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Floc-Flotation of Malachite Fines with an Octyl Hydroxamate and Kerosene Mixture

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Abstract: Malachite fines are easily produced in the grinding process, leading to low malachite flotation recovery. Floc-flotation of malachite fines with an octyl hydroxamate and kerosene mixture was studied to improve the flotation recovery, using microflotation, microscopy image observations, contact angle measurements, and Extended Derjguin–Landau–Verwey–Overbeek (EDLVO) analysis. The results showed that the addition of octyl hydroxamate as an emulsifier of kerosene enhanced the aggregation of malachite fines and improved malachite flotation recovery. In addition, when kerosene droplets were smaller and of uniform size distribution, the spreading of kerosene droplets on the malachite surface improved. The enhanced spreading of kerosene droplets led to higher coverage of kerosene on the malachite surface, resulting in improved hydrophobic aggregation and flotation recovery.

Keywords: Floc-flotation; emulsifier; malachite flotation; octyl hydroxamate; spreading

1. Introduction

With the depletion of copper sulfide minerals, malachite has attracted increasing interest. Since malachite is a relatively soft mineral, with a Moh's hardness of 3.5–4 [1], fines are easily produced in the crush and grinding process. Froth flotation poorly responds to fine mineral particles, mainly because the collision efficiencies between fine particles and bubbles are low, resulting from their low momentum in the flotation pulp [2]. Hydrophobic flocculation is one of the effective methods to increase the apparent sizes of the fine particles, which can be used before flotation to promote the flotation of fine minerals [3,4]. The process of floc-flotation includes dispersion, selective hydrophobization, formation of hydrophobic flocs, and flotation. Floc-flotation has been widely investigated in mineral processing, including floc-flotation of galena [5], sphalerite [6], molybdenite [3,7], coal [8–10], hematite [11–13], apatite [14], and scheelite [15]. However, no investigation has yet been reported on the hydrophobic flocculation and floc-flotation of malachite fines in aqueous suspensions.

Three key parameters govern hydrophobic flocculation, namely particle hydrophobicity, kinetic energy input, and nonpolar oil participation [3,15,16]. Particles with higher hydrophobicity induce stronger hydrophobic attraction and result in more powerful hydrophobic flocculation [17]. Mechanical agitation (shear field) of fine particles suspensions inputs sufficient kinetic energy for particles to overcome the potential energy barrier [15]. Nonpolar oil droplets greatly promote hydrophobic flocculation through forming oil bridges between hydrophobic particles and increasing particle hydrophobicity [17]. The coverage of nonpolar oil on the mineral surface is affected by the dispersion and spreading properties of nonpolar oil. For example, in the flotation of molybdenite fines by mechanically prepared neutral oils emulsions, the floatability of molybdenite fines in the presence of transformer oil is markedly better than that in the presence of kerosene and diesel oil due to the superior dispersion performance of transformer oil [18].

Regarding the effect of the spreading property of nonpolar oils, because of the viscosity effects, long hydrocarbons show slow spreading rate on the mineral surface (e.g., coal), leading to decreased flotation yield. Therefore, surface-active reagents can improve the spreading of oil on the mineral surface, which is beneficial to its flotation [19,20]. Octyl hydroxamate, a selective collector for malachite, is a surfactant that can adsorb at the kerosene–water interface and lower the interfacial tension. However, no investigation studied the effect of octyl hydroxamate on the dispersion and spreading of nonpolar oil in the malachite flotation. Thus, in the current research, the effects of using octyl hydroxamate as a collector and emulsifier of kerosene in the floc-flotation of malachite fines were studied, making use of contact angle measurements, optical microscopy observations, microflotation, and EDLVO theoretical analysis. We hypothesize that the addition of octyl hydroxamate in the emulsification process can enhance the interaction between kerosene and the mineral, and thus be beneficial to floc-flotation of malachite fines.

2. Experimental

2.1. Materials

The natural malachite samples were obtained from the Lupe mine, Mexico. A chunk mineral was selected for contact angle measurements. The remaining chunk minerals were crushed, hand-sorted, and wet ground to obtain different fractions for different applications, namely, particles of −25 µm (d_{50} = 4.2 µm) for the hydrophobic flocculation and microflotation (Figure 1), and finer particles, d_{50} and d_{85} of 1.7 and 2.9 µm, for the zeta potential measurements. According to X-ray diffraction (XRD, Bruker D8, Bruker AXS, Inc., Madison, WI, USA.), the sample constituted high purity malachite ($Cu_2CO_3(OH)_2$) and minor amounts of pseudomalachite ($Cu_5(PO_4)_2(OH)_4$). Atomic absorption spectroscopy (AAS) assayed the sample with 54.3 wt % Cu and 0.5 wt % P. Based on the XRD characterization, the P and Cu were assumed to be from pseudomalachite and combination of malachite and pseudomalachite, respectively; thus, it could be estimated that the sample contains 4.3 wt % of pseudomalachite, 90 wt % of malachite, and 5.7 wt % of other gangue minerals. Considering pseudomalachite and malachite behave similarly in flotation, a grade of 94.3% was assumed. Potassium octyl hydroxamate was synthesized and purified in the laboratory, according to the methods described by Raghavan and Fuerstenau [21]. The kerosene was from the Fisher Scientific without further purification. Hydrochloric acid (HCl), sodium hydroxide (NaOH), and potassium chloride (KOH) of ACS reagent grade were used to adjust the solution pH. Potassium chloride of ACS reagent grade was used as background electrolyte in zeta potential measurements. Distilled water was used in all the experiments.

