

## Article

# Application of Waste Engine Oil for Improving Ilmenite Flotation Combined with Sodium Oleate Collector

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**Abstract:** Collectors commonly have synergetic effects in ores flotation. In this work, a waste engine oil (WEO) was introduced as a collector to an ilmenite flotation system with sodium oleate (NaOL). The results show that the floatability of ilmenite was significantly improved by using WEO and NaOL as a combined collector. The recovery of ilmenite was enhanced from 71.26% (only NaOL) to 93.89% (WEO/NaOL combined collector) at the pH of 6.72. The optimum molar ratio of NaOL to WEO was about 2.08 to 1. The WEO and NaOL also have synergetic effects for the collection of ilmenite, because to obtain the ilmenite recovery of 53.96%, the dosage of 45 mg/L NaOL is equal to 38.56 mg/L WEO/NaOL combined collector (30 mg/L NaOL + 8.56 mg/L WEO). In other words, 15 mg/L of NaOL can be replaced by 8.56 mg/L of WEO. It is an effective way to reduce the dosage of the collector and reuse WEO. Therefore, it is a highly valuable and environmentally friendly approach for WEO reuse. WEO mainly consists of oxygen functional groups, aromatics, and long-chain hydrocarbons, especially for the RCONH<sub>2</sub> and RCOOH, thereby forming a strong interaction on the ilmenite surface. The adsorption mechanism of waste engine oil and sodium oleate on the ilmenite surface is mainly contributed by chemical adsorption. Therefore, WEO exhibits superior synergistic power with NaOL as a combined collector. Herein, this work provided an effective collector for ilmenite flotation and a feasible approach for reducing NaOL dosage and recycling WEO.

**Keywords:** ilmenite; flotation; waste engine oil; combined collector; adsorption mechanism



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## 1. Introduction

Titanium, a significant strategic metal, has been extensively used in aerospace, ship-building, medical devices, and other fields [1,2]. Ilmenite is rich in titanium resources; thereby, it is considered as the major mineral resource of titanium in China [3]. However, the separation of ilmenite faces many challenges due to the complex composition and low grade for ilmenite. The conventional separation of titanium includes gravity separation, magnetic separation, and electric separation. However, these techniques were only suitable for the +74 μm fraction. It is difficult to achieve effective separation of ilmenite for the −74 μm fraction by conventional methods [4]. Flotation is an effective separation technique to retrieve fine mineral particles, and it is widely used in the mineral industry [5–7]. The versatility of this process depends on the proper use of reagents, which are added into the pulp to induce wettability differences between ilmenite and other minerals in the ore. The sodium oleate (NaOL), as a typical and commercial collector for ilmenite flotation [6,8], has the characteristics of strong collecting ability but large dosage. The main optimization approach for ilmenite flotation is NaOL modification or combination with other reagents [9–15]. However, the route of NaOL modification is long and costly. The mixture of NaOL and D-phenylalanine performed positive synergistic adsorption in diasporite [10]. Xu et al. claimed that dodecyl amine-hydrochloride/NaOL has better hydrophobicity and collection performance than a single agent in muscovite flotation [11].

Herein, the combination of NaOL with other reagents is more appropriate for improving the collecting ability and reducing the reagents' cost. Even though, those collectors are still expensive.

Waste engine oil (WEO) is contaminated by impurities, oxidized, or decomposed matters, when using various vehicles, ships, and other machinery [16]. Approximately 40 million metric tons is produced every year; about 60% of the products become WEO all over the world [17]. It will bring a series of hazards if the WEO is not handled properly [18,19]. To reduce its harmful effects, the WEO should be recycled and reused. However, traditional approaches need to use corrosive and toxic substances, or strict conditions, such as vacuum distillation [20]. It will not only cause serious environmental pollution, it will also endanger human survival environment and health as well as waste valuable resources again. Therefore, how to effectively reuse WEO has become an important global imperative problem. The WEO has multiple substances such as hydrocarbons, esters, heteroatom compounds, and so on [21]. The WEO has potential application in flotation. The effect of WEO as a collector on the coal gasification waste flotation separation was investigated. The coal gasification waste was divided to cleaner concentrate carbons for fuel use and qualified tailings for building materials with a WEO collector. The goals of "Carbons Recycle" and "Waste Disposal by Waste" were realized [22].

In this work, a WEO was firstly introduced to enhance the collecting property of ilmenite with NaOL as a collector. The chemical compositions and structural features of the WEO were investigated by gas chromatography/mass spectrometry (GC/MS) and Fourier transform infrared spectroscopy (FTIR). The synergistic adsorption mechanism of WEO/NaOL combined collector on the ilmenite surface was analyzed by zeta potential, FTIR, and X-ray photoelectron spectroscopy (XPS). This work provided an economical and effective collector for ilmenite flotation. Meanwhile, it is a suitable way to recycle WEO, reduce NaOL dosage, and improve the ilmenite recovery.

