Original Article

Investigation into the flotation of malachite, calcite and quartz with three phosphate surfactants

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ABSTRACT

The flotation response of malachite, calcite and quartz to bis (2-ethylhexyl) phosphate (DEHPA), dibutyl phosphate (DBP) and tributyl phosphate (TBP) was evaluated by microflotation experiments. The results showed that DEHPA exhibited an impressive flotation selectivity for malachite against calcite/quartz in the pH range of 6.0–9.0 and achieved superior malachite flotation recovery over DBP and TBP. The flotation mechanism of DEHPA to malachite was further investigated through adsorption, contact angle, zeta potential, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The findings inferred that DEHPA reacted with the surface copper atom of malachite via its O atoms of $P-OH$ and $P=O$ to form the hydrophobic surface complexes of Cu(II)-DEHPA. The double active center of the $-P(=O)OH$ group might be contributed to the stronger affinity of DEHPA and DBP to malachite than that of TBP with the single active center of the $-P=O$ group. TBP returned the lowest malachite recovery among the three phosphate surfactants, even it has more hydrophobic carbon atoms than those of DBP.

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1. Introduction

Copper is extensively used in daily necessities, industries and national defenses. Copper oxide minerals are of a significant resource for copper production [1,2]. Currently, there are two basic technologies for the processing of copper oxide minerals, leaching/solvent extraction/electrowinning process and froth flotation. The former usually is a time-consuming and costly process with high pollution and low processing capacity [3,4]. In many cases, flotation technology is a better choice for the separation and enrichment of copper oxide minerals [5–8]. Malachite $\text{Cu}_2(\text{OH})_2\text{CO}_3$ is the most common CuO mineral in the copper oxide deposits. For possessing dissolubility and hydration, malachite exhibits a poor floatability during froth flotation process [9,10]. It is well established that in froth flotation, collectors play a bridge role between mineral particles and bubbles [11,12]. Thus, to develop high-performance collectors for malachite flotation is of great importance for improving its separation and enrichment.

For flotation recovery of malachite, there are two general technologies, pre-sulfidization flotation with sulfydryl collectors such as xanthates [13–18] and direct flotation with oxide mineral collectors including fatty acids, fatty amines, petroleum sulfonates and hydroxamic acids [18–22]. In most...
cases, the former is more effective than the latter. However, the pre-sulfidization flotation suffers from the insufficient or excessive sulfidization, leading to the unsatisfactory flotation separation efficiency of malachite [13,14,19,20]. Therefore, to separate and enrich malachite through direct flotation approaches has been widely investigated, and the high-selective collectors toward malachite have been far from being satisfactory [23,24]. A great number of investigations showed that the phosphoric acid compounds exhibited strong affinity toward metal oxides through the formation of M–O–P bonds [25–27], and their surfactants have been widely used in the flotation of metal oxide minerals. Bulatovic et al. thought the dialkyl phosphoric acid esters were effective collectors for the flotation recoveries of titanium minerals [28,29]. And they found that octyl diphosphonic acid possessed pretty good selectivity for niobate flotation [29]. Kirchberg and Wotting observed that alkyl phosphoric acids with 5-7 carbon atoms in their alkyl group were powerful flotation collectors for fine cassiterite [30]. Despite the widespread application of phosphorus surfactants in froth flotation of metal oxide minerals, little is known about their flotation separation of malachite from calcite or quartz.

In this paper, bis (2-ethylhexyl) phosphate (DEHPA) was introduced as a flotation collector to enrich malachite, calcite or quartz. Its flotation performances were compared with those of dibutyl phosphate (DBP) and tributyl phosphate (TBP) by micro-flotation tests. Subsequently, the adsorption mechanism of DEHPA toward malachite surfaces was investigated through adsorption, contact angle, zeta potential, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Materials

DEPHA and TBP were purchased from Aladdin and DBP was obtained from Xiya Reagents. Their molecule structures were shown in Fig. 1. Other reagents used in the experiments were purchased from commercial suppliers and they were all analytical reagent grade. Distilled water was used in all the experimental processes.

Malachite, calcite and quartz with high purity were obtained from Guili, Guangxi Province, China [31]. After being ground and sieved, the mineral particles with a diameter ranging from +37 to −74 μm were used in the micro-flotation and adsorption tests. The finer part of −5 μm was used for the measurements of zeta potential, FTIR and XPS.

