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ИССЛЕДОВАНИЕ ЭЛЕКТРОКИНЕТИЧЕСКИХ ПАРАМЕТРОВ КОМПОЗИЦИОННЫХ КОАГУЛЯНТОВ-ФЛОКУЛЯНТОВ

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В работе проведено систематическое исследование электрокинетических параметров композиционных коагулянтов-флокулянтов, полученных на основе комбинации полиалюминия хлорида (оксихлорида алюминия) и органических полимеров. Экспериментальные результаты, полученные с помощью метода измерения потока тока и метода электрофореза, свидетельствуют о том, что комбинация полиалюминия хлорида и катионного органического полимера может эффективно повысить способность нейтрализации заряда. Приведённые данные прямо указывают на то, что в результате комбинирования полиалюминия хлорида и катионного органического полимера положительный заряд частиц взвеси заметно увеличивается, благодаря чему характеристики двойного электрического слоя на твердой поверхности с отрицательным зарядом улучшаются. Наиболее важным фактором является усиление способности композиционного коагулянта к нейтрализации заряда, в этой связи эффективность применения композиционного реагента выше по сравнению с эффективностью полиалюминия хлорида. Кроме того, благодаря наличию длинной молекулярной цепи, добавление катионного органического полимера в полиалюминия хлорид может усилить мостиковую коагуляцию частиц. Результаты эксперимента показывают, что при смешивании полиалюминия хлорида с природным катионным органическим полимером - хитином и промышленным катионным органическим полимерным продуктом С109Р, его электрический заряд может быть значительно повышен. Этот факт, несомненно, заслуживает внимания при разработке составов коагулянтов-флокулянтов для улучшения их способности к нейтральности заряда в процессах коагуляции и агломерации частиц взвеси. При проведении эксперимента по использованию анионных органических полимеров за основу принимали положение теории коагуляции-флокуляции о том, что основной функцией анионного органического полимера в композитном реагенте является функция мостика между твердыми частицами. При этом эффективное воздействие на данное свойство системы вряд ли может привести к снижению способности нейтрализовать заряд полиалюминия хлорида. Экспериментальные данные, касающиеся исследования композиционного реагента, содержащего полиалюминия хлорид и промышленные анионные органические полимерные продукты AH200P и AN910SH, подтверждают тот факт, что такая комбинация не приводит к снижению способности нейтрализации заряда.

Ключевые слова: коагуляция, флокуляция, электрокинетические параметры, метод измерения потока тока, метод электрофореза, полиалюминия хлорид, катионные и анионные органические полимеры

STUDY ON ELECTROKINETIC PARAMETERS OF COMPOSITE COAGULANTS-FLOCCULANTS

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In this work the electrokinetic parameters of composite coagulants-flocculants based on combination of polyaluminum chloride (aluminum oxychloride) and organic polymers were studied systematically. The experimental results, obtained by the streaming current and electrophoresis methods, witness that the combination of polyaluminum chloride and cationic organic polymer can effectively enhance the charge neutrality capacity. The results obtained directly indicate that after the combination of polyaluminum chloride and cationic organic polymer, the positive charge of suspended particles obviously enhances, and the ability of double electrical layer on solid surface with negative charge improves. The most important factor is that the charge neutrality capacity of composite coagulant is stronger, thus, in comparison with polyaluminum chloride efficiency, the efficiency of composite reagent is higher. Moreover, due to the existence of long molecular chain, adding cationic organic polymer into polyaluminum chloride can enhance the bridging coagulation between its particulate matters. The experimental results indicate that if to combine polyaluminum chloride with natural cationic organic polymer - chitin and industrial cationic organic polymer product C109P, its electric charge can be largely enhanced This fact undoubtedly deserves attention when developing compositions of coagulants-flocculants to improve their ability to charge Lei Sun, Hui Zhao, Heng Zhong, Dongsheng Xia, A.V. Nevsky

neutrality in the processes of coagulation and agglomeration of suspended particles. When executing experiment on the use of anionic organic polymers, the regulation of the coagulation-flocculation theory that the main function of an anionic organic polymer in a composite reagent is the function of a bridge between solid particles was taken as a basis. At the same time, an effective influence on this property of the system can hardly lead to a decrease in the ability to neutralize the charge of polyaluminium chloride. Experimental data relating to the study of the composition reagent containing polyaluminium chloride and industrial anionic organic polymer products AH200P and AN910SH, confirm the fact that this combination does not reduce the ability to neutralize the charge.

