

## Flotation of niobite, fersmite, and ilmenorutile

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**Abstract:** The flotation of niobite, fersmite, and ilmenorutile was studied using 3 collectors with various concentration and pulp pH. The collecting property of different representative collectors was investigated. Experimental results show that diphosphonic acid is an effective collector for valuable niobium-containing minerals. A flotation recovery of 90.87%-91.7% is obtained with 75 mg/L diphosphonic acid at pH 2-4. The chemical adsorption of diphosphonic acid on these 3 minerals' surface might lead to the high recovery efficiency of the minerals, which is proved by IR and X-ray photoelectron spectroscopy spectra.

**Key words:** flotation; collector; diphosphonic acid; niobite; fersmite; ilmenorutile

### 1. Introduction

Niobite, fersmite, and ilmenorutile are 3 important niobium-containing industrial minerals. The separation of niobium minerals from its gangues is important for their further exploitation. Flotation is a cost-effective mineral processing method and is widely used to enrich niobium-containing minerals. Other methods, such as gravity concentration and magnetic separation, are also applied. However, recovery and concentrate grade from the latter methods are far from satisfactory [1].

Highly selective collectors have been developed recently to enrich niobium-bearing minerals, which has resulted in several unique flotation characteristics. The phosphoro-organic compounds based on diphosphonic acid derivatives have been proposed as collectors for the flotation of the complex mineral assemblages. Their high efficiency has been demonstrated for these minerals [2-4]. A family of chelating agents, that is, hydroxamic acids, has been tested extensively for flotation of rare earth minerals [5-6]. In selective flotation of cassiterite finely disseminated in complex ores, styrolphosphonic acid has shown to be an effective collector [7]. Thus, alkyl and aryl arsenic acids, phosphonic acids, TF-279, and hydroxamic acids are considered to be the typical collectors for niobium-containing minerals, which were used in this study [8-15].

In our previous studies [8-9, 15-17], different collectors and depressants have been studied in three niobium-containing systems. These systems are fersmite/limonite-nephelite-dolomite, ilmenorutile/fluorite-hematite, and niobite/dolomite, respectively. This paper continued the study of the flotation of niobite-bearing mineral by using collectors of benzyl arsenic acid (BAA), diphosphonic acid (DA), and C<sub>7-9</sub> alkyl hydroxamic acid (AHA) with various concentration and pulp pH. The purpose was to find out the best collector for the 3 minerals. The adsorption mechanism of the best collector on the 3 niobium-containing minerals' surface was studied by IR and X-ray photoelectron spectroscopy (XPS).

### 2. Experimental

#### 2.1. Preparation of niobium-containing minerals

Preparation of these niobium-containing minerals was necessary for the study of floatability. Table 1 shows the purifying process used for different minerals and their major physical characteristics are shown in Table 2

#### 2.2. Reagents

Benzyl arsenic acid (BAA), diphosphonic acid (DA), and C<sub>7-9</sub> alkyl hydroxamic acid (AHA) were employed as collectors in this study. All the reagents used were of analytical grade and acquired from Al-

drich Chemical Co., Inc.

**Table 1. Purifying process of the 3 samples**

Sample	Source	Purifying process
Fersmite	Synthesis	Synthesis, grinding and screening
Niobite	Synthesis	Synthesis, grinding and screening
Ilmenorutile	Xinqi region, Jiangsu Province, China	Comminution, ore sorting, porcelain ball grinding, shaking table, wet high intensity magnetic separation, and screening

**Table 2. Physical characteristics of the 3 samples**

Density / (g·cm <sup>-3</sup> )	Purity	Color	Particle size / mesh
4.75	99.48%	Colorless and transparent crystal or white powder.	
5.86	95.84%	Gray crystals with a particle size of about 2.0 mm	-325
4.34	95.3%	Iron black or black	

### 2.3. Flotation experiment

The XFGC-80 flotation cell with a volume of 70 mL was used in this study. A 2-g sample was employed in each flotation test with 70 mL of distilled water. The pulp temperature was controlled at 28±2°C and the impeller rotation speed was fixed at 2000 r/min. After 3 min conditioning, the pulp pH was adjusted by HCl or NaOH to the required value. The collector was then added into the pulp and conditioned for 2 additional minutes. The flotation time was kept for 3 min. Corning pH meter 430 acquired from Corning, NY was used to measure the pulp pH.

