Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1090918

57 (2016) 6217–6223
March

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Effect of cations on simultaneous enhancement of dewaterability and settleability of activated sludge under mild thermal treatment

Jie Yu[a,*], Yan Zhao[a], Xianfa Ma[b], Chaoqin Bai[c]

[a]*Faculty of Architectural, Civil Engineering and Environment, Ningbo University, Ningbo 315211, China, Tel. +86 137 3843 3519; Fax: +86 574 8760 0337; emails: yujie@nbu.edu.cn (J. Yu), zhaoyan@nbu.edu.cn (Y. Zhao)*
[b]*Zhejiang Huanke Environment Consultancy Co., Ltd., Hangzhou 310007, China, email: maxianfa01@163.com*
[c]*Faculty of Architecture, Henan University of Science and Technology, Luoyang 471023, China, email: bcq1980@163.com*

Received 18 February 2015; Accepted 28 August 2015

ABSTRACT

Dewatering and settling are of great importance during activated sludge treatment. The activated sludge fetched from a thickening tank of the wastewater treatment plant was dosed with 0.01–0.10 M cations under mild thermal treatment below 100℃. Specific resistance to filtration and sludge volume index were measured to evaluate the dewaterability and settleability, respectively. Results show that dewaterability and settleability were deteriorated under mild thermal treatment, but improved markedly with the addition of cations, and advanced further together with mild thermal treatment, indicating that the cations transformed the effect of mild thermal treatment from deterioration to enhancement. Calcium and Fe^{3+} were found to be the most effective cations in strengthening the sludge dewatering and settling under mild thermal treatment, and could act immediately after the addition. It is speculated that the cations interact with the binding sites of the polymer substances and cells released by mild thermal treatment, forming polymer–cation–cell complexes, intensifying the flocs inner connection and inducing a superb aggregation. The dewaterability and settleability were thus enhanced by cations under mild thermal treatment.

Keywords: Cations; Activated sludge; Dewaterability; Settleability; Mild thermal treatment

1. Introduction

Increasing amounts of waste activated sludge is threatening the environment, demanding proper and efficient treatment. Sludge settling and dewatering are of high importance, but also difficult issues due to the special characteristics of sludge [1]. The settling and dewatering are commonly performed by gravity sedimentation with the aid of flocculants and mechanical dewatering successively. This procedure hardly reduces the water content below 80%, failing to meet the disposal demand (such as compost, landfill, and incineration) [2].

Several advanced methods were developed to improve the dewaterability and/or settleability, including biological hydrolysis [3], photocatalysis [1], freezing and thawing [4], ozonation [5], sonication [6], and thermal treatment [7]. Among these methods, thermal treatment was widely studied as it is effective and practically viable. Temperature is an essential parameter relating to the dewatering performance and

*Corresponding author.

energy consumption. The dewaterability was improved markedly above 150℃ [8]. The introduction of some chemicals, such as H_2SO_4, $Ca(OH)_2$, and H_2O_2, could further strengthen the dewaterability and lower the temperature to 100℃ or so [7,9]. Recently, researchers adopted mild thermal treatment below 100℃ assisted by additives, like Fe(II)-$S_2O_8^{2-}$, to enhance the dewaterability and obtained promising result, paving way for the application of a new energy-saving method in sludge deep dewatering [10].

Cations play a significant role in the sludge flocculation, settling, and dewatering [11]. They could act in the following ways: charge neutralization, compressing the colloidal double layers, and bridging the negatively charged flocs [12,13]. Besides, Ca^{2+} could specifically interact with alginate, promoting flocs formation [14]. It is likely that various types of interactions are involved simultaneously with different importance, leading to the discrepant performances of cations. The multivalent cations, such as Fe^{3+}, Ca^{2+}, and Mg^{2+}, show a remarkable role in inducing the flocs aggregation and improving the dewaterability and settleability, while the role of the monovalent cations varies with the experimental procedures [11].

This study introduced cations into the sludge under mild thermal treatment, aiming to explore an easy and efficient method for sludge settling and dewatering intensification. To the best of our knowledge, little work has been performed concerning the synchronous improvement of dewaterability and settleability by various cations under mild thermal treatment.