Key words: coagulation, flocculation, electrokinetic parameters, streaming current technique, electrophoresis method, polyaluminum chloride, cationic and anionic organic polymers

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INTRODUCTION

Coagulation and flocculation techniques are widely used in natural and wastewater treatment. Despite sharing of these technologies there is difference between coagulation and flocculation processes. To coagulate means to curdle and it basically refers to a chemical process in which the destabilization of nonsettleable particles takes place. These particles form clumps with the help of a coagulant. On the other hand, flocculation means to form flocs. It can be described as a physical or a mechanical process in which the coagulated clumps or flocs are joined together to form masses as a cloud and then a precipitate. In coagulation, the forces responsible for keeping the particles apart after they contact, are reduced. Flocculation brings the de-established colloidal particles together and they form large aggregates. Coagulation is achieved by neutralizing the particles and thus, the repelling force between the particles is greatly reduced. After employing the flocculation process, the coagulated particles form a large agglomeration, which is also known as floc.

In general, coagulation can be easily achieved with the help of such coagulants as, e.g. inorganic salts of aluminum or iron. These salts neutralize the charge on the particles that are responsible for water turbidity. These salts also hydrolyze to form insoluble precipitates entrapping the particles. While flocculation occur these agglomerations of destabilized particles take the form of large particles which settle down, and this result can be achieved by adding to water the high molecular weight, water soluble organic polymers. For water treatment, the step of coagulation is generally followed by step of flocculation. One of the urgent tasks of advanced coagulants and flocculants development is the investigation of the combination methods of these reagents. Therefore, the research of new type of efficient reagent by the combination of commonly used polyaluminum chloride and some organic polymers has significant meaning and was the task of this R&D.

The study on the process that coagulant or its hydrolysate acts on the surface of colloid to cause destabilization is one of the core problem concerning basic investigation of coagulants. Coagulation process actually includes two successive processes: coagulant or its hydrolysate absorbs charge neutralization on the surface of particulate matter to make the colloid lose stability, which is called condensing process; the relevant colloidal particle gradually forms larger floc through mutual collision or coagulant and its hydrolysate's bridging action under the certain hydraulic condition, which is called coagulation process [1, 2]. Generally speaking, coacervation process is the necessary premise of coagulation process; if there is no fine destabilization of colloidal solids, coagulation processes is hard to be happen or form the larger floc. Under normal conditions, various aquatic particles bring negative charge, so if the coagulant wants to achieve the goal that makes destabilization for particulate matter to implement charge neutrality, it has to have the certain positive charge [3, 4]. According to DLVO theory (which is named after Boris Derjaguin and Lev Landau, Evert Verwey and Theodor Overbeek), colloidal critical coagulation concentration is inversely proportional to sixth power of ionic charge valence number [5-7]. Therefore, in order to improve aggregation efficiency and to save reagent dosage, searching the coagulant with positive charge as high as possible becomes the main goal of the R&D regarding this aspect [8-10].

The present researchers consider that the best flocculation species in PAC is Al₁₃, namely, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. Compare to traditional aluminum salt, when it gets the best condensation (electrophoresis value (mobility) of colloidal solids, EM), the dosage of PAC can be decreased 50-60% [11]. This kind of effective agglomeration of PAC is closely related to higher positive charge of Al₁₃. Of course, it is necessary to make the synergistic effect in the process of condensation and coagulation if want to realize the fine coagulate effect [12]. The efficiency of coagulation process generally requires the substance own higher molecular weight; although compared to traditional aluminum salt, PAC's apparent molecular weight has improved (PAC's mid grain size with 2.5 of degree of alkalization(B) is more than 10 nm and can reach to 58%), compared to polymerized silicate and organic polymer, its molecular weight is much smaller [13]. So in order to enhance the bridging coagulability of PAC, developing various composite coagulants becomes a kind of reasonable development trend based on PAC. The correct proportion for each component in composite coagulant is one of the ivestigation goals [14, 15].