### 2.4. IR and XPS analyses

Infrared spectra were measured using a JEOL JIR 5500 FT-IR spectrophotometer with an MCT detector. The differential spectrum between minerals untreated and treated by diphosphonic acid was measured into the CaF<sub>2</sub> infrared cell over the 400 and 4000 cm<sup>-1</sup> region.

The X-ray photoelectron spectroscopy (XPS) investigation was carried out using a Vacuum Generator Escalab Mk II spectrometer with Al K<sub>α1,2</sub> radiation as an excitation source ( $h\nu=1486.6$  eV). The electron analyzer was operated in fixed analyzer transmission mode with a constant pass energy of 20 eV. All measurements were performed at pressures lower than 10<sup>-8</sup> Pa in the analysis chamber.

The experimental samples used for IR and XPS analyses were niobium-containing mineral particles with and without diphosphonic acid treatment. The sample untreated was ground to 2 μm in an agate mortar and 1.0 g sample was then collected for analysis. The preparation procedure for a treated niobium-containing mineral sample is described below.

(1) The mineral sample was ground to 2 μm in an agate mortar to increase the surface area for diphosphonic acid adsorption on mineral sample surface.

(2) 150 mL diphosphonic acid of 1% concentration

was prepared in a 200-mL beaker at pH 5.0 or 3.0 (for ilmenorutile).

(3) 2.0 g of the ground mineral sample was added into the beaker. The pulp was then agitated for 2 h at about 25°C and pH 5.0 or 3.0 (for ilmenorutile).

(4) A centrifugal filter was used to separate solids from the pulp.

(5) The separated solid was washed by deionized water at pH 5.0 or 3.0 (for ilmenorutile). This process was repeated 5 times to reduce the solvent reagent concentration in the liquid.

(6) The solid sample was dried at 30°C and kept in a dryer for analysis.

## 3. Results and discussion

### 3.1. Benzyl arsenic acid (BAA)

The collecting efficiency of BAA for niobite, fersmite, and ilmenorutile was investigated by mineral flotation tests. The effect of BAA on the recovery of niobium minerals at different pH values is shown in Fig. 1. The optimum pH for niobite, fersmite, and ilmenorutile treated by BAA collector is 5.0, 6.0, and 6.0, respectively. The maximum recovery of niobite is 44.16% at pH 5.0 with 300 mg/L BAA. Fersmite reaches the maximum recovery of 15.9% at pH 6.0 with 20 mg/L BAA. The maximum recovery of ilmenorutile is 74.64% at pH 6.0 in the presence of 50 mg/L BAA.

The effects of BAA concentration on the collecting efficiency of the 3 minerals at their optimum pH values are shown in Fig. 2. It is shown that the collecting efficiency increases with the increase of BAA concentration. The collecting efficiency of ilmenorutile increases slowly when the BAA concentration is less than 35 mg/L. The collecting efficiency of ilmenorutile increases abruptly when the BAA concentration is 35-50 mg/L. Further increasing the BAA

concentration leads to a slightly increase of the ilmenorutile collecting efficiency. It is obvious that the recovery of ilmenorutile is 75% using 50-500 mg/L BAA.

