New Insight on the Combined Effects of Hydrothermal Treatment and FeSO₄/Ca(ClO)₂ Oxidation for Sludge Dewaterability Improvement: Moisture Distribution and Noncovalent Interaction Calculation

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ABSTRACT: A combination of hydrothermal treatment and FeSO₄/Ca(ClO)₂ oxidation was developed in our previous work and was proved to be significantly useful for improving the sludge dewaterability. The dewatering mechanism of the sludge after the combined treatment of hydrothermal treatment and FeSO₄·7H₂O/Ca(ClO)₂ was obtained for the first time based on the moisture distribution analysis. Moreover, the noncovalent interaction between the hydrophilic sites of sludge EPS in sludge and water molecules was studied for the first time by using density functional theory. The electrostatic potentials of three representative EPS molecules, that is, dextran, poly-gamma-glutamate, and poly-L-lysine, were calculated and analyzed. AIM and RDG of the representative EPS-water complex models were calculated to study the noncovalent interaction mechanism. The moisture distribution and noncovalent interactions analyzed in this paper will provide information for improving sludge dewatering performance.

1. INTRODUCTION

Many methods have been reported for sludge treatment and utilization.¹⁻⁴ However, these methods have quite high requirements for the moisture content of sludge, generally lower than 45%. The dewatering problem has restricted the disposal of sludge because of its difficulty and high energy consumption. The key factor of the sludge dewatering problem is the extracellular polymeric substances (EPSs) and the oxygen-containing groups in it, causing the hydrophilicity of sludge. Methods have been conducted to improve sludge dewaterability, for example, electric field,⁵ floculant,⁶,⁷ cationic surfactant,⁸ biomass and advanced oxidation process (AOP)⁹,¹⁰ acidification and ultrasound,¹¹ and hydrothermal treatment.¹²,¹³

Hydrothermal treatment¹⁴,¹⁵ can decompose EPS, thus greatly improving the dewaterability of sludge. Acids and alkali are usually applied as auxiliary agents, causing high corrosion which limited the application of hydrothermal treatment. AOP technology¹⁶,¹⁷ has been widely used in recent years, which can produce hydroxyl radicals (*OH). However, its effect is limited. Therefore, based on our previous work,¹⁸ a combined method of hydrothermal and FeSO₄/Ca(ClO)₂ oxidation was developed to improve sludge dewaterability. The results showed that the combined method has a pretty high effect for improving sludge dewaterability. To further analyze the main causes of the difficulty in sludge dewatering and provide information for improving sludge dewatering performance, the moisture distribution of sludge and the noncovalent interactions between sludge EPS and water molecules are analyzed in this paper.

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spaces of flocs and organisms), surface water (held on to the surface of solid particles by adsorption and adhesion), and bond water (bound by chemical linkage). Mahmoud et al. studied the limits of sludge dewaterability by using different sludge dewatering methods, that is, mechanical dewatering, electro-dewatering, and thermal dewatering. The results showed that the limits of sludge dewaterability are closely related to the moisture types in sludge. Thus, it is necessary to further study the moisture distribution of sludge and analyze the relationship between the moisture type in sludge and sludge dewaterability.

Noncovalent interactions were reported to exist between sludge EPS and other molecules, for example, hydrogen bond interaction, van der Waals forces, and steric interactions. Till now, the mechanism study of sludge EPS at the molecular level is nearly blank. The mechanism studies of lignite at the molecular level can be used as references. Generally, a large number of oxygen-containing groups in lignite make its surface hydrophilic. Hydrogen bond interactions can be formed between water molecule and the oxygen-containing groups, which cause the high water content of lignite. Nishino et al. found that carboxyl is the preferred adsorption site, and the adsorption amount of water vapor is closely related to the carboxyl content. There are varying bond energy degrees of the hydrogen bonds formed with the oxygen-containing group, which proves the existence of different types of water adsorption sites. However, till now, there is no theoretical study on the hydrophilia of different function groups in sludge EPS.