## 2. Material and Methods

### 2.1. Characteristics of the Material

The ilmenite sample was obtained from Panzhihua, Sichuan Province, China. The ilmenite sample was ground by a ball mill. The micro-flotation was carried out with  $-74 + 38 \mu\text{m}$  particle size samples. Table 1 and Figure 1 illustrated the chemical constituents and mineral components of ilmenite by X-ray fluorescence spectrometer (XRF, Holland) and X-ray diffraction (XRD, Holland), respectively. As shown in Figure 1, the ilmenite was of high purity. As shown in Table 1, the Ti and Fe are the main elements of ilmenite. The purity of ilmenite is 93.38% (by calculation), as the  $\text{TiO}_2$  grade of the ilmenite sample is 49.12%, and the theoretical grade of  $\text{TiO}_2$  in ilmenite is 52.63%.

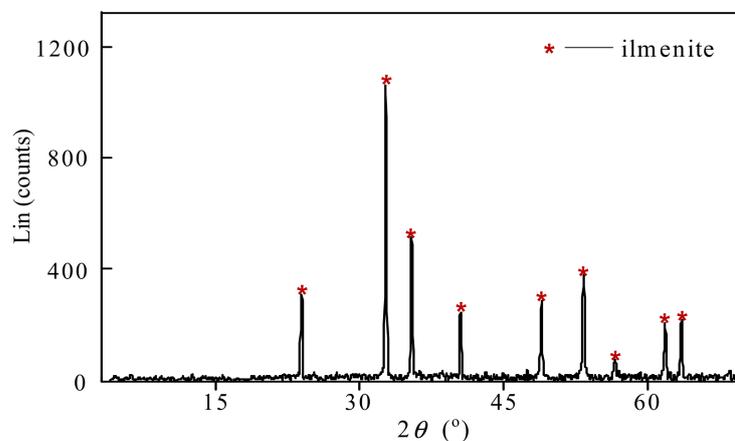


Figure 1. The XRD patterns of the ilmenite sample.

**Table 1.** The chemical composition of the ilmenite sample.

Element.	FeO	TiO <sub>2</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	MnO	Others
Content (%)	37.67	49.12	3.15	2.83	4.14	0.75	0.60	1.74

The WEO was collected from a repair shop in Zhengzhou, Henan Province, China. Chemical reagents were analytically pure. The NaOL collector was purchased from Aladdin Industrial Corporation, China. The pH of the pulp was adjusted using HCl and NaOH solution. The resistivity of ultrapure water was more than 18.2 MΩ/cm.

## 2.2. Flotation Tests

Flotation tests have been reported in the literature [23,24]. First, 2.0 g of ilmenite and 40 mL of deionized water were added into the XFG flotation cell with an agitating rate of 1600 r/min. The pH of the pulp was adjusted by NaOH or HCl solution. The pulp was stirred for 2 min. Subsequently, the WEO was added into the flotation cell and stirred for 1 min; then, NaOL was added into the flotation cell and stirred for 2 min. For contrast, a parallel test was carried out that consisted of only adding NaOL into the flotation cell and stirring for 3 min. The flotation was maintained for 3 min. Finally, the concentrate and tailings were dried and weighed to calculate the flotation recovery.

## 2.3. Adsorption Mechanism Tests

The zeta potentials of samples were measured by a Zetasizer Nano ZS90 analyzer (Malvern, Worcestershire, Britain). The suspension was prepared by mixing 20 mg of ilmenite and 40 mL of ultrapure water. The collector was introduced to the suspension and adjusted to several pH values; then, the mixture was transferred to the sample tube. The KNO<sub>3</sub> solution ( $1 \times 10^{-3}$  mol/L) was used as background electrolyte [25]. The conductivity and pH of the suspension were continuously monitored during the whole measurement. Each of the samples was measured at least five times, and the final results were averaged.

The FTIR spectra of ilmenite and reagents were recorded by an FTIR spectrometer (Nicolet iS10, Thermo Electron, NJ, USA). First, 2.0 g of ilmenite was introduced into 40 mL of solution at the corresponding pH and stirred for 5 min; then, it was mixed with NaOL or/and WEO for 10 min. After static stratification, they were washed and filtered with deionized water three times. Subsequently, the ilmenite sample and absorbed reagents were dried in a vacuum desiccator. Meanwhile, the dried ilmenite, WEO, and NaOL were analyzed by FTIR. Then, a 1 mg mineral sample and 100 mg of spectroscopic grade KBr were mixed and pressed to tablets for FTIR measurements.

