



Article Flotation Separation of Cassiterite from Calcite Using Low-Molecular-Weight Citrus Pectin as Depressant

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Abstract: This paper presents the development of an environmentally friendly, small molecular depressant citrus pectin for improving the recovery of cassiterite resources. Citrus pectin extracted from citrus peel was utilized as the depressant, and it demonstrated significant potential in separating calcite from cassiterite in micro-flotation tests. The molecular weight of the citrus pectin extracted in this paper decreased from 11,485,412 Da to 32,959 Da compared to commercial pectin, resulting in the depressant efficiency of the reagent. The results of a zeta potential and adsorption test indicated that citrus pectin had less and weaker adsorption on the cassiterite surface and could be replaced with NaOL. The chemical adsorption process of citrus pectin on the surface of calcite was determined through FTIR spectroscopy analysis. XPS analysis results indicated that the interaction between the carboxyl groups of citrus pectin and calcium atoms enables adsorption to occur. The AFM revealed that citrus pectin displayed a uniform and dense pattern of point-like adsorption on the surface of calcite. Micro-flotation experiments showed that cassiterite recovery of 80% can be obtained at a citrus pectin dosage of 10 mg/L. Citrus pectin has the advantages of being low-cost, highly selective, and environmentally suitable, making it a promising alternative to conventional reagents.

Keywords: cassiterite; calcite; citrus pectin; flotation; depressant

1. Introduction

Tin is one of the crucial strategic metal elements possessing strong anti-corrosion qualities and exceptional electrical conductivity. Tin products play an essential role in many modern fields, such as electronic soldering, gas sensors, nuclear power generation, and the aerospace industries [1–3]. Cassiterite (SnO₂) is a widespread primary tin mineral, usually in the form of small-diameter particles associated with other gangue minerals, especially calcite [4,5]. Flotation is a feasible and effective method to concentrate cassiterite [6]. The existing fatty acid-based trapping agents have low selectivity for calcite [7]. It is of great significance to study the preparation of highly selective, physico-chemically stable, and environmentally friendly depressants for cassiterite recovery [8].

At present, commonly used calcite depressants are divided into inorganic and organic depressants. Compared with inorganic depressants, organic depressants such as oxalic acid, citric acid, carboxymethyl cellulose, sodium phytate, starch, and calcium lignosulfonate [9] have stronger depressing properties on calcite [10–12]. However, some organic depressants suffer from drawbacks such as decreased selectivity, a limited pH separation range, a high consumption level, and damage to human health and the environment. [13]



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Hence, the development of an environmentally friendly selective depressant that effectively reduces calcite recovery during the flotation process is of significant practical importance in improving the separation of cassiterite and calcite.

Pectin is an α -1, 4-linked D-galacturonic acid-based (Figure 1) natural green polysaccharide obtained from plant cell walls [14]. Pectin is renewable [15], non-toxic [16], biodegradable, and compatible [15]. Based on these qualities, researchers have tried to apply pectin to flotation in recent years [17]. Jiao et al. [18] proposed the use of commercial pectin as a depressant, and the free carboxyl groups on its molecular chain could bind to the calcium ions on the calcite surface. Wang et al. [19] researched the flotation behavior of commercial pectin-treated galena and chalcopyrite in the presence and absence of copper sulfate. But commercial pectin has a large molecular weight and low solubility, which limits its depressant properties [20]. The molecular weight of pectin can be controlled in the laboratory acid extraction process, which addresses the challenge of implementing this type of polymer [21]. Citrus pectin is abundant, accessible, and inexpensive compared to pectin from other sources [22].



Figure 1. Pectin molecular formula.

Overall, citrus pectin is a non-toxic, low-cost, naturally degradable depressant. This paper attempts to investigate the potential of small molecule citrus pectin extracted from citrus peel as a depressant for cassiterite during flotation. The optimal citrus pectin dosage and depression mechanism on the surface of calcite are also researched. To examine the potential interaction mechanism on the calcite surface, this research employs zeta potential, contact angle, Fourier Transform Infrared (FTIR) X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). This research provides theoretical guidance and proposes solutions for the development of new cassiterite flotation chemicals.