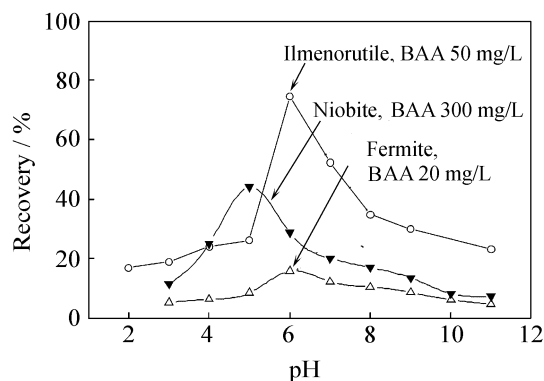


Fig. 1. Effect of pH on the recovery of the 3 niobium-containing minerals treated with BAA.

The collecting efficiency of niobite increases slowly when the BAA concentration is 20-50 mg/L. The collecting efficiency of niobite increases slightly when the BAA concentration is 50-600 mg/L. It is obvious that the recovery of niobite is about 50% using 50-600 mg/L BAA.

The collecting efficiency of fersmite increases slowly when the BAA concentration is less than 50 mg/L, and then increases abruptly when the BAA concentration is 50-400 mg/L. Further increasing the BAA amount leads to a slightly increase of the fersmite collecting efficiency. It is obvious that the recovery of fersmite is less than 52% using 400-750 mg/L BAA.

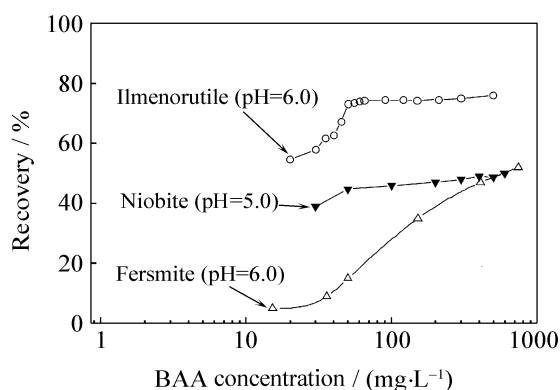


Fig. 2. Effect of BAA concentration on the recovery of the 3 niobium-containing minerals at optimum pH values.

### 3.2. Diphosphonic acid (DA)

The effects of DA on the flotation of niobium-containing minerals in different pH pulps are shown in Fig. 3. The collecting efficiencies of niobite, fersmite, and ilmenorutile are constant at the low pH range (less than 5.0). With the increase of pH (higher than 6.0), the collecting efficiencies of all the minerals decrease. The recoveries are reduced to 20%-30% at

pH 8.0 for these 3 minerals. It is clear that DA is an effective collector for these 3 minerals at acidic pulp. The recoveries range from 90.87% to 91.7% for ilmenorutile, 88.1% to 87.86% for niobite, and 82% to 85% for fersmite at pH 2-4 in the presence of 20-140 mg/L DA.

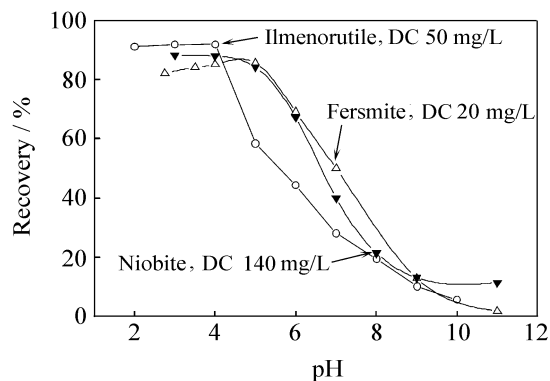


Fig. 3. Effect of pH on the recovery of the 3 niobium-containing minerals treated with DA.

