Investigation of Mechanism of Adsorption of Xanthate and Hydroxamate on Malachite

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Keywords	Abstract
Malachite *Surface potential* *Adsorption* *Synergism* *Froth flotation*	Copper oxide minerals such as malachite do not respond well to the traditional copper sulfide collectors, and require alternative flotation schemes. In many copper ore mines, significant copper oxide minerals, especially malachite, are associated with sulfide minerals. Considering that xanthates are most widely used in the flotation of sulfide minerals as well as copper sulfide minerals and, hydroxamate has shown a good selectivity for copper oxide minerals. Use of the synergistic effect of xanthate and hydroxamate can be an effective way to increase the flotation efficiency of copper oxide minerals along with sulfide minerals. In this work, we investigate the individual interactions of potassium amyl xanthate (PAX) and potassium alkyl hydroxamate (HXM) with the natural malachite and explore their synergistic effects on the malachite flotation. The results of solubility of malachite in collector solutions, changes in the malachite surface potential, adsorption kinetics, adsorption densities, dynamic contact angles, FT-IR analyses, and small-scale flotations, are discussed. The results obtained demonstrate that PAX and HXM are chemically co-adsorbed on the malachite surface, and the amount of PAX adsorbed on the malachite surface is considerably increased in the mixed PAX/HXM systems because of the co-adsorption mechanism. The flotation results confirm that the mixed PAX/HXM exhibit a superior flotation performance of malachite compared to the individual system of PAX or HXM. Based on these results, the mixed PAX/HXM exhibit a remarkable synergism effect on malachite surface hydrophobicity.

1. Introduction

A majority of copper is extracted from copper sulfide minerals. However, copper oxide minerals account for a significant portion of copper production [1]. Two most important copper recovery methods from copper oxide ores are leaching and flotation [2]. For the copper oxide ores with low copper content or high carbonate gangue, the froth flotation has become the most economic method for the concentration and recovery of copper [3]. Copper oxide minerals are not successfully recovered using the traditional concentration methods by thiol-based collectors. They require a special treatment in a froth flotation circuit. The conventional method involves sulfidization (at -500 to -600 mV) followed by

flotation. Sodium sulfide (Na$_2$S), sodium hydrosulfide (NaSH), and ammonium sulfide ((NH$_4$)$_2$S) are used as the sulfidizing agents and the thiol-based reagents are used as the collectors [2]. The conventional method is attractive but it suffers from two major disadvantages [2]:

a) Difficulty to control the dosage of the sulfidizing agent; an excess amount leads to the depression of copper oxide minerals, while its insufficient amounts result in poor recoveries.

b) Varying response of copper oxides to sulfidization, which results in a failure for an acceptable recovery.

Malachite, a sparingly soluble mineral, is the most abundant copper oxide mineral found in the supergene zone of copper deposits, and often

accompanies sulfide minerals. It dissolves plenty of ions in the flotation pulp. These ions affect the chemistry of the flotation pulp, and therefore, its flotation performance. Formation of smaller stable bubbles and compressing the electrical double layer of minerals are some of the positive effect, and consumption of flotation reagents and formation of metal hydroxides precipitate barriers are the negative effects [3]. Furthermore, hydrogen bonding of water molecules with the malachite surface followed by extensive hydration of the malachite leads to an ineffective flotation of malachite [4].

A number of different collectors including fatty acids, fatty amines, petroleum sulphonates, and hydroxamates have been evaluated for oxide copper flotation without sulfidization [5]. Chelating agents appear to be good collector alternatives for the flotation of copper oxide [6, 7]. There has been an appreciable amount of research work mainly conducted on the application of hydroxamates for oxide copper flotation; however, these reagents have yet to find industrial applications [8].

Various manufactures such as Hoechst, Cyanamid, Cytec, Ausmelt, Axis House, and Russian and Chinese companies have developed hydroxamates for mineral collectors [8].

Most recently, Axis House has developed a series of linear hydroxamate collectors under the brand names of AM2, AM28, and AM810. Extensive investigations show that these collectors have a great promise for upgrading the sulfidic and oxidized copper minerals [9]. Hydroxamate collectors such as AM28 can be used successfully in the flotation system to recover the copper oxide minerals from mixed copper sulphide/oxide without reducing the recovery of the sulfide minerals [5]. An investigation has shown that copper sulfides and oxides from blended ore minerals can be successfully floated using mixtures of hydroxamates and xanthate collectors [10].

It has been found that the linear alkyl hydroxamates are much better reagents than the branched alkyl hydroxamates with similar molecular weights for copper oxide flotation [11]. Marion et al. have observed the highest malachite recovery and a higher flotation kinetics using the C8-alkyl hydroxamates as the collector [1]. Interaction of n-octanohydroxamate with the surface of malachite has led to the formation of a cupric hydroxamate layer on the malachite detected by Raman spectroscopy [12].

