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Selective flotation separation of ilmenite from titanaugite using n-octylphosphonic acid as collector in acidic pulp

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Abstract: n-octylphosphonic acid (OPA) was introduced as a novel collector for ilmenite flotation and its effectiveness was compared with the conventional chelating collector, benzohydroxamic acid (BHA). Micro-flotation tests demonstrated that OPA was a highly effective and selective collector for separating ilmenite from titanaugite over acidic conditions (optimal pH around 3), which was also supported by adsorption amount measurements. X-ray photoelectron spectroscopy (XPS) tests indicated that the chemisorption of OPA onto ilmenite surface was much stronger than that of BHA. Solution chemistry diagram analyses indicated that OPA could dissociate well at pH 3.0 and mostly exist in anion form. DFT calculations further confirmed that OPA was much easier to adsorb onto ilmenite surface with shorter bond length and lower adsorption energy in comparison with BHA. Therefore, OPA maintained good collecting ability and selectivity for ilmenite flotation in the strongly acidic pulp, providing valuable insights into new collector design and development.

Key words: ilmenite; titanaugite; flotation separation; n-octylphosphonic acid

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1 Introduction

Titanium (widely regarded as a strategic and rare metal) and its derived alloys have excellent properties and are broadly used in aerospace, shipbuilding, medicine, coatings, and other fields [1−4]. China is abundant in titanium resources, which makes up about 27% of global total titanium reserves [5]. However, the main mineral source of titanium in China is ilmenite, which is primarily found in igneous ores and located in the Panxi region of Sichuan Province [6]. Generally, ores containing ilmenite in China comprise several gangue minerals such as titanaugite, chlorite, amphibole, feldspar, and others, resulting in poor ilmenite grade and difficulty in their beneficiation. To address this, flotation is an effective way that has been reported frequently [6−10]. However, as the main gangue mineral, titanaugite and ilmenite (target mineral) have similar surface properties and active sites, which can deteriorate ilmenite flotation behavior. At present, industrial practice for ilmenite concentrate production is normally carried out under acidic pulp conditions using H_2SO_4 solution as the pH regulator due to the following reasons: (1) the acidic conditions contribute to the dissolution of Ca and Mg on the surface of titanaugite, which makes the relative content of active sites reduce and titanaugite depress; (2) on the other hand, the acidic

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conditions are conducive to the high exposure of Fe^{2+} sites on the surface of ilmenite, which makes the difference in floatability of ilmenite and titanaugite increase [9,11,12]

Based on industrial practice for decades, the cleaning process of ilmenite-containing ores by flotation is conducted under strongly acidic pulp conditions with pH 2.8−3.9 [13], which has posed great challenges for collectors used throughout flotation. To date, many researchers have worked on collectors for ilmenite flotation and developed collectors with good performance at neutral or mildly alkaline pH, like phosphoric esters [14], NaOL [15], BHA-NaOL [16], BHA-DDA [17], Fe-BHA [18], and 2-ethyl-2-hexenoic hydroxamic acid [19]. However, these collectors performed poorly in strongly acidic pulps, indicating that the practical demands for ilmenite flotation in industrial production are not taken into extensive consideration. Moreover, it should be noted that these reagents are currently in the laboratory research stage and how to promote their industrialization in ilmenite flotation remains challenging. To address such gap, it is believed that if the collector to be developed can exhibit good performance for ilmenite flotation within a wide pH range (especially from weakly acidic environments to strongly acidic environments), it will be more promising and applicable to be promoted in industrial production of ilmenite concentrate. Therefore, aiming to meet the high demands on collectors for ilmenite flotation in industrial practice, particularly under the strongly acidic pulp conditions, is the starting point of current research.

It is hypothesized that the pK_a value of a collector must be low enough so that it can dissociate well under the strongly acidic pulp conditions [20−22] and then meet the collecting requirements for ilmenite flotation. The pK_a of n-octylphosphonic acid (OPA) is 2.69 [23], and thus it could be a promising collector candidate to float ilmenite in the strongly acidic pulps. Therefore, in this study, OPA was used as a novel collector for the selective separation of ilmenite from titanaugite under acidic conditions, and the conventional chelating collector, benzhydroxamic acid (BHA), was used as well for comparison. The collecting ability and selectivity of both collectors were compared with micro-flotation experiments. The associated adsorption mechanism of OPA and BHA was further explored by employing adsorption amount measurements, solution chemistry calculations, XPS tests, and DFT calculations.

2 Experimental

2.1 Materials and reagents

Ilmenite and titanaugite specimens were obtained from Panzhihua, Sichuan Province, China. Pure minerals of ilmenite and titanaugite were produced by repeated purification of the ore specimens by grinding, shaking table recleaning, and magnetic separation. The minerals with 38−74 μm were screened from the pure minerals for flotation tests. The X-ray fluorescence (XRF) and X-ray powder diffraction spectra (XRD) results of ilmenite and titanaugite are shown in Table 1 and Fig. 1. The major mineral component of ilmenite specimen, as shown by the XRD pattern, is just ilmenite, and the titanaugite specimen contains tiny amounts of chlorite, amphibole, and feldspar in addition to the main component of titanaugite. The purity of both minerals reached more than 90%, meeting the requirements for mineral flotation tests.

