Natural organic matter(NOM) removal from surface water by coagulation

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Abstract: Poly-aluminum-chloride-sulfate(PACS) with different SO_4^{2-}/Al^{3+} mole ratios and bacicity(γ) of 2.0 was synthesized using $AlCl_3 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$ and Na_2CO_3 as raw materials. The effect of SO_4^{2-}/Al^{3+} ratio on the performance of PACS for removal of natural organic matter(NOM) with humic-rich actual water was examined. It was found that PACS with SO_4^{2-}/Al^{3+} mole ratio of 0.0664 achieved the best NOM removal results and was selected to investigate its performance in comparison with PAC, $FeCl_3$ and alum($Al_2(SO_4)_3 \cdot 18H_2O$). The experimental results showed that the optimum NOM removals were achieved at pH 5.0—8.2 and the dose of about 5.0 mg/L as Al both for the selected PACS and PAC, at pH 5.0—6.0 and the dose of about 7.0 mg/L as Fe for $FeCl_3$, and at pH 5.0—7.0 and the dose of about 7.0 mg/L as Al for alum, respectively. At the optimum conditions, the selected PACS achieved the best NOM removal result, followed by PAC, $FeCl_3$, and then alum. The concentration of residual aluminum in treated water by the selected PACS and PAC under the optimum coagulant conditions was approximately 115 µg/L, which can completely comply with the regulated limits.
Keywords: coagulation; humic-rich water; NOM removal; residual aluminum

Introduction

Natural organic matter(NOM) in rivers and lakes is a complex mixture of molecules with varying molecular weight and chemical nature and originates from a variety of sources (degradation of terrestrial and aquatic organisms, biological activity in the water body, human inputs etc.). NOM is by far the largest source of organic material in raw water, and it comprises both particulate and dissolved components. Dissolved NOM (operationally defined as the fraction that passes through a 0.45-µm pore filter) usually comprises the largest portion, although very high-molar-mass organic acid molecules are often considered as to have colloidal properties (Edzwald, 1993; Randtke, 1988). NOM is primarily composed of humic substances, such as humic acids(HA) and fulvic acids (FA) that result from decomposition of terrestrial and aquatic biomass, but it can contain a range of organic species and microorganisms and their discharges (Randtke, 1988). NOM has been associated with unpleasant taste and odor, growth substrates for bacteria, potential transport of adsorbed hydrophobic organic and inorganic contaminants, increased coagulant and disinfectant demands, and most important for the drinking water treatment industry, disinfection by-products (DBPs) that include such as halogenated substances as trihalomethanes(THMs; Randtke, 1988; White, 1997; Exall, 2000). Health problems may be associated with the ingestion of organic compounds in drinking water or, in the case of volatile organic such as THMs, by inhalation and absorption through the skin (Andelmann, 1990; Tate, 1990). So, attention to the removal of NOM from surface water has increased in recent years.

Coagulation is an essential method to reduce the concentration of NOM in surface water and coagulants most commonly used are aluminum or iron salts. In order to evaluate the effect of coagulant type and dose, and pH on

coagulation performance in terms of the removal of NOM from surface water, poly-aluminum-chloride-sulfate (PACS) and polyaluminum chloride (PAC) were prepared and were examined their NOM removal effectiveness in comparison with alum($Al_2(SO_4)_3 \cdot 18H_2O$) and $FeCl_3$ using a actual surface water. During research, NOM removal was examined in terms of the removal of total organic carbon (TOC), dissolved organic carbon(DOC) and UV absorption at a wavelength of 254 nm(UV_{254}).