In our previous work, the characteristics of the EPS at the molecular level were studied using density functional theory (DFT) calculation, that is, electrostatic potential (ESP) analysis, bond order analysis, and bond dissociation enthalpy (BDE) analysis. The results showed that the key factor of the hydrophilicity of sludge is the oxygen-containing groups in EPS. However, the mechanism study of noncovalent interactions between the function groups in sludge EPS and the water molecules is nearly blank. According to Wu et al., in molecules (AIMs) and reduced density gradient (RDG) analyses were carried out to study the noncovalent interaction mechanism between water molecules and hydrophilic sites on the lignite surface, which provides information for the noncovalent interaction study of sludge EPS in this paper.

This paper aims to study the moisture distribution of sludge before and after the combined method of hydrothermal treatment and FeSO₄·Ca(ClO)₄ oxidation, as well as the noncovalent interaction mechanism between the hydrophilic sites of sludge EPS and water molecules. An improved moisture distribution analysis method proposed in our previous work combining thermal drying and bond strength analysis was used in this paper to study the moisture distribution of sludge. The dewatering mechanism of sludge after the combined treatment of hydrothermal treatment and FeSO₄·7H₂O/Ca(ClO)₄ was determined for the first time based on the moisture distribution analysis. Moreover, the noncovalent interaction between EPS in sludge and water on the molecular level was studied for the first time by using density functional theory (DFT). Three representative model molecules of sludge EPS were established, that is, dextran, poly-gamma-glutamate, and poly-l-lysine. The ESP analysis of EPS molecules was calculated and analyzed. The EPS–water complex models were also constructed. AIM and the RDG of the EPS–water complex models were calculated to study the noncovalent interaction mechanism between hydrophilic sites of sludge EPS and water molecules.

2. EXPERIMENTAL SECTION

In our previous work, the material characteristics of the sludge and hydrothermal dewatering (HTD) method were described. The combined method of hydrothermal and FeSO₄·7H₂O/Ca(ClO)₄ were used for improving sludge dewaterability. A high-pressure reactor was used for hydrothermal and the temperatures were controlled to 150, 180, and 210 °C. The concentrations of Ca(ClO)₄ were set as 0.02, 0.04, and 0.06 g/g DS. The molar ratios of FeSO₄·7H₂O/Ca(ClO)₄ were set as 1.0, 1.25, and 1.5. In this work, the moisture distribution characteristics and the noncovalent interaction between EPS and water were focused. Thus, the moisture distribution measurement method and DFT calculation of the noncovalent interaction between EPS and water in sludge were mainly introduced.

2.1. Experimental Methods. The thermal drying method was used in this work to study the moisture distribution of sludge. It was first reported by Smollen to quantify the bound water content of sludge. The drying system is improved based on the system used in Deng’s report. The thermal drying system and procedure was the same as described in the previous literature. The weight data of sludge samples were recorded every 15 s until it came to be constant. The samples were then taken out from the thermal drying system and put into an oven at 105 °C for 12 h.

2.2. Calculation Methods. 2.2.1. Model Construction and Geometry Optimization. Three representative model molecules in EPS of sludge, that is, dextran, poly-gamma-glutamate, and poly-l-lysine, were taken into account in analyzing the intermolecular interactions with water. The structure of the three model molecules were described in our previous work. All the EPS–water complex models constructed in this work are shown in Figure 1. The geometry optimization and vibrational frequency were carried out at the M062X-D3/S-311+G(d,p) level by Gaussian 09 program. The frequency calculation confirms that there is no imaginary frequency appeared.

Figure 1. EPS–water complex models constructed in this work. (a) Complex A (dextran–water complex), (b) Complex B (poly-gamma-glutamate–water complex), and (c) Complex C (poly-l-lysine–water complex).
The interaction between the complex and the water was calculated under the same level as the geometric optimization calculation, that is, M062X-D3/6-311+G(d,p). The method is considered to have high applicability and reliability to the calculation of the noncovalent interaction.31,32

2.2.2. ESP. The principle of ESP analysis was introduced in our previous work. Multiwfn 3.533 was applied to analyze ESP on the van der Waals surface of the three representative model molecules of the EPS in sludge. The wave functions used were generated at the B3LYP/6-311G(d,p) level. The van der Waals surface refers to the electron density equal to 0.001 e/bohr.34 AIM was analyzed based on Multiwfn 3.5. AIM was analyzed based on Multiwfn 3.5. The wave functions are generated at the M062X-D3/6-311+G(d,p) level, which is the same as the computational level of geometric optimization.