Table 1 Main chemical components of purified ilmenite and titanaugite specimens (mass fraction, %; LE: other elements, mainly as O, V, S, etc.)

Component	Ti	Fe	Ca	Mg	Al	Si	Mn	LE
Ilmenite	28.86	29.78	0.6	2.85	0.7	1.56	0.47	35.18
Titanaugite	2.08	9.81	10.5	7.27	4.69	19.84	0.16	45.65

Analytically pure OPA and BHA were supplied by Shanghai Aladdin Biochemical Technology Co., China. The solution medium for all tests was deionized water. The pH of the solutions was adjusted with NaOH and H_2SO_4.

2.2 Micro-flotation test

The micro-flotation tests were conducted in a hanging trough-type flotation machine (Jilin Prospecting Machinery Factory) with a stirring speed of 1700 r/min. 2 g of mineral specimen was weighed, and 35 mL of deionized water was measured and placed in the flotation tank for each test. The pulp was stirred well and NaOH or H_2SO_4 solution was added to adjust the pH of the pulp. The collector was added and stirred for 3 min to ensure they were completely dispersed. Flotation was carried

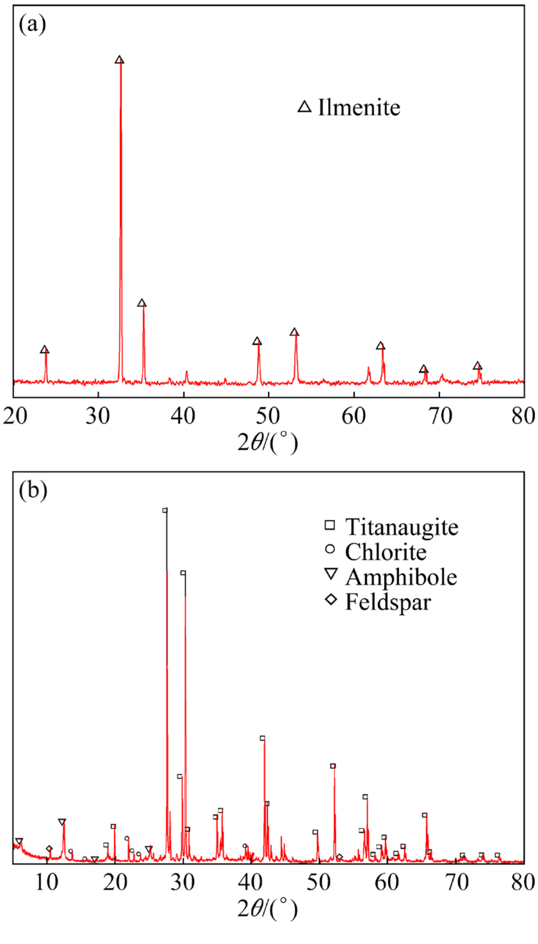

Fig. 1 XRD patterns of ilmenite (a) and titanaugite (b)

out for 3 min and the froth products were manually scraped off. The concentrates and tailings under different flotation conditions were filtered, dried, and weighed to calculate the flotation recovery. In the flotation tests of mixed binary minerals, ilmenite concentrate was dried, weighed, and chemically analyzed, and the grade and recovery of ilmenite and titanaugite were calculated. Each flotation test was repeated three times and the average value (± standard deviation) was finally reported in this work.

2.3 Adsorption amount measurement

The adsorption amount measurements were conducted by Multi N/C 3100 Analyzer (Analytikjena, Jena, Germany). Total organic carbon (TOC) measurement was used to determine the residual concentration of the collector in the supernatant after its adsorption on mineral surface, and the residual concentration was used to calculate the adsorption amount of the flotation reagent on mineral surface. Apart from the last-hand scraping step, the specimen preparation procedure was essentially the same as the flotation procedure. The suspension was then centrifuged in a centrifuge for 30 min at 10000 r/min, and the supernatant was filtered through a 0.45 μm needle filter, which was then measured in a TOC analyzer. As the initial and residual concentrations were known, the amount of the agent that had been adsorbed onto mineral surface could be calculated as follows:

$$\Gamma=\frac{(C_\mathrm{i}-C_\mathrm{r})V}{\eta m} \tag{1}$$

where Γ is the adsorption amount of the reagent on each mineral, mg/g; η is the carbon content (%) in molecule of the reagent; C_i and C_r are the initial and residual TOC contents of the reagent in the supernatant, mg/L, respectively; m is the mass of the mineral specimen, g; V is the liquid volume, L [24].

