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ИЗУЧЕНИЕ МЕХАНИЗМА ДЕЙСТВИЯ КОМПОЗИЦИОННЫХ КОАГУЛЯНТОВ-ФЛОКУЛЯНТОВ

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Исследование посвящено изучению адсорбционных характеристик различных типов композиционных коагулянтов-флокулянтов в сочетании с полиалюминия хлоридом (оксихлоридом алюминия) с органическим полимером. Было изучено влияние этих коагулянтовфлокулянтов на снижение мутности растворов, а также исследованы характеристики процесса когезии и коагуляции. На основании полученных экспериментальных данных обсуждены характер и механизм когезии и коагуляции для различных типов композиционных коагулянтов-флокулянтов. Установлено, что изотерма адсорбиии катионных композиционных коагулянтов-флокулянтов соответствует закону адсорбции Ленгмюра и характеризуется параметрами адсорбции монослоя, что повышает их способность к нейтрализации электрического заряда. Анионные композиционные коагулянты-флокулянты повышают адсорбционную способность и способность к образованию мостиковых связей с помощью органических полимеров, демонстрируя при этом свойства, характерные для многослойной адсорбции. В частности, было отмечено, что при одинаковых условиях скорость флокуляции и скорость осаждения композиционных коагулянтов-флокулянтов выше, чем у полиалюминия хлорида. Этот факт объяснен полезными свойствами органического полимера за короткое время образовывать крупные хлопья, благодаря наличию в его молекуле длинной цепи. Крупные хлопья обладают значительной потенциальной энергией взаимодействия с небольшими частииами, что делает возможным эффективное столкновение между частииами, приводяшее к значительному усилению проиесса коагуляции. Изучено влияние времени хранения композиционных коагулянтов-флокулянтов на эффективность процесса коагуляции. Результаты эксперимента свидетельствуют о том, что после длительного хранения коагуляционные свойства реагентов в некоторой степени ухудшаются, однако композиционные коагулянты-флокулянты имеют преимущества в этом аспекте по сравнению с полиалюминия хлоридом. Следует сделать вывод, что в целом качество композиционных коагулянтов-флокулянтов в отношении их стабильности оставалось на высоком уровне.

Ключевые слова: коагуляция, флокуляция, полиалюминия хлорид, катионные и анионные органические полимеры, изотерма адсорбции, мутность

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STUDY ON COMPOSITE COAGULANTS-FLOCCULANTS MECHANISM ACTION

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This research deals with the investigation of adsorption characteristics of different types of composite coagulants-flocculants, combined by polyaluminum chloride (aluminum oxychloride) with organic polymer. The effect of this composite coagulants-flocculants on solution's turbidity removal and characteristics of cohesion and coagulation process have been studied too. On the basis of experimental data obtained the character and mechanism of cohesion and coagulation for different types of composite coagulants-flocculants were discussed. It was stated out that the adsorption isotherm of cationic composite coagulants-flocculants conforms to Langmuir adsorption law, and it characterized by monolayer adsorption parameters, which increases their ability to neutralize electric charge. The anionic composite coagulants-flocculants enhance the adsorption value and bridging ability with the help of organic polymers, showing multilayer adsorption characteristics. It was observed specifically, that under the same conditions the flocculation rate and sedimentation rate of composite coagulants-flocculants are higher than polyaluminum chloride has. This fact was explained by the advantages of organic polymer due to its long chain which is able to form larger floc within short time. The large floc has strong attractive potential energy for tiny particles, which make the opportunity of effective collision between particles what leads to sharply increased coagulation. The influence of storage time period on composite coagulants-flocculants coagulation effectiveness has been examined. The experimental results witness that the coagulation characteristics of reagents will be reduced to some extent after long-term storage, but composite coagulantsflocculants have advantages in this aspect over polyaluminum chloride. It should be concluded that, in general, the quality of composite coagulants-flocculants in relation to their stability remained at a high level.