2. Materials and methods

2.1. Activated sludge

The raw activated sludge was fetched from a thickening tank of the wastewater treatment plant in Xihu Beer Chaori Limited Company of Hangzhou, China. The main characteristics of the activated sludge were tested according to CJ/T 221-2005 (China standard for municipal sludge analysis). It contains about 85.3% water with a pH of 7.24, soluble chemical oxygen demand of 105.8 mg/L and mixed liquor suspended solids of 144.4 g/L.

2.2. Experimental procedures

The sludge was washed twice, screened through a 24-mesh sieve, filtered by a vacuum pump to eliminate most of the water and stored at 4℃ before use. The experiments were carried out in a double-walled glass vessel of 1.9 L under atmospheric pressure, equipped with a stirrer and a condenser (Fig. 1). First, about 1.0 L of deionized water and a certain amount of cations (analytical grade KCl, NaCl, $CaCl_2$, $MgCl_2$, or $FeCl_3$) were added into the reactor and preheated to a fixed temperature. The temperature was monitored by a thermometer and kept constant by hot oil circle through the jackets. Then, the sludge was added to form a 1.2-L mixture with 3.0% (w/w) dry solid (DS) content. The expected temperature, 60, 80, or 90℃, was achieved rapidly. The slurry was stirred at 260 rpm for 1 min and then at 160 rpm for homogenization. The samples were taken periodically and analyzed after 10-min cooling.

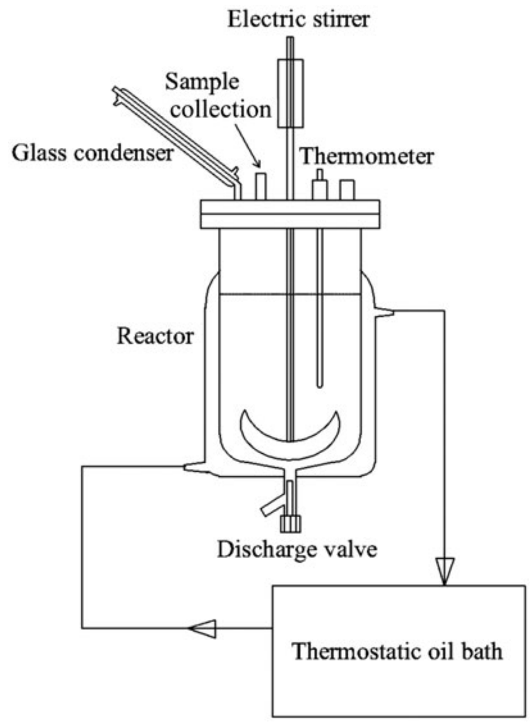

Fig. 1. Schematic diagram of reaction apparatus for sludge.

2.3. Analytical methods

The sludge dewaterability in terms of specific resistance to filtration (SRF) was measured by a special Buchner funnel [15]. The filtration was carried out under 0.05 MPa with a 0.45-μm cellulose membrane. About 50 mL of sludge was filtered and the volume of filtrate was recorded with time. The SRF was calculated by the following equation:

$$r = 2PA^2b/uc \quad (1)$$

where r is the SRF, P is the pressure, A is the filter area, b is the slope of time–filtrate volume curve, u is the filtrate viscosity, and c is the DS content of the cake per filtrate volume.

The sludge volume index (SVI) was determined to evaluate the settleability of sludge according to the Standard Methods for the Examination of Water and Wastewater, 20th edition. About 50 mL of sample was poured into a 50-mL cylinder, and the 30-min settled sludge volume was divided by the suspended solids to be the SVI.

The analyses were performed at least three times and the average results were presented. The sludge was also subjected to a B series biological microscope (Chongqing Optec Instrument Co., Ltd., China) and the micrographs were taken at a magnification of 10 × 10.

3. Results

3.1. Single mild thermal treatment

The SRF and SVI varied markedly for the sludge treated at 60, 80, and 90˚C, as shown in Fig. 2. Sharp elevations of the SRF and SVI were observed within the first 8 h, followed by a gentle increase, indicating the immediate detrimental effect of mild thermal treatment on the sludge dewaterability and settleability. The SRF was increased from 6.8×10^9 cm/g to 9.9×10^9, 2.5 ×, and 3.8×10^{10} cm/g as the temperature increased from 25˚C to 60, 80, and 90˚C, respectively. Meanwhile, the SVI reached 1.5, 1.5, and 2.5 times of the control value (16.53 mL/g). Higher temperatures led to higher SRF and SVI, i.e. worse dewaterability and settleability. The sludge dewaterability was found