2.2. Micro-flotation tests

A 240 mL Hallimond tube was used to perform the micro-flotation tests. The flotation procedure was according to our previous experiment [24]. After conducting flotation for 3 min under 200 ± 2 mL/min N2, the froth and underflow products were separately collected, filtered, dried and then weighed. The flotation recovery was calculated by Eq. (1).

\[ \varepsilon = \frac{m_1}{m_1 + m_2} \times 100\% \]  

Here, \( \varepsilon \) is the recovery of malachite, calcite or quartz, \( m_1 \) and \( m_2 \) are the weight of the froth and underflow products (g), respectively. The listed recovery was the average of two independent tests.

2.3. Zeta potential measurements

Zeta potential of malachite, calcite or quartz particles with or without DEPHA in 1 × 10⁻⁵ mol/L KCl solution was recorded at 298 ± 1.5 K on the Brookhaven Zeta Plus analyzer (USA) [24]. 50 mg mineral samples and DEPHA solutions were mixed. To obtain the desired pH of the suspension, several drops of dilute KOH or HCl solutions were injected. Afterwards, the suspension was agitated for 5 min and its zeta potential was independently measured eight times. Their average value was reported with a common variation of ±5 mV.

2.4. Adsorption and contact angle measurements

To a 150 mL conical flask, 0.1 g malachite, 20 mL distilled water, desired pH regulators (dilute KOH or HCl solutions), DEPHA solutions, and extra distilled water were sequentially added to reach 100 mL. After shaking the suspension for 4 h at 298 ± 1.5 K, the malachite pulp was filtered, and the residual concentration of DEPHA in the filtrate was measured according to the concentration of total organic carbon recorded by the Total Organic Carbon analyzer (TOC-VCCH, Shimadzu, Japan). The adsorption amount of DEPHA on malachite surfaces was calculated via Eq. (2).

\[ Q_d = \frac{V(C_0 - C_d)}{WS} \]  

Here, \( Q_d \) is the amount of DEPHA covered on malachite (mol/m²), \( C_0 \) is DEPHA's initial concentration (mol/L), \( C_d \) is the residual concentration of DEPHA (mol/L), \( V \) is the volume (L), \( S \) is malachite's specific surface area with a value of 0.346 m²/g, and \( W \) is the mass of malachite (g). Each adsorption test was repeated twice, independently, and the average result was reported.

The contact angles of malachite surfaces with/without DEPHA modification were measured via water drop method on the Zhongchen JC2000C device (China) [12]. The average value of five separate measurements was reported.

![Fig. 1 – Molecule structures of DEPHA (a), DBP (b) and TBP (c).](image-url)
2.5. FTIR and XPS measurements

$2 \times 10^{-4}$ mol/L DEHPA solutions were blended with $2 \times 10^{-4}$ mol/L CuSO₄ solutions in a volume proportion of 1:2. After being stirred, a blue precipitate appeared from the mixture. 50 mg malachite particles were stirred in 100 mL $2 \times 10^{-4}$ mol/L DEHPA solutions for 5 h at 298 ± 1.5 K. Afterwards, the malachite particles and the blue precipitates were separately filtered, rinsed a couple of times with water, desiccated in a vacuum chamber for 5 days, and then delivered for FTIR and XPS detections.

The Nicolet FTIR-740 spectrometer (USA) was adopted for FTIR record by KBr disk method. And the wavenumber was ranged from 500 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

The ESCALAB 250 Xi instrument and Avantage soft of Thermo Scientific (USA) were used to record and analyze the XPS spectra [24]. And the XPS binding energy was calibrated by setting the C 1s XPS peak at 284.6 eV.

3. Results and discussion

3.1. Micro-flotation findings

Fig. 2 shows the flotation response of malachite, calcite and quartz to pH with $1 \times 10^{-5}$ mol/L DEHPA, DBP or TBP. The results of Fig. 2 (a) indicate that in the presence of $1 \times 10^{-5}$ mol/L DEHPA, the flotation recovery of malachite was over 90% in the pH range of 6–11, while quartz recovery was less than 25%. As for the calcite, a relatively low flotation recovery was observed at pH 6–9. When the pH values were higher than 9, calcite recovery increased sharply and reached the maximum of >82% at pH around 10. The flotation results indicated that DEHPA exhibited excellent flotation selectivity toward malachite against calcite and quartz at pH 6–9.