2.2.3. AIM Analysis. In the AIM theory, the topological analysis is often used. According to Bader,35 the position where the electron density gradient disappears to zero is called the critical points (CPs). CPs can be divided into four different types. Bond CPs (BCPs) is a key CP which is usually found among the pairs of atoms that are attracted to each other. CPs with only one negative eigenvalue are known as the ring CPs (RCPs), showing spatial exclusion. The bond path between a BCP and the pairs of atoms reflects the various bonding pathways of the atoms.36 AIM was analyzed based on Multiwfn 3.5. The wave functions are generated at the M062X-D3/6-311+G(d,p) level, which is the same as the computational level of geometric optimization.

2.2.4. RDG Analysis. In the RDG theory, the RDG function is applied to describe the noncovalent interaction effect. The expression is shown in the following terms37

\[ \text{RDG}(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}} \]  

where \( \rho(r) \) represents electron density, \( \nabla \rho(r) \) denotes the first derivative of electron density.

MULTIWFN program was used for the RDG analysis of the optimized EPS−water complex model. Based on the Multiwfn outputs, the RDG isosurface maps were obtained by VMD. In order to clearly show the intermolecular interactions between the EPS molecule and the water molecule, only the grid regions between the EPS molecule and water are displayed on the RDG isosurface map.

3. RESULTS AND DISCUSSION

3.1. Effect of Hydrothermal and FeSO₄·7H₂O/Ca(ClO)₂ Addition on Moisture Distribution in Sludge. 3.1.1. Calculation Theory of the Moisture Distribution in Sludge. The drying test is usually used to measure the moisture distribution in sludge based on the different drying rates. A typical drying curve and its corresponding moisture type is illustrated in Figure 2.19 An improved moisture distribution analysis method combining thermal drying and bond strength analyses was proposed in our previous work.20 Based on the method, the drying and bond strength curves of untreated sludge and upgraded sludge is obtained as shown in Figure 3.

Four phases can be observed in both drying and bond strength curves, that is, phase I (X₁−), phase II (X₂−X₃), phase III (X₃−X₄), and phase IV (0−X₄). Phase I represents the free water in sludge, where the drying rate remains constant and the bond strength between the moisture and solid phase remains zero. Phase II denotes the interparticle water in sludge, where the drying rate decreases gradually and the bond strength between the moisture and solid phase is between 0 and 4500 kJ/kg. Phase III represents the surface water in sludge, where the drying rate decreases further to zero and the bond strength between the moisture and solid phase exceeds 4500 kJ/kg. Phase IV is bound water in sludge, where the drying rate remains zero. Thus, the corresponding moisture distributions of untreated sludge and upgraded sludge are given in Figure 4.

3.1.2. Effect of Hydrothermal and FeSO₄·7H₂O/Ca(ClO)₂ Addition. Based on the method described in Section 3.1.1, moisture distributions are illustrated in Figure 4. Four types of water can be observed in sludge, that is, free water, interparticle water, surface water, and bond water. Generally, water that can be removed relatively easily using mechanical dewatering includes free water and part of interparticle water.20 Thus, the sum of bond water, surface water, and interparticle water were also used as an evaluation parameter (Wbsi) for sludge dewatering performance in this study.

In our previous work,20 Pearson correlation coefficients of operating parameters on sludge dewaterability (CST, SRF, and Wbsi) were analyzed by using SPSS software. The results showed that the temperature is the main factor. In this work, Pearson correlation coefficients of operating parameters on the sludge dewatering performance (Wbsi) were also analyzed. The results showed that Wbsi was correlated with the temperature on level \( p < 0.05 \), which is consistent with the results of our previous work.18 Moreover, Wbsi was correlated with Wc and SRF on level \( p < 0.01 \). Wbsi was inferred to highly correlated with sludge dewaterability. That is, the change of the moisture distribution in sludge is the main reason for the improvement of the sludge dewatering performance.