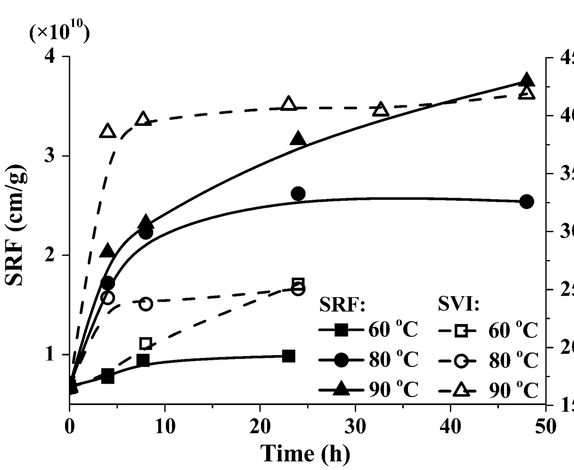

Fig. 2. SRF and SVI variations with time under mild thermal treatment at 60, 80, and 90˚C.

to be degenerated under thermal treatment below 150˚C [8], while the deterioration of settleability by thermal treatment has rarely been reported before. The mild thermal treatment could break up the bindings among polymeric substances, making the flocs hard to settle [10]. Besides, more interstitial water would be trapped in the dispersed flocs, leading to a poor dewatering performance.

3.2. Effect of cations under mild thermal treatment

Cations play an important role in the dewatering and settling process [11,12]. Several common cations, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, and Fe^{3+}, were introduced and the functions of different cations with mild thermal treatment on the dewaterability and settleability were investigated. Since very similar evolution of the SRF or SVI was observed for the sludge treated at 60, 80, and 90˚C with cations, 80˚C was chosen for further exploration.

The effect of various cations on the sludge SRF is presented in Fig. 3. The SRF was reduced quickly within the first 5 min, and then reached a plateau for most of the cations. That is, the sludge dewaterability was improved remarkably by cations and the change seemed to occur within a relatively short time. Further enhancement of the dewaterability was achieved by raising the temperature from 25 to 80˚C. For example, with increasing temperature from 25 to 80˚C, the SRF was reduced by 63.6 and 90.5% in the first 5 min for the sludge with 0.05 M Ca^{2+} and 1/30 M Fe^{3+}, respectively. This indicates that the cations transformed the impact of mild thermal treatment on the dewaterability from deterioration to enhancement. Among these cations, 0.05 M Ca^{2+} improved the dewaterability to the largest extent at 25˚C while the most effective cation at 80˚C was 1/30 M Fe^{3+}.

The evolution of the SVI was consistent with that of the SRF for the sludge with cations at 25 and 80˚C (Fig. 4). The SVI was decreased sharply with the addition of cations at 25˚C, and further lowered at 80˚C. When the temperature was increased from 25 to 80˚C, about 11.5 and 35.5% reduction of SVI was observed in the first 5 min for the sludge with 1/30 M Fe^{3+} and 0.05 M Ca^{2+}, respectively. The settleability was improved evidently by cations, and advanced further together with mild thermal treatment. Among these cations, 1/30 M Fe^{3+} led to the optimal sludge settleability.

It is concluded that the cations could transform the negative effect of mild thermal treatment and further improve the dewaterability and settleability simultaneously. Among the cations, Ca^{2+} and Fe^{3+} performed better than others.

