



Effects of organic matter and dewaterability changes on sludge calorific value during acid treatment

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Received: 6 September 2023 / Accepted: 4 November 2023 / Published online: 5 December 2023
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Abstract

Acid treatment can increase the sludge calorific value to some extent by separating inorganic elements. In order to determine the mechanism by which acidification affects the sludge calorific value from an organic perspective, we investigated the changes in organic matter and dewaterability under different pH conditions. The results of this study showed that acidification conditioning retained organic matter while removing a greater amount of inorganic elements. Furthermore, acid treatment significantly increased the zeta potential and particle size of sludge particles and facilitated the precipitation of biological organic components from the supernatant to the surface of sludge particles. Acid-treated sludge exhibited a lower moisture content and a higher proportion of organic matter, and sludge treated with H₂SO₄, HCl, and HNO₃ exhibited respective increases in calorific values of 12.14%, 7.92%, and 8.01% under pH 2. The calorific value of the acid-treated sludge was higher, making it more suitable for subsequent incineration. The findings of this study serve as a reference and foundation for efficient sludge incineration.

Keywords Sludge incineration · Acid treatment · Sludge recycling · Calorific value · Extracellular polymeric substances (EPS) · Fourier transform infrared (FTIR)

Introduction

With the accelerated pace of urbanization and industrialization in China, the scale of urban wastewater treatment has been steadily increasing, resulting in a continuous rise in sludge production. According to statistics, in 2019, China's sludge production exceeded 60 million tons, and it is projected to surpass 90 million tons annually by 2025 (Guo et al. 2022). Sludge composition contains harmful substances such as mineral salts, organic pollutants, pathogenic

bacteria, and heavy metals. Without proper disposal and management, these components can pose a threat to the ecological environment and seriously endanger human health (Djandja et al. 2021). Disposal technologies for sludge include sanitary landfills, land utilization, composting, and incineration (Raheem et al. 2018). Among these, sludge incineration is a rapid and effective method that can quickly reduce volume and destroy organic matter. This approach has been widely applied globally (Kuo et al. 2007; Huber et al. 2016). However, it is imperative to underscore that sludge, owing to its high moisture and ash content, coupled with its low calorific value, poses a formidable challenge to the incineration process (Xu et al. 2023).

In practical applications, co-incineration of sludge with fuels is commonly employed, often requiring the addition of more than 30% of fossil fuels such as coal to meet the requirements of combustion and energy balance. This approach of introducing external fossil energy not only greatly increases the cost of sludge disposal but also exacerbates the emission of smoke pollutants. Furthermore, the high moisture content of sludge often results in a large volume, causing inconvenience in handling and transportation. Enhancing the dewatering capability of sludge is considered

Responsible Editor: Guilherme Luiz Dotto

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crucial for reducing cake moisture content and sludge management costs (Wong et al. 2015; Cai et al. 2018). In recent years, a large amount of aluminum and iron salts have been used as conditioning agents for flocculation, phosphorus removal, and deep dehydration of sewage sludge. Consequently, the content of Fe and Al in sludge has been increasing, which has further contributed to the reduction of organic components in sludge. In the face of these challenges, it has become crucial to find pretreatment methods that can reduce the moisture content of sludge and increase the proportion of its organic components.

The following are various commonly used pre-treatment methods: thermal treatment (Neyens and Baeyens 2003), ultrasonic treatment (Mobaraki et al. 2018), microwave irradiation (Liu et al. 2016), electrochemical conditioning (Mahmoud et al. 2018), as well as the addition of coagulants or flocculants (Wei et al. 2018), oxidants (Kim et al. 2016), and alkalis (Wei et al. 2019). However, thermal treatment consumes huge quantities of energy, has high operational expenses, demands costly operational equipment, and is prone to emitting odors and causing secondary pollution to the environment. Ultrasonic treatment, microwave pretreatment, and electrochemical pretreatment require more energy and more sophisticated instruments and are consequently difficult to implement in practical applications. Fenton oxidation technology also has obvious limitations, such as its intricate operation and higher process expenses. The application of ozone oxidation technology has also encountered obstacles due to the instability of ozone itself, high operational costs, and strict regulatory requirements. In addition, the use of coagulants or flocculants introduces metallic components, increases the proportion of inorganic components in the sludge, and reduces the calorific value of the sludge during combustion. Most importantly, these above-mentioned methods can seriously degrade the organic components in sludge after treatment, thus lowering its calorific value and making it unsuitable for subsequent incineration.

In contrast to these methods, acidification conditioning stands out as a cost-effective and uncomplicated approach widely employed in the pretreatment of sludge (Wei et al. 2019). It can effectively increase the calorific value of sludge to some extent (Liang et al. 2023). Metal oxides and hydroxides in sludge can be dissolved and released under acidic conditions, so the simple chemical method of acid conditioning can be fully utilized for extracting Fe, Al, Ca, and other metal elements in sludge and releasing them into the liquid phase (Raynaud et al. 2012; Keeley et al. 2016). The significant extraction of inorganic elements from the solid phase to the liquid phase results in a relative increase in the organic content of the sludge, thus increasing its calorific value. However, it is important to note that this is a study conducted on the effects of acidification conditioning on the calorific value of sludge from an inorganic perspective. The

specific variations in other factors related to sludge calorific value, such as organic constituents and moisture content during this process, still need to be further investigated. This will contribute to gaining a deeper understanding of the mechanism by which acidification affects the calorific value of sludge.

The aim of this study was to explore the mechanism of the effects of acidification conditioning on the sludge calorific value from an organic perspective. The variations in organic matter and dehydration performance under different pH conditions during acid treatment were investigated to infer their impacts on the calorific value of sludge. Various characteristics of the sludge were examined to assess the dewatering effectiveness and changes in organic components, including the concentrations of suspended solids (SS) and volatile suspended solids (VSS), the zeta potential and diameter of sludge flocs, as well as the moisture content (W_c) and calorific value (H_{hv}) of sludge cakes. Additionally, the study was extended to evaluate extracellular polymeric substances (EPS), fluorescent components, surface functional groups, and the surface microstructure within the sludge, thereby inferring the approximate effects of acid treatment on the biological organic components and moisture in the sludge. The findings of this research can serve as a reference and the basis for efficient sludge incineration.

Materials and methods

Sludge and reagents

The sludge used in the experiment was collected from the secondary sedimentation tank of a wastewater treatment plant in the urban area of Dongguan City. After sample collection, it was immediately transported to the laboratory and stored in a refrigerator at a temperature of 4°C. To remove excess supernatant and increase the concentration of the sludge, gravity sedimentation was used. Prior to analysis and experimentation, the original sludge was thoroughly mixed by rapid mixing. The pH value of the raw sludge was 6.98.

