Permanganate/bisulfite (PM/BS) conditioning–horizontal electro-dewatering (HED) of activated sludge: Effect of reactive Mn(III) species

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ABSTRACT

A novel activated sludge (AS) conditioning method through permanganate/bisulfate (PM/BS) process was proposed. The method involved a new conditioner of reactive Mn(III) intermediate. Moreover, a Mn(III) conditioning–horizontal electro-dewatering (Mn(III) C–HED) process was established to improve AS dewatering performance. Underlying mechanisms were unraveled by investigating changes in physicochemical characteristics, scanning electron microscope (SEM) morphology, and transformation of water and organic matters. The optimum dewatering conditions for Mn(III) C–HED process with the final water content of 86.94% were determined as the combination of KMnO_4 0.01 mol/L AS and NaHSO_3 0.05 mol/L AS at 20 V for 120 min. Results showed that Mn(III) C–HED process effectively reduced free water and bound water with the corresponding removal ratios of 51.68% and 87.62% at the anode-side as well as 36.55% and 85.08% at the cathode-side, respectively. During the PM/BS process, the produced Mn(III), Mn^{2+} , and MnO_2 exerted chemical and physical effects on AS conditioning and dewatering. Mn(III) disintegrated extracellular polymeric substances (EPS) fractions and cells in AS, as well as induced partial bound water release. Additionally, flocculation effect induced by Mn^{2+} and MnO_2 skeleton building also benefited AS dewatering. AS cells were further disrupted under the effect of a horizontal electric field. Accordingly, EPS within the AS matrix was solubilized, tightly bound (TB)-EPS or loosely bound (LB)-EPS was converted to their corresponding outer EPS fractions, and AS dewaterability improved. Additionally, changes in pH and temperature at HED stage damaged the AS cells and changed the floc properties, thereby leading to easy separation of liquid and AS particles.

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1. Introduction

Sludge is a by-product of wastewater treatment and its dewatering is an essential step to make the transportation and disposal of sludge physically and economically feasible (Subramanian et al., 2010; Devlin et al., 2011; Xiao et al., 2016). In China, the dramatic increase in municipal wastewater treatment capacity has produced a substantial amount of sewage sludge over the recent dozen years (Dai, 2012), which may account for approximately up to 60% of the total operation cost of a wastewater treatment plant (Low et al., 2000). However, sewage sludge is generally difficult to dewater

due to its high water content (WC) ($\geq 95\%$) and fine particles, colloidal (Raynaud et al., 2012), compressible (Shi et al., 2015), and porous fractal network and gel-like structure (Mahmoud et al., 2010; Dursun and Dentel, 2009). Together with more stringent disposal regulations, this phenomenon has caused an urgent demand for more efficient sludge conditioning and dewatering methods.

To reinforce the poor dewaterability of sludge, various conditioning methods (Mahmoud et al., 2013; Skinner et al., 2015), such as the addition of calcined aluminum salts (Zhen et al., 2011), acid/alkaline pretreatment (Neyens et al., 2004), advanced oxidation processes (Zhen et al., 2012), ultrasonication (Feng et al., 2009), electrolysis (Yuan et al., 2011), thermal pretreatment (Bougrier et al., 2008), microwave irradiation (Yu et al., 2009), and

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Abbreviation			
AS	activated sludge	FW	free water
AMW	apparent molecular weight	FWC	free water content
BBD	Box-Benhen Design	HED	horizontal electro-dewatering
BS	bisulfate	LB-EPS	loosely bound extracellular polymeric substances
BW	bound water	Mn(III) C	Mn(III) conditioning
BWC	bound water content	MMPs	magnetic micro-particles
CM-HED	coupling magnetic conditioning–horizontal electro-dewatering	MW	molecular weight
CPAM	cationic polyacrylamide	PM	permanganate
CST	capillary suction time	PSD	particle size distributions
DS	dry solid	RSM	response surface methodology
DSC	differential scanning calorimetry	SEM	scanning electron microscope
EPS	extracellular polymeric substances	TB-EPS	tightly bound extracellular polymeric substances
EEM	excitation-emission matrix	TOC	total organic carbon
FRI	fluorescence regional integration	TSS	total suspended solids
		TWC	total water content
		VSS	volatile suspended solids
		WC	water content

enzymatic treatment (Ayol, 2005), have been employed to change the sludge structure for the easy separation of solid and liquid portions (Tuan et al., 2012). Although these methods may have high dewatering potentials, their application has been limited by factors including sludge volume increase or high energy requirement for operation and complexity of implementation.

Recently, Sun et al. (2015, 2016) reported a novel approach to yield the reactive Mn(III) species through the permanganate/bisulfate (PM/BS) process. These reactive species could oxidize the organic contaminants at extraordinarily high rates. When PM/BS process was used to oxidize the phenol, ciprofloxacin, and methyl blue at pH_{ini} 5.0, the oxidation rate constants (k_{obs}) reached 60–150 s^{−1} that were 5–7 orders of magnitude faster than conventional advanced oxidation processes for water treatment. Some of reactions during the PM/BS process may be expressed as follows (Sun et al., 2015):

With the advantages of high oxidizing speed and wide operative pH range, the PM/BS process may involve a new category of advanced oxidation technologies in terms of contaminant oxidation by reactive Mn(III) species, rather than hydroxyl and sulfate radicals. Although soluble Mn(III) is known to be a strong one-electron oxidizing agent and its high oxidizing speed for organic contaminants in water has been proved recently (Sun et al., 2015), as far as we know, no studies have employed PM/BS process to produce Mn(III) species as a conditioner to promote the sludge dewaterability.