Key words: coagulation, flocculation, polyaluminum chloride, cationic and anionic organic polymers, adsorption isotherm, turbidity

INTRODUCTION

The basic research on flocculant PAC with inorganic polymer has suggested that compared with traditional aluminum salt and PAC, on the molecular and water particle morphology and structure of physical chemistry, etc. they all have very big difference, which also determines that the process of cohesion and coagulation of PAC is completely different from the traditional characteristics of the coagulants [1-5]. PAC has a relatively stable form of hydrolytic polymerization (such as Al13) and these forms not only has high positive charge, but has very strong charge neutrality capacity for the aquatic particulates; because of its high molecular weight and hydroxy complex structure, the surface of the particles has a strong adsorption characteristics and bridging coagulation effect between particles [6-12]. On the basis of mechanism study on cohesion and coagulation of PAC, agglutination technology system with a brand-new concept attracts scientists more and more attention, which is trinitarian adaptation system (so called FRD system) with efficient flocculant (F), efficient flocculation reactor (R) and economical auto-dosing system (D). The highly efficient flocculant is the core of this system [13-16]. The inevitable trend for the development of coagulant is from traditional aluminum salt to PAC to PAC compound. Therefore, it is an important subject to study the characteristics and action mechanism of considered reagents in order to use them for development and modernization local waste-water treatment facilities as component of textile plants resource-saving water management systems [17-23].

EXPERIMENTAL PART

The equipment

The major instruments include NDH-20D type of light scattering turbidity meter, UV-5500 type of UV-visible light spectrophotometer and MY-3000 type of six-joint coagulation tester.

The materials

The investigated by us composite coagulantflocculant (abbreviate as PACP) was combined by polyaluminum chloride (PAC) and organic polymer (OP).

The major materials include polyaluminum chloride (PAC), kaolin and organic polymer. They were used for preparation of composite coagulant-flocculant contained PAC plus organic polymer (OP) and for preparation of composite coagulant-flocculant contained PAC, polyacrylamide (PAM) (abbreviate as PAC-PAM) plus OP.

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.

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. Coagulant with non-ionic organic polymer (NOP) was investigated as well. The NOP has the code of industrial product as N505P and was produced by Japan Sanyang Huacheng Joint-stock Company (SAN-FLOC).

The investigated coagulant-flocculant was made by our team, and the method are as follows: to put 100 mL 0.2mol/L AlCl₃ solution into beaker, under the quick magnetic stirring, then slowly drop 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 methods

Experiment of coagulation efficiency

Coagulation beaker experiment was the most direct method to verify the coagulating property of coagulant, and it can simulate hydraulic conditions in the process of actual water treatment, which has very important meaning for the production practice.

Preparation of simulative turbid liquid: (1) to mix tap water and deionized water based on 1:1proportion; its initial pH value was 7.50, hardness is 60mg/L(calculated by CaCO₃), and basicity µ_{bis} 1.2·10⁻³mol/L (bicarbonate alkalinity); (2) to measure a certain quantity of kaolin and to add it into (1) for stirring well after soaking by deionized water, making its concentration is 100mg/L;

(3) to measure a certain quantity of humic acid, and to add it into (2) for stirring well after dissolving through deionized water, making its concentration is 100 mg/L.

For turbidity measurement: to take 2000 mL simulated water samples into square organic glass beaker, and add the matter under 150 rpm of high-speed stirring for 15 min, and then make 40 rpm of slow stirring for 15 min, finally to stop stirring, and make static sedimentation for 15min; to take probe of supernate under the 2 cm of surface to measure its turbidity.

Experiment of adsorptive properties evaluation

It was need to put 250 mL of water sample into 300 mL breaker; after adding matter under strongly magnetic stirring for 2 min, then to take water samples and filter them through 0.45 of positive filter membrane; put a certain volume of filter liquor into 50 mL of volumetric flask, and then add it into 0.5 mol/L HNO₃, heating it for two hours at 60 °C of water bath; after cooling, to make the volume constant by deionized water. We've used Al-Ferron colorimetric method to measure content of total aluminum. Adsorbent aluminum amount is the difference value between general Lei Sun, Hui Zhao, Heng Zhong, Dongsheng Xia, A.V. Nevsky

aluminum content measured in the condition that no kaolin in water.

RESULTS AND DISCUSSION

PACP adsorptive property

The adsorptive property of coagulant or its hydrolysate on surface of particulate matter not only has important influence on charge neutrality character, but directly relates to exertion of bridging behavior between particulate matters. In order to explore PA1's cohesion and coagulation mechanism, it is necessary to research its adsorptive property.

In the following step, it makes the adsorption experiment for several kinds of types of PACP on the surface of kaolin particle when they have different dosages. Although adsorbing capacity is calculated by sampling and measuring within 1min after adding the matter; within the short time, the adsorption process can't reach to the equilibrium state; due to the charge neutralityadsorption and destabilization in the process of condensation is very quick, that is, it will be finished between several microseconds and seconds. Therefore, the absorption experiment under the non-equilibrium state is good for understanding instantaneousadsorption-condensation condition of various coagulants on the surface of colloidal particle, and it is closer to reality.