The XPS (Thermo 250XI, Waltham, MA, USA) was used to determine the spectrum of ilmenite powder adsorbed in the reagents. The specimen preparation for XPS was consistent with the sampling method of FTIR.

The organic compounds in WEO were analyzed by GC/MS (GC-2014C, Japan) The method was used to identify the chemical composition of WEO [16]. The furnace program performed from 70 to 300 °C at a rate of 10 °C/min, and then, the temperature was maintained at 300 °C for 10 min. The peak area normalization method was applied to calculate the corresponding content of component in WEO.

## 3. Results and Discussion

### 3.1. Effects of WEO on Ilmenite Flotation

As exhibited in Figure 2a, the concentrate recovery of ilmenite flotation was significantly improved by adding WEO, with the WEO dosage of 30 mg/L and the NaOL dosage of 60 mg/L. With the pH increasing, the ilmenite recovery climbs up and then declines, and the recovery increment ranges from 15.05% (pH = 2.38) to 25.30% (pH = 4.96). The optimized ilmenite flotation recovery reached 93.89% from 71.26% with adding WEO at the pH of 6.72. Therefore, WEO can significantly improve the concentrate recovery of ilmenite flotation with the presence of the NaOL. Compared to the pH of 6.72, the recovery declines as the pH increases (pH = 9.02 and pH = 11.72), with the NaOL dosage of 60 mg/L.

However, the recovery increment is still over 16% with adding 30 mg/L of WEO. Therefore, the WEO is a suitable collector for improving the flotation behavior of ilmenite with the presence of the NaOL.

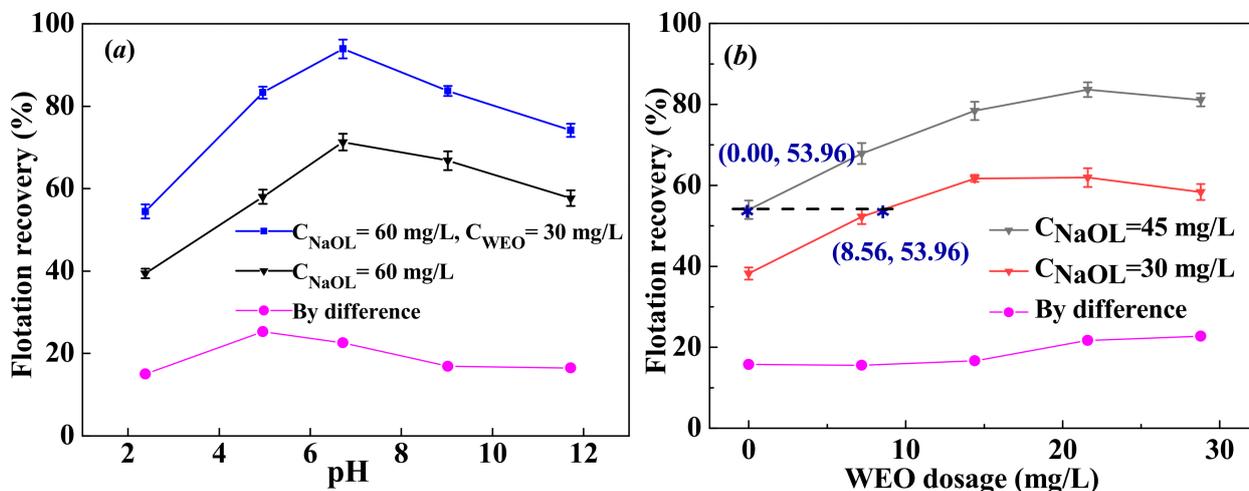


Figure 2. The flotation recovery of ilmenite at different pH (a) and collector dosage (b).

This does not mean that a WEO dosage would always promote the recovery. The dosage of WEO and NaOL has an optimal value, which is most conducive to the production of ilmenite. The ratio of the combined collector is an important index for ilmenite flotation [26]. As shown in Figure 2b, as the dosage of WEO increased, the ilmenite recovery climbed up and then declined. The ilmenite recovery reached the top point when the combined collector was prepared by 45 mg/L NaOL and 21.60 mg/L WEO, or 30 mg/L NaOL and 14.40 mg/L WEO. Therefore, the optimum molar ratio of NaOL to WEO was about 2.08 to 1.