For more than 20 years, laboratory and pilot studies have proven that electric field assisted-dewatering technologies, such as non-pressurized electro-dewatering, pressurized (vacuum or pressure) electro-dewatering, and compression electro-dewatering, are efficient approaches for water removal in sewage sludge (Chu et al., 2004; Saveyn et al., 2005; Tuan et al., 2008; Tuan and Sillanpää, 2010a, b; Mahmoud et al., 2010, 2011, 2016; Tuan et al., 2012; Feng et al., 2014; Qian et al., 2015, 2016; Conrardy et al., 2016; Yu et al., 2017). As a gradually expanding technology, electro-dewatering can reduce the amount of interstitial water and

vicinal water (Tuan and Sillanpää, 2010b) while saving the treatment costs (Mahmoud et al., 2010). And Mahmoud et al. (2010) proposed that the horizontal electro-dewatering (HED) technique would be promising for large-scale applications due to its simplicity in construction, high efficiency, and ease of operation in comparison with the conventional vertical electric field. Zhou et al. (2001) claimed that the WC of activated sludge (AS) ranged from 97% to 92% under the effect of horizontal electric field. Chu et al. (2004) applied the HED process to dewater the digested sludge, and the WC values were 95.8%–92.3%. Moreover, Qian et al. (2016) used the magnetic micro-particles (MMPs) and magnetic field as a coupling conditioning unit prior to HED, in which the WC of AS after coupling magnetic conditioning–horizontal electro-dewatering (CM–HED) at the optimum conditions reached 89.98%.

Based on aforementioned advancements on the PM/BS and HED processes, it could be interesting to conduct the sludge dewatering with their combination: Mn(III) conditioning (Mn(III) C)–HED process. Thus, the AS was treated by Mn(III) C–HED process and the corresponding dewatering effect was systematically investigated in this study. The objectives of this study were to: (a) determine the operating parameters (conditioners dosage, electric voltage, and dewatering time), in terms of the dewatering effect and energy consumption through response surface methodology (RSM); (b) obtain insights into the migration and distribution of water and organic matter in activated sludge matrix along different stages of Mn(III) C–HED process; (c) unravel the mechanism and clarify the enhancement of AS dewatering performance by analyzing the physicochemical characteristics, morphological properties, water distribution, and EPS of AS matrix treated by Mn(III) C–HED process; and (d) provide a novel pre-treatment and dewatering technique for AS.

2. Materials and methods

2.1. Test materials

The AS used in this study was collected from the secondary sedimentation tank in a municipal wastewater treatment plant in Beijing, China, immediately transferred to the laboratory within 1 h and then stored at 4 °C after screened through a 4.0-mm sieve to remove grit (Zhen et al., 2013). The supernatant was decanted to acquire the denser AS samples that were used in this study. Table 1 shows the characteristics of AS samples collected at different times. The total suspended solids (TSS, g/L), volatile suspended solids

Table 1

Main characteristics of AS used in this study before conditioning.

Sample	TSS (g/L)	VSS (g/L)	WC (%)	pH	Zeta potential (mV)	CST (s)
#1	13.5 ± 0.01	8.6 ± 0.01	98.63 ± 0.01	6.90 ± 0.01	−9.47 ± 0.85	29.4 ± 0.99
#2	13.8 ± 0.01	9.1 ± 0.01	98.67 ± 0.01	6.87 ± 0.01	−9.72 ± 0.66	27.3 ± 0.69

#1: RSM optimization of Mn(III) C–HED process; #2: Characterization of AS during Mn(III) C–HED process.

(VSS, g/L), and WC were determined from the weight loss of AS samples that were dried at their respective temperatures in accordance with the standard method (APHA, 2005). The pH was measured using a pH meter (PB-10, Sartorius Stedim Biotech Co., Ltd., Beijing, China). The zeta potential was measured using Zetasizer Nano Z system (Malvern Co., UK) in accordance with electrophoresis theory. The sample for zeta potential test was the extracted supernatant after centrifuging AS samples for 15 min at 3000 rpm (Dursun, 2007). The capillary suction time (CST) was tested by a CST meter (304B, Triton Electronic Co., Ltd., UK) using chromatography paper (17 CHR, Whatman International Ltd., England). All tests mentioned and the subsequent experiments were conducted within a maximum of 5 d and in triplicate to ensure reproduction.

Sodium bisulfate (NaHSO_3 , 58.5%–65.0%) and potassium permanganate (KMnO_4 , >99.5%) were purchased from Beijing Chemical Works (Beijing, China) and have been applied as the sludge conditioner. All the chemical reagents were analytical grade and used as received without further purification.

2.2. Experimental procedure

As depicted in Fig. 1, the two successive stages during the experimental procedure are Mn(III) C and HED.

At Mn(III) C stage, 250 ml of AS was transferred into a 500-ml beaker. The reaction was initiated immediately by adding an appropriate amount of potassium permanganate once a specified constant sodium bisulfate was applied. AS was continuously agitated by magnetic stirrers at 300 rpm for 5 min to ensure homogeneity throughout the reaction. The conditioned AS was then drained under gravity in a cylinder-shaped plexiglass cell with a diameter of 70 mm and a height of 140 mm (Fig. 1b). The bottom of the cell was covered with a polypropylene filter cloth with a 5 μm aperture for water removal, and the filtrate was collected using a beaker on a balance. Drainage continued until no more than two drops of filtrate were collected within 10 min (2 h were necessary). At the HED stage, the electroosmotic dewatering apparatus in the horizontal electrical field is presented in Fig. 1c. It was opened to the atmosphere and there was no pressure difference between the two electrodes. The materials of electrodes were Ta_2O_5 -coated metal oxide IrO_2 . A nylon filter cloth (5 μm aperture) was used to cover the cathode-side, and the water flowed across it. The cross-sectional area of the loading compartment was 85 mm $\times$ 42 mm, and the distance between the two electrodes was 65 mm. Different

voltages were provided by a variable DC power supply (DH1719A-4, Dahua Elec-tronic, Co., Ltd., China) during HED stage of 60–120 min. The filtrated water was regularly collected in a conical flask for following measurement.