2.4 XPS test

The preparation of specimens for X-ray photoelectron spectroscopy (XPS) was similar to flotation. The specimen was first ground to −2 μm and weighed to 2 g in a 50 mL beaker, and then deionized water was added. After stirring, the slurry pH was adjusted to the desired value and then the collector was added. Conditioning time was kept the same as flotation tests, and finally, ilmenite samples treated with OPA/BHA were collected and dried in a vacuum oven. The XPS tests were performed on a Thermo Scientific ESCALAB 250Xi with Al as the photoelectron emission source and with a controlled vacuum of $133.322\times(10^{-9}$–$10^{-8})$ Pa. The results were analyzed using Thermo Scientific Avantage 4.52 software, and all elemental binding energies were calibrated against the C 1s binding energy of 284.8 eV.

2.5 DFT calculation

The density functional theory (DFT) calculations were carried out within the Castep module in Materials Studio 2018. Periodic models of ilmenite bulk phases using XRD crystal structures were obtained from the American Mineralogical Crystal Structure Database [25]. Surface energy calculations indicated that the (104) surface was a reasonable solution surface for ilmenite [26], and the (104) plane is usually chosen as the representative surface in the investigation on the adsorption mechanism of water molecules and reagents on ilmenite surface [19,27]. A crystalline surface model with a vacuum layer thickness of 40 Å was optimized and used to calculate the vacuum adsorption energy. First-principles approach using density generalized theory calculations to construct common exposed surfaces of ilmenite, BHA molecule, and OPA anion structures, and perform structure optimization and calculate adsorption energies of both collectors [27]. The core electrons were described by ultrasoft pseudopotential with an energy cutoff of 380 eV. Under the comprehensive consideration of affordable calculation cost and acceptable calculation accuracy, the exchange correlation potential was modeled using Generalized Gradient Approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE). For self-consistent iteration, the density mixing electronic minimizer was used with a self-consistent field tolerance of 2.0×10^{-6} eV/atom. The structural models all use Na^+ as the equilibrium charge, and the spin polarization was considered for all the calculations. The adsorption energy (ΔE_{ads}) between the reagent and ilmenite (optimized (1 0 4) surface) is quantified as follows [28]:

$$\Delta E_{\text{ads}}=E_{\text{complex}}-(E_{\text{adsorbate}}+E_{\text{mineral}}) \tag{2}$$

where E_{complex} is the energy of the optimized ilmenite−reagent system; $E_{\text{adsorbate}}$ is the total energy of the reagent; E_{mineral} is the total energy of the ilmenite surface.

3 Results and discussion

3.1 Micro-flotation analysis

Figure 2 shows the effects of OPA and BHA on the flotation recovery of ilmenite and titanaugite under various pH conditions.

As shown in Fig. 2, when the concentration of collector was 4×10^{-4} mol/L, the recovery of ilmenite with OPA was significantly higher than that with BHA. The difference in recoveries between ilmenite and titanaugite was more than 60% in the pH range of 2.0−4.0 when using OPA as the collector, while the greatest difference in recoveries between the two minerals with BHA was only 56.3% over the entire pH range (pH 2−7). The optimal pH condition for ilmenite separation from titanaugite using OPA as the collector was about 3.0. The recoveries of ilmenite and titanaugite in such condition were 79.55% and 4.35%, respectively, and the biggest recovery difference reached about 75%. Comparatively, the optimal ilmenite flotation pH with BHA was 6.0, and the greatest difference in flotation recoveries between ilmenite and titanaugite was about 56%.

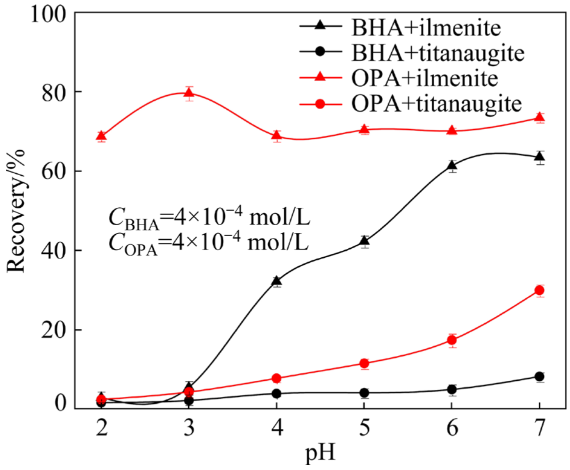

Fig. 2 Effects of BHA and OPA on flotation recovery of ilmenite and titanaugite under different pH conditions

Figure 3 suggests the effects of collector concentrations on flotation recoveries of ilmenite and titanaugite under their respective optimal pH condition (OPA at pH=3.0 and BHA at pH=6.0). The recovery of ilmenite increased steadily and finally levelled off as the collector concentration increased. And at the same concentration, the recovery of ilmenite with OPA was much higher than BHA. After the concentration of OPA reached 4×10^{-4} mol/L, continuing increase of OPA dosage