The chemical reagents were purchased from Guangzhou Chemical Reagent Factory, including sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3), all of which were of analytical grade.

Experimental procedures

Sixty milliliters of activated sludge was taken and poured into a 100 mL beaker. The beaker was placed on a magnetic stirrer, and the pH of the activated sludge was adjusted to 2, 3, 4, 5, and 6 using a sulfuric acid (H_2SO_4) aqueous solution at a concentration of 2 mol/L, while simultaneously a blank sample was set up. The pH adjustment and stirring reaction

of activated sludge were carried out at 300 r/min for 20 min. After that, it was left to stand undisturbed for 10 min. The change in acidity value of activated sludge was detected using a pH meter, and the relevant labels were written. The same procedural methods were applied for hydrochloric acid (HCl) and nitric acid (HNO₃) as comparative experiments.

Extraction of extracellular polymeric substances (EPS)

To investigate the changes in biopolymers within the extracellular polymeric substances (EPS) layer of the sludge, soluble EPS (S-EPS), loosely bound EPS (LB-EPS), and tightly bound EPS (TB-EPS) were extracted from the sludge samples (Li and Yang 2007; Domínguez et al. 2010; Liu et al. 2017).

Firstly, 30 mL of the sludge samples was taken into a 50 mL centrifuge tube. The tube was centrifuged at 4 °C and 8000 g for 15 min to collect the supernatant as S-EPS. Next, a 0.05% sodium chloride (NaCl) solution with a temperature of 70 °C was used to resuspend the precipitate to its original volume. Subsequently, a vortex oscillator (XW-80A) was employed to mix the suspension for 1 min until it was uniformly dispersed. Then, the mixture was centrifuged at 4 °C and 8000 g for 15 min, collecting the supernatant as LB-EPS. Finally, the precipitate was resuspended back to its original volume using a 0.05% NaCl solution. The suspension was incubated in a water bath at 60 °C for 30 min, followed by centrifugation at 4 °C and 8000 g for 15 min to obtain the supernatant as TB-EPS.

S-EPS, LB-EPS, and TB-EPS were filtered using a 0.45 μm filter before being analyzed for proteins and polysaccharides. The protein concentration was measured using the Lowry-Folin method, with bovine serum albumin as the standard (Lowry et al. 1951). The polysaccharide concentration was evaluated using the phenol–sulfuric method, with glucose as the standard (Herbert et al. 1971).

Three-dimensional fluorescence spectroscopy analysis

The three-dimensional fluorescence spectra were measured using a RF-6000 fluorescence spectrophotometer (Shimadzu, Hong Kong). The excitation-emission matrix (EEM) spectra were monitored within the excitation wavelength range of 220 to 500 nm and the emission wavelength range of 280 to 550 nm. The excitation and emission slits were set to 5 nm, and the scanning speed was maintained at 12,000 nm/min.

The analysis of typical organic compounds and fluorescence intensity in the sludge was performed using the fluorescence region integration (FRI) method (Chen et al. 2003). The equations used for calculation were shown in Eqs. (1) and (2).

$$\Phi_{i,n} = MF_i \iint_{exem} I(\lambda_{ex}\lambda_{em}) d\lambda_{ex} d\lambda_{em} \quad (1)$$

$$\Phi_{T,n} = \sum_{i=1}^5 \Phi_{i,n} \quad (2)$$

where $\Phi_{i,n}$ was the integrated standard volume of fluorescence region *i*, λ_{ex} was the excitation wavelength, λ_{em} was the emission wavelength, $I(\lambda_{ex}\lambda_{em})$ was the fluorescence intensity corresponding to the excitation and emission wavelengths, $\Phi_{T,n}$ was the integrated standard volume of the total fluorescence region, MF_i was the multiplicative factor, which was the reciprocal of the ratio between the integrated area of fluorescence region *i* and the total integrated area of fluorescence regions.

Moisture content and calorific value analysis

The acidified sludge samples were dehydrated using the vacuum filtration method. The vacuum degree during filtration was 0.06 MPa, and the duration was 5 min. Subsequently, the sludge cake was placed in a drying oven at 105 °C until a constant weight was achieved. Based on the change in mass before and after drying, the sludge cake's moisture content (W_c) was calculated using Eq. (3).

$$W_c = \frac{W_1 - W_2}{W_1} \times 100\% \quad (3)$$

where W_1 was the weight of the sludge cake after filtration, W_2 was the weight of the sludge cake after drying at 105 °C.

The calculation of the calorific value of sludge commonly requires the oxygen content of the sludge. However, the presence of metals in the sludge can interfere with oxygen measurements. Therefore, in this study, the formula proposed by Zhou was used to calculate the calorific value (H_{hv}) of the sludge (Zhou et al. 2011). The equation was shown as Eq. (4).

$$H_{hv} = \frac{25368V_s}{T_s} - 1918.8 \quad (4)$$

where V_s was the volatile solids content in the sludge, T_s was the total solids content in the sludge.

Analytical methods

The measurement of SS (suspended solids) and VSS (volatile suspended solids) in the sludge samples was conducted using standard methods (APHA et al. 2005). The pH value was determined using a pH meter (PH-100B, Lichen, China).

Zeta potential analysis and dynamic light scattering (DLS) particle size analysis of the supernatant from raw sludge and acidified sludge samples were performed at 25 °C

using an Omni instrument (Brookhaven, USA). The parameters D10, D50, and D90 represent the diameters of the corresponding percentages of particles less than the diameters stated.

The surface functional groups (Fourier transform infrared spectroscopy, FTIR) of the sludge were measured using a Fourier transform infrared spectrometer (Nicolet iS50, Thermo Fisher Scientific, USA) with a scanning range of 4000–400 cm^{-1} and a resolution of 4 cm^{-1} . The microscopic structures (scanning electron microscope, SEM) of the raw sludge and acidified sludge samples were observed using a scanning electron microscope (Zeiss Sigma 300, Germany). The thermogravimetric (TG) analysis was performed on a TG209F1 Libra unit, and samples were heated in an atmosphere of nitrogen at 10 $^{\circ}\text{C}/\text{min}$ between 30 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$.