2.3. Measurement of bound water content (BWC)

BWC was measured through differential scanning calorimetry (DSC) approach (Lee and Lee, 1995). The temperature of AS sample initially decreased to -60°C at a rate of $10^\circ\text{C}/\text{min}$, assuming that all the free water in this sample was frozen. Then, the temperature increased to 40°C at the same rate. The free water content (FWC) can be obtained by integrating the peak area of the endothermic curve below the baseline that represented the heat absorbed to melt the frozen free water. BWC can then be calculated by the difference of the FWC to the total water content (TWC) (APHA, 2005) as follows:

$$\text{BWC} = \text{TWC} - \Delta H / \Delta H_0 \quad (4)$$

where ΔH is the amount of energy absorbed in the AS samples; and ΔH_0 is the standard melting heat of ice (334.7 J/g) (Feng et al., 2014).

2.4. Supernatant/filtrate characteristics

The supernatant/filtrate was collected at each stage and the following measurements were conducted at room temperature (25°C). Conductivity was recorded using a conductivity meter (EC215, Beijing Kanggaote Science and Technology Co., Ltd., Beijing, China). The total organic carbon (TOC) was measured with a TOC analyzer (TOC-V CSN, Shimadzu, Japan).

The excitation–emission matrix (EEM) fluorescence spectrum was obtained through a luminescence spectrometry (F-7000, Hitachi, Japan), and EEM spectra were obtained using scanning emission spectra from 220 nm to 600 nm at 1 nm increments by varying the excitation wavelength from 200 nm to 400 nm at 5 nm increments (Qian et al., 2016). Five Ex/Em regions (Table 2) of the EEM spectra were determined through fluorescence regional integration (FRI) analysis (Chen et al., 2003). In brief, the cumulative EEM area volumes were first normalized to the relative regional areas. The normalized EEM area volumes ($\Phi_{i,n}$ and $\Phi_{T,n}$, referring to the values of regions I, II, III, IV, and V and the entire region) and the percent fluorescence response ($P_{i,n} = \Phi_{i,n} / \Phi_{T,n} \times 100\%$) were calculated according to the method proposed by Chen et al. (2003).

A waters liquid chromatography system, which consisted of a

Fig. 1. Sketch of the experimental setup for AS Mn(III) C–HED process: (a), Raw AS, (b), Mn(III) C, (c), HED.

Table 2
Five Ex/Em regions for FRI analysis.

Region	Ex/Em	Fluorescence substances
I	200–250/300–330	Tyrosine
II	200–250/330–380	Tryptophan
III	200–250/380–500	Fulvic acid-like materials
IV	250–400/300–380	Soluble microbial byproduct-like materials
V	250–400/380–500	Humic acid-like materials

Waters 2487 Dual λ Absorbance Detector, Waters 1525 pump system, was used to quantify the molecular weight (MW). The organic materials were separated by a Shodex KW 802.5 gel chromatography column (Shoko, Japan). The mobile phase buffered with 5 mM phosphate to pH 6.8 and 0.01 M NaCl was filtered through a 0.22 μ m membrane and then degassed for 30 min by ultrasonication before use. A total of 600 μ L sample was injected at a flow rate of 0.8 ml min⁻¹. Apparent molecular weight (AMW) was calibrated according to polystyrene sulfonate standards (Sigma-Aldrich, USA) of MWs 1.8–32 kDa (Zhang et al., 2017).

2.5. Extraction and analytical methods of EPS fractions

The different EPS layers, namely, slime, loosely bound (LB)-EPS, and tightly bound (TB)-EPS of AS, were extracted through centrifugation and ultrasonication method (Yu et al., 2008; Qian et al., 2016). After all the EPS layers were extracted, the particulates in each layer were filtered through polyether sulfone membranes with a pore size of 0.45 μ m. After extraction, the contents of TOC, EEM fluorescence spectra, and MW of different EPS fractions were recorded following the aforementioned method.

2.6. AS morphology

During the observation of AS morphology, the AS samples were analyzed by freeze-drying treatment under vacuum at -60 °C for 72 h and then coated with gold for SEM observation (Quanta 200, FEI, USA). In addition, the particle size distributions (PSD) of AS were determined through a small-angle light scattering test with a laser scattering instrument (Malvern Mastersizer 3000, Malvern UK). The median particle size (d_{50}), d_{10} , d_{90} , and mass fractal dimension (D_F) can be derived from the PSD curves.

3. Results and discussion

3.1. Response surface methodology (RSM) optimization of Mn(III) C-HED process

Box–Behnken Design (BBD) was adopted to optimize the conditioning and HED conditions (Mahmoud et al., 2011). The potassium permanganate concentration, sodium bisulfate concentration, voltage, and dewatering time were considered as independent variables, namely, X_1 , X_2 , X_3 , and X_4 , respectively. The WC of the dewatered AS and energy consumption were selected as the responses Y_1 and Y_2 , respectively. The Y_2 value could be calculated by the following equation:

$$Y_2 = \sum_{i=1}^n U_i I_i \Delta t \quad (5)$$

where U_i and I_i are the applied voltage (V) and electric current (A) recorded at the i th measurement, respectively. Δt is the time interval between two recorded measures (s), and n is the number of recorded measures.

Table 3 presents the range and levels of the four factors. Twenty nine runs were required for a complete experimental design

Table 3
Code and level of factors chosen for the trials.

