

Exploring the effect of sodium hexametaphosphate in coal slime flotation

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Abstract: In this paper, the influence of sodium hexametaphosphate (SHMP) in coal slime flotation was studied, and the interaction between SHMP and coal slime flotation particles was revealed through XRD test, contact angle measurement, zeta potential test, scanning electron microscopy analysis, XPS analysis, and DLVO theoretical calculation. The experimental results show that when the dosage of SHMP is 1500 g/t, the recovery rate of clean coal combustibles increases by 9.61 %. SHMP reduces the hydrophobicity of clay minerals (kaolinite) in coal slime flotation and also enhances the dispersibility of coal slime particle. Scanning electron microscopy and energy dispersive analysis showed that SHMP reduced the number of clay particles (kaolinite) on the coal surface, thereby reducing the ash content of the clean coal. In this paper, SHMP is mainly used to modify the surface of kaolinite so as to reduce the hydrophobicity of the mineral, that is, to improve the recovery rate of clean coal combustibles in coal slime flotation.

Keywords: sodium hexametaphosphate, coal slime, flotation, DLVO

1. Introduction

Coal occupies an important position in global energy. Coal-rich, oil-poor, and gas-poor are the main descriptors of the status quo of the energy structure. The shortage of oil and gas resources leaves coal in a very important position (Egorov and Strizhak, 2017). Coal is the main fuel energy in China, and in order to meet the energy demand with about 39 % of electricity coming from the combustion of coal, coal consumption will increase in proportion to the increase in electricity consumption (Glushkov et al., 2018; Vershinina et al., 2018). The direct combustion of coal will cause environmental pollution problems, dust pollution, and the production of toxic and harmful gases, which greatly restrict the clean utilization of coal resources (Meng et al., 2021). In the process of mining, crushing, and separation, the surface of fine coal slime particles is in contact with air, and the surface oxidation of coal slime leads to a significant decrease in flotation efficiency (Chen et al., 2022). The main washing methods of fine coal slime include foam flotation, oil agglomeration, flocculation, and enhanced gravity separation (Sahinoglu, 2018). Flotation is the main method for the separation of fine-grained coal slime in the coal industry, and the difficulty of flotation separation mainly depends on the unique interface characteristics between coal and gangue minerals (Yu et al., 2017).

Froth flotation is a technology that separates particles based on their selective adhesion to air bubbles, and it is the most efficient method for sorting fine and ultrafine slimes (Yu et al., 2020; zhao et al., 2022). Coal and clay minerals are the main fine particles in high ash coal slime, and their efficient separation is one of the difficult problems to solve in the coal preparation industry (Li et al., 2019). Clay minerals are common gangue minerals in coal preparation which are associated with coal slime, and their complex surface and interface reactions are the main factors affecting coal slime separation (Bai et al., 2020). Clay minerals are extremely fine and have a significant impact on coal slime flotation (Wang

et al., 2015). In the process of coal slime flotation, fine clay minerals enter the foam layer with the liquid during flotation to contaminate the clean coal, and fine clay minerals will also increase the dosage of chemicals and the viscosity of pulp, resulting in the decrease of flotation efficiency (Forbes et al., 2014). The surface of clay minerals is naturally negatively charged, and the fine clay particles adhere to the coal particles through electrostatic action, thereby reducing the hydrophobicity of the surface of the coal particles (Liu et al., 2020; Ndlovu et al., 2013). Therefore, the existence of clay minerals in the process of coal slime flotation has become the bottleneck of clean utilization of coal today.

Many scholars have conducted relevant research on the deterioration of coal slime caused by the existence of clay minerals in slime. Dispersants (Liu and Peng, 2015), inhibitors (Zhao, 2014), etc. are added to the flotation system to eliminate the adverse effects of clay minerals in coal slime flotation. It can be seen in previous studies that sodium hexametaphosphate ($\text{NaPO}_3)_6$, SHMP) is widely used as an inhibitor or dispersant in mineral flotation, which has an impact on the zeta potential of gangue, increases the dispersion of coal slime, and improves the flotation selectivity (Li et al., 2020; Zhang et al., 2001). When SHMP is added to coal slime flotation, the influence of polyaluminium chloride on quartz entraining in fine coal slime flotation can be eliminated (Liang et al., 2019). SHMP can not only reduce the adsorption of anionic surfactants on the surface of kaolinite, but also improve the hydrophilicity of coal and inhibit its flotation (Wang et al., 2014; Choi et al., 1993). The researchers studied sodium hexametaphosphate (SHMP) and sodium silicate (SS) as dispersants to reduce the effect of kaolinite on the flotation of chalcopyrite in seawater through flotation experiments, and the results showed that there is kaolin in seawater. Both dispersants could restore chalcopyrite flotation (Ramirez et al., 2018). To mitigate the detrimental effects of clay minerals on mineral flotation, colloidal interactions were altered by adding inhibitors to generate electrostatic forces and/or steric repulsion.

In previous studies, researchers only studied the effect of SHMP addition on gangue mineral coating on coal surface, without XPS analysis, hydrolysis analysis and DLVO theoretical calculation analysis of SHMP, which has some shortcomings. In this paper, the effects of SHMP on the surface of coal and clay minerals (kaolinite) particles are studied. The surface contact angle, zeta potential, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy and X-ray energy spectroscopy (SEM/EDS) were investigated under the condition of adding a certain amount of SHMP. DLVO theoretical calculations were applied to reveal the effect of SHMP on interparticle interactions. Based on the above research, it can be further explained that the addition of sodium hexametaphosphate (SHMP) can improve the recovery rate of combustibles in coal slime flotation. At the same time, the research of this paper is expected to provide certain significant guidance for subsequent researchers.

2. Materials and methods

2.1. Materials

The raw coal samples used in this paper were collected from -0.125 mm grain slime after TBS (Teeter Bed Separator) separation in a coal preparation plant in Guizhou. It can be seen in Figure 1a that the main mineral components of the coal slime are quartz, pearl clay, kaolinite, and double kaolinite, among which pearl clay, kaolinite, and double kaolinite are clay minerals that are easy to sludge, resulting in large consumption of flotation reagents. They are easily mixed into the flotation clean coal, which increases the ash content of the clean coal. It can be seen in Table 1 that the ash content of coal slime is 39.75 %. The raw coal sample is separated with 1.30 g/cm³ of heavy liquid to obtain coal with lower ash content, and then the obtained low-ash coal is ground and used as the subsequent test coal. From Table 1 and Figure 1b, it can be concluded that the ash content of coal is 4.6 %, and gangue minerals can be effectively removed by heavy liquid separation, resulting in reduced interference to the experiment.