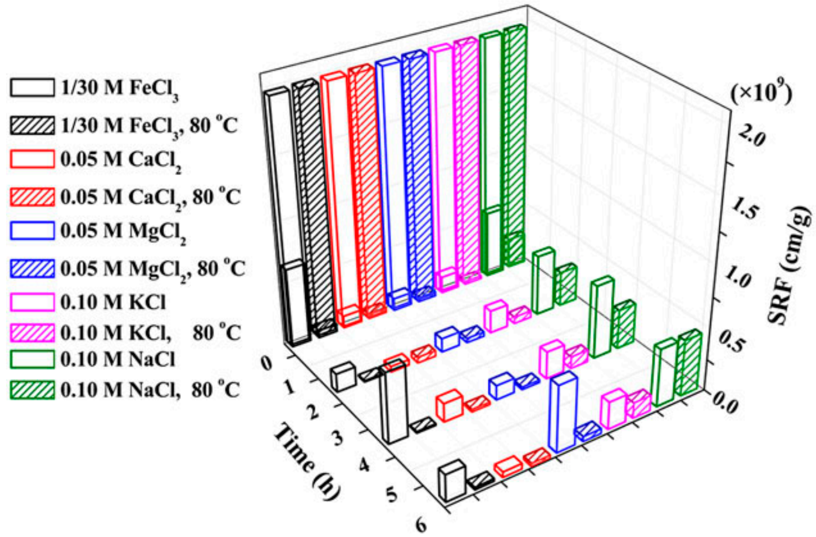

Fig. 3. SRF evolution of sludge with NaCl, KCl, $MgCl_2$, $CaCl_2$, and $FeCl_3$ at 25 and 80˚C.

3.3. *Effect of cations adding time*

Calcium chloride was added into the sludge at different intervals to verify the efficiency of cations in mild thermal treatment. The SRF was decreased dramatically when $CaCl_2$ was added at the beginning of thermal treatment, as presented in Fig. 5. When $CaCl_2$ was added at 2, 4, and 6 h, the SRF was elevated at first, and then decreased as soon as $CaCl_2$ was added, revealing that $CaCl_2$ could depress the dewaterability degeneration induced by mild thermal treatment rapidly. It is reasonable to add $CaCl_2$ into the sludge initially during mild thermal treatment as the lowest SRF was achieved.

Similarly, the SVI was increased at 80˚C, and depressed immediately after the introduction of $CaCl_2$, indicating that $CaCl_2$ could counteract the settleability deterioration caused by mild thermal treatment and improve the settleability significantly (Fig. 6). Outstanding settleability could be obtained by adding $CaCl_2$ at the beginning of the reaction. These results show that cations could ameliorate the sludge dewaterability and settleability during the mild thermal treatment as soon as they were added, and were supposed to be adopted at the beginning of the reaction.

4. Discussion

Cations are a key factor in sludge dewatering and settling process. The multivalent cations had been reported to improve the dewaterability and settleability remarkably at room temperature [16,17]. However, the role of monovalent cations is debatable, since either promotion or inhibition effects are reported by adding Na^+ and K^+ into the sludge [11]. Since activated sludge exhibits colloidal properties with negative charges, the cations neutralize the surface charge and compress the colloidal double layers, leading to the formation of bigger flocs [12]. The multivalent cations, especially divalent cations, could further aid in flocs aggregation and stabilization via interacting with the extracellular polymer substances, like polysaccharides and protein, and bridging the functional groups, while the monovalent cations may cause deterioration of the flocs properties by displacing multivalent cations from binding sites within the flocs [13,18,19]. Different interaction mechanisms can consequently induce the discrepant performances between monovalent and multivalent cations.

In the current work, the cations showed a positive effect in strengthening the sludge dewatering and settling under mild thermal treatment, and multivalent cations performed better than monovalent cations. The role of Na^+ and K^+ could probably be attributed to the neutralization of the flocs negative charge and compression of colloidal double layers by the cations [12]. The bridge role of multivalent cations, to a large extent, could explain their better performance than monovalent ones [11].

The micrographs were also taken to present the flocs status (Fig. 7). The untreated sludge was relatively dispersed as shown in Fig. 7(a). The negatively charged flocs repulsed each other, hindering the aggregation [12]. With the addition of cations, the flocs were compressed and bridged by the cations, inducing the flocs agglomeration and the improvement of

