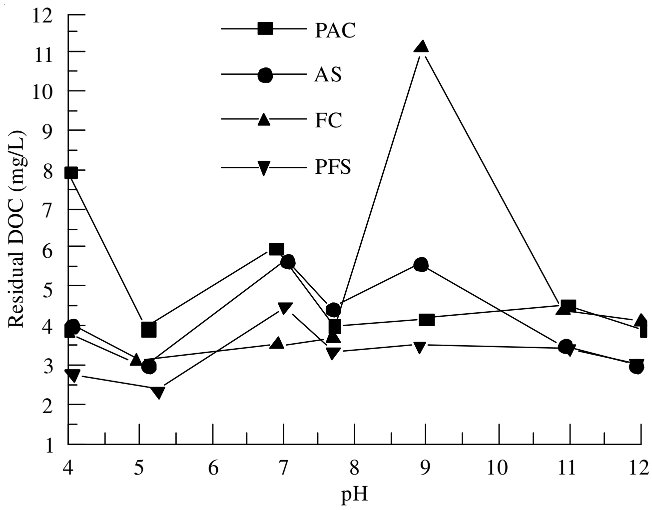

Fig. 5. Effects of pH for DOC removal

Effects of pH on coagulation: In the coagulation processes of water treatment, pH and alkalinity are main influencing factors of treatment effect. When the pH is low, the main existing form of inorganic salt coagulant in water is the type of positively-charged ions and the main reaction mechanism is charge neutralization. But with the pH increasing, inorganic salt coagulant is gradually turned into various hydroxide polymers and compounds, then the main reaction mechanism is adsorption and charge neutralization. When the pH is high enough, eventually, inorganic salt coagulant is turned into hydroxide precipitate. At this point, the main mechanism for the removal of organism is co-precipitation.

The test data in some waterworks which use the Yangtze river raw water as source water shows that the alkalinity of Yangtze river raw water is kept at about 120 mg/L and the pH is greater than 7.5 all the year, so the Yangtze river raw water has the characteristic of high alkalinity. It is well known that high-alkalinity water can replenish the OH^- additionally consumed in the hydrolysis reaction of coagulant through carbonate equilibrium in the carbonate system and this can make water maintain at high pH value and influence the hydrolysis form of coagulant. Some studies have shown that the high-alkalinity water has the poor effects of the organic matter removal[9].

In high alkalinity and hardness water treatment, if we can make a breakthrough in original traditional softened technology in which the pH of water is adjusted to 10 and adjust pH to more than 11, then it will generate $Mg(OH)_2$. It can improve the removal rate of organic matter in water by taking advantage of the characters of $Mg(OH)_2$ sedimentation (positive electricity and amorphous structure) in alkaline condition. Surely, this kind of strengthen the softening coagulation method is recommended as one of the removal methods of disinfection by-products precursor by USEPA[10].

In March 2011, the effects of polyaluminum chloride (PAC), aluminum sulfate (AS), ferric chloride (FC) and polymeric ferric sulfate (PFS) to coagulation were studied by changing the pH of raw water. The dosage of coagulant is 0.06 mmol/L (measured by the content of Fe or Al). And the test results are shown in Figs. 3-5.

The results reveal that the pH of raw water (pH is around 8) is in the best fit pH range of turbidity removal to all the coagulant. However, to different coagulant, the best fit pH range of turbidity removal has some difference as well. Compared with aluminum sulfate, the best fit pH range of other coagulant is much broader, for example, when reducing turbidity, the best fit pH for aluminum sulfate is about 7-9. But the best fit pH for polyaluminum chloride and ferric chloride is about 7-10 and for polymeric ferric sulfate is about 6-9. When the pH is low, the main form of aluminum sulfate in water is Al^{3+} and the removal of turbidity is through the static adsorption for particulate matter. But at this time, there has formed polymeride for polymeric ferric sulfate and polyaluminum chloride, so the effect resulting from pH on hydrolysis of these coagulant is much smaller. When pH is low, the removal of particulate matter by using polyaluminum chloride or ferric chloride is not only the static adsorption, but also charge neutralization, so the turbidity removal efficiency is much better. The difference at the best fit pH range between ferric chloride and aluminum sulfate may cause by the different molecular weight-Fe is higher than Al, although the main form of ferric chloride in low pH water is Fe^{3+}, the attractiveness of Fe^{3+} is much stronger than Al^{3+}. In addition, the hydrolysis product of Fe^{3+} has lower solubility than the hydrolysis product of Al^{3+} and $Fe(OH)_3$ is not the typical amphoteric compound, so it is also cause the difference in the best fit pH range.