Based on Figure 4a, compared to untreated sludge, the moisture distribution of the upgraded sludge changed obviously. The content of surface water decreased and content of free water increased obviously. This is because the EPS in sludge was degraded with the combined effect of hydrothermal and FeSO₄/Ca(ClO)₂ and part of the water absorbed in EPS was released. Kobayashi et al.38 studied the effect of hydrothermal treatment on the particle distribution of the sludge. The results showed that the initial sludge is assumed to be a floccule consisting of 100−200 μm-sized particles. When the sludge was subjected to

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**Figure 2.** Typical drying curve. Reprinted (Adapted or Reprinted in part) with permission from [19]. Copyright [2004] [Elsevier].
hydrothermal treatment, the particle size of the treated sludge decreased drastically, which confirmed the degradation of sludge EPS and the increasing content of free water in sludge. The content of free water, which can be removed relatively easily using mechanical dewatering, was increased. The sludge dewatering performance was thus improved. Moreover, the treatments affect the moisture distribution in this order: combined effect > individual hydrothermal > individual FeSO₄/Ca(ClO)₂, which is consistent with the trend of effect on sludge dewatering performance in our previous work.¹⁸

Compared to the untreated sludge, the hydrothermal temperature has great influence on sludge water distribution. The content of free water increased obviously, which indicated the improved sludge’s dehydrating properties. That is, the hydrothermal temperature promoted the improvement of sludge’s dehydrating properties. However, based on Figure 4b, for the hydrothermal temperatures of 150, 180, and 210 °C, the change of sludge moisture distribution was not obvious. Compared to the sludge treated at 150 °C, the content of free water of the sludge treated at 180 and 210 °C increased. Also, as described in our previous work,¹⁸ the dewatering performance of sludge treated at these two conditions was the best, and the dewatering performance is better for molar ratio 1.25. Thus, the 0.04 g/g DS calcium hypochlorite concentration is recommended for sludge treatment. Moreover, molar ratio 1.25 is recommended considering both the dewatering performance and economical condition.

Sludge dewaterability (Wc), pH, and free radical analysis at different conditions are listed in Table 1. The pH ranges from 5.9 to 7.4, which indicated the study was conducted at an approximately neutral pH value. Great sludge dewaterability was achieved at this neutral pH period. Moreover, as can be observed in Table 1, the free radicals’ concentrations were closely related to the pH value. The lower the pH value, the higher the free radical concentration, which was agreed with Zhu et al.⁹ that

Figure 3. Drying and bond strength curves: (a,c,e) drying curves, and (b,d,f) bond strength curves.
3.2. DFT Study of Noncovalent Interactions between EPS and Water.

3.2.1. ESP Analysis of EPS Molecule.

According to the results based on our previous work,18 EPS is the main reason that restrained the deep dewatering of sludge. To analyze the interactions between EPS and water, hydrophilicity and hydrophobicity sites of EPS were first studied by ESP analysis based on DFT calculations. ESP can be used to analyze the sites of electrophilic and nucleophilic attacks based on its negative and positive ESP, respectively. Thus, sites with minimum ESP were generally the sites of the electrophilic attack. To represent EPS, exopolysaccharide and peptide molecular models were analyzed. The ESP distribution maps of these molecule models with their local minima and maxima are illustrated in Figure 5.

The global minima ESP value \( V_{\text{min}} = -44.98 \text{ kcal/mol} \) can be observed at the carbonyl of poly-l-lysine. Also other local minima ESP value can be observed at regions of EPS molecules, that is, the carbonyl region \(-43.7 \text{ kcal/mol} \) and carbonyl region \(-32.37 \text{ kcal/mol} \) of poly-gamma-glutamate, the

Figure 4. Detailed moisture distribution of untreated sludge and upgraded sludge: (a) comparison of untreated and upgraded sludge, (b) the effect of hydrothermal temperature, and (c) the effect of FeSO₄/Ca(ClO)₂ addition.

