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Effect of fresh aluminum hydroxide gels on algae removal from micro-polluted water by polyaluminum chloride coagulant

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ABSTRACT

Polyaluminum chloride (PAC) coagulant, a most commonly used inorganic coagulant, was prepared using fresh aluminum hydroxide gels under the low energy consumption. The aim of this study was to investigate the influence of fresh aluminum hydroxide gels on the characteristics of PAC and the algae removal from micro-polluted water. The results suggested that PAC with the basicity values (OH/Al) of 2.5 and 2.0 synthesized by this method possessed the high content of middle polymeric aluminum (Al_{b2}). And fresh aluminum hydroxide gels contributed to the formation of Al_{b2}. Adding fresh aluminum hydroxide gels in the aging period temporarily increased the small/middle polymeric aluminum (Al_b) content that rapidly reduced with the time extending since fresh aluminum hydroxide gels accelerated the aluminum hydrolysis. The excessive fresh aluminum hydroxide gels would aggravate the decrease of Al_b content. The presence of fresh aluminum hydroxide gels in PAC slightly reduced the coagulation efficiency, but the performance deterioration resulted from overdosing was weakened in the cases. Besides, the residual aluminum concentrations in the treated water were always low as fresh aluminum hydroxide gels induced the generation of colloidal aluminum hydroxide particles. Charge neutralization was not the only coagulation mechanism in this treatment.

1. Introduction

Polyaluminum chloride (PAC) is the versatile coagulant in the portable water treatment throughout the world [1]. The conventional industrial preparation method of PAC has the defects of high energy consumption, rigorous preparation condition and high impurity content [2]. In order to overcome these weaknesses, granular aluminum is considered to react with alkaline before it is dissolved by hydrochloric acid (HCl), which can be operated under moderate temperature and atmospheric pressure [2]. However, granular aluminum is not cost-effective to be applied in the industrial scale, and other cheap aluminum ore should substitute the pure aluminum in the preparation. Besides, the small/middle polymeric aluminum (Al_b) content of PAC prepared using calcium aluminate by this method is always lower than that of it prepared by conventional method especially at high basicity values [3]. Increasing Al_b content is able to improve the coagulation efficiency in most of the studies [4]. And in the preparation, fresh aluminum hydroxide gels as the intermediate product are formed after adding acid solution into the sodium aluminate [3]. But their effect on characteristic of PAC has rarely found in the research.

Coagulation as an important water treatment technology has been applied in the algae treatment where PAC plays a vital role [5]. To the best of our knowledge, however, no publication has concentrated on the influence of fresh aluminum hydroxide gels on the treatment of algae, especially for the treatment of algae from micro-polluted water.

In this research, PAC was prepared by fresh aluminum hydroxide gels with the heating by sunlight. The effect of fresh aluminum

Abbreviations: Al_a, mononuclear aluminum; Al_b, small/middle polymeric aluminum; Al_{b1}, small polymeric aluminum; Al_{b2}, middle polymeric aluminum; Al_c, high polymeric or colloidal aluminum; Al_m, mononuclear aluminum; Al_2, dimeric aluminum; Al_{13}, tridecamer $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}]$; Al_{un}, undetectable aluminum species; HCl, hydrochloric acid; NaOH, sodium hydroxide; NMR, nuclear magnetic resonance; NOM, natural organic matter; OH/Al, basicity value; PAC, polyaluminum chloride.

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hydroxide gels on characteristics of PAC was studied via considering the distributions and transformations of aluminum species in the preparation and aging periods. The micro-polluted water containing algae was prepared to investigate the influence of fresh aluminum hydroxide gels on coagulation performance of PAC in terms of removal rate, residual turbidity, residual aluminum concentration, floc characteristic and zeta potential.

2. Materials and methods

2.1. Coagulants preparation

All the chemical reagents were analytical grade chemicals. Deionized water was used to make all the solutions of reagents. The powdered $Al(OH)_{3(s)}$ reacted with NaOH solution (40%) to prepare sodium aluminate solution under rapidly stirring and temperature of 100 °C. And then a certain amount of HCl solution was added into sodium aluminate solution according to the desired basicity value. In the process, the large quantities of fresh aluminum hydroxide gels were formed, and the half-finished PAC solution was prepared. In the pre-experiment, the high temperature and modest heating time could accelerate the dissolution of gels [6]. However, it consumed more energy, and the stability of production was far from satisfactory. In this study, the half-finished PAC solution with fresh aluminum hydroxide gels was placed in the sunlight without further artificial heating in the preparation until gels were dissolved. The weather in the period was presented in the Fig. S1. As the comparison, part of the half-finished PAC solution with fresh aluminum hydroxide gels was placed in the room (about 17 °C) without sunlight and part of it was placed in the water bath (temperature of 22 °C). The prepared PAC solution were respectively denoted as $PAC_{2.5}$, $PAC_{2.0}$, $PAC_{1.5}$, $PAC_{1.0}$, $PAC_{0.5}$ and PAC_0 according to the basicity values of 2.5, 2.0, 1.5, 1.0, 0.5 and 0.

