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Exploration on the mechanism of enhancing low-rank coal flotation with cationic surfactant in the presence of oily collector

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ABSTRACT

It is difficult to yield a high combustible matter recovery in the flotation of low rank coal with common oily collectors. This study focuses on the enhancement in flotation performance of low rank coal by combining diesel oil with didodecyldimethylammonium bromide (DDAB), as well as its corresponding intensifying mechanism. The adsorption of DDAB and/or diesel oil on the pure coal and quartz surfaces was investigated based on the zeta potential and FTIR analyses, while the floatability of the coal and quartz samples before and after pretreatment was evaluated by the attachment time and flotation results. The results indicated that DDAB had great effects on the zeta potentials of coal and quartz, and the isoelectric points of these two samples were observed at the DDAB concentrations of about 0.007 and 0.006 g/L, respectively. Additionally, according to the FTIR analyses, the physical and chemical adsorptions were proposed to interpret the adsorption of DDAB, and diesel oil and mixed diesel oil/DDAB on the coal surface, respectively. Meanwhile, the diesel oil's adsorption of on the coal surface was enhanced by the conditioning process with the mixed DDAB/diesel oil. In contrast, diesel oil adsorption on the quartz was very little in quantity. As a result, a great difference in surface hydrophobicity between the coal and the quartz was attained, and an excellent flotation performance was obtained by using the mixed DDAB/diesel oil. However, a too low surface tension of flotation pulp caused by the excessive DDAB seems to be unfavorable to the flotation of coal samples. In this case, water with less surface tension was readier to spread on the coal surface than diesel oil, thereby making the coal hydrophilic and meanwhile hindering the diesel oil's spreading on its surface.

1. Introduction

Coal is greatly important to human beings owing to its huge reserves and role as an energy fuel [1]. Over the past decades, coal as the major primary energy fuel has supported China's rapid economic and social developments [2]. With the depletion of high-quality coal resources, the low-medium rank/oxidized coals has been reconsidered for exploitation and utilization to guarantee China's sustainable development of the coal industry, which involves lignite, long-flame coal, weakly caking coal, non-caking coal, and oxidized coal [3]. However, the fine coal has been ever-increasing with the deterioration of geological conditions and the continuous improvement in the mechanization of mining. Moreover, the combustion of low-quality coals poses a great threat to the survival and development of humans due to the environmental pollution resulted from its ash and sulfur content. As a result, increased attention has been paid to the efficient and clean utilization of low-quality coals in the field of mineral processing.

In comparison to gravity separation, froth flotation, an efficient physicochemical technique, is widely applicable for the beneficiation of coals less than 0.5 mm in particle size [4–7]. For high-coalification-degreed coals with natural surface hydrophobicity, they respond well to the conventional froth flotation processes, thereby easily obtaining a high yield or combustible matter recovery. However, the low-medium rank/oxidized coal is always rich in oxygen that exists as oxygenated functional groups, thereby giving rise to a hydrophilic surface [7–11]. What's more, the coal with low degree of metamorphism is susceptible to oxidation on the surface when exposed in the air, resulting in the formation of oxygenated functional groups and hence increasing its hydrophilic sites [12–15]. These attributes will make the common oily collector, diesel oil and kerosene, difficult to spread on the coal surface, thus leading to its poor flotation performance [7,11,13,16]. Furthermore, a stable wetting film can form on the surface of low rank coal due to the hydrogen bonds between these hydrophilic groups and polar water molecules, which further increases its hydrophilicity [13,17]. On

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the other hand, the low rank coal is characterized by easily breaking into fine particles, which results in a larger specific surface area. Consequently, it is difficult for low-medium rank coal to float using common oily collectors, and the dosage of oily collector is usually maintained at a high level range to achieve a satisfactory yield [11,14,17–19].

In order to intensify the flotation of low-medium rank/oxidized coal, one way is pretreatment for coals. In this process, the floatability of low-medium rank/oxidized coal could be improved by grinding, which removed the oxidation layer and hence produce some fresh hydrophobic surfaces [20–22]. Similar research indicated that the flotation performance could be further enhanced by dry-grinding with collectors, which was attributed to the increase in coal hydrophobicity caused by the adsorption of collectors on its surfaces and pores before the conditioning processes in flotation cell [23,24]. Besides, it was reported that the thin clay layer and oxidized layer could be also removed from the oxidized coal surface by the ultrasound treatment [25–28], thereby resulting in the increase of flotation kinetics and combustible matter recoveries [29]. Apart from this effect, the ultrasound treatment was also used for the conditioning process of flotation pulp [4,30], and improving the distribution of reagents in the flotation pulp [30,31]. Reinforcing prior arguments, there are many research studies regarding enhancing the floatability of coals by the treatments of thermal, and microwave heating [7,32–34], and particle surface modification [8,18,35].