Table 1 Comprehensive table of industrial analysis of slime and coal

sample	Mad(%)	Aad(%)	Vad(%)	FCad(%)
slime	1.85	39.75	16.62	41.78
coal	0.08	4.6	24.74	70.58

ad=air drying basis; daf=dry ashless basis; M=moisture content; A=ash content; V=volatile matter content; FC=fixed carbon content

High-purity kaolinite (purity > 99 %) was purchased from Guangdong Southern Canton Chemical New Material CO., LTD, China. and was tested as the pure clay mineral in this study. Its XRD pattern is shown in Figure 1c. XRF is used to assist in the determination of the chemical composition of kaolinite. The analysis results of XRF are shown in Table 2. The analysis results of XRD and XRF show that the kaolinite sample contains a small amount of impurities which will not have a significant impact on the experiment, thus the purity is high.

The particle size distribution of coal and kaolinite was analyzed by a laser particle sizer (Malvern Mastersizer 2000). Before measuring the particle size, the samples were dispersed by ultrasonic treatment for 2 min, and the data measured by laser degree were plotted and analyzed to obtain the particle size distribution of coal and kaolinite, so as to obtain d_{90} coal and kaolinite respectively.

It can be seen in Figure 2 that d_{90} low-ash coal and kaolinite are smaller than 70.963 μm and 25.179 μm , respectively, and the average particle sizes of coal and kaolinite are 23.376 μm and 4.018 μm , respectively. Kerosene, sec-octanol, and sodium hexametaphosphate were used as collector, foaming agent, and conditioner, respectively, and distilled water was used in all experiments to investigate the effect of sodium hexametaphosphate (SHMP) on coal slime flotation.

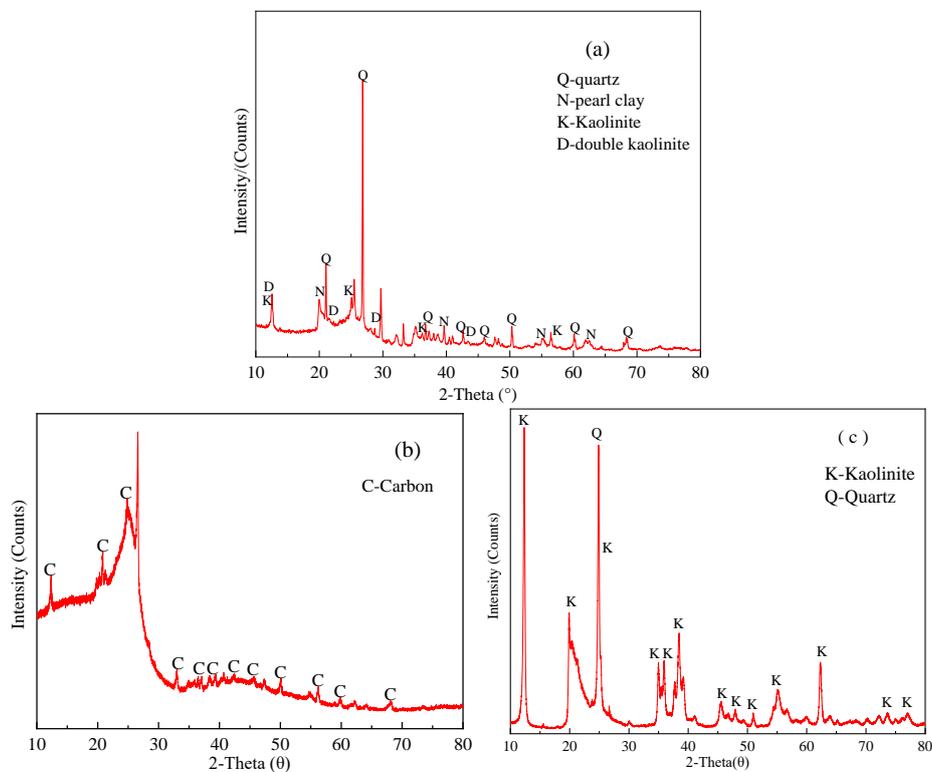


Fig. 1. XRD patterns of slime (a), low ash coal (b) and kaolinite (c)

Table 2 XRF analysis result table of kaolinite

Element	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	Loss on ignition
content/%	45.10	37.70	1.20	0.06	0.06	0.05	0.03	2.10	13.70

2.2. Flotation test

The variable experiments of SHMP in this paper were carried out using a 1.0 L flotation cell (XFG, Wuhan Exploration Machinery Factory, China). The flotation pulp concentration was 100 g/L, the impeller revolution was fixed at 1800 r/min, and the aeration rate was 0.06 m³/h. The amount of collector (kerosene) and foaming agent (sec-octanol) were fixed at 1000 g/t and 500 g/t, respectively. The dosages of SHMP were 0 g/t, 500 g/t, 1000 g/t, 1500 g/t, 2000 g/t, and 2500 g/t, respectively. All experiments were carried out at room temperature. The coal slime samples were pre-slurried for 1 min.

The addition times of SHMP, kerosene and sec-octanol were 3 min, 3 min, and 2 min, respectively; the aeration time was 30 s; and the foaming time was 3 min. Then the flotation product was filtered, dried and weighed, and the ash content of the flotation product and raw coal slime was measured using a muffle furnace. Each flotation test was repeated three times, and the average value was taken. The calculation formula of the recovery rate of clean coal combustibles is:

$$E_j = \frac{R_j(100 - A_j)}{100 - A_y}$$

In the formula: E_j is the recovery rate of clean coal combustibles; R_j is clean coal yield; A_j is clean coal ash content; A_y is feed ash content.

