

Article

Study on Selective Adsorption Behavior and Mechanism of Quartz and Magnesite with a New Biodegradable Collector

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Abstract: Research on the efficient flotation desilication of low-grade magnesite is of great significance for the sustainable development of magnesium resources. Traditional collectors usually have some disadvantages, such as poor selectivity, severe environmental pollution, and weak water solubility. To strengthen the desilication flotation process of magnesite ore, the biodegradable surfactant, cocamidopropyl amine oxide (CPAO), was first utilized as the collector for the separation of the magnesite and quartz. The selective adsorption behavior and mechanism of the quartz and magnesite with the CPAO as the collector were studied through the micro-flotation experiments of the single mineral and the artificially mixed mineral, contact angle and atomic force microscopy (AFM) measurements, fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) analyses. The flotation results indicated that the CPAO showed good selectivity and could effectively separate magnesite and quartz. When the concentration of the CPAO was 10.0 mg/L in the natural pulp pH (about 7.2), the concentrates with 97.67% MgO recovery and 45.62% MgO grade were obtained. The contact angle and AFM measurements indicated that the CPAO could selectively adsorb on the quartz surface rather than the magnesite surface to improve the interface difference between them, especially its surface hydrophobicity. The results of the FTIR and XPS analyses indicated that the CPAO is selectively adsorbed on the surface of the quartz, mainly through electrostatic interaction and hydrogen bonding. In conclusion, the CPAO had good selectivity and great potential as an effective collector in the reverse flotation desilication progress of magnesite.

Keywords: flotation; magnesite; quartz; biodegradable collector; cocamidopropyl amine oxide; selective adsorption



Citation: Liu, W.; Zhao, Q.; Zhang, R.; Zhao, P.; Liu, W.; Han, C.; Shen, Y. Study on Selective Adsorption Behavior and Mechanism of Quartz and Magnesite with a New Biodegradable Collector. *Separations* **2023**, *10*, 590. <https://doi.org/10.3390/separations10120590>

Academic Editor: Gavino Sanna

Received: 2 November 2023

Revised: 20 November 2023

Accepted: 23 November 2023

Published: 1 December 2023



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1. Introduction

Magnesite is a magnesium-containing carbonate mineral with superior refractory and bonding qualities, which has emerged as one of the important raw materials for the production of refractory materials [1,2]. Meanwhile, magnesite is also widely used in automobiles, construction materials, aviation, chemical raw materials, and refining magnesium and magnesium-containing compounds [1,3–5]. It is widely known that in the discovered magnesite deposits, the quartz is the most commonly associated gangue [1]. Excessive quartz contained in magnesite can seriously affect the quality of refractory materials prepared, especially during the melting process, the quartz transforms into low melting point silicates, which seriously deteriorates the strength of refractory materials [6]. In recent years, with the annual consumption of high-quality magnesite, it has become urgent to remove the quartz from the low-grade magnesite [7]. Research on the efficient flotation desilication of low-grade magnesite is of great significance for improving product quality, reducing environmental impact, and enhancing the sustainable development of magnesium resources [8,9].

Reverse flotation desilication with the simple reagent system is one of the most common methods to separate magnesite from the quartz [1,10]. During this process, a small amount of the quartz particles rise with the bubbles in the pulp, which are the flotation tailings. While magnesite particles are mainly left in the pulp as flotation concentrates. The collector plays a critical role in achieving effective flotation separations of minerals [11,12]. Cationic amine collectors are widely used in the reverse flotation desilication systems of magnesite, with the most common being dodecylamine (DDA) [1,8]. While the DDA as a collector of reverse flotation desilication has exposed many defects in industrial production, such as poor selectivity, foam stickiness, toxicity, refractory, etc., [3,13,14]. Therefore, in recent years, researchers have conducted a lot of work on the novel reverse flotation desilication collectors for magnesite, and have developed various cationic collectors, such as hydroxyl-containing cationic collectors (N-dodecylisopropanolamine, N,N-Bis(2-hydroxypropyl)laurylamine, N-(2-hydroxy-1,1-dimethylethyl) dodecylamine, 2-[2-(Tetradecylamino)ethoxy]ethanol, etc.), polyamine cationic collectors (N-dodecylethylenediamine, N-(2-hydroxyethyl)-N-dodecylethanediamine, etc.), quaternary ammonium salt cationic collectors (N-hexadecyltrimethylammonium chloride, Palmitoyl trimethylammonium chloride, 1,4-bis(dodecyl-N,N-dimethylammoniumbromide)butane, etc.), and others (N,N-Dipropyl-dodecyl amine, N-[3-(dimethylamino) propyl]dodecanamide, pentaethoxylated laurylamine, Dimethylaminopropyl lauramide, etc.) [9,13,15–18]. Compared to the DDA, the above-mentioned collectors have exhibited certain advantages in the field of reverse flotation desilication of magnesite, but their application and promotion in industrial practice were hindered because of harsh synthesis conditions, high production costs, toxicity, refractory, etc. Therefore, developing highly selective, low-cost, and environmentally friendly collectors for magnesite reverse flotation desilication remains a research hotspot for the sustainable development of magnesite resources.

Cocamidopropyl amine oxide (CPAO, Figure 1) is a biodegradable surfactant, that has the advantages of good water solubility, foam stability, large foam volume, low irritation, and so on, and is widely used in fields such as daily chemical products, textiles, sterilization, and so on [19,20]. The primary raw material of the CPAO is natural coconut oil, and its price is relatively low [20]. Although the CPAO has great surface activity, there are no reports of it being used in mineral processing yet. As is well known, the dodecylamine (DDA) is the most common cationic collector, commonly used for the separation of minerals such as silicates, carbonates, phosphates, potassium salts, metal oxide ores, and so on [21,22]. Compared to the DDA, the CPAO has advantages such as easy biodegradation, good low-temperature stability, and low toxicity, making it a potential cationic collector for mineral desilication.