Factors		Level		
		-1.00	0.00	1.00
X_1	Potassium permanganate concentration (mol/L)	0.01	0.03	0.05
X_2	Sodium bisulfate concentration (mol/L)	0.05	0.15	0.25
X_3	Voltage (V)	20	30	40
X_4	Time (min)	60	90	120

(Table 4). The optimization goal was to maximize the solid content and minimize the energy consumption of the dewatered sludge by using Design Expert 8.0.5.

The results of the experiments designed by BBD and the corresponding ANOVA are presented in Tables 4 and 5, 6, respectively. After data fitting, a second-order polynomial equation was obtained as follows:

$$Y_1 = 84.24 - 1.66 * X_1 - 4.69 * X_2 - 3.41 * X_3 - 1.52 * X_4 - 3.20 * X_1 * X_2 - 1.42 * X_1 * X_3 - 0.68 * X_1 * X_4 - 1.85 * X_2 * X_3 - 0.52 * X_2 * X_4 + 0.27 * X_3 * X_4 \quad (6)$$

$$Y_2 = 702.00 + 152.00 * X_1 + 314.25 * X_2 + 366.75 * X_3 + 208.50 * X_4 - 51.00 * X_1 * X_2 + 80.25 * X_1 * X_3 + 128.25 * X_1 * X_4 + 198.00 * X_2 * X_3 + 117.75 * X_2 * X_4 + 37.50 * X_3 * X_4 + 225.12 * X_1^2 + 14.00 * X_2^2 + 14.75 * X_3^2 - 3.63 * X_4^2 \quad (7)$$

where Y_1 and Y_2 are the predicted responses (WC, %; energy consumption, kWh/kg water removed) and X_1 , X_2 , X_3 , and X_4 are the coded independent variables (potassium permanganate concentration, mol/L; sodium bisulfate concentration, mol/L; Voltage, V; Time, min). The predicted results obtained from the above equation are also shown in Table 4. The significance of the second-order polynomial equation was assessed by the F-ratio at probability (p-value) to test the statistical significance of the estimated correlations. According to the simulation results based on the model, the optimum dewatering conditions were determined to be the combination of KMnO₄ dosage 0.01 mol/L AS and NaHSO₃ dosage 0.05 mol/L AS at 20 V for 120 min. The WC of AS was reduced to 86.94% under these conditions, and the energy consumption during the electro-dewatering process was 0.0034 kWh/kg water removed, which could cost 0.00030 US dollar/kg water removed. In the study of Mahmoud et al. (2011), an electro-dewatering (EDW) with mechanical pressure resulted in a similar water content of AS to this study at the following conditions: voltage 20 V, pressure 200 kPa, time 120 min, while its energy consumption was about 0.09 kWh/kg water removed.

In addition, the chemical cost for PM/BS process was 0.28 US dollar/kg dry solids (DS) (Table 7), which was more expensive than the traditional cationic polyacrylamide (CPAM) conditioning (Qian et al., 2016). However, the former effectively decreased the WC of AS.

In order to quantify the improvement due to Mn(III) conditioning, the same AS was dewatered by HED directly without pretreatment by PM/BS process. The WC of dewatered AS was 91.33% at 40 V voltage and 120 min duration of an electric field, which was higher than the WC of Mn(III) C–HED treated AS.

However, as indicated in Eqs. (1)–(3), the reactions of sulfite and permanganate salts could result in the MnO₂ formation during AS conditioning process. If all KMnO₄ could translate to MnO₂, one gram dry AS solid contains about 0.059 mg MnO₂, which has a low effect on the final dry solid content or water content of dewatered AS. Thus, the water content was determined without deduction of the yielded MnO₂ mass in this study. During the Mn(III) C–HED process, most of the soluble ions (Mn²⁺, SO₄²⁻) were left in

Table 4
Design and response values.

No. Exp	KMnO ₄ (mol/L AS)		NaHSO ₃ (mol/L AS)		Voltage (V)		Time (min)		Y ₁ (%)		Y ₂ (kWh/kg water removed)	
	X ₁	x ₁	X ₂	x ₂	X ₃	x ₃	X ₄	x ₄	Observed	Predicted	Observed	Predicted
1	0.01	−1.00	0.15	0.00	30	0.00	120	1.00	84.71	85.06	0.0013	0.0010
2	0.03	0.00	0.15	0.00	20	−1.00	60	−1.00	86.50	89.44	0.0005	0.0002
3	0.05	1.00	0.15	0.00	30	0.00	120	1.00	80.82	80.38	0.0019	0.0017
4	0.01	−1.00	0.15	0.00	40	1.00	90	0.00	81.25	83.91	0.0014	0.0013
5	0.01	−1.00	0.05	−1.00	30	0.00	90	0.00	88.05	87.39	0.0005	0.0005
6	0.01	−1.00	0.25	1.00	30	0.00	90	0.00	83.67	84.41	0.0014	0.0014
7	0.05	1.00	0.15	0.00	40	1.00	90	0.00	75.68	77.75	0.0020	0.0018
8	0.01	−1.00	0.15	0.00	20	−1.00	90	0.00	87.01	87.89	0.0004	0.0006
9	0.03	0.00	0.15	0.00	40	1.00	60	−1.00	80.48	82.08	0.0010	0.0010
10	0.05	1.00	0.25	1.00	30	0.00	90	0.00	72.57	74.69	0.0015	0.0016
11	0.03	0.00	0.15	0.00	30	0.00	90	0.00	83.61	84.24	0.0009	0.0009
12	0.03	0.00	0.05	−1.00	20	−1.00	90	0.00	90.96	90.49	0.0004	0.0003
13	0.03	0.00	0.05	−1.00	30	0.00	120	1.00	88.80	87.93	0.0006	0.0006
14	0.03	0.00	0.25	1.00	40	1.00	90	0.00	74.91	74.29	0.0020	0.0019
15	0.05	1.00	0.15	0.00	20	−1.00	90	0.00	87.11	87.41	0.0007	0.0008
16	0.03	0.00	0.15	0.00	30	0.00	90	0.00	85.05	84.24	0.0010	0.0009
17	0.03	0.00	0.05	−1.00	40	1.00	90	0.00	88.28	87.37	0.0008	0.0007
18	0.05	1.00	0.05	−1.00	30	0.00	90	0.00	89.75	90.47	0.0009	0.0011
19	0.01	−1.00	0.15	0.00	30	0.00	60	−1.00	87.98	86.74	0.0008	0.0009
20	0.03	0.00	0.05	−1.00	30	0.00	60	−1.00	91.06	89.93	0.0004	0.0004
21	0.03	0.00	0.15	0.00	20	−1.00	120	1.00	84.77	85.86	0.0005	0.0006
22	0.03	0.00	0.25	1.00	20	−1.00	90	0.00	84.97	84.81	0.0007	0.0006
23	0.03	0.00	0.15	0.00	30	0.00	90	0.00	85.43	84.24	0.0007	0.0009
24	0.05	1.00	0.15	0.00	30	0.00	60	−1.00	86.81	84.78	0.0008	0.0009
25	0.03	0.00	0.15	0.00	30	0.00	90	0.00	84.61	84.24	0.0009	0.0009
26	0.03	0.00	0.25	1.00	30	0.00	120	1.00	80.07	77.51	0.0016	0.0016
27	0.03	0.00	0.15	0.00	30	0.00	90	0.00	83.74	84.24	0.0007	0.0009
28	0.03	0.00	0.25	1.00	30	0.00	60	−1.00	84.40	81.59	0.0008	0.0008
29	0.03	0.00	0.15	0.00	40	1.00	120	1.00	79.85	79.58	0.0012	0.0016