![Figure 4](image_url)

Figure 5. ESP map: (a) dextran, (b) poly-gamma-glutamate, and (c) poly-l-lysine. Cyan dots represent the local minima of EPS and orange dots denote the maxima of EPS.

![Figure 5](image_url)

Table 1. Sludge Dewaterability \( W_c \), pH, and Free Radicals Analysis

| samples          | \( W_c \) (%) | pH  | DMPO *OH concentration (10⁻⁷ mol/mL) 5 min | DMPO **OH concentration (10⁻⁷ mol/mL) 10 min |
|------------------|---------------|-----|------------------------------------------|---------------------------------------------|
| HT-180-ADD-1.25-0.04 | 51.72         | 5.93| 6.373                                    | 3.454                                       |
| HT-180-ADD-1.25-0.02 | 54.69         | 7.03| 3.895                                    | 2.072                                       |
| HT-180-ADD-1.25-0.06 | 55.51         | 5.88| 8.781                                    | 5.184                                       |
| HT-180-ADD-1.00-0.04 | 54.25         | 7.42| 3.207                                    | 1.592                                       |
| HT-180-ADD-1.50-0.04 | 53.73         | 6.02| 3.993                                    | 2.218                                       |
branched-chain hydroxyl region (−39.65, −26.47, −23.7, and −17.71 kcal/mol), and hemiacetal region (−17.35 kcal/mol) of the dextran molecule. Moreover, the local minima ESP value can also be observed near the N atom in the amino regions of the poly-l-lysine molecule. In the negative potential region of EPS molecules, the local minima of the ESP value are related to the O and N atoms in the molecule. These negative potential regions overlap each other, forming the negative potential surface of the molecule.

The global maximum ESP value ($V_{\text{max}} = 49.14$ kcal/mol) can be observed near the H atom in the amino region of the poly-gamma-glutamate molecule. Other local maximum ESP values can be observed at regions of EPS molecules, that is, the H atom in the carboxyl region (48.56 kcal/mol) of the poly-gamma-glutamate molecule, the H atom in the hydroxyl region (47.46 kcal/mol) of the dextran molecule, and the H atom in the amino region (45.89 kcal/mol) of the poly-l-lysine molecule. In the positive potential region of EPS molecules, the local maximum of the ESP value is related to the H atom in the molecule.

The ESP analysis of exopolysaccharide and peptide molecules is very important for understanding and predicting intermolecular or intramolecular interactions, especially noncovalent interactions. Because of the large number of oxygen-containing groups in EPS of sludge, the most significant noncovalent interaction is the hydrogen bond. Regions in EPS molecules with the local maxima ESP value can be potential hydrogen bond donors, for example, H atom in the amino group of poly-gamma-glutamate, H atom in the hydroxyl group of dextran, and H atom in the amino group of poly-l-lysine. Moreover, regions in EPS molecules with a local minimal ESP value can act as a hydrogen bond receptor, for example, the lone pairs in the O atom of the carbonyl group in poly-l-lysine, O atom in the carboxyl and carbonyl groups of poly-gamma-glutamate, and O atom in the branched-chain hydroxyl of dextran. The association between H atoms (local maximum points) and O atoms (local minimum points) and actual measurable hydrogen bond-donating and -accepting tendencies has been experimentally confirmed. When the water molecule approaches the surface of EPS, the positive and negative potential ESP of EPS and water molecules will attract each other to form the stable structure of the EPS–water adsorption complex.