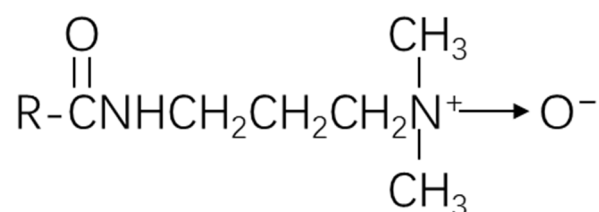


Figure 1. The molecular structure of CPAO (R contains the group of lauric acid, myristic acid, and palmitic acid).

In this study, the biodegradable surfactant CPAO was first used as the collector for the separation of the magnesite from the quartz. The flotation performance of the CPAO for the separation of the magnesite and quartz was investigated through the micro-flotation experiments of the single mineral and the artificially mixed mineral. Furthermore, the selective adsorption behavior and mechanism of the magnesite and quartz with the CPAO were also investigated by contact angle tests and atomic force microscopy (AFM) measurements, fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) analyses.

2. Materials and Methods

2.1. Materials

The samples of the magnesite and quartz used for the experiments were obtained from Anshan City, Liaoning Province, China. The large pieces of high-quality ore were crushed to 3~5 mm by the hammer, and high-grade ore samples were selected by hand. The selected small particles of high-purity samples were then ground in a ceramic ball mill and sieved with a $-74 + 38 \mu\text{m}$ standard sieve to obtain qualified-grade products. The samples of the quartz were soaked with the HCl (analytical pure, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) three times, to remove impurities to improve quality, and then washed with ultrapure (UP) water until neutral pH was obtained, and finally dried at low temperature in a vacuum drying oven for use in subsequent tests. The magnesite samples with qualified particle sizes were magnetically separated three times by a magnetic separator (SLon-1.0T, SLon Magnetic Separator Co., Ltd., Ganzhou, China) and then subjected to shaking table sorting (LYN(S)-1100 $\times$ 500, Wuhan Exploration Machinery Co., Ltd., Wuhan, China) for further purification to obtain qualified products. Finally, they were also dried at a low temperature in a vacuum drying oven for use in subsequent tests. The results for the X-ray diffraction (XRD) and chemical analysis (X-ray fluorescence spectrometric, thermogravimetric analysis method, and inductively coupled plasma) of the magnesite and quartz samples are presented in Table 1 and shown in Figure 2. It can be concluded from these results that the purity of the obtained magnesite and quartz samples was higher than 98%, which satisfied the requirement of the following tests.

Table 1. Chemical compositions of pure minerals (wt. %).

Sample	MgO	CaO	SiO ₂	Al ₂ O ₃	SO ₃	LOI
Magnesite	47.28	0.31	0.36	0.08	0.03	51.94
Quartz	0.11	0.09	99.48	0.32	—	—

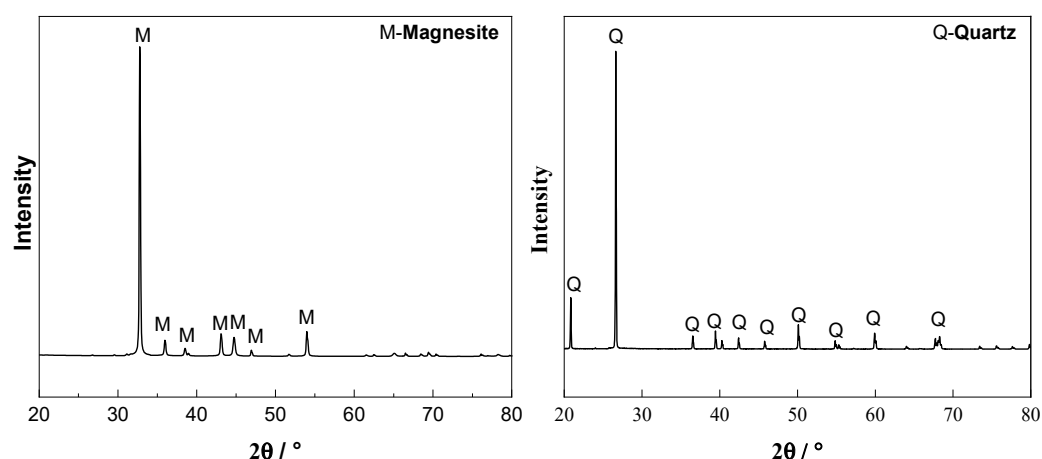


Figure 2. XRD patterns of the magnesite and quartz.

The CPAO was purchased from Shanghai Maclean Biochemical Co., Ltd., Shanghai, China. The hydrochloric acid (HCl) and sodium hydroxide (NaOH) used to adjust the pH of the pulp were purchased from Sinopharm Chemical Reagent Co., Ltd. The potassium bromide used for the IR detection background was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China. All the tests requiring water in the study were conducted using the UP water (18 MΩ·cm) to avoid the influence of other ions, which was prepared using ultra-pure water mechanisms (TS-DI-40L/H) from the Dow Water Treatment Equipment Engineering Co., Ltd., (Dongguan, China).