2.2. Characterization methods

2.2.1. Ferron assay

Aluminum species distributions of PAC were measured by the Al-Ferron timed spectro-photometric method which was based on the different reaction time of various aluminum species with the Ferron reagent (8-hydroxy-7-iodoquinoline-5-sulfonic acid). The monomeric species (Al_a) reacted with Ferron within 60 s, and small/middle polymeric species (Al_b) reacted with Ferron within 120 min. The high/insoluble polymeric aluminum species (Al_c) needed much more time to react with Ferron, or they did not react with Ferron at all. Al_c content was obtained by the difference between the content of Al_T and that of Al_a combined with Al_b [7].

2.2.2. ^{27}Al NMR spectroscopy

^{27}Al NMR spectroscopy could be also used to analyze aluminum species distribution (Bruker Co., Switzerland). The instrumental settings and experimental conditions were represented in the previous study. Sodium aluminate solution (0.2 mol/L) diluted by deuterium oxide (D_2O) was used as an inner standard, and its chemical shift was 80 ppm. The characteristic peaks of 0, 3-4 and 62.5 ppm represented mononuclear aluminum (Al_m), dimeric aluminum (Al_2) and $AlO_4Al_{12}(OH)_{24}(H2O)_{12}^{7+}$ (Al_{13}), respectively. The concentrations of aluminum species were determined by the ratio of the integrated intensity of their corresponding peaks to that of peak at 80 ppm. The content of undetectable species (Al_{un}) was calculated by deducting the sum of the detected aluminum species from the Al_T [7].

2.3. Coagulation tests

Coagulation tests were performed by a ZR4-6 six-paddle gang stirrer (Shenzhen Zhongrun Water Industry Technology and Development Co., Ltd, China) to analyze the coagulation performance of $PAC_{2.5}$, $PAC_{2.0}$ and PAC_0 in the treatment of algae from micro-polluted water. *Microcystis aeruginosa* was obtained from the Freshwater Algae Culture Collection at the Institute of Hydrobiology (China). BG11 medium was used as the algae inoculums [8]. The algae were cultured in a constant temperature incubator (Shanghai Boxun Industry & Commerce Co., Ltd, China) under the temperature of 25 ± 2 °C, and illumination of 3000 lx was provided for 12 h every day. The algae with inoculums collected at two cultivation time were used for coagulation tests. The turbidity values of collected solution were 3 ± 0.5 NTU with pH of 7.21 and 10 ± 0.5 NTU with pH of 8.15 respectively. Jar tests were performed at room temperature and natural pH. The self-prepared PAC was added into the water, and the dosage was given as the concentration of aluminum in milligrams per liter (mg Al/L). The commercial PAC with the basicity value of 2.0, as a comparison, was also used in the algae treatment. The water was mixed at a high speed of 300 rpm for 1 min and at a low speed of 40 rpm for 10 min, and then it was allowed to settle for 30 min. Turbidity and pH of water/treated water were measured using a 2100P turbidity meter (HACH, Loveland, USA) and a HQ11 pH meter (HACH, Loveland, USA). Zeta-potential was measured by ZS90 Malvern potential analyzer (Malvern, UK) at the natural pH. The supernatant was acidized using HNO_3 solution and was heated at 100 °C for 5 min before the residual aluminum in the supernatant was measured by chrome azurol S colorimetric analysis according to the national standard of China (GB/T5750.6-2006). The flocs were dried in a vacuum drier, and the morphology of flocs was observed using a VEGA II LMU SEM (TES-CAN Company, Czech). Fractal dimensions of the flocs were calculated by photographic image analysis method using Image-pro Plus 6.0 software [9].

3. Results and discussion

3.1. Aluminum species distributions in polyaluminum chloride coagulant

In this study, PAC is prepared by fresh aluminum hydroxide gels under sunlight. Although the preparation time of this method is long, the temperature of 100 °C is only required in the reaction between powdered $Al(OH)_{3(s)}$ and NaOH for about 20 min and no other artificial heating is needed in the rest of time until PAC is prepared (fresh aluminum hydroxide gels were dissolved). But in the conventional industrial preparation of PAC, the powdered $Al(OH)_3$ or other bauxite firstly reacts with HCl under 100 °C for two hours, and then calcium aluminate is added to adjust the basicity value with the temperature of 80 °C and time of four hours [3]. To compare these preparation conditions, PAC prepared in this study possesses the advantages of short heating time and low energy consumption. Besides, it is often found that high pure PAC solution (without drying) as the product is directly used in the drinking water treatment in the town [3]. And the time interval between preparation and application of PAC solution is long enough for the dissolution of fresh aluminum hydroxide gels. Thus, preparing PAC via fresh aluminum hydroxide gels would be a promising method that could be applied in the industrial scale.

Aluminum species distribution is an important factor to characterize aluminum-based coagulants. Al_b contributing to the coagulation performance is the vital aluminum species and Al_{13} is considered as the most effective component among them [4,10]. It is described that aluminum species distributions of self-prepared PAC are similar with PAC prepared by the conventional method at the range of basicity value from 0 to 2.0 (Table 1 and Table S1). The maximum Al_b content of self-prepared PAC is obtained at basicity value of 2.0. But Al_b content abnormally decreases in the $PAC_{2.5}$ due to the presence of insoluble fresh aluminum