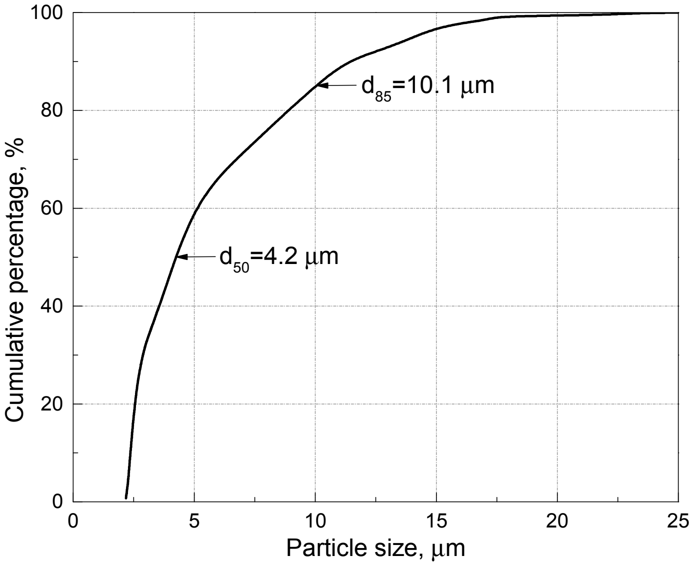

Figure 1. Cumulative percentage of malachite particle size for hydrophobic flocculation and microflotation.

2.2. Preparation of Kerosene Emulsion

Two kinds of kerosene emulsion were prepared in the experiments to promote the hydrophobic flocculation. The first kind of kerosene emulsion was prepared by mixing 1 g kerosene with 99 mL distilled water, followed by ultrasonic treatment for 10 min using a HORIBA ultrasonic processor (HORIBA, Kyoto, Japan). To prepare the second kind of kerosene emulsion, 0.05 wt % of octyl hydroxamate was added in the emulsification process so that a layer of octyl hydroxamate covered on kerosene droplets surface. According to the particle size analysis using a Malvern Mastersizer 2000 (Malvern Panalytical Ltd, Malvern, UK), the d_{50} of the first and second kind of kerosene emulsion were 2.14 and 0.53 µm, respectively.

2.3. Hydrophobic Flocculation

The hydrophobic flocculation of malachite fines in aqueous suspensions was performed in a mixing tank of 10 cm inner diameter with four 1 cm width baffles. The mixing head was connected with a mixer controller (Servodyne, Woodland, CA, USA), and the shaft was equipped with a S-shape impeller of 6 cm width and 2 cm height. 1 g of malachite sample was mixed with 99 mL distilled water and the pH was regulated by adding hydrochloric acid or sodium hydroxide solution, followed by the addition of given amount of octyl hydroxamate with conditioning time of 3 min. After that, a desired amount of kerosene emulsion was added, and then the suspensions were strongly conditioned at 900 rev/min for 15 min. After the conditioning, flocs of malachite fines in aqueous suspensions were obtained.

2.4. Microflotation

The microflotation of malachite fines was conducted by using a 150 mL modified Hallimond tube, which was equipped with a 20 µm frit and a magnetic stirrer. A malachite suspension from the hydrophobic flocculation was transferred to the Hallimond tube and diluted to 120 mL. After that, the flotation was conducted for 5 min with 20 mL/min nitrogen gas. The floated (concentrate) and unfloated (tailing) products were separately collected, filtered, dried, and weighed, and the mass ratio of the floated product was calculated as flotation recovery.

2.5. Contact Angle Measurement

The spreading of kerosene droplets on malachite surface and contact angle of the malachite sample was measured by a goniometer (DSA-25, Kruss, Hamburg, Germany) equipped with a CM4210 optics module with zoom lens and was operated using the captive bubble method in the ADVANCE software

(Version 1.1.0.2). After being wet-polished with 80, 400, 800, and 1200 grit SiC paper, the lump of the malachite sample was further polished with 1 μm of alumina gel on a polishing cloth. In some cases, lumps of the prepared malachite sample were immersed in solutions of 2×10^{-4} mol/L octyl hydroxamate at pH 9 for 15 min. Then, the malachite sample was dried and then immersed in distilled water. After that, a drop of kerosene was introduced with a microsyringe through a U-shaped needle underneath the mineral surface. The spreading of the kerosene droplets was recorded with time. In other cases, the prepared malachite sample was immersed in solutions of 2×10^{-4} mol/L octyl hydroxamate at pH 9 for 15 min. A droplet of kerosene was introduced at the tenth minutes and maintained at the tip of the U-shaped needle for 5 min to adsorb the octyl hydroxamate in the solution. After that, the droplet of kerosene was transferred to the malachite surface and the contact angle was recorded with time. For each condition, at least four measurements were performed and the average contact angle is reported. In terms of measuring the contact angle of malachite, an air bubble was introduced to contact with malachite treated by 2×10^{-4} mol/L octyl hydroxamate at pH 9 for 15 min.

2.6. Zeta Potential Measurements

A ZetaProbe Analyzer (Colloidal Dynamics, Sydney, Australia) with electroacoustic technology was employed to measure the zeta potential of the malachite particles and kerosene emulsions in aqueous solutions at various pHs and in the absence and presence of octyl hydroxamate. Based on the stimulated electro-acoustic sonic amplitude (ESA) values of the malachite particles, the zeta potential was calculated using the O´Brien equation [22,23]. In a typical measurement, 5 g of malachite sample and a given amount of octyl hydroxamate were conditioned with 250 mL KCl (1×10^{-3} mol/L) solutions in the cell of the ZetaProbe for 10 min and the suspension was allowed to equilibrate for 5 min at each pH prior to taking a measurement. In some cases, the prepared kerosene and 1×10^{-3} mol/L KCl were added to measure its zeta potential. Then, the zeta potential values were recorded and reported by the equipment. The suspension pH was regulated by the equipment through the automatic titration of 0.1 mol/L KOH and HCl solutions.

2.7. Observation of Kerosene Emulsions and Malachite Hydrophobic Aggregates

A Leica DMLP optical microscope equipped with digital camera was applied to observe oil droplets in emulsions and hydrophobic aggregates in aqueous suspensions. To prepare the samples, kerosene emulsion or malachite aggregates suspensions were dropped on a glass plate, and a thin glass slide was put on the drop to fix the emulsion or suspension. The images of representative kerosene droplets and malachite aggregates were taken during the observation.