Each component in composite coagulant will make the contribution to overall structure and cohesion-coagulation efficiency, but the function on different aspects may have positive and negative effect [16]. Therefore, factors that need to be considered when studying complex flocculants must focus on strengthening an effect without causing adverse effects or controlling adverse effects to a limited extent [17]. The study of bringing the polysilicic acid into PAC and PFC (Polymerization Ferric Chloride) to prepare compound type of organic polymer coagulant has already was indicated that due to polysilicic acid itself has negative charge, the introduction will make the PAC and PFC charge neutrality capacity reduce, but under the proper proportion, the advantage brought by its enhancement for bridging coagulation of PAC and PFC is more than the loss, and the comprehensive result is positive effect [18]. The recombination of organic polymer (OP) and PAC also has the problem about the influence of OP and PAC on charge neutrality capacity [19, 20].

In this research we use the electrophoretic technique and streaming current to measure the technology parameters, to compare PAC and electric characters of various types of PACP, discuss the influence of different types of OP on charge of PAC, and make the further analysis on the influence of cationic organic polymer (COP) on PAC condensation-coagulation process [21-23].

EXPERIMENTAL

The equipment

The major instruments were the SC-3000 type of Streaming Current Detector (SCD), ZD-100 type of agitator and Malvern Mastersizer-3000 type laser diffraction particle size analyzer.

The materials

The major materials include PAC, kaolin and organic polymer. The kaolin used in this experiment was taken from Henan province of China with an average grain size of 1.28 μ m and about 16 m²/g surface square. Organic polymer includes the cationic organic polymer and anionic organic polymer. Coagulant with cationic organic polymer (COP) was used. The source of natural cationic polyacrylamide (CPAM) with cationic organic polymer is chitin, the molecular weight is 8-12 million, and the COP that has the code of industrial product as C109P, it was made by Japan Lanyang Huacheng Joint-stock Company (SANFLOC). Coagulant with anionic organic polymer (AOP) was used by us too. The AOP has the code of industrial product as AH200P which is made by Japan Sanyang Huacheng Joint-stock Company (SANFLOC) and it has the code of industrial product as AN910SH which was made in France.

The investigated coagulant-flocculant was made by our team, and the method are as follows: to put 100 mL 0.2 mol/L AlCl₃ solution into beaker, under the quick magnetic stirring, then slowly drop organic polymer solution to the predetermined organic polymer/aluminum (O/A) proportion, and then drop 0.5 mol/L NaOH solution at speed of 0.04 mL/min, finally to record the volume of alkali liquor used.

The procedure of preparation of turbid liquid and experimental method of coagulation process was as follows. We've used simulated water samples contained 100 mg/L of kaolin. The measurement of turbidity was executed by pipette transfer to probe the supernate under 2 cm of the surface and measurement of the rest turbidity.

The methods

Electrophoresis method was used to make the experimental representation for charge characteristics of COP

It was used deionized water and kaolin to make 100 mg/L turbid liquid, and then NaHCO₃, NaNO₃ and HCl were used to adjust ion strength as $1 \cdot 10^{-3}$ mol/L and pH value as 6.50. We put the certain volume of above turbid liquid into beaker, and under the high-speed stirring quantitatively adding of COP water solution was made; after 2 min time interval we examine the samples at relevant electrophoresis mobility, EM

 $(\mu m \cdot cm/(s \cdot V))$ measured by laser electrophoresis apparatus. At the same time we make comparison for cationic (COP) and non-ionic (NOP) polymers.

Experiment of coagulation and measurement of the ζ *electric potential*

The procedure of coagulation experiment was as putting the substance in 800 mL beaker of water under 150 rpm of quick stirring, continue to make quick stirring for 1 min, and the sample ζ electric potential of particulate matter measurement by Malvern Mastersizer-3000 type laser diffraction particle size analyzer, and then slowly stir it at 40 rpm for 15 min, finally stop stirring and make steady depositing for 15 min.

RESULTS AND DISCUSSION

Streaming current character of PACP

In water treatment technology, the traditional index to measure is the degree of elimination of colloid stability, i.e. ζ -electric potential. But the measurement of ζ -electric potential is more difficult with higher precision, and it is difficult to make online continuous detection. In recent years, streaming current (SC) technique is gradually widely used for researching electrical property of coagulant and the interaction of coagulant for the colloidal particle surface. Streaming current and ζ electric potential are both related to the double electrode layer of solid surface: ζ electric potential is under the electric field action, solid is relative to quiet liquid move, and the electric potential generated on sliding surface between slide and liquid; streaming current is generated by relative movement between adsorbed layer and diffusion layer under the exogenous process. Theoretical research indicates that under the outside pressure, there is following relationship between ζ – electric potential generated form flow of capillary tube and streaming current:

$$I = \pi \epsilon p r^2 \zeta / (\eta l) \tag{1}$$

1)

where: I – streaming current, p – pressure difference on the both sides of capillary tube, r – radius of capillary tube, ϵ – permittivity of water; η – viscosity of water, l – length of capillary tube.