Fig. 2 (b) demonstrates that $1 \times 10^{-5}$ mol/L DBP recovered approximate 65% malachite over the pH range of 7–9. And malachite recovery decreased to below 60% at pH ∼ 6 or over 10. However, the lower flotation recovery for calcite or quartz was observed across the experimental pH range of 6–11. Obviously, the flotation performance of DBP for malachite was inferior to that of DEHPA.

In Fig. 2 (c), $1 \times 10^{-5}$ mol/L TBP recovered less than 45% malachite, 35% calcite or 25% quartz at pH 6–11. This meant that TBP owned weak collecting power toward malachite, calcite and quartz.

The flotation response of malachite, calcite or quartz as a function of the initial concentration of DEHPA, DBP or TBP at pH ∼ 7 was listed in Fig. 3. It shows that the recoveries of the three minerals increased as increasing collector concentration from $1 \times 10^{-6}$ to $1 \times 10^{-5}$ mol/L. At $1 \times 10^{-5}$ mol/L collector, the recovery of malachite was near 95%, 63% and 43% for DEHPA, DBP and TBP, respectively, while, the flotation recoveries of calcite or quartz were below 30%.

Therefore, Figs. 2 and 3 indicate that the flotation performances of the three phosphate collectors toward malachite could be determined as: DEHPA > DBP > TBP. Specifically, DEHPA exhibited excellent flotation selectivity for malachite versus calcite and quartz over the pH range of 6–9.

For DEHPA and DBP, they possess the active center of −P(=O)OH, and DEHPA returned the higher malachite flotation recoveries for its longer carbon chain and stronger hydropho-
biciry. TBP owns the -P=O functional group which might exhibit weak affinity to copper atom in comparison to the -P(O)OH group, returning the lowest malachite recoveries among the three phosphate surfactants, even it has more hydrophobic-carbon atoms than those of DBP [32].

3.2. Zeta potential results

Fig. 4 shows the isoelectric point (IEP) of the malachite fine particles occurred at pH ~ 8.4, near the reported values [12,33]. In the presence of $1 \times 10^{-4}$ mol/L DEHPA, malachite's $\zeta$ (zeta potential) significantly moved to more negative values, and its IEP emerged at pH ~ 6.7, which implied the adsorption of DEHPA onto the copper atom sites (positive charges sites) of malachite interfaces.

The pKa (the negative logarithm of acid dissociation constant) value of DEHPA was about 1.72 [12,33,34], indicating that the dominated species of DEHPA in aqueous solutions at pH > 6 is its anion ((C8H17O)2POO$^-$). Thus, at pH 6.0–8.4, electrostatic attraction might drive the adsorption of DEHPA onto malachite surfaces. Given that malachite particles were negatively charged at pH > 8.4, the electrostatic attraction was unlikely to be the main driving force for malachite adsorption of anionic DEHPA. However, it was experimentally observed from Fig. 4 that the anionic DEHPA did adsorb onto malachite surfaces at pH > 8.4. These phenomena clearly inferred that DEHPA adsorption overcame the electrostatic repulsive force, recommending a coordination bonding effect of anionic DEHPA to the interface Cu atom on malachite.

3.3. Adsorption results

The adsorption quantities of DEHPA on malachite as a function of pH or DEHPA dose are shown in Fig. 5. Fig. 5 (a)

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**Fig. 3** – Flotation recoveries of malachite, calcite and quartz as a function of DEHPA (a), DBP (b) and TBP (c) initial concentration (at pH ~ 7).

**Fig. 4** – The zeta potential of malachite fine particles with and without $1 \times 10^{-4}$ mol/L DEHPA.
presents that under $1 \times 10^{-5}$ mol/L DEHPA, the preferable pH for malachite adsorption of DEHPA occurred around 7.0. Fig. 5 (b) demonstrates that at pH $\sim$7.0, malachite adsorption towards DEHPA swiftly increased with the increasing concentration until reaching $1 \times 10^{-5}$ mol/L DEHPA. Sequentially, the increase of DEHPA’s adsorption amount turned very slow.