Note: Y₁: WC (%) of dewatered AS; Y₂: Energy consumption (kWh/kg water removed) of electro-dewatering process.

Table 5
ANOVA for the quadratic model of final water content.

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	530.00	10	53.00	16.60	<0.0001 (significant)
A	33.10	1	33.10	10.37	0.0047
B	264.23	1	264.23	82.78	<0.0001
C	139.20	1	139.20	43.61	<0.0001
D	27.63	1	27.63	8.66	0.0087
AB	40.96	1	40.96	12.83	0.0021
AC	8.04	1	8.04	2.52	0.1300
AD	1.85	1	1.85	0.58	0.4564
BC	13.62	1	13.62	4.27	0.0536
BD	1.07	1	1.07	0.34	0.5696
CD	0.30	1	0.30	0.095	0.7617
Residual	57.46	18	3.19		
Lack of Fit	54.91	14	3.92	6.16	0.0461 (significant)
Pure Error	2.55	4	0.64		
Cor Total	587.46	28			

Note: R² = 90.22%; R_{adj}² = 84.79%; A: KMnO₄ dosage; B: NaHSO₃ dosage; C: voltage; D: time.

supernatant/filtrate of AS matrix, which highly increased the salinity of these reject water. The treating process, such as coagulation–calcium precipitation–adsorption/filtration (Daniellaregina and Marialúciacpda, 2008; Silva et al., 2012; Jones and Knocke, 2017) could be employed to deal with this kind of water.

3.2. Variations of physicochemical characteristics and SEM morphology along the Mn(III) C–HED process

3.2.1. Zeta potentials and conductivity of AS matrix

Table 8 presents the changes in zeta potentials and conductivity of AS before and after Mn(III) conditioning. Both the zeta potential and conductivity of AS matrix increased after Mn(III) conditioning.

The increase in soluble cations in AS matrix can lead to AS flocs coagulation by compressing the electrical double layer on their surface and the reduction in absolute value of zeta potential value. According to the DLVO theory, such decrease can weaken the electrostatic repulsion among AS flocs and promote their flocculation (Jucker et al., 1998). Moreover, the implication of the reduction in absolute value of zeta potential also inferred the abatement in the ionized polymer on the surface of AS flocs and the weakening polarity effect between the water molecules (Liao et al., 2001). Thus, the hydrophobicity of AS flocs was strengthened, which can lead to the decrease in their bound water and accelerate their coagulation accordingly (Pere et al., 1993; Liao et al., 2001).

Table 6
ANOVA for the quadratic model of energy consumption.

Source	Sum of squares	df	Mean Square	F Value	p-value
Model	4.266E+006	14	3.047 E+005	9.24	<0.0001 (significant)
A	2.772E+005	1	2.772E+005	8.40	0.0117
B	1.185E+006	1	1.185E+006	35.91	<0.0001
C	1.614E+006	1	1.614E+006	48.92	<0.0001
D	5.217E+005	1	5.217E+005	15.81	0.0014
AB	10404.00	1	10404.00	0.32	0.5833
AC	25760.25	1	25760.25	0.78	0.3919
AD	65792.25	1	65792.25	1.99	0.1798
BC	1.568E+005	1	1.568E+005	4.75	0.0468
BD	55460.25	1	55460.25	1.68	0.2158
CD	5625.00	1	5625.00	0.17	0.6859
A ²	3.287E+005	1	3.287E+005	9.96	0.0070
B ²	1271.35	1	1271.35	0.039	0.8472
C ²	1411.22	1	1411.22	0.043	0.8391
D ²	85.24	1	85.24	2.583E-003	0.9602
Residual	4.620E+005	14	32997.05		
Lack of Fit	4.197E+005	10	4.1969.47	3.97	0.0979 (not significant)
Pure Error	42264.00	4	10566.00		
Cor Total	4.728E+005	28			

Note: R² = 90.23%; R_{adj}² = 80.46%; A: KMnO₄ dosage; B: NaHSO₃ dosage; C: voltage; D: time.

Table 7
Economic feasibility of chemical cost.

