Research article

Further exploring on aqueous chemistry of micron-sized lignite particles in lignite–water slurry: Effects of humics adsorption

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ABSTRACT

The aqueous chemistry of micron-sized lignite particles has essential influences on the dispersion stability of water-lignite slurry. In this work, the adsorption behaviors of dissolved humics on lignite surface in lignite–water slurry were studied through batch adsorption experiments. The influences of adsorbed humics on the surface properties, particle size distribution and dispersion stability of lignite particles in water-lignite slurry were examined by advanced analysis techniques, EDLVO theory and settlement tests. The adsorption results indicate that the adsorption capacity of humics on lignite increases from $4.11 \, mg \cdot g^{-1}$ to $8.25 \, mg \cdot g^{-1}$ with the humics concentration increasing from $100 \, mg \cdot L^{-1}$ to $200 \, mg \cdot L^{-1}$. The adsorption process can be well described by the pseudo-second order kinetic model. The adsorbed humics significantly improves the hydrophilicity and electronegativity of lignite surface and reduces the apparent particle size of lignite. The EDLVO calculation and settlement tests reveal that the total interaction energy of the humics-adsorbed lignite particles at 18 nm of separation distance is enhanced from $0.85 \times 10^{-17} \, J$ to $1.45 \times 10^{-17} \, J$ with the initial humics concentration increasing from $100 \, mg \cdot L^{-1}$ to $200 \, mg \cdot L^{-1}$. The dispersion stability of micron-sized lignite particles is improved with humics adsorption on lignite surface.

1. Introduction

Lignite, a kind of low rank coal, is abundant in China, being estimated approximately 130 billion tons inventory [1]. With the rapid economic development, increasing consume of high rank coal has led to a drastic increase in the demand for lignite. However, lignite presents a high moisture content (25–70%), high ash content, low calorific value and poor thermal stability. These inherited defects seriously limit their utilization in the industrial processes, due to low power plant efficiency, high CO_2 and solid residues emission, increased transportation cost and spontaneous combustion during storage [2,3]. Notably, lignite possesses many remarkable advantages, such as low mining cost, high volatile matter content, high reactivity, and low content of sulfur, nitrogen and heavy metals [4,5]. Therefore, the scientific research on the efficient and clean utilization of the abundant lignite resources has been expected.

Coal–water mixture (CWM) often exists in the processing technologies including coal washing processes (flotation and jigging), coal-water slurry (CWS), and disposal of coal [6–11]. The interaction of lignite with water can result in the dissolution of humics, since lignite contains high content of organic humics. And that is why lignite can be used as a raw material of soil conditioners or organic fertilizers [12,13]. Coal–water mixture is commonly found in the flotation processing of lignite. And lignite flotation is harder to operate than high rank coal due to the more hydrophilic functional groups on lignite surface [14]. In addition, the preparation of coal–water slurry from low rank coal for combustion and gasification is a promising technology in lignite cleaning utilization [15–17]. Consequently, it is of great significant to make certain of the slurryability and dispersion stability of coal–water slurry. Notably, the surface properties and particle size distribution of lignite have been confirmed to have a remarkable influence on the slurryability and dispersion stability of coal–water slurry [18]. Some researchers have found that the oxygen-containing functional groups and moisture on lignite surface obviously affected the surface properties and subsequent flotation behavior, slurryability or burning properties in lignite flotation and lignite cleaning technology [19–24]. Li and Park et al. have noted that the hydrophobicity and slurryability of lignite could be evidently improved owing to the decrease of oxygen-containing functional groups after pyrolysis or torrefaction treatment [25,26].

Actually, the oxygen-containing functional groups are mainly born of humics in lignite, and the adsorbed-water in lignite is due to the

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binding site of humics. Humics is a kind of hydrophilic matter and possess lots of oxygen-containing functional groups such as carbonyl, carboxyl, quinonyl, phenolic hydroxyl and alcohol hydroxyl [27,28]. Once lignite is immersed into water, a mass of oxygen functional groups would be exposed to water. In our previous work of research group, we found that humics dissolution has pronounced impacts on the aqueous chemistry and dispersion properties of lignite–water slurry [29]. Interestingly, the dissolved humics could be further adsorbed on the lignite surface. Therefore, it is significant to study the adsorption behaviors of humics on the micro-sized lignite particles and the effects of humics adsorption on the properties of lignite–water slurry.

In order to investigate the influences of interactions between dissolved humics and lignite that might occur in the lignite flotation or the lignite cleaning technology, it is absolutely necessary to obtain more information about the effects of humics adsorption on the aqueous chemistry of micron-sized lignite particles. In this work, the adsorption behaviors of humics on the micron-sized lignite particles in the lignite–water slurry were studied by the batch adsorption experiments at the various humics concentration. The effects of humics adsorption on the particle sizes and surface properties of lignite were investigated using advanced analysis techniques including optical microscope, Fourier transform infrared spectroscopy (FTIR), Zeta potential test and contact angle analysis. The dispersion behavior of lignite–water slurry after lignite adsorbing humics were examined EDLVO calculation and settlement tests.