3.2.2. AIM Analysis of EPS–water Complexes. Based on the ESP analysis of exopolysaccharide and peptide molecules in EPS, geometry optimization was conducted to obtain stable EPS–water adsorption complexes with the lowest electron energy, where the hydrogen atoms/the oxygen atoms of moisture molecules toward local minimum/local maximum ESP points of the EPS molecule. The AIM molecular structure of the three optimized EPS–water complexes are illustrated in Figure 6, in which CPs and bond paths are also illustrated. BCPs are also observed, and the BCPs and the two interacting atoms are connected by the corresponding bond paths. This confirms the existence of hydrogen bonds. According to Figure 6a, three hydrogen bonds can be observed, that is, O10···H26−O24, O24···H19−O18, and O24···H8−C3. For O10···H26−O24, O10 in hydroxyl was acted as a hydrogen bond acceptor. For O24···H19−O18, H19 in hydroxyl acted as a hydrogen bond donor. For O24···H8−C3, H8 acted as a hydrogen bond donor.

Based on the different hydrogen bond donors, two types of hydrogen bonds can be observed in the adsorption complexes as shown in Figure 6, that is, O···H–O and C···H–O. The geometries of these two types of hydrogen bonds are different from each other, as listed in Tables 2 and 3. The H···O distances of O···H–O and C···H–O range from 1.86 to 2.32 Å and from 2.51 to 2.65 Å, respectively. The angles of O···H–O and C···H–O range from 144.9 to 158.1°. Compared to the sum of the van der Waals radius of oxygen and hydrogen atoms (1.52 + 1.2 = 2.72 Å), the H···O distances of the two types of hydrogen bonds are smaller, which indicates the existence of hydrogen bonds between the EPS and water. Generally, the hydrogen bond is believed to be stronger when its angle is closer to be a straight line (180°) and the H···O distance is shorter. Based on Tables 2 and 3, the hydrogen bond of O···H···O is usually stronger than the hydrogen bond of C···H···O. Thus, O···H···O is identified as the typical hydrogen bond, and C···H···O is defined as the weak hydrogen bond.

To quantitatively investigate the hydrogen bond strength between sludge molecules and water molecules, Tables 2 and 3 give the calculation results of $\rho(r_{\text{bcp}})$ and $V(r_{\text{bcp}})$ at BCPs, where $\rho(r_{\text{bcp}})$ represents the electron density and $V(r_{\text{bcp}})$ denotes the potential energy density. Bond energy $E_{\text{HB}}$ was then calculated based on the equation proposed by Espinosa et al. and the results are listed in Tables 2 and 3. The highest $E_{\text{HB}}$ can be observed in the O12···H5−O7 hydrogen bond in complex C, which indicated that the interaction between the sludge molecule and water molecule is dominated by electrostatic attraction. However, the smallest $E_{\text{HB}}$ can be observed in the O24···H19−O18 hydrogen bond in complex A. Based on Tables 2 and 3, for C···H···O, $E_{\text{HB}} < 15$ kJ/mol. $E_{\text{HB}}$ of typical hydrogen bonds O···H···O were 3−5 times stronger than that of weak hydrogen bonds C···H···O.

Figure 6. BCPs (orange dots) and bond paths (red lines) of three EPS–water complexes: (a) complex A (dextran–water complex), (b) complex B (poly-gamma-glutamate–water complex), and (c) complex C (poly-l-lysine–water complex).
Generally, the higher the $E_{\text{HB}}$, the stronger the hydrogen bond between water molecules and functional groups in sludge molecules will be.\textsuperscript{25} Thus, $E_{\text{HB}}$ is an indicator to characterize hydrophilia of the oxygen-containing group. According to data in Tables 2 and 3, the hydrophilic intensity order of different oxygen-containing groups in EPS was obtained, that is, carbonyl groups in poly-L-lysine > hydroxyl groups in dextran > carboxyl groups in poly-gamma-glutamate.

### Table 2. Characteristics of the Hydrogen Bond O–H···O in EPS···water Complexes

| complexes | BCP | hydrogen bonds | H–O distance (Å) | H-bond angle (deg) | $\rho(r_{\text{HB}})$ (a.u.) | $V(r_{\text{HB}})$ (a.u.) | $E_{\text{HB}}$ (kJ/mol) |
|-----------|-----|----------------|-----------------|--------------------|-----------------|-----------------|-----------------|
| A         | a2  | O24–H19–O18    | 2.03            | 144.9              | 0.0206          | −0.0156         | −22.71          |
| A         | a3  | O10–H26–O24    | 1.86            | 158.1              | 0.0271          | −0.0234         | −31.68          |
| B         | b2  | O18–H11–O10    | 1.95            | 148.6              | 0.0235          | −0.0190         | −26.67          |
| C         | c1  | O12–H5–O7      | 2.32            | 146.5              | 0.0292          | −0.0246         | −33.76          |