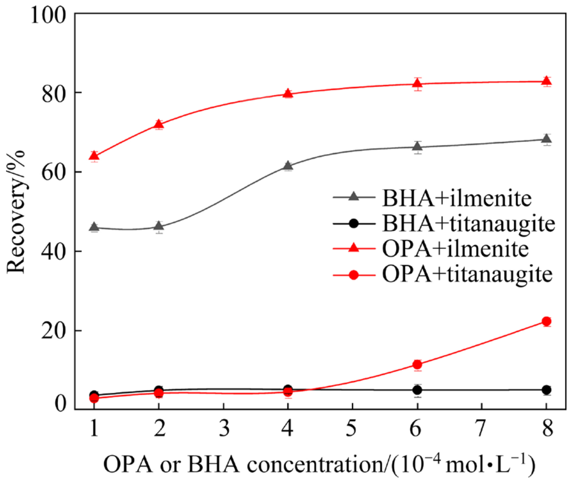

Fig. 3 Effects of OPA (at pH=3.0) and BHA (at pH=6.0) concentrations on flotation recoveries of ilmenite and titanaugite

had little effect on the recovery of ilmenite. At this time, the recovery difference between ilmenite and titanaugite was 75.2%, and the two minerals can be separated selectively using OPA as the collector. The effect of BHA concentration on ilmenite recovery was similar to that of OPA. As a result, for the flotation separation of ilmenite and titanaugite, the optimal concentrations of OPA and BHA collectors were both 4×10^{-4} mol/L.

Flotation tests of mixed binary minerals (ilmenite:titanaugite=1:1, mass ratio, TiO_2 grade 24.35%) were carried out to further evaluate the performances of OPA and BHA in ilmenite flotation separation from titanaugite. Herein, the pH conditions were controlled under their respective optimal conditions (OPA at pH 3.0 and BHA at pH 6.0), and the results are presented in Fig. 4.

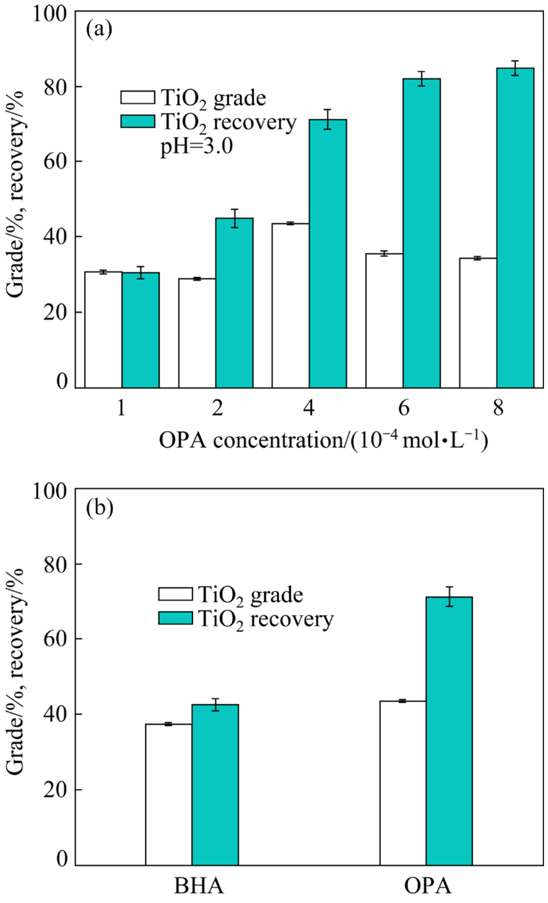

Fig. 4 Effect of OPA concentration (a) and different collectors (b) on flotation index of mixed binary minerals ($C_{BHA}=4\times10^{-4}$ mol/L, pH=6.0; $C_{OPA}=4\times10^{-4}$ mol/L, pH=3.0)

Figure 4(a) indicated that the TiO_2 grade of concentrate increased initially and then decreased as the OPA concentration increased, and meanwhile, TiO_2 recovery remained an increasing trend. TiO_2 grade reached a maximum of 43.65% and the recovery was 71.25% when the OPA concentration was 4×10^{-4} mol/L. The recovery increased somewhat as the concentration of OPA was further increased, but the grade of TiO_2 dropped gradually, and thus the optimal concentration for selective separation of ilmenite from titanaugite using OPA as collector was 4×10^{-4} mol/L. Comparative flotation studies of mixed binary minerals with OPA and BHA as the collector, respectively, were conducted under their respective optimal pH conditions (OPA at pH 3.0 and BHA at pH 6.0), and the results are illustrated in Fig. 4(b). TiO_2 grade and recovery were 37.5% and 42.63%, respectively, when BHA was employed as the collector. TiO_2 grade and recovery were 43.65% and 71.25%, respectively, when OPA was used as the collector. OPA thus had much better selectivity and collecting ability than BHA, allowing for good performances of OPA in the flotation separation of ilmenite from titanaugite under the strongly acidic conditions.

3.2 Adsorption amount

The amount of flotation collector adsorbed on mineral surface can be used to detect changes in flotation recovery [29]. Figure 5 shows the adsorption capacity of BHA and OPA on the surface of ilmenite and titanaugite under different pH conditions.