Both of the results presented in Figure 2a,b proved that the WEO/NaOL combined collector has a stronger collecting capacity for ilmenite compared to a single NaOL collector. Moreover, as seen in Figure 2b, to obtain the ilmenite recovery of 53.96%, the dosage of 45 mg/L NaOL is equal to 38.56 mg/L WEO/NaOL combined collector (30 mg/L NaOL + 8.56 mg/L WEO), indicating that the WEO and the NaOL also have synergistic effects for the collection of ilmenite. On the other hand, when the dosage of NaOL is 45 mg/L or the dosage of WEO is 38.56 mg/L, the flotation recovery of ilmenite can achieve 53.96%. In other words, 15 mg/L of NaOL can be replaced by 8.56 mg/L of WEO. It is an effective way to reduce the dosage and cost of the collector by adding WEO. It is also an efficient approach for WEO reuse, because waste was converted to valuable flotation collectors. Therefore, it is a highly valuable and environmentally friendly approach for WEO reuse.

### 3.2. Adsorption Mechanism Analysis

#### 3.2.1. Zeta Potential Shifts

The zeta potentials of ilmenite treated by NaOL or/and WEO in different solutions are shown in Figure 3. The isoelectric point of pure ilmenite is close to  $\text{pH} = 6.0$  [27,28]. When NaOL was used as a single collector, the zeta potentials of ilmenite are negatively shifted, indicating the adsorption of NaOL on the ilmenite surface [8]. When both WEO and NaOL were used at  $\text{pH} < 8.0$ , the zeta potentials of the ilmenite surface are more negatively than that treated only by NaOL. It indicates that the cooperation of NaOL and WEO can promote the flotation performance at  $\text{pH} < 8.0$ . However, the WEO is not suitable for ilmenite flotation at  $\text{pH} > 8.0$ . The results showed that the combined collector and the ilmenite have stronger adsorption at  $\text{pH} < 8.0$  [29].

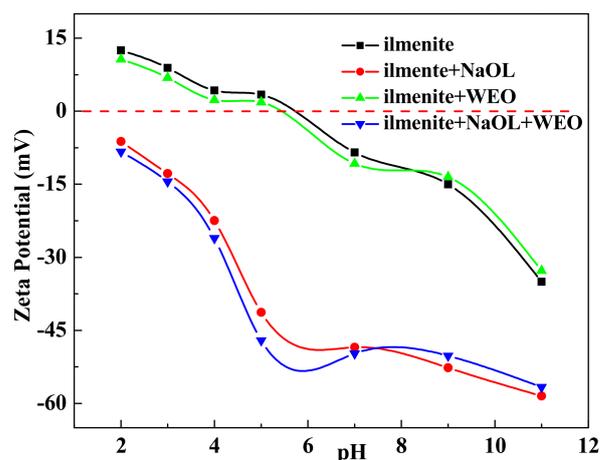


Figure 3. Effect of pH on zeta potentials of ilmenite treated by NaOL or/and the WEO.

### 3.2.2. Infrared Absorption Shifts

The FTIR spectra of WEO, NaOL, ilmenite, and ilmenite treated with WEO or/and NaOL are presented in Figure 4. As shown in Figure 4a, the FTIR spectrum of ilmenite was basically consistent with the chemical bond vibration mode reported previously [30]. In the FTIR spectrum of NaOL, the bands at 2923 and 2853  $\text{cm}^{-1}$  belong to the C–H stretching vibration ( $-\text{CH}_2-$  and  $-\text{CH}_3$ ), while the band at 721  $\text{cm}^{-1}$  was attributed to  $-(\text{CH}_2)_n-$  deformation. The peaks at 1561, 1464, and 1427  $\text{cm}^{-1}$  were caused by  $-\text{COO}-$  vibration [14,15]. In the FTIR spectrum of WEO, the bands at 2920, 2852, 1462, and 1377  $\text{cm}^{-1}$  were attributed to the C–H vibration of methyl/methylene, while the peak at 722  $\text{cm}^{-1}$  was attributed to C–H bending vibration of the substituted aromatics and aromatic hydrocarbon [31,32]. It indicates that non-polar alkanes/olefins exist in WEO, which can increase its fixation degree on the ilmenite surface and improve the floatability of the ilmenite surface. The peak at 1700  $\text{cm}^{-1}$  belongs to the C=O stretching vibration of carboxyl and carbonyl [33], while the bands at 1605 and 1156  $\text{cm}^{-1}$  originated from the C–N stretching vibration and C=N stretching vibration of amide component, respectively [34]. The polar component is beneficial to the adsorption of active sites on the ilmenite surface. Therefore, the synergistic effect of the polar and non-polar components in WEO is conducive to the ilmenite flotation.

