Research paper

Decrease in hydrophilicity and moisture readsorption of Manglai lignite using lauryl polyoxyethylene ether: Effects of the HLB and coverage on functional groups and pores

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A B S T R A C T

Decrease in hydrophilicity of lignite and moisture readsorption after adsorption of a series of lauryl polyoxyethylene ether ($C_{12}(EO)_n$) were studied with the measurement of wetting heat and moisture readsorption ratio. Effect of the hydrophilic lipophilic balance (HLB) of $C_{12}(EO)_n$ on efficiency of the decrease in lignite hydrophilicity was investigated. X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption/desorption were used to disclose the coverage characteristics of the different functional groups and the aggregations in pores of lignite by the adsorbed surfactant. Results indicated that both wetting heat and moisture readsorption ratio of lignite decreased significantly using different $C_{12}(EO)_n$. The size order of wetting heat of lignite after adsorption of different $C_{12}(EO)_n$ with variation of the HLB values were almost consistent with that of moisture readsorption. The low HLB values of $C_{12}(EO)_n$ especially with HLB of around 13.62 and 12.49/9.75 are most efficient respectively for the decrease in wetting heat and moisture readsorption of lignite. Coverage of oxygen-containing groups by surfactant was mainly devoted to the decrease in hydrophilicity of lignite. Among those oxygen groups in lignite surface, the COO/COOH and C-O/OH were responsible for adsorption priorities. Aggregations of surfactant in pores were beneficial for decreasing moisture readsorpiton of lignite surface due to the decreased storing space of moisture.

1. Introduction

Utilization of lignite in industrial processes, such as combustion in power plant, storage and transportation, requires a low amount of water to maximize the efficiency and save coal [1–3]. A wide variety of drying and dewatering technologies for low rank coal have been developed for this aim [1]. The phenomenon of moisture readsorption of the dried lignite in air leads to a loss of drying efficiency. Moisture readsorption of lignite results from the strong interaction of water molecules with the polar oxygen functional groups on the lignite surface, such as phenolic hydroxyl, carboxyl, carbonyl and methoxyl groups [4–7]. Abundant pore structures also provide enough storing space for the moisture readsorbed [8]. Generally, inhibition of moisture readsorption of lignite focuses on three points below: (a) eliminating the oxygen-containing groups on the lignite surface by chemical methods to weaken its adsorption capacity for moisture; (b) shielding the oxygen-containing groups with a hydrophobic medium to prevent the contact of lignite surface with moisture; (c) reducing the pore volume of lignite by physical or chemical methods to decrease the storing space for moisture. Conventional hydrothermal dewatering (HTD) [9,10] and mechanical thermal expression (MTE) [11–13] could effectively decrease moisture readsorption of lignite as a result of the decrease in the concentration of oxygen functional groups and in the pore volume of lignite [14], but the conducted conditions requires high temperature and pressure resulting of the unnecessary energy cost and the waste water which is difficult to recycle [15].

Application of surfactant to decrease moisture readsorption of lignite could be achieved basing on its capacity of modifying the hydrophilicity of lignite. Surfactants containing amphiphilic molecular structure have been widely used to modify the characteristics of the phase interface, such as in coal flotation and ultrafine coal dewatering [16–18]. The adsorption of surfactant on lignite surface could decrease the hydrophilicity of lignite and moisture readsorption by shielding the hydrophilic sites of lignite with hydrophobic surfactant layer. The contact angles of different ranks of coal were found to be decreased significantly after adsorption of surfactants [19].

The concentrations of oxygen functional groups on the lignite surface and the surfactants species could both affect the extent of the

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decrease in hydrophilicity of lignite [20]. Lignite contains a variety of functional groups, which can differ in their adsorption capacities for different surfactants; for example, the effective thickness of the adsorbed cationic surfactant CTAB on surface carboxyl groups was found to be thicker than that on other oxygen-containing lignite functional groups [21]. Thus the extent of hydrophilicity modification could depend on the proportions of different oxygen functional groups present, just as the water-holding capacity of lignite depends on the relative proportions of different oxygen-containing groups [22]. In addition, surfactant also differ their effectiveness of reducing the hydrophilicity of lignite; cationic surfactant has been demonstrated to be much more effective than anionic surfactant for the decrease in hydrophilicity of lignite [23]. However, most cationic surfactants are quaternary ammonium compounds, and the introduction of nitrogen on the lignite surface may have undesirable environmental consequences. In consideration of this point, the nonionic surfactant may be alternative choice. The hydrophilic lipophilic balance (HLB) values of nonionic surfactant, as one important indicator of the activities, should be given necessary attention.

The lauryl polyoxyethylene ether ($C_{12}(EO)_n$), one of the most common nonionic surfactants, were chosen in this study. All the elements contained in $C_{12}(EO)_n$ molecules are environment friendly having little effect on the further utilization of lignite. Compared to the conventional drying technology hydrothermal dewatering (HTD) and mechanical thermal expression (MTE), method of $C_{12}(EO)_n$ adsorption need lower equipment investment and more convenient operating conditions which is cost-effective. Understanding the distribution characteristics of nonionic surfactant on different functional groups and pore structures of lignite are beneficial for controlling the decrease in hydrophilicity and moisture readsorption. Decrease in hydrophilicity of lignite after adsorption of a series of $C_{12}(EO)_n$ were measured by calorimetric methods, and the moisture readsorption were also investigated. Effect of the HLB of $C_{12}(EO)_n$ on efficiency of the decrease in lignite hydrophilicity was analyzed. XPS analysis and nitrogen adsorption/desorption were adopted to disclose the distribution of $C_{12}(EO)_{15}$ on the different functional groups and pore structures. In addition, surface tension of $C_{12}(EO)_n$ solution with different concentration were also analyzed before the adsorption experiments of lignite.

