Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 34(2024) 995−1002

Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Flotation behavior of ilmenite using 1,10-phenanthroline as novel collector

Pan CHEN[1], Jia-yan LIU[1], Wei-si LI[1,2], Ji-hua ZHAI[3], Yao-hui YANG[2]

1. School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China;
2. Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Sciences, Chengdu 610000, China;
3. College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China

Received 9 October 2022; accepted 28 February 2023

Abstract: 1,10-phenanthroline (Phen) was introduced as the novel collector for the selective separation of ilmenite from titanaugite. Micro-flotation showed that Phen was a more effective collector for ilmenite flotation from pH 2 to 12 compared with benzohydroxamic acid (BHA), and the maximum increase in ilmenite recovery (~20%) was observed at pH 6. Titanaugite kept at very low level of floatability (recovery < 5%) during micro-flotation test. FTIR and XPS analyses indicated that Phen and BHA adsorbed onto ilmenite surface via chemisorption and the interaction between Phen and ilmenite was intenser than that of BHA. XPS results also showed that Phen reacted with both iron (ferrous and ferric) and titanium on the ilmenite surface. A five membered ring structure appeared to form during the adsorption of Phen onto the ilmenite surface.

Key words: ilmenite; 1,10-phenanthroline; flotation; benzohydroxamic acid

1 Introduction

Titanium has been widely used in paints, aerospace, aviation, alloy production, and medical and chemical industries due to its characteristics of light weight, high strength, strong corrosion resistance and stable chemical properties [1−5]. Although the 9th abundant element in the Earth's crust, titanium is regarded as a rare metal due to its wide distribution across the globe and the difficulty in its upgrading/processing from titanium containing ores [6]. Ores containing ilmenite and rutile are two main sources of industrial and market value for titanium processing. Specially, ilmenite contributes to about 90% of the global consumption of titanium minerals, and the gross ilmenite reserves are more than 14 times higher than rutile [7]. Therefore, titanium industry is and will continue to be primarily reliant on ilmenite resources.

Many technologies have been developed in mineral processing of ores containing ilmenite, such as gravity separation, magnetic separation, electrostatic separation and flotation [8,9]. With deep mining, the ores containing ilmenite have gradually become lean and fine, and flotation has been the requisite technique for ilmenite upgrading [10−13]. The main gangue associated with ilmenite in Panzhihua city, China, is titanaugite, and it is believed that ilmenite and titanaugite have similar physical and chemical properties on surface [14−17], which increases the difficulty in their selective separation. Therefore, a collector with good selectivity as well as high collecting ability is required in ilmenite flotation.

Fatty acids/soaps are widely used in ilmenite flotation but the major drawback of them is their unsatisfactory selectivity. With interests of the

---

Corresponding author: Ji-hua ZHAI, Tel: +86-13549641056, E-mail: jihuazhai@cdut.edu.cn; Yao-hui YANG, E-mail: peacefulsw@163.com
DOI: 10.1016/S1003-6326(23)66448-9

strong bonding ability and high selectivity, chelating collector can be used to improve the separation efficiency of ilmenite from gangues. Benzohydroxamic acid (BHA) is one of the common chelating collectors in flotation of oxide ores and its performance (single use or combined use with other collectors) in ilmenite flotation has been reported as well [18−21]. Some other developed chelating collectors for ilmenite flotation within recent years include dodecylimino-dimethylenediphosphoinc acid [22], *α*-hydroxyoctyl phosphonic acid [12] and 2-ethyl-2-hexenoic hydroxamic acid [23]. In addition, coffee oil [24], undecyl propyl ether amine [25], styrene phosphonic acid [26], succinamate and phosphoric acid esters [27], were also the reported collectors for ilmenite flotation. 1,10-phenanthroline (Phen) has a structure that can coordinate with metal ions and thus has the potential to be used as the collector for ilmenite flotation. This has been supported by the important role of Phen in coordination chemistry, where Phen is used as the bidentate ligand for many transition metal ions with the formation of complex in a $[M(Phen)]^{2+}$ pattern [28−30]. However, research on the use of Phen as the collector for ilmenite flotation has not been studied.

Therefore, the present study focused on the evaluation of using Phen as the novel collector for ilmenite flotation separation from titanaugite. The performance of Phen was studied by micro-flotation tests and associated mechanism was explored via Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) analyses as well as density functional theory (DFT) calculation. It is hoped from this study that a more efficient chelating collector, in comparison with BHA (a widely used chelating collector in oxide ores processing), can be found for ilmenite flotation.

2 Experimental

2.1 Materials

The raw ore samples were obtained from Panzhihua area, Sichuan Province, China. To obtain the high-purity minerals of ilmenite and titanaugite, they were repeatedly purified by magnetic separation and gravity separation, followed by screening. The samples with a size fraction of 38−74 μm were employed for the flotation tests. The XRD and XRF results of ilmenite and titanaugite used in this work (Fig. 1 and Table 1) show that the purity of ilmenite and titanaugite samples is high enough to meet the requirement for micro-flotation and subsequent tests.