If bring Ohm law into above formula, we can get the expression of streaming potential:

$$\mathbf{E}_{s} = (\mathbf{p} \epsilon \zeta / (\eta) \left[1 / (\mathbf{L}_{0} + 2\mathbf{L}_{s}/\mathbf{r}) \right]$$
(2)

where: E_s – streaming potential; L_0 – conductivity of water; L_s – conductivity of surface of water.

The equations (1) and (2) reveal the inner relationship between ζ electric potential and streaming current and streaming potential to explain two of them are the descriptions for the same essential phenomenon and different sides, and under the certain experimental condition, the streaming current (or streaming potential) and ζ electric potential have linear relation.

Streaming current character of coagulant combined by PAC and COP (PACPc)

The Fig. 1 and Fig. 2 respectively illustrate the changes of response value of streaming current (SC) with the adding concentration after putting PAC, its chitin, and C109P's copolymer coagulant PACP into water. Due to it does not put particulate matter into another one, so initial response value of SC is surface structure charge of SCD's piston and sleeve, and streaming current generated from double electrode layer of special ion in adsorption water. From the data illustrated by these figures we can see the following. 1) With the increase of the adding amount, the SC value of various coagulants all increase relatively, and they all gradually turns to positive value from negative value. 2) Under the condition that additive dosage of aluminum is quite, the SC response value of PACPc is obviously larger than the PAC, and the larger the O/A ratio (O – organic polymer, A – aluminum), the bigger the SC response value. On the contrary, when the SC reaches to the same response value, PACPc's dosage is less than PAC, and the dosage of PACPc with large O/A ratio is less than the small O/A ratio. The results for the state (SC = 0) that reaches to the isoelectric point as an example, the dosage of PAC and two types of PACP are shown in Table 1.

Table 1

| The composition | change of chitin, | PAC and PACPc in |
|-----------------|-------------------|------------------|
| | isoelectric poin | ıt |

Таблица 1. Изменение содержания хитина, РАС и РАСРс в изоэлектрической точке

| Parameter | Chitin/PAC | | | C109P/PAC | | |
|-----------|------------|------|------|-----------|------|------|
| O/A | 0 | 0.10 | 0.20 | 0 | 0.05 | 0.10 |
| Dosing | 5.63 | 3.97 | 3.18 | 5.70 | 4.27 | 3.84 |





Рис. 1. Изменение величины потока тока (SC) в зависимости от состава системы (хитин-РАСРс) и концентрации Al



Fig. 2. The changes of streaming current (SC) values vs. system composition (C109P -PACPc) and Al concentration Рис. 2. Изменение величины потока тока (SC) в зависимости от состава системы (C109P -PACPc) и концентрации Al

The above result directly verifies that after the recombination of PAC and COP, the positive charge obviously enhances, and the ability of double electrode layer on solid surface with negative electricity obviously improves. Thus, we can think that compared to PAC coagulation efficiency, PACPc will be higher, and one important factor is that charge neutrality capacity of composite coagulant is stronger.

In order to further discuss the mutual influence between charges of two elements in PACPc, it considers that bring few PAC into COP solution to make the composite coagulant with the main element of COP (recorded as PPAC). The weight ratio of total aluminum and organic matter can be recorded as A/O, and then we've used SCD to measure the character of streaming current (the results are shown in Fig. 3 and Fig. 4. From the data of these figures, we can see the following. 1) The SC response value of COP and the composite product of it and PAC increases with the increase of adding dosage. 2) Compared with the COP, when the adding dosage (expressed as COP) is same, PPAC with the introduction of PAC has higher SC value. When it reaches to zero electric point, adding dosage of PPAC with COP and different O/A ratio are shown in Table 2. We can find that at this time, the PPAC (PAC/chitosan) dosage with A/O = 0.10 is 56.7% of chitin, and the PPAC (PAC/C109P) dosage with A/0 = 0.10 is 76.7% of C109P. 3) When the adding dosage is the same, SC value will not has proportional increase with the enlargement of A/O, for example, for the recombination of C109P and PAC, when A/O ratio is between 0 and 0.10, the SC value has sharply increase, but when A/O is between 0.10 to 0.20, SC value slightly increase. 4) Compared to chitin and C109P, they need very different dosage for reaching to same SC value, at the isoelectric point, the dosage of chitin is about six times of C109P, which verifies that cation property of C109P is much stronger than chitin.