Results and discussion

Effects of acidification on moisture and calorific value

As shown in Fig. 1, the moisture content (W_c) of the acid-treated sludge cakes exhibited a decreasing trend within the pH range of 6 to 2. This indicated that the addition of acid enhanced the dewatering performance of the sludge to a certain degree. When the pH reached 2, the sludge cakes treated with sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) experienced reductions in moisture content amounting to 3.24%, 5.92%, and 5.60%, respectively.

Following the acid treatment, the calorific value (H_{hv}) of the sludge increased relative to their respective raw groups. When the pH reached 2, the sludge treated with H_2SO_4 , HCl, and HNO_3 exhibited respective increases in calorific values of 12.14%, 7.92%, and 8.01% (see Fig. 1). The increase in the calorific value of acid-treated sludge indicated that the addition of acid effectively enhanced the proportion of organic components within the sludge, which corresponded

to Liang's research (Liang et al. 2023). This fact confirmed that acid treatment can maximize the preservation of organic matter in sludge while improving its dewaterability.

Effects of acidification on SS and VSS

The volatile suspended solids (VSS) and suspended solids (SS) of the sludge displayed a progressive decrease under the conditions of acid addition and pH reduction (see Fig. 2). The reduction was more pronounced at pH 2, where the SS content decreased by 12.82%, 11.41%, and 12.66% following treatment with sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3), respectively. This phenomenon can be attributed to the infusion of a significant amount of hydrogen ions (H^+) into the solution of activated sludge during the acidification process. The H^+ induced the decomposition of SS and VSS in the sludge, with a stronger acidity leading to more intense decomposition. The decomposition of SS and VSS can convert bound water into free water, thereby enhancing the dewatering performance of the sludge.

It was worth noting that while both VSS and SS showed a decreasing trend, the reduction rate of VSS was considerably more moderate (see Fig. 2). Especially at pH 2, the treatment with H_2SO_4 , HCl, and HNO_3 resulted in a reduction of 6.02%, 7.14%, and 7.83% in VSS, respectively. Under acidic conditions, the molecular structure of organic components underwent a transformation, converting some macromolecular organic matter into smaller molecules. Although this process resulted in the hydrolysis of organic matter into the liquid phase, most of the smaller molecules were likely to agglomerate and precipitate on the surface of the sludge after centrifugation or filtration. As a result of the retention of a significant portion of organic matter, the rates of decline in VSS were slower. Therefore, the significant decrease in SS can be attributed to the extraction of inorganic elements from the solid phase during the

Fig. 1 The calorific value (H_{hv}) and the moisture content (W_c) of sludge cakes at different pH values of sludge (a: H_2SO_4 ; b: HCl; c: HNO_3)

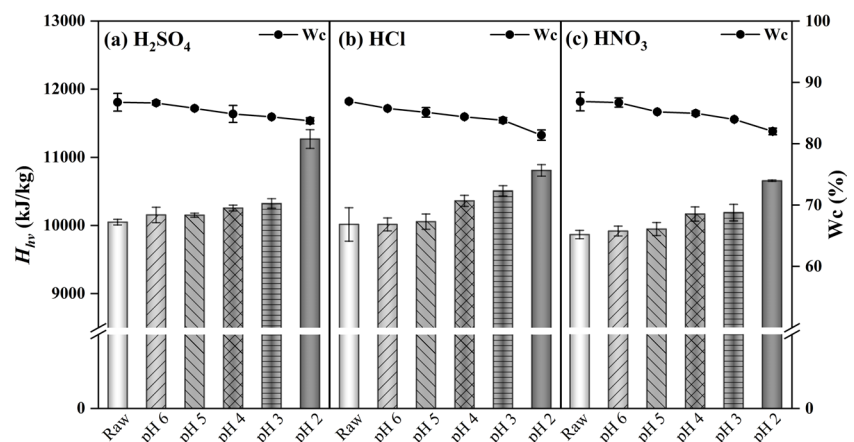
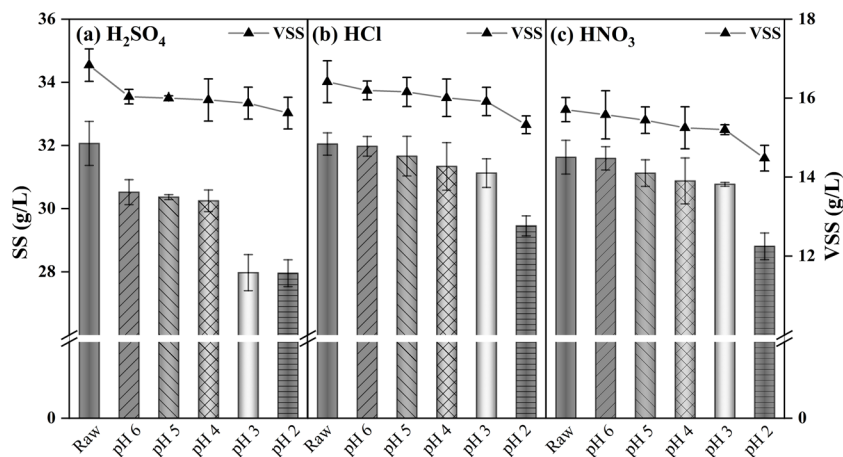


Fig. 2 The volatile suspended solids (VSS) and suspended solids (SS) at different pH values of sludge (a: H₂SO₄; b: HCl; c: HNO₃)



acidification process, with these elements being released into the supernatant in ion form.

After acid treatment, there was a noticeable rise in the volatile ratio (VSS/SS) compared to their respective raw groups (see Fig. 3a). The VSS/SS of sludge treated with H₂SO₄, HCl, and HNO₃ increased by 4.81%, 3.13%, and 3.11%, respectively. According to thermogravimetric analysis (TG), the weight loss ratio related to the organic matter of sludge was similarly increased throughout the acid treatment (see Fig. 3b). These facts showed the effectiveness of acid treatment in removing inorganic elements from the sludge while preserving organic matter as much as possible post-dehydration. This process significantly augmented the proportion of organic constituents in the sludge, thereby enhancing its calorific value and incineration performance.

Effects of acidification on zeta potential and particle size

As the absolute value of the zeta potential decreases, the stability of the system weakens, and the tendency for sludge particles to aggregate increases. This change in stability can be attributed to the presence of negative charges on the surface of the sludge particles, which originate from the anionic functional groups such as hydroxyl, carboxyl, and phosphate groups in the sludge matrix. The existence of these negative charges creates a significant electrostatic repulsion between the particles, effectively hindering the flocculation and stabilization of the sludge particles (Wong et al. 2015).