In the flotation test of pure minerals, Phen and BHA, which were obtained from Tokyo Chemical Industry, were used as collectors. Hydrochloric acid and sodium hydroxide solutions were used as the pH regulators. All the reagents were analytically

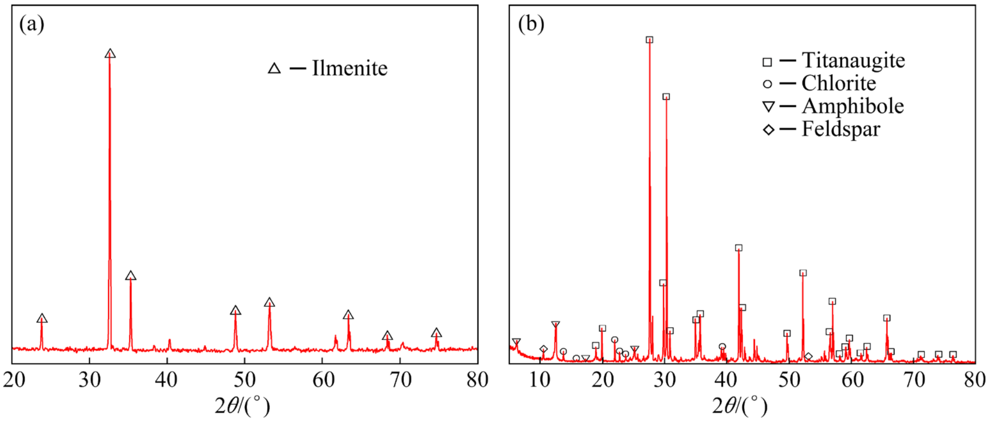

Fig. 1 XRD patterns of ilmenite (a) and titanaugite (b) used in this study

Table 1 Major chemical compositions of purified ilmenite and titanaugite samples (Le: other elements, mainly as O, V, S, etc.) (wt.%)

Sample	Ti	Fe	Ca	Mg	Al	Si	Mn	Le
Ilmenite	28.86	29.78	0.60	2.85	0.70	1.56	0.47	35.18
Titanaugite	2.08	9.81	10.50	7.27	4.69	19.84	0.16	45.65

pure. Deionized water (resistivity 18.3 MΩ·cm) was used throughout the test.

2.2 Micro-flotation

The flotation test was carried out in an XFG tank flotation machine with a volume (flotation cell) of 40 mL, and the impeller speed was controlled at 1700 r/min. For each experiment, 2 g mineral samples and 35 mL of deionized water were added to the flotation cell for mixing and stirring for 1 min. The slurry was then rinsed with hydrochloric acid or sodium hydroxide solution to adjust the pH to the designed value of 2−12. The required amount of collector was added, and the mixture was stirred for 3 min. After 3 min of flotation, the scraped foam products (concentrate) and unfloated (tailing) particles were dried and weighed to calculate the recovery. The reported results are the average recovery of three independent tests.

2.3 FTIR test

Ilmenite samples used for micro-flotation were first ground to be less than 2 μm. For each test, 2 g fine ilmenite samples were used and placed into a 40 mL flotation cell, and then mixed with 35 mL deionized water at 1700 r/min. The slurry was then adjusted to pH 6 and subsequently 2.0×10^{-4} mol/L Phen or BHA was added to the slurry followed by conditioning for 30 min. The slurry was then filtered to obtain the conditioned ilmenite solids which were processed by washing four times with deionized water. The solids were then dried in a vacuum environment at 55 °C for 24 h. Finally, the FTIR spectra of Phen, BHA, pure ilmenite and ilmenite treated with Phen and BHA were recorded by a Bruker Alpha (Thermo, USA) FTIR spectrophotometer which employed the pressed pellet mode with KBr for sample preparation.

2.4 XPS test

A Thermo Scientific ESCALAB 250Xi instrument manufactured by the Thermo Fisher Scientific Co., USA, was used to conduct the XPS measurement. Samples for XPS tests were prepared in the same way that was used for FTIR tests. As for XPS measurement, the take-off angle was 90° and the vacuum pressure was controlled within $133.322\times(10^{-9}-10^{-8})$ Pa. The binding energies recorded were referred to the neutral C 1s peak (284.8 eV) for compensation of potential surface charging effects. The software of Thermo Scientific Avantage 4.52 was used to collect and process all the data used in this study.