3. Results and Discussion

Figure 2 presents the flotation recovery of malachite with the addition of two kinds of kerosene emulsions as a function of octyl hydroxamate concentration. The flotation recovery increased as the octyl hydroxamate concentration was increased, exhibiting flotation recovery around 15% in the absence of octyl hydroxamate. With the addition of octyl hydroxamate, malachite recovery raised drastically, inferring that prehydrophobicization of the malachite surface is essential when kerosene is adopted in the floc-flotation. With the utilization of octyl hydroxamate in the emulsification process, higher flotation recovery of malachite was achieved, indicating that it is beneficial to add octyl hydroxamate in the emulsification process. It needs to be noted that, in the presence of 2×10^{-4} mol/L octyl hydroxamate, the addition of 0.05 wt % octyl hydroxamate emulsified kerosene introduced only 6.4% more octyl hydroxamate, which is negligible to this system. In addition, mixture of octyl hydroxamate and kerosene may provide high selectivity when malachite was accompanied by other minerals since octyl hydroxamate had been proved to be a relatively high selective collector for malachite flotation [24,25], and kerosene adsorbs onto minerals surface through hydrophobic interaction.

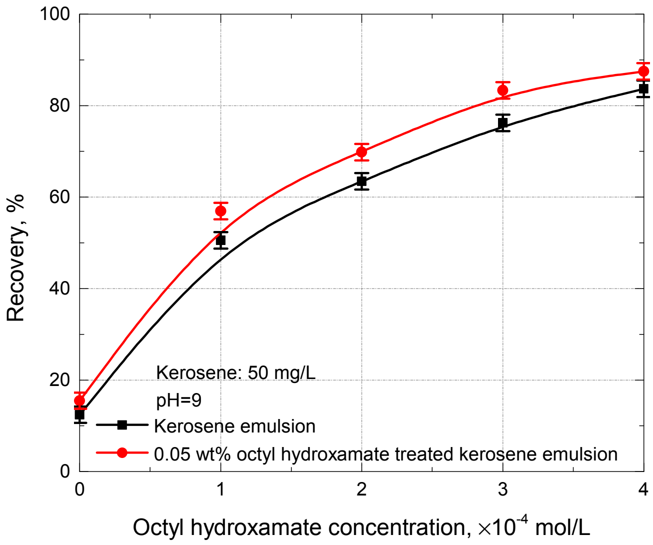

Figure 2. Flotation recovery of malachite with the addition of two kinds of kerosene emulsions as a function of octyl hydroxamate concentration.

Figure 3 gives the flotation recovery of malachite with the addition of two kinds of kerosene emulsions at pH 9. The flotation recovery increased steadily with the increase of kerosene dosage, reaching the maximum of around 97% when octyl hydroxamate treated kerosene emulsion was used, indicating that kerosene has a remarkable influence on the malachite flotation. In the conditioning process, octyl hydroxamate was first adsorbed onto malachite surface to make the mineral surface prehydrophobic, so that the kerosene droplets were capable of interacting with its surface. The coating of kerosene can substantially enhance flocculation through the formation of oil bridges between hydrophobic particles and increasing particle hydrophobicity [3]. With the utilization of octyl hydroxamate in the emulsification process, higher flotation recovery of malachite was achieved. This phenomenon is more evident in the presence of greater dosage of kerosene, with a recovery increase around 12.5% at 80 mg/L kerosene. It suggests that the addition of 0.05 wt % octyl hydroxamate in the emulsification process promotes the floc-flotation.

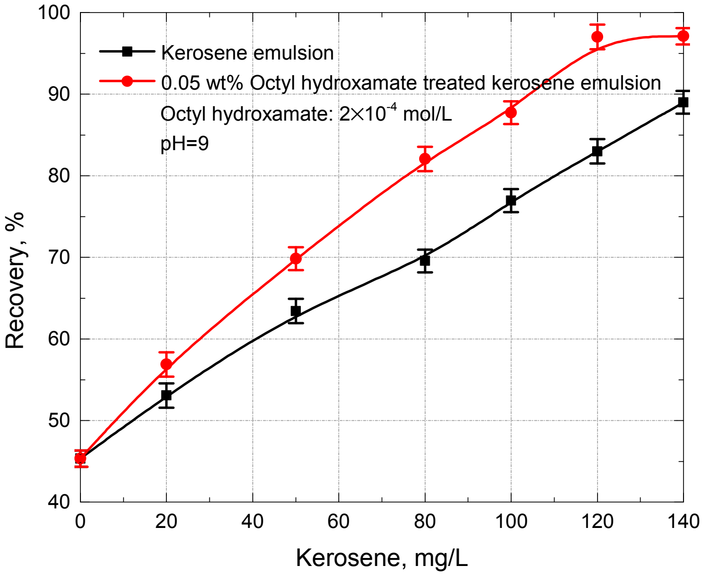

Figure 3. Flotation recovery of malachite with the addition of two kinds of kerosene emulsions as a function of kerosene dosage.

Two kinds of kerosene emulsions were prepared to enhance the flocculation process by using an ultrasonic processor in the presence and absence of 0.05 wt % octyl hydroxamate. In order to understand the roles of oil droplets size distribution in the flocculation process, the optical microscopy images of the two kinds of kerosene emulsions were photographed and are shown in Figure 4. The kerosene emulsion produced by ultrasonic processor in the presence of 0.05 wt % octyl hydroxamate was smaller than that in the absence of 0.05 wt % octyl hydroxamate. In addition, the droplets were highly uniform in size. This is because octyl hydroxamate adsorbs at the kerosene–water interface and lowered the interfacial tension. Therefore, at the same dosage of kerosene, the kerosene emulsion prepared in the presence of 0.05 wt % octyl hydroxamate had much more kerosene surfaces to contact malachite particles and then to enhance the hydrophobic flocculation, and therefore the flotation performance.