From Fig. 4a, it can be noted that the addition of acid to the sludge resulted in a significant increase in the sludge's zeta potential. When the pH reached 2, the zeta potential of the sludge treated with sulfuric acid increased

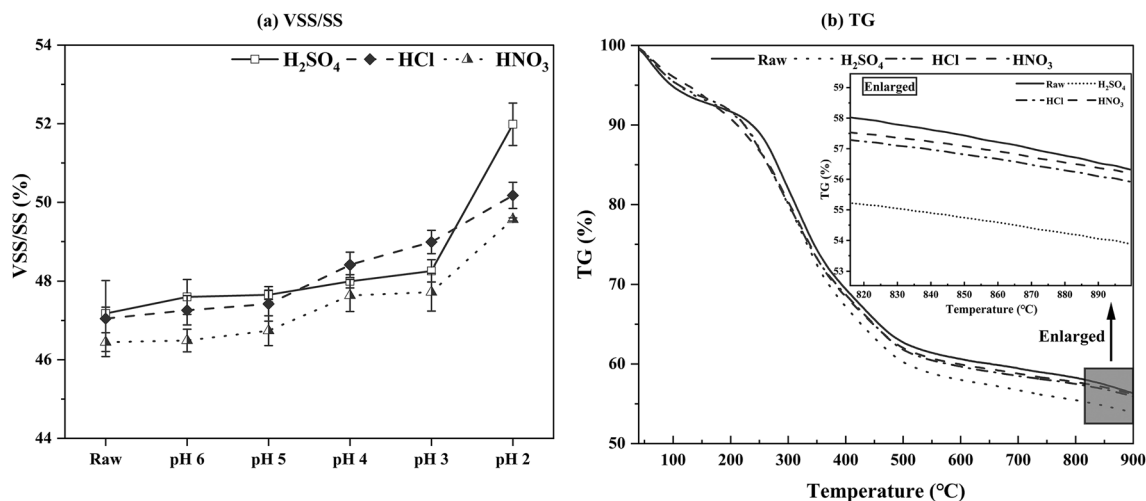


Fig. 3 The volatile ratio (VSS/SS) and thermogravimetric analysis (TG) at different pH values of sludge (a: VSS/SS; b: TG, H₂SO₄—pH 2; HCl—pH 2; HNO₃—pH 2)

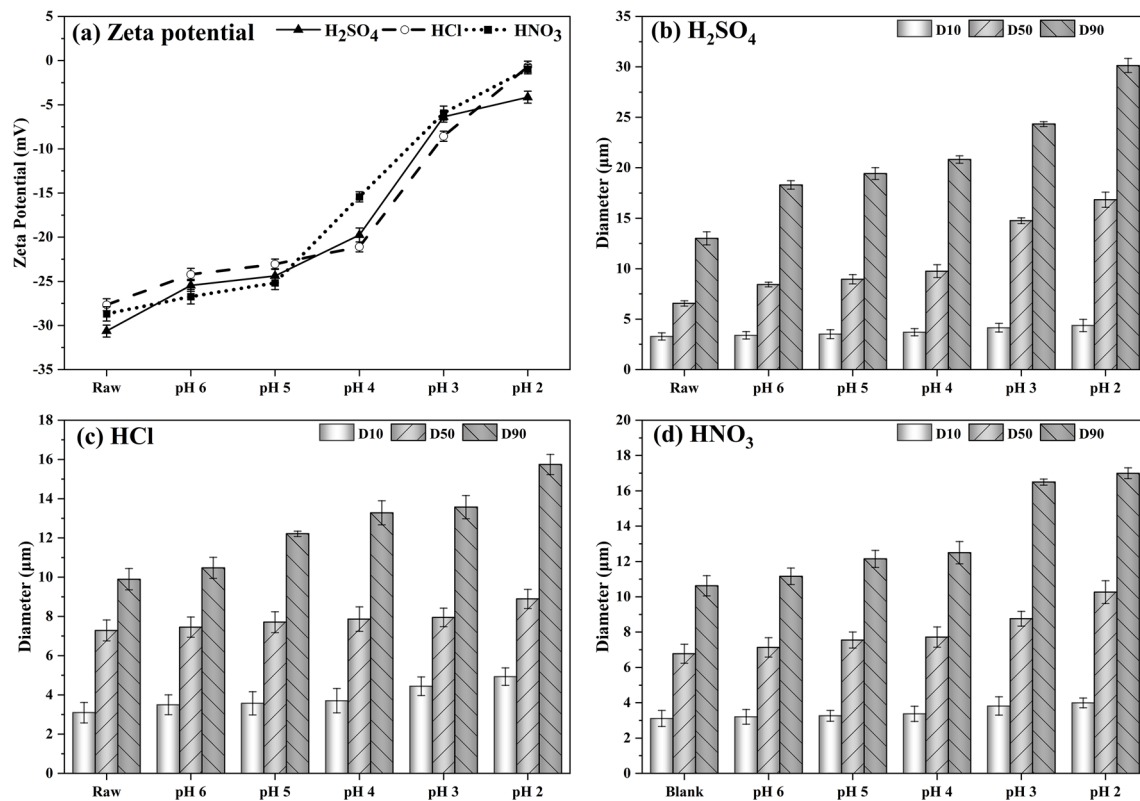


Fig. 4 Zeta potential and particle size of sludge at different pH values (a: zeta potential of H₂SO₄, HCl, and HNO₃; b: particle sizes of H₂SO₄; c: particle sizes of HCl; d: particle sizes of HNO₃)

from -30.63 to -4.15 mV; the zeta potential of the sludge treated with hydrochloric acid increased from -27.66 to -0.69 mV; and the zeta potential of the sludge treated with nitric acid increased from -28.68 to -0.96 mV. This change can be attributed to the interaction between the H⁺ in the solution and the negative charge on the surface of the sludge flocs. Simultaneously, protonation reactions occurred within the organic matter in the sludge under acidic conditions, leading to a decrease in the charge density and an increase in the zeta potential on the sludge surface.

The increase in the zeta potential of sludge contributed to the aggregation and flocculation of sludge particles, leading to the enlargement of the size of sludge particles, particularly in terms of D50 and D90 (see Fig. 4b–d). In the dewatering process of sludge, the super-colloids within the size range of 1–100 μm play a vital role (Higgins and Novak 1997). A progressive increase in the size of sludge particles classified as super-colloids during acid treatment was observed in our study, which effectively enhanced the filtration and dewatering performance of the acid-treated sludge (Jin et al. 2004; Shao et al. 2009). Therefore, the addition of acid not only improved the flocculation process of the sludge but also exerted a positive influence on its dewatering capability.