Table 2 The composition change of chitin, C109P and PAC in isoelectric point

Таблица 2. Изменение содержания хитина, С109Р и РАС в изоэлектрической точке

| Parameter | PAC/Chitin | | | PAC/C109P | | | | | |
|-----------|------------|------|------|-----------|------|------|--|--|--|
| O/A | 0 | 0.10 | 0.20 | 0 | 0.05 | 0.10 | | | |
| Dosing | 7.12 | 4.04 | 3.64 | 1.20 | 0.92 | 0.86 | | | |



Fig. 3. The changes of streaming current (SC) values vs. system composition (chitin-PPAC) and chitin concentration Рис. 3. Изменение величины потока тока (SC) в зависимости от состава системы (хитин-PPAC) и концентрации хитина



Fig. 4. The changes of streaming current (SC) values vs. system composition (C109P-PPAC) and C109P concentration Рис. 4. Изменение величины потока тока (SC) в зависимости от состава системы (C109P-PPAC) и концентрации C109P

The experimental results indicate that if the PAC combines with cationic organic polymer chitin and C109P, its electric charge can largely enhance, and this is undoubtedly good for improving charge neutrality capacity in the process of agglomeration and coagulation. However, after recombination of two types of them, their charges has no simply added relationship, so O/A ratio should control in a proper range to make the OP van effectively enhance the charge neutrality Lei Sun, Hui Zhao, Heng Zhong, Dongsheng Xia, A.V. Nevsky

capacity. Of course, in the process of agglomeration and coagulation, the introduction of OP still can enhance the bridging capacity of PAC, which needs further experimental research.

Streaming current character of coagulant combinated by PAC and AOP (PACPa)

The two types of anionic organic macromolecule AH200P and AN910SH detect streaming current respectively with PAC (B = 42%) through different O/A ratio after recombination. The data of Table 3 show the change of PAC near isoelectric point and PACPa's SC response value with the adding concentration. We can see from the data in the table that when the PAC and the PACPa with different O/A ratio have the same dosing quantity (calculated as Al), their SC value has no change. In order to make the comparative analysis easy, it makes linear regression treatment for data in Table 3 to calculate the relevant dosage of PAC and various types of PACPa in isoelectric point; refer to Table 4. We can see from Table 4 that in the isoelectric point, dosage of PAC is mostly same as relevant PACPa, namely, the discrepancy is less than 5% (the difference between AH200P and AN910SH is caused by the difference of experimental condition).

The above results indicate that the introduction of AOP hardly has impact on SC response value of PAC, but this can't ensure that AOP has no influence on charge of PAC. In order to further analyze this phenomenon, it takes electrophoresis method to make the experimental representation for charge property of AH200P, and the results are shown in Fig. 5.

Table 3

The streaming current response value of the composite PACP, PAC and AOP near the isoelectric point *Таблица 3.* Величина отклика потока тока композиционных составов РАСР, РАС и АОР вблизи изоэлектри-

| Al(mg/L) | AH200P/PAC | | | | AN910SH/PAC | | | |
|----------|------------|------------|------------|------------|-------------|------------|------------|------------|
| | O/A = 0 | O/A = 0.01 | O/A = 0.02 | O/A = 0.04 | O/A = 0 | O/A = 0.01 | O/A = 0.02 | O/A = 0.04 |
| 4.6 | -0.20 | -0.16 | -0.19 | -0.18 | -0.44 | -0.40 | -0.40 | -0.40 |
| 5.1 | -0.10 | -0.08 | -0.09 | -0.09 | -0.31 | -0.28 | -0.30 | -0.28 |
| 5.6 | -0.02 | 0.02 | -0.01 | -0.01 | -0.19 | -0.16 | -0.17 | -0.15 |
| 6.1 | 0.05 | 0.08 | 0.07 | 0.06 | -0.09 | -0.07 | -0.06 | -0.06 |
| 6.6 | 0.13 | 0.16 | 0.16 | 0.15 | 0.00 | 0.02 | 0.00 | 0.02 |
| 7.1 | 0.19 | 0.21 | 0.21 | 0.19 | 0.07 | 0.09 | 0.08 | 0.09 |
| 7.6 | 0.23 | 0.26 | 0.26 | 0.24 | 0.16 | 0.18 | 0.16 | 0.17 |