2. Materials and Methods

2.1. Mineral Preparation and Experimental Process

In the experiments, single-mineral samples of cassiterite and calcite were obtained from the Guangxi Zhuang Autonomous Region in China. The large mineral samples were first crushed to reduce their size [23]. The size fraction measuring between -74 and +38 µm was subjected to micro-flotation analysis. Some samples within the -38 µm size range were ground down even further to a size of -5 µm for surface analysis measurements [24]. The X-ray diffraction (XRD) analysis is shown in Figure 2. The cassiterite and calcite samples were of higher purity and met the requirement for single-mineral flotation experiments. The experiments used high-quality chemicals and reagents. Sodium oleate (NaOL), which was used as the collector, was purchased from Aladdin Industrial Corporation. HCl and NaOH were used to adjust the pH values of the solutions [25], and they were obtained from Sigma-Aldrich, Darmstadt Germany. Ultrapure water with a resistivity greater than 18.2 MΩ/cm was used.



Figure 2. X-ray diffraction of cassiterite (a) and calcite (b).

Single-mineral flotation experiments were performed in an XFG flotation machine (40 mL, Wuhan Exploration Machinery Company, Wuhan China) with an impeller speed of 1700 r/min [26]. The process for flotation was as follows: (1) 2.0 g of a single-mineral sample (2.0 g of cassiterite or 2.0 g of calcite) was added to a plexiglass cell, which was then filled with 40 mL of ultrapure water and agitated for 1 min to obtain a uniform pulp; (2) pH regulators, citrus pectin, and NaOL were gradually added at intervals of 3 min, as indicated in the flowchart presented in Figure 3; and (3) the concentrate and tailing products were gathered for drying in order to determine flotation recovery.



Figure 3. Single-mineral flotation flow chart.

Three identical flotation experiments were conducted for each condition, and the final value was determined as the average of the three recovery values obtained. The standard deviation was calculated using the mean value of the three measurements and represented as an error bar.

2.2. Extraction and Detection of Citrus Pectin

Citrus pectin was extracted according to a reported method [27]. A beaker containing 200 mL of ultrapure water was used as the solvent. This water was employed to extract the pectin from citrus peels. To the beaker containing the ultrapure water, 10 g of citrus peel powder was added, which was carried out to achieve a homogeneous mixture. The pH of the solution was then adjusted to 1.8 using citric acid. Subsequently, the beaker was subjected to extraction in a water bath set to a temperature of 85 °C for a duration of 90 min. The elimination of citrus peel residue from the crude pectin solution was achieved via centrifugation. The citrus pectin solution was then concentrated using a rotation evaporator, and precipitation was accomplished using anhydrous ethanol, which was then washed

three times with 70% ethanol. The pectin was then left to naturally dry at room temperature, resulting in the production of pectin powder.

The galacturonic acid (GalA) content of pectin was analyzed using a colorimetric method with a UV spectrophotometer [28]. A standard sample or test samples (0.5 mg/mL) were dispersed in ultrapure water through gentle magnetic stirring. Then, 6 mL of analytical-grade H₂SO₄ (98%) was added to a 1 mL sample in a test tube held on ice and thoroughly mixed. The solution was placed in a boiling water bath for 20 min before being allowed to cool. Next, 200 μ L of a 0.15 (w/v) carbazole–ethanol solution was added, and the mixture was vigorously vortexed. The resulting pink color remained stable for approximately 1 h. The absorbance was measured at 525 nm using a standard GalA curve.

FTIR (Thermo Electron Corporation, Waltham, Massachusetts, USA) was utilized to analyze the functional groups of citrus pectin and commercial pectin. A mass ratio of 1:100 of KBr powder was mixed with the samples. The average molecular weights of citrus pectin and commercial pectin were determined using gel permeation chromatography (GPC, Agilent, Santa Clara, CA, USA).

2.3. Interaction Measurements

Zeta potential was used to study the interactions between the flotation reagents and the mineral particle surface with a Zetasizer Nano ZS90 (Malvern, Britain). To 50 mL of ultrapure water, 0.5 g samples with a particle size of less than 5 μ m were added, and the slurry pH was adjusted with a 0.1 M HCl or 0.1 M NaOH solution. The reagent dosages were calculated based on the micro-flotation experiments. The obtained slurry settled for a period of time before the supernatant was used to measure zeta potential at 25 °C.

A contact angle analyzer (Theta Flex, Biolin Scientific, Gothenburg, Sweden) was employed to measure the contact angles of the cassiterite and calcite samples treated with the flotation reagent using the sessile drop method. The mineral samples underwent polishing using an automated polishing machine to achieve a sleek surface. It was imperative to ensure that the sample surface was immaculately clean and free of any contaminants prior to conducting the test. An average value was obtained by running each test at least three times.