### 3.4. Contact angle

Contact angle is an important index for characterizing the hydrophobicity of a mineral surface. The hydrophobization ability of a collector toward a given mineral surface is closely related to its flotation performance [12,33].

The newly-polished malachite exhibited the contact angle of $42 \pm 1^\circ$. After $1 \times 10^{-5}$ mol/L DEHPA modification of 10 min, malachite’s contact angle increased as shown in Fig. 6. Fig. 6 also demonstrates that the maximum water contact angle of malachite emerged at pH around 7.0 with a value of $93.5 \pm 0.5^\circ$, which corresponded to the preferable pH for malachite adsorption of DEHPA.

### 3.5. FTIR

The FTIR spectra for DEHPA, Cu-DEHPA sediments, and malachite without/with DEHPA treatment are respectively shown in Fig. 7.

Fig. 7 (a) indicates that for DEHPA, its C–H vibrations of the −CH$_2$ and CH$_3$ groups arose on about 2865, 2930 and 2961 cm$^{-1}$. The peaks near 1031 and 886 cm$^{-1}$ were respectively attributed to its PO–C and P–OC vibrations [35]. The characteristic band being close to 2326 cm$^{-1}$ was related to its PO–H oscillation [36]. And its P=O and P–O–H adsorption bands separately appeared close to 1226 and 1690 cm$^{-1}$ [37–41]. For Cu-DEHPA sediments, the adsorption peaks near 2864, 2930 and 2960 cm$^{-1}$ were due to the C–H vibrations. The P=OCu vibration bands appeared close to 1182 cm$^{-1}$ [37]. The peaks at $\sim$1029 and 1098 cm$^{-1}$ belonged to PO–C vibrations and those at 884 cm$^{-1}$ due to P–OC oscillations. The characteristic bands near 3448 and 1633 cm$^{-1}$ resulted from the O–H vibrations of water molecules [4,40].

After modification with DEHPA, the C–H adsorption bands at around 2850, 2920 and 2960 cm$^{-1}$ appeared on malachite as presented in Fig. 7(b) [41]. The vibration peak at $\sim$1628 cm$^{-1}$ might be related to O–H of water molecules. It should be noted that malachite possesses strong IR adsorption bands which covered those of Cu-DEHPA surface complexes, thus making their characteristic absorption peaks less pronounced [41].

### 3.6. XPS results

The XPS for the Cu-DEHPA precipitation and malachite modified by DEHPA are shown in Figs. 8–10 and Tables 1–3. The survey XPS results in Fig. 8 and Table 1 demonstrate that the mole ratio of carbon, oxygen, phosphorus and copper in the Cu-DEHPA precipitates was of 31.95:9.00:2.10:1.00, suggesting that the chemical composition of the Cu-DEHPA precipitates was of Cu(DEHPA)$_2$H$_2$O. This meant two DEHPA species might combine with one copper atom to form Cu-DEHPA complexes [42]. After malachite was treated with DEHPA, its atomic con-
Fig. 7 – FTIR spectra of (a) DEHPA before or after its response to Cu²⁺ and (b) malachite before and after DEHPA adsorption.

Fig. 8 – The scanning XPS of malachite before (a) and after (b) DEHPA adsorption, and Cu-DEHPA precipitate (c).

Fig. 9 – High-resolution Cu 2p 3/2 XPS for malachite (a) before and (b) after DEHPA treatment, and (c) Cu-DEHPA precipitate.

centration of carbon and phosphorus increased, while that of copper and oxygen reduced, signifying the adsorption of malachite towards DEHPA.

As shown in Fig. 9 and Table 2, the Cu 2p3/2 XPS peaks of the Cu-DEHPA precipitation were observed at ~934.71 and 932.43 eV, which might be separately assigned to the Cu(II)-DEHPA¹ with the [43] and Cu(II)-DEHPA² with the configuration. The Cu 2p3/2 XPS peaks for malachite appeared around 934.65 eV, belonging to Cu(II) oxides [43]. After treatment with DEHPA, malachite surface existed two XPS adsorption bands at ~934.72 and 932.65 eV, the former might be designated as the Cu(II)-DEHPA¹ with the configuration and the Cu(II) species in malachite bulk phase. The other might be assigned to the Cu(II)-DEHPA² with the configuration. The Cu atom in Cu(II)-DEHPA² is more convenient to share electrons from its four-membered ring structure than that in Cu(II)-DEHPA¹, resulting in lower Cu binding energy. It should

Table 1 – Relative atomic concentration of elements as confirmed by XPS.