Adsorption studies and infrared analysis show that potassium octylhydroxamate is chemisorbed on the malachite surface at the pH range of 6-10. This suggests that a pair of HCO_3^- and OH^- ions are displaced for each hydroxamate ion to be adsorbed. [6]. The interaction between octylhydroxamate and malachite has been examined by Zili et al. (2019). Their findings show that in the pH range of 6-9, octylhydroxamate mainly exists in the molecular form and reacts with the chemisorbed $Cu(OH)^+$ and $Cu(CO_3)_2^{2-}$ on the malachite surface. Since the octylhydroxamate anion is the predominant species above pH 9, the reaction between the octylhydroxamate anion and the chemisorbed $Cu(CO_3)_2^{2-}$ and $Cu(OH)^+$ at the malachite surface is responsible for the flotation of malachite [13].

The hydroxamate ions chemisorb on the malachite surface in a way that two oxygen atoms of each hydroxymate anion bond to a Cu atom on the malachite surface, and the deprotonated N-atom interacts with a second (adjacent) Cu atom on the malachite surface or with a Cu- hydroxamate molecule [14].

Hydrogen bonding between the hydroxamate ions is one of the reasons for the formation of multi-layers. H–bonding between oxygen and hydrogen of one hydroxamate with the hydrogen and oxygen of another molecule extends to two- and three-dimensional networks between the hydroxamate ions. [11].

Also studying the flotation of chrysocolla by alkyl hydroxamate suggests that insoluble surface complexes formed between surface copper ions and hydroxamates are responsible for its flotation [15].

It is now very well-accepted that the xanthate adsorption on sulfide minerals occurs through a corrosion type mixed potential mechanism. According to the mixed potential theory, an anodic reaction can occur only if there is a cathodic reaction proceeding at a finite rate at that potential [16]. For the flotation systems, the cathodic reaction is usually given by the reduction of oxygen. The corresponding anodic reaction involves interaction of xanthate on the sulfide minerals in three ways: (a) chemisorption of the xanthate ion (X^-), (b) reaction of xanthate with the sulfide mineral (MS) to form metal xanthate (MX_n), and (c) oxidation of xanthate to dixanthogen (X_2) at the mineral surface [16, 17].

The mechanism by which xanthate is adsorbed onto a copper plate has been studied by Mielczarki (1987). For the lowest sub-monolayer coverages, the adsorbed xanthate molecules are randomly oriented. Then with the growth of the adsorption layer, the degree of random orientation of the molecules increases, being different for different

xanthates. The observations show a heterogeneous structure of amyl xanthate in the adsorption layer consisting of regions with either a monolayer or multi-layer coverage [19].

Lee et al. (2009) have evaluated the use of xanthate collector for copper sulfide and the hydroxamate collector for copper oxide flotation as well as a mixture of xanthate and hydroxamate to simultaneously recover copper sulfide and oxide minerals from Minto's sulfide ore. Their findings proved that N-octylhydroxamate could be used successfully to recover the copper oxide minerals in mixed copper sulfide/oxide blends without reducing the recovery of the sulfide minerals [5].

The use of xanthates as a collector of non-sulfide minerals, in particular, oxides, has not been extensively investigated [20].

Davidson (2009) with the aim of achieving flotation conditions for natural ore to optimize copper recovery has investigated the adsorption kinetic of xanthate and hydroxamate individually on the malachite and borrnite surfaces and used the statistical method (response surfaces) to determine the operational conditions. The results obtained demonstrated that xanthate adsorption on malachite was pH-dependent and that the maximum adsorption density on malachite occurred at pH 9.5. Hydroxamate was adsorbed more rapidly on the surface of malachite than xanthate. The results suggest that the adsorption mechanism involves the chemisorption of a first layer followed by a multi-layer formation through surface reactions. The numbers of the hypothetical collector layers formed were 6 and 9 for malachite-xanthate and malachite-hydroxamate, respectively. The model predicted 98% copper recovery using 202.7g/t of xanthate, 674.99 g/t of hydroxamate, and 61.9 g/t of DETA [11].

Over time, and with continuous mining, the composition of ores has become more complex. Single collectors can barely meet the dual requirement of recovery and selectivity in mineral flotation [22].

The excellent performance of mixed collectors in practical applications has inspired numerous researchers to explore the potential combination modes and their underlying mechanisms [23].

The combined use of collectors with a high flotation performance and a high selectivity can usually fulfill the multiple requirements [24]. In comparison to the individual collectors, the use of mixtures can reduce the total amount of collectors used. Moreover, some collectors with very high surface activity can be quite expensive in industrial applications, which can limit their large-scale applications. By contrast, a combination of surface-active and expensive surfactant with a comparatively less surface-active and a cheaper surfactant in different