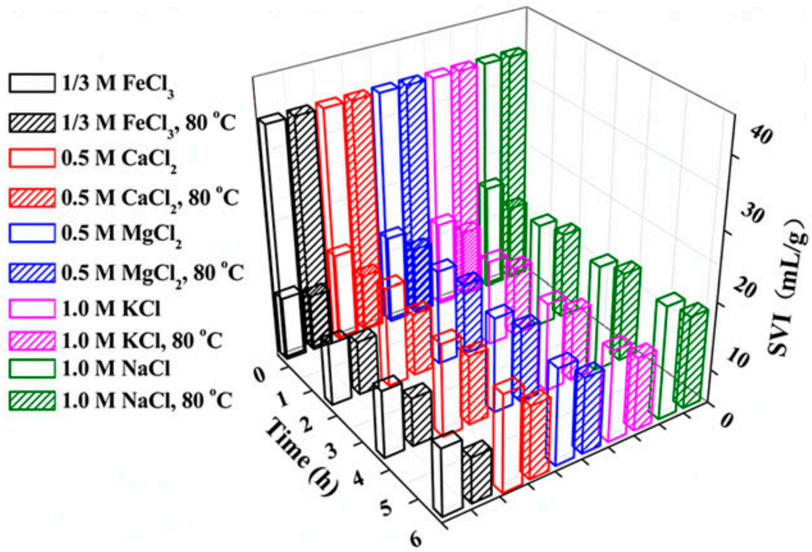

Fig. 4. SVI evolution of sludge with NaCl, KCl, $MgCl_2$, $CaCl_2$, and $FeCl_3$ at 25 and 80˚C.

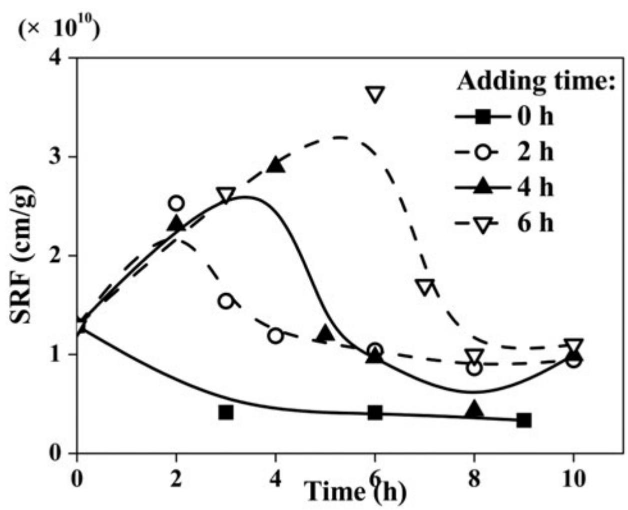

Fig. 5. SRF evolution of sludge at 80˚C with 0.05 M $CaCl_2$ added at 0, 2, 4, and 6 h.

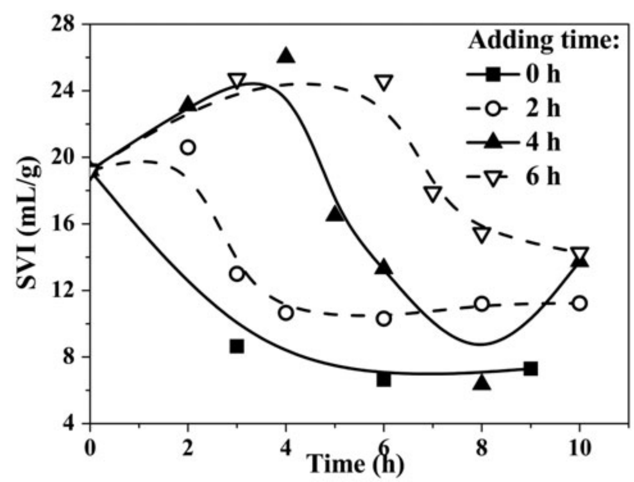

Fig. 6. SVI evolution of sludge at 80˚C with 0.05 M $CaCl_2$ added at 0, 2, 4, and 6 h.

dewaterability and settleability (Figs. 7(b), 3, and 4). Contrarily, a further dispersion of the flocs was observed for mild thermal-treated sludge (Fig. 7c). Mild thermal treatment had been demonstrated to cause the flocs rupture and the release of extracellular and intracellular polymer substances, deteriorating the dewaterability and settleability consequently (Fig. 2) [20,21]. However, some polymer substances released by mild thermal treatment are supposed to act as bioflocculants in the presence of cations [10,22]. Besides, the cells of the bacterium isolated from sludge had been verified to flocculate with $CaCl_2$ even if the cells were killed by thermal treatment [13]. So, it is assumed that cations could react with the binding sites of the cells and polymer substances released by mild thermal treatment, forming polymer–cation–cell complexes and intensifying the flocs inner connection. The buildup of the new compact network induced dramatic improvement of the sludge dewaterability and settleability (Figs. 7(d), 3, and 4). The exposure of the binding sites and the formation of polymer–cation–cell complexes are among the most important mechanisms for the superb performance of sludge with cations under mild thermal treatment.