Effects of acidification on EPS and EEM

The majority of the sludge is predominantly composed of negatively charged extracellular polymeric substances (EPS), which are highly hydrophilic gel-like biopolymers (Keiding et al. 2001; Liao et al. 2001; Mikkelsen and Keiding 2002). The main components of EPS are proteins and polysaccharides, and the dewaterability of sludge is mainly related to their concentrations (Sheng and Yu 2006; Yu et al. 2008). High contents of proteins and polysaccharides increase the negative charge and repulsive forces on the sludge surface, leading to an increase in the viscosity and stickiness of the sludge. This, in turn, worsens the sedimentation and compressibility of sludge flocs, resulting in poorer dewatering performance (Sheng et al. 2010). Therefore, in sludge treatment, controlling the concentrations of proteins and polysaccharides in EPS is crucial for enhancing the dewatering capability of sludge.

EPS can be divided into three components: S-EPS, LB-EPS, and TB-EPS, with increasing adsorption capacity in that order (Laspidou and Rittmann 2002; Liu and Fang 2003). As shown in Figs. 5 and 6, as the pH gradually decreased, the concentrations of proteins and polysaccharides also decreased. The phenomenon indicated that acidic

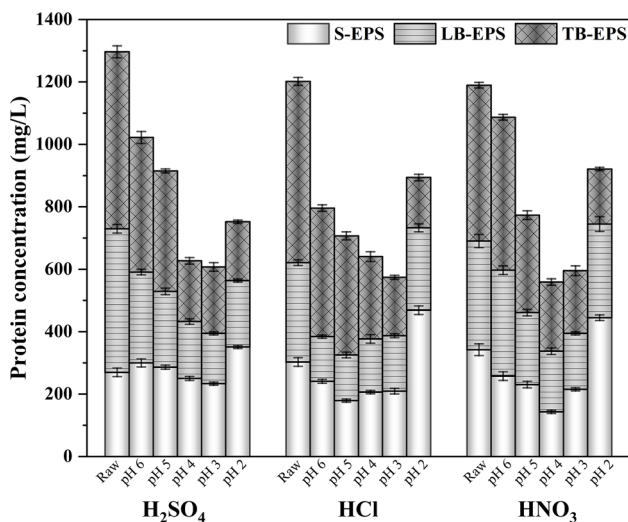


Fig. 5 Protein concentration of sludge treated with acid at different pH values

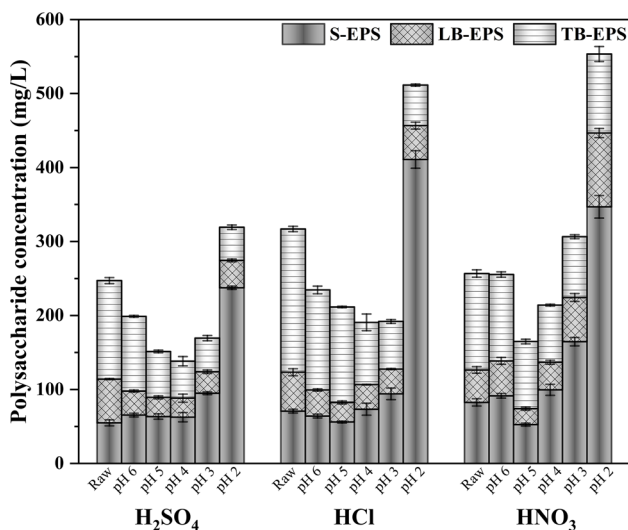


Fig. 6 Polysaccharide concentration of sludge treated with acid at different pH values

conditions can change the structure of proteins and polysaccharides, reducing their solubility in solution. This process facilitated the aggregation and precipitation of protein and polysaccharide molecules on the sludge surface. Consequently, a continuous decrease in organic matter concentration was detected in the supernatant of the sludge, which was beneficial for sludge dewatering.

For sludge treated with sulfuric acid (H₂SO₄) and hydrochloric acid (HCl), the protein concentration reached its lowest value at pH 3, measuring 607.35 mg/L and 574.17 mg/L, respectively. In the case of sludge treated with nitric acid (HNO₃), the protein concentration was lowest at pH 4, measuring 559.09 mg/L (see Fig. 5). As

for polysaccharides, sludge treated with H₂SO₄ and HCl exhibited the lowest polysaccharide concentration at pH 4, measuring 138.29 mg/L and 190.79 mg/L, respectively. However, for sludge treated with HNO₃, the lowest polysaccharide concentration was observed at pH 5, measuring 151.32 mg/L (see Fig. 6).

The intensity of the acidic environment directly affects the extent of sludge disintegration and the leaching of organic matter. Under highly acidic conditions (pH 2), the concentration of proteins and polysaccharides in the supernatant of the sludge increased, especially in S-EPS. This phenomenon can be attributed to the significantly increased hydrolysis reaction caused by the excessively low pH value, which led to the disintegration of sludge flocs and the release of organic matter into the solution. The decomposition of organic matter is usually accompanied by the release of bound water, which further enhances the sludge's dewatering performance (Chen et al. 2001; Xu et al. 2009; Guo et al. 2011). It was noteworthy that a slight increase in EPS concentration did not worsen the sludge's dewatering ability but rather contributed to removing water more effectively under pH 2 (see Fig. 1). Sludge with higher EPS content and lower zeta potential generally exhibited lower shear sensitivity and dispersion at concentrations below a certain threshold. This meant that such sludge was less likely to disperse under external disturbance, demonstrating better stability and higher dewaterability (Houghton and Stephenson 2002; Mikkelsen and Keiding 2002).

Fluorescence Regional Integration (FRI), a widely employed method for fluorescence spectrum analysis, divides the fluorescence spectrum into five distinct regions based on the characteristics of fluorescent substances. As shown in Fig. 7, the species of organic matter in the S-EPS, LB-EPS, and TB-EPS of the raw sludge were fundamentally similar. Peak A (Ex/Em = 220 nm/305 nm) and Peak B (Ex/Em = 220 nm/340 nm) were located in Region I and Region II, respectively. The fluorescence intensity in these regions primarily correlates with the content of aromatic proteins such as tyrosine and tryptophan. Peak C (Ex/Em = 225 nm/385 nm) in Region III corresponds to fulvic acid-like substances. Peak D (Ex/Em = 280 nm/305 nm) located in Region IV corresponds to soluble microbial products (SMP), while Peak E (Ex/Em = 340 nm/420 nm) in Region V is associated with humic acid-like substances (Baker 2001; Chen et al. 2003; Guo et al. 2014). Comparing the fluorescence intensity ($\Phi_{i,n}$) across different regions in the raw sample, it can be deduced that dissolved microbial products (Region IV) were the main organic components of the EPS in the raw sludge, whereas the concentration of fulvic acid-like substances (Region III) was comparatively lower. Protein-like substances associated with aromatic amino acid structures (Region I and Region II) were predominantly distributed within the LB-EPS (see Fig. 8).