	Market Price (USD/t)	Dosage (g/kg DS)	Economic feasibility (USD/kg DS)	Total cost (USD/kg DS)
Potassium permanganate	1881.33	114.52	0.22	0.28
Sodium bisulfate	144.72	377.03	0.06	

Note: The market price for potassium permanganate was from Zhengzhou Dike chemical Co., Ltd., China. The market price for sodium bisulfate was from Guangzhou Yuanyifeng trade Co., Ltd., China. RMB exchange rate with the US dollar (USD):1 USD = 6.91 RMB.

Table 8
Zeta potential and conductivity of AS before and after Mn(III) conditioning.

	Zeta potential (mV)	Conductivity (mS/cm)
Raw AS	−9.718 ± 0.25	1.076 ± 0.02
Mn(III) C	−5.729 ± 0.20	9.482 ± 0.06

3.2.2. AS floc size and mass fractal dimension

The changes in d_{10} , d_{50} , d_{90} and D_F values were presented in Table 9. Many previous studies reported that soluble Mn(III) was a strong oxidizing agent, which can be employed in contaminant transformation and sequestration (Sun et al., 2015, 2016; Sisley and Jordan, 2006). In this study, the Mn(III) oxidization effect may disintegrate the AS flocs into small ones and induce the decrease in d_{10} , d_{50} , and d_{90} values at Mn(III) C stage. However, the slight decrease in the AS flocs size implied that both effects of disintegration and coagulation of AS flocs occurred simultaneously during Mn(III) conditioning stage, and the former was relatively stronger than the latter. According to Eq. (2), the Mn²⁺ ions produced during Mn(III) oxidization conditioning can play an important role in AS flocculation (Higgins and Novak, 1997) through bridge formation between biopolymers of microbial cells. This result was consistent with the previous studies (Stratford, 1992), which revealed that the

divalent cations, such as calcium, magnesium and manganese, can be taken as “contact ions” (Mahmoud et al., 2010) in the binding sites of bacteria for agglutination.

After the HED treatment, AS floc size increased at both anode-side and cathode-side, especially at the anode-side. As the horizontal electric field was used, the water in AS matrix, commonly with cations, was driven toward the negative electrode (cathode-side) under the effect of electro-osmosis, whereas the negatively charged AS particles moved toward the anode-side under the effect of electrophoresis (Mahmoud et al., 2011, 2016). Thus, the vicinal water content in AS decreased more significantly at the anode-side than at the cathode-side and the hydration layer of the AS particle surface, which was beneficial to the flocculation. Thus, this effect combined with Mn²⁺ coagulation led to the sharp increase in particle size at the anode-side. In addition, the changes in the D_F values of AS flocs indicated that their compactness slightly decreased along the Mn(III) C–HED process.

3.2.3. AS SEM morphology

The morphology of AS flocs was presented as SEM images of Fig. 2. Raw AS flocs showed a coarse and flocculent surface with large interstices and voids for water to flow through (Fig. 2a). Under the effects of Mn(III) oxidation and Mn²⁺ flocculation, the conditioned AS flocs by Mn(III) showed a smooth and compact surface with smaller voids than raw AS. The MnO₂ particles produced according to the reaction in Eq. (3) may contribute to such morphology and can also act as skeleton builders, which were beneficial to produce small holes and provide the access for water removal (Zhang et al., 2017). In the inset of Fig. 2b, the cracked microbial cells indicated the oxidation effect of Mn(III).

After the HED stage, the shrinking structure of AS occurred due to the disruption of cells and release of bound water under the effect of electric field (Tuan and Sillanpää, 2010b). Some pores were

Table 9
Particle size and mass fractal dimension of AS at different Mn(III) C–HED stages.

	Raw AS (μm)	Mn(III) C (μm)	Anode-side (μm)	Cathode-side (μm)
d_{10}	17.61	16.10	19.30	16.47
d_{50}	48.48	45.55	57.39	49.96
d_{90}	104.53	101.43	140.81	123.98
D_F	2.28	2.26	2.21	2.24

Fig. 2. SEM morphology of AS at different Mn(III) C–HED stages.

observed in AS due to the H_2/O_2 production from water electrolysis (Eqs. (8), (9)). Weber and Stahl (2002) reported that the sludge near the anode-side has a more porous structure than that near the cathode-side. In this study, AS flocs at the anode-side showed a rough surface but presented a relatively compact structure at the cathode-side, which was caused by more MnO_2 particles formed at the anode-side (Eq. (10)). In addition, according to Equations (8) and (9), the pH at the cathode-side increased whereas that at the anode-side decreased (Mahmoud et al., 2010) as well as contributed the rough surface of AS flocs at the anode-side. During the HED stage, a considerable ohmic loss occurred in this electro-chemical cell, which caused heating in the dewatering device and thus a decreasing liquid viscosity (Mahmoud et al., 2011, 2016; Navab-Daneshmand et al., 2015).

At the cathode-side:

At the anode-side:

3.3. Variations of water distribution along the Mn(III) C–HED process

The DSC thermograms for the AS samples at different dewatering stages are presented in Fig. 3. A large exothermic phase change occurred from -5°C to -20°C for the AS sample at the cooling stage. However, no obvious exothermic peak was observed for the temperature below -20°C . The areas above the baseline were 237.8 J/g for raw AS and 256.0 J/g for the AS samples at the Mn(III) C stage. The exothermic peak areas of the AS samples after HED were 243.3 and 236.4 J/g at the anode-side and cathode-side, respectively. The crossed fraction in the curve of the exothermic peak was attributed to the large heat release of the water in the AS samples (Qian et al., 2016). While heating at the same rate of $10^\circ\text{C}/\text{min}$, much heat absorption occurred near the range of 0 – 20°C . The amount of heat absorption in this region was slightly larger than that released at the cooling stage.