With the pH increasing to 10 around, the turbidity has an increase as well. It is because that as the increasing of OH^-, the Ca^{2+} in natural water is turned largely into $CaCO_3$ colloid, then the turbidity rises and even exceeds the turbidity of raw water. When increasing the pH to 11, it may generate $Mg(OH)_2$ sedimentation and the sedimentation may adsorb other impurities particles, organic matter and $CaCO_3$ particles in the water, then the turbidity of water reduces significantly.

In the pH range of raw water, the removal rate of organic matter is low no matter using what kind of coagulant. The best pH value for the removal of organic matter by aluminous coagulant is about 5 and for iron coagulant is about 4-6. It is because that in the above pH range the existence form of iron and aluminum is present in poly state or low poly state compound and although the dissolved organic matter can be removed by the role of charge neutralization and adsorption. The formative flocculation is very loose can't be removed by sedimentation but can be removed by 0.45 μm micro filtration membrane. So in this pH range the turbidity of settled water is also high but the organic content decreases. However, with the pH value increasing to 6, the capacity of various coagulants for the removal of organic matter reduces gradually. This may be caused by the increasing high poly state of hydrolyses of aluminous and iron coagulant and then as the adsorption bridging play a leading role, the effects for the removal of dissolved organic matter in water is not very well.

All the organics of the submerged water starts regimenting when the pH beyond 9-10. On one hand, because of the produced hydroxide precipitate of various kinds of coagulants in alkaline environment; on the other hand, along with the pH value to further improve and beyond 11, magnesium hydroxide gradually begin to generate and these sediments are of good characters in absorption and coagulation to achieve a better removal result for organics in the water through absorption and co-precipitation mechanism.

From the experiment results, a better removal result of NTU but a less effective function on those organics can be observed when different kinds of coagulates were employed in the pH of original water. Adjustment of pH could be one of effective channels to improve the removal of organics. It can be achieved on one side by reducing the pH level to a proper range to remove the organics for various coagulants or improve the pH to the level that magnesium hydroxide came into being to achieved the removal of organic by enforcing the softening sediment on the other side. But it was not suitable to popularize its implication in Chongqing area nowadays owing to the increase cost of chemicals as well as the infrastructure in the water plant. Furthermore, it complex the operation process.

Temperature on the effects of coagulation: polyaluminum chloride and polyaluminum chloride-polydimethyldiallylammonium chloride are used in the coagulation experiments, respectively, in the early spring cold seasons and summer hot season and the results are shown in Figs. 6 and 7. Many studies show that temperature has a great influence on the coagulation effect[11]. When the water temperature is low, the ion product of water constant is also low; OH^- is less as well, at the same time, metal salt hydrolysis is less entirely, the hydrolysis rate is also slower. Polyaluminum chloride already partially hydrolyzed before dosing, it's hydrolyzed affected by temperature after dosing less than aluminum sulfate's impact.