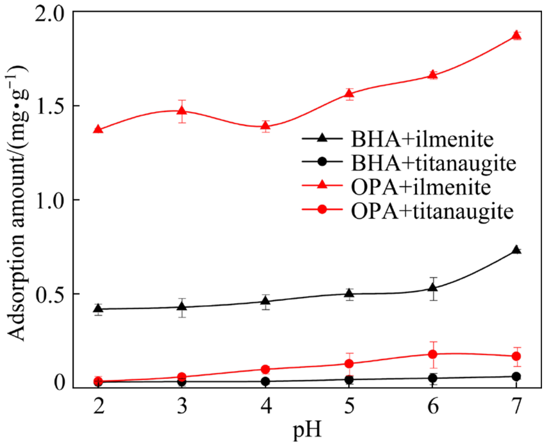

Fig. 5 Adsorption amount of BHA and OPA on surface of ilmenite and titanaugite under different pH conditions

As shown in Fig. 5, over the entire experimental pH range, the adsorption amount of OPA on ilmenite surface was at least 8 times higher than that of BHA. At pH 3.0, the adsorption amount of OPA on ilmenite surface was 1.47 mg/g, which was much higher than that of BHA (0.06 mg/g). It demonstrated that OPA can efficiently adsorb onto ilmenite surface under the strongly acidic conditions. Meanwhile, the adsorption amount of OPA on ilmenite surface at pH 3.0 was much higher than that adsorbed on the surface of titanaugite (0.43 mg/g), demonstrating that OPA exhibited good selectivity between ilmenite and titanaugite. The results of surface adsorption amount measurements were consistent with the results of micro-flotation tests, both indicating that OPA can selectively and efficiently adsorb onto ilmenite surface under the strongly acidic conditions. As a result, the hydrophobicity difference between ilmenite and titanaugite was enhanced, and a high-efficient flotation separation of ilmenite from titanaugtie was achieved [18].

However, as the total organic carbon (TOC) method is not a direct method to measure the adsorption amount of collector on mineral surface, ilmenite flotation behavior may not always be consistent with the adsorption measurement results in some cases, which has been reported for ilmenite and hematite as well [30,31]. In this study, Fig. 5 also revealed that the adsorption amounts of OPA on ilmenite surface increased from pH 4 to 7 but ilmenite flotation recovery increased slightly (Fig. 2). And the significant adsorption amounts of collector on mineral surface should be further determined. While using BHA as the collector, the effects of pH on ilmenite flotation recovery (Fig. 2) were overall consistent with adsorption amount measurement results (Fig. 5), which was ilmenite recovery increased as pH increased from 2 to 7, and meanwhile BHA adsorption amount on ilmenite surface increased. As collector adsorption amount onto mineral surface was a reference for qualitative discussion of adsorption behaviors of different collectors (not a linear correlation with their flotation effectiveness), this was why the adsorption amounts of OPA collectors on ilmenite surfaces were much larger than those of BHA collectors, but small differences in their flotation recovery were observed.

3.3 Solution chemistry

A solution chemistry diagram is helpful in exploring the mechanism of collector adsorption onto mineral surfaces and identifying the primarily functional species of specific collectors under certain pulp conditions [32−34]. Figure 6 shows the logarithm diagram of BHA and OPA as a function of solution pH at a concentration of 4×10^{-4} mol/L.

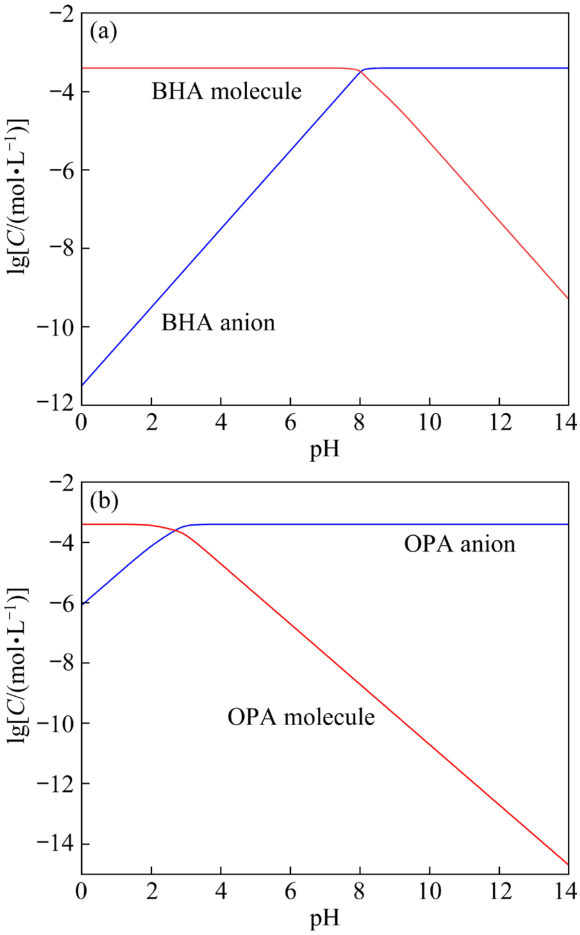

Fig. 6 Species distribution curves of BHA (a) and OPA (b) against pH at concentration of 4×10^{-4} mol/L