Adsorptive property of PACPc

The results illustrated in Fig. 1 indicate that, with the increase of adding dosage (expressed as Al content), the adsorbing capacity of PAC and PACPc gradually increases. When the adding dosage is same, compared with PAC, the adsorbing capacity of PACPc obviously decreases; the larger the O/A ratio, the lower the adsorbing capacity, and the more obvious the difference when the adding dosage is more. Seen from the regressive calculation result of L-shape isotherm, adsorption characteristics of PAC and PACPc basically accord with the Langmuir type of adsorption isotherm with mono-layer absorption character. This is maybe because that positive charge of PACPc is stronger than the original PAC, so when the mono-layer absorption is saturated, the repulsive force between positive charges prevents the further absorption on the particle surface of of PAC in the system, only forming monolayer absorption. It should be noted that these adsorption isotherms are rather sharp and in future we plan to test other models for describing the adsorption process besides the Langmuir model.

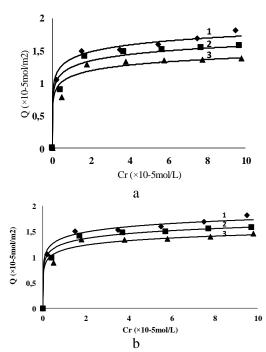


Fig. 1. Adsorption characteristics of PAC and its composite PACPc with: a) chitin: 1 - PAC; 2 - PACPc (O/A=0.1); 3 - PACPc (O/A=0.2);
b) C109P: 1 - PAC; 2 - PACPc (O/A=0.05); 3 - PACPc (O/A=0.01)
Рис. 1. Адсорбционные характеристики РАС и его композиционного состава РАСРс с: а) хитином; б) C109P

Adsorptive property of PACPa

The data in Fig. 2 show the experimental results of the change of PAC, anionic organic polymer AH200P and AN910SH, and adsorbing capacity of compound PACPa with the adding concentration of Al (III). Form Fig. 2, we can find that adsorbing capacity of PAC and PACPa increases with the increase of dosage. But the obvious character that PACPa is different from PAC is that with the increase of dosage, adsorption curve of PAC trends to be gentle and the adsorbing capacity has less increase, but PACPa's adsorbing capacity increases with the increase of dosage, also, PACPa with large O/A ratio has large adsorbing capacity. This indicates that PACPa has strong adsorption capacity. If matching the experimental data based on L-shape isothermal equation, it will get the regression parameter. Seen form the computed result, we can find that experimental data and fitting result of PACPa with O/A = 0.02 has large difference, and the absorption of PAC and PACPa with O/A = 0.01 generally accords with Frundlich type, and their regression parameterl/n is less than one, which indicates that after adding the matter, there is the certain repulsive force between molecules because of electrostatic interaction at the beginning.

The difference of adsorption characteristic of PACPa and PAC is mainly caused by two aspects, on the one hand, the consistency of AOP and PAC make

the positive charge of PAC reduce, which makes the repulsive force between adsorbed molecules reduce, and it is good for the adsorption; on the other hand, AOP is the linear molecule with gigantic molecular weight, and it can form composite products with high molecular weight together with PAC, the more the molecular weight, the larger the attraction between molecules, and the stronger the adsorbent trend.

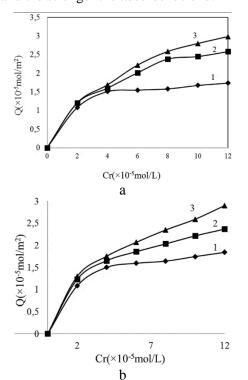


Fig. 2. Adsorption characteristics of PAC and its composite PACPa with: a) AH200P; b) AN910SH
Рис. 2. Адсорбционные характеристики PAC и его композиционного состава PACPa с: a) AH200P; б) AN910SH

PACPc coagulation efficiency

In comparison with experiment about coagulation and turbidity removal of PACPc and PAC with different O/A ratio, Fig. 3 demonstrates the characteristics of composite products denoted respectively as PACP-1 and PACP-2. One can clearly see that under the condition that the dosage of aluminum is same and coagulation experiment condition is consistent, PAC-Pc's turbidity removal effect is obviously better than that of PAC, and the larger the O/A ratio, the better the PACPc's turbidity removal effect. We also find from the experiment that in the coagulation process of PACPc, and the formation of flocs is quick; in the process of standing, floccus settling is fast; based on the analysis on PACPc's coagulation effect, it indicates that after the recombination of COP and PAC; on the one hand, the positive charge in the molecular chain and positive charge of PAC makes phase addition to enhance charge neutrality capacity; on the other hand, the compound generated by COP and PAC has a large particle size which can be bridged between the unstable particles. It is good for forming the larger floc, which enhances the function of removing the small particles in the water through the sweep function of the flocs.

