



Characterization of flocculation-conditioning ferric hydroxide gel with differently charged polyacrylamides



Y.L. Wang^{a,*}, W.L. Yan^a, X. Qian^a, Y.Q. Sheng^a, Y.J. Chen^b

^a College of Environmental Science Engineering Research Center for Water Pollution Source Control and Eco-Remediation, Beijing Forestry University, Beijing 100083, China

^b Beijing Waterworks Group Co., Ltd., Beijing 100031, China

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ABSTRACT

Three types of polyacrylamide (PAM) flocculants of cationic PAM WD4960, non-ionic PAM M351, and anionic PAM WDA110 had different performances on the Ferric hydroxide gel (FHG) dewaterability and that M351 was the best one. The optimum dosages of these PAMs did not completely depend on the FHG total suspended solid (TSS) content of 0.2–1.5 g/L. The amount of PAM absorbed on the FHG surface linearly increased with an increase in its dosage, and saturation adsorption did not occur at the tested PAM dosages. The rise in PAM dosage can increase the size of conditioned FHG flocs/aggregates, while can decrease their compactness. The conditioned FHG aggregates at the optimum M351 dosage exhibited a moderate size, the smoothest surface, and the least compact structure among the three types of PAM. Conditioning the raw FHG with the cationic PAM of WD4960 increased its positive charge and decreased its hydrophilicity and specific surface area (S). However, M351 or WDA110 conditioning only increased the negative surface charge and hydrophilicity and decreased the S value of the conditioned FHG. The osmotic pressure variations indicated that, as a hydrogel, the optimum WD4960-conditioned FHG had stronger potential to absorb water from outside than the M351 or WDA110-conditioned FHG. Compared with that in the raw FHG, the free water content (FWC) reduction in the M351- or WD4960-conditioned FHG contributed entirely to the increase in bound water content (BWC) and the water release outside the hydrogel.

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1. Introduction

Water treatment residuals (WTRs), such as alum sludge, ferric sludge, and their mixtures, have been recognized as difficult to dewater [1,14,19,21]. Synthetic polymer or metal salt conditioning is an efficient process most frequently used to improve WTR dewatering, and the proper use of flocculation conditioners is a critical aspect of sludge dewatering [18]. The single or combined usage of polymers and metal salts with different charges and molecules has been demonstrated to be effective in WTR conditioning [2,6,7,9,14,18,19,21].

In a previous study [3], suggested that the alum sulfate coagulated sludge is gelatinous in character. The gel-like network structure of alum sludge, ferric sludge, and their mixtures was also identified in their respective rheological tests [1,7,17,19]. Furthermore, the gel-like network structure played an important role in the

conditioning and dewatering behaviors of WTR or sewage sludge [1,8]. Alum or ferric salt is frequently used to coagulate impurities in raw water, and the coagulant products enter the WTR and represent its main solid materials [1,3,19]. Therefore, the prime determinant of the gel-like structure of the WTR is the alum or ferric hydroxide precipitate and their mixtures contained in this sludge, which should be considered as the key components corresponding to the conditioning and dewatering behaviors of WTR. Using a non-ionic polymer as conditioner [3,14], observed strong similarities in the conditioning and dewaterability behavior of an alumino-humic sludge and an aluminum hydroxide suspension at a concentration equivalent to the coagulant fraction within the sludge. They also suggested that the optimum conditioning dosage is linked to the mass of alum hydroxide precipitate in alum sludge.

According to previous studies [3,14], it can be inferred that the conditioning and dewatering behaviors of aluminum suspensions could resemble those of WTR. However, studies on the effects and characteristics of ferric hydroxide suspension in conditioning WTR are still limited, and the similarity or discrepancy between the conditioning and dewatering behaviors of ferric hydroxide sus-

* Corresponding author. Fax: +86 10 62336596.

E-mail address: wangyil@mail@126.com (Y.L. Wang).

pension and WTR needs to be identified. The experimental results of [19] determined the differences in the structure and characteristics of WTRs conditioned with cationic, non-ionic, or anionic polymers. A cationic polyacrylamide (PAM) of WD4960 is considered the more ideal conditioner for WTRs than M351 and WDA110. The corresponding transition from an alum/ferric hydrogel to a cross-linked gel occurs during the WD4960-conditioning process. Following previous studies, the present study focuses on the effects of differently charged PAM during ferric hydroxide gel (FHG) conditioning to explore variations in the dewaterability, geometrical, and surface physicochemical characteristics and gel structures of the conditioned FHGs. The results of this study can reveal the conditioning and dewatering behavior of ferric hydroxide suspension, and improve the current understanding on WTR conditioning and dewatering.

2. Materials and methods

2.1. Preparation for FHG

FHG was prepared using the method of titration–hydrolysis–coagulation in boiled water [20]. The corresponding procedure was as follows: the saturated FeCl_3 solution was added drop-wise to the boiled deionized water until the color of the formed suspension turned brown–red. This brown–red suspension was boiled again for 1 min to 2 min and was cooled to room temperature. The original FHG suspension was diluted to different total suspended solid (TSS) contents of 0.2, 0.6, 1.0, 1.2, and 1.5 g/L with deionized water. The pH of raw WTRs in a water plant of Beijing, China was 7.06 [19]. The aforementioned FHG suspension was also alkalinized to this pH value with addition of 0.25 mol/L NaOH solution.