BHA has a pK_a of 8.1, and Fig. 6(a) indicates that when pH is less than 8.1, BHA is mostly in molecule form. The concentration of neutral molecules of BHA is $1\times10^{-3.4}$ mol/L at the optimal flotation pH of 6.0, accounting for more than 99% concentration. Under such condition, ilmenite recovery and adsorption amount of BHA on ilmenite surface were 61.3% and 0.18 mg/g, respectively, according to the results of micro-flotation and adsorption amount measurement. It indicates that a small amount of BHA can adsorb on ilmenite surface and that BHA molecules play a major role. Thus, the molecule form of BHA is supposed to adsorb on ilmenite surface in later DFT calculations. When the pH is 3.0, the concentration of BHA anions is just $1\times10^{-8.5}$ mol/L. In this case, ilmenite recovery and the adsorption amount of

BHA on ilmenite surface were only 5.55% and 0.06 mg/g, respectively, indicating that BHA is unable to collect ilmenite effectively under the strongly acidic conditions.

The pK_a value of OPA is 2.69, and as provided in Fig. 6(b), the concentration of OPA anions is $1\times10^{-3.4}$ mol/L at the optimal flotation pH of 3.0, accounting for 99.53% concentration. Ilmenite recovery and the adsorption amount of OPA on ilmenite surface were 79.55% and 1.47 mg/g, respectively. It demonstrates that under the strongly acidic conditions, OPA can dissociate well and the OPA anions can effectively adsorb on the surface of ilmenite, making the surface hydrophobic and allowing ilmenite to be floated with the bubbles. As OPA anions play a crucial role, they are thus supposed to adsorb on ilmenite surface in the following DFT calculations.

3.4 XPS spectra

The interaction between flotation reagents and minerals manifests itself as changes in relative contents and chemical states of elements (active sites) on mineral surfaces, which can be detected by XPS tests [1]. As a result, XPS tests were conducted to further study the adsorption process of BHA and OPA on ilmenite surface and the full XPS spectra of pure ilmenite and ilmenite treated with BHA or OPA are shown in Fig. 7.

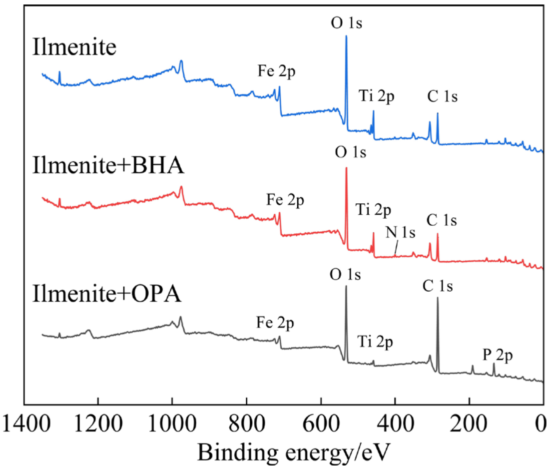

Fig. 7 Full XPS spectra of pure ilmenite and ilmenite treated with BHA or OPA

Figure 7 indicated that the N1s peak and P2p peak appeared on ilmenite spectra after interaction with BHA and OPA, respectively, indicating the adsorption of collector on ilmenite surface. As affected by collector adsorption, the changes in binding energies and atomic fractions of elemental C, O, P, N, Fe, and Ti on ilmenite surface are summarized in Table 2 (BHA) and Table 3 (OPA), respectively.

Table 2 Binding energy (E_b) and atomic fraction (x) of elements on ilmenite surface before and after BHA treatment

Element	Ilmenite		Ilmenite+BHA		ΔE_b/	Δx/
	E_b/eV	x/%	E_b/eV	x/%	eV	%
C 1s	284.8	21.0	284.8	25.2	0	4.2
O 1s	531.0	64.1	530.6	58.4	−0.4	−5.7
P 2p	–	–	–	–	–	–
N 1s	–	–	400.8	2.1	400.8	2.1
Fe 2p	710.9	8.5	710.8	8.2	−0.1	−0.3
Ti 2p	458.2	4.6	458.2	6.1	0.0	1.5

Table 3 Binding energy and atomic fraction of elements on ilmenite surface before and after OPA treatment

Element	Ilmenite		Ilmenite+OPA		ΔE_b/	Δx/
	E_b/eV	x/%	E_b/eV	x/%	eV	%
C 1s	284.8	21.0	284.8	56.7	0	35.7
O 1s	531.0	64.1	531.7	31.2	0.7	−32.9
P 2p	–	–	133.6	7.4	133.6	7.4
N 1s	–	–	–	–	–	–
Fe 2p	710.9	8.5	710.6	3.2	−0.3	−5.3
Ti 2p	458.2	4.6	458.4	1.3	0.2	−3.3