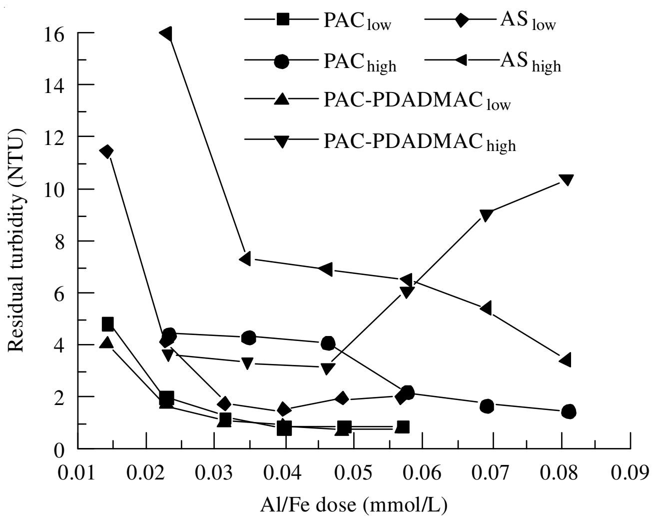

Fig. 6. Effects of temperature for turbidity removal

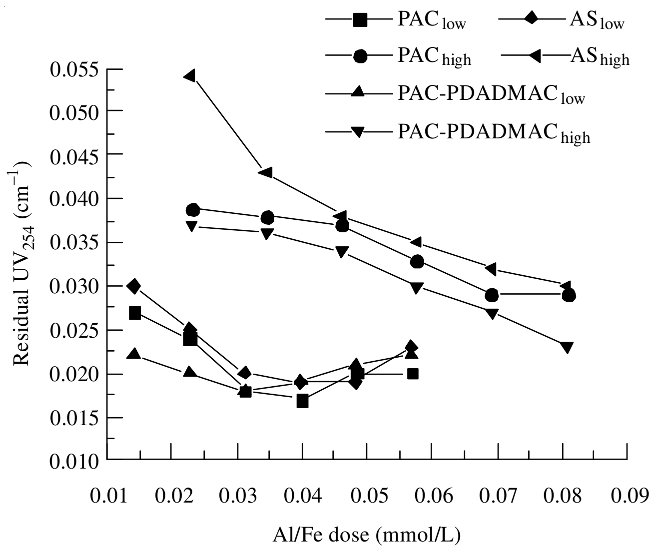

Fig. 7. Effects of temperature for UV_{254} removal

Therefore, the polyaluminum chloride treatment effect in cold seasons with a low dosage is significantly better than aluminum sulfate, while in the hot season this advantage is not obvious. The test results show that to achieve better treatment effect in the hot season the polyaluminum chloride, aluminum sulfate and polyaluminum chloride-polydimethyldially-lammonium chloride dosages are higher than in cold seasons. This is due to higher turbidity in summer Yangtze water caused by heavy rain and other reasons and then the COD_{Mn} in the water is also higher than before. As a result, drug consumption increased compared to the low temperature seasons. Consequently, the effect of water quality conditions on coagulation is more obvious compared with the impact of temperature effects.

Conclusion

When using four kinds of coagulant of the polyaluminum chloride, polymeric ferric sulfate, aluminum sulfate and ferric chloride to treat raw water in the Yangtze river in Chongqing, it is known that the turbidity removal effect of polyaluminum chloride is good, polymeric ferric sulfate in removing organic effect is good and no matter what kind of coagulant is used, when compounding with polydimethyl-diallylammonium chloride, coagulation efficiency are improved greatly. In the raw water pH condition, the turbidity removal effect are better, while the organic matter removal effect is poorer. By adjusting the pH, the optimal pH for aluminum coagulants to remove organic matters in the Yangtze river water is 5 or so. And the optimal pH for iron coagulants to remove organic matters is 4-6 or so. When at the pH more than 11, generating $Mg(OH)_2$ precipitation, organic matter removal rates greatly improve. In different seasons, the raw water quality conditions have a stronger influence on coagulation effects than temperature.

For the main urban areas of Yangtze river Chongqing raw water, organic matter removal rate can be increased through coagulants optimization, lowering pH to the optimal pH range of various coagulants or increasing pH to strengthening the softening precipitation. Currently in Chongqing water plant, the best way to enhance coagulation, under the condition of reaction process and water quality is to find optimum coagulant.

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