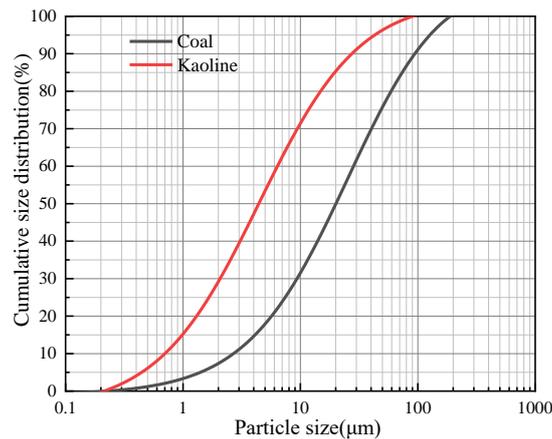


Fig. 2. Particle size distribution of coal and kaolinite

2.3. Contact angle measurement

The sample particle size of coal and kaolinite was ground to $<38 \mu\text{m}$, and three groups of particles were prepared for the test. One group of samples treated with water was used for blank measurements, and the other two groups of samples were treated with kerosene (1000 g/t) and SHMP and kerosene (1000 g/t and 1500 g/t), respectively. Firstly, six samples of 150 mg powder were weighed into the tablet model, and then the pressure of 60 MPa was applied on the tablet press for 3 min. Finally, the mold was released to obtain a small disc with a diameter of 1 cm. The contact angles of the six samples were measured with an automatic titration contact angle meter (HARKE-SPCAX3, Harko, Beijing). First, the deionized water drop was photographed on the surface of the small wafer, and then the contact angle was measured by image analysis. The average value was taken for three measurements in each test, and all measurements were performed at room temperature.

2.4. Zeta Potential Test

The zeta potential of coal and kaolinite was measured by Coulter Delsa440sx zeta analyzer. The suspension was prepared by weighing 40 mg of sample smaller than $38 \mu\text{m}$ and adding 40 mL 0.01 mol/L KCl liquor. The suspension was stirred with a magnetic stirrer for 2 min, and then the suspension was stirred with different amounts of SHMP for another 2 min. The suspension was then left for 1 min, and the upper suspension containing fine minerals was transferred to the electrophoresis tank using a syringe for zeta potential testing. Each test was repeated three times, and the average of the three tests was taken as the zeta potential data under this condition.

2.5. SEM analysis

For SEM/EDS analysis, the coal was first subjected to strict wet screening to obtain samples with a particle size of $74\text{--}125 \mu\text{m}$. Then 2 g coal and 0.2 g kaolinite were mixed and stirred in distilled water in a 40 mL beaker for 10 min. Finally, the suspension was passed through a sieve with a pore size of $74 \mu\text{m}$ and gently rinsed with distilled water, and the samples on the sieve were dried in an oven at $40 \text{ }^\circ\text{C}$. After plating the sample with a layer of gold, the kaolinite overlying the coal surface was observed using

SEM (ZEISS Gemini 300) at 2000 magnification. In addition, EDS was used to determine the elemental composition of the selected points, and the covering phenomenon of kaolinite on the coal surface was observed with or without a certain amount of SHMP.

2.6. XPS test

In order to better study the effect of SHMP on the surface of coal and kaolinite, X-ray photoelectron spectroscopy (XPS) was used to analyze the surface of coal and kaolinite after treatment. XPS peak fitting software was used to analyze the data. Physical displacements occurred during the testing of non-conductive samples, and the degree of displacement varied according to the conductivity of the sample (Wang et al., 2021). The binding energy can be corrected for the C-C bond of 284.8 eV in the C element.

2.7. DLVO theoretical calculation

The classical DLVO theory, which studies particle-particle interactions in flotation systems, can well explain colloidal particle interactions, including van der Waals interaction energy (V_W) and electrostatic interaction energy (V_E) (Gui et al., 2016; Liu et al., 2019). DLVO theory is also a powerful tool for conducting interfacial interaction studies. The total potential energy V_T of the interaction between particles is expressed by the following formula: $V_T = V_E + V_W$, where V_E is the electrostatic interaction energy, J ; and V_W is the van der Waals interaction energy, J .

(1) The electrostatic interaction energy is expressed as (1):

$$V_E = \frac{\pi \epsilon_0 \epsilon_a R_1 R_2}{R_1 + R_2} (\varphi_1^2 + \varphi_2^2) \left(\frac{2\varphi_1 \varphi_2}{\varphi_1^2 + \varphi_2^2} \ln \left[\frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)} \right] + \ln[1 - \exp(-2\kappa H)] \right) \quad (1)$$

where ϵ_0 is the dielectric constant of the solution (for water $\epsilon_0 = 80$) (Oats et al., 2010), ϵ_a is the dielectric constant of free space ($8.854 \times 10^{-12} \text{ C}^2\text{mJ}^{-1}$) (Yoon, 2000), and R_1 and R_2 are spherical. The radius of coal particles and kaolinite, and the values of R_1 and R_2 , are $23.376 \mu\text{m}$ and $4.018 \mu\text{m}$, respectively; φ_1 and φ_2 are the surface potentials of coal and kaolinite, respectively, in mV; H is the distance between spherical coal particles and kaolinite; and κ is the Debye length, and its calculation expression is (2) (Hu et al., 2019):

$$K^{-1} = \frac{0.304}{\sqrt{C_{\text{KCl}}}} \quad (2)$$

where C_{KCl} is the concentration of KCl solution, the concentration is $1 \times 10^{-4} \text{ mol/L}$, the value of K^{-1} is 30.4, the unit is nm

(2) The expression of van der Waals interaction energy is (3) (Xu and Yoon, 1989):

$$V_W = -\frac{A}{6H} \frac{R_1 R_2}{R_1 + R_2} \quad (3)$$

In the formula: A is the Hamaker constant, and its expression is (4):

$$A = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (4)$$

In the formula: subscripts 1, 2, and 3 represent coal, kaolinite and medium (water), respectively, where A_{11} , A_{22} and A_{33} are the hammaker constants of coal, kaolinite and water in vacuum, respectively, and their value is 6.1×10^{-20} , 9.7×10^{-20} , $3.7 \times 10^{-20} \text{ J}$ (Hao et al., 2018; Bremmell et al., 2005).

3. Results and discussion

3.1. Sludge flotation test results

In this experiment, the effect of SHMP addition on clean coal ash content, coal tailings ash content, clean coal yield, and clean coal combustible recovery rate was studied. It can be seen in Figure 3a that with the increase in SHMP dosage, the ash content of clean coal gradually decreases and tends to be flat, the ash content of tail coal gradually increases and then tends to be flat, and the change rate of ash content of clean coal is higher than that of tail coal ash. It can be seen in Figure 3b that with the increase in SHMP

dosage from 0 g/t to 1500 g/t, the yield and recovery of clean coal increased significantly, and when the dosage of SHMP gradually increased, the yield and recovery of clean coal gradually become flat.