Table 4

The composition change and linear regression correlation coefficients (R) of PAC with PACPa in isolectric point *Таблица 4*. Изменение состава и коэффициенты линейной регрессии (R) для PAC и PACPa в изоэлектрической точке

| ской точке | | | | | | | | |
|-----------------------|------------|--------|--------|-------------|--------|--------|--------|--------|
| Parameter | AH200P/PAC | | | AN910SH/PAC | | | | |
| O/A | 0 | 0.01 | 0.02 | 0.04 | 0 | 0.01 | 0.02 | 0.04 |
| D ₀ (mg/L) | 5.82 | 5.61 | 5.71 | 5.74 | 6.68 | 6.65 | 6.65 | 6.57 |
| R | 0.9936 | 0.9934 | 0.9939 | 0.9934 | 0.9947 | 0.9966 | 0.9966 | 0.9928 |





We can see from Fig. 5 that the three types of OP charge characters has obvious difference. The C109P increases with the increase of dosing quantity. Electrophoresis mobility of particulate matter gradually rise and show stronger cationic characteristic. The N505P increases with the increase of dosing quantity, and EM has no obvious change and show the non-ionic character; AH200P increases with the increase of dosing quantity, and its EM decreases slowly and show certain anionic character. The comparison of their charge character is shown in Table 5.

In this table ΔEM is the increment of OP from 0 to 0.2 mol/L is the increment of EM; I is the relative charge density, expressed as the ratio of the absolute

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| T | able 5 |
|--|--------|
| Comparison of charge characteristics of several or | ganic |
| polymers | |

Таблица 5. Сравнение характеристик заряда некоторых органических полимеров

| Parameter | C109P | N505P | AH200P |
|-----------|-------|-------|--------|
| ΔΕΜ | 2.60 | 0.22 | -0.54 |
| Ι | 11.8 | 1 | 2.45 |

value of ΔEM to the absolute value of ΔEM of N505P, i.e. I = $|\Delta EM|/|\Delta EM|_{N505P}$.

As shown in Fig. 5, AH200P has negative charge, but its electric density is not high, also, its influence on surface charge of particulate matter are less obvious than cationic C109P. Therefore, we can think that AOP's influence on SC response value of PAC does not generate obvious influence, and the reasons are possibly as follows. 1) Anionic degree of hydrolysis with organic polymer is generally lower (generally is 20-30%), and molecular chain has less groups with negative electricity after dissolution; generally, the electric density is less. 2) The main content $Al_{13}[(Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}]$ in PAC has strong positive charge. 3) When the organic polymer recombines with PAC, the proportion of introduction is less.

However, AOP is the content with negative charge after all, so its introduction necessarily makes positive electricity of PAC reduce; due to the limitation of sensitivity of streaming current detector, this slight influence can't display.

As seen from theory of flocculation, the main function of AOP in composite coagulant is bridging function between particulate matters, and the effective development of this function should be not likely to sharply reduce charge neutrality capacity of PAC. Experimental study about the streaming current character of PAC, AH200P and AN910SHcomposite coagulant verifies that the recombination of PAC and AOP will not make its charge neutrality capacity reduce, which provides the possibility for compounding composite coagulant with high-effect in organic and organic polymer.

Charge character of PACPc and the relationship between it and cohesive coagulating property