In order to further research mutual synergistic effect of COP and PAC in the process of coagulation, we bring few PAC into the solution of C109P and chitin to manufacture composite coagulant with main element of COP (denoted respectively as PPAC-1 and PPAC-2), expressed as PAC content in PPAC as the weight ratio of aluminum and organic matter (denoted as A/O), and make the coagulation test comparison with the situation when only add COP, as shown in Fig. 4.

The results show that bringing PAC into COP solution also largely improves COP coagulation effect in exclusive use; when use level us 1.62 mg/L (calculated as C109P), the rate of the turbidity of C109P is 66.7%; PPAC-1 of AJ0 = 0.05 is 83.3%; PPAC-1 of A/0 = 0.10 is 88.9%. Similarly, for the condition of PPAC-2, when dosage is 2.70 mg/L (calculated as chi-tin), the rate of turbidity removal of chitin is 3.3%, but the PPAC-2 of A/0 = 0.1 is 44.4%; PPAC-2 of A/0 = 0.2 is 88.9%. We also can see from this that compared with same A/O. The influence of PAC on coagulate effect of chitin is more obvious than the influence on C109P. This can be explained by the fact that C109P itself is more active than chitin (compare Fig. 4-a and Fig. 4-b).

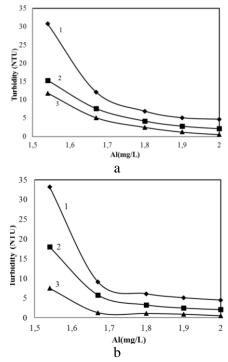


Fig. 3. Comparison of flocculation effect between PAC and: a) PACPc-1; b) PACPc-2

Рис. 3. Сравнение эффекта флокуляции между РАС и: a) PACPc-1; б) PACPc-2

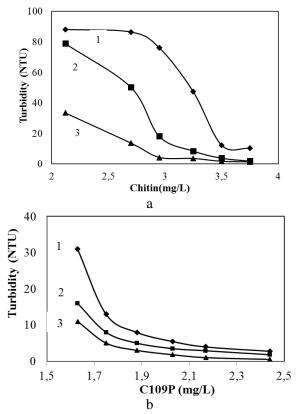


Fig. 4. Comparison of flocculation effect between PAC and: a) PACPc-1; b) PACPc-2 Рис. 4. Сравнение эффекта флокуляции между PAC и: a) PACPc-1; б) PACPc-2

Coagulation efficiency of PACPa

Anionic organic polymer (AOP) is a polyelectrolyte with a certain amount of negative charge on the molecular chain after hydrolysis, and its molecular weight is usually several times to tens of times more than that of COP. After recombination of AOP and PAC, charge neutrality capacity of PAC cannot be increased but even weakened; and coagulation phenomena is based on the premise of certain degree of charge neutrality, so the recombination of AOP and PAC has much more complex condition. The results in Fig. 5 show changing curve of coagulation and turbidity removal effect with the increase of dosage (expressed in Al content) of composite products that AH200P and AN910SH respectively combined with PAC (denoted as PACPa-1 and PACPa-2 respectively). The experimental results show that compared with PAC, the coagulation effect of PACPa has a turning point; when dosing quantity is less than this point, the coagulation effect of PACPa is worse than PAC; when dosing quantity is larger than this point, the coagulation effect of PACPa is better than PAC. This indicates that AOP has certain influence on the charge of PAC, especially when the additive dosage is less and the electric neutralization becomes the main factor in the process of coagulation, the effect is more prominent, and the recombination of AOP and PAC needs to have a proper O/A ratio.

To change the O/A ratio, under the condition that ensures the dosage can reach to the certain degree of charge neutrality, and further compare with the coagulate effect of PACPa and PAC, as shown in Fig. 6. The results indicate that in the scope of above dosage, coagulate effect of PACPa is obviously better than PAC, and for PACPa, the larger the O/A proportion, the better the effect of coagulation and turbidity removal. In the process of experiment, we also find that PACPa has high speed to form floc, and the volume of floc is larger and the steady depositing is relatively quick. Based on the analysis on the influence of AOP on coagulate effect of PAC, it thinks that AOP slightly reduces the charge neutrality capacity of PAC, and the stronger coagulate effect of PACPa forms large floc mainly depends on the condition that the longer molecular chain of AOP makes destabilization and bridges between particulate matters, and then removes the fine particulate matters in water completely through sweep function.