2.2. Methods

2.2.1. Flotation Experiments

The micro-flotation experiments were carried out on an XFGII 5-35 flotation machine with a 30 mL flotation cell, which was produced by the Jilin Exploration Machinery Plant. First, 3 g of single mineral samples or artificially mixed mineral samples (magnesite:quartz = 1:1) and the UP water were placed in the flotation cell. The mixed pulp samples were stirred for 2 min at 1600 rpm at room temperature. Then, the pH regulator (HCl or NaOH) was added into the suspension and stirred for 2 min. After that, the collector was added with a subsequent 1 min stirring, and then the flotation scraping operation time was 5 min. Finally, the froth products and the cell products were collected, filtered, dried, and weighed, respectively. The products of the artificially mixed mineral were analyzed for the MgO in the Analytical and Testing Center of Northeastern University (Shenyang, China), and the recovery was calculated by the following equations [8,17].

$$\varepsilon = \frac{\beta \times m}{\alpha \times M} \times 100\%$$

where ε is the MgO recovery, %; m is the weight of the product at the tank, g; M is the total weight of the raw mineral, g; and α is the MgO grade of the raw mineral, %.

2.2.2. Contact Angle Measurements

As known from the literature, the flotability of minerals is often characterized by the hydrophobicity of the mineral surface [23]. Measuring the contact angle value of a mineral or mineral treated by flotation reagents is a common method to judge the strength of their surface hydrophobicity and indirectly evaluate their flotation behavior. In this study, a contact angle measuring instrument JC2000A, which was produced in Shanghai Zhongchen Digital Technology Equipment Co., Ltd. (Shanghai, China) was used to conduct the contact angle measurements. The pure samples of the magnesite and quartz were first sliced out flat plane by using the slicer and then polished smoothly with the sandpaper. The prepared samples of the magnesite and quartz were cleaned and then soaked in the UP water or a certain concentration of the CPAO solutions for 10 min, respectively. Subsequently, the samples of the magnesite and quartz were taken out and dried in a vacuum drying oven at a low temperature of approximately 50 °C. Finally, the dried samples were placed on the platform of the contact angle measuring instrument to conduct the contact angle measurements, and each sample was measured three times (the measurement effective error was $\pm 1.0^\circ$), with the average reading used to determine the final contact angle value of the sample [22].

2.2.3. AFM Analysis

An atomic force microscopy (AFM) is often used to react with the sample's surface morphology by measuring the force of the interaction between the probe and the sample and is commonly used to detect the absorption performed between minerals and the flotation reagent. In this study, a Bruker MultiMode 8 AFM with a scan range of $1.0 \mu\text{m} \times 1.0 \mu\text{m}$ and 256 lines were used to examine the cross-section height and images of the magnesite and quartz. The small, smooth, and square samples prepared by the pure minerals were cleaned with the UP water in an ultrasonic cleaner to remove impurities and then dried. The dried samples were immersed for 30 min in the presence and absence of a certain CPAO concentration solution. Subsequently, the samples were dried in a vacuum drying oven at a temperature of 35 °C [8]. Finally, the final prepared samples were pasted on the slide and were measured using the AFM.

2.2.4. FTIR Analysis

The Nicolet 740 FTIR spectrometer, which was produced in Waltham, MA, USA, was utilized to perform the FTIR measurements for studying the adsorption behavior and mechanism between collector and mineral. The pure samples of the magnesite or quartz

were ground in a clean agate mortar to obtain the sample less than $-5\ \mu\text{m}$. Subsequently, the procedure for the sample preparation was similar to that used in the flotation experiments. The flotation products were dried in a vacuum drying oven at a low temperature of approximately $50\ ^\circ\text{C}$. The KBr disc pellet is the common method of the FTIR measurements and was used in the study. The dried samples were combined in a ratio of 1:100 with potassium bromide and then compressed to obtain suitable samples of the FTIR measurements. Finally, each sample's FTIR wavenumber, which ranged from 450.0 to $4000.0\ \text{cm}^{-1}$, was measured and analyzed [24].

2.2.5. XPS Analysis

A thermo PHI VersaProbe 4 spectrometer (Waltham, MA, USA) was used to detect the X-ray photoelectron spectra of the CPAO with and without their interaction with the minerals. The samples to be measured were prepared in a similar way to the FTIR analysis. After scanning all the elements in the sample, the high-resolution spectra of the contained elements were scanned individually by the high-magnification X-ray photoelectron energy after scanning all the elements in the sample. The obtained spectra were analyzed using the XPS Peak 4.1 software. The C1s peak of $284.8\ \text{eV}$ was also used as a reference [25].

3. Results and Discussion

3.1. Micro-Flotation Experiments of Single Minerals

Flotation recovery is a common index for evaluating the collector's ability to collect minerals [26]. For this purpose, first, the effect of the pulp pH on the CPAO's collection of the magnesite and quartz was investigated (Figure 3). As seen in Figure 3, the change in the pulp pH showed little effect on the magnesite recovery at the $10.0\ \text{mg/L}$ CPAO concentration as a function of the pH. The recovery of magnesite was always at a relatively low level, and in the test pH range, the recovery of magnesite was always below 4%. It can also be seen from Figure 3 that contrary to magnesite, the flotation recovery of the quartz was extremely affected by the pH of the pulp; it first increased and then decreased as the pulp pH value increased. With the increase in the pulp pH value from 4 to 10, the recovery of the quartz was above 80%; its value reached 97.1% at the natural pH. As the pH value continued to increase, its recovery rapidly decreased to 5% . When the pH of the pulp was neutral or weakly alkaline, the flotation performance of the CPAO on the quartz and magnesite had a huge difference. When the pulp pH was about 7.2 , the flotation performance difference between the magnesite and quartz using the CPAO as the collector was the largest, in which the recovery of the quartz was 98.02% and the recovery of the magnesite was 3.60% .