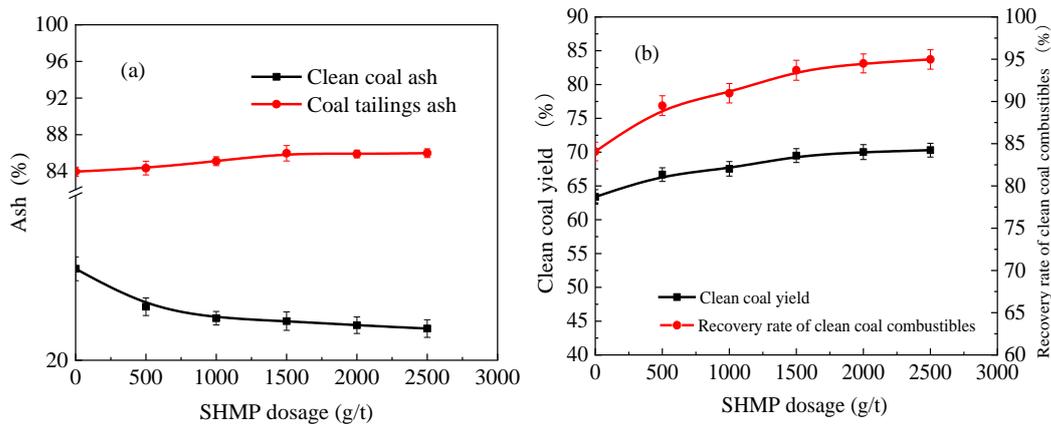


Fig. 3. (a) The effect of different SHMP dosage on clean coal and coal tailings ash content; (b) The effect of different SHMP dosage on clean coal yield and clean coal combustible recovery.

It can be seen in Figure 4a that when the dosage of SHMP is 0 g/t and 1500 g/t, the ash content of the clean coal drops to 22.22 % and 20.95 %, respectively. After flotation, the ash content of 0 g/t SHMP and 1500 g/t SHMP clean coals were both lower than 25.00 %, both of which can be used as coal for power generation. It can be seen in Figure 4b that the recovery rate of clean coal combustibles with 1500 g/t SHMP is increased by 9.61 % compared with 0 g/t SHMP. The test results show that the addition of SHMP has a significant effect on the quality of clean coal, and the adsorption of SHMP enhances the dispersion of clay minerals in the suspension, thus reducing their impact on coal slime flotation (Jiang et al., 2012). Therefore, adding a certain dosage of SHMP is beneficial for improving the recovery rate of clean coal combustibles, reducing the emission of tail coal, and improving the utilization rate of coal energy.

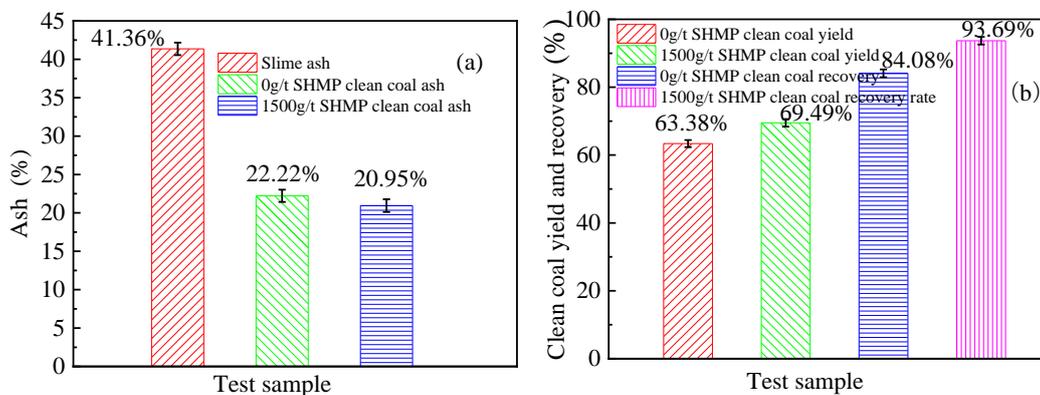


Fig. 4. (a) Slime ash, 0 g/t SHMP clean coal ash, and 1500 g/t SHMP clean coal ash; (b) 0 g/t SHMP and 1500 g/t SHMP clean coal yield, 0 g/t The recovery rate of SHMP and 1500 g/t SHMP clean coal combustibles.

3.2. Analysis of surface wettability of coal and kaolinite

Contact angle is an effective tool to study differences in wettability of mineral surfaces (Zhen et al., 2019; Yang et al., 2019). Figure 5 shows the contact angles of coal and kaolinite after water, kerosene, and kerosene plus SHMP treatments. The contact angle of coal is 74.60°, the contact angle of kerosene after quenching and tempering is 107.60°, and the contact angle of kerosene plus SHMP after quenching and tempering is 103.93°. The contact angle of kaolinite is 13.47°, the contact angle after kerosene conditioning is 19.13°, and the contact angle after kerosene plus SHMP conditioning is 12.40°. Compared with kerosene plus SHMP, the contact angles of coal and kaolinite decreased by 3.67° and 6.73° respectively after adding kerosene, indicating that SHMP has a great influence on the adsorption of

kerosene on the surface of kaolinite. Therefore, adding a certain dosage of SHMP can reduce the adsorption of kerosene on the surface of kaolinite, thereby saving chemicals and improving the quality of clean coal.

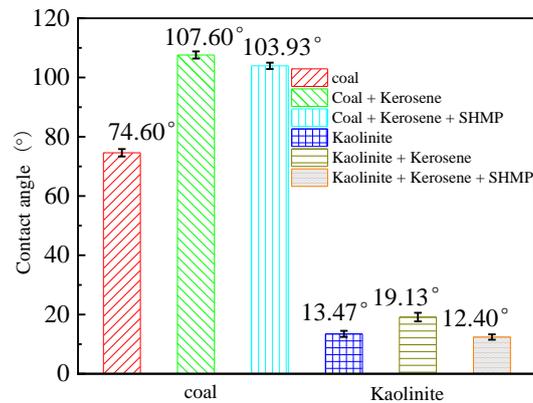


Fig. 5. Contact angle size diagram of coal and kaolinite after water, kerosene, and kerosene plus SHMP mixture

3.3. Zeta potential analysis of coal and kaolinite

Zeta potential is an important means to characterize the electrical properties of mineral surfaces, and it plays a significant role in studying the attachment or adsorption of mineral particles on the surface (Zhao et al., 2019). The electrostatic force makes the mineral particles attract or repel each other, so the surface charge of the mineral plays a regulating role. The zeta potentials of coal and kaolinite were measured under different dosages of SHMP, and their electrostatic force changes were studied. It can be seen in Figure 6 that with the increase in SHMP dosage, the zeta potential of coal first decreased and then increased, reaching a minimum value at 1500 g/t. With the increase in SHMP dosage, the zeta potential of kaolinite also decreased first and then increased. When the amount of SHMP is 1500 g/t, the zeta potential of coal is similar to that of kaolinite, and the electrostatic repulsion between coal and kaolinite is at its maximum. Therefore, under this condition, kaolinite on the surface of slime can be effectively removed, and the recovery rate of combustibles of clean coal reaches the maximum, which is consistent with the study in Figure 4b.