Fig. 3. DSC thermograms of AS at different Mn(III) C–HED stages.

Table 10

Water distribution in AS at different Mn(III) C–HED stages.

	TWC (kg/kg DS)	FWC (kg/kg DS)	BWC (kg/kg DS)
Raw AS	48.67	46.30	2.38
Mn(III) C	9.49	7.90	1.59
Anode-side	6.88	5.73	1.15
Cathode-side	8.45	6.91	1.54

The water contents of the AS samples at the different Mn(III) C–HED stages obtained from DSC are shown in Table 10. The raw AS contained 2.38 kg of bound water per kg of DS mass. This value was in agreement with the result of Qian et al. (2016). As indicated in Table 10, 0.79 kg/kg DS BW transferred to FW at the Mn(III) C stage, which can be ascribed to the EPS degradation and AS flocs disruption by Mn(III) oxidation as well as the coagulation effect of Mn^{2+} . This result was different from previous reports that the conditioning with inorganic or organic flocculants (polymers, iron or aluminium salts) could hardly disintegrate EPS structure and convert bound water into free water to improve the degree of sludge dehydration (Niu et al., 2013; Chen et al., 2016; Zhang et al., 2017). After gravitational drainage, 38.40 kg/kg DS free water was removed through the water access under the skeleton building effect of MnO_2 . This result was in accordance with previous studies that the gravitational settling dewatering was only effective in removing free water (Mahmoud et al., 2010).

At the subsequent HED stage, both FWC and BWC decreased, and the corresponding rates were 27.47% (anode-side) and 12.53% (cathode-side) for FWC, whereas 27.67% (anode-side) and 3.14% (cathode-side) for BWC, respectively. As mentioned in section 3.2.3, the water electrolysis, variations of pH, and temperature under the effect of horizontal electric field at HED stage can reduce the liquid density, viscosity, and the surface tension of AS matrix then led to EPS and cell disruption (Mahmoud et al., 2010; Tuan and Sillanpää, 2010b). Therefore, the bound water released from the HED treated AS flocs and the free water was driven toward the cathode-side by the electro-osmotic flow, which resulted in the much lower water content in AS at the anode-side than at the cathode-side (Tuan and Sillanpää, 2010a). During the whole Mn(III) C–HED process, the reduction rates of TWC, BWC, and FWC for AS flocs were 85.86% , 87.62% , and 51.68% for anode-side; 82.64% , 85.08% , and 36.55% for cathode-side, respectively.

Fig. 4. Variations of TOC in EPS of AS at different Mn(III) C–HED stages.

3.4. Changes in organic matter along the Mn(III) C–HED process

3.4.1. TOC content in AS EPS

Fig. 4 presents the variations of TOC values in the three-layer EPS fractions during the entire process. After Mn(III) conditioning, the TOC contents in slime, LB-EPS, and TB-EPS increased with 22.97, 7.63, and 0.09 times, respectively. At the following HED stage, TOC content in AS EPS increased at both anode-side and cathode-side.

This result implied that Mn(III) oxidation can decompose the bacterial cells in AS flocs and improve organic compounds in EPS matrix. Under the effect of horizontal electric field, AS cells were further disrupted, then their cytoplasm released and contributed to the EPS layer-fractions. Moreover, the most TOC increase occurred for slime among these three EPS layers during the Mn(III) C–HED process. In comparison with raw AS, the LB-EPS or TB-EPS ratio in total EPS decreased, whereas slime EPS ratio increased along the Mn(III) C–HED process. This result indicated that both LB-EPS and TB-EPS were compressed and the inner EPS fractions transformed to the outer ones during the above process, which can facilitate the AS dewatering (Niu et al., 2013).

In addition, the TOC values in EPS of AS flocs at the cathode-side were higher than at anode-side. Under the effect of electro-osmosis, the released un-charged intra-cellular materials at anode-side also can migrate to the cathode-side of HED cell along with water (Tuan and Sillanpää, 2010a). The more water migration, the more these dissolved organics. Combined with Table 10, lower EPS content implied lower water content in AS flocs and higher dewatering effect.

3.4.2. Distribution and migration of EEM-identified organics

As indicated in Fig. 5a–c, four peaks of A, B, C, and D were identified in the EEMs of slime in raw AS flocs, which were identified as tryptophan-like protein (peak A), aromatic protein (peak B) (Chen et al., 2003), visible fulvic acid-like (peak C), and UV fulvic acid-like substances (peak D) (Qian et al., 2016). Only two peaks of A and B were observed in EEMs of LB-EPS and TB-EPS of raw AS, and

Fig. 5. EEM fluorescence spectra of the Slime (a), LB-EPS (b), and TB-EPS (c) at different Mn(III) C–HED stages.

the intensities of these two peaks were stronger in TB-EPS. Along the Mn(III) C–HED process, A and B peaks in the EEMs of AS EPS mostly appeared. Moreover, Mn(III) conditioning can strengthen these two peaks in the outer EPS layers, and much more increase in peak A occurred in slime. For TB-EPS in AS flocs, the peaks A and B were weakened after Mn(III) C stage. This phenomenon implied that Mn(III) oxidation led to the cell disruption and EPS disintegration, which converted into dissolved organics and other EPS fractions, especially for TB-EPS, thus the sludge dewatering was improved (Yu et al., 2008).

As the conditioned AS was treated by HED, the slime EPS in AS flocs at anode-side contained weakened peak A and B, as well as peaks D and E, whereas slightly enhanced peak A occurred at cathode-side, and peak E also remained. For the LB-EPS and TB-EPS, the peaks A and B were weakened for AS flocs at anode-side but were strengthened at cathode-side. This phenomenon was consistent with the variation of TOC contents near both electrodes, demonstrating the migration of un-charged organic substances toward the cathode-side with the electro-osmotic flow (Tuan and Sillanpää, 2010b).