To determine the concentration of pectin in citrus pectin, the total organic carbon (TOC) analyzer was used to quantify the total organic carbon content via catalytic combustion and oxidation at a high temperature. A standard sample of known reagent concentration was used to establish the standard curve, which should cover the range of the adsorption amount for accurate results. Two independent tests were conducted for each group, and the adsorption capacity of the mineral was computed.

At pH 9.0 (suitable pH value for flotation), a 2.0 g sample was dissolved in 40 mL of ultrapure water, with or without the addition of citrus pectin. The mixture was then stirred at 1700 rpm for a period of 3 min. The mineral samples followed filtering, washing, and a 12-h, 50 $^{\circ}$ C drying process. The mixture was then examined using XPS, for which data were then fitted using the "Avantage" software (V6).

The citrus pectin-treated mineral samples were prepared for AFM (Bruker, Karlsruhe, Germany) scanning as follows: cassiterite and calcite samples were immersed in a 10 mg/L citrus pectin solution for 3 min, respectively, and then washed repeatedly with ultrapure water to clean the mineral surfaces of any remaining reagents. High-purity nitrogen was employed to blow-dry the Samples for testing.

3. Results and Discussion

3.1. Characterization of Citrus Pectin

As depicted in Figure 4, the obtained FTIR for the commercial pectin and citrus pectin showed similar characteristics, especially in the region between $1600-1630 \text{ cm}^{-1}$ and $1740-1760 \text{ cm}^{-1}$, which corresponds to the free and esterified carboxyl groups [29,30]. Additionally, bands originating from the stretching vibration of the methyl (CH₃) group

in the methyl ester around 2800–3000 cm⁻¹ correspond to C–H absorption [31]. The stretching of hydroxyl (O–H) groups was responsible for the wider band ranging from 2400 to 3600 cm⁻¹ due to moisture present in both the commercial pectin and citrus pectin samples [29,32].



Figure 4. FTIR analysis of citrus pectin and commercial pectin.

As shown in Figure 5, the citrus pectin had a heavy molecular weight average of 32,959 Da, a number average molecular weight of 11,106 Da, and a polymer dispersity index of 2.9677. Compared to the heavy average molecular weight of commercial pectin (11,485,412 Da), citrus pectin had a low molecular weight. Notably, the extracted small molecule citrus pectin had a galacturonic acid content of 60.725%, indicating that it had fewer impurities and could be utilized as a flotation depressant.



Figure 5. Gel chromatography test chart of commercial pectin (a) and citrus pectin (b).

3.2. Micro-Flotation Experiment

The effect of the NaOL dosage on the flotation performance of cassiterite and calcite at pH 8.5 was investigated. As shown in Figure 6a, with an increasing concentration of NaOL, the flotation recovery of two minerals exhibited a rapid increase. Both the cassiterite and calcite minerals exhibited favorable floatability, indicating that it could be hard to separate cassiterite from calcite without the use of a depressant. The flotation recovery of cassiterite

exhibited a rapid increase with the NaOL concentration, reaching a peak value of 96.51% at 30 mg/L. Subsequently, as the NaOL concentration continued to rise, the recovery rate of cassiterite fluctuated around this maximum value. On the other hand, the recovery of calcite displayed a gradual increment with the NaOL concentration within the range of 10–60 mg/L, eventually reaching a maximum value of 95.01%. At a NaOL concentration of 30 mg/L, the recovery of calcite and cassiterite was recorded at 78.02% and 96.51%, respectively, indicating a significant difference between the two minerals. Consequently, 30 mg/L was identified as the optimal concentration of NaOL for the flotation process based on these findings.



Figure 6. The influence of NaOL (**a**) and citrus pectin (**b**) dosages on the floatability of cassiterite and calcite.