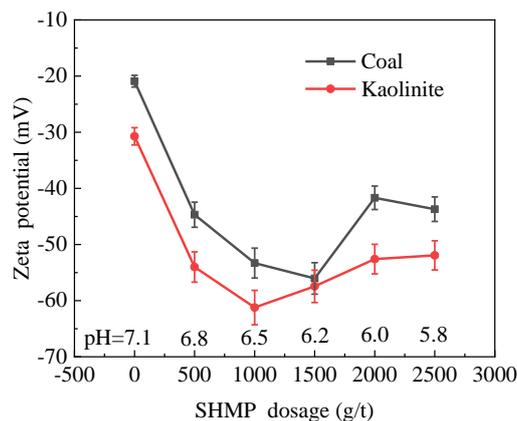


Fig. 6. The effect of different SHMP dosage on the zeta potential of coal and kaolinite

From the results of the zeta potential test, it can be seen that SHMP is adsorbed on the surface of coal and kaolinite. With the increase in SHMP dosage, the surface potential of coal and kaolinite gradually becomes negative. Figure 7 shows the hydrolysis distribution of SHMP with pH changes. It can be seen in Figure 7 that when the amount of SHMP increases from 0 g/t to 2500 g/t, the pH value of the solution is between 5.8 and 7.1. When it is 6.2, the main ion species of SHMP are H_2PO_4^- followed by HPO_4^{2-} and H_3PO_4 , and the H_2PO_4^- dissociated from SHMP can be adsorbed on the surface of the sample through hydrogen bonds. It can be seen in Figures 6 and 7 that the anions dissociated from SHMP can be

adsorbed not only on the surface of coal, but also on the surface of kaolinite. From the change trend of zeta in Figure 6, it can be seen that the anion of SHMP has the largest adsorption capacity on the kaolinite surface.

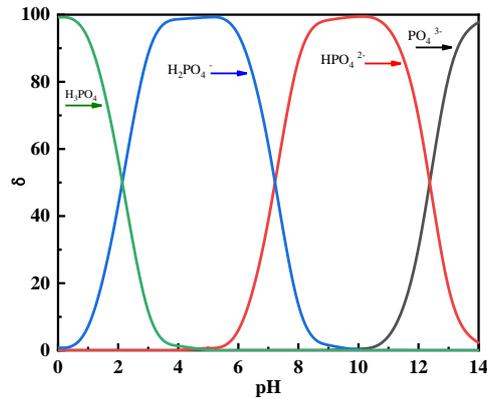


Fig 7. Hydrolysis profile of SHMP as a function of pH

3.4. SEM analysis

SEM/SED analysis was performed to observe the coverage of kaolinite on the surface of coal at the dosages of 0 g/t and 1500 g/t SHMP. Figure 8a shows that a large amount of hydrophilic kaolinite covers the surface of the coal, which reduces the hydrophobicity of the coal surface. Some small kaolinite particles gather together, and some cover the coal surface alone. The main elements of these fine muds analyzed by EDS are C, O, Al, S, etc., while the main elements on the coal surface are C and O, and the main elements in Figure 8b are C and O. These results show that when the dosage of SHMP is 1500 g/t, the coal surface is mainly low-ash particles, and the addition of SHMP can effectively remove high-ash particles.

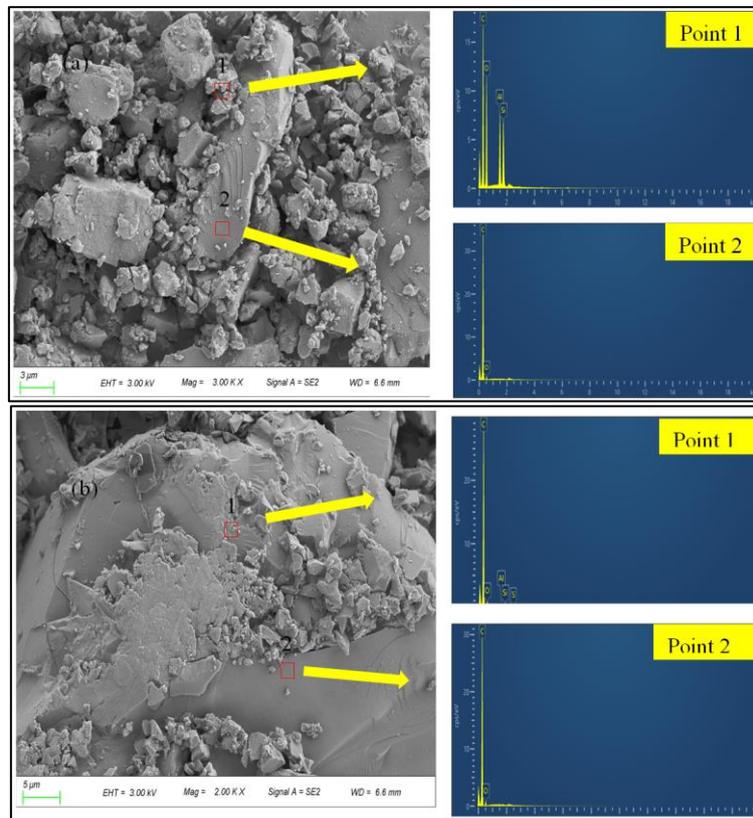


Fig. 8. (a) shows the coverage of kaolinite on the coal surface at the dosage of 0 g/t of SHMP; (b) shows the coverage of kaolinite on the coal surface at the dosage of 1500 g/t of SHMP

3.5. XPS test

Figure 9a-f shows the narrow C1s energy spectra of coal and kaolinite particles before and after the action of different agents. XPS peak is used to fit the C1s peaks, and the peaks with binding energies of about 284.6 eV, 285.4 eV, 286.6 eV and 289.1 eV correspond to C-C/C-H, C-O, C=O, and COOH (Fen-Rong, et al., 2011; Wang et al., 2013).