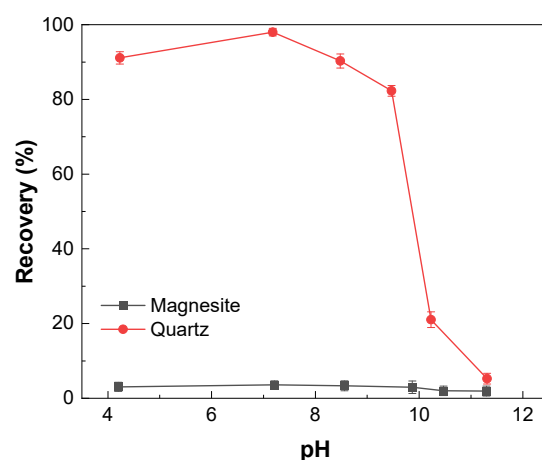


Figure 3. Flotation recovery of the magnesite and quartz in the presence of the $10.0\ \text{mg/L}$ CPAO as a function of pulp pH.

The effect of the CPAO concentration on the recovery of the magnesite and quartz at natural pulp pH is shown in Figure 4. As seen from Figure 4 with the increase of the CPAO concentration from 2.5 mg/L to 15.0 mg/L, the recovery of magnesite showed an increasing trend. In the range of the test CPAO concentration, increasing the concentration of the CPAO had a very limited effect on the recovery of magnesite, and the recovery of magnesite was always kept at a low level and lower than 5%. Figure 4 also shows that the recovery of the quartz increased at first and then tended to be stable with the increase in the CPAO concentration. When the concentration of the CPAO increased from 2.5 mg/L to 10.0 mg/L, the recovery of the quartz increased with the increase in the CPAO concentration. The recovery of the quartz reached 98.02% at the 10.0 mg/L of CPAO, and when the concentration of the CPAO continued to increase, the recovery had no significant transformation. The results show that when the concentration of the CPAO was 10.0 mg/L, the flotation performance of the CPAO on the quartz reached its maximum, and too much reagent would not further increase the recovery of the quartz.

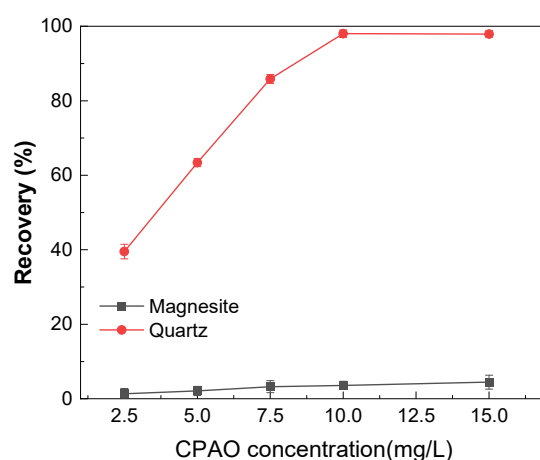


Figure 4. Flotation recovery of the magnesite and quartz as a function of the CPAO concentration at natural pulp pH.

By comparing the recoveries of the quartz and magnesite at the same concentration, it can be concluded that the CPAO had strong selectivity when the dosage of the reagent was sufficient. When the dosage of the CPAO reached 10.0 mg/L, the recoveries of the quartz and magnesite were 98.02% and 3.60%, respectively, with a difference of more than 90%, which could effectively achieve the separation of magnesite and quartz. While the traditional cationic collector DDA, was used as the collector under the same conditions, the recovery of the quartz was 92.55% and lower than that of the CPAO, and the recovery of the magnesite was 22.43% and higher than that of the CPAO.

3.2. Micro-Flotation Experiments of Artificially Mixed Minerals

To further determine the separation performance of the CPAO in the magnesite–quartz system, the artificially mixed ore flotation experiments were used to measure the separation performance of the CPAO for the magnesite and quartz. The separation results of the quartz and magnesite by the 10.0 mg/L CPAO for different pH conditions are shown in Figure 5.

It can be seen from Figure 5 that the MgO grade decreased with the increase of the pulp pH when the pH was in the range of 7 to 12. When the pulp pH was about 7, the MgO grade was 45.62%, and with the pulp pH increased to 11.3, the MgO grade dropped to 23.68%. This could be due to the ability of the CPAO to collect the quartz was decreasing with the increase in the pulp pH value. When the pH was about 11, the flotation performance of the CPAO for the quartz and magnesite was similar. As the pulp pH increased from 4 to 11, the recovery of the MgO in concentrate increased, and the recovery of the MgO consistently exceeded 95% within the entire pH study range. Since this flotation process was reverse flotation, the concentrate stayed in the flotation cell. With an increase in pH,

the ability of the CPAO to collect the quartz was weakened, and the mass of the quartz in the flotation cell was increased. In summary, the optimal pulp pH of the CPAO as a collector for the magnesite and quartz was between a natural pH and a weakly alkaline pH. The natural pulp pH was chosen and used in the subsequent study, at this point, the obtained concentrate grade was 45.62%, and the recovery rate of that was 97.67%.

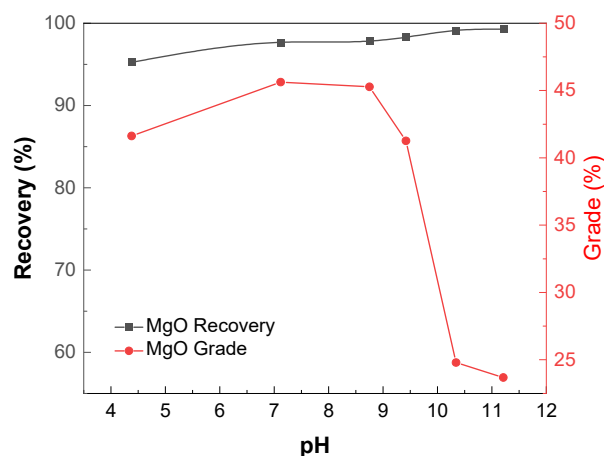


Figure 5. Flotation recovery and grade of the MgO as the function of the pulp pH with 10.0 mg/L CPAO.