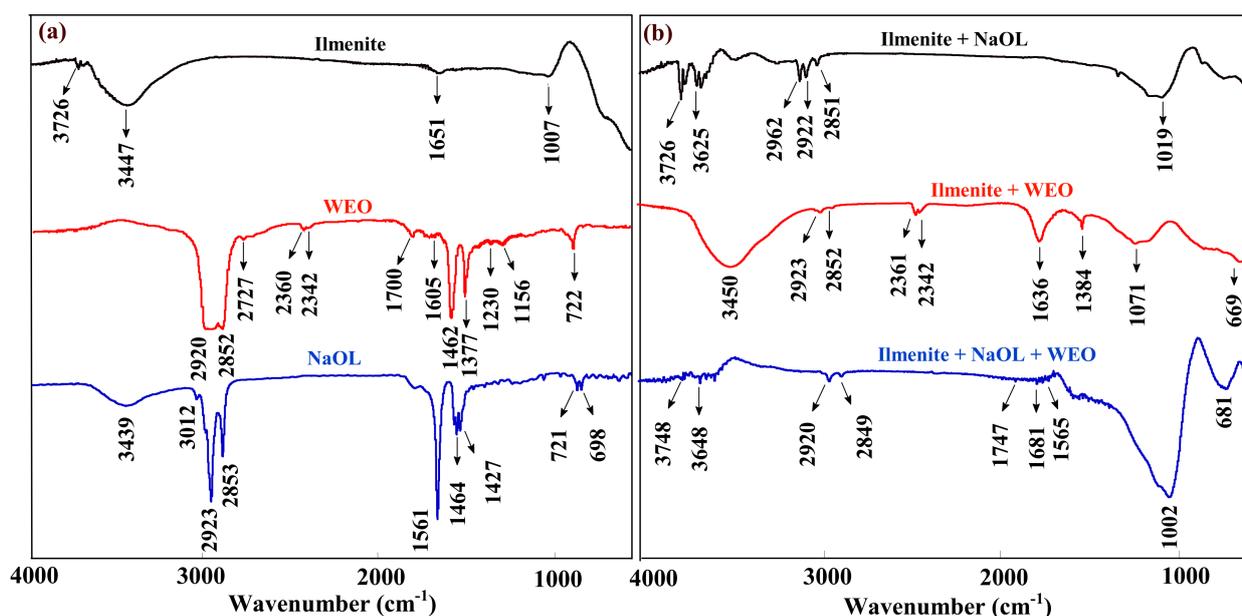


Figure 4. FTIR spectra of (a) ilmenite, WEO, and NaOL, and (b) ilmenite treated with WEO or/and NaOL.

Figure 4b performed the FTIR spectra of ilmenite treated with NaOL or/and WEO. Comparing the FTIR spectrum of ilmenite with ilmenite treated by NaOL, new bands at 2962, 2922, and 2851  $\text{cm}^{-1}$  were found on the spectrum of the ilmenite surface treated with NaOL. The band at 2962  $\text{cm}^{-1}$  moved to a lower wavenumber by 50  $\text{cm}^{-1}$  compared to that in the FTIR spectrum of NaOL. It can be inferred that NaOL is adsorbed on the ilmenite surface [35]. Compared with the FTIR spectrum of ilmenite, characteristic peaks of WEO (at approximately 2923, 2852, 2361, 2342, 1384, and 669  $\text{cm}^{-1}$ ) were observed on the spectrum of ilmenite treated by WEO. The new band at 1636  $\text{cm}^{-1}$  was shifted by 31  $\text{cm}^{-1}$  on ilmenite treated by WEO. This proves that WEO can react on the ilmenite surface. Comparing the FTIR spectrum with WEO, the new bands at 1747 and 1681  $\text{cm}^{-1}$  were shifted by 47 and 76  $\text{cm}^{-1}$  on the spectrum of ilmenite treated by NaOL and WEO. Other peaks at 2920, 2849, and 681  $\text{cm}^{-1}$  may be the superposition of NaOL and WEO. These results indicated the combined collector adsorbed on the ilmenite surface via the form of chemical adsorption.

