



Influence of surfactant for improving dewatering of brown coal: A comparative experimental and MD simulation study

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ABSTRACT

Experimental method and molecular dynamics (MD) simulations were used to investigate the filtration dewatering process of brown coal in the presence of the surfactant TRITON X-100 (TX-100). A significant reduction in filter cake moisture content was observed upon addition of TX-100 in the dewatering experiments. It was observed that a narrow TX-100 concentration range of below the critical micelle concentration (CMC) was best for dewatering. The enhancement in filtration dewatering characteristics could be attributed to the wetting characteristic changes of the brown coal surface caused by surfactant adsorption, as indicated by measurement of contact angles. Monolayer adsorption of TX-100 at the lignite surface was investigated by MD simulations. The TX-100 molecules repelled water molecules near the coal surface and adsorbed at the water-lignite interface with the ethoxylate closer to the coal surface than the octylphenol. The mobility of water molecules was enhanced in presence of TX-100 according to the results of mean square displacement (MSD) and diffusion coefficient. It was inferred that adsorption of TX-100 resulted in a more hydrophobic brown coal surface, in agreement with the dewatering and contact angle experiments.

1. Introduction

Brown coal reserves are estimated at 1025 billion tons worldwide, accounting for nearly 40% of all coal reserves [1]. However, its high moisture content hinders the efficient use of brown coal. The high moisture content increases the costs of transportation and storage of the coal. Besides, the high moisture affects the thermal efficiency of power generation [2,3]. When brown coal is burned in conventional power stations, up to 20% of the inherent chemical energy of the lignite is wasted because of the evaporation of water [4]. Tao et al. [5] reported that a 1% reduction in the moisture content of American coal can cause a 1.4% increase in the calorific value. Thus, more efficient dewatering processes for brown coal have been developed in recent years [6,7]. Thickening, filtration, and thermal treatments are the most commonly used processes for coal dewatering. In the thickening process, gravity is used to separate particles in water by sedimentation. Due to the low specific gravity of coal ($\sim 1.3 \text{ g/cm}^3$), the residual moisture content of the treated product is approximately 30 wt%, which is not enough for utilization of brown coal. Although thermal dewatering technology has been proposed for removing additional water, this process is costly and results in significant pollution generation [4,8,9]. The filtration process uses pressure to separate the solid coal and water, and is inexpensive and efficient [10]. Many investigations regarding the filtration process

have been reported [11,12]. Once the pressure is carried to the slurry, filtrate is quickly removed from the cake until a certain point above which the residual water remains constant. To increase dewatering efficiency, many methods have been proposed aid in the filtration process. Previous studies [13–17] have shown that the addition of a small amount of appropriate surfactant to the dewatering filtrate of fine coal significantly improved dewatering efficiency. The mechanism of improvement appeared to involve hydrophilic lipophilic balance (HLB), point of zero charge (PZC), pH, and surface tension. In essence, the adsorption characteristics of the surfactant on the coal surface likely play a critical role in the dewatering process. Although there have been many experimental studies on lignite, a theoretical description of interactions within the lignite/surfactant/water system during filtration dewatering at the molecular level is lacking.

Molecular dynamics (MD) is an effective tool to investigate the microscopic properties of materials. It should be noted that several investigations regarding lignite/water interactions have been performed using MD simulation. Kumagai et al. [18] modeled the structure of Yalloum lignite. The volume of the lignite model decreased as water was removed. Vu et al. [19] used MD to study the interactions between brown coal and water as a model system of a lignite matrix. It was indicated that the diffusion of water molecules near to lignite was reduced due to hydrogen bonding interactions. Zhang et al. [20] used MD

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Table 1
Proximate analysis of lignite (wt%).

Moisture, ad ¹	Ash, ad ¹	Volatile matter, daf ²	Fixed carbon, daf ²
9.10	19.82	62.75	37.25

¹ Air-dry basis.

² Dry ash-free basis.

methods to investigate the structure and dynamics of lignite during moisture removal with different initial moisture contents. The interactions among water molecules and functional groups in the coal, such as hydroxyl, carboxyl, and carbonyl groups have also been studied.

The two-phase filtration dewatering system with the addition of surfactant is very complex. In this study, a molecular level description of the interactions of the lignite/surfactant/water system is provided by MD simulation. The results will be useful for understanding the mechanisms governing filtration dewatering. In addition, filtration dewatering experiments were carried out to experimentally verify the MD simulation results.

