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Adsorption behavior and mechanism of Bi(III) ions on rutile−water interface in the presence of nonyl hydroxamic acid

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Abstract: The adsorption behavior and mechanism of Bi(III) ions on the rutile−water interface were investigated through micro-flotation, Zeta potential measurement, adsorption amount measurement and X-ray photoelectron spectroscopy (XPS). According to the results of micro-flotation, Bi(III) ions could largely improve the rutile flotation recovery (from 62% to 91%), and they could increase the activating sites and reduce the competitive adsorption between nonyl hydroxamic acid negative ions and OH^- ions, which determined that Bi(III) ions were capable of activating rutile flotation. The adsorption of Bi(III) ions onto the rutile surface led to the shift of Zeta potential into the positive direction, which was good for the adsorption of nonyl hydroxamic acid anions. In addition, the results of XPS indicated that the chemical environment around Ti atom had not changed before and after the adsorption of Bi(III) ions. Based on the adsorption mechanism of Bi(III) ions, it was deduced that firstly Bi(III) ions occupied the vacancies of the original Ca^{2+}, Mg^{2+} and Fe^{2+} ions on the rutile surface; secondly Bi(III) ions covered on the rutile surface in the form of hydroxides.

Key words: rutile; flotation; activation of Bi(III) ions; competitive adsorption; activation sites

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1 Introduction

Rutile is not only one of the raw materials that are necessary for high-grade welding electrodes, but also the most suitable raw material for the production of rutile titanium dioxide [1,2]. However, the majority of rutile ores belong to refractory ores, and thus flotation is one of the most efficient methods of solving the problem related to the fine embedded grain size, the complexity of the mineral and easiness to muddy [3].

With the rapid development of flotation, many effective collectors have been applied to the process of flotation separation of the oxide ores successfully. Many reviews indicated that alkyl hydroxamic collectors have a high selectivity on oxide ores such as cassiterite, cheelite, and rutile [4−7]. Furthermore, their affinity to metal or metal oxide is far stronger than fatty acid, thereby forming more stable metal complexes [8−10]. Unfortunately, the flotation recovery is a little lower when using alkyl hydroxamic collectors in spite of higher concentration. In order to improve the recovery, the consumption of collectors in abundance must be enhanced due to the lack of activating sites for collector adsorption on the mineral surface. And we tried to add surface activating sites with two common surface modification approaches: to change the valence state or structure of present surface elements and to introduce new activating elements to the mineral surface.

A selective control of surface properties is conductive to the design of solid surface, so the anchoring group plays a key role in functional materials and adjusting the interaction between mineral and activating sites of the mineral surface. Pb(II) and Cu(II) ions are effective activators that have already been widely used to modify mineral surface properties. The

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flotation recovery of sphalerite can be greatly improved in the presence of copper ions. The copper xanthates had lower solubility than zinc xanthates, resulting in a more hydrophobic surface of sphalerite particles to attach air bubbles [11]. Copper ions could also activate the flotation of pyrite, which was suppressed by lime in alkaline condition, because they led to the formation of new metal sulfide phases on pyrite surfaces [12]. FAN and ROWSON [13] found that $Pb(NO_3)_2$ could be used as activator to improve ilmenite floatability effectively and selectively. The Pb^{2+} and $Pb(OH)^+$ species could be attached onto ilmenite surfaces selectively, achieving improvement in the flotation recovery of ilmenite.

In this work, Bi(III) ions (novel activator) were introduced to add the activation sites on the rutile surface, and subsequent flotation reflection to nonyl hydroxamic acid was investigated as well. According to the measurement results of XPS and Zeta potential, the adsorption mechanisms of Bi(III) ions on the rutile surface and subsequent reflection to nonyl hydroxamic acid (collector) were further discussed.

2 Experimental

2.1 Materials

In this work, rutile samples obtained from Zaoyang, Hubei, China were firstly crushed and ground to particles (38−74 μm) and then purified by sieving, and tabling with low/high-intensity magnetic separation methods. The pure rutile samples were washed several times with distilled water and finally dried at room temperature. According to the analysis of particle size (Fig. 1), the average particle size of rutile was 53.98 μm, which was measured through a laser particle-size analyzer (Mastersizer 2000). As a result, all the reagents were analytically pure in this work.

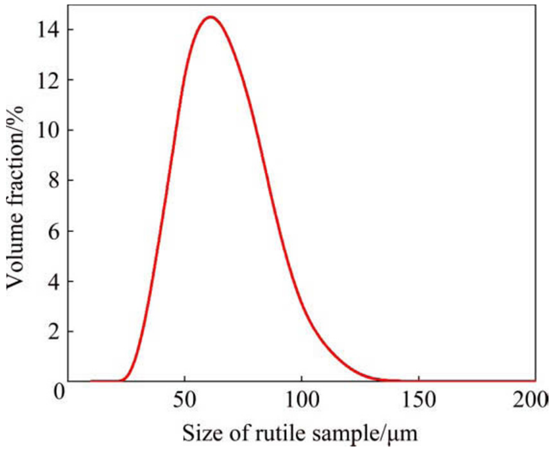

Fig. 1 Size contribution of rutile sample

An analysis of chemical compositions of rutile was carried out by a wavelength dispersive X-ray fluorescence (XRF) spectrometer S4 Pioneer. The results of XRD and XRF are shown in Fig. 2 and Table 1, respectively. The parameter setting and the method of XRD and XRF were previously described in Ref. [14]. From the XRD results in Fig. 2 and the XRF results in Table 1, the purity of rutile samples was calculated to be 93.8%.

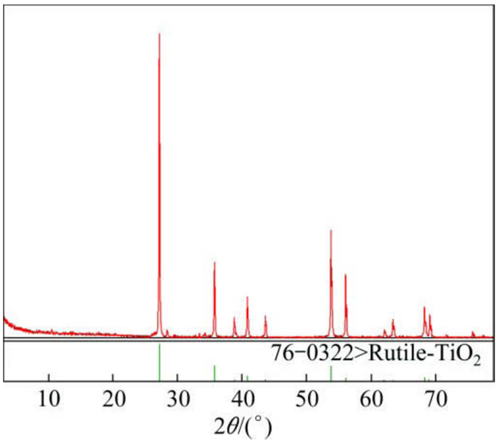

Fig. 2 XRD pattern of rutile

Table 1 Multi-element analysis result of pure rutile mineral (mass fraction, %)

TiO_2	FeO	Fe_2O_3	SiO_2	CaO	MgO	Al_2O_3
93.80	1.53	1.33	2.07	0.17	0.31	0.99

2.2 Experimental methods

2.2.1 Micro-flotation tests

The purified rutile particles (2 g) were placed in a plexiglass cell (40 mL) that was then filled with distilled water so as to adjust the pH value. After 2 min, the bismuth nitrate and the collector were added, respectively. Next, the suspension was agitated for 2 and 3 min, respectively, and then the pH was measured before the flotation (4 min). The concentrates and tailings were weighed after filtration and drying, and finally the flotation recovery was calculated.

2.2.2 Adsorption experiment

The rutile samples (2.0 g) were place in a plexiglass cell (40 mL) that was then filled with distilled water. Then, the pH value was adjusted by 1% hydrochloric acid solution. After constant stirring for 2 min, bismuth nitrate was added. The suspension was agitated for 5 min. Next, the samples were centrifuged and filtered to separate liquid and solid phases after extraction. After washing twice with distilled water, the filter liquor was moved to a 100 mL volumetric flask. Finally, the adsorption amount was calculated by the following equation:

$$Q_e=\frac{V(C_0-C_e)}{WS} \tag{1}$$