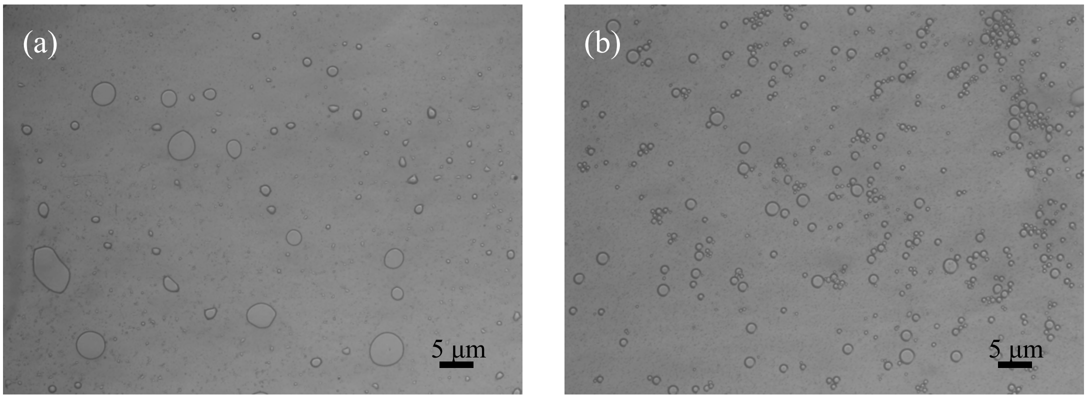

Figure 4. Optical microscopy images of the kerosene emulsions prepared by ultrasonic processor (**a**) without the addition of octyl hydroxamate (**b**) with the addition of 0.05 wt % octyl hydroxamate.

Figure 5 presents the spreading of kerosene droplets at the malachite surface measured with the captive bubble method, showing that the spreading of kerosene droplets was a relatively slow process, which continued for 900 s. The kerosene droplets spread fast within 120 s, followed by a gradual spreading in the subsequent 780 s. Kerosene droplet treated with octyl hydroxamate exhibited greater contact angle compared to that without the treatment of octyl hydroxamate after 30 s. Within 900 s, the spreading rate of kerosene in the presence of octyl hydroxamate is higher. This suggests that kerosene droplets treated by octyl hydroxamate interact more strongly with the malachite surface, resulting in higher coverage of kerosene on the malachite surface, which increases the hydrophobicity, and therefore flotation recovery.

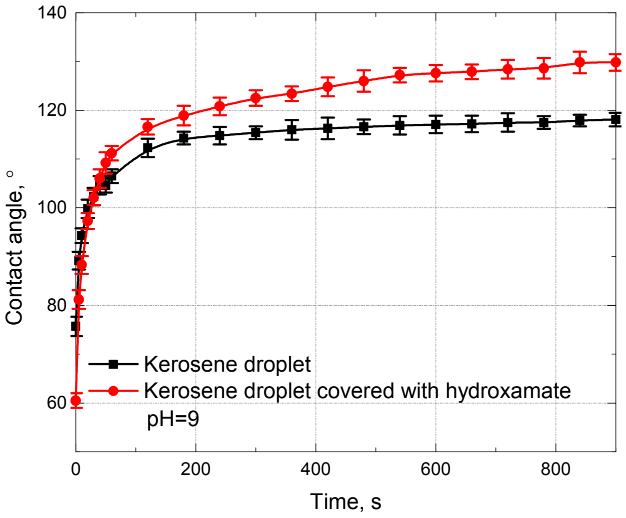

Figure 5. Spreading of kerosene droplets on the malachite surface measured with the captive bubble method.

Figure 6 gives the optical microscope images of malachite aggregates in the presence of two kinds of 50 mg/L kerosene emulsions with the addition of 2×10^{-4} mol/L octyl hydroxamate to make the malachite surface prehydrophobic. The aggregates in the presence of octyl hydroxamate-treated kerosene emulsion were larger than those in the presence of kerosene emulsion without treatment by octyl hydroxamate, which is in accordance with the results in Figures 4 and 5. With the addition of 0.05 wt % octyl hydroxamate-treated kerosene in the aggregation process, more oil surfaces contacted malachite particles and the oil droplets spread more readily on the malachite surface, leading to higher coverage of kerosene on the malachite surface, and as a consequence, greater hydrophobicity and aggregation.

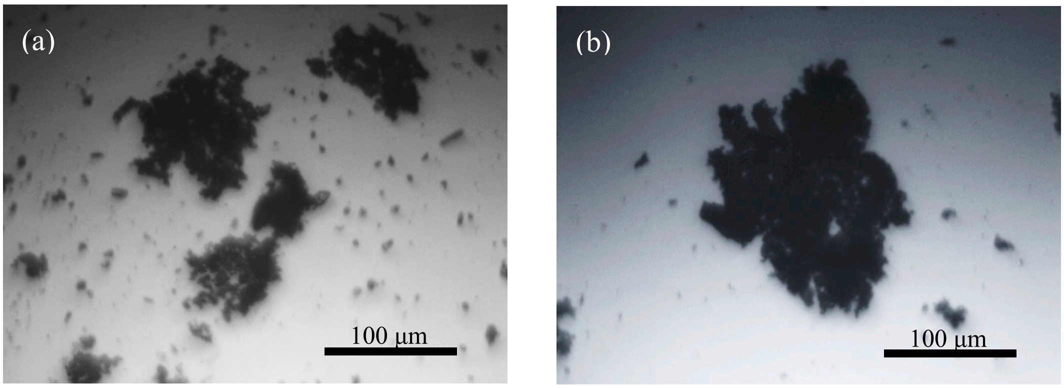

Figure 6. Optical microscopy images of the malachite aggregates (**a**) with the addition of kerosene emulsion; (**b**) with addition of 0.05 wt % octyl hydroxamate treated kerosene emulsion.

Figure 7 presents the zeta potentials of malachite particles in the absence or presence of 2×10^{-4} mol/L octyl hydroxamate as a function of pH. The zeta potentials of malachite decreased steadily with increasing solution pH, exhibiting its isoelectric point (IEP) at around 8.1, which was in good agreement with that reported at pH 7.8 in another study [26]. In the lower pH range, the zeta potential increased with the decrease of pH because the adsorption of H^+, and it decreased with the increase of pH in higher pH range, resulting from the adsorption of OH^-. In the presence of octyl hydroxamate, the zeta potential also decreased as increasing pH, the IEP of malachite particles shifted to the proximity of 7.7, and octyl hydroxamate anion adsorbed onto negatively charged malachite surface, implying the chemisorption of octyl hydroxamate on malachite surface [27]. Above pH 10, the adsorption of octyl hydroxamate decreased due to the repulsion between octyl hydroxamate anion and highly negatively charged malachite surface. In addition, the zeta potential of malachite in the presence of 2×10^{-4} mol/L octyl hydroxamate at pH 9 was −7.98 mV.