The effect of the CPAO concentration on the flotation separation of the magnesite and quartz was investigated under the natural pulp pH (about 7.2), and the results are shown in Figure 6.

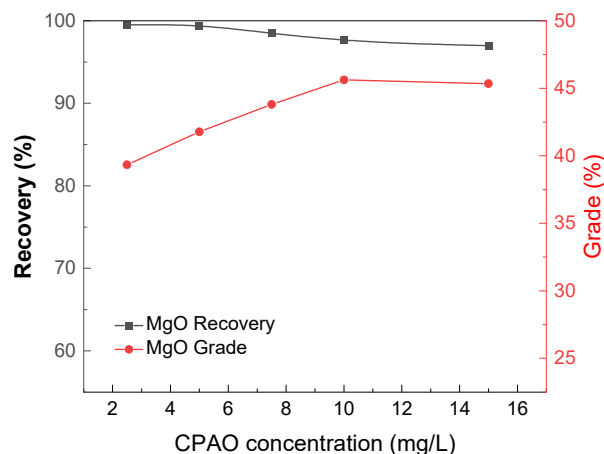


Figure 6. Flotation recovery and grade of the MgO as the function of the CPAO concentration.

As can be seen from Figure 6, with the increase in the additional dosage of the CPAO, the recovery of the MgO slightly decreased. It could be due to the floating ability of the magnesite enhanced with the increase in the CPAO concentration, and more magnesite entered the foam product. However, when the concentration of the CPAO reached 15.0 mg/L, the recovery of the MgO was still over 96%. Additionally, with the increase in the CPAO concentration, the MgO grade of the obtained concentrate gradually increased to a certain value and then slowly changed. When the CPAO concentration increased from 2.5 mg/L to 10.0 mg/L, the MgO grade of the obtained concentrate increased from 39.33% to 45.62%. However, when the CPAO concentration exceeded 10 mg/L, the MgO grade of the obtained concentrate did not continue to improve as the CPAO concentration increased. It could be due to the fact that under that amount of the CPAO, the vast majority of the quartz had been floated out, and as the amount of the CPAO was too large, some magnesite was also floated out, so the MgO grade of the obtained concentrate could not continue to increase.

The performance of the CPAO in the magnesite–quartz flotation system was analyzed, and the optimal separation indexes of the concentrate could be obtained with the natural pulp pH (about 7.2) and 10.0 mg/L CPAO as the collector, which the MgO recovery and grade of that were 97.67% and 45.62%, respectively. In summary, the CPAO has great potential as an effective collector in the reverse flotation desilication progress of magnesite.

3.3. Contact Angle Measurements

The contact angle is an important indicator of the hydrophobicity of the mineral surface, and the value of the contact angle has a positive correlation with the hydrophobicity of the mineral surface [27]. The improvement of the surface hydrophobicity of the quartz and magnesite could be understood by comparing the changes in the surface contact angle of the quartz and magnesite before and after treatment with the CPAO. Figure 7 shows the contact angle of the quartz and magnesite before and after treatment with the CPAO.

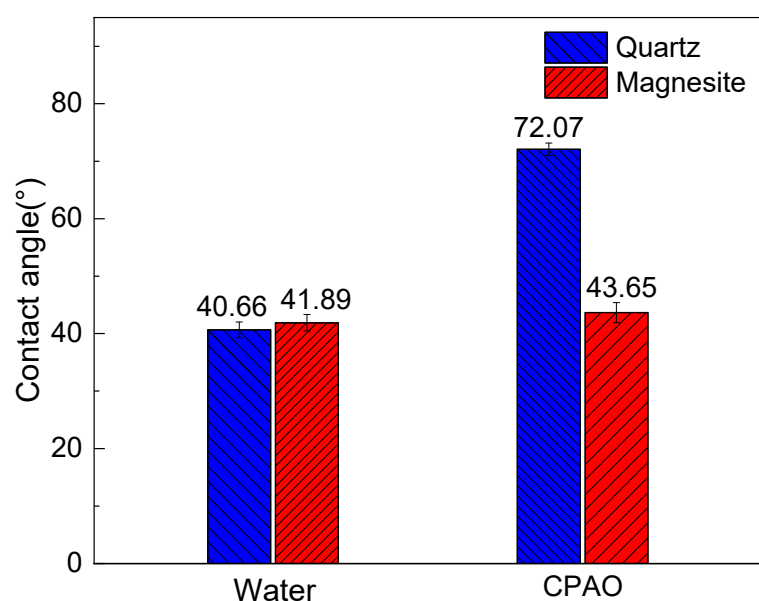


Figure 7. Contact angles of the quartz and magnesite before and after treatment with 10.0 mg/L CPAO.

It can be seen from Figure 7 that the contact angles of the quartz and magnesite before the treatment with the collector were 40.66° and 41.89°, respectively. The results were similar to those of previous relevant reports, and the contact angles of the magnesite and quartz were low, indicating that the natural flotability of the magnesite and quartz was poor [10,12,28]. After treatment with the 10.0 mg/L CPAO, the contact angle of the quartz surface changed significantly and increased from 40.66° to 72.07°, whereas the contact angle of the magnesite surface had little change and only increased from 41.89° to 43.65°. It can be concluded that CPAO could effectively improve the surface hydrophobicity of the quartz but had little effect on the surface hydrophobicity of magnesite. After treatment with the appropriate CPAO, the surface hydrophobicity of the quartz and magnesite was very different, and the surface hydrophobicity of the quartz was much higher than that of magnesite, so the two show a large difference in flotability, to achieve the purpose of separating the quartz and magnesite. To sum up, the surface hydrophobicities of the quartz and magnesite were improved to different degrees after treatment with the CPAO. The surface hydrophobicity of the quartz was greater, which means that the flotation performance of the quartz and magnesite after the treatment with the CPAO was greatly different. This above could also be used to explain the results of the single mineral flotation tests and artificial mixed ore flotation tests.