2. Experimental

2.1. Materials

Lignite from Manglai in China was selected for this work. The lignite was milled and sieved into 48–75 μm particles and dried in a vacuum oven at 373 K for 2 h prior to use. All lignite samples used in this study were dried lignite. Surfactants used in this study were lauryl polyoxyethylene ether series ($C_{12}(EO)_n$; n = 4, 7, 9, 15, 20, 23; purity > 98%). The non-ionic surfactant is a hydrophilic ethylene oxide chain (EO) with varying length attached to dodecyl (hydrophobic group), as indicated in Fig. 1. In order to reveal the effect of HLB on the decrease in hydrophilicity of lignite, the HLB values of $C_{12}(EO)_n$ was calculated according to the Griffin's method (Eq. (1)) [24,25].

$$HLB = 20\, M_H/(M_H + M_L) \qquad (1)$$

where M_H is the molecular weight of hydrophilic head of surfactant molecule, g/mol; M_L is the molecular weight of hydrophobic end of surfactant molecule, g/mol. The obtained HLB values of $C_{12}(EO)_n$
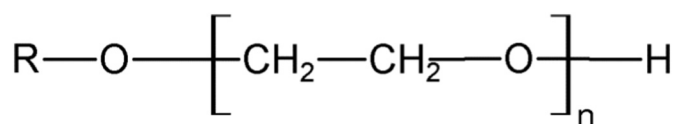

Fig. 1. Chemical structure of lauryl polyoxyethylene ether (R: dodecyl, n: the EO groups).

(n = 4, 7, 9, 15, 20, 23) are 9.75, 12.49, 13.62,15.62, 16.52 and 16.90 respectively.

2.2. Adsorption process

Adsorption experiments were conducted in 500 mL flat-bottom flasks immersed in a thermostatic magnetic shaker bath. For this, 0.4 g of dried sample was agitated with 400 mL of an aqueous solution with a known solution concentration of $C_{12}(EO)_n$ (50, 100, 200, 300 and 400 mg/L). The flasks were shaken by shaker at a constant speed (800 r/min) for 10 h at 298 K. At the end of adsorption period, the deposit was separated by filtration with qualitative filter paper and vacuum dried at 373 K until the change of weight was < 0.5 wt% within 30 min (usually 2 h).

2.3. Characterization

The wetting heat of solid particle samples immersed in water was obtained using a C80 micro-calorimeter (Setaram, France), which is a new type of Calvet calorimeter. The thermostatic mode at 303 K and membrane-mixing stainless steel cell (volume: 8.5 mL) were adopted. Next, 0.1 g of dried sample was sealed in a cell under an aluminum foil membrane which divided the mixing cell into two parts. Then, 2 mL liquid was poured into upper portion of the cell. The cell was placed in a calorimeter, and the aluminum-foil membrane was pricked when system reached a balance. Wetting process usually finished within 2 h and wetting heat was finally obtained by integration of the heat-flow curve. The error in wetting heat was less than ± 0.5 J/g.

The FTIR spectrum was measured using a Bruker Tensor 27 FTIR Instrument and KBr pellets (100 mg, 1 wt%) was adopted. The measured region extended from 4000 to 600 cm^{-1}. A blank scan before measurement was taken to eliminate the influence of background. The resolution was 2 cm^{-1}.

XPS measurements were carried out to investigate the distribution of surfactant adsorbed onto the coal surface. Experiments were conducted using an ESCALAB 250Xi instrument (Thermo Fisher). The pressure in the sample chamber was below 2×10^{-7} Pa during tests. Monochromatic Al radiation ($K_\alpha\, h\nu$ = 1486.6 eV) was used as the X-ray source. The survey scan had a resolution of 1 eV. The high-resolution spectra were recorded with a pass energy of 30 eV and an energy step size of 0.1 eV for the scan of C 1 s, O 1s, Si 2p, Ca 2p and S 2p. Binding energies were corrected by the containment carbon (C 1 s = 284.6 eV). The Shirley method was used to deduct the effect of background [26]. Data processing was performed using XPS Peak 4.1 software.

The surface tension of surfactant solution was measured with the Wilhelmy plate (Pt alloy) method using an automatic surface/interface tensiometer (QBZY-3 from China). All the surfactant solution was prepared freshly before the measurements. The measurement environment was room temperature (298 K). After measurement of each solution, the plate was cleaned by absolute ethyl alcohol and water, and finally burned in an alcohol flame. The error in surface tension of surfactant solution was less than ± 0.2 mN/m.

The nitrogen adsorption and desorption measurement was carried out at 77 K on a TriStar II 3020 specific surface and porosity analyzer (Micromeritics Instrument Corporation, USA). Before each measurement, sample was vacuum-degassed at 378 K for 4 h. Then, adsorption/desorption isotherms were obtained at different relative pressure values (P/P$_0$: 0.05–0.95). The specific surface area was calculated using the BET (Brunauer Emmett Teller) method in the relative pressure range P/P$_0$ of 0.05–0.30. The pore size distribution was analyzed using the BJH (Barrett Joyner Halenda) method with a pore diameter range of 1.7–300 nm.

In order to investigate the influence of adsorption of surfactants on lignite surface hydrophilicity modification, moisture readsorption of dried lignite samples was measured. The coal samples were placed respectively in numbered weighing bottles. Next, the weighing bottles