2. Experimental

2.1. Materials

Lignite used in this work was obtained from Yunnan province, China. The typical elemental composition, proximate analysis and humics content of lignite were determined respectively according to GB/T 476-2001, GB/T 212-2008 and GBT 11957-2001, and the results are summarized in Tables 1 and 2. Seen from Table 1, the oxygen content of lignite reaches to 26.00%, which indicates that lignite contains a large amount of organic matter. The moisture and free humics in lignite are up to 61.60% and 42.20%, respectively, as indicated in Table 2. The lignite was dried in a vacuum drying oven at 30 °C for 48 h, and then grinded by a high-energy planetary ball mill for 3 min. The lignite particles are smaller than 15 μm and approximately 50% of the particles are smaller than 2.7 μm.

Unless specifically noted, all chemicals used in this work were analytical reagents and purchased from Tianjin Kermel Reagent Technologies Co., Ltd., China. The humics was bought from Tianjin Zhiyuan Chemical Reagent Co. Ltd., China. Hydrochloric acid and sodium hydroxide were used to adjust solution pH.

2.2. Adsorption experiments

All the adsorption experiments were conducted using a batch equilibration approach at 25 °C. The 100 mL Erlenmeyer flasks containing lignite and humics solution were shaken for a certain time in a thermostatic rotary shaker operating at 150 rpm, and then the mixture was centrifuged for 5 min at 3500 rpm. The concentration of lignite was

Table 2
Kinetic parameters for adsorption of humics on the lignite.

C_{humics} (mg·L^{-1})	Pseudo first-order model			Pseudo second-order model			
	q_e	k_1	R^2	q_e	k_2	v_0	R^2
100	3.76	0.23	0.9795	3.78	0.29	4.08	0.9969
125	4.89	0.15	0.9251	4.93	0.11	2.67	0.9902
150	5.93	0.15	0.9256	6.56	0.03	1.16	0.9944
175	6.85	0.16	0.9704	7.14	0.04	1.91	0.9906
200	8.11	0.17	0.9954	8.57	0.04	2.79	0.9995

fixed at 4 g·L^{-1} and the solution pH was 7. The concentration of humics in the supernatant was determined by an ultraviolet and visible spectrophotometer (UV–Vis). The humics-adsorbed lignite was subsequently dried in the vacuum drying oven at 30 °C for 48 h and then stored in vacuum oven. The adsorption capacity q (mg·g^{-1}) of humics onto lignite was calculated by the following equation:

$$q = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where C_0 is the initial concentration of humics (mg·mL^{-1}), C_t is the humics concentration at t min (mg·mL^{-1}), V is the volume of humics solution (mL), and m is the weight of lignite (g).

The effect of humics concentration on adsorption was investigated through varying the initial concentration of humics from 100 to 200 mg·L^{-1}, since the amount of humics dissolved from lignite were up to 154.70 mg·L^{-1} under the condition of lignite concentration 4 g·L^{-1}, solution pH 12 and dissolving time 30 min at 30 °C. The adsorption kinetics were performed by collecting samples at definite intervals time in the range of 0–150 min. All the experiments were conducted in triplicate to get more accurate results and the average value was reported. Statistical analysis was conducted with Origin pro 8.5 software.

2.3. Characterizations

The concentration of humics was determined by the photometric method. The photometric measurements were performed at 465 nm with a model TU-1901 double-beam ultraviolet and visible spectrophotometer (UV–Vis, PERSEE, China) with deionized water as reference. The standard curve of humics was tested as: $y = 0.0097x - 0.0034$, and its regression coefficient was 0.9998.

The size distribution of lignite particles was obtained from the optical microscope equipped with statistical analysis software (ZEISS Axio Scope. A1, Germany). And D_{50} was defined as the apparent particle size relevant to 50% of cumulative distribution. The main functional groups on lignite surface were analyzed using a Nicolet Nexus 670 Fourier transform infrared spectrometer (Thermo Electron Corporation, America). The KBr pellet technique was used, and approximately 1 mg sample was thoroughly mixed with 100 mg of spectroscopic grade KBr and pressed into pellets for recording the spectra.

Zeta potentials of lignite particles were measured with a JS94H2 model microscopic electrophoresis apparatus (Powereach.com, China). A suspension concentration of 0.1 g·L^{-1} for lignite was used. Each test was repeated five times and the average value was reported. The static contact angles of dried lignite were measured on a JC2000D model

Table 1
Proximate analysis, elemental composition and humics content of lignite.

Proximate analysis				Elemental analysis (%daf)					Humics content (%)	
Total moisture (%ar)	Ash (%d)	Volatile matter (%daf)	Fixed carbon (%daf)	C	H	O_{diff}	N	S	Total humics	Free humics
61.60	19.91	58.75	41.25	67.12	3.54	26.00	1.56	1.78	45.79	42.20

Note: free humics refers to the soluble organic fractions; Total humics refers to the soluble and the insoluble organic fractions associated with calcium and magnesium ions.