3.4. AFM Analysis

An atomic force microscopy (AFM) can respond to the surface morphology of the sample through the force of the interaction between the probe and the sample before it is applied [29]. It can therefore be used to visually detect the absorption of minerals before and after interaction with the reagent. The surface morphology of the quartz and magnesite before and after treatment with a concentration of the 10.0 mg/L CPAO is shown in Figure 8. The NanoScope Analysis 2.0 software was used to analyze the microscopy of two mineral samples.

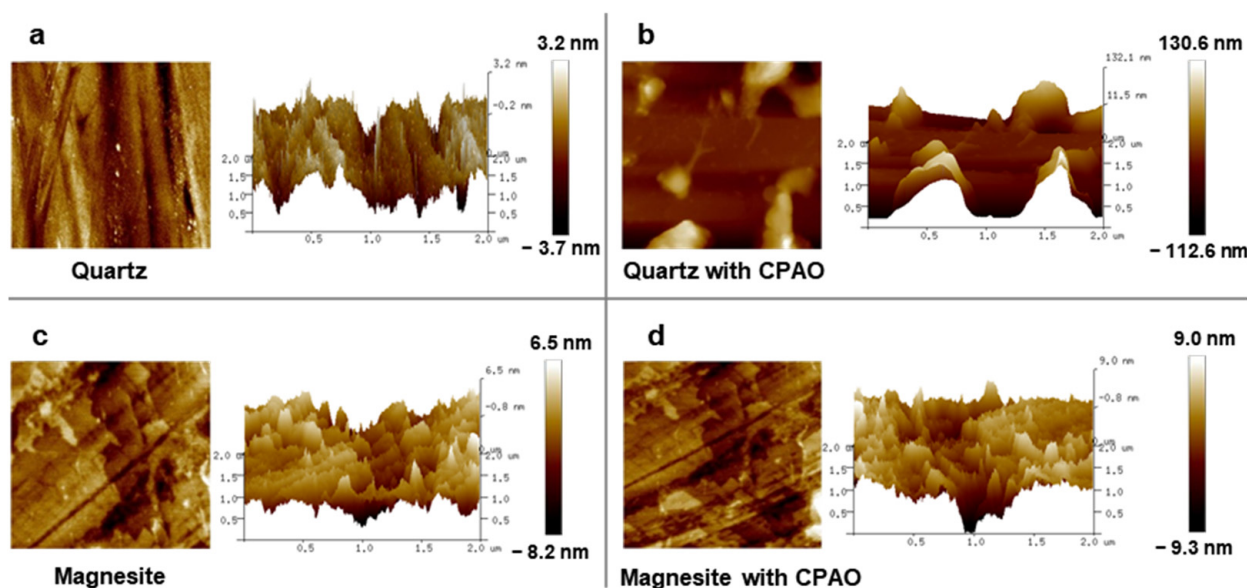


Figure 8. AMF images of the quartz and magnesite before (a,c) and after (b,d) treatment with CPAO.

Figure 8a shows the two-dimensional and three-dimensional surface morphology of the quartz before treatment with the CPAO. It can be seen from the two-dimensional image that the quartz surface was mainly composed of yellow particles and a small amount of white quartz particles. From the three-dimensional morphology, the quartz surface was uneven, and the quartz particles were unevenly distributed. The absolute altitude of the particles on the quartz surface was 3.2 nm. Figure 8b shows the two-dimensional and three-dimensional surface morphologies of the quartz treated with the CPAO. As can be seen from the three-dimensional image in Figure 8b, the surface of the quartz was no longer quartz particles, but a layer of oil was wrapped around the quartz particles. From the three-dimensional morphology, it could be concluded that the quartz surface topography was not uneven, but only a few raised parts. It indicated that the collector adsorbed and filled on the quartz surface, making the uneven surface filled with the collector molecules [30,31]. It could also be seen that the absolute altitude of the quartz surface changed from 3.2 nm to 130.6 nm, which was due to the CPAO was adsorbed on the surface of the quartz particles. The thickness of the originally raised quartz particles had increased. The changes on the quartz surface also indicated that the CPAO adsorbed on the quartz surface particles in some form. Based on the analysis results of contact angle detection, it could be inferred that one end of the CPAO adsorbed on the quartz surface particles in some form, and the hydrophobic end was exposed to the outside, thus improving the hydrophobic surface of the quartz surface [32–34]. It can also be seen from Figure 8c,d) that the absolute altitude of the magnesite surface changes little before and after the CPAO treatment, indicating that the CPAO hardly adsorbs on the magnesite surface. The above results were consistent with the results of flotation experiments, indicating that the CPAO had good selectivity for the quartz.

3.5. FTIR Analysis

The FTIR analysis can detect the functional groups of chemicals and minerals. By comparing the changes of functional groups on the mineral surface before and after treatment of the chemical reagent, the adsorption mode of the chemical reagent on the mineral surface can be preliminarily judged [35]. To investigate the adsorption mode of the CPAO on the quartz surface, the FTIR analysis was conducted on the quartz surface before and after treatment with the CPAO. Figure 9 shows the infrared spectra of the CPAO and the quartz surface before and after treatment with 10 mg/L CPAO.