1 Materials and methods

1.1 Materials

Deionized water (0.055 µS/cm, Milli-Q PLUS, Millipore) was used in all the experiments. All chemicals used were commercially available with purities $\geqslant$ 99.0%. The coagulation tests employed land surface water. The raw water was taken in September 2002 from a brown water lake (Hohlohsee, Northern Black Forest, Germany; HO22). The original samples were filtrated(0.45 µm, cellulose nitrate) and stored in the dark at 4 ℃. Basic sample parameters are given in Table 1. As can be seen, the water had very low pH, very high levels of DOC and high the specific UV absorbance(SUVA) value. Experience with numerous surface waters showed that a SUVA of 2 indicates a non-humic water and a SUVA of greater than 6 indicates a humic-rich water (Edzwald, 1990). The SUVA value for the tested raw water was 5.05 suggesting high humic water.

In this study, the raw water was diluted to reach a DOC concentration of about 10 mg/L as the test water for coagulation experiment.

1.2 Preparation of PACS

PACS was produced using $AlCl_3$, $Al_2(SO_4)_3$ and Na_2CO_3 as raw materials. Briefly, a Na_2CO_3 solution (~ 30.0%) was slowly added to a mixed solution of $AlCl_3$ and $Al_2(SO_4)_3$ (~ 6.75% Al and mole SO_4^{2-}/Al^{3+} ratio of 0—

0.15) with stirring at room temperature to obtain the desired mole ratio OH/Al(γ) of 2.0. After addition, the mixture was stirred until no bubbles formed and the solution became transparent, and then it was allowed to rest for more than 24 h before the properties of the coagulant were examined. During the preparation of PACS coagulants, when $Al_2(SO_4)_3$ was not added, the product was PAC. PACS products had the following properties: total aluminum concentration = 3.64%—3.71% as Al, γ = 2.0, pH = 2.82 and specific gravity(20℃) = 1.182—1.184 g/L.

Table 1 Raw water characteristics

Parameter	Value
Dissolved organic carbon(DOC), mgC/L	29.3
Total organic carbon(TOC), mgC/L	33.7
Turbidity, NTU	1.49
pH, 15℃	3.15
Conductivity, 15℃, μS/cm	50.6
Mn, mg/L	0.037
Fe, mg/L	0.483
UV_{254}, Abs/m	148
UV_{436}, Abs/m	15.5
Color	Brown
SUVA, L/(mg-m)	5.05

All the synthesized coagulants were diluted with deionized water to a concentration of 1 g/L Al before used. However, alum and $FeCl_3$ were diluted with deionized water to a concentration of 10 g/L as Al or Fe before used.

1.3 Jar tests and analysis

Jar tests were carried out at room temperature (ca. 20℃). 500 ml of the test water was added to each of the one-liter beakers and a Janke and Kunkel five-paddle stirrer (IKA-Labortechnik, Reihenrührwerk RER, Germany) was used for mixing. The solutions were stirred rapidly at 150 r/min for 2 min during coagulant addition, followed by slow stirring at 40 r/min for 15 min and quiescent settling for 30 min. Following settling, a supernatant sample was withdrawn and filtered through 0.45 μm membrane before being analyzed for TOC, DOC, UV_{254} and residual aluminum.

During experiments, the pH of the water was adjusted to a given value with 1 mol/L NaOH or 1 mol/L HCl solutions and was measured using pH-meter CG840(Schott). TOC and DOC were measured using a total organic carbon analyzer (TOC-Vcsn, Shimadzu Corporation). UV_{254} absorbance was measured at 254 nm wavelength using a Lambda 5 UV/VIS spectrophotometer (Perkia-Elmer Corporation). Residual aluminum was measured at 167.016 nm wavelength using Vista CCD Simultaneous ICP AES (Varian Optical Spectroscopy Instrument, Mulgrave, Victoria, Australia). The detection limit is 1.0 μgAl/L.