Table 2 demonstrated that after BHA treatment, the atomic fraction of C increased by 4.2%, whereas the contents of O and Fe decreased by 5.7% and 0.3%. Furthermore, a new element N at 400.8 eV appeared on ilmenite surface, indicating the adsorption of BHA on ilmenite surface [18]. Previous studies have shown that the adsorption of BHA onto ilmenite surface was a chemical process [35,36]. The changes in the binding energy of Fe 2p and Ti 2p were 0.1 and 0.0 eV, respectively, indicating that the chemisorption of BHA to Fe (active site) on ilmenite surface was weak. As indicated in Table 3, the atomic fraction of C on ilmenite surface increased by 35.7% following OPA treatment, and meanwhile, the newly emerged P element on ilmenite surface had a relative content of 7.4%. The contents of Fe and Ti fell by 5.3% and 3.3%, respectively. All these showed that, following OPA treatment, the changes in atomic fraction were larger than those after BHA treatment. Moreover, the changes in the binding energy of Fe 2p and Ti 2p after OPA treatment were 0.3 and 0.2 eV, respectively, which were much more obvious than those after BHA treatment. This revealed that the chemisorption between Fe and Ti sites on ilmenite surface with OPA species was stronger than that of BHA, which was consistent with the results of micro-flotation tests and adsorption amount measurements.

A high-resolution XPS spectra of Fe $2p_{3/2}$ is shown in Fig. 8. On the surface of pure ilmenite, the binding energies of ferrous and ferric species are at 710.68 and 713.48 eV, respectively [37,38]. The binding energies of ferrous and ferric on ilmenite surface changed after treatment with BHA and OPA. The peak changes in ferrous and ferric binding energies on ilmenite surface after BHA treatment were 0.01 and 0.86 eV, respectively. Comparatively, the peak changes in ferrous and ferric binding energies after OPA treatment were 0.03 and 1.08 eV, respectively, showing stronger chemisorption between OPA and Fe sites on the surface of ilmenite. Titanium on ilmenite surface was composed of Ti—O—Ti and Ti—O—Fe, as demonstrated in the high-resolution Ti $2p_{3/2}$ spectra in Fig. 8, with matching peaks of 458.08 and 458.88 eV, respectively [39,40]. The peak changes in Ti—O—Ti and Ti—O—Fe binding energies on the surface of ilmenite after BHA treatment were 0.06 and 0.1 eV, respectively. Comparatively, the peak changes in Ti—O—Ti and Ti—O—Fe binding energies after OPA treatment were 0.25 and 1.0 eV, respectively, demonstrating stronger chemisorption between OPA and Ti sites on ilmenite surface as well.

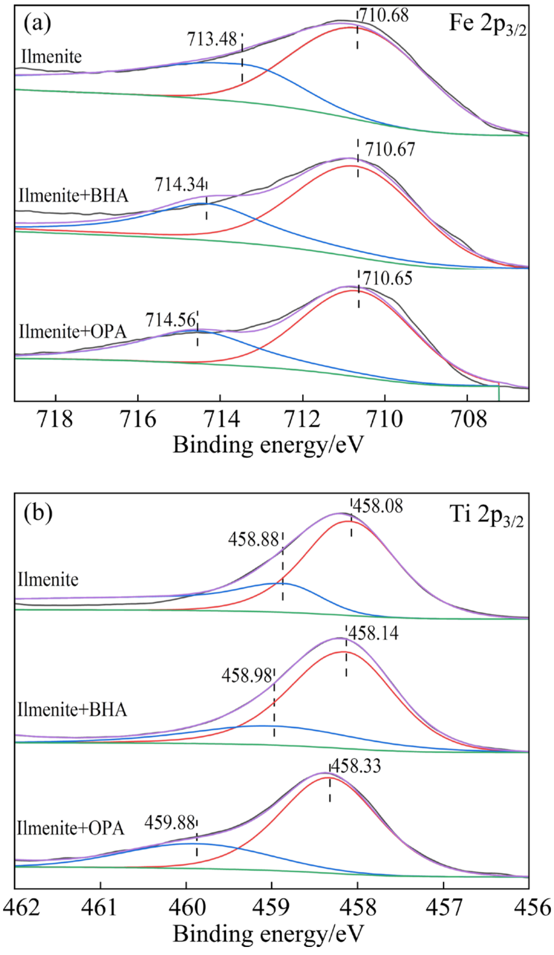

Fig. 8 High-resolution XPS spectra of Fe $2p_{3/2}$ (a) and Ti $2p_{3/2}$ (b)

3.5 DFT analysis

To better understand the adsorption mechanism of collectors onto ilmenite surface at the atomic level, adsorption models of BHA (molecule form) and OPA (anion form) on ilmenite (104) surface were constructed and associated adsorption energies (an effective index for evaluating the adsorption strength of collector on mineral surface) were calculated. The easier the collector adsorbs on mineral surface, the greater the chemical connection between the collector and mineral surface, and the lower the adsorption energy will be [41]. The adsorption configuration is more stable in adsorption model if the bond length between the collector and the active sites on mineral surface is shorter [42]. The adsorption model and adsorption energy of BHA and OPA^- on the commonly exposed surface of ilmenite (104) are shown in Fig. 9 and Table 4, respectively.