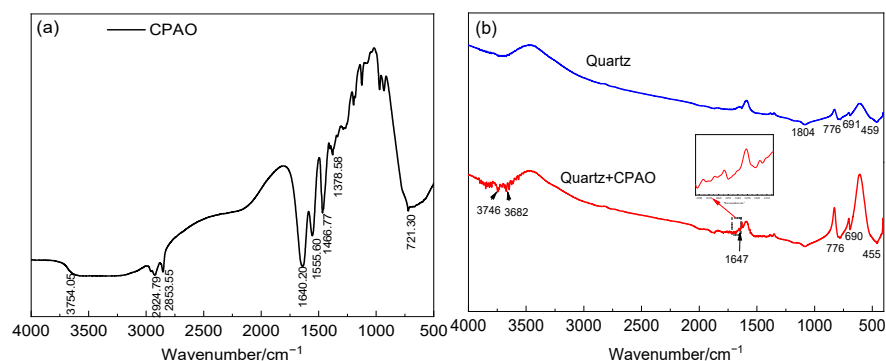


Figure 9. Fourier infrared spectra of the CPAO and quartz, (a) CAPO, (b) quartz before and after treatment with CPAO.

It can be seen from Figure 9a that N–H stretching vibrational absorption peak in amide group at 3784.05 cm^{-1} ; strong absorption peaks at 2924.79 cm^{-1} and 2853.55 cm^{-1} for methyl and methylene stretching vibrations; stretching vibrational absorption peak in C=O double bond in amide group at 1640.20 cm^{-1} ; in-face bending vibrational absorption peak in the N–H bond at 1555.60 cm^{-1} and 1466.77 cm^{-1} ; in-face wobbling vibrational absorption peak in methylene group at 1378.58 cm^{-1} for the N–H stretching vibration absorption peak in the amide group; and at 721.30 cm^{-1} for the in-face rocking vibration peak of the methylene group [35].

It can be seen from Figure 9b that before treatment with the CPAO, the infrared spectrum of the quartz was mainly the characteristic peaks (Si–O bond absorption peak) of the quartz [36]. The peak around 1084 cm^{-1} corresponded to the asymmetric stretching vibration absorption peak of the Si–O bond, the peaks around 776 cm^{-1} and 691 cm^{-1} corresponded to the symmetric vibration absorption peaks of the Si–O–Si bond, and the peak around 459 cm^{-1} corresponded to the bending vibration absorption peak of the O–Si–O bond [24,37]. After treatment with the CPAO, the infrared spectrum of the quartz had no new peaks except for the characteristic peaks of the quartz and CPAO. In the spectrum of the quartz treated with the CPAO, the peak that appeared around 1647 cm^{-1} corresponded to the C=O characteristic absorption peak of the amide group from CPAO, and a large number of peaks appeared in the vicinity of $3800\text{--}3500\text{ cm}^{-1}$, which might be the O–H of H_2O or N–H of CPAO [15,38]. From the above, it could be inferred that the CPAO was adsorbed on the quartz surface, the adsorption process between them did not involve chemical reactions [39]. It also can be seen that there was a red shift phenomenon of the peak in the spectrum of the quartz treated with the CPAO. The bending vibration absorption peak of the O–Si–O bond shifted from 459 cm^{-1} to 455 cm^{-1} , indicating that the O–Si–O bond participated in the adsorption process, and might have hydrogen bonding with the CPAO [36]. Therefore, it could be concluded that the CPAO adsorbed on the surface of the quartz mainly through electrostatic interaction and hydrogen bonding, which also explains the significant impact of the CPAO on mineral flotation performance by slurry pH.

3.6. XPS Analysis

According to the infrared spectroscopy, the adsorption mechanism of the CPAO on the quartz surface was inferred. To further study the adsorption mechanism, the XPS detection was performed on the quartz surface before and after treatment with the CPAO. The XPS results are shown in Table 2. The atomic binding energy on the quartz surface before and after treatment with the CPAO is shown in Figures 10 and 11.

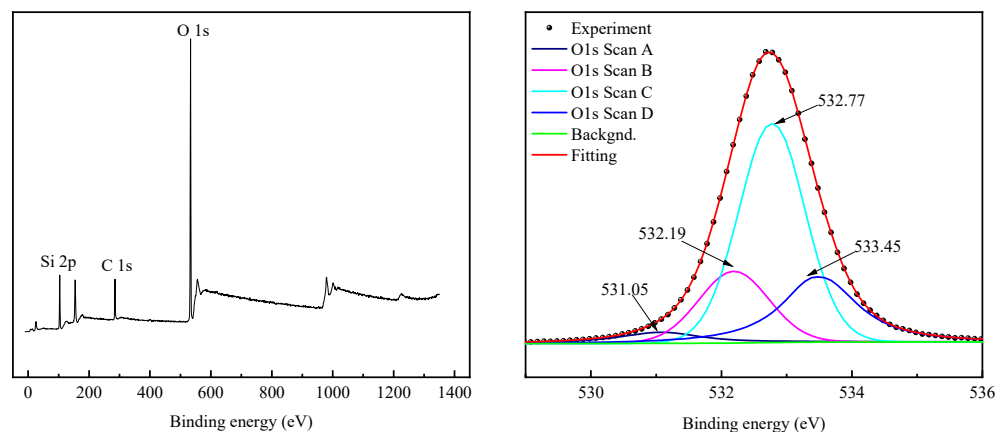


Figure 10. The binding energy of elements on the quartz surface before treatment with CPAO.

