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The removal efficiency and reaction mechanism of aluminum coagulant on organic functional groups-carboxyl and hydroxyl

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HIGHLIGHTS

- ▶ SOM with the carboxyl functional group could be coagulated effectively.
- ▶ SOM with the hydroxyl functional group could not be coagulated.
- ▶ Pre-hydroxide degree of coagulant has an important effect on SOM of MW = 3000.
- ▶ Pre-hydroxide degree of coagulant has no effect on SOM of MW higher than 450 000.

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ABSTRACT

In order to remove the synthetic organic matter in drinking water and wastewater efficiently, aluminium chloride ($AlCl_3$) and polyaluminum chloride (PAC) with different *B* values ($B = 0.5, 1.5, 2.3$) were used to coagulated polyacrylic acids (PAAs) and polyvinyl alcohols (PAs) in this study. The effect of molecular weight and functional groups on the coagulation behavior was investigated by the experiments of the removal efficiency, floc size and fourier transform infrared spectrometer (FTIR) analysis of the formed flocs. The results indicated that aluminum salt coagulants had a fairly high removal efficiency for the carboxyl containing organic matter water but almost no removal efficiency for hydroxyl containing organic matter water. When organic matter interacts with aluminum salt coagulants, the molecular weight (MW) of organic matter affects the coagulation performance. For MW = 450 000 of PAA, the dissolved organic carbon (DOC) removal efficiency can reach 94% at the dose of 8 mg/L. However, for MW = 1800, no DOC removal occurred for all tested coagulants. FTIR analysis indicated that during the coagulation process of PAA, the COOH existed in PAA molecule was transformed into COO^-.

1. Introduction

Water pollution, as a global environmental problem, has drawing increasing attention throughout the world. With the high-speed development of modern industry especially petrochemical, pesticides and pharmaceutical industries, the amount and type of organic compounds in water environment have increased dramatically. In addition, the direct discharge of different kinds of produced industrial wastewater and sewage into original water bodies has induced the quality deterioration of raw water and water distribution system [1]. So far, more than two thousand kinds of organic chemical pollutants have been detected in water/wastewater all around the world. As indicated by other researchers, 765 species have been detected in drinking water, among which, 20 species have been identified as carcinogens, 23 species were suspected carcinogens, 18 species were promote cancer materials and 56 species were mutagen materials [2]. As a consequence, more attention should also be given to the deterioration of water quality caused by synthetic organic matter (SOM) in recent years. Subsequently, the removal of organic matter (OM) has become an increasingly important issue in water treatment due to the formation of disinfection by-products (DBPs) caused by the incompletely removed OM. Effective treatment process is needed to remove OM from water/wastewater and to reduce the toxicity of effluents.

Coagulation/flocculation has been widely used process in water and wastewater treatment processes, in which, coagulants play an important role for removing suspended particles and organic materials [3,4]. Different with biological treatments, no toxic intermediate were produced during the flocculation process. Moreover, relatively high cost to effectiveness ratio was achieved during the large scale flocculation operation [5–7]. Enhanced coagulation was used by Liu et al. [8] to remove natural organic matter and to control the formation of disinfection by-products in Luwen drinking water treatment plant which was a typical experiment with conventional processes employed to treat source water

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Table 1
Synthetic raw water characteristics and methods of measurement.

		Dissolved organic carbon (DOC) (mg/L)	Turbidity (NTU)	Zeta potential (mV)	pH
PAA	MW = 450 000	45.43–46.05	0.45–0.50	−23.0 to −26.5	5.21–5.26
	MW = 3000	48.04–50.89	0.38–0.51	−29.4 to −30.8	4.54–5.21
	MW = 1800	48.77–49.25	0.47–0.50	−28.5 to −29.7	5.18–5.23
PA	MW = 11 000–31 000	35.92–36.10	0.47–0.51	−12.5 to −13.4	6.67–6.74
	MW = 88 000–97 000	36.09–36.13	0.45–0.50	−13.3 to −14.8	6.75–6.78

heavily polluted by natural organic matter. The combined usage of $KMnO_4$ and $FeCl_3$ significantly enhanced COD_{Mn} removal, meanwhile removed COD_{Mn} by coagulation increased from 0.60 mg/L to 2.22 mg/L whereas that by chlorination decreased from 1.66 mg/L to 0.67 mg/L [8].