3 Results and discussion

3.1 Flotation results

Flotation behavior of ilmenite (Fig. 2) shows that Phen has better collecting ability than BHA throughout the studied pH range. Ilmenite recovery using Phen as the collector increased sharply from pH 2 to 6, reached the plateau (maximum at about 73%) from pH 6 to 8, and then decreased when pH>8. Similar trend was found as well for ilmenite when using BHA as the collector, with the maximum of about 55% at pH 8. Therefore, Phen can remarkably enhance ilmenite recovery than BHA (about 20% higher, in Fig. 2). However, no significant change in titanaugite flotation recovery (all below 6%) was observed over the entire pH range when using Phen or BHA as the collector (Fig. 2), although BHA indicated slightly higher recovery of titanaugite than Phen.

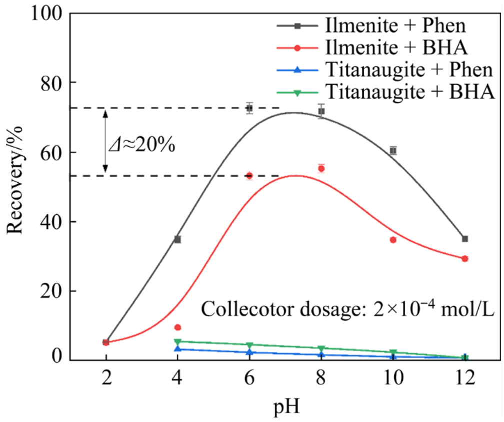

Fig. 2 Flotation recovery of ilmenite and titanaugite as function of pH (Phen and BHA concentration of 2×10^{-4} mol/L, respectively)

Phen and BHA concentration has obvious influence on ilmenite recovery but quite limited effect on titanaugite recovery (at pH 6, see Fig. 3). Flotation recovery of ilmenite enhanced remarkably with the increase of Phen or BHA concentration, and the recovery reached the maximum and kept stable when Phen concentration was over 2×10^{-4} mol/L. To achieve the similar ilmenite recovery, BHA concentration should be over 4×10^{-4} mol/L (Fig. 3). Therefore, flotation tests showed that Phen was a better collector for ilmenite upgrading by flotation than BHA.

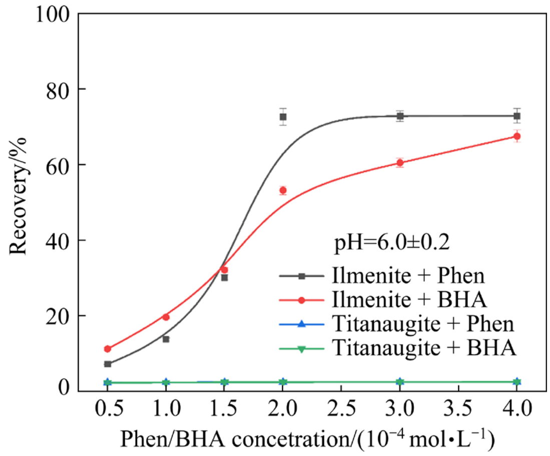

Fig. 3 Effect of collector concentration on recovery of ilmenite and titanaugite

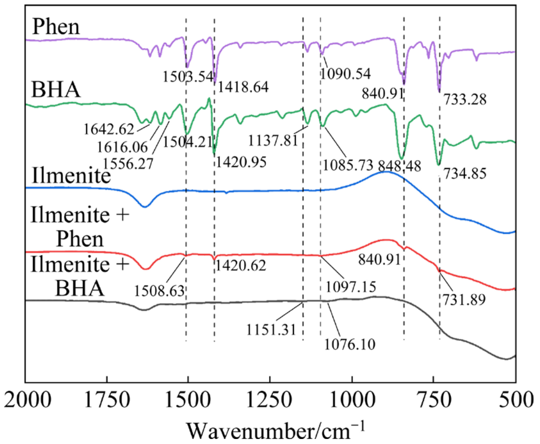

Fig. 4 FTIR spectra of ilmenite before and after Phen or BHA treatment

3.2 FTIR analysis

The FTIR spectra of Phen, ilmenite and ilmenite treated with Phen at pH 6 are presented in Fig. 4. The Phen bands at 1503.54, 1090.54 , and 733.28 cm^{-1} are attributed to the C═N symmetric tensile vibration, C—C vibration and out-of-plane bending vibration of C—H, respectively [31,32]. After being treated with Phen, new bands of ilmenite emerged at 1508.63, 1420.62, 1097.15, 840.91 and 731.89 cm^{-1}. Specially, the new bands at 1508.63 cm^{-1} due to the C═N symmetric tensile vibration, at 1097.15 cm^{-1} due to C—C vibration and at 731.89 cm^{-1} due to the out-of-plane bending vibration of C—H shifted by 5.09, 6.61, and 1.39 cm^{-1}, respectively, compared with the FTIR spectrum of Phen. These changes in FTIR spectra of ilmenite treated with Phen indicated that Phen chemisorbed onto the ilmenite surface.