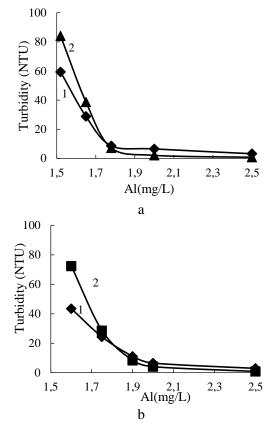


Fig. 5. Comparison of flocculation effect between PAC and: a) PACPa-1; b) PACPa-2 Рис. 5. Сравнение эффекта флокуляции между РАС и: a) PACPa-1; б) PACPa-2

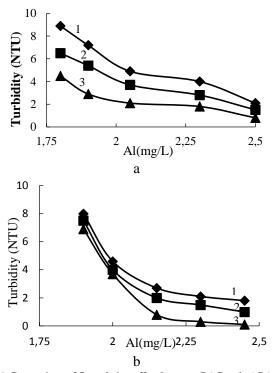


Fig. 6. Comparison of flocculation effect between PAC and: a) PACPa-1(AH200P/PAC); b) PACPa-2(AN910SH/PAC)
Рис. 6. Сравнение эффекта флокуляции между PAC и: a) PACPa-1 (AH200P / PAC); б) PACPa-2 (AN910SH / PAC)

Comparision of precipitation process and coagulation process of PACP and PAC

From the above experiment, we can see that comparing with PACP and PAC, their adsorption characteristic and effect of coagulation and turbidity removal have obvious difference, which indicates that their interaction mechanism with particulate matter in the process of condensation and coagulation is different. The purpose of this experiment is to explore the different character of PACP and PAC in the process of condensation and coagulation (including the formation of floc in the process of flocculation process and the sediment of floc in the precipitation process, etc.), making the further understanding for the difference of coagulating property of PACP and PAC.

Experimental subject:

PAC(B = 42% cAl = 0.02mol/L);

PACP: it is formed by anionic organic polymer AH200P and PAC through O/A=0.02.

Confirmation of dosage

It takes coagulation jar experiment, that is, respectively add 2000 mL of simulated water sample into two beakers; under the condition of quick stirring (130 rpm), add the same quantity of PACP and PAC (expressed as Al content) into two beakers, and then continue to stir it quickly for 1min, and stir it slowly (40 rpm) for 15 min; stop stirring and make steady depositing for 15min, finally use supernate to measure rest turbidity. Change the adding dosage and repeat the above experiment, and ensure the proper dosage through the relevant relation curve of residual turbidity under the different dosage, and the result is shown in Fig. 7.

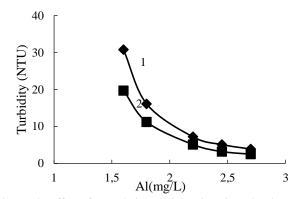


Fig. 7. The effect of coagulation PACP and PAC on the change of Al dosing quantity Рис. 7. Влияние коагуляции РАСР и РАС на изменение коли-

чества дозы Al

From Fig. 7 one can see that the effect of coagulation and turbidity removal of PACP and PAC both reduce with the increase of adding amount, but PACP is obviously better than PAC. The standard is then the rest turbidity reaches to 20 NTU (according to the experience of coagulation beaker experiment, if the rest turbidity is more than 20 NTU, generally, in the process of coagulation, the fine floc does not form), and the amount of PACP is about 85% of PAC. In order to facilitate the comparison of coagulation process for PACP and PAC, it determines the adding dosage of following experiments is 1.90 mg/L (expressed as Al content).

Comparison of coagulation/flocculation process between PACP and PAC

The mixture and process are corresponding to condensation and coagulation in the whole process of coagulation. The function of mixture is to rapidly spread matter into water evenly and reacts with particulate matter in water to make them produce the certain destabilization. The mixing process requires stronger turbulence (velocity gradient G = 500~1000S-1), and mixing time is generally less than 2min. The process that relevant particulate matter forms large floc under mutual collision and the function of coagulant is the process of flocculation. The process requests a proper turbulence condition (generally the velocity gradient G = 30~100s-1) and a certain response time (T = 15~20min) to ensure the sufficient reaction in the process of coagulation.

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The experiment mainly studies the response time's influence on coagulation process of PACP and PAC. The experimental method is to add matter under the condition of high-speed stirring (130rpm); the mixing time is fixed at 1min; in each group of experiment, the slow stirring (40rpm) time is set as different values, and settling time is fixed at 10min; the relationship of rest turbidity and response time is shown in Fig. 8.