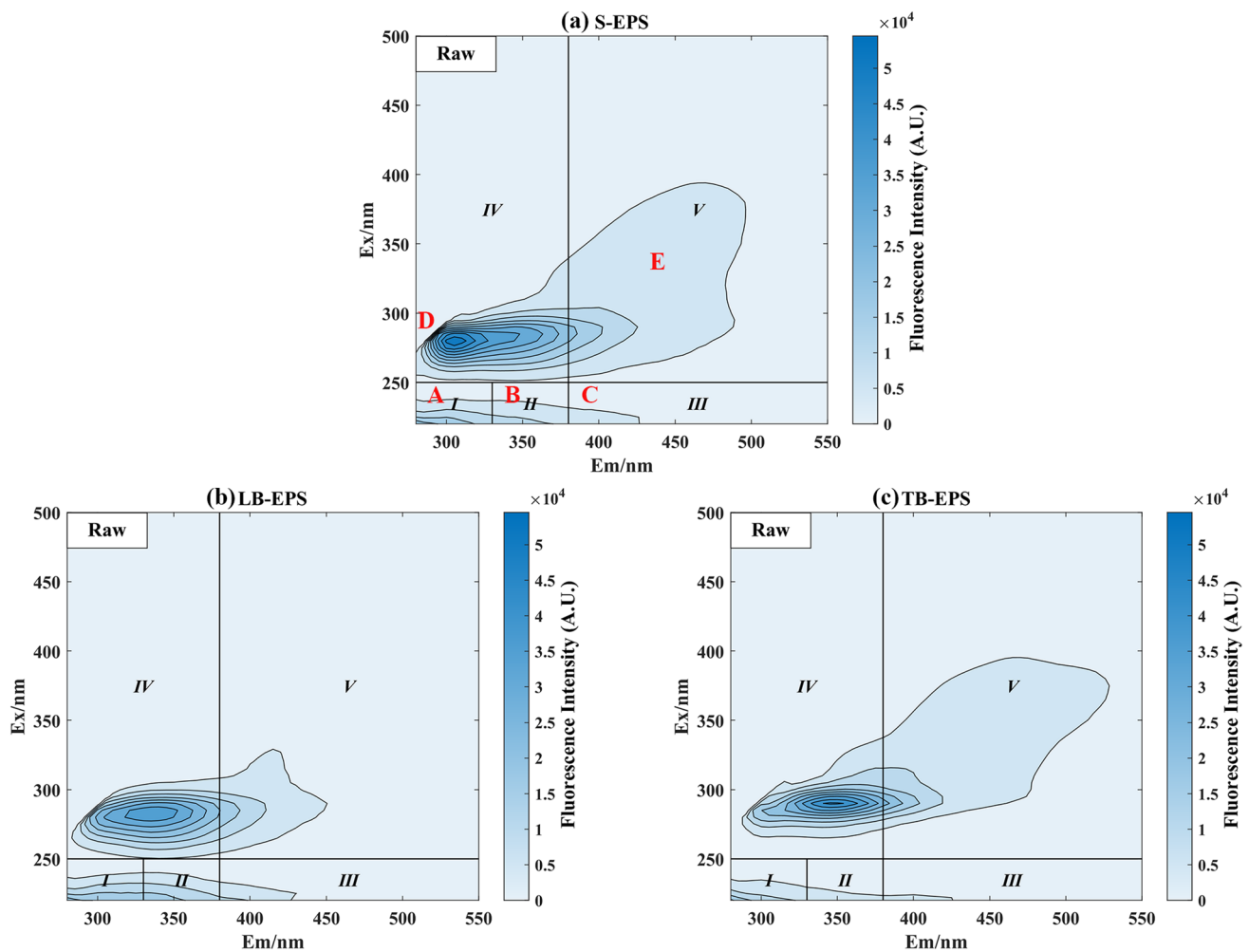


Fig. 7 Fluorescence spectra of raw sludge (**a**: S-EPS; **b**: LB-EPS; **c**: TB-EPS)

Upon acidification treatment, a notable diminishing trend in $\Phi_{i,n}$ was observed within the EPS components of each layer compared to the raw sludge. This further confirmed that acid treatment effectively converted and decomposed the fluorescent organic components contained in S-EPS, LB-EPS, and TB-EPS. Particularly in the S-EPS, the total fluorescence intensity ($\Phi_{T,n}$) of the five regions exhibited a relatively significant change upon the pH being lowered to 5–6, whereas $\Phi_{T,n}$ of the loosely bound EPS and tightly bound EPS (LB-EPS and TB-EPS) showed a lesser reduction. This indicated that the hydrolysis of sludge EPS under acidic conditions occurred from the outer layers towards the inner layers, with the soluble EPS (S-EPS) being the most susceptible to hydrolysis. Due to the enhanced acidity in an environment with a pH of 3–4, the sludge underwent stimulation of the acid, resulting in floc disruption and leaching of organic components, leading to a slight increase in $\Phi_{T,n}$. However, under extremely acidic conditions (pH 2), because of the further enhancement of acid hydrolysis, $\Phi_{i,n}$

of each component experienced a certain degree of reduction (see Fig. 8). The decomposition of fluorescent components caused lower concentrations of sludge EPS, facilitating the separation of free water and enhancing the dewatering performance of acid-treated sludge (Sheng et al. 2010).