The optimum pH for the collecting of niobite, fersmite, and ilmenorutile by DA is 3.0, 5.0, and 3.0-4.0, respectively. The effect of DA concentration on the minerals' collecting efficiency at their optimum pH was studied by the mineral flotation with the DA concentration of 1-1000 mg/L, as shown in Fig. 4. It shows that the recovery of ilmenorutile is kept at 93% when the pH is 3.0 and the DA concentration is in the range of 75-400 mg/L. The recovery of niobite is in the range of 85%-90% when the pH is 3.0 and the DA concentration is 300 mg/L. The recovery of fersmite is about 92% when the DA concentration is in the range of 90-200 mg/L. The collecting efficiency of DA for these 3 minerals decreases in the following order: fersmite>ilmenorutile>niobite. This result is in good agreement with that obtained with fersmite by Zheng *et al.* [1] and Ren *et al.* [10].

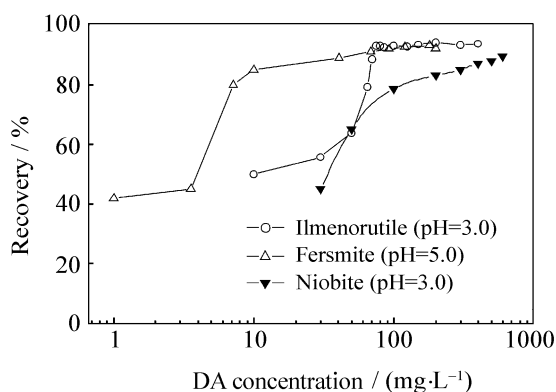


Fig. 4. Effect of DA concentration on the recovery of the 3 niobium-containing minerals at the optimum pH value.

### 3.3. C<sub>7-9</sub> alkyl hydroxamic acid (AHA)

The effects of AHA on the recovery of the 3 nio-

bium-containing minerals at different pH are shown in Fig. 5. It is shown that AHA exhibits a stronger collecting ability for fersmite and niobite than for ilmenorutile. With the increase of pH, the collecting efficiency of all minerals by AHA increases, in the range of 3-7 for fersmite and niobite and 2-6 for ilmenorutile. Further increasing the pH leads to the decrease of collecting efficiency. This might be due to that 3 niobium-containing minerals surface sorption to AHA is weaker at strong acidic pulp and strong base pulp.

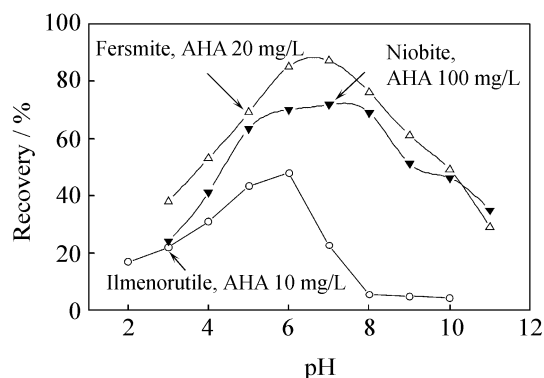


Fig. 5. Effect of pH on the recovery of the 3 niobium-containing minerals with AHA.

The effect of AHA concentration on the recovery of these 3 minerals at their optimum pH value is shown in Fig. 6. It is shown that the collecting efficiency increases with the increase of AHA concentration. The collecting efficiency can reach 87%-89% for ilmenorutile with AHA in the range of 50-70 mg/L, 81%-86% for niobite with more than 120 mg/L AHA, and 92% for fersmite with AHA in the range of 46-90 mg/L. The efficiency of AHA for these 3 minerals varies in the following order: fersmite>ilmenorutile>niobite.

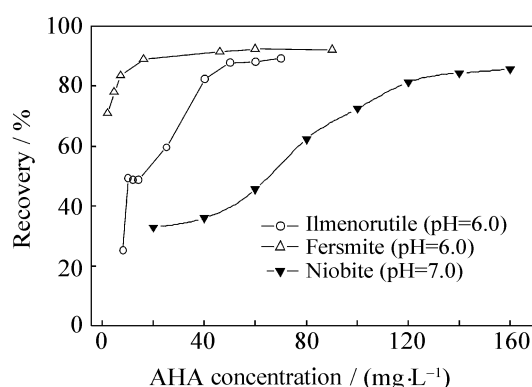


Fig. 6. Effect of AHA concentration on the recovery of the 3 niobium-containing minerals at the optimum pH value.