2 Results and discussion

2.1 Effect of SO_4^{2-}/Al^{3+} molar ratio of PACS on its removal efficiency for NOM

The tested water was treated by PACS at a dose of 3.0 mg/L as Al and the TOC, DOC and UV_{254} removal results are shown in Fig.1. It can be seen that SO_4^{2-}/Al^{3+} molar ratio in PACS has a great effect on the removal efficiency for NOM. And the various of the removal of TOC, DOC and UV_{254} with SO_4^{2-}/Al^{3+} molar ratio were very similar. When the SO_4^{2-}/Al^{3+} ratio of PACS is 0.0664, the best coagulating result was achieved. With either a decrease or an increase of the SO_4^{2-}/Al^{3+} ratio, NOM removal efficiency decreases. The highest removal of TOC, DOC and UV_{254} was approximately 74%, 72% and 81% respectively, when PACS with SO_4^{2-}/Al^{3+} ratio of 0.0664 was used. The results demonstrated that a humic-rich water showed a great NOM removal following coagulation, which is consistent with findings of other researchers(Edzwald, 1990).
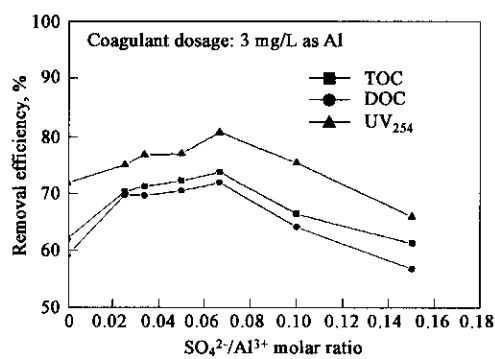

Fig.1　Effect of SO_4^{2-}/Al^{3+} molar ratio of PACS with γ value of 2.0 on TOC, DOC and UV_{254} removal efficiency

Based on the results above, PACS with SO_4^{2-}/Al^{3+} molar ratio of 0.0664 was selected for the subsequent comparison of PACS with PAC having γ value of 2.0, alum and $FeCl_3$ for treatment of the tested water.

2.2 Effect of pH on coagulation performance

The effect of pH on the removal of NOM at the dosage of 5 mg/L as Al for both PACS and PAC, at the dosage of 7.5 mg/L as Al for alum, and at the dosage of 7.5 mg/L as Fe as for $FeCl_3$ is given in Fig.2. It can be seen that for all the tested coagulants, the efficiency of TOC, DOC and UV_{254} removal depends on the pH of coagulation. The optimum NOM removals were achieved in the ranges of pH 5.0—8.2, 5.0—8.2, 5.0—6.0 and 5.0—7.0 for PACS, PAC, $FeCl_3$ and alum, respectively. This is consistent with findings of other researchers(Pernitsky, 1999). The results mean that polymerized metal coagulants can widen their optimum coagulation pH range when used in water and wastewater treatment. The explanation to above results was given as follows: At very low pH, very few NOM molecules can be accommodated around each metal species because NOW contains few anionic sites and NOM is tightly wound. As the pH is raised, more anionic sites are generated by deprotonation of acidic carboxyl groups, and at the same time, the molecules unwind and become more linear, which