After the addition of the citrus pectin depressant (Figure 6b), the floatability of calcite was dramatically reduced. Less than 10% calcite was floated at 5 mg/L of citrus pectin. However, the addition of the citrus pectin had virtually no effect on the cassiterite recovery. About 81.8% of the cassiterite could still be floated even at a citrus pectin dosage of 10 mg/L. The pH influence on the floatability of cassiterite and calcite is shown in Figure 7. In the presence of NaOL only, both cassiterite and calcite showed high recovery in the pH range of 6–11 (Figure 7a). After the citrus pectin and NaOL were added, the floatability of cassiterite was maintained at more than 85%, while the pH rose from 8 to 9 (Figure 7b). When the pH value exceeded 10, the recovery of cassiterite also was depressed. A fixed pH of 9.0 was chosen as a suitable condition. In the single-mineral floation test, when the pulp pH was 9, the concentration of NaOL was 30 mg/L, and the concentration of citrus pectin was 10 mg/L, the recovery of cassiterite was 85.92%, and the recovery of calcite was 2.95%. In the presence of the citrus pectin depressant, there was a significant difference in the recovery of the two minerals, demonstrating excellent floation separation between cassiterite and calcite.

3.3. Zeta Potential Result

The reagent can change the surface charge of the mineral, and this process can be captured using zeta potential. To maintain consistency with flotation experiments, the zeta potential of the samples was determined across the pH spectrum of 6–11. In the case of cassiterite (Figure 8a), the zeta potential remained consistently negative within the test range without exhibiting an isoelectric point. The negative potential of cassiterite decreased with the rising pH levels of the solution, which was attributed to the increase in negatively charged OH⁻ present in the solution. As shown in Figure 8b, the isoelectric point of calcite was obtained within a pH of 8.5, which was in line with earlier findings [33].



Figure 7. The influence of pH on the floatability of cassiterite and calcite in the presence of NaOL (**a**) and citrus pectin and NaOL (**b**).



Figure 8. The zeta potentials of cassiterite (**a**) and calcite (**b**) as a function of pH in the absence and presence of flotation reagents.

After the addition of the citrus pectin, the zeta potential of both minerals underwent negative shifts due to the negatively charged carboxyl functional groups. However, compared with cassiterite, the calcite suffered a much shaper drop (21.2 mV) in its zeta potential, which meant that citrus pectin had a stronger affinity for calcite. After the reaction of citrus pectin and NaOL, the zeta potential of the cassiterite surface fell by 6.2 mV compared to the treatment of only citrus pectin. Conversely, the zeta potential of the calcite surface remained unchanged. These results indicated that NaOL can be adsorbed on the surface of pectin-treated cassiterite. Citrus pectin demonstrated a more powerful interaction with calcite than cassiterite, which led to a strong depressant of calcite in the flotation process. Therefore, this result suggested that the pre-adsorption of citrus pectin formed a strong passivation layer on the calcite surface, which led to the inability of NaOL to adsorb on the calcite surface.

3.4. Contact Angle Result

As shown in Figure 9, the contact angles of water on pure calcite and cassiterite were $35.17 \pm 1^{\circ}$ and $40.70 \pm 1^{\circ}$, consistent with previous reports [34,35]. After the interaction between minerals and citrus pectin, the contact angle of the cassiterite sample increased to $50.15 \pm 1^{\circ}$, signifying the enhanced hydrophobicity of the cassiterite surface due to the action of citrus pectin. In contrast, the contact angle of the calcite sample decreased to $30.21 \pm 1^{\circ}$, suggesting that citrus pectin rendered the calcite surface more hydrophilic, illustrating a distinction between the two minerals. The application of citrus pectin and

NaOL resulted in cassiterite's contact angle reaching 70.1 \pm 1°, thus significantly augmenting its surface hydrophobicity. At the same time, calcite remained hydrophilic, and the contact angle was about 36.19 \pm 1°, which also made calcite unable to float during the flotation process. Higher concentrations of citrus pectin resulted in a more hydrophilic calcite surface and a lower recovery rate in the flotation process. The disparity in surface hydrophilicity between cassiterite and calcite directly influenced the separation of the two minerals.



Figure 9. Contact angles of water on cassiterite and calcite surfaces before and after treatment with citrus pectin and NaOL.

3.5. Adsorption Experiment

The experiments conducted established the high efficiency of citrus pectin as a depressant for the separation of cassiterite and calcite. This section focuses on investigating the adsorption behavior of citrus pectin towards these minerals. The adsorption extent of citrus pectin on the mineral surface corresponds to its effect on the floatability of the minerals. Six standard concentrations of citrus pectin solution were prepared: 10 mg/L, 20 mg/L, 40 mg/L, 70 mg/L, 100 mg/L, and 120 mg/L. The standard curve was constructed using the citrus pectin concentration versus organic carbon content, and the standard curve equation was y = 0.71152 + 0.35841x with a variance of $R^2 = 0.99826$, indicating high accuracy in the test results (Figure 10).