### Table 3. Characteristics of the Hydrogen Bond C–H···O in EPS···water Complexes

| complexes | BCP | hydrogen bonds | H–O distance (Å) | H-bond angle (deg) | $\rho(r_{\text{HB}})$ (a.u.) | $V(r_{\text{HB}})$ (a.u.) | $E_{\text{HB}}$ (kJ/mol) |
|-----------|-----|----------------|-----------------|--------------------|-----------------|-----------------|-----------------|
| A         | a1  | O24–H8–C3      | 2.65            | 112.8              | 0.0069          | −0.0046         | −7.21           |
| B         | b3  | O9–H6–C3       | 2.51            | 102.0              | 0.0104          | −0.0069         | −10.85          |

![Figure 7](image)

**Figure 7.** RDG isosurface maps and scatter diagrams of three complexes: (a,c,e) color mapped RDG isosurface graphs, and (b,d,f) scatter diagrams. The isovalue is set to 0.5. The surfaces are colored on a blue-green-red scale according to the values of sign ($\lambda_2$) ranging from −0.03 to 0.02 a.u. Blue represents strong attractive interactions, green represents vdW interactions, and red indicates strong steric effects.

### 3.2.3. RDG Analysis of EPS···water Complexes

Color mapped RDG isosurface graphs and scatter diagrams of RDG versus sign ($\lambda_2$) for three complexes are illustrated in Figure 7. The color presented by different values on the equivalent face can be used to identify weak interactions between different types of molecules. For $\lambda_2 < 0$, the interactions are bonded interactions. For $\lambda_2 > 0$, the interactions are unbonded interactions. The electron density can be used to reflect the...
bond strength. For a negative value of \( \lambda_2 \rho \), the greater the absolute value the stronger the attractive interaction will be and its representative interaction is hydrogen bond. For a positive value of \( \lambda_2 \rho \), the greater the absolute value the stronger the unbonded interaction will be and its representative interaction is the steric effect. For the near zero value of \( \lambda_2 \rho \), the representative interaction is weak van der Waals interactions.

A RDG value of 0.5 is selected for the isosurface graphs in Figure 7. In the isosurface graphs, a blue-green-red color range, as shown in the color bar, was used to describe the value of sign \( \lambda_2 \rho \) from −0.03 to 0.02 a.u. Blue represents strong attractive interactions, green represents van der Waals interactions, and red represents the steric effect. Generally, there is no obvious boundary between the weak hydrogen bond and van der Waals interactions on the isosurface graphs. On the scatter diagrams, the more scatter points distributed on the line of 0.5 a.u. RDG, the stronger the corresponding interactions.

As shown in complex A, B, and C in Figure 7, for exopolysaccharide and peptide molecular in sludge EPS, differences can be observed in the interactions between water and these molecules. For complex A (dextran--water complex), the steric effect can be observed between the carbon atom and the oxygen of the water molecule. Moreover, two different hydrogen bonds also exist (corresponds to the two spikes ranges from −0.03 to −0.025 a.u. in the scatter diagram). The spike on the left side corresponds to the O10--H26--O24 hydrogen bond with greater bond energy, and the spike on the right side corresponds to the O24--H19--O18 hydrogen bond. Therefore, the hydrophilia of the hydroxyl groups in dextran can be proved again. For complex B (poly-gamma-glutamate--water complex), it is a typical van der Waals interaction. The interaction between poly-gamma-glutamate and water molecules is dominated by van der Waals attraction. Most areas of the isosurface are green and brown-green (corresponds to the spike located in low electron density and low gradient regions in the scatter diagram), representing the van der Waals interactions between molecules. For complex C (poly-l-lysine--water complex), based on the blue isosurface (corresponds to the spike ranges from −0.04 to −0.02 a.u. in the scatter diagram) between the carbonyl and water molecule, a relatively weak hydrogen bond can be inferred to exist. Weak van der Waals interactions can be observed between the hydrogen of the carbonyl and the oxygen of the water molecule, as well as between the oxygen of the carbonyl and the hydrogen of the carbon atom. A small but a non-negligible steric effect also exists (corresponds to the spike ranges from 0.01 to 0.02 a.u. in the scatter diagram).