Metal coagulants are widely used conventional coagulants, such as polymeric and monomeric forms of Al and Fe salts [9]. Aluminum based coagulants such as $Al_2(SO_4)_3$, $AlCl_3$ and polyaluminumchloride (PAC) are the most widely applied inorganic coagulants, which remove pollutants by charge neutralization, adsorption, entrapment and complexation mechanism [10]. In recent years, researches of prehydrolyzed aluminum coagulants have been rapidly developed. Application of prehydrolyzed aluminum coagulants (PAC in particular) is on the rise, especially in China, Japan, Russia and Western Europe [11], for its advantages over conventional aluminum salts including less sludge production and less dependence on temperature or pH [12]. Yang et al. [13] used three different PAC (B = 1.5, 2.0, 2.3) to treat the surface water in a reservoir in Jinan in the eastern China. The result showed that PAC (B = 2.0) was optimum for removal of hydrophilic natural organic matter (NOM), while PAC (B = 1.5) and PAC (B = 2.3) were more suitable for hydrophobic NOM fraction removal. Meanwhile, PAC (especially with B = 2.0) samples were demonstrated to reduce the concentration of total dissolved Al and monomeric Al with comparatively higher toxicity to human health: PAC (B = 2.0) showed lower concentration for each kind of residual Al species [13].

In recent years, although there has been a lot of works on the application of coagulation and Al-based coagulants, there still have no reports related to the removal of SOM by coagulation process so far. On one hand, the properties of SOM are more complex due to the various organic functional groups existed in SOM. If the function mechanism between the coagulants and the functional groups in SOM is clearly understood, organic matters in drinking water and wastewater can be efficiently removed and the removal efficiency of coagulation process can be significantly improved. On the other hand, in present study, no evidence has been found to prove that the organic matter removal from water is only influenced by the molecular weight (MW) of SOM. Therefore, it merits more efforts to investigate the characteristics of organic materials which are directly corresponding to the OM removal during coagulation process.

Main objective of this study was to investigate whether the enhanced coagulation could remove the SOM efficiently or not and to examine the effect of functional groups and MW of organic matter on coagulation process. Furthermore, the influence of aluminum based coagulants prehydrolysis was also explored. The reaction mechanism between aluminum/iron based coagulants and other organic functional groups (aldehyde, benzene ring, halogen and so on) will be investigated in later study.

2. Materials and methods

2.1. Preparation and synthesis of coagulants

PAC was synthesized by slow titration at room temperature[1] [12,14]. A solution of $AlCl_3{\cdot}6H_2O$ was slowly titrated with a Na_2CO_3 solution under rapid stirring conditions. Different input quantity of Na_2CO_3 resulted in three B values[2]: 0.5, 1.5, 2.3. The resulting samples were denoted as PAC05, PAC15 and PAC23, respectively. At the end of the reaction the products were homogeneous and transparent with a final concentration of 10.0 g/L (Al) [15]. The hydrolysis degree of polymeric salt can be controlled during manufacturing and the pre-hydrolysis process can minimize the complicated reactions caused by metal salt hydrolysis. Therefore, dosage of polymeric salts provides a simpler and more precise way to control the coagulation process [16–18].

The $AlCl_3$ solution of 10 g/L (Al) was obtained by dissolving 8.9485 g of $AlCl_3{\cdot}6H_2O$ in deionized water and metered its volume to 100 mL. PAC and $AlCl_3$ were dosed according to the Al concentration (mg/L) during coagulation processes.

2.2. Test waters

All reagents used in this experiment were of analytical grade. Deionized water was used to prepare all solutions.

Polyacrylic acid (PAA) was purchased from Shanghai crystal pure industrial Co., Ltd., China. Three kinds of MW PAA[3] were chosen to prepare the test water. Stock PAA was prepared by dissolving certain quality of PAA to deionized water. The concentrations of stock PAA solutions were 14 g/L, 14 g/L and 7 g/L, respectively. The synthetic test water of PAA (MW = 450 000) was prepared by diluting the stock PAA solution to 100 mg/L. Synthetic test water of PAA (MW = 1800 and 3000) was prepared by diluting the stock PAA solution to 200 mg/L.

Polyvinyl alcohol (PA) was purchased from Alfa Aesar Chemical Co., Ltd., Tianjin, China. Two kinds of molecular weight PAA (MW = 11 000–31 000 and 88 000–97 000) were chosen to prepare the test water. Stock PA was prepared by dissolving certain quality of PA to deionized water. The concentration of stock PA solution was 7 g/L. The synthetic test water of PA was prepared by diluting the stock PA solution to a concentration of 200 mg/L.

The synthetic water characteristics and the corresponding methods of measurement were shown in Table 1.

2.3. Coagulation experiments

Coagulation experiments were performed in a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co., Ltd., China) at room temperature. The tested procedure involved a first rapid mixture of 1.5 min at 200 rpm, a 40 rpm coagulation stage for 15 min, and a final settlement period for 30 min. The Al-based coagulant was added after 30 s of rapid mixture. Following depositing, water samples were collected from 2 cm below solution surface for subsequent turbidity, zeta potential and pH measurements. Portion collected water sample was filtered through a 0.45 μm microfiltration membrane for the measurement of DOC.

2.4. Coagulation kinetics

The evolution of floc size was monitored by a laser diffraction instrument Mastersizer 2000 (Malvern, UK) during the coagulation

[1] 25 ± 1 °C.

[2] B value = OH^-/Al^{3+}.

[3] MW = 1800, 3000 and 450 000.