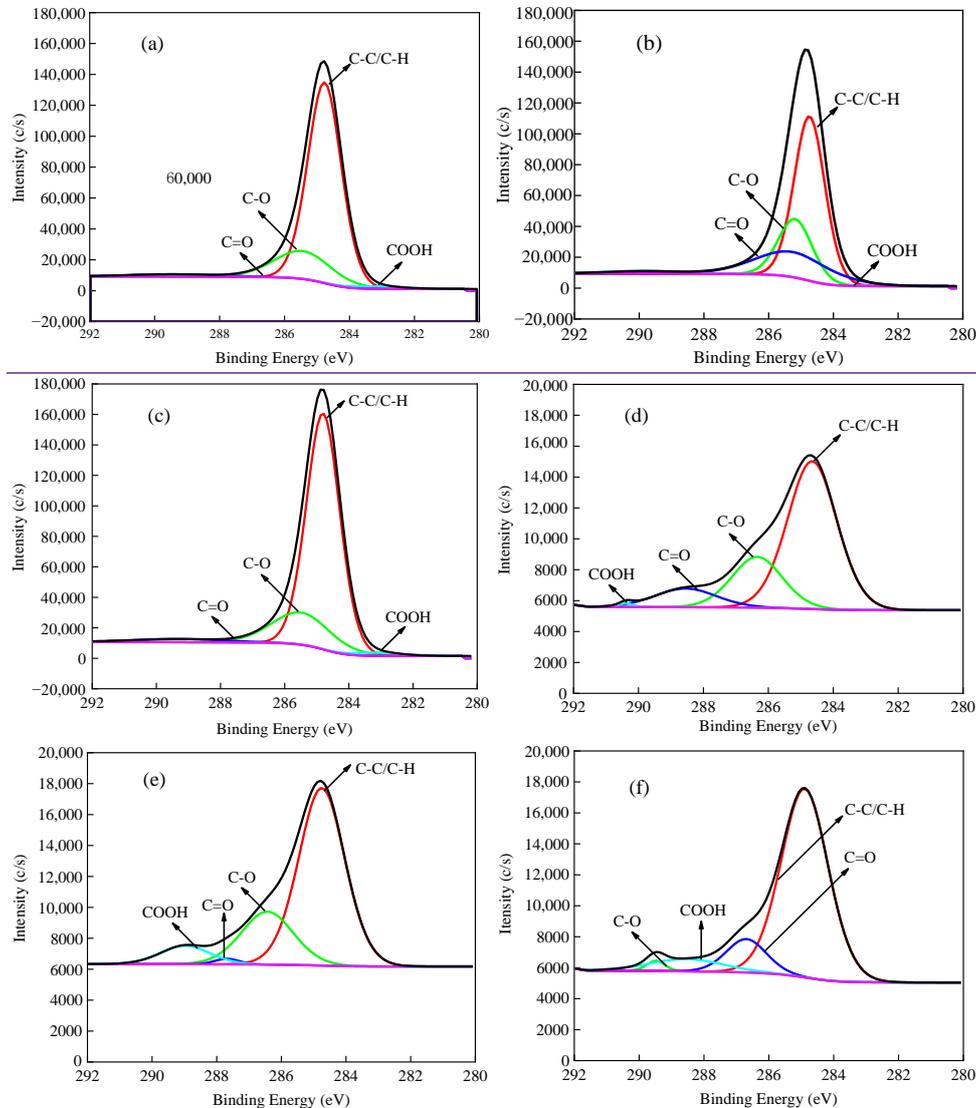


Fig. 9. (a) Fitting result of coal C1s peak; (b) Fitting result of coal+kerosene C1s peak; (c) Fitting result of coal+kerosene+SHMP C1s peak; (d) Fitting result of kaolinite C1s peak; (e) fitting result of kaolinite+kerosene C1s peak; (f) fitting result of kaolinite+kerosene+SHMP C1s peak

The relative contents of the four components were calculated according to the fitted peak areas in Figure 9a-f. The calculation results are shown in Table 3. It can be seen in Table 3 that when kerosene is added, the C-C/C-H group content of coal increases from 77.49 % to 94.04 %, an increase of 16.55 %; and the C-C/C-H group content of kaolinite increases from 65.94 % to 79.29 %, an increase of 13.35 %; while C-O, C=O, and COOH gradually decrease. When kerosene + SHMP is added, the C-C/C-H group content of coal decreases from 94.04 % to 85.16 %, decreasing by 8.88 %; the C-C/C-H group content of kaolinite decreases from 79.29 % to 66.63 %, a reduction of 12.66 %; and the contents of C-O, C=O and COOH groups increased compared with kerosene. Hydrocarbon chains and aromatic cycloalkanes are both hydrophobic, while oxygen-containing functional groups are hydrophilic (Niu et al., 2017). The adsorption of kerosene on the surface of coal and kaolinite promoted the exposure of C-C/C-H to the mineral surface and enhanced the surface hydrophobicity of mineral particles. The addition of SHMP

weakened the adsorption of kerosene on coal and kaolinite, and the decrease of C-C/C-H content on kaolinite surface was greater than that on the coal surface. In conclusion, the addition of SHMP reduces the adsorption of kaolinite to kerosene, that is, the hydrophobicity of kaolinite decreases. SHMP not only reduces the reagent consumption, but also improves the quality of clean coal in coal slime flotation.

Table 3. The relative content of the fitted front area of each functional group

Test name	C-C/C-H (%)	C-O (%)	C=O (%)	COOH (%)
Coal	77.49	18.46	2.59	1.46
Coal + Kerosene	94.04	3.22	1.42	1.31
Coal + Kerosene + SHMP	85.16	10.46	2.86	1.51
Kaolinite	65.94	23.22	10.38	0.45
Kaolinite + Kerosene	79.29	12.94	1.13	6.64
Kaolinite + Kerosene + SHMP	66.63	13.62	11.84	7.91