Figure 10. Standard curve of relation between organic carbon concentration and citrus pectin concentration.

The study investigated the impact of an initial concentration of sodium oleate on the adsorption capacity at 25 °C and a 4-h adsorption time (Figure 11). The results indicated that, at a low concentration, there was only mild fluctuation in the adsorption capacity of both groups, indicating that the concentration hardly affected their adsorption capacity. As a result, an initial concentration of 50 mg/L was selected to test the adsorption time.



Figure 11. The effect of initial concentration on the adsorption amounts of citrus pectin on cassiterite and calcite surfaces.

A further investigation was conducted to explore the influence of adsorption time on the adsorption capacity of citrus pectin on the surfaces of cassiterite and calcite. The test results are presented in Figure 12. As the adsorption time increased, the adsorption capacity on the surfaces of cassiterite and calcite initially increased and then reached a plateau. Notably, the adsorption rate on the surface of calcite demonstrated a rapid rise, with the fastest adsorption rate occurring at approximately 20 min. On the other hand, cassiterite reached its adsorption rate at around 40 min. The maximum adsorption capacity for calcite was measured at 38.81 mg/g, while that for cassiterite was 29.56 mg/g, reflecting a difference of 9.25 mg/g between the two minerals. Subsequently, the citrus pectin adsorbed on the surface of calcite exhibited desorption, while the adsorption capacity on the surface of cassiterite remained relatively unchanged.



Figure 12. The effect of adsorption time on the adsorption amounts of CP on cassiterite and calcite surfaces.

Dynamic adsorption experiments revealed differences in the interaction of citrus pectin with calcite and cassiterite. The adsorption of citrus pectin on the surface of cassiterite was limited, and pre-adsorption on the cassiterite surface did not hinder the adsorption of NaOL. However, citrus pectin occupied adsorption sites on the calcite surface, forming a thick adsorption layer and thereby hindering the adsorption of NaOL.

3.6. FTIR Result

To further elucidate the adsorption mechanism of citrus pectin on the calcite surface, FTIR spectra were recorded both before and after the treatment with citrus pectin.

In the infrared spectra presented in Figure 13a, it was observed that the pure cassiterite minerals exhibited two distinct characteristic peaks at 626 cm⁻¹ and 501 cm⁻¹, which can be attributed to the antisymmetric vibration characteristics of Sn–O bonds present in cassiterite [7,36]. Upon the treatment that applied citrus pectin to cassiterite, there were no observable characteristic peaks associated with citrus pectin. While slight shifts in the characteristic peaks of cassiterite were noted, they were deemed negligible. Overall, it can be concluded that citrus pectin did not undergo chemisorption on the surface of cassiterite.



Figure 13. Functional groups of mineral surfaces before and after interacting with citrus pectin: (a) cassiterite and (b) calcite.

In the infrared spectrum depicted in Figure 13b, the pure calcite minerals exhibited distinct absorption peaks that correspond to specific vibrational modes. Firstly, the in-plane bending vibration of the CO_3^{2-} ion in calcite was observed at 711 cm⁻¹, then the out-of-plane bending vibration at 875 cm⁻¹, and finally the asymmetric stretching vibration at 1421 cm⁻¹ [34,37]. These three peaks were considered characteristic absorption features of calcite. Additionally, it was worth noting two characteristic peaks present in the spectrum of citrus pectin. These peaks correspond to the C–H stretching vibration absorption peak on galacturonic acid at 2935 cm⁻¹ and the C–O stretching vibration absorption peak of the esterified carboxyl group at 1737 cm⁻¹. Upon studying the infrared spectra of calcite treated with citrus pectin, it was observed that not only the three characteristic peaks of calcite but also these two characteristic peaks of citrus pectin were apparent. Notably, three characteristic absorption peaks belonging to calcite also appeared to exhibit minor shifts in their amplitudes. The adsorption of citrus pectin showed different behaviors towards cassiterite and calcite, indicating its selective adsorption towards the two minerals, which was consistent with the flotation results and zeta potential testing.