Similarly, Fig. 4 also gives the FTIR spectra of BHA and ilmenite treated with BHA at pH 6.0. The characteristic BHA bands at 1556.27 and 1504.21 cm^{-1} are assigned to the vibration of the benzene ring [18,33]. Additionally, the bands at 1642.62, 1616.06, 1137.81 and 1085.73 cm^{-1} are resulted from C═N, C═O, C—N and N—O stretching vibrations, respectively [18,33,34]. After treatment with BHA, new peaks of ilmenite appeared at 1151.31 and 1076.10 cm^{-1}, which corresponded to the peaks of BHA spectrum at 1137.81 and 1085.73 cm^{-1}, respectively. The shifts in these peaks (13.5 and 9.63 cm^{-1}, respectively) confirmed that BHA was chemically adsorbed on the ilmenite surface as well.

FTIR results confirmed the chemisorption of both Phen and BHA on ilmenite, and Fig. 4 was also indicative that the newly formed bands of ilmenite treated with Phen were intenser than BHA. Moreover, more characteristic bands of Phen appeared on spectra of ilmenite treated with Phen in comparison with that of BHA. Hence, more Phen was assumed to adsorb onto ilmenite surface than BHA and thus resulted in a better flotation performance of Phen (Figs. 2 and 3).

3.3 XPS analysis

In order to further explore the adsorption mechanism of Phen on ilmenite surface, XPS analysis was performed. Table 2 gives the relative contents of elements on ilmenite surface before and after treatment with Phen and BHA.

Table 2 Relative contents of elements on ilmenite surfaces (at.%)

Sample	C 1s	O 1s	N 1s	Fe 2p	Ti 2p
Ilmenite	26.4	56.8	0	10.2	6.0
Ilmenite + Phen	31.0	51.8	1.6	9.1	6.4
Ilmenite + BHA	27.2	54.6	1.3	10.2	6.7

Table 2 shows that carbon content on ilmenite surface increased by 4.6%, from 26.4% to 31.0% after ilmenite was treated with Phen, and the content of nitrogen increased by 1.6% as well. Meanwhile, the contents of iron and oxygen on the ilmenite surface decreased by 1.1% and 5.0%, respectively. After BHA treatment, the contents of carbon and titanium increased by 0.8% and 0.7%, respectively. Meanwhile, nitrogen content increased by 1.3% whereas oxygen content decreased by 2.2%. These changes in surface atomic contents of ilmenite confirmed the adsorption of Phen and BHA onto ilmenite surface, and meanwhile, more Phen can adsorb onto ilmenite surface in compassion with BHA, which agrees well with their flotation behavior.

Table 3 lists the changes in binding energy of iron and titanium on ilmenite surface before and after Phen or BHA treatment. The binding energy of Fe 2p shifted negatively by 0.4 eV after treatment with Phen, whereas 0.2 eV change was found for ilmenite treated with BHA. This change in Fe 2p binding energy indicates the chemical environmental change caused by the chemisorption of Phen and BHA onto ilmenite surface, and moreover, Phen appeared to be intenser than BHA. As for Ti 2p, the binding energy shifted negatively by 0.3 and 0.1 eV for ilmenite treated with Phen and BHA, respectively. This indicates that titanium can also serve as the active site using Phen as the collector.

Table 3 Binding energy of elements on ilmenite surface

Sample	Binding energy/eV				
	C 1s	O 1s	N 1s	Fe 2p	Ti 2p
Ilmenite	284.8	530.2	−	710.8	458.2
Ilmenite + Phen	284.8	530.1	399.5	710.4	457.9
Ilmenite + BHA	284.8	530.3	400.5	710.6	458.1

Sample	Chemical shift/eV				
	C 1s	O 1s	N 1s	Fe 2p	Ti 2p
Ilmenite	−	−	−	−	−
Ilmenite + Phen	−	−0.1	−	−0.4	−0.3
Ilmenite + BHA	−	0.1	−	−0.2	−0.1

The Fe 2p peak fitting diagram of ilmenite before and after Phen treatment is shown in Fig. 5. The Fe 2p peak is generally divided into two main peaks, namely, Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$ [35,36], and more specifically, two valence states of Fe(II) and Fe(III) were analyzed. That is, the binding energies at 710.56 and 723.65 eV in Fig. 5 are Fe(II) of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively; the binding energies at 714.16 and 727.26 eV are Fe(III) of Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$, respectively. After treatment with Phen, the binding energies of Fe(II) and Fe(III) on ilmenite surface have shifted correspondingly: Fe(II) and Fe(III) belonging to Fe 2p$_{3/2}$ changed 0.37 eV, and those of Fe(II) and Fe(III) belonging to Fe 2p$_{1/2}$ shifted 0.32 and 0.37 eV, respectively. On the basis of such binding energy change, both Fe(II) and Fe(III) on ilmenite surface are the active sites and react with Phen.