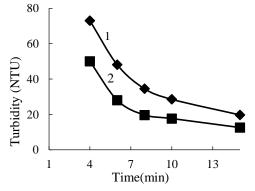


Fig. 8. Comparison of flocculation process efficiency between PACP and PAC Рис. 8. Сравнение эффективности процесса флокуляции

между РАСР и РАС

It can be seen from Fig. 8 that response time has obvious impact on coagulation process of PACP and PAC, and its influence on PAC is larger than PACP. If the rest turbidity reaches to 20NTU, made this as standard, PAC needs 14min; however, PACP only needs 7min', thus, the response time shrink a half,

which indicates that the forming speed that PACP generates alum floc during coagulation/flocculation process is largely faster than PAC, and this fully reflects the high efficiency of PACP.

Comparison of settling character of alum floc formed by PACP and PAC

Precipitation process is the important link of operation technique of coagulation. The implementation of precipitation process has direct relationship to the size and character of floc generated by coagulation/flocculation process: if the floc is large and dense, its settling property is good; if the floc is small or the floc is large but its structure is loosen, will be bad for the implementation of precipitation process. The purpose of this experiment is to research the settle ability of floc generated in the process of coagulation of PACP and PAC (it mainly refers to the larger floc which can settle within 30min, and the tiny particulate matter and floc which are difficult to settle are caused by insufficient coagulation/flocculation process and matter amount). Experimental method: it was need to add matter under the condition of high-speed stirring (130rpm), blend them for l min, and then turn to slow stirring (40rpm) to make flocculation process for 10min. After stirring stop, in the process of steady depositing, take samples to measure and test the rest turbidity in regular terms, the relationship between settling time and residual turbidity is shown in Fig. 9.

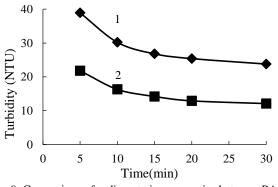


Fig. 9. Comparison of sedimentation properties between PACP and PAC Рис. 9. Сравнение осадительных свойств РАСР и РАС

From Fig. 9 we can see that in the process of coagulation, the settle ability of floc generated by PACP and PAC has obvious difference: the floc generated by PACP mostly fully settles within 5min, and the rest turbidity reaches to 20 NTU, later on, the rest turbidity slightly decreases, which is because the fine particle and tiny floc settle slowly; floc generated by PAC settles slowly, after 30min, its rest turbidity is still more than 20 NTU. We also can find from the paired observation in the process of flocculation experiment that the floc generated by PAC.

The research of compare experiment on the process of coagulation/flocculation process and sedimentation process fully reflect the efficiency of PACP, and this kind of high efficiency is undoubtedly related to the OP's function in PACP. The function generated by OP during coagulation/flocculation process can be known from coagulation kinetics that according to the basic equation of particulate matter's collision and coagulation in the process of coagulation/flocculation process, coagulation speed N is in direct proportion to the third power of particle radius R. OP takes advantage of the function of its long chain to make it can form larger floc of R within short time, which largely increases the opportunity of mutual collision between particulate matters, so coagulation speed sharply quickens. Moreover, the large floc has strong attractive potential energy for tiny particle, which makes the opportunity of effective collision between particles (can

cause the collision of coagulation) sharply increase; on the other hand, after forming large floc, under the function of OP, according to micro-vortex coagulantion enhancement theory, the size of vortex also relatively increases, thus, the energy consumption can reduce relatively. In order to adapt to the requirement of PACP for coagulation condition, reactive pool takes multi-level method, which provides the formation of floc with most suitable hydraulic condition.

The influence of storage time period on PACP coagulation effectiveness

Compared with PACP and PAC, coagulation performance can get large improvement, however, if you want to make it become a kind of efficient coagulant with application and development potential, it has to own the certain stability. In the scope of the concentration applied in this text (0.2-0.02mol/L) and O/A ratio (0-0.2), under the indoor temperature, PACPc (composite products between chitin or C109P and PAC) and PACPa (composite products between AH200P or AN910SH and PAC) not generate muddy or settling phenomenon within a half of a year. In order to verify whether the PACP still can maintain better coagulate effect after long time of storage, we make the comparison of coagulation experiment for chitin composite type of PACPc (O/A=0.1) and AH200P composite type of PACPa (O/A=0.02), and the relevant PAC; the results are shown in Fig. 10.