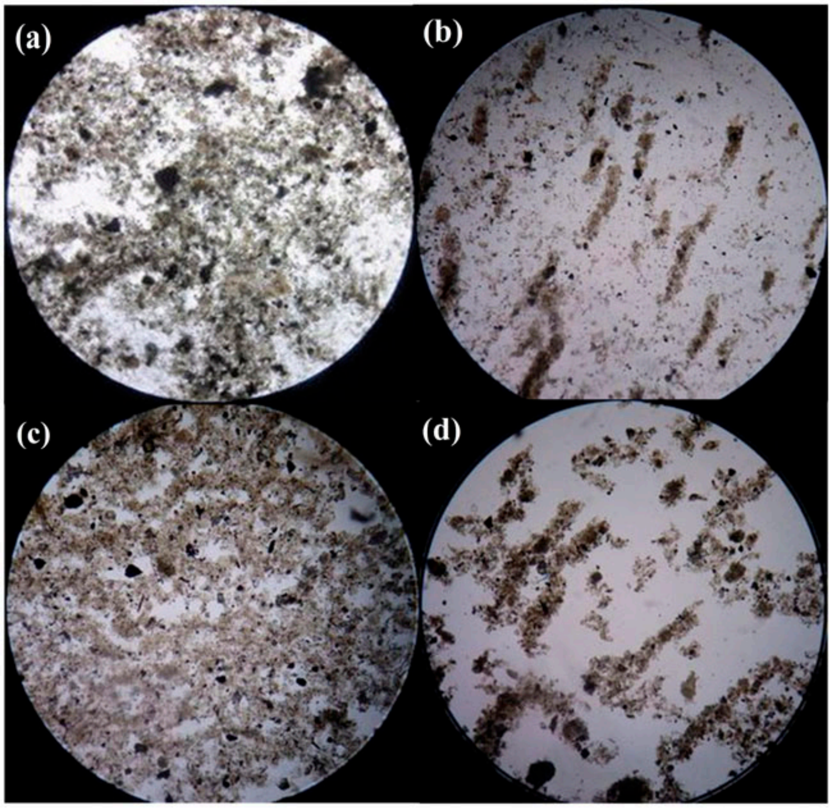

Fig. 7. Micrographs (10 × 10) of the activated sludge: (a) raw activated sludge, (b) sludge with cations, (c) mild thermal-treated sludge, and (d) sludge with cations under mild thermal treatment.

This study provides an effective method to improve the sludge dewaterability and settleability simultaneously. It gives an alternative for sludge deep dewatering and process simplification. The energy consumption, calculated as the sum of the energy consumptions for heating water and solids of the sludge, is much lower compared to those of other advanced dewatering technologies [23]. For instance, the energy consumption for heating sludge from 25 to 80℃ is about 226.4 kJ/kg, while thermal drying requires at least 2,260 kJ/kg for the latent heat of water evaporation. Moreover, the utilization of adjacent waste heat will facilitate the engineering application. So, it is promising to introduce multivalent cations to the sludge treatment process under mild thermal treatment, especially for the sludge designated as hazardous waste, and mild thermal treatment at 60℃ was recommended from the aspect of economy.

Considering the role of mild thermal treatment, we infer that other sludge disintegration approaches, such as sonication, freezing and thawing, might enhance the settling and dewatering as well with the aid of cations. This speculation has been partly verified [6]. More investigations are needed to get an advanced and overall understanding.

5. Conclusions

The cations could transform the impact of mild thermal treatment on the dewaterability and settleability from deterioration to improvement, and strengthen the sludge dewatering and settling significantly under mild thermal treatment. Multivalent cations performed superior to monovalent ones, indicating that different cations act in various ways with flocs. The cations could work immediately after the addition during mild thermal treatment, such that it is suggested to add them at the beginning. It is hypothesized that some polymer substances and cells released by mild thermal treatment could interact with the cations, forming polymer–cation–cell complexes and strengthening the inner link of flocs. The dewaterability and settleability were thus improved simultaneously. The combination of cations and mild thermal treatment gives an efficient and energy-saving alternative for sludge deep dewatering and settling.

Acknowledgments

The authors gratefully acknowledge the anonymous reviewers and the editor for their thoughtful suggestions on revising and improving this work. This work was financially supported by the National Natural Science Foundation of China (Project No. 51408325), the Department of Education of Zhejiang Province (Project No. Y201431005), the Discipline Project of Ningbo University (Project No. XKL14D2061), and K.C. Wong Magna Fund in Ningbo University.

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