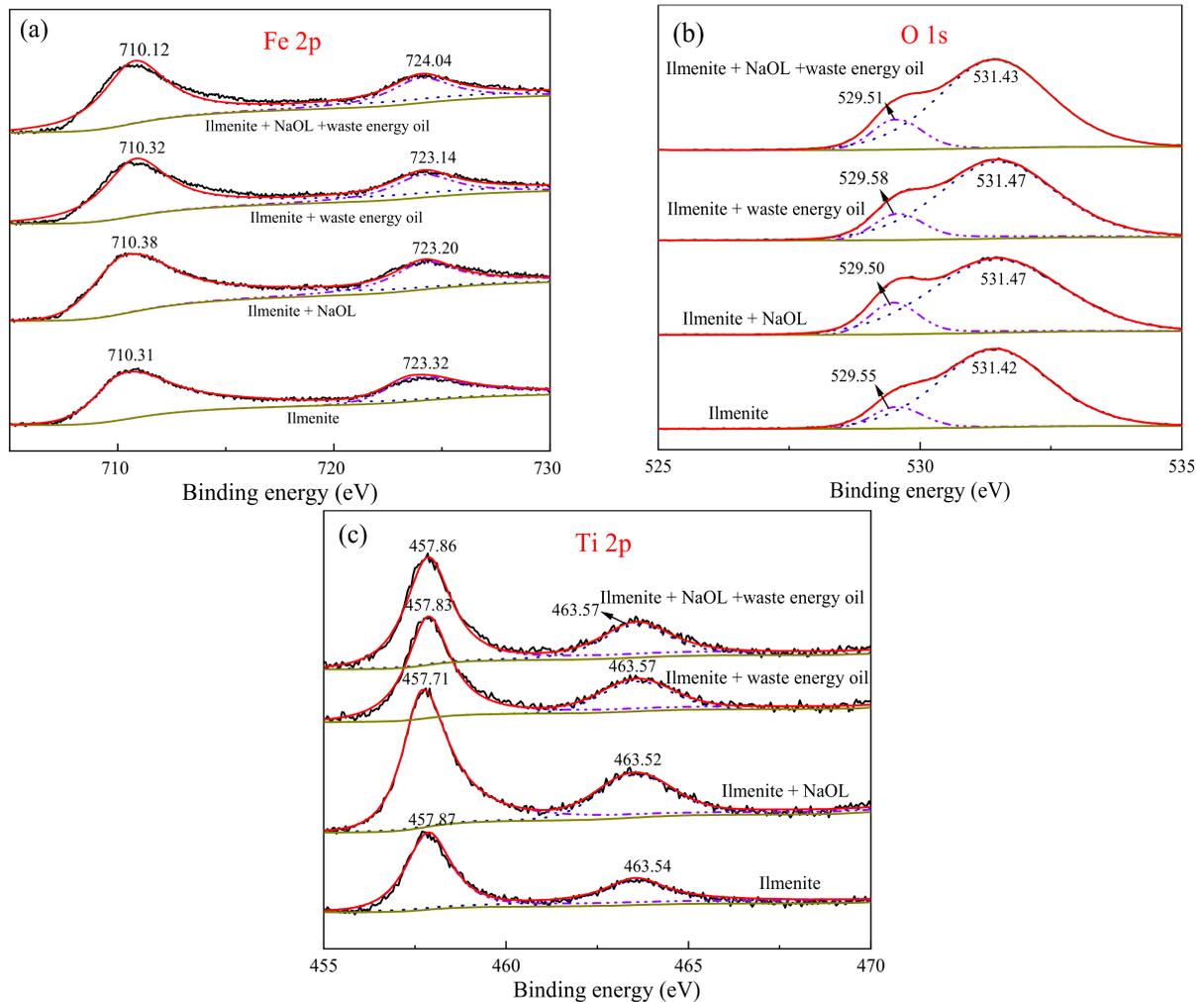
### 3.2.3. Concurrent Forms of Elements

The synergistic collection mechanism of NaOL or/and WEO on the ilmenite surface was investigated by XPS. Table 2 listed the chemical shift of the binding energy on the ilmenite surface treated by NaOL or/and WEO. As listed in Table 2, after ilmenite was treated by the combined collector, the chemical shift of Ti was not obvious, while the chemical shift of Fe on the ilmenite surface changed by 0.72 eV. This result indicated that the combined collector could react with the active site of Fe on the ilmenite surface because the chemical environment for Fe was transformed [35].

**Table 2.** Binding energies of elements on the ilmenite surface treated with WEO or/and NaOL (eV).

Sample	Binding Energy (eV)						Chemical Shift (eV)					
	Fe 2p3/2	Fe 2p1/2	O 1s	O 1s	Ti 2p3/2	Ti 2p1/2	Fe 2p3/2	Fe 2p1/2	O 1s	O 1s	Ti 2p3/2	Ti 2p1/2
Ilmenite	710.31	723.32	531.42	529.55	457.87	463.54	-	-	-	-	-	-
Ilmenite + NaOL	710.38	724.2	531.47	529.5	457.71	463.52	0.07	0.88	0.05	-0.05	-0.16	0.02
Ilmenite + WEO	710.32	723.14	531.47	529.58	457.83	463.57	0.01	-0.18	0.05	0.03	0.04	0.03
Ilmenite + NaOL + WEO	710.16	724.04	531.43	529.51	457.86	463.57	-0.15	0.72	-0.01	-0.04	-0.01	0.03