Effects of acidification on FTIR and SEM

In order to further investigate the impact of acid treatment on sludge flocs, Fourier transform infrared spectroscopy (FTIR) was used to analyze the functional groups on the surface of the sludge samples. As can be seen in Fig. 9, the broad infrared peak band within the range of 3100–3700 cm^{-1} is usually caused by the vibration of O–H groups of carboxyl groups, phenols, and alcohols and the vibration of N–H groups of amide (Zhai et al. 2012). Specifically, the broad peak near the wavenumber of 3423.26 cm^{-1} corresponds to the stretching vibration of hydroxyl groups (–OH) in carboxylic acids (Lu et al. 2013). Hydroxyl groups are

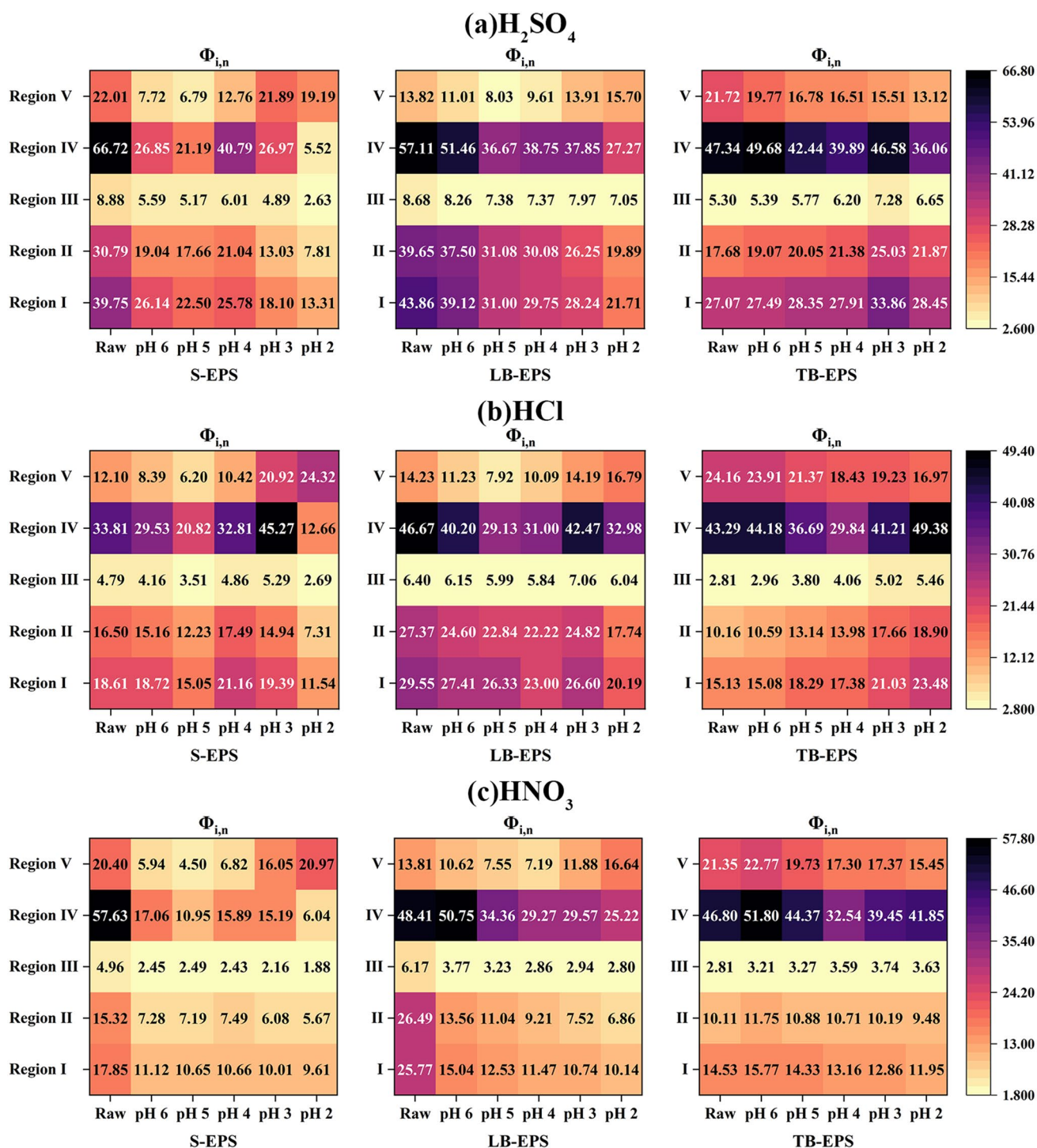


Fig. 8 Fluorescence intensity of each region of sludge at different pH values (**a**: H₂SO₄; **b**: HCl; **c**: HNO₃; Unit: $\times 10^7$ A.U. nm²)

typical hydrophilic functional groups capable of forming hydrogen bonds with water molecules. After acid treatment, this infrared peak at 3423.26 cm^{-1} exhibited a certain degree of reduction, indicating the removal of O–H bonds from the sludge under acidic conditions. This reduction in hydroxyl groups weakened the hydrophilicity of the sludge,

facilitating the separation and removal of water from the sludge.

The infrared peak near 1454.56 cm^{-1} exhibited an increase in intensity for sludge treated with sulfuric acid and hydrochloric acid, while it disappeared in the nitric acid-treated sludge. This peak is considered the typical

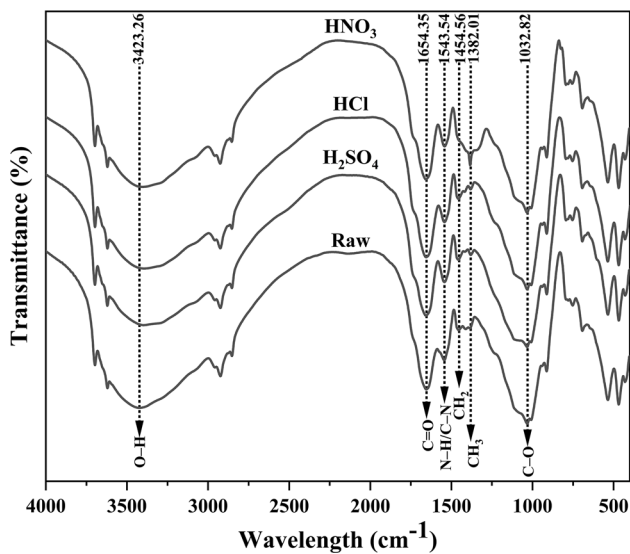


Fig. 9 Infrared spectra of sludge under different acid treatments (H_2SO_4 —pH 2; HCl —pH 2; HNO_3 —pH 2)

position for the shear vibrations of CH_2 in cellulose and saturated fatty acids (Fan et al. 2014). At 1382.01 cm^{-1} , the infrared peak intensity of the acid-treated sludge was also enhanced, particularly more significantly in the case of nitric acid-treated sludge. This peak is attributed to the symmetric stretching vibrations of CH_3 groups in nitrate or carboxylate groups and aromatic nitro groups (Fan et al. 2017). After acid treatment, the C–H bonds in the sludge were essentially retained, and even the formation and strengthening of C–H peaks were detected. The preservation and intensification of C–H peaks suggested the accumulation of aliphatic compounds in the sludge.