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<th>Substances</th>
<th>Relative atomic concentration/%</th>
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<tr>
<td></td>
<td>C 1s</td>
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<tr>
<td>Cu-DEHPA precipitate</td>
<td>72.53</td>
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<tr>
<td>Malachite</td>
<td>26.96</td>
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<tr>
<td>Malachite after DEHPA adsorption</td>
<td>35.05</td>
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<tr>
<td>Δ⁰</td>
<td>6.09</td>
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</table>

Δ is defined as the difference value of atomic concentration.
be noted that during the interaction of DEHPA with malachite, its surface copper atoms acted as the reactive entities with the partly-exposed dangling bonds, which were significantly different from the free cupric ions in aqueous solutions during the generation of Cu-DEHPA precipitation, probably resulting in the higher proportion of Cu(II)-DEHPA\textsuperscript{2} in the precipitates than that in the DEHPA complexes on malachite surfaces.

The P atom of DEHPA has a valence of 5 \cite{44-46}. Fig. 10 and Table 3 show that the P 2p XPS bands for the Cu-DEHPA precipitation and the DEHPA-treated malachite were divided into two peaks at \( \sim134.15 \) eV and 133.36 eV, respectively. The lower-energy peak might be belonged to P(V) in the Cu(II)-DEHPA\textsuperscript{2} configuration and the higher was owing to P(V) in the Cu(II)-DEHPA\textsuperscript{1}. The P 2p and Cu 2p3/2 XPS adsorption bands implied that there might be two bonding models of DEHPA with copper atom in the Cu-DEHPA precipitation and Cu-DEHPA surface complexes. Surely, to confirm the exact bonding structure between DEHPA and copper needs further investigations.

4. Conclusions

The flotation performances of DEHPA to malachite, calcite and quartz were compared with those of DBP and TBP by micro-flotation tests, and DEHPA’s adsorption mechanism towards malachite was further explored via adsorption, contact angle, zeta potential, FTIR and XPS. Based on the experimental findings, the following conclusions were recommended:

The micro-flotation results demonstrated the collecting affinity of the three phosphate collectors toward malachite could be determined as: DEHPA > DBP > TBP. And, DEHPA exhibited excellent flotation selectivity for malachite versus calcite and quartz over the pH range of 6–9.

Contact angle results illustrated that the hydrophobicity of malachite surface was significantly improved after DEHPA treatment. Adsorption experiments indicated that the preferable pH for malachite adsorption of DEHPA emerged at pH around 7.0, corresponding to that of contact angle findings. Zeta potential inferred that DEHPA might adsorb onto malachite surfaces via electrostatic interaction under pH 6–8.4. At pH > 8.4, the coordination bonding effect might be the dominated driving force for malachite adsorption of DEHPA.

FTIR and XPS inferred that DEHPA reacted with the surface copper atom of malachite via its O atoms of P=O and P=O. The double active center of the P=O group might be contributed to the stronger affinity of DEHPA to malachite than that of TBP with the single active center of the P=O group. The Cu(II)-DEHPA chemisorption layers on malachite surfaces improved the hydrophobicity of malachite particles and realized their flotation enrichment.

Acknowledgement

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<table>
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<th>Table 2 – High-resolution of Cu 2p 3/2 XPS.</th>
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<tr>
<td>Malachite</td>
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<td>Malachite covered by</td>
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<tr>
<td>DEHPA</td>
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<tr>
<td>Cu-DEHPA</td>
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<td>precipitate</td>
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<th>Table 3 – High-resolution P 2p XPS.</th>
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<td>Malachite</td>
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<tr>
<td>Cu-DEHPA</td>
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Fig. 10 – High-resolution P 2p XPS bands for (a) malachite after DEHPA treatment and (b) Cu-DEHPA precipitate.