2.2. FHG conditioning

FHG conditioning was performed using three types of PAM: WD4960, M351, and WDA110 (Shanghai Weidu Water Treatment Technology Ltd.). WD4960 is a cationic PAM with a molecular weight (MW) of 20–25 MDa and a surface charge density (SCD) of +2.53 meq/g suspended solid (SS). M351 is a non-ionic PAM with an MW similar to that of WD4960 and an SCD of –0.0750 meq/g SS. WDA110 is an anionic PAM with an MW over 15 MDa and an SCD of –1.22 meq/g SS.

FHG conditioning with PAM was performed through a jar test using a six-paddle stirring apparatus (JTY-6, Tangshan Dachang Chemicals Ltd., China). Several 500 mL fresh FHG samples in 1 L beakers were injected with 0.1% PAM solution under stirring for 5 s at a mixing intensity of 800 rpm. Then the mixture was successively agitated at 800 rpm for 1 min and at 62 rpm for 5 min. After mixing, the conditioned FHG aggregates and the corresponding supernatant were withdrawn from the beakers for subsequent testing. The capillary suction time (CST) of the FHG aggregates was determined using a Triton 304B instrument. A JC2000A instrument (Powereach Co., Shanghai, China) was used to measure the contact angle (CA) of the FHG aggregates [13]. The D650 (an absorbance at 650 nm) and conductivity of the supernatant were tested. The zeta potential (ZP) of the colloids was also measured using a Zetasizer 2000 (Malvern, UK). After the supernatant was filtrated using a 0.45 μm cellulose membrane, its viscosity was measured using a Brookfield DV-III rheometer. Its residual PAM contents were derived from the viscosity–PAM content standard curves. All the determined coefficients (R^2) of the three corresponding standard curves were greater than 99%.

2.3. Geometric characterization

The particle sizes of raw and conditioned FHG aggregates were measured using a Mastersizer 2000 instrument (Malvern) with a small-angle laser-light scattering instrument. The corresponding representative diameter of the flocs/aggregates, such as median diameter (d_{50}), was derived from the tests.

A GE-5 digital microscope (Aigo, China) was employed to obtain images of the FHG aggregates. The conditioned FHG aggregate samples were carefully transferred from the jar test beakers to a small glass dish filled with a small amount of deionized water using a wide-mouthed pipette. These aggregates were then distributed evenly and separately for image recording with a microscope. Several parameters, such as area, perimeter, and longest diameter, were selected to characterize the non-spherical morphology of the aggregates using the Image-pro Plus 5.0 software. The image fractal dimensions, including the one-dimensional fractal dimension (D_1) and two-dimensional fractal dimension (D_2), were also identified. D_1 was calculated by regression analysis of the logarithm of the perimeters versus the logarithm of the corresponding longest diameters. D_2 was calculated by regression analysis of the logarithm of the projected areas versus the logarithm of the corresponding perimeters.

2.4. Gel structure characterization

2.4.1. Moisture distribution

The bound water content (BWC) was determined using the differential scanning calorimetry (DSC) approach [10,15]. Prior to the DSC test, the raw or conditioned FHG sample was subjected to centrifugation at 1000 g for 10 min. The supernatant, as a part of FWC, was decanted. In determining the thermograms using a differential thermal analyzer (DSC204, Netzsch, Germany), the settled FHG sample was first cooled at a rate of 10 °C/min to –50 °C and then heated back to 25 °C at the same rate. The amount of adsorbed or released heat during measurement was determined through the peak of an endothermic or exothermic curve. If bound water does not freeze at the given threshold temperature of –50 °C, then the heat released by the settled FHG sample is proportional to its FWC amount. As indicated in Eq. (1), the BWC was determined through its difference from the total water content (TWC), which was measured by drying overnight at 105 °C. The DSC tests were conducted in duplicate.

$$W_B = W_T - \frac{\Delta H}{\Delta H_0} - W_{F\text{-decanted}} \quad (1)$$

Where W_B , W_T and $W_{F\text{-decanted}}$ are the BWC, TWC and decanted FWC in the FHG samples, respectively (kg/kg TSS). ΔH is the amount of heat released by the FHG samples during the DSC test, and ΔH_0 is the standard melting heat of ice (334.7 kJ/kg).

2.4.2. Osmotic pressure

According to Keiding and Rasmussen [16], the osmotic effects of biosolids in dewatering were adapted to gel theory. In this study, the osmotic pressure for the raw and conditioned FHGs was also estimated.

The simplest equation for the osmotic pressure π [8] is

$$\pi = \Delta C \times R \times T \quad (2)$$

where ΔC is the concentration difference (mol/m^3), R is the universal gas constant ($\text{Pa} \times \text{m}^3/\text{K}/\text{mol}$), and T is the absolute temperature (K).

Similar to the π of biosolids as proposed by Keiding and Rasmussen [16], the colligative property of the osmotic pressure in the FHG matrix can be determined through the counter-ions of the charged FHG surfaces. The charge density of the counter-ions can

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