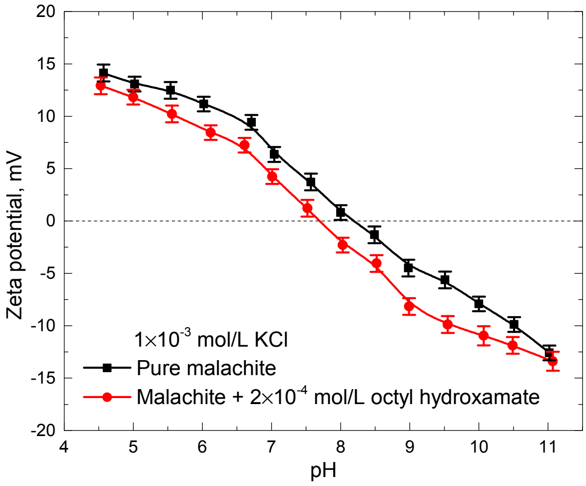

Figure 7. Zeta potential of malachite in the presence and absence of 2×10^{-4} mol/L octyl hydroxamate.

Figure 8 gives the zeta potential of kerosene and octyl hydroxamate-treated kerosene emulsion, showing that the zeta potentials of kerosene decreased steadily with increasing the solution pH. With the addition of octyl hydroxamate, the zeta potential of kerosene moved to more positively values, which may be caused by the binding of the neutral octyl hydroxamate molecules to kerosene since octyl hydroxamate molecules and anions coexist throughout the pH range [13]. The zeta potential of kerosene in the absence and presence of 0.05 wt % octyl hydroxamate at pH 9 were −89.91 and −103.31 mV respectively.

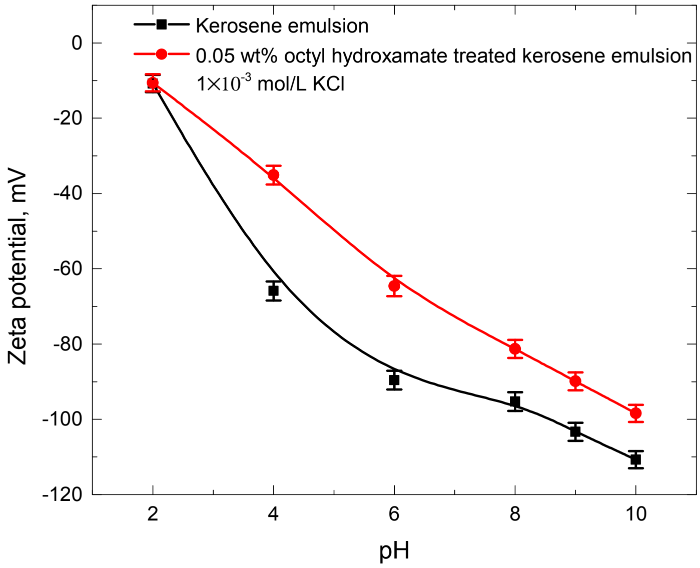

Figure 8. Zeta potential of kerosene emulsion and 0.05 wt % octyl hydroxamate-treated kerosene emulsion.

In the oil-assisted flotation system, where oil droplets interact with hydrophobic particles, the interactions can be explained using EDLVO theory since hydrophobic interaction plays a significant role [28]. In an attempt to investigate the energetics of the studied malachite–collector–kerosene system, the EDLVO theory calculation was performed. In the EDLVO theory, the total interaction energy comprises van der Waals interaction (V_{W}), electrical (Coulombic) interactions under constant potential (V_{E}), and hydrophobic or hydration interaction (V_{H}) [13,29,30]. The total interaction energy can be calculated by the following equation:

$$V_{TED} = V_W + V_E + V_H \tag{1}$$

where V_{TED} is the total interaction energy, V_W is the Van der Waals interaction, V_E is the electrostatic interaction, and V_H is the hydrophobic interaction.

The values of the above interaction energies are calculated based on the following expressions:

$$V_W = -\frac{AR_1R_2}{6H(R_1+R_2)} \tag{2}$$

where R_1 and R_2 are the equivalent spherical radius of malachite particles and oil droplets. The Hamaker constant A is obtained through the Lifshitz approach [31]. For malachite particle_1 and oil droplet_2 interacting in aqueous solution_3, A_{132} is given as

$$A_{132} = \frac{3}{4}k_BT\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right) + \frac{3h_pv_e}{8\sqrt{2}}\frac{\left(n_1^2-n_3^2\right)\left(n_2^2-n_3^2\right)}{\sqrt{\left(n_1^2+n_3^2\right)}\sqrt{\left(n_2^2+n_3^2\right)}\left\{\sqrt{\left(n_1^2+n_3^2\right)}+\sqrt{\left(n_2^2+n_3^2\right)}\right\}} \tag{3}$$

where k_B denotes the Boltzmann constant (1.381×10^{-23} J/K), T is the absolute temperature, ε denotes the static dielectric permittivity, n is the refractive index in the visible range, h_p is the Planck's constant (6.626×10^{-34} $m^2 \cdot kg/s$), ν_e is the main electronic absorption frequency (approximately 3×10^{15} s^{-1}).