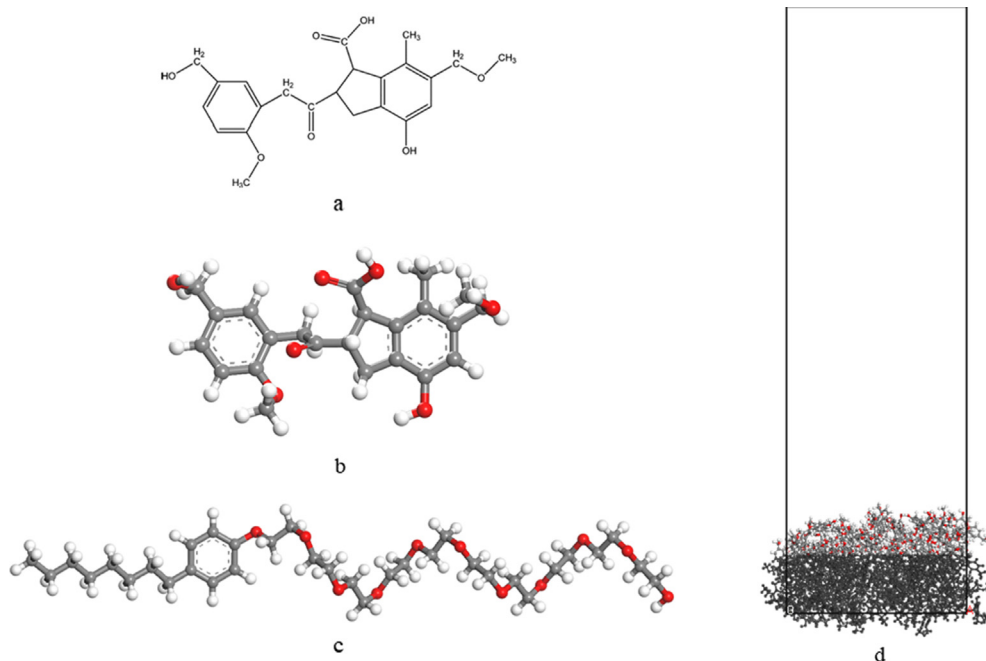
2. Experimental and methods

2.1. Materials

Lignite from Zhaotong, Yunnan Province, China was selected for this study and was crushed by a cone crusher. The crushed sample was ground, and sieved to obtain the $-38\ \mu\text{m}$ size fraction. Proximate analysis was then performed, and the results are shown in Table 1, where M_{ad} is the moisture content, A_{ad} is the ash content V_{daf} is the volatile content, and FC_{daf} is the fixed carbon content.

To eliminate the mineral matter effects of coal for XPS measurements, the lignite was demineralized using a dilute HF and HCl solution [21,22]. Subsequently, the sample was dried in a vacuum oven at $100\ ^\circ\text{C}$ for 24 h. This purified coal sample was used throughout the study.

Triton X-100 (TX-100) was obtained from DOW Chemical Company, and is a branched chain octylphenol with 9.5 mol of ethylene oxide per molecule with critical micelle concentration (CMC) of 189 mg/L at $25\ ^\circ\text{C}$ [16].



2.2. Dewatering experiment

Dewatering was achieved using the Buchner Vacuum process. In all experiments, coal pulp containing 100 g of coal and 300 g of distilled water with varying amounts of TX-100 was prepared. The mixture was stirred for 30 min with a magnetic bar. The prepared slurry was poured into a Buchner funnel 110 mm in diameter containing filter paper with a pore size of $10\ \mu\text{m}$. The dewatering tests were performed at a constant vacuum pressure of 60 kPa. Dewatering was performed for 5 min after the removal of water from the top of the cake. After filtration, the filter cakes were weighted and dried in an oven at $105\ ^\circ\text{C}$ to enable the calculation of moisture content.

2.3. Contact angle

The contact angle between the lignite and surfactant solution was determined using a DSA100 video optical contact angle measuring device. Before the contact angles were measured, 200 mg of the coal sample was placed under a pressure of 40 MPa for 2 min using desktop powder tablet compressing machine and an ID13 cylindrical tablet mold. When removed, a circular test piece with polished plane was fabricated with a diameter of 13 mm and thickness of 2 mm [23–27].