is the result of repulsion of the many negative charges. At this time, in one hand, cationic metal species interacts electrostatically with anionic NOM to form insoluble charge-neutral product because of charge neutralization; on the other hand, each NOM may attach several times to the same metal species, and also can attach to other metal species (Gregor, 1997). In this way, organic molecules are linked together to form flocs and then can be easily removed from water. As the pH is raised further, say higher than optimum pH value, the increase of pH favored the hydrolysis of metal-ions, and decreased the formation of positively charged ions. Thus, the ability for coagulants to neutralize the negative charge on NOM became small, and NOM could not be removed effectively.
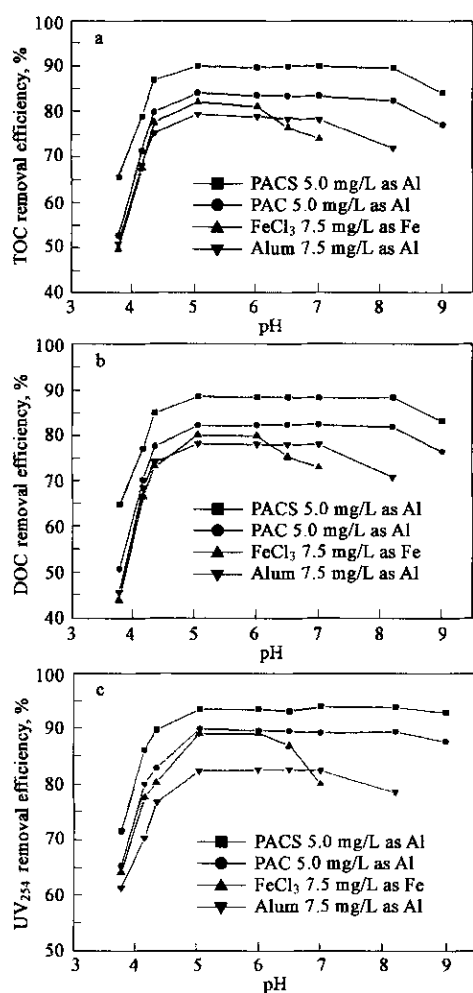

Fig.2   Effect of pH on TOC(a), DOC(b), UV$_{254}$ (c) removal efficiency

2.3   Effect of the dosages of coagulants on coagulation performance

The effect of the dosages of coagulants on their coagulation performance was carried out at pH 6.5 for PACS, PAC and alum, and at pH 5.5 for FeCl$_3$. The results are shown in Fig.3. It can be seen that the removal patterns of TOC, DOC and UV$_{254}$ using PACS, PAC, FeCl$_3$ and alum under the tested dosage range were similar. The optimum

coagulation doses for TOC, DOC and UV$_{254}$ removal were about 5.0 mg/L as Al both for PACS and for PAC, 7.0 mg/L as Fe for FeCl$_3$, and 7.0 mg/L as Al for alum, respectively. Under-dosing or over-dosing of coagulants results in significant deterioration in NOM removal. During testing, macro-floc formation could be noted under the around optimum coagulant dosage range, otherwise, no noticeable flocs occurred. At the optimum coagulation conditions, PACS had the best TOC, DOC and UV$_{254}$ removal, followed by PAC and then FeCl$_3$. Alum showed the least NOM removal at optimum pH range. Similar results for turbidity removal have been noted by other researchers (Hanson, 1990; Morris, 1984). The optimal coagulation of PACS and PAC are believed to correspond to prehydrolyzed metal-ion coagulants with the higher cationic charge and larger polymeric species (Jiang, 2003). Thus, coagulating species with high cationic charge and large polymeric species should be perform better than those with low cationic charge and species. Because PACS has higher cationic charge and larger polymer size than PAC at the same pH value(Gao, 2000; 2001; 2003), PACS gave higher DOC and UV$_{254}$ removal efficiency than PAC at the same conditions.

2.4   Residual aluminum in the treated water

Residual aluminum in the water following coagulation by aluminum salts should be minimized because that aluminum is suspected harmful to human and living organisms. Aluminum ion can lead to maladies such as Alzheimer's Syndrome, Osteoporosis, Anemia and Anorexia after its concentration in body accumulated to a certain level (Wen, 2002). PACS with SO$_4^{2-}$/Al^{3+} molar ratio of 0.0664 and γ value of 2.0 and PAC with γ value of 2.0 were selected to evaluate the effect of dosages of coagulants on residual aluminum in the water following coagulation and the results are shown in Fig.4. As can be seen that under-dosing or over-dosing of coagulants results in significant deterioration in residual aluminum. The residual aluminum deteriorates much more when over-dosing than under-dosing. At the optimum coagulant dose, the concentration of residual aluminum in treated water was approximately 115 μg/L, which can completely comply with the regulated limits.