We can find from the experimental results that coagulate effect of chitin compound type of PACPc and AH200P compound type of PACPa is still obviously better than PAC. If compare with additive dosage of PAC and PACP with same residual turbidity (denoted as Al): based on data of Fig. 10-a, we can know that when the rest turbidity reaches to 20NTU, the additive dosage of chitin compound type of PACPc (O/A=0.1) is 1.46mg/L, but the additive dosage of PAC is 1.67 mg/L, also, the dosage of PACPc decreases by 12.6% than PAC; according Fig. 3-a, when the rest turbidity is 4NTU, the additive dosage of new chitin compound type of PACPc (O/A=0.1) is 1.70 mg/L, and PAC needs 2.0mg/L; at this tine, the dosage of PACPc decreases by 15.0% than PAC; compared with AH200Pcompound type of PACPa, based on data of Fig. 10-b, when the rest amount is 20NTU, the dosage of PACPa(O/A=0.02) decreases by 15.4% than PAC after six-month placement; the newly manufactured PACP reduces by 20.8% than PAC (when the rest turbidity reaches to 3NTU, as shown in Fig. 10-a).

The comparison of experimental result of above coagulation indicates that although coagulate effect of compound type of PACP will be reduced after long-term placement, it is also better than PAC. The reduction of such coagulate effect for PACP is possibly related to the change of organic polymer structure and the change of PACP form distribution, but it needs the further experiment research.

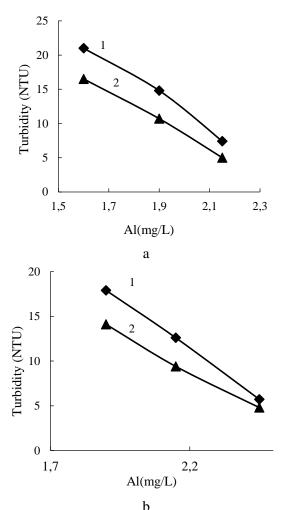


Fig. 10. Comparison of PAC flocculation after six months of storage: a) chitin - PACPc; b) AH200P - PACPa

Рис. 10. Сравнение РАС флокуляции после хранения в течение шести месяцев: а) хитин - РАСРс; б) АН200Р – РАСРа

CONCLUSION

As it was found under the same conditions, the adsorption capacity of PACPc is less than PAC, and the larger the organic polymer/aluminum ratio, the smaller the adsorption capacity. The adsorption isotherm of PACPc conforms to Langmuir adsorption isotherm and shows the characteristics of monolayer adsorption. Under the same conditions, the adsorption capacity of PACPa is greater than that of PAC, and the adsorption capacity increases with the increase of organic polymer/aluminum ratio. The adsorption of PACPa corresponds to multilayer adsorption type. Lei Sun, Hui Zhao, Heng Zhong, Dongsheng Xia, A.V. Nevsky

The flocculation effect of PACPc and PACPa is obviously better than that of PAC, but the flocculation mechanism of PACPc is not the same: the flocculation effect of PACPc is enhanced mainly because of the combination of the two components, and the flocculation effect of PACPa is enhanced mainly because of the presence of organic polymer macromolecule.

Compared with PAC, the flocs formed in the flocculation process of organic composite PACP are much faster, and the flocs settled rapidly.

The influence of storage time period on composite coagulants-flocculants coagulation effectiveness have been examined. The experimental results witness that the coagulation characteristics of reagents will be reduced to some extent after long-term storage, but composite coagulants-flocculants has advantages in this aspect over polyaluminum chloride. It should be concluded that, in general, the quality of composite coagulants-flocculants in relation to their stability remained at a high level.

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REFERENCES ЛИТЕРАТУРА

- 1. Gao B.Y., Chu Y.B., Yue Q.Y., Wang B.J., Wang S.G. Characterization and coagulation of a polyaluminum chloride (PAC) coagulant with high Al-13 content. *J. Environ. Manag.* 2004. V. 76. P. 143-147.
- 2. Gao B.Y., Yue Q.Y., Wang B.J. The chemical species distribution and transformation of polyaluminum silicate chloride coagulant. *Chemosphere*. 2002. V. 46. P. 809-813.
- 3. Jiang J.Q., Graham J.D. Pre-polymerised inorganic coagulants and phosphorus removal by coagulation A review. *Water SA*. 1998. V. 24. P. 237-244.
- Bilanovic D., Shelef G., Sukenik A. Flocculation of microalgae with cationic polymers - effects of medium salinity. *Biomass.* 1988. V. 17. P. 65-76.
- Deng S.B., Bai R.B., Hu X.M. Characteristics of a bioflocculant produced by Bacillus mucilaginosus and its use in starch wastewater treatment. *Appl. Microbiol. biotechnol.* 2003. V. 60. P. 588-593.
- 6. **Tang H.X.** Flocculation morphology for hydroxyl polymer of polyaluminum chloride. *Acta Sci. Circumst.* 1998. V. 18. P. 1-10.
- 7. **Gao B.Y., Chu Y.B., Yue Q.Y.** Characterization and coagulation of a polyaluminum chloride (PAC) coagulant with high Al-13 content. *J. Environ. Manag.* 2005. V. 76. P. 143-147.