3.7. XPS Result

The high-resolution XPS spectra of Ca 2p and C 1s for calcite with and without the citrus pectin treatment are shown in Figure 14. Double peaks at 346.68 eV and 350.28 eV appeared in the fitting peaks of calcite, which could be responsible for the Ca 2p 3/2 and Ca 2p 1/2 in calcite, respectively. When the citrus pectin depressant was interacting with calcite, new fitted peaks appeared at 347.48 eV and 350.98 eV, which belonged to the Ca–COOH group [38]. After the citrus pectin treatment, a calcite Ca 2P peak appeared to obviously shift, and a new fitted peak was formed, indicating that the interaction between citrus pectin and the calcite surface was very strong, which was also consistent with the results of the zeta potential analysis. As shown in Figure 14c, the peaks at 289.28 eV, 286.38 eV, and 284.78 eV were shown in the high-resolution spectra of C 1s of calcite, which corresponded to the carbon in the carbonate of the calcite, the inescapable hydrocarbon contamination from the environment, and hydrocarbons, respectively [39]. The XPS spectrum of citrus pectin after treatment revealed the presence of a peak corresponding to Ca–COOR.



Figure 14. High-resolution Ca 2p and C 1s spectra of calcite (**a**,**c**), and calcite treated with citrus pectin (**b**,**d**).

Prior to interaction with citrus pectin (Figure 15), the Sn element in pure cassiterite exhibited two distinct fitting peaks: one at 494.98 eV, corresponding to Sn 3d 5/2, and another at 486.48 eV, representing Sn 3d 3/2 [40]. Following the interaction with citrus pectin, the characteristic peaks of Sn on the cassiterite surface remained relatively unchanged, suggesting weak surface bonding between citrus pectin and cassiterite. In summary, XPS analysis indicated that there was a strong chemical interaction between citrus pectin and calcite, and the Ca site on the calcite created a new chemical bond with the carboxyl group in citrus pectin.



Figure 15. High-resolution Sn 3D spectra of cassiterite (**a**) and cassiterite treated with citrus pectin (**b**).

3.8. AFM Result

To gain deeper insight into the adsorption mechanism of citrus pectin on calcite, AFM surface morphologies were examined. AFM scans were performed at $2 \times 2 \mu m$ with a setpoint of 0.4 mN. As demonstrated in Figure 16, they revealed that the average roughness Ra of untreated calcite amounted to 0.915 nm (Figure 16a). Furthermore, it was polished, showing that the calcite surface is characterized by a high degree of smoothness.

However, after the treatment with citrus pectin, the surface of the calcite exhibited a unique phenomenon whereby it was covered with dense, block-type protrusions. And the surface roughness Ra increased from 0.915 nm to 2.862 nm, indicating that citrus pectin was adsorbed on the surface of the calcite. The interaction between citrus pectin and calcite led to the formation of an adsorption layer on the surface of the citrus-pectin-treated calcite. This layer effectively prevented the further adsorption of the collector, ultimately leading to a notable decline in calcite recovery. It is evident that the adsorption mechanism of citrus pectin on calcite is an intricate process that needs to be further studied and understood.



Figure 16. Two- and three-dimensional images of calcite surface morphology before (**a**,**c**) and after (**b**,**d**) citrus pectin treatment.

4. Conclusions

This study entailed the acid extraction of small molecule citrus pectin from fresh citrus peel as compared to commercial pectin. Citrus pectin exhibited a smaller molecular weight and higher solubility, which achieved better selective depressant effects in the flotation process while reducing the recovery rate of calcite. The development and implementation of citrus pectin can potentially improve the recovery and utilization of cassiterite resources. The principle of selective depressant of citrus pectin was verified.

- During the analysis of the surface wettability of cassiterite and calcite, the surface of cassiterite became hydrophobic after being treated with citrus pectin and NaOL, while the surface of calcite became hydrophilic after the same treatment. The difference in surface wettability between cassiterite and calcite was the prerequisite for separation.
- 2. The analysis of the zeta potential of cassiterite and calcite showed that NaOL cannot be adsorbed on the surface of calcite treated with citrus pectin.
- 3. The results of FTIR and XPS analysis on the surface of cassiterite and calcite showed that the chemical reaction between citrus pectin and calcite forms a Ca–COOR bond on the surface of calcite, while the interaction between citrus pectin and cassiterite was physical adsorption.
- 4. The difference between citrus pectin with cassiterite and calcite can also be seen from the static adsorption and adsorption morphology. The citrus pectin was dispersed on cassiterite, while the adsorption capacity on calcite was dense and concentrated.

The different adsorption modes of citrus pectin on cassiterite and calcite lead to the different behaviors of the two in the flotation process. The use of citrus pectin not only enhances the efficiency of cassiterite resource recovery but also offers treatment options for citrus peel.

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