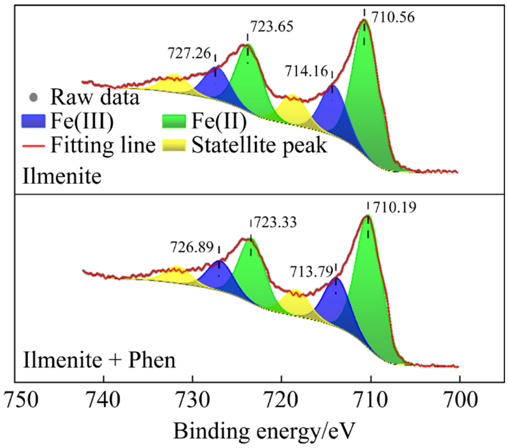

Fig. 5 High-resolution XPS spectra of Fe 2p

The peak fitting diagram of Ti 2p spectra before and after Phen treatment is shown in Fig. 6. The titanium on ilmenite surface is considered with two chemical environments: Ti−O−Fe and Ti−O−Ti [37,38]. Before Phen treatment, the binding energies were 458.15 and 463.78 eV for Ti−O−Ti of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, and 459.48 and 465.18 eV for Ti−O−Fe of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$, respectively. After treatment with Phen, the binding energy shifts of Ti−O−Ti and Ti−O−Fe on Ti 2p$_{3/2}$ were 0.28 and 0.10 eV, respectively, while those of Ti−O−Ti and Ti−O−Fe on Ti 2p$_{1/2}$ were 0.20 and 0.55 eV, respectively. Therefore, it was further confirmed that titanium on ilmenite surface was also the active site for Phen adsorption.

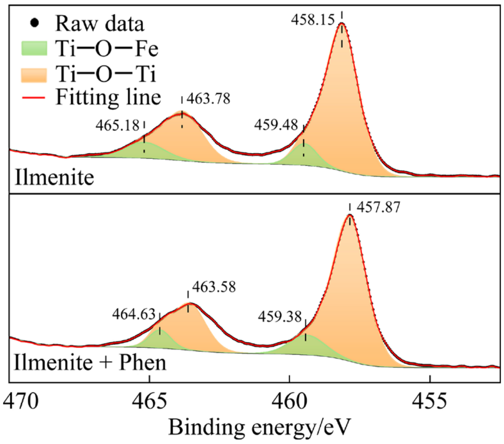

Fig. 6 High-resolution XPS spectra of Ti 2p

3.4 Adsorption model

Results of the micro-flotation tests indicated that Phen possessed better collection ability to ilmenite compared with BHA, and the preferable pH value for the flotation was 6.0. FTIR and XPS analyses confirmed the chemisorption of Phen onto ilmenite surface, and XPS results further showed that iron and titanium were the active sites on ilmenite surface. Figure 7 gives optimized geometries and Mulliken charges of Phen. The initial molecular structure of the collector molecule was optimized by PM3 (Parameterized Model Revision 3) method. The obtained geometries were further optimized and calculated through DFT methods in aqueous solutions at the B3LYP/6-31G level in Gaussian 03.

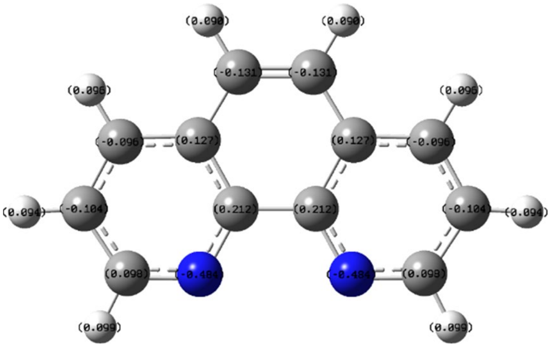

Fig. 7 Optimized geometries and Mulliken charges of Phen at B3LYP/6-31G level

Figure 7 showed both nitrogen atoms charged negatively at 0.484 electron, indicating that N atoms in Phen molecules had certain electronic supply abilities. Therefore, it was assumed that nitrogen in Phen molecular structure reacted with iron (ferrous and ferric) and titanium on ilmenite surface to form a five membered ring structure. A schematic model for Phen adsorption onto ilmenite surface was thus proposed as shown in Fig. 8. This process was controlled by chemisorption as confirmed by FTIR and XPS. Physical adsorption as a function of electrostatic attraction was unlikely to happen for such process as the isoelectric point of ilmenite usually situated at about pH 5 [8,39]. The optimum pH for ilmenite flotation at pH 6 using Phen as the collector meant the negatively charged ilmenite surface under such condition, which was repulsed to negatively charged nitrogen atoms of Phen.