3.6. Calculation of interaction energy between coal and kaolinite

DLVO theory was used to reveal the role of SHMP in separating coal and kaolinite in flotation. Figure 10 is presented as a function of separation distance for the interaction energy of coal and kaolinite at 0 g/t and 1500 g/t SHMP. It can be seen in Figure 10 that the van der Waals interaction energy (V_W) is negative and independent of the addition of SHMP. The electrostatic interaction energy (V_E) is positive. After adding SHMP, V_{E2} is greater than V_{E1} , indicating that the repulsive force between coal and kaolinite particles is stronger after adding SHMP. It can be seen in Figure 10 that when 0 g/t SHMP is added, the total interaction energy V_{T1} between coal and kaolinite is negative, and when 1500 g/t SHMP is added, the total interaction energy V_{T2} between coal and kaolinite is positive. With the addition of 0 g/t SHMP, the mutual attraction between coal and kaolinite particles occurred. In comparison, with the addition of 1500 g/t SHMP, the total interaction energy is positive and larger, indicating that the particles are more dispersed (Tang et al., 2016). In the flotation test, when the amount of SHMP increased from 0 g/t to 1500 g/t, the inhibitor hindered the adsorption of kerosene on the surface of kaolinite, resulting in a decrease in the hydrophobicity of kaolinite. At the same time, the addition of SHMP increased the interaction and enhanced the dispersion, so that the recovery rate of combustibles of clean coal increased by 9.61 %. Therefore, the addition of SHMP in coal slime flotation can improve the recovery rate of combustibles of clean coal. In the flotation test, when the amount of SHMP increased from 0 g/t to 1500 g/t, the inhibitor hindered the adsorption of kerosene on the surface of kaolinite, resulting in a decrease in the hydrophobicity of kaolinite. At the same time, the addition of SHMP increased the interaction and enhanced the dispersion, thus increasing the recovery of the combustion body of clean coal by 9.61 %. Therefore, the addition of SHMP in slime flotation can improve the combustible body recovery of clean coal.

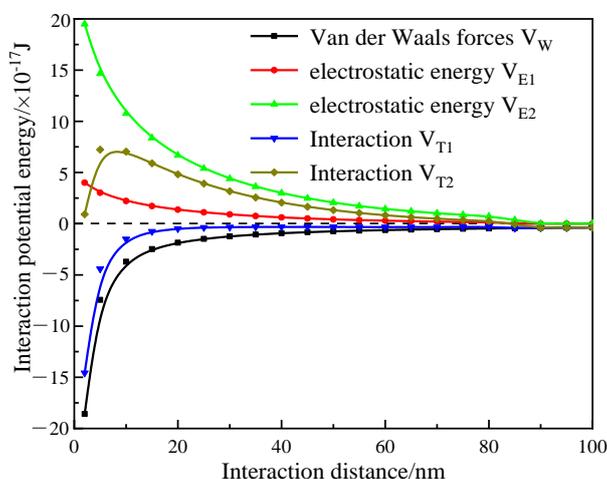


Fig. 10. Interaction energy of coal and kaolinite

4. Conclusion

The addition of SHMP improved the recovery rate of combustibles in coal slime flotation. The effect of SHMP on the separation of coal and minerals was calculated using contact angle measurement, XPS analysis, zeta potential measurement, scanning electron microscope analysis, XPS analysis, and DLVO theory. The results showed that:

1. SHMP has a great influence on the adsorption of kerosene on the surface of kaolinite. SHMP is adsorbed on the surface of kaolinite, which hinders the adsorption of kerosene on the surface of kaolinite and makes kaolinite more hydrophilic;

2. When the dosage of SHMP increased to 1500 g/t, the recovery rate of clean coal combustibles increased by 9.61 %. SHMP can inhibit the hydrophobicity of the kaolinite surface after kerosene modification, and SHMP also enhances the dispersion of slime particles. When the dosage of SHMP is 1500 g/t, the zeta potential of coal and kaolinite is similar and the absolute value is larger, indicating that the electrostatic repulsion between coal and kaolinite particles is larger;

3. Through scanning electron microscope and energy spectrum analysis, it can be seen that the addition of SHMP reduced the amount of clay minerals on the coal surface and reduced the ash content of clean coal. The addition of SHMP increased the total interaction energy between coal and minerals, indicating that SHMP enhanced particle dispersion in slime flotation.

Acknowledgments

The authors acknowledge financial supports from the Cultivation project of Guizhou University (No.[2020]13) and National Natural Science Foundation of China (51864010).

References

- EGOROV, R.I., STRIZHAK, P.A. *The light-induced gasification of waste-derived fuel*. Fuel 2017, 197, 28–30.
- GLUSHKOV, D., PAUSHKINA, K., SHABARDIN, D., STRIZHAK, P. *Environmental aspects of converting municipal solid waste into energy as part of composite fuels*. J. Clean. Prod. 2018, 201, 1029–1042.
- VERSHININA, K.Y., LAPIN, D.A., LYRSCHIKOV, S.Y., SHEVYREV, S.A. *Ignition of coal-water fuels made of coal processing wastes and different oils*. Appl. Therm. Eng. 2018, 128, 235–243.
- MENG, Z., YANG, Z., YIN, Z., LI, Y., JU, X., YAO, Y. *Interaction between dispersant and coal slime added in semi-coke water slurry: An experimental and DFT study*. Appl. Surf. Sci. 2021, 540, 148327.
- CHEN, J., SUN, Y., LIU, L., GE, W., SHEN, L., MIN, F. *Interactions between Mg²⁺-doped kaolinite and coal: Insights from DFT calculation and flotation*. Appl. Surf. Sci. 2022, 600, 154071.
- SAHINOGLU, E. *Cleaning of high pyritic sulfur fine coal via flotation*. Adv. Powder Technol. 2018, 29, 1703–1712.
- YU, Y., CHENG, G., MA, L., HUANG, G., WU, L., XU, H. *Effect of agitation on the interaction of coal and kaolinite in flotation*. Powder Technol. 2017, 313, 122–128.
- YU, Y., LI, A., XU, Z., ZHOU, A., LI, Z., ZHANG, N., QU, J., ZHU, X., LIU, Q. *New insights into the slime coating caused by montmorillonite in the flotation of coal*. J. Clean. Prod. 2020, 242, 118540.
- ZHAO, B., HU, S., ZHAO, X., ZHOU, B., LI, J., HUANG, W., CHEN, G., WU, C., LIU, K. *The application of machine learning models based on particles characteristics during coal slime flotation*. Adv. Powder Technol. 2022, 33, 103363.
- LI, M., XIA, Y., ZHANG, Y., DING, S., RONG, G., CAO, Y., XING, Y., GUI, X. *Mechanism of shale oil as an effective collector for oxidized coal flotation: From bubble-particle attachment and detachment point of view*. Fuel 2019, 255, 115885.
- BAI, H., LIU, Y., ZHAO, Y., CHEN, T., LI, H., CHEN, L., SONG, S. *Regulation of coal flotation by the cations in the presence of clay*. Fuel 2020, 271, 117590.
- WANG, L., PENG, Y., RUNGE, K., BRADSHAW, D. *A review of entrainment: Mechanisms, contributing factors and modelling in flotation*. Miner. Eng. 2015, 70, 77–91.
- FORBES, E., DAVEY, K.J., SMITH, L. *Decoupling rheology and slime coatings effect on the natural flotability of chalcopyrite in a clay-rich flotation pulp*. Miner. Eng. 2014, 56, 136–144.
- LIU, J., EJTEMAEI, M., NGUYEN, A.V., WEN, S., ZENG, Y. *Surface chemistry of Pb-activated sphalerite*. Miner. Eng. 2020, 145, 106058.
- NDLOVU, B., FARROKHPAY, S., BRADSHAW, D. *The effect of phyllosilicate minerals on mineral processing industry*. Int. J. Miner. Processing 2013, 125, 149–156.