#### 4. Fundamental study

The floatation results are consistent with our former work [8-9, 15-17], which showed DA is the best col-

lector among DA, BAA, and AHA. The mechanism of the surface sorption of collector, DA, on niobium-containing minerals was further studied by IR and XPS.

The reagent adsorption characteristics and bonding atoms of the functional group can be identified by IR [18]. XPS functions by irradiating a sample material with monoenergetic soft X-rays to eject electrons. The relative concentrations of electrons can be determined from the photoelectron intensities. The unique feature of XPS is its ability to identify different chemical states, which is valuable for studies of adsorbed species, oxidation/corrosion products, thin-film growth processes, etc. [19].

Diphosphonic acid consists of phosphorus, carbon, hydrogen, and oxygen. Neither oxygen nor carbon should be used as the criterion for the presence of diphosphonic acid due to the possibility of carbon pollution of mineral surface and inherent oxygen component of the mineral. Hydrogen could not be detected by XPS due to the absence of inner layer of electrons. Therefore, phosphorus is the most proper indicator of diphosphonic acid [20].

#### 4.1. IR analysis of DA, fersmite and fersmite treated by DA

The peaks at 1465, 2854, 2925, and 2957  $\text{cm}^{-1}$  are ascribed to methyl and submethyl vibration, which are present in DA-treated fersmite, as shown in Fig. 7.

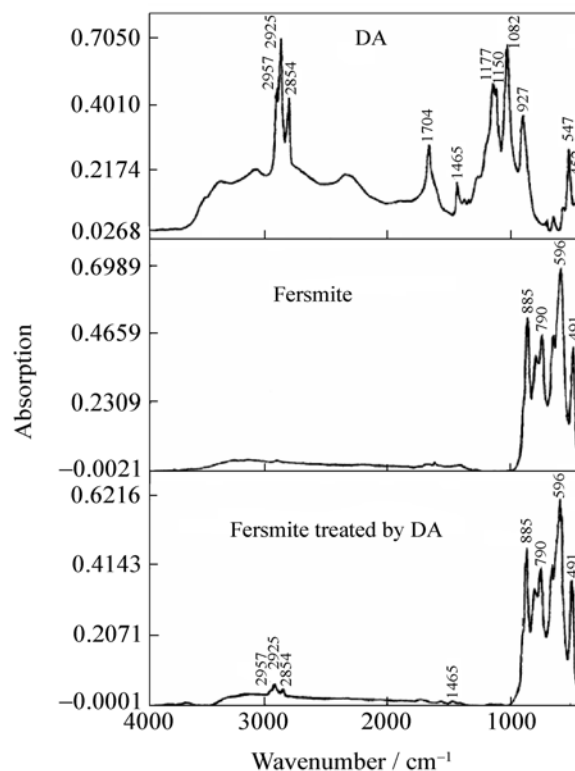


Fig. 7. IR spectra of DA, fersmite, and fersmite treated by DA [10, 15].

The absorption peaks at 1178, 1142, 1087, and 934  $\text{cm}^{-1}$  associate with vibrations of  $-\text{P}-\text{O}-$  and  $-\text{P}=\text{O}$ , which are more displayed on the differential spectrum in Fig. 8. The characteristic peak of  $-\text{P}-\text{O}-$  in DA is at 1062  $\text{cm}^{-1}$ , which is shifted to 1087  $\text{cm}^{-1}$ . This shift indicates that DA is adsorbed on the surface of fersmite [10, 15].