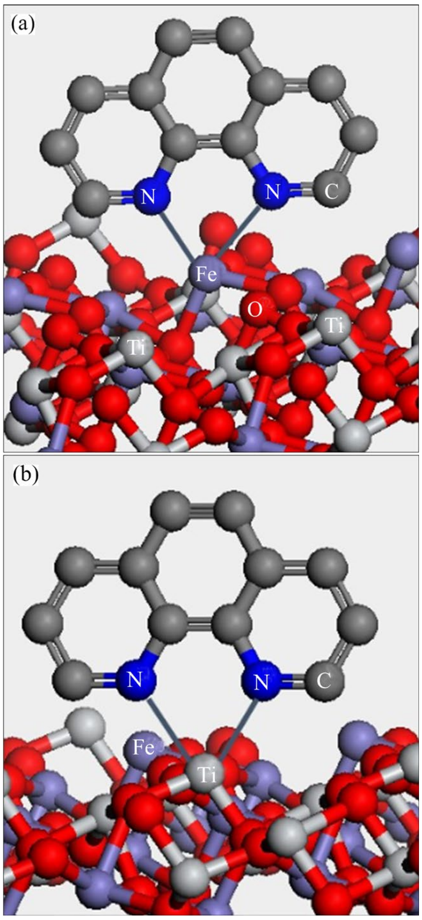

Fig. 8 Schematic of adsorption model for Phen on Fe (a) and Ti (b) active sites on ilmenite surface at pH 6

4 Conclusions

(1) Phen was a more effective collector for ilmenite flotation compared to BHA, which is widely used in flotation of oxide ores. Titanaugite remained very low levels of floatability (flotation recovery <5%) when using Phen and BHA as the collectors. An increase up to ~20% in ilmenite recovery using Phen as the collector was observed at pH 6 when compared with that of BHA.

(2) FTIR showed that Phen and BHA adsorbed onto ilmenite surface via chemisorption, and the newly formed bands of ilmenite treated with Phen was intenser than BHA. Moreover, more characteristic bands of Phen appeared on spectra of ilmenite treated with Phen in comparison with those of BHA.

(3) XPS further confirmed the chemisorption of Phen and BHA onto ilmenite surface, and Phen was intenser than BHA when reacted with active sites on ilmenite surface. Moreover, Phen could react with both iron and titanium (active sites) on

ilmenite surface and a formation of five membered ring structure was proposed by this study.

CRediT authorship contribution statement

Pan CHEN: Conceptualization, Literature reviewing, Writing − Original draft; **Jia-yan LIU:** Conducting flotation tests, Mechanism exploration, Writing − Review & editing; **Wei-si LI:** FTIR and XPS analysis, Writing − Review & editing; **Ji-hua ZHAI:** Conceptualization, Material acquisition, Writing − Review & editing; **Yao-hui YANG:** Conceptualization, Adsorption model 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.

Acknowledgments

The authors acknowledge the support of the National Natural Science Foundation of China (No. 52074357), and the National Key Research and Development Program of China (No. 2019YFC1803500).

References

[1] DU Yu-sheng, MENG Qing-you, YUAN Zhi-tao, MA Long-qiu, ZHAO Xuan, XU Yuan-kai. Study on the flotation behavior and mechanism of ilmenite and titanaugite with sodium oleate [J]. Minerals Engineering, 2020, 152: 106366.

[2] MEHDILO A, IRANNAJAD M, REZAI B. Effect of chemical composition and crystal chemistry on the zeta potential of ilmenite [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013, 428: 111−119.

[3] ZHAI Ji-hua, CHEN Pan, WANG Hong-bin, HU Yue-hua, SUN Wei. Flotability improvement of ilmenite using attrition-scrubbing as a pretreatment method [J]. Minerals, 2017, 7: 13.

[4] YAN Zheng-pei, ZHANG Ying, ZHENG Shi-li, ZHANG Yang, SUN Pei, SONG Zi-wei, SAFDAR F, QI Tao. Preparation of titanium mineral from vanadium titanomagnetite concentrates by hydrogen reduction and acid leaching [J]. Transactions of Nonferrous Metals Society of China, 2022, 32: 3099−3109.

[5] YAN Wen-gao, WANG Hua-ming, TANG Hai-bo, CHENG Xu, ZHU Yan-yan. Effect of Nd addition on microstructure and tensile properties of laser additive manufactured TC11 titanium alloy [J]. Transactions of Nonferrous Metals Society of China, 2022, 32: 1501−1512.

[6] WANG Shu-hong, LI Jin, WU Shu-zhuang, YAN Wen, HUANG Wei-xia, MIAO Li, CHEN Zhong. The distribution characteristics of rare metal elements in surface sediments from four coastal bays on the northwestern South China Sea [J]. Estuarine, Coastal and Shelf Science, 2016, 169: 106−118.

[7] USGS. Titanium statistics and information [EB/OL]. https://pubs.usgs.gov/periodicals/mcs2022/mcs2022-titanium-minerals.pdf2022.

[8] ZHAI Ji-hua, CHEN Pan, SUN Wei, CHEN Wei, WAN Si. A review of mineral processing of ilmenite by flotation [J]. Minerals Engineering, 2020, 157: 106558.

[9] MEHDILO A, IRANNAJAD M. Surface modification of ilmenite and its accompanied gangue minerals by thermal pretreatment: Application in flotation process [J]. Transactions of Nonferrous Metals Society of China, 2021, 31: 2836−2851.