4. CONCLUSIONS

A combined method of hydrothermal and FeSO₄·7H₂O/ Ca(CIO)₂ was developed for improving sludge dewaterability in our previous work. In this paper, the dewatering mechanism of sludge after the combined treatment of hydrothermal treatment and FeSO₄·7H₂O/ Ca(CIO)₂ was obtained for the first time. The content of surface water in sludge was converted into free water, which indicated that the EPS in sludge was degraded and part of the water absorbed in EPS was released. The increase of free water is the main reason for the improvement of sludge dewatering performance.

The noncovalent interaction between EPS in sludge and water on the molecular level was studied for the first time by using density functional theory (DFT). With hydrothermal and FeSO₄/ Ca(CIO)₂, the content of surface water decreased and content of free water increased obviously, which indicated that the EPS in sludge was degraded and part of the water absorbed in EPS was released. The treatments affect the moisture distribution in this order that: combined effect > Individual hydrothermal > Individual FeSO₄/ Ca(CIO)₂. The optimal operating conditions were consistent with the optimal operating conditions analyzed in our previous work.

The high internal water content of sludge is caused by noncovalent interactions between the EPS and the moisture molecule of the sludge, especially for the hydrogen bond between exopolysaccharide/peptide molecule and water molecule. The RDG analysis was used to calculate the noncovalent interactions of EPS--water complexes. Based on the ESP analysis of the three representative EPS molecules as well as the AIM and RDG analysis of the three complexes, noncovalent interactions between hydrophilic sites on EPS molecular surfaces and water molecules were obtained. Based on the ESP analysis, regions in EPS molecules with a local maxima ESP value can be potential hydrogen bond donors, for example, H atom. Regions in EPS molecules with a local minimal ESP value can act as a hydrogen bond receptor, for example, the lone pairs in the O atom near oxygen-containing groups.

Two types of hydrogen bonds can be observed, that is, typical hydrogen bond O–H···O and weak hydrogen bond C–H···O. Generally, the hydrogen bond formed between the oxygen-containing group in dextran/poly-gamma-glutamate/poly-l-lysine and water molecule is the typical hydrogen bond O–H···O. The hydrogen bond formed between the carbon ring in Dextran and water molecule is the weak hydrogen bond C–H···O. The oxygen-containing group site is more hydrophilic than the carbon chain. The hydrophilic intensity order of different oxygen-containing groups in EPS was obtained, that is, carbonyl groups in poly-l-lysine > hydroxyl groups in dextran > carboxyl groups in poly-gamma-glutamate. The noncovalent interaction results based on RDG analysis are similar to AIM analysis. In addition to the hydrogen bond, the van der Waals interactions and steric effects were also existed between water molecules and exopolysaccharide/peptide molecules.

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ABBREVIATIONS

AOP advanced oxidation process
DS dry sludge
EPS extracellular polymeric substances
DFT density functional theory
ESP electrostatic potential
AIM atom in molecules
RDG the reduced density gradient
BDE bond dissociation enthalpy
HTD hydrothermal dewatering
CPs critical points
BCPs bond critical points
RCPs ring critical points
CST capillary suction time
SRF capillary suction time
vDW van der Waals
a.u atomic unit

Nomenclature

$W_{\text{bu}}$ an evaluation parameter for sludge dewatering performance
$W_c$ water content
$\rho$ electron density
$V$ potential energy density
$\eta_{\text{BCPs}}$ at BCPs
$E_{\text{HB}}$ bond energy
$\lambda_2 < 0$, bonded interactions; $\lambda_2 > 0$, unbonded interactions

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