Fig. 6a, c and 6e presented the $\Phi_{T,n}$ values of three-layer fractions along the Mn(III) C–HED process. A sharp increase in $\Phi_{T,n}$ values after the Mn(III) conditioning occurred for slime and LB-EPS but

decrease for TB-EPS. At the HED stage, the $\Phi_{T,n}$ values of three-layer EPS fractions decreased at the anode-side, whereas the $\Phi_{T,n}$ values for slime EPS decreased continuously at the cathode-side but increased sharply for LB-EPS and TB-EPS. Moreover, the $\Phi_{T,n}$ ratios of EPS layer fractions to total EPS increased for slime and LB-EPS along Mn(III) C stage but sharply decreased for TB-EPS, which indicated that the TB-EPS fractions were compressed.

For the $\Phi_{i,n}$ values (Fig. 6a, c and 6e) of EPS fractions, the tyrosine (Region I), tryptophan (Region II), and fulvic acid-like materials (Region III) for slime and LB-EPS increased after Mn(III) conditioning, whereas soluble microbial byproduct-like materials (Region IV) and humic acid-like materials (Region V) of three-layer EPS fractions remained stable. In addition, $\Phi_{i,n}$ values of all regions mostly decreased in TB-EPS at the same time. At the HED stage, almost all $\Phi_{i,n}$ values of three-layer EPS fractions decreased at the anode-side. However, all $\Phi_{i,n}$ values of slime EPS generally slightly decreased at the cathode-side but they showed a completely opposite variation for the LB and TB-EPS.

According to previous studies (Xiao et al., 2016; Shao et al., 2010), high tryptophan-like protein and soluble microbial byproduct-like materials in LB-EPS may not be beneficial for sludge filterability. However, the effective dewatering by Mn(III) C–HED process indicated that the Mn^{2+} coagulation and MnO_2 skeleton

Fig. 6. $\Phi_{i,n}$, $\Phi_{T,n}$, and FRI distributions of the Slime (a)(b), LB-EPS (c)(d), and TB-EPS (e)(f) at different Mn(III) C–HED stages.

Fig. 7. Molecular weight distribution of the slime (a), LB-EPS (b), and TB-EPS (c) at different Mn(III) C–HED stages.

building effect can exceed such over-oxidation effect of Mn(III) on AS, which can be an effective pretreatment for HED.

In Fig. 6b, d and 6f, the $P_{i,n}$ values of the five regions of slime, LB-EPS, and TB-EPS showed a similar trend during the entire process. After the raw AS was conditioned by Mn(III), the $P_{i,n}$ values of region I and region IV increased, region II remained stable, whereas the other two regions generally decreased.

3.4.3. High performance size-exclusion chromatography (HPSEC) analysis

To ascertain the key organic compounds distribution in AS during the Mn(III) C–HED stages, the MW of organics was analyzed. Zhang et al. (2017) suggested that three main molar mass fractions can be distinguished: macromolecular fraction (>5000 Da) mainly composed of carbohydrates and proteins, mid molecular fraction (1000–5000 Da) mainly composed of humic substances, and low molecular fraction (<1000 Da) mainly composed of building blocks and organic acids. The MW distributions of three-layer EPS fractions in AS during Mn(III) C–HED process are presented in Fig. 7. Four MW peaks were observed in different EPS fractions: 300 Da, 1500 Da, 4000 Da, 40,000 Da.

As depicted in Fig. 7a–c, each intensity of MW significantly intensified in slime EPS and slightly increased in LB-EPS after Mn(III) treatment. However, the signals of four MW peaks weakened in TB-EPS simultaneously. These observations were consistent with the variations of $\Phi_{i,n}$ values for corresponding regions (Fig. 6d, f, and 6h). Moreover, at the subsequent HED stage, nearly all peaks obviously increased at the anode-side in three-layer EPS. However, for the cathode-side, similar increases were observed in the slime and LB-EPS. In addition, the intensity of low and middle MW compounds sharply weakened in TB-EPS, whereas the high molecular weight organic compounds increased simultaneously, which was confirmed by the strengthening intensity of MW peak on 40,000 Da. Moreover, the increase in peak 40,000 Da in three-layer EPS fractions during the entire process indicated the high content of protein, which was detrimental to AS filterability (Xiao

et al., 2016; Shao et al., 2010). Combined with the results of water distribution in AS (Table 10), HPSEC analysis further confirmed that the Mn^{2+} and MnO_2 effects overcame the influence of protein increase, induced a high water removal efficiency during the Mn(III) C–HED process.

4. Conclusion

In this study, a novel PM/BS conditioning–HED process was applied to improve the AS dewatering performance.

The produced manganese forms during the PM/BS process induced a combined conditioning effect on AS. Mn(III) oxidation led to the cell disruption and EPS disintegration, which induced partial bound water release. Moreover, Mn^{2+} ions can play an important role in AS flocculation through bridge formation between biopolymers of microbial cells. In addition, the increase in soluble cations in AS matrix can compress the electrical double layer, weaken the polarity effect between water molecules, and strengthen the hydrophobicity thus facilitated the AS dewatering. As for the MnO_2 , which can act as skeleton builders and lead to a more porous and incompressible structures of AS, provided passages for water removal.

Under the effect of horizontal electric field, AS cells were further disrupted, then their cytoplasm were released together with part of bound water. Both LB-EPS and TB-EPS were compressed and the inner EPS fractions transformed to the outer ones during HED stage, which was beneficial to AS dewatering. In addition, the application of an electric field produced electrochemical reactions, which led to the changes in pH, temperature and manganese species. These effects caused damage to AS cells and changed flocs properties. Moreover, water migrated from anode-side to cathode-side and then was removed.

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