[10] FAN Xian-feng, ROWSON N. Fundamental investigation of microwave pretreatment on the flotation of massive ilmenite ores [J]. Developments in Chemical Engineering and Mineral Processing, 2000, 8: 167−182.

[11] FAN Xian-feng, WATERS K, ROWSON N, PARKER D. Modification of ilmenite surface chemistry for enhancing surfactants adsorption and bubble attachment [J]. Journal of Colloid and Interface Science, 2009, 329: 167−172.

[12] LI Fang-xu, ZHONG Hong, ZHAO Gang, WANG Shuai, LIU Guang-yi. Adsorption of α-hydroxyoctyl phosphonic acid to ilmenite/water interface and its application in flotation [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016, 490: 67−73.

[13] SONG Quan-yuan, TSAI S C. Flotation of ilmenite using benzyl arsonic acid and acidified sodium silicate [J]. International Journal of Mineral Processing, 1989, 26: 111−121.

[14] ZHU Yang-ge. Research on the theory and technology of micro-fine ilmenite flotation [D]. Changsha: Central South University, 2011. (in Chinese)

[15] ZHU Yang-ge, ZHANG Guo-fan, FENG Qi-ming, YAN Dai-cui, WANG Wei-qing. Effect of surface dissolution on flotation separation of fine ilmenite from titanaugite [J]. Transactions of Nonferrous Metals Society of China, 2011, 21: 1149−1154.

[16] FANG Shuai, XU Long-hua, WU Hou-qin, SHU Kai-qian, XU Yan-bo, ZHANG Zhen-yue, CHI Ru-an, SUN Wei. Comparative studies of flotation and adsorption of Pb (II)/benzohydroxamic acid collector complexes on ilmenite and titanaugite [J]. Powder Technology, 2019, 345: 35−42.

[17] TIAN Jia, XU Long-hua, YANG Yao-hui, LIU Jing, ZENG Xiao-bo, DENG Wei. Selective flotation separation of ilmenite from titanaugite using mixed anionic/cationic collectors [J]. International Journal of Mineral Processing, 2017, 166: 102−107.

[18] XU Long-hua, TIAN Jia, WU Hou-qin, LU Zhong-yuan, YANG Yao-hui, SUN Wei, HU Yue-hua. Effect of Pb^{2+} ions on ilmenite flotation and adsorption of benzohydroxamic acid as a collector [J]. Applied Surface Science, 2017, 425: 796−802.

[19] YANG Yao-hui, XU Long-hua, LIU Ya-chuan, HAN Yue-xin. Flotation separation of ilmenite from titanaugite using mixed collectors [J]. Separation Science and Technology, 2016, 51: 1840−1846.

[20] GAO Zhi-yong, JIANG Zhe-yi, SUN Wei, GAO Yue-sheng. Typical roles of metal ions in mineral flotation: A review [J]. Transactions of Nonferrous Metals Society of China, 2021, 31: 2081−2101.

[21] LI Fang-xu, ZHOU Xiao-tong, LIN Ri-xiao. Flotation performance and adsorption mechanism of novel 1-(2-

hydroxyphenyl)hex-2-en-1-one oxime flotation collector to malachite [J]. Transactions of Nonferrous Metals Society of China, 2020, 30: 2792−2801.

[22] GUAN Chang-ping, YIN Zhi-gang, ZHAI Ji-hua, HU Yue-hua, CHEN Pan, SUN Wei. Surface modification of ilmenite by a novel surfactant dodecylimino-dimethylenediphosphoinc acid and its sequent influence on ilmenite floatability [J]. Separation Science and Technology, 2020, 55: 358−368.

[23] XU Hai-feng, ZHONG Hong, TANG Qing, WANG Shuai, ZHAO Gang, LIU Guang-yi. A novel collector 2-ethyl-2-hexenoic hydroxamic acid: Flotation performance and adsorption mechanism to ilmenite [J]. Applied Surface Science, 2015, 353: 882−889.

[24] WANG Sen, XIAO Wei, MA Xiao, LI Jiu-zhou, CHEN Li-juan, YAO Hui. Analysis of the application potential of coffee oil as an ilmenite flotation collector [J]. Minerals, 2019, 9: 505.

[25] LIU Xing, HUANG Guang-yao, LI Cheng-xiu, CHENG Ren-ju. Depressive effect of oxalic acid on titanaugite during ilmenite flotation [J]. Minerals Engineering, 2015, 79: 62−67.

[26] ZHONG Kang-nien, CUI Lin. Influence of Fe^{2+} ions of ilmenite on its flotability [J]. International Journal of Mineral Processing, 1987, 20: 253−265.

[27] BULATOVIC S, WYSLOUZIL D M. Process development for treatment of complex perovskite, ilmenite and rutile ores [J]. Minerals Engineering, 1999, 12: 1407−1417.