The electrostatic double layer energy between malachite particles and oil droplets using the Derjaguin approximation is expressed as [32]:

$$V_E = \pi\varepsilon_0\varepsilon_r \frac{R_1 R_2}{R_1 + R_2}\left(\psi_1^2 + \psi_2^2\right)\left\{\frac{2\psi_1\psi_2}{\psi_1^2 + \psi_2^2}\ln\left[\frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)}\right] + \ln[1 - \exp(-2\kappa H)]\right\} \tag{4}$$

where ε_0 is the permittivity of vacuum (8.854×10^{-12} $C^2/J/m$), ε_r denotes the dielectric constant of the aqueous medium (78.54 at 25 °C), ψ_1 and ψ_2 are the surface potentials or the stern layer potentials of the particles and droplets, which can be approximated by zeta potentials. κ^{-1} is the Debye length (9.6 nm in 1×10^{-3} mol/L KCl) and can be calculated using Equation (5).

$$\kappa = \left(\frac{\sum_i C_{i,0} e^2 Z_i^2}{\varepsilon_0 \varepsilon_r k_B T}\right)^{\frac{1}{2}} \tag{5}$$

where $C_{i,0}$ denotes the ion strength in the medium, e is electronic charge (1.602×10^{-19} C), and Z_i denotes the ion valence.

The empirical hydrophobic interaction energy equation between asymmetric spheres can be described as [13]:

$$V_H = -\frac{K_{132} R_1 R_2}{6H(R_1 + R_2)} \tag{6}$$

The hydrophobic parameter of malachite particle_1 and oil droplets_2 in aqueous medium_3, K_{132}, can be obtained with geometric mean combing rule and expressed as follows [33].

$$K_{132} \approx \sqrt{K_{131} K_{232}} \tag{7}$$

where K_{131} is the hydrophobic parameter of two malachite_1/aqueous solution_3 interfaces; Similarly, K_{232} is the hydrophobic parameter of two kerosene_2/aqueous solution_3 interfaces. Mao showed that the K_{232} of oil droplets is approximately 6×10^{-18} J without surfactant, which decreased slightly when the concentration of surfactant was lower than 10^{-4} mol/L [13,34]. Therefore, the value of K_{232} was simplified as 6×10^{-18} J as an approximation in this work. The K_{131} was obtained by adopting empirical expression Equation (8) from Yoon and Luttrell [35].

$$log K_{131} = -3.194 \times cos\theta_w - 18.229 \tag{8}$$

where θ_w denotes the water contact angle of malachite mineral. In this study, the contact angle of malachite mineral with the addition of 2×10^{-4} mol/L octyl hydroxamate at pH 9 was measured by the captive bubble method and the value was 34.5°.

The interaction energies between malachite particles and kerosene droplets/octyl hydroxamate treated kerosene droplets are shown in Figures 9 and 10, respectively. The energies of van der Waals, electrical double layer and hydrophobic interaction were calculated based on Equations (1)–(8). The EDLVO interaction energy estimation could be used to predict the adhesion of kerosene droplets onto the hydrophobic malachite particles. The calculated energies of van der Waals, electrical double layer, and hydrophobic interaction all showed negative values, suggesting that these interaction forces are attractive. The magnitude of the attractive force decreased following the order $V_H > V_E > V_W$. The closer the separation distances of malachite and kerosene droplets, the stronger the attraction between them. Although malachite and kerosene surface were negatively charged, the electrostatic interaction between malachite fines and kerosene droplets was attractive because the surface charge of malachite was small. The total interaction energies in the two cases are negative, indicating the attractive interaction force between these particles; thus, the emulsified kerosene droplets and kerosene droplets emulsified with octyl hydroxamate can collide and adhere onto the malachite particle surface, making the surface more hydrophobic, forming large hydrophobic aggregates, and resulting in improved flotation recovery. However, the interaction strength between emulsified kerosene droplets and malachite particles is greater than that between 0.05 wt % octyl hydroxamate emulsified kerosene droplets and malachite surface. Combined with the microflotation results, it is inferred that the interaction strength calculated by EDLVO theory doesn't play a significant role in this system, which is in accordance with that reported by [18].

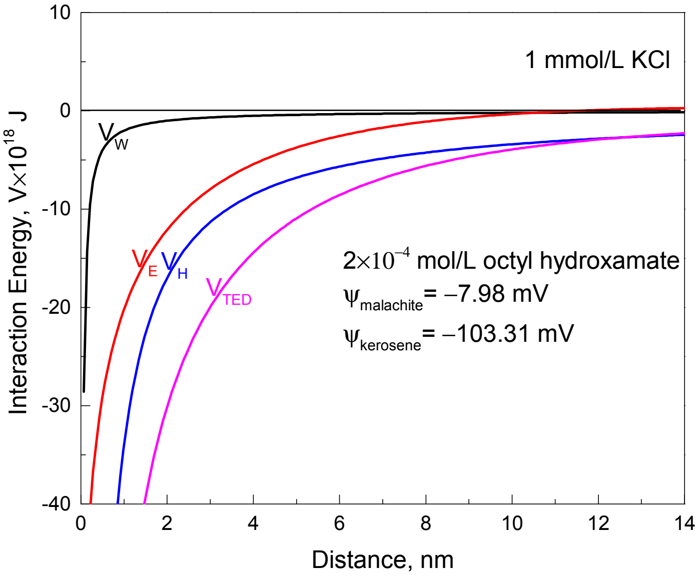

Figure 9. The interaction energy between malachite particles and emulsified kerosene droplets as a function of separation distance, malachite radius: 2.10 µm and kerosene radius: 1.07 µm.

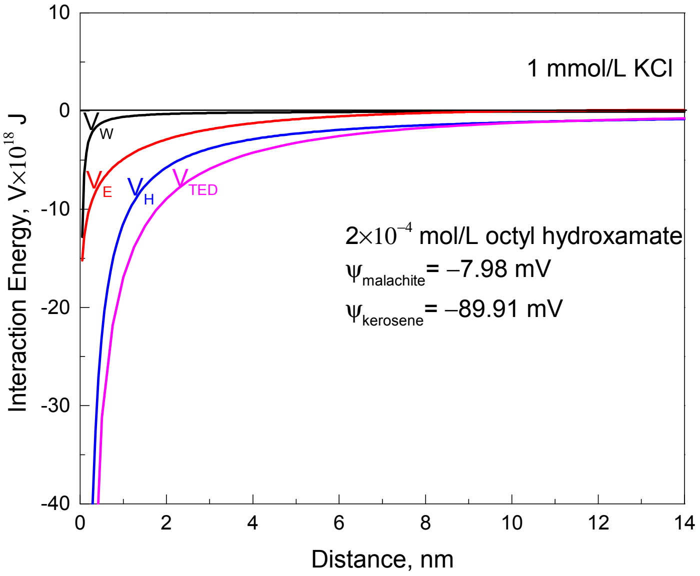

Figure 10. The interaction energy between malachite particles and 0.05 wt % octyl hydroxamate treated kerosene droplets as a function of separation distance, malachite radius: 2.10 µm and kerosene radius: 0.27 µm.