The infrared peak at 1654.35 cm^{-1} in the sludge spectrum is the stretching vibrations of C=O bonds in amide compounds or aromatic hydrocarbon structures, indicating the existence of C–N bonds in the protein amide I band (Silva et al. 2012; Dai et al. 2019). It is worth noting that after acid treatment, the peak at this position exhibited a sharpened and intensified trend. Likewise, the infrared peak of acid-treated sludge at 1543.54 cm^{-1} also displayed an enhanced trend, attributed to the stretching vibrations of N–H and C–N bonds in the CO–NH group of the protein amide II band (Zhang et al. 2011; Patel et al. 2019). The intensified and sharpened changes at 1654.35 cm^{-1} and 1543.54 cm^{-1} suggested that acid treatment can to some extent enrich protein amide compounds to the surface of the sludge, consequently increasing the concentration of organic matter in the sludge. The infrared peak within the range of $900\text{--}1300\text{ cm}^{-1}$ is commonly attributed to the stretching and bending vibrations of C–O bonds in polysaccharides (Zhai et al. 2012; Li et al. 2018). After acid treatment, the infrared peaks of the sludge at 1032.82 cm^{-1} showed an increased height and

sharpness, indicating more polysaccharides were adsorbed on the sludge.

The addition of acid did not significantly change the typical infrared peak positions of proteins and polysaccharides; on the contrary, these peaks displayed a certain degree of intensity enhancement. That suggested that acid can improve the adsorption and enrichment capacity of relevant biomolecular substances on the surface of sludge particles. This further revealed that acid treatment promoted the precipitation of bioorganic components from extracellular polymeric substances (EPS).

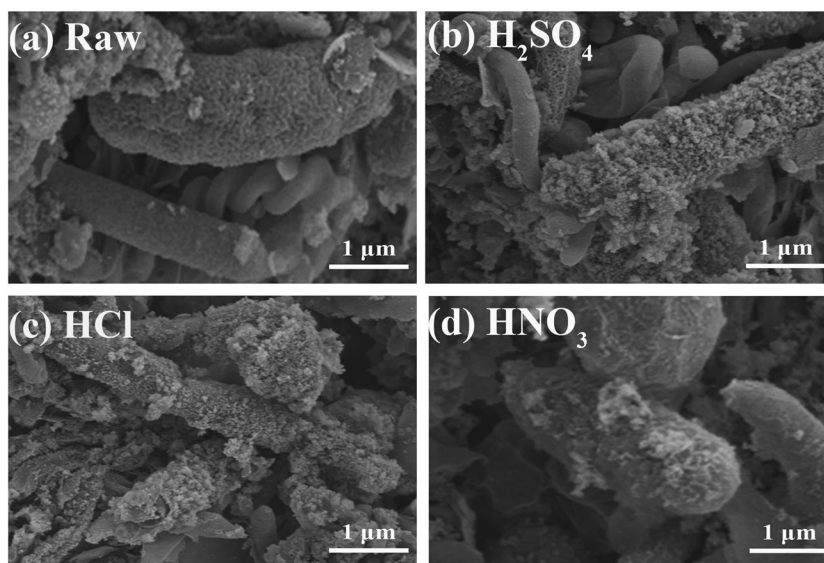
As shown in Fig. 10, the surface of the raw sludge particles and microorganisms was relatively smooth by means of scanning electron microscopy (SEM). However, after acid treatment, a noticeable change was observed, with the presence of precipitated substances attached to the surfaces of both particles and microorganisms. These findings demonstrated that the addition of acid can change the structure of the organic components and reduce their solubility in solution, thus prompting the aggregation and precipitation of organic molecules on the surfaces of particles and microorganisms.

Conclusion

The addition of sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) caused a significant rise in the zeta potential and particle size of the sludge, which facilitated the flocculation between sludge particles. Acid treatment effectively decomposed or converted the hydrophilic O–H bonds within the sludge and the organic components in extracellular polymeric substances (EPS). The volatile suspended solids (VSS) and suspended solids (SS) were also partially decomposed during acid treatment. The SS and VSS content decreased by 12.82% and 6.02% (H_2SO_4), 11.41% and 7.14% (HCl), and 12.66% and 7.83% (HNO_3) at pH 2 following treatment, respectively. These changes led to the release of bound water in the sludge, which reduced the moisture content (W_c) of the sludge cake and improved its dewatering performance under acidic conditions. The sludge cakes treated experienced reductions in moisture content amounting to 3.24% (H_2SO_4), 5.92% (HCl), and 5.60% (HNO_3) under pH 2, respectively.

Furthermore, acid treatment can effectively retain the organic matter, significantly increasing the proportion of organic components in the sludge. The volatile ratio (VSS/SS) of sludge treated with H_2SO_4 , HCl, and HNO_3 increased by 4.81%, 3.13%, and 3.11%, respectively. The addition of acid can change the structure of biomolecules, lowering their solubility in solution and promoting the precipitation of organic components from the supernatant to the surface of sludge particles. The acid-treated sludge had a lower moisture

Fig. 10 The surface microstructure images of sludge under different acid treatments (a: Raw; b: H_2SO_4 —pH 2; c: HCl —pH 2; d: HNO_3 —pH 2)



content and a higher proportion of organic matter, causing an increase in its calorific value (H_{hv}). When the pH reached 2, the sludge treated with H_2SO_4 , HCl , and HNO_3 exhibited respective increases in calorific values of 12.14%, 7.92%, and 8.01%. Acid-treated sludge exhibited a lower moisture content, a higher proportion of organic matter, and a higher sludge calorific value, making it more suitable for subsequent incineration. This meant that acid-treated sludge was beneficial for energy recovery and resource utilization in sludge disposal.

Author contribution Lieyang Lv: writing—original draft, writing—review and editing, investigation, methodology, visualization. Meiqi Yang: investigation, data curation, validation. Wei Liu: funding acquisition, conceptualization, supervision.

Funding This study was financially supported by China Energy Engineering Group Guangdong Electric Power Design Institute Co., Ltd (CG-2021-K-016).

Data Availability The data that support the findings of this study are openly available on request.

Declarations

Ethics approval, consent to participate, and consent for publication Not applicable. The manuscript does not report on or involve any animals, humans, human data, human tissue, or plants, nor does it contain any individual personal data.

Competing interests The authors declare no competing interests.

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