The Fe 2p level split into two peaks of Fe 2p3/2 and Fe 2p1/2 because of the spin-orbit coupling [36]. Figure 5a illustrated the high-resolution spectrum of Fe 2p and its separation fitting peaks. Among these peaks, the separated peaks for the ilmenite samples treated by collectors were attributed to Fe<sup>3+</sup> and Fe<sup>2+</sup> species, respectively [37]. Compared with original ilmenite, the binding energy of Fe 2p changed from 710.31 to 710.16 eV and from 723.32 to 724.04 eV separately when ilmenite was treated by the combined collector. This shows that the combined collector contributed possibly its electron to iron species for the change of chemical environment to Fe ions on the ilmenite surface [38,39]. The O 1s spectra of ilmenite treated with NaOL or/with WEO are presented in Figure 5b. The O 1s spectrum of ilmenite was fitted to two components, namely the Ti-O bond (529.55 eV) and Fe-O bond (531.42 eV) [23]. Figure 5c was the high resolution of the Ti 2p spectra of ilmenite treated by NaOL and/or WEO. Comparing ilmenite treated by the combined collector with ilmenite, the binding energy of Ti 2p3/2 and Ti 2p1/2 centered from 457.87 to 457.86 eV and from 463.54 to 463.57 eV, respectively [40]. Since the binding energy was comparatively slight, it indicated that the Ti atom may be not the reaction site on the ilmenite surface after ilmenite was treated by the combined collector. Based on the related report, in weak acid or weak alkaline solutions, titanium ions mainly existed on Ti(OH)<sub>4</sub> in a stable form, while ferrous ions could be active sites in the form of Fe<sup>2+</sup> and FeOH<sup>+</sup> for collector absorption [41,42]. The XPS result was consistent with the FTIR result. According to the results of XPS analyses, Fe ions on the ilmenite surface acted as the active sites to react with the combined collector, indicating there was chemical adsorption between the combined collector and ilmenite.



**Figure 5.** The high resolution of Fe 2p (a), O 1s (b), and Ti 2p (c) spectra on the ilmenite surface treated with WEO or/and NaOL.

### 3.3. Interactive Mechanism of WEO/NaOL on Ilmenite Surface

The interactive mechanism between the combined collector and ilmenite were related with the aqueous species of WEO, NaOL, and the crystal structure of ilmenite [43]. Figure 6 illustrates the chromatogram of WEO, and Table 3 lists the relative content of identified chemicals. As shown in Figure 6, the chromatogram was attributed to the benzene derivatives at low retention time, oxygenated compounds at medium retention time, and long-chain hydrocarbons at high retention time. As illustrated in Table 3, WEO was mainly composed of chemicals with the carbon number of 19 to 38, especially the carbon atom ranges from 24 to 28 [22], which accounted for half of the total. These compounds in WEO determined the adsorption characteristics on the ilmenite surface. The results showed that benzene derivatives and oxygenated compounds in WEO can largely bond with the active sites of ilmenite, and its long-chain hydrocarbons can enhance the hydrophobic property on the ilmenite surface.