- Moghaddam S.S., Moghaddam M. R.A., Arami M. Coagulation/flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology. J. Hazard. Mater. 2010. V. 175. P. 651-657.
- Zhou Dandan, Xu Zhengxue, Wang Yao. Simultaneous removal of multi-pollutants in an intimate integrated flocculation-adsorption fluidized bed. *Environ. Sci. Pollut. Res.* 2015. V. 22. P. 3794-3802.
- 10. **Divakaran R., Pillai V.N.S.** Flocculation of kaolinite suspensions in water by chitosan. *Water Res.* 2001. V. 35. P. 3904-3908.
- Bezawada J., Hoang N.V. Production of extracellular polymeric substances (EPS) by Serratia sp.1 using wastewater sludge as raw material and flocculation activity of the EPS produced. J. Environ. Manag. 2013. V. 128. P. 83-91.
- 12. Hierrezuelo J., Vaccaro A., Borkovec M. Stability of negatively charged latex particles in the presence of a strong cationic polyelectrolyte at elevated ionic strengths. J. Colloid Interface Sci. 2010. V. 347. P. 202-208.
- 13. Kovaleva O.Y., Navrotskii, V.A., Shulevich Y.V. Synthesis and hydrodynamic behavior of stoichiometric complexes of cationic polyelectrolytes with amphiphilic anions. *Russ. J. Appl. Chem.* 2005. V. 78. P. 1190-1193.
- Zhao Shan, Huang Guohe, Fu Haiyan Enhanced Coagulation/Flocculation by Combining Diatomite with Synthetic Polymers for Oily Wastewater Treatment. *Separat. Sci. Technol.* 2014. V. 49. P. 27-33.
- Aljuboori A.H.R, Idris A., Al-Joubory H.H.R., Uemura Y., Ibn Abubakar B.S.U. Flocculation behavior and mechanism of bioflocculant produced by Aspergillus flavus. J. Environ. Manag. 2015. V. 150. P. 466-471.
- Liu Wei Jie, Wang Kai, Li Bao Zhen Production and characterization of an intracellular bioflocculant by Chryseobacterium daeguense W6 cultured in low nutrition medium. *Biores. Technol.* 2010. V. 144. P. 1044-1048.
- 17. Divakaran R., Pillai V.N.S. Flocculation of kaolinite suspensions in water by chitosan. *Water Res.* 2001. V. 148. P. 414-421.
- Yang Zhen, Yang Hu, Jiang, Ziwen Flocculation of both anionic and cationic dyes in aqueous solutions by the amphoteric grafting flocculant carboxymethyl chitosan-graft-polyacrylamide. J. Hazard. Mater. 2013. V. 254. P. 36-45.
- Tang Hongxiao, Luan Zhaokun. Features and mechanism for coagulation-flocculation processes of polyaluminum chloride. J. Environ. Sci. 1995. V. 7. P. 204-211.
- Borchate S.S., Kullkarni G.S., Kore V.S. A review on applications of coagulation-flocculation and ballast flocculation for water and wastewater. *Internat. J. Innovat. Eng. Technol.* 2014. V. 4. P. 216-222.
- He Lili, Xu Xinyang. Polymeric Aluminum Ferric Chloride Calcium Composite Flocculant: Preparation, Characteristics and Coagulation Performance. Internat. conf. on frontiers of environment, energy and bioscience. 2013. P. 734-740.
- 22. Тагазоvа Т.V., Dimakas Lukas, Nevsky A.V., Bautista Dioni Production of coagulants for textile enterprises wastewater treatment. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 1997. V. 40. N 3. P. 55 58 (In Russian). Тарасова Т.В., Димакас Лукас, Невский А.В., Баутиста Диони. Получение коагулянтов для очистки сточных вод текстильных предприятий. Изв. вузов. *Химия и хим. технология.* 1997. Т. 40. Вып. 3. С. 55 58.
- 23. Nevsky A.V., Meshalkin V.P., Sharnin V.A. Analysis and Synthesis of Water Resource-Saving Chemical Processes. M.: Science PH. 2004. 212 p.

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