The EDLVO theory delineated the adherence of kerosene droplets and octyl hydroxamate-treated kerosene droplets onto the hydrophobic malachite surface. In terms of the spreading phenomenon, the schematic representation of the enhancement of kerosene spreading on malachite surface by using octyl hydroxamate as an emulsifier is presented in Figure 11. With the addition of octyl hydroxamate to the kerosene emulsification process, octyl hydroxamate adsorbed on the kerosene droplets surface with the polar group orienting to the water side and hydrophobic tail orienting to the kerosene side. After kerosene droplets adhering to malachite surface, at the three-phase contact line, the octyl hydroxamate on kerosene chemically adsorbs onto the malachite surface and coadsorbs with the preadsorbed octyl hydroxamate, which may provide an additional force to enhance the spreading of kerosene.

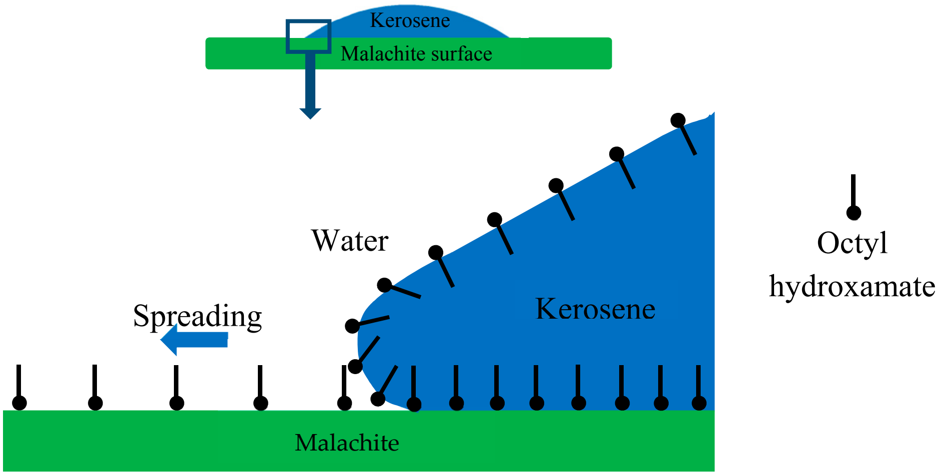

Figure 11. Schematic representation of enhancement of kerosene spreading on malachite surface by using octyl hydroxamate as an emulsifier.

4. Conclusions

1. The addition of octyl hydroxamate as an emulsifier of kerosene enhanced the aggregation of malachite fines, resulting in improved malachite flotation recovery.

2. With the addition of octyl hydroxamate in the emulsification process, kerosene droplets were smaller and much more uniform in size, which provided more kerosene surfaces to contact malachite particles, resulting in enhanced hydrophobic flocculation, and therefore improved flotation performance.

3. The EDLVO theoretical analyses exhibited stronger attractive interaction strength between malachite particles and kerosene droplets compared to that between malachite particles and 0.05 wt% octyl hydroxamate-emulsified kerosene droplets, implying the adherence of kerosene droplets onto the malachite surface. Combined with microflotation results, it is inferred that interaction strength calculated by the EDLVO theory doesn't play a significant role in the system. The octyl hydroxamate adsorbed on the kerosene surface could chemically adsorb onto the malachite surface and coadsorb with preadsorbed octyl hydroxamate, providing an additional force to enhance the spreading of kerosene. Thus, greater coverage of kerosene on the malachite surface was achieved, and as a consequence, hydrophobic flocculation and flotation recovery were enhanced.