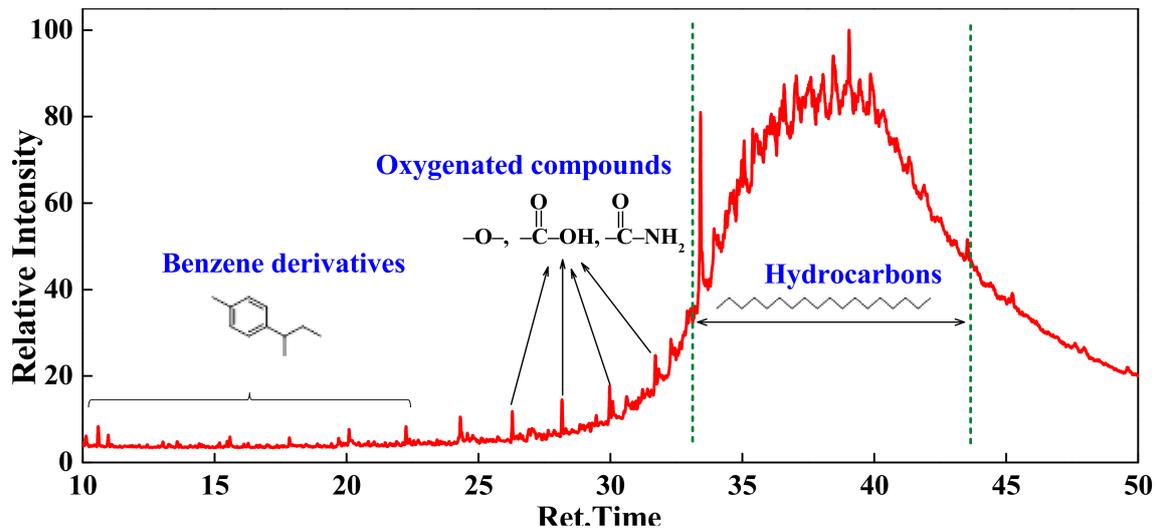
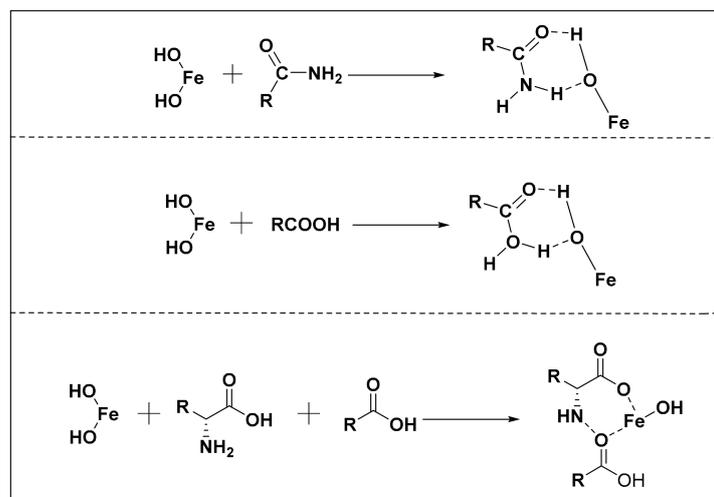


Figure 6. The GC/MS chromatogram of WEO.

Table 3. The chemical composition of C19 to C38 of WEO.

Carbon Number	Relative Content (%)	Carbon Number	Relative Content (%)
C19	0.51	C28	7.16
C20	3.10	C29	3.33
C21	1.98	C30	0.97
C22	4.79	C32	1.64
C23	2.16	C33	1.96
C24	11.63	C34	4.23
C25	11.47	C35	7.58
C26	9.57	C37	0.93
C27	10.04	C38	0.96

Under weak acid or alkali conditions (pH = 6.0–9.0), WEO and NaOL existed mainly in these three forms: (1) amphoteric species with negatively charged ( $-COO^-$ ,  $-CO-NH^-$ ,  $-O^-$ ) and positively charged ( $-NH_2^+$ ) groups; (2) saturated alkanes with different carbon length; (3) species with unsaturated double or triple bonds. As stated in XPS analysis, the active site on the ilmenite surface was principally iron in weak acid or weak alkaline solution. Therefore, as shown in Figure 7, WEO and NaOL in the solution could act on the ilmenite surface in different forms and react with iron active sites to form related molecules. It could be speculated that the  $-COO^-$  groups for WEO and NaOL could contribute the frontier electrons of O atoms to Fe atoms on the ilmenite surface. The reactions could involve the chelation adsorption as  $-CO-NH^-$ ,  $-O^-$ , and other related components between combined collector and ilmenite. NaOL could be adsorbed in the ilmenite surface by forming hydrogen bonds between  $-C=O$  and  $-NH_2$  groups in WEO. It was concluded that the adsorption mechanism between combined collector and ilmenite primarily included chemical adsorption, electrostatic interaction, and hydrogen bond adsorption. The mixture of NaOL and WEO increased the adsorption capacity of the ilmenite surface.



**Figure 7.** The association equations of combined collector (NaOL and WEO) on the ilmenite surface.

#### 4. Conclusions

A new WEO/NaOL combined collector was prepared and efficiently used for ilmenite flotation. The NaOL dosage was significantly reduced when the WEO was used for ilmenite flotation to replace some of the NaOL. The optimum molar ratio of NaOL to WEO was about 2.08 to 1. The WEO and NaOL also have synergetic effects on the ilmenite flotation, as the recovery of adding 8.56 mg/L WEO is equal to 15 mg/L NaOL, while the initial NaOL dosage was 30 mg/L. The combination of NaOL and WEO could increase their adsorption capacity on the ilmenite surface and improve the collection performance. The application of the WEO/NaOL combined collector on ilmenite flotation can achieve the goal of “reusing WEO” and “reducing NaOL dosage” in ilmenite flotation, which also has potential application in the future industry.

**Author Contributions:** Formal analysis Q.Y., F.T., G.F., W.P., G.Z. and P.L.; investigation F.T., G.F. and H.H.; methodology Y.C., H.H., W.P., G.Z. and P.L.; Writing—original draft, Q.Y.; Writing—review & editing, G.F. and P.L. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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