Distilled water droplets and wetting agents dropped on the surface of lignite samples was imaged and analyzed using the optical contact angle meter (DSA100) via the “contact angle using” and “circle fitting” modes. The contour line of the wetting result is shown on the image of the drops and measurement of contact angles was automatically acquired and displayed. Each data point reported herein represents a mean of five measurements.

2.4. Molecular dynamics simulation methodology

The COMPASS force field was employed in MD simulations [28–32]. The molecular model of brown coal was built based on the models developed by Wender et al. [33], Kumagai et al. [18] and Tang et al. [34], as shown in Fig. 1a. In Fig. 1b, the structure of the brown coal model was optimized. 80 optimized lignite molecules were put into a periodic box. In the case of a constant pressure-temperature ensemble with the Berendsen thermostat and barostat, the system was equilibrated [35]. The temperature of the system was maintained at 298 K

Fig. 1. (a) Molecular model of lignite. (b) The structure of a single lignite model. (c) TX-100 molecular model. (d) The structure of 80 optimized lignite model molecules. The fixed atoms in lignite model are shown in black. The red balls are O, grey are C, and white are H. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and the pressure was set to 0.1 MPa. A time step of 1.0 fs was employed to integrate the motion equations. The Ewald Summation method and a van der Waals interaction cutoff of 12.5 Å were used to account for long-range electrostatic interactions. After an equilibration time of 500 ps in the NPT ensemble, the brown coal model was constructed as shown in Fig. 1d.

The molecule model of TX-100 was shown in Fig. 1c. It should be noted that 10 mol of ethylene oxide per molecule was employed. The coal-water-TX system, which included 80 brown coal macromolecules, 5000 water molecules, and 3 TX-100 molecules, was packed into a rectangular simulation cell with dimensions of $44.74 \times 44.74 \times 150$ Å³ (X × Y × Z). The simple point charge (SPC) water model was adopted [36].

The simulation was performed in the NVT ensemble level at 298 K using a Nose thermostat with time step of 1.0 fs. A van der Waals interaction cutoff of 12.5 Å and the Ewald summation method, with an accuracy of 10^{-3} kcal/mol, were employed to account for long-range electrostatic interactions. The bottom of the lignite model was frozen during the simulation to reduce computational cost as shown in Fig. 1d. The simulation was run for 1 ns and the final results were obtained from simulations of 500 ps.

3. Results and discussion

3.1. Dewatering studies

The results of the dewatering of the coal pulp as a function of TX-100 surfactant dosage are observed in Fig. 2. The cake moisture content was 22.14% without the addition of TX-100. It was observed that TX-100 enhanced the dewatering effect as the cake moisture first decreased with increasing TX-100 concentration to a minimum value of approximately 17%. Subsequently, the moisture content increased with increasing TX-100 concentration.

It should be noted that the minimum cake moisture occurred at a concentration of 150 mg/L, which is near the critical micelle concentration (CMC) of TX-100 as shown in Fig. 2. The best dewatering efficiency was obtained in a narrow range of TX-100 concentration just below the CMC. This observation is in agreement with previous studies [17,37], and can be explained by the changing lignite surface wettability, which was verified by the following contact angle experiments. It is likely that at TX-100 concentrations below the CMC, adsorption occurs simultaneously through hydrophobic interactions between the hydrocarbon chain of TX-100 and the hydrophobic coal as well as through polar interactions between the ethoxylated TX-100 and hydrophilic functional groups at the surface of the coal. Due to abundance

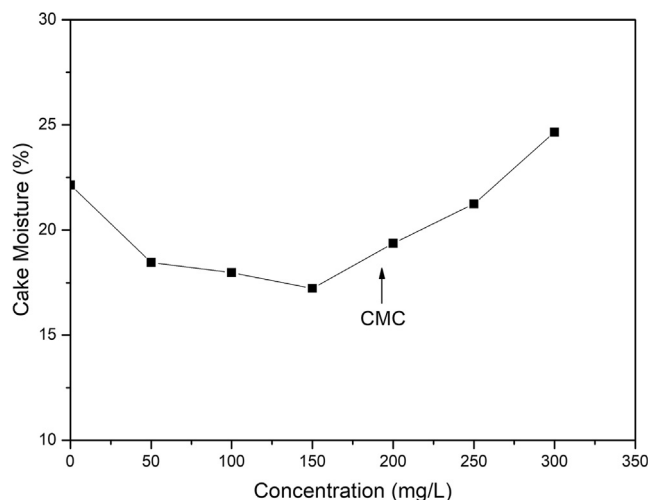


Fig. 2. Moisture content of filter cakes as a function of TX-100 concentration.