[28] SAMMES P G, YAHIOGLU G. 1,10-Phenanthroline: A versatile ligand [J]. Chemical Society Reviews, 1994, 23: 327−334.

[29] SUMMERS L A. The phenanthrolines [M]// Advances in heterocyclic chemistry. Amsterdam: Elsevier, 1978: 1−69.

[30] BENCINI A, LIPPOLIS V. 1, 10-Phenanthroline: A versatile building block for the construction of ligands for various purposes [J]. Coordination Chemistry Reviews, 2010, 254: 2096−2180.

[31] SCHILT A, TAYLOR R. Infra-red spectra of 1: 10-phenanthroline metal complexes in the rock salt region below 2000 cm^{-1} [J]. Journal of Inorganic and Nuclear Chemistry, 1959, 9: 211−221.

[32] ZHENG Xiao-ling, ZHANG Han-hui, WEI Ke-mei. Synthesis and spectroscopic characterization of lanthanum and glycine amino acid with 1,10-phenanthroline [J]. Spectroscopy and Spectral Analysis, 2000, 20: 852−854. (in Chinese)

[33] HAN Gui-hong, DU Yi-fan, HUANG Yan-fang, YANG Shu-zhen, WANG Wen-juan, SU Sheng-peng, LIU Bing-bing. Efficient removal of hazardous benzohydroxamic acid (BHA) contaminants from the industrial beneficiation wastewaters by facile precipitation flotation process [J]. Separation and Purification Technology, 2021, 279: 119718.

[34] MENG Qing-you, YUAN Zhi-tao, YU Li, XU Yuan-kai, DU Yu-sheng. Study on the activation mechanism of lead ions in the flotation of ilmenite using benzyl hydroxamic acid as collector [J]. Journal of Industrial and Engineering Chemistry, 2018, 62: 209−216.

[35] ABAZOVIĆ N D, MIRENGHI L, JANKOVIĆ I A, BIBIĆ N, ŠOJIĆ D V, ABRAMOVIĆ B F, ČOMOR M I. Synthesis and characterization of rutile TiO_2 nanopowders doped with iron ions [J]. Nanoscale Research Letters, 2009, 4: 518−525.

[36] SILVEIRA J E, PAZ W S, GARCIA-MUNOZ P, ZAZO J A, CASAS J A. UV-LED/ilmenite/persulfate for azo dye mineralization: The role of sulfate in the catalyst deactivation [J]. Applied Catalysis B: Environmental, 2017, 219: 314−321.

[37] GUO Shi-mei, LIU Jiu-rong, QIU Song, WANG Yi-ran, YAN Xing-ru, WU Nan-nan, WANG Shen-yu, GUO Zhan-hu. Enhancing electrochemical performances of TiO_2 porous microspheres through hybridizing with $FeTiO_3$ and nanocarbon [J]. Electrochimica Acta, 2016, 190: 556−565.

[38] PHOOHINKONG W, PAVASUPREE S, MEKPRASART W, PECHARAPA W. Synthesis of low-cost titanium dioxide-based heterojunction nanocomposite from natural ilmenite and leucoxene for electrochemical energy storage application [J]. Current Applied Physics, 2018, 18: S44−S54.

[39] CHEN Pan, ZHAI Ji-hua, SUN Wei, HU Yue-hua, YIN Zhi-gang. The activation mechanism of lead ions in the flotation of ilmenite using sodium oleate as a collector [J]. Minerals Engineering, 2017, 111: 100−107.

钛铁矿在捕收剂 1,10-菲罗啉作用下的浮选行为

陈 攀 [1]，刘佳燕 [1]，李维斯 [1,2]，翟计划 [3]，杨耀辉 [2]

1. 中南大学 资源加工与生物工程学院，长沙 410083；
2. 中国地质调查局 成都矿产综合利用研究所，成都 610000；
3. 成都理工大学 材料与化学化工学院，成都 610059

摘　要：引入 1,10-菲罗啉(Phen)作为钛铁矿与钛辉石选择性分离的新型捕收剂。浮选实验表明，与苯甲羟肟酸(BHA)相比，在 pH 2~12 之间，Phen 是钛铁矿浮选更加有效的捕收剂，并且在 pH 6 时钛铁矿的回收率提高最大(约为 20%)。在浮选过程中，钛辉石的可浮性保持在非常低的水平(回收率<5%)。FTIR 和 XPS 分析表明，Phen 和 BHA 以化学吸附的方式吸附在钛铁矿表面，并且钛铁矿与 Phen 之间的相互作用比 BHA 更强。XPS 结果还表明，Phen 在钛铁矿表面与铁(亚铁和铁)和钛发生反应，在 Phen 吸附到钛铁矿表面的过程中形成五元环结构。

关键词：钛铁矿；1,10-菲罗啉；浮选；苯甲羟肟酸

(Edited by Xiang-qun LI)