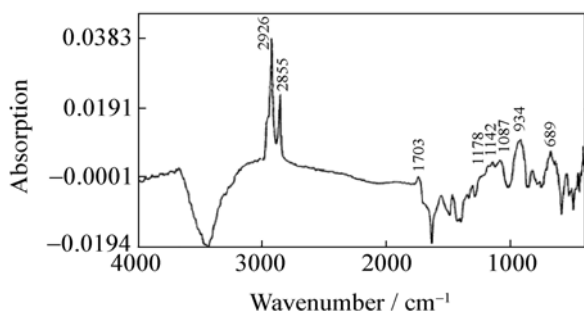


Fig. 8. Differential spectrum between untreated fersmite and fersmite treated by DA [10, 15].

#### 4.2. XPS analysis of DA and fersmite treated by DA

The effect of reagent adsorption on  $\text{P}_{2p}$  peak was shown in Fig. 9. The  $\text{P}_{2p}$  peak is at 132.95 eV for DA and 136.80 eV for the treated fersmite with the difference of 3.85 eV. Fig. 9 suggests that the  $\text{P}_{2p}$  peak position changes for fersmite treated by DA and the chemical displacement of phosphorus occurs. It can be concluded that DA is chemically adsorbed on fersmite surface, increasing the atomic concentration of phosphorus.

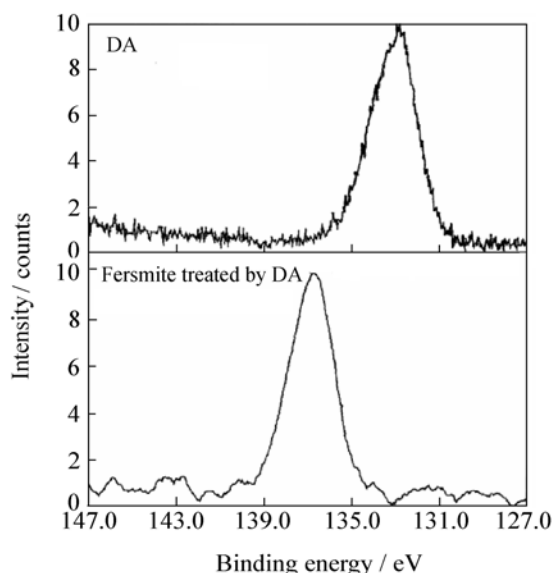


Fig. 9.  $\text{P}_{2p}$  peak for DA and fersmite treated by DA [10, 15].

#### 4.3. IR analysis of DA, niobite, and niobite treated by DA

The IR spectra of DA, niobite, and niobite treated by DA are shown in Fig. 10.

Fig. 10 clearly shows that the 3 characteristic ab-

sorption peaks appear for niobite treated by DA, which are associated with methyl and submethyl vibration at 2854, 2924, and 2957  $\text{cm}^{-1}$ , respectively. The absorption peaks at 1049, 1115, and 1169  $\text{cm}^{-1}$  associated with vibrations of  $-\text{P}-\text{O}-$  and  $-\text{P}=\text{O}$  are more clearly displayed in Fig. 10. Since the characteristic  $-\text{P}-\text{O}-$  peak for DA is at 1062  $\text{cm}^{-1}$ , the significant peak position shift to 1049  $\text{cm}^{-1}$  indicates that DA is adsorbed on the surface of niobite, but the peak position shift is not as distinct as that for fersmite and ilmenorutile [10, 17]. Similar results have been obtained with ilmenorutile treated by DA. Our former results demonstrated that the  $-\text{P}-\text{O}-$  characteristic peak shifted from 1062 to 1032  $\text{cm}^{-1}$  when DA was used as collector to float ilmenorutile (IR was elided) [9].