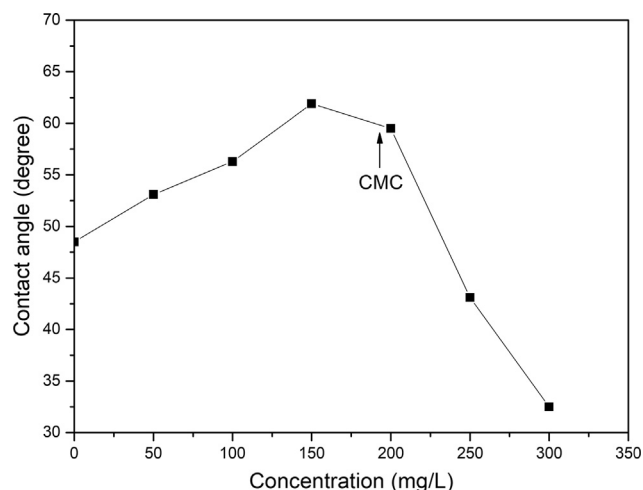


Fig. 3. Variation of contact angle on the brown coal surface as a function of TX-100 concentration.

of oxygen-containing functional groups on the lignite surface, at low surfactant concentrations the overall interaction is dominated by polar interactions. The hydrophobicity of the coal was enhanced with increasing TX-100 concentration. At TX-100 concentrations above the CMC, the surfactant molecules adsorbed through hydrophobic chain-chain interactions resulting in the extension of ethylene oxide chains into the solution, rendering the coal surface more hydrophilic. The concentration of the octylphenol ethoxylate is important for the effective filtration dewatering of brown coal. From the results presented here, it is clear that a low concentration of TX-100 (below its CMC) is beneficial for the dewatering of lignite.

At TX-100 concentrations below the CMC, monolayer adsorption occurs more readily. Therefore, the monolayer adsorption structure of TX-100 on the lignite model was used in the following MD simulations.

3.2. Contact angle

The contact angles as a function of TX-100 concentration on the lignite surface are obtained in Fig. 3.

The lignite shows a contact angle of 48.5° in the absence of TX-100. As the concentration of TX-100 was gradually increased, the contact angle first increases and then decreases at a critical point. The maximum contact angle of 61.9° at approximately 150 mg/L, near the CMC of TX-100. The results of the contact angle measurements are in agreement with the dewatering studies, especially the remarkable change of wettability in vicinity of the CMC.

3.3. Molecular dynamics simulation of TX-100

3.3.1. Adsorption structure of TX-100

The aggregated structure of TX-100 on the brown coal surface is shown in Fig. 4. The density distributions of lignite, TX-100, and water molecules along the Z axis with being normal to the lignite surface were calculated and shown in Fig. 5. Fig. 6 indicates the density distributions of the head (ethoxylate) and tail (octylphenol) groups of TX-100.

It is indicated that a hemi-micellar structure forms on the brown coal surface in Fig. 4. Most ethylene oxide groups adsorb on the lignite surface. In addition, the alkyl chains are clearly highly intertwined with each other. Fig. 5 shows that the TX-100 peak distribution appears at 27.75 Å, which is closer to the lignite surface than most water molecules along the Z-axis exceeding 31 Å. It is meaning that TX-100 primarily exists at the water/coal interface. It can be inferred that some water molecules were repelled from lignite surface because of adsorption of TX-100. It should be noted that there is a weak shoulder with ~34 Å, indicating the presence of structured water molecules close to