3   Conclusions

This study developed a series of poly-aluminum-chloride-sulfate (PACS) coagulants with SO$_4^{2-}$/Al^{3+} mole ratios ranged from 0.0 to 0.150 and γ of 2.0. The performance of PACS for removing NOM with humic-rich actual water was found to be highly dependent on the SO$_4^{2-}$/Al^{3+} mole ratios. The PACS with SO$_4^{2-}$/Al^{3+} ratio of 0.0664 achieved the best NOM removal results and was selected to further investigate its coagulation performance in comparison with PAC with γ value of 2.0, FeCl$_3$ and alum. It was found that the optimum NOM removals were achieved at pH 5.0—
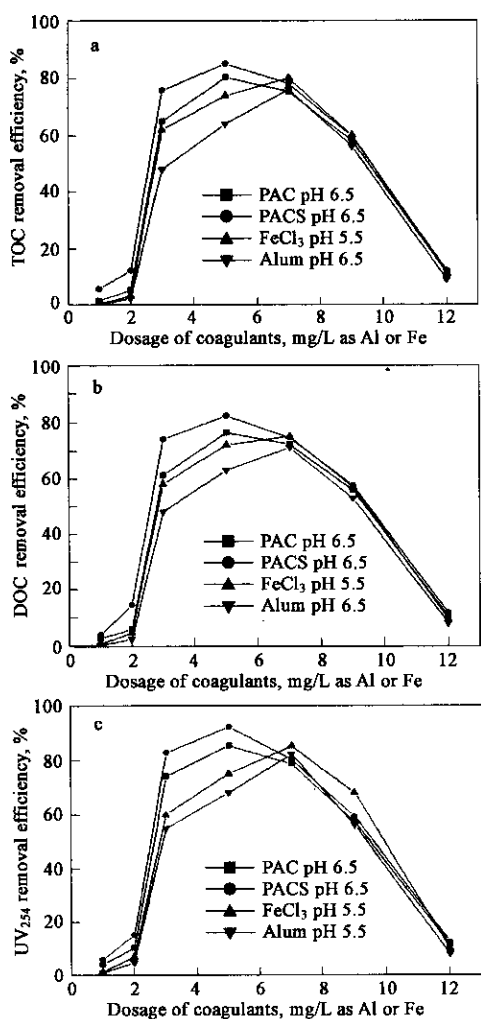
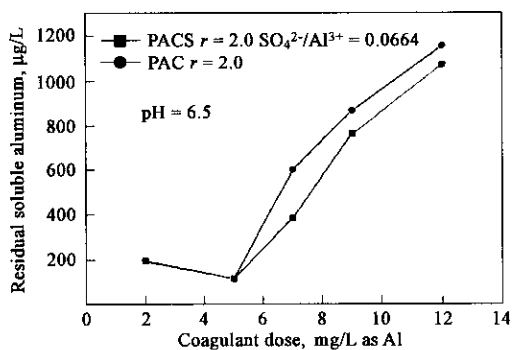Fig.3 Effects of dosage of coagulants on TOC(a), DOC(b) and UV_{254}(c) removal

Fig.4 Effect of dosages of coagulants on residual aluminum

8.2 and the dose of about 5.0 mg/L as Al both for the selected PACS and PAC, at pH 5.0—6.0 and the dose of about 7.0 mg/L as Fe for $FeCl_3$, and at pH 5.0—7.0 and the dose of about 7.0 mg/L as Al for alum, respectively. At the optimum conditions, the selected PACS had the best NOM removal, followed by PAC and then $FeCl_3$. Alum showed the least NOM removal at optimum pH range. The concentration of residual aluminum in treated water by the selected PACS and PAC under the optimum conditions was approximately 115 $\mu g/L$, which can completely comply with

the regulated limits.

There is some evidence that the superior treatment performance of the selected PACS is due to the high cationic charge and larger size of the polymeric species present in the prehydrolyzed chemical. The strength and stability of this charge and its larger size may explain the good performance of the selected PACS for removing NOM.

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