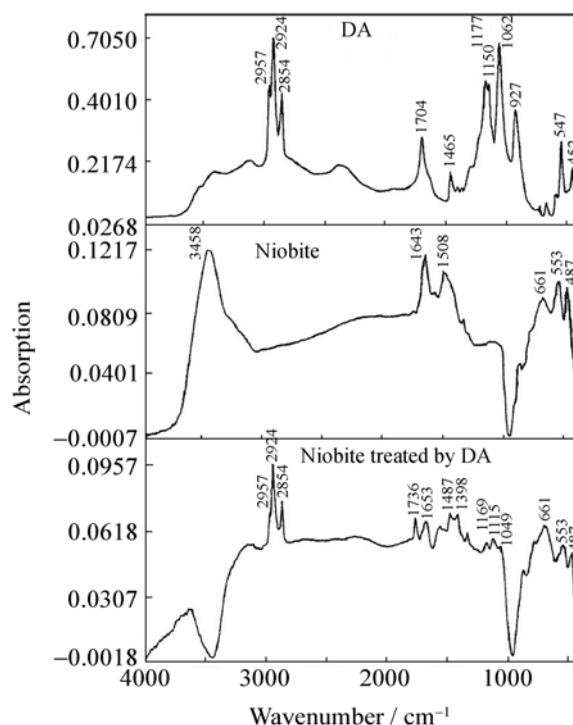


Fig. 10. IR spectra of DA, niobite, and niobite treated by DA [10, 17].

#### 4.4. XPS analysis of DA and niobite treated by DA

The  $\text{P}_{2p}$  peak for the DA and the treated niobite is compared in Fig. 11. The  $\text{P}_{2p}$  peak is at 132.95 eV for DA and 135.80 eV for the treated niobite with the difference of 2.85 eV. This suggests that DA is chemically adsorbed on niobite's surface, increasing the atomic concentration of phosphorus [10, 17]. Similar results have been obtained with ilmenorutile treated by DA. It was reported that the binding energy of the  $\text{P}_{2p}$  peak of ilmenorutile changed by 0.45 eV (XPS was elided) and the  $\text{P}_{2p}$  peak of fersmite changed by 3.85 eV (see Fig. 9) after being treated with DA [9-10]. These results indicate that the change in  $\text{P}_{2p}$  peak posi-

tion for treated niobite is not as pronounced as that for treated fersmite, but the change is more distinct than that for the treated ilmenorutile.

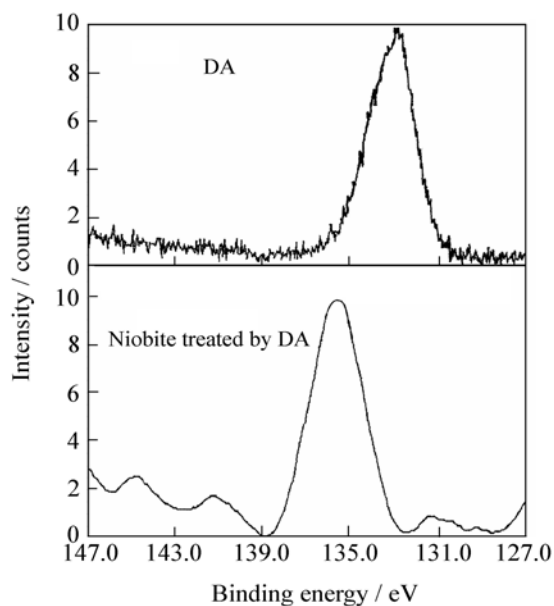


Fig. 11.  $P_{2p}$  peak for the DA and the treated niobite [10, 17].

## 5. Conclusions

(1) The recovery efficiency of BAA to these 3 minerals decreases in the following order: ilmenorutile>niobite>fersmite.

(2) The recovery efficiency of these 3 minerals is the same when AHA and DA are used. They have the same order as the following: fersmite>ilmenorutile>niobite.

(3) The recovery efficiency order of three collectors is DA>AHA>BAA.

(4) DA is the best collector at the same concentration

(5) IR and XPS spectra indicate that the adsorption of DA on these three minerals surface is chemical adsorption.

(6) The chemical adsorption might indicate the high recovery efficiency of the minerals.

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