It can be seen from Fig. 9 and Table 4 that the bond length between active sites (titanium and/or iron) on ilmenite surface and oxygen of the functional group of OPA was much shorter than that of BHA. Moreover, the adsorption energy of OPA (−463.25 and −483.69 kJ/mol) was substantially lower than that of BHA (−235.96 and −197.35 kJ/mol). All these theoretical calculations confirmed that OPA was much easier to adsorb onto ilmenite surface and the associated adsorption configuration was more stable than BHA.

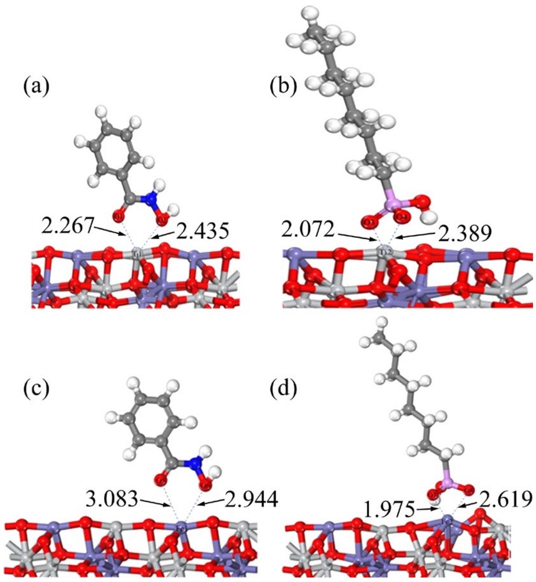

Fig. 9 Adsorption configurations of BHA (a, c) and OPA^- (b, d) on ilmenite (104) surface with active sites of iron and titanium: (a, b) Ti; (c, d) Fe

Table 4 Adsorption energy and bond length of BHA and OPA^- on ilmenite (104) surface

Reagent species	Bond	Bond length/ Å	Energy/ ($kJ\cdot mol^{-1}$)
BHA	Ti—O	2.267/2.435	−235.96
	Fe—O	3.083/2.944	−197.35
OPA^-	Ti—O	2.072/2.389	−463.25
	Fe—O	1.975/2.619	−483.69

4 Conclusions

(1) OPA exhibited better collecting ability and selectivity than BHA, especially within the strong-medium acidic conditions (pH 2−5), and the optimal flotation pH for OPA was around 3.0. Flotation experiments of mixed binary ilmenite/titanaugite minerals further confirmed that OPA can selectively collect ilmenite from titanaugite in the strongly acidic pulp.

(2) Adsorption amount measurements indicated that more OPA could adsorb onto ilmenite surface in comparison with BHA, and only tiny OPA/BHA adsorbed onto titanaugite surface. XPS tests revealed that the adsorption of OPA onto ilmenite surface was a chemical process and such interaction between OPA and ilmenite was stronger (higher changes in binding energies and relative contents of active sites on ilmenite surface) than that of BHA.

(3) DFT calculations further indicated that compared to BHA, OPA was much easier to adsorb onto ilmenite surface and the adsorption configuration was more stable (with shorter bond length and lower adsorption energy). In conclusion, OPA can selectively collect ilmenite under the strongly acidic conditions, and this provides a reference for new collector design so that the newly developed collector can be more suitable to float ilmenite from gangues on an industrial scale.

CRediT authorship contribution statement

Pan CHEN: Conceptualization, Investigation, Writing − Original draft; **Jia-yan LIU:** Investigation, Methodology, Analysis; **Ji-hua ZHAI:** Conceptualization, Methodology, Supervision, Writing − Review & editing; **Yao-hui YANG:** Supervision, Writing − Review & editing; **Wei SUN:** Formal analysis, Writing − Review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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酸性矿浆中以辛基膦酸作捕收剂选择性浮选分离钛铁矿和钛辉石

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摘　要：引入辛基膦酸(OPA)作为钛铁矿浮选的新型捕收剂，并与传统螯合捕收剂苯甲基羟肟酸(BHA)进行比较。单矿物浮选实验表明，OPA 是一种在酸性条件下(最佳 pH 值约为 3)从钛辉石中分离钛铁矿的高效选择性 捕收剂，吸附量测试也证实如此。X 射线光电子能谱(XPS)测试结果表明，OPA 在钛铁矿表面的化学吸附作用比 BHA 更强。溶液化学组分图分析表明，OPA 在 pH 为 3.0 时可以很好地解离，并且主要以阴离子形式存在。DFT 计算进一步证实，与 BHA 相比，OPA 更容易吸附在钛铁矿表面，键长更短，吸附能更低。因此，在强酸性矿浆溶液中，OPA 对钛铁矿保持了良好的捕收能力和选择性，这对新型捕收剂的设计和开发有一定的借鉴作用。

关键词：钛铁矿；钛辉石；浮选分离；辛基膦酸

(Edited by Xiang-qun LI)