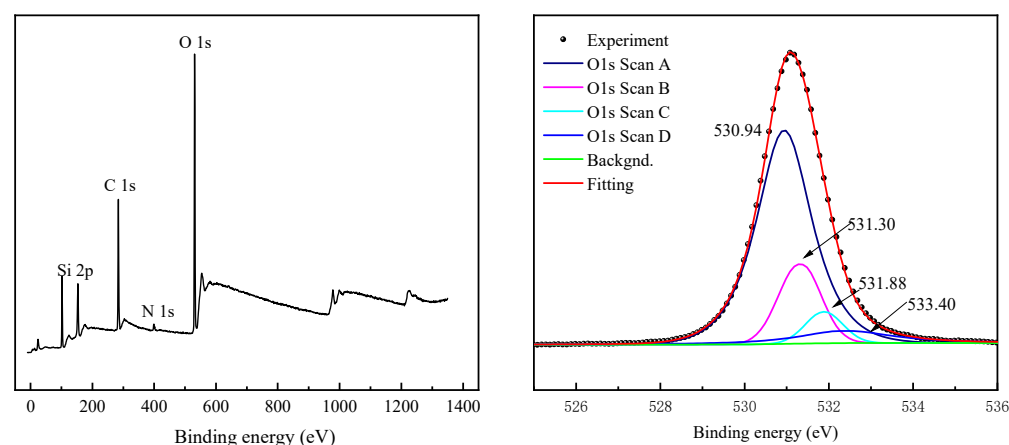


Figure 11. The binding energy of elements on the quartz surface after treatment with CPAO.

Table 2. XPS characterization of reference compounds on the samples.

Species	Atomic Concentration (%)				Binding Energy (eV)		
	C 1s	O 1s	Si 2p	N 1s	C 1s	O 1s	Si 2p
Quartz	17.51	48.38	30.92	-	284.80	532.95	103.27
Quartz with CPAO	40.38	34.09	23.77	1.76	284.80	532.26	103.19

It can be seen from Table 2 and Figures 10 and 11 that the quartz surface only contained C, O, and Si elements before treatment with the collector. Wherein C was inevitably derived from the conductive adhesive used in the XPS experiments, O and Si were derived from the quartz surface. After treatment with the CPAO, the N element, about 1.76%, was checked on the quartz surface. The content of the Si element decreased from 30.92% to 23.77%, the content of the O element decreased from 48.38% to 34.09, and the content of the C element increased from 17.51% to 40.38%. It could be inferred that CPAO was adsorbed on the quartz surface. It can also be seen that the binding energy of the O 1s peak migrated from 532.95 eV to 532.26 eV, and that of other elements had little change, indicating that the O

element on the quartz surface participated in the adsorption process between the CPAO and the quartz surface [36,40].

Peak fitting was performed on the full spectrum and O 1s peaks of the quartz surface and the quartz surface treatment with the CPAO, and the results are shown in Figures 10 and 11. In Figure 10, the O 1s peak on the quartz surface consisted of four peaks, namely Si–O (531.05 eV), Si–O–Si (532.19 eV), Si–OH (532.87 eV), and H₂O (533.45 eV) [36]. From Figure 11, after treatment with CPAO, no new O 1s peaks appeared on the quartz surface, but the binding energy of the O 1s peaks migrated to 530.94 eV (Si–O), 531.30 eV (Si–O–Si), and 531.88 eV (Si–OH), respectively. The results show that the NH groups in the CPAO could form strong hydrogen bonds with Si–O, Si–O–Si, or Si–OH groups on the quartz surface [15]. Therefore, the adsorption modes of CPAO on the quartz surface included the strong hydrogen bonds formed by the NH groups in the CPAO molecules and O atoms on the quartz surface and the electrostatic adsorption [24].

4. Conclusions

The biodegradable surfactant, CPAO, was first used as a collector for the separation of the magnesite and quartz. The micro-flotation experiments indicated that the flotation performance of the CPAO on the magnesite and quartz was extremely different, at the 10.0 mg/L CPAO in the natural pulp pH, the recovery of the quartz was 98.02%, while that of magnesite is only 3.60%. The optimal separation indexes of the concentrate were obtained with the natural pulp pH (about 7.2) and the 10.0 mg/L CPAO as the collector, and the MgO recovery and grade were 97.67% and 45.62%, respectively. The flotation tests indicated that the CPAO had good selectivity and great potential as an effective collector in the reverse flotation desilication progress of magnesite. The contact angle measurements indicated that the CPAO could selectively adsorb on the quartz surface to enhance its surface hydrophobicity. The AFM analysis also confirmed that CPAO could selectively adsorb on the quartz surface rather than the magnesite surface to improve the interface difference between them. The results of the FTIR and XPS analyses indicated that the O element on the quartz surface participated in the adsorption process between the CPAO and quartz surface, and the CPAO selectively adsorbed on the surface of the quartz mainly through electrostatic interaction and hydrogen bonding.

Author Contributions: Conceptualization, W.L. (Wenbao Liu) and Y.S.; methodology, W.L. (Wenbao Liu) and Q.Z.; software, R.Z.; validation, P.Z. and Q.Z.; formal analysis, C.H.; investigation, P.Z., W.L. (Wengang Liu) and Q.Z.; resources, W.L. (Wenbao Liu); data curation, R.Z. and W.L.; writing—original draft preparation, W.L. (Wenbao Liu) and Q.Z.; writing—review and editing, W.L. (Wenbao Liu) and Q.Z.; visualization, C.H., P.Z. and R.Z.; supervision, W.L. (Wenbao Liu); project administration, Y.S.; funding acquisition, W.L. (Wenbao Liu). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Nos. 52104250, and 52274254), the Fundamental Research Funds for the Central Universities (No. N2201005), the China Postdoctoral Science Foundation (2022M720927), the Supported by Guizhou Provincial Science and Technology Projects (Qiankehe Support [2023] General 142).

Data Availability Statement: Data are contained within the article.

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

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