Another way is the use of surfactants, modifiers and special collectors in flotation for coals, especially for low-medium rank coals. It was reported [8,13,35–37] that the collectors containing oxygenated functional groups could be used to improve the flotation of low rank/oxidized coals by conquering the negative effect of oxygen-containing functional groups on the coal surface, such as alcohol hydroxyl, phenolic hydroxyl, carbonyl and the others. This behavior could be attributed to the interaction (i.e., hydrogen bonds) between the polar heads in the collectors and oxidized sites on the coal surface, which was stronger than that between nonpolar chain (benzene ring and aliphatic chain) and the carbonaceous sites on the coal surface [13,18,36]. A similar research [38] indicated that the mixed diesel oil/2-ethylhexanol could greatly enhance the performance of both conventional and oily-bubble flotation of the low rank coal. Apart from the above-mentioned reasons, 2-ethylhexanol as an emulsifier was believed to promote the dispersion of diesel oil by adsorbing at the oil/water interface, and meanwhile to reduce the energy required by the oily collector spreading on the coal surface owing to 2-ethylhexanol's adsorption at the coal/oil interface [13,37]. Moreover, the cationic collectors or surfactants also played an important role in the flotation of low rank/oxidized coals [11,13,16,39,40]. In the flotation pulp, the surfaces of low rank/oxidized coals and air bubble are usually negatively charged, which results in an electrostatic repulsion between particles and bubbles. Whereas the cationic surfactants could alter the zeta potential of these coals, thereby enhancing the adsorption of common oily collectors thus improving their surface hydrophobicity [13,16,39–41]. However, it should be noted that these cationic surfactants also had an unexpected effect on the zeta potential of gangue minerals, which is detrimental to attain a good selectivity for coal particles in flotation [42,43].

In this investigation, a cationic surfactant, didodecyldimethylammonium bromide (DDAB), was used for the expected enhancement in the flotation performance of coal samples in the presence of diesel oil (oily collector). To explore the effect of DDAB on the floatability of coal and gangue mineral more precisely, the pure coal (ultra-low-ash coal) and pure quartz were used as the experimental samples. The adsorption of diesel oil and/or DDAB on the coal and quartz samples was analyzed by the zeta potential and FTIR analyses, while the hydrophobicity of these two samples before and after conditioning process was evaluated by the attachment time analysis and flotation results.

Table 1
Proximate and ultimate analyses of coal sample [38].

Proximate analysis, %				Ultimate analysis, %				
M_{ad}	A_{ad}	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}
4.65	16.45	36.27	63.73	70.70	3.95	22.07	0.95	2.33

Table 2
Particle size distribution of coal samples.

Size, mm	Yield, %	Ash, %	Oversize		Undersize	
			Yield,%	Ash,%	Yield,%	Ash,%
0.50–0.25	18.16	17.04	18.16	17.04	100.00	16.97
0.25–0.125	15.19	11.45	33.36	14.49	81.84	16.95
0.125–0.074	24.70	8.27	58.05	11.85	66.64	18.20
0.074–0.045	11.27	11.29	69.33	11.75	41.95	24.05
−0.045	30.67	28.74	100.00	16.97	30.67	28.74
Total	100.00	16.97				

2. Experimental

2.1. Materials

The coal sample less than 0.5 mm in particle size was provided by the Meizhiyou Coal Preparation Plant in Shaanxi Province of China, which is a long-flame coal with a volatile matter content of 36.27%. The detailed results of proximate and ultimate analyses for the coal samples are listed in Table 1, where M_{ad}, A_{ad}, V_{daf} and FC_{daf} represent the moisture content, ash content, volatile matter content, and fixed carbon content, respectively. Whereas C_{daf}, H_{daf}, O_{daf}, N_{daf}, and S_{daf} respectively refer to the content of carbon, hydrogen, oxygen, nitrogen, and sulfur elements. In addition, the particle size distribution of coal samples is given in Table 2. It was found that the yield of coal samples with particle size fractions of 0.074–0.125 mm (the optimal size range for fine-coal flotation) was 24.70%, with the lowest ash content of 8.27%. However, the coal samples of −0.045 mm in particle size (of −0.045 mm) accounted for 30.67% and its ash content was the highest (28.74%), which is unfavorable to obtain the efficient separation of fine clean coal from ultrafine slime in flotation. Furthermore, the identification for the mineral phases present in the raw coal was conducted with an X-ray Diffraction analyzer (Bruker, Germany) equipped with a Cu Kα source. For a typical XRD analysis, the powder samples were first ground to −0.045 mm, and the software Jade 6 was employed for the data analysis. Fig. 1a shows the results of XRD analyses for the raw coal, and it suggested that the main mineral matter in the coal sample was quartz, followed by calcite, with fewer amounts of kaolinite and pyrite. As is known that coal and gangue minerals, especially quartz, are negatively charged in the flotation pulp. Therefore, it was envisaged that the quartz will be of a great influence on the coal flotation in the presence of the cationic surfactant DDAB ($C_{26}H_{56}BrN$, purchased from Shanghai Macklin Biochemical Co., Ltd.). To explore the effect of DDAB on the coal flotation more precisely, the pure coal and quartz samples were used as experimental materials in this study. The pure coal samples with an ash content of 2.88% were collected by a float-and-sink experiment in which the organic heavy liquid with a density of 1.4 g/cm^3 was prepared by mixing benzene and carbon tetrachloride, and the pure quartz samples were provided by Damao Chemical Reagent Factory in Tianjin, China. The results of XRD analyses for both samples are presented in Fig. 1b and c. In addition, the pure coal and quartz samples were ground to 0.045 mm in diameter for the FTIR and zeta potential measurements, while the coal and quartz samples with the size fraction of 0.074–0.125 mm were collected by screening for the attachment time measurements.

Furthermore, to eliminate the influence of other cations on the experiments, the deionized water was used to prepare the DDAB aqueous