In the above, the streaming current experiment was undertaken to express the electric charge character of PACPc and PACPa. Compared with PAC, the positive charge of PACPc obviously enhances, but the influence of AOP on positive charge of PAC is relatively less. In order to further investigation the relationship between electric charge character of composite coagulant of PAC and COP, and condensation and coagulation property, the following experiment studies PAC with different degree of alkalisation B, and the relationship between the change of ζ -electric potential during reaction between PACPc and particulate matter, and rest turbidity. We've made the experiment of coagulation and measured the ζ electric potential. Fig. 6, 7, 8 represent the data respectively for AlCl₃, PAC (recorded as PAC10) with B = 1.0, and PAC (recorded as PAC18) with B = 1.8, and ζ electric potential of PACPc with recombination of C109P, and the experimental results concerning the dosage of rest turbidity. According to the changeable trend of dosage, each curve shown in figure can be divided into three zones, namely: I) the zone with no clear condensation and coagulation; II) condensation and coagulation; III) re-stability zone. Compared with ζ potential curve and residual turbidity curve in the figure, and the comparison between B value series, we can find the following characteristic features. 1) With the increase of additive dosage, PAC with different B and its relevant ζ electric potential of PACPc are all show the gradually increasing trend, and they will turn to positive value from negative value when get the certain additive dosage; at the same time, the residual turbidity also reduces with the increase of the ζ electric potential, and it reaches to the minimum value when the ζ electric potential is near to the zero. 2) In the scope of additive dosage used for experiment, residual turbidity of $AlCl_3$ with B = 0 and its composite product has no obviously increasing trend when they have large dosage, but B = 1.0 and B = 1.8 series of residual turbidity begin to rise when they have large dosage, and this kind of trend for latter is larger than the former. 3) When the dosage (expressed as Al) is same, ζ electric potential of particulate matter related to PACPc is higher than AlCl₃ and PAC, and then larger the O/A ratio, the higher the relevant ζ electric potential. The above contents indicate that condensation and coagulation of composite product of PAC and C109P basically accord with mechanism of adsorption and charge neutralization. In addition, in the process of experiment, when observe the speed of forming floc and settling velocity of floc, it finds that PAC with high B is better than the PAC with low B, and organic compound type is superior to that of aluminum salt or PAC, also, the higher O/A ratio is better than the lower O/A ratio.

The experiments by streaming current and electrophoresis both prove that the recombination of PAC and COP can effectively enhance its charge neutrality capacity. Moreover, due to the existence of long molecular chain, bringing COP into PAC can enhance



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Fig. 6. Coagulation and flocculation characteristics of AlCl₃ and C109P composite coagulant: a) zeta potential vs. Al concentration; b) residual turbidity vs. Al concentration

Рис. 6. Коагуляционно-флокуляционные характеристики AlCl₃ и композиционного коагулянта C109P: a) дзета-потенциал в зависимости от концентрации Al; б) остаточная мутность в зависимости от концентрации Al



Fig. 7. Coagulation and flocculation characteristics of PAC10 and C109P composite coagulant: a) zeta potential vs. Al concentration; b) residual turbidity vs. Al concentration.

Рис. 7. Коагуляционно-флокуляционные характеристики РАС10 и С109Р композиционного коагулянта: а) дзета-потенциал в зависимости от концентрации Al; б) остаточная мутность в зависимости от концентрации Al



Fig. 8. Coagulation and flocculation characteristics of PAC18 and C109P composite coagulant: a) zeta potential vs. Al concentration; b) residual turbidity vs. Al concentration Puc. 8. Коагуляционно-флокуляционные характеристики PAC18 и C109P композиционного коагулянта: a) дзета-потенциал в зависимости от концентрации Al; б) остаточная мутность в зависимости от концентрации Al

CONCLUSION

The experimental results, obtained by the streaming current and electrophoresis methods, prove that the combination of polyaluminum chloride and cationic organic polymer can effectively enhance the charge neutrality capacity. Adding the cationic organic polymer into polyaluminum chloride can enhance the bridging coagulation between its particulate matters.

The combination of polyaluminum chloride and cationic organic polymer enhances the positive charge, and the ability of double electrode layer on solid surface with negative electricity improves. The most important factor is that the charge neutrality capacity of composite coagulant is stronger, thus, in comparison with polyaluminum chloride efficiency, the efficiency of composite reagent is higher. Moreover, due to the existence of long molecular chain, adding cationic organic polymer into polyaluminum chloride can enhance the bridging coagulation between its particulate matters.

The data obtained, indicate that if to combine polyaluminum chloride with natural cationic organic polymer – chitin and industrial cationic organic polymer product – C109P, its electric charge can be largely enhanced. This fact is undoubtedly positive for improving charge neutrality capacity in the process of agglomeration and coagulation as a whole.

The experimental results concerning investigation the composite reagent containing polyaluminum chloride plus industrial anionic organic polymer products – AH200P and AN910SH verify that there combination will not make the charge neutrality capacity reduced.

In general we hope that this work's results will be another contribution [24] to practical application at the stage of design water resource-saving chemical processes at textile and other industrial enterprises as

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recommendations for water-recycling systems implementation [25].

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