- LIU, D., PENG, Y. *Understanding different roles of lignosulfonate in dispersing clay minerals in coal flotation using deionised water and saline water.* Fuel 2015, 142, 235–242.
- ZHAO, B. *Experimental study on ash reduction by inhibitor during flotation.* Clean Coal Technol. 2014, 20, 36–38.
- LI, Y., XIA, W., PAN, L., TIAN, F., PENG, Y., XIE, G., LI, Y. *Flotation of low-rank coal using sodium oleate and sodium hexametaphosphate.* J. Clean. Prod. 2020, 261, 121216.
- ZHANG, G.F., FENG, Q.M., LU, Y.P., LIU, G.Y., OU, L.M. *Effect of sodium hexametaphosphate on flotation of bauxite.* J. Cent. South Univ. Technol. (Nat. Sci.) 2001, 32, 127–130.
- LIANG, L., TAN, J., LI, B., XIE, G. *Reducing quartz entrainment in fine coal flotation by polyaluminum chloride.* Fuel 2019, 235, 150–157.
- WANG, L.Y., QIANG, M.L., XIAN, Y.Y. *Application and Mechanism Study of Sodium Hexametaphosphate in Coal Flotation.* Coal Technology, 2014.
- CHOI, I.K., WEN, W.W., SMITH, R.W. *The effect of a long chain phosphate on the adsorption of collectors on kaolinite.* Miner. Eng. 1993, 6, 1191–1197.
- RAMIREZ, A., ROJAS, A., GUTIERREZ, L., LASKOWSKI, J.S. *Sodium hexametaphosphate and sodium silicate as dispersants to reduce the negative effect of kaolinite on the flotation of chalcopyrite in seawater.* Miner. Eng. 2018, 125, 10–14.
- WANG, Y., LI, Y., XIA, W., PENG, Y., XIE, G. *Adsorption of sodium oleate on coal surface with different oxidation degrees and its effect on flotation.* Colloids Surf. A: Physicochem. Eng. Asp. 2021, 611, 125801.
- GUI, X., XING, Y., RONG, G., CAO, Y., LIU, J. *Interaction forces between coal and kaolinite particles measured by atomic force microscopy.* Powder Technol. 2016, 301, 349–355.
- LIU, C., ZHANG, W., SONG, S., LI, H. *Effects of lizardite on pentlandite flotation at different pH: Implications for the role of particle-particle interaction.* Miner. Eng. 2019, 132, 8–13.
- OATS, W.J., OZDEMIR, O., NGUYEN, A.V. *Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation.* Miner. Eng. 2010, 23, 413–419.
- YOON, R.H. *The role of hydrodynamic and surface forces in bubble–particle interaction.* Int. J. Miner. Processing 2000, 58, 129–143.
- HU, P., LIANG, L., LI, B., XIA, W. *Heterocoagulation between coal and quartz particles studied by the mineral heterocoagulation quantifying system.* Miner. Eng. 2019, 138, 7–13.
- XU, Z., YOON, R. *The role of hydrophobia interactions in coagulation.* J. Colloid Interface Sci. 1989, 132, 532–541.
- HAO, H., LI, L., YUAN, Z., LIU, J. *pH-controlled dispersion of micro-fine siderite from hematite and quartz.* Powder Technol. 2018, 339, 710–716.
- BREMMELL, K.E., FORNASIERO, D., RALSTON, J. *Pentlandite–lizardite interactions and implications for their separation by flotation.* Colloids Surf. A: Physicochem. Eng. Asp. 2005, 252, 207–212.
- JIANG, S.Y., ZHANG, K., PEI, J.Y., LIU, J.T. *Inhibition mechanism and application of Sodium Hexametaphosphate to coal slime.* China Coal 2012, 38, 83–85.
- ZHEN, K., ZHANG, H., LI, C., LI, X. *Effect of oxidized diesel oil on the flotation response of the low-rank coal by plasma oxidation method.* Fuel 2019, 245, 13–20.
- YANG, L., ZHU, Z., LI, D., YAN, X., ZHANG, H. *Effects of particle size on the flotation behavior of coal fly ash.* Waste Manag. 2019, 85, 490–497.
- ZHAO, X., MENG, Q., YUAN, Z., ZHANG, Y., LI, L. *Effect of sodium silicate on the magnetic separation of ilmenite from titanite by magnetite selective coating.* Powder Technol. 2019, 344, 233–241.
- FEN-RONG, L., WEN, L., HUI-QING, G., BAO-QING, L., ZONG-QING, B., RUI-SHENG, H. *XPS study on the change of carbon-containing groups and sulfur transformation on coal surface.* J. Fuel Chem. Technol. 2011, 39, 81–84.
- WANG, B., PENG, Y., VINK, S. *Diagnosis of the Surface Chemistry Effects on Fine Coal Flotation Using Saline Water.* Energy Fuels 2013, 27, 4869–4874.
- NIU, C., XIA, W., XIE, G. *Effect of low-temperature pyrolysis on surface properties of sub-bituminous coal sample and its relationship to flotation response.* Fuel 2017, 208, 469–475.
- TANG, J.C., DUTTON, J.J., PIEC, I., GREEN, D., FISHER, E., WASHBOURNE, C.J., FRASER, W.D. *LC-MS/MS application for urine free pyridinoline and free deoxypyridinoline: Urine markers of collagen and bone degradation.* Clin. Mass Spectrom. 2016, 1, 11–18.