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References

1. Petrov, T.G.; Protopopov, E.N.; Shuyskiy, A.V. Decorative grown malachite. Nature and technology. *Russ. J. Earth Sci.* **2013**, *13*, 1–7. [CrossRef]
2. Sivamohan, R. The problem of recovering very fine particles in mineral processing—A review. *Int. J. Min. Process.* **1990**, *28*, 247–288. [CrossRef]
3. Song, S.; Zhang, X.; Yang, B.; Lopez-Mendoza, A. Flotation of molybdenite fines as hydrophobic agglomerates. *Sep. Purif. Technol.* **2012**, *98*, 451–455. [CrossRef]
4. Song, S.; Trass, O. Floc flotation of Prince coal with simultaneous grinding and hydrophobic flocculation in a Szego mill. *Fuel* **1997**, *76*, 839–844. [CrossRef]
5. Song, S.; Lopez-Valdivieso, A.; Reyes-Bahena, J.L.; Bermejo-Perez, H.I.; Trass, O. Hydrophobic flocculation of galena fines in aqueous suspensions. *J. Colloid. Interf. Sci.* **2000**, *227*, 272–281. [CrossRef] [PubMed]
6. Song, S.; Lopez-Valdivieso, A.; Reyes-Bahena, J.L.; Lara-Valenzuela, C. Floc flotation of galena and sphalerite fines. *Min. Eng.* **2001**, *14*, 87–98. [CrossRef]
7. Yang, B.; Song, S.; Lopez-Valdivieso, A. Kinetics of hydrophobic agglomeration of molybdenite fines in aqueous suspensions. *Physicochem. Probl. Miner. Process.* **2015**, *51*, 181–189.
8. Song, S.; Valdivieso, A.L. Hydrophobic flocculation flotation for beneficiating fine coal and minerals. *Sep. Sci. Technol.* **1998**, *33*, 1195–1212. [CrossRef]
9. Song, S. Experimental studies on hydrophobic flocculation of coal fines in aqueous solutions and flotation of flocculated coal. *Int. J. Oil. Gas. Coal. T.* **2008**, *1*, 180–193. [CrossRef]
10. Liang, L.; Tan, J.; Li, Z.; Peng, Y.; Xie, G. Coal flotation improvement through hydrophobic flocculation induced by polyethylene oxide. *Int. J. Coal Prep. Util.* **2016**, *36*, 139–150. [CrossRef]
11. Pascoe, R.D.; Doherty, E. Shear flocculation and flotation of hematite using sodium oleate. *Int. J. Min. Process.* **1997**, *51*, 269–282. [CrossRef]
12. Shibata, J.; Fuerstenau, D.W. Flocculation and flotation characteristics of fine hematite with sodium oleate. *Int. J. Min. Process.* **2003**, *72*, 25–32. [CrossRef]
13. Li, H.; Liu, M.; Liu, Q. The effect of non-polar oil on fine hematite flocculation and flotation using sodium oleate or hydroxamic acids as a collector. *Min. Eng.* **2018**, *119*, 105–115. [CrossRef]
14. Yang, B.; Huang, P.; Song, S.; Luo, H.; Zhang, Y. Hydrophobic agglomeration of apatite fines induced by sodium oleate in aqueous solutions. *Results Phys.* **2018**, *9*, 970–977. [CrossRef]
15. Chen, W.; Feng, Q.; Zhang, G.; Li, L.; Jin, S. Effect of energy input on flocculation process and flotation performance of fine scheelite using sodium oleate. *Min. Eng.* **2017**, *112*, 27–35. [CrossRef]
16. Duzyol, S.; Ozkan, A. Correlation of flocculation and agglomeration of dolomite with its wettability. *Sep. Sci. Technol.* **2011**, *46*, 876–881. [CrossRef]
17. Song, S.; Lopez-Valdivieso, A.; Ding, Y. Effects of nonpolar oil on hydrophobic flocculation of hematite and rhodochrosite fines. *Powder. Technol.* **1999**, *101*, 73–80. [CrossRef]
18. Lin, Q.Q.; Gu, G.H.; Wang, H.; Liu, Y.C.; Fu, J.G.; Wang, C.Q. Flotation mechanisms of molybdenite fines by neutral oils. *Int. J. Min. Met. Mater.* **2018**, *25*, 1–10. [CrossRef]
19. Moxon, N.T.; Bensley, C.N.; Keast-Jones, R.; Nicol, S.K. Insoluble oils in coal flotation: the effects of surface spreading and pore penetration. *Int. J. Min. Process.* **1987**, *21*, 261–274. [CrossRef]
20. Burkin, A.R.; Bramley, J.V. Flotation with insoluble reagents. ii. Effects of surface-active reagents on the spreading of oil at coal-water interfaces. *J. Chem. Technol. Biot.* **2010**, *13*, 417–422.
21. Raghavan, S.; Fuerstenau, D. The adsorption of aqueous octylhydroxamate on ferric oxide. *J. Colloid. Interf. Sci.* **1975**, *50*, 319–330. [CrossRef]
22. O'brien, R. The electroacoustic equations for a colloidal suspension. *J. Fluid. Mech.* **1990**, *212*, 81–93. [CrossRef]
23. Rao, F.; Song, S.; Lopez-Valdivieso, A. Electrokinetic studies of minerals in aqueous solutions through electroacoustic measurement. *Surf. Rev. Lett.* **2009**, *16*, 65–71. [CrossRef]
24. Lee, K.; Archibald, D.; McLean, J.; Reuter, M.A. Flotation of mixed copper oxide and sulphide minerals with xanthate and hydroxamate collectors. *Min. Eng.* **2009**, *22*, 395–401. [CrossRef]
25. Marion, C.; Jordens, A.; Li, R.; Rudolph, M.; Waters, K.E. An evaluation of hydroxamate collectors for malachite flotation. *Sep. Purif. Technol.* **2017**, *183*, 258–269. [CrossRef]

26. Li, Z.; Rao, F.; García, R.E.; Li, H.; Song, S. Partial replacement of sodium oleate using alcohols with different chain structures in malachite flotation. *Min. Eng.* **2018**, *127*, 185–190. [CrossRef]
27. Fuerstenau, D.W.; Pradip. Zeta potentials in the flotation of oxide and silicate minerals. *Adv. Colloid. Interfac.* **2005**, *114*, 9–26. [CrossRef]
28. Piñeres, J.; Barraza, J. Energy barrier of aggregates coal particle-bubble through the extended DLVO theory. *Int. J. Min. Process.* **2011**, *100*, 14–20. [CrossRef]
29. Chrysikopoulos, C.V.; Syngouna, V.I. Attachment of bacteriophages MS2 and ΦX174 onto kaolinite and montmorillonite: Extended-DLVO interactions. *Colloid. Surf. B.* **2012**, *92*, 74–83. [CrossRef] [PubMed]
30. Hunter, R. *Foundations of Colloid Science*, 2nd ed.; Oxford University Press: Oxford, UK, 1986.
31. Lifshitz, E.M. The theory of molecular attractive forces between solids. *J. Exp. Phys. Ussr.* **1956**, *29*, 94–110.
32. Hogg, R.; Healy, T.W.; Fuerstenau, D.W. Mutual coagulation of colloidal dispersions. *Trans. Faraday. Soc.* **1966**, *62*, 1638–1651. [CrossRef]
33. Yoon, R.H.; Flinn, D.H.; Rabinovich, Y.I. Hydrophobic interactions between dissimilar surfaces. *J. Colloid. Interf. Sci.* **1997**, *185*, 363–370. [CrossRef]
34. Mao, L. Application of Extended DLVO Theory: Modeling of Flotation and Hydrophobicity of Dodecane. Ph.D. Thesis, Virginia Tech, Blacksburg, VA, USA, 1998.
35. Yoon, R.H.; Luttrell, G.H. *Development of the Selective Hydrophobic Coagulation Process*; Fourth Quarterly Technical Progress Report, July 1, 1992–September 30, 1992 (No. DOE/PC/91164-T1); Virginia Center for Coal and Minerals Processing: Blacksburg, VA, USA, 1992.