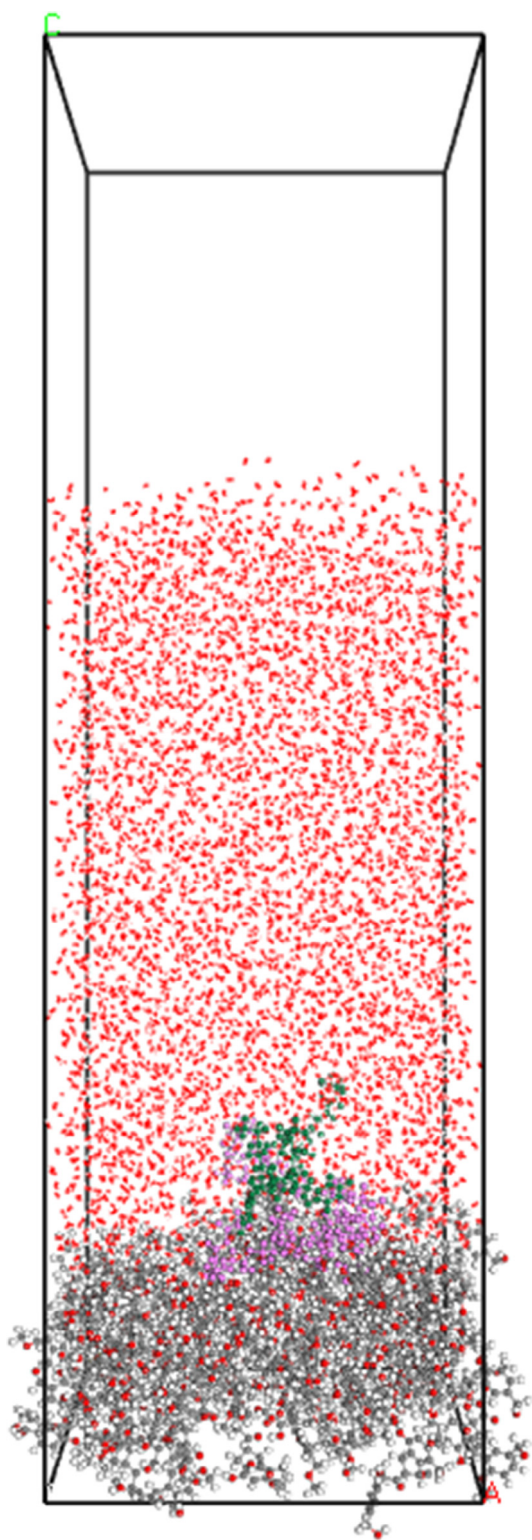


Fig. 4. Simulation snapshot of TX-100 (Octylphenol: green and Ethoxylate: purple) aggregates on the lignite surface (O: red, C: gray, and H: white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lignite surface. This water layer may be the near-surface water film controlled by the hydrogen bonding [38].

The Z-dependent density profiles for the ethoxylate and octylphenol groups of TX-100 were also plotted to reveal the configuration of TX-100 on the lignite surface (Fig. 6). Obviously, the peak distribution of

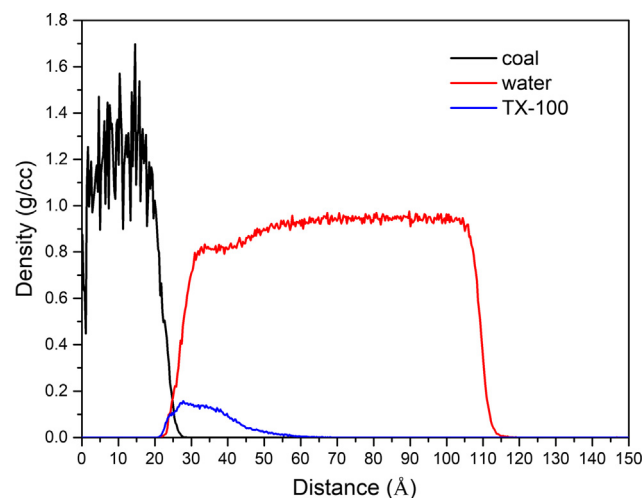


Fig. 5. Density distributions of coal, TX-100 and water molecules along the Z axis.

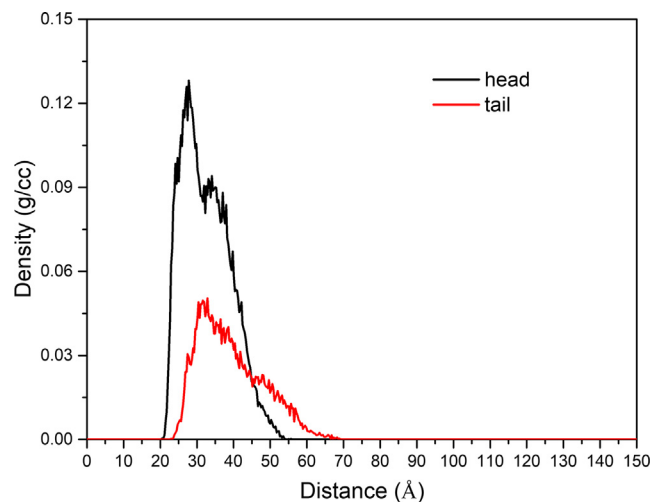


Fig. 6. Density profiles of the TX-100 head and tail groups along the Z-axis direction.

the ethoxylate group was closer to the lignite surface than that of the octylphenol group. Thus, it can be inferred that the polar interactions between the ethoxylated group of TX-100 and hydrophilic sites on the lignite surface is the dominant adsorption force. In other words, the ethylene oxide groups of TX-100 preferentially adsorb on the hydrophilic sites of brown coal, leaving the hydrophobic portion exposed to the bulk solution. This result certifies that stronger hydrophobicity lignite surface was obtained after adsorbing TX-100, which is agreement with dewatering and contact angle experiments.

3.3.2. Mobility of water molecules

The change of the lignite cake moisture content can be partly represented by dynamic properties of water molecules around coal surface. The dynamic property could also be gained from translational motion of water molecules. This motion is obtained by calculating the mean square displacement (MSD)[39]. The MSD curves of water molecules in the lignite/water system and lignite/water/TX-100 system have been calculated from Eq. (1), as shown in Fig. 7.

$$\text{MSD} = N^{-1} \left\langle \sum_i |r_i(t) - r_i(0)|^2 \right\rangle \quad (1)$$

where N , $r_i(0)$ and $r_i(t)$ are atom number, position vector at an initial

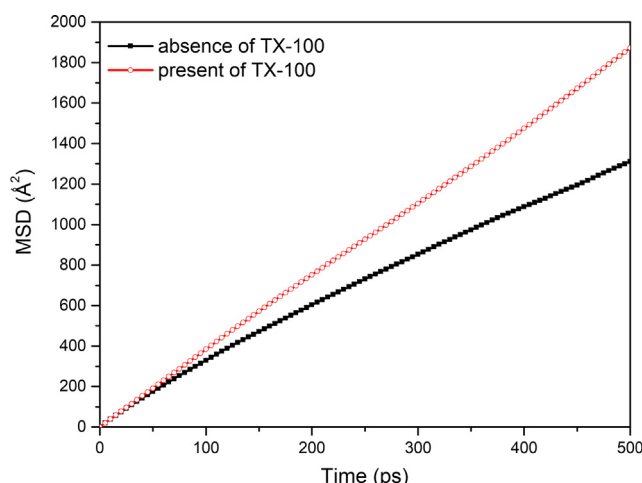


Fig. 7. MSD curves of water molecules in the absence and presence of TX-100.

time and position vector after time t , respectively. The angular brackets represent ensemble averaging.

The diffusion coefficient (D) can represent the intensity of water molecules mobility [40]. It is denoted as Eq. (2),

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i \rightarrow j} N \langle |r_i(t) - r_i(0)|^2 \rangle \quad (2)$$

In Fig. 7, it was obviously observed that the mobility of water molecules was enhanced in presence of TX-100. In the mixed system, the diffusion coefficients with and without TX-100 were 6.14×10^{-5} and $4.26 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively. The increased mobility of water molecules indicates stronger hydrophobicity after adsorbing TX-100. The results are in agreement with experiments of dewatering and contact angle.

4. Conclusions

The filtration dewatering process of brown coal in the presence of TRITON X-100 (TX-100) was studied by experimental method and MD simulation.

It is observed that the minimum in the cake moisture occur at the concentration around CMC of TX-100. In addition, as the concentration of TX-100 gradually increases, the contact angle first increases and then decreases with maximum contact angle at about CMC of TX-100. The dewatering and contact angle experiments show that wetting characteristics change of the brown coal surface causes the enhancement of surfactant in filtration dewatering process.

Monolayer adsorption of TX-100 at lignite surface was investigated by means of Molecular dynamics simulations. The density distributions of lignite, TX-100 and water molecules along the Z-axis showed that TX-100 molecules adsorbed at the water-coal interface. It means that TX-100 molecules repelled water molecules near lignite surface. The aggregated structure of adsorbed TX-100 molecules shows that the ethoxylate groups are closer to the coal surface than that of octylphenol groups. The mobility of water molecules was enhanced in presence of TX-100 according to the results of mean square displacement (MSD) and diffusion coefficient. It was inferred that adsorption of TX-100 brought out more hydrophobic brown coal surface, which was agreement with filtration dewatering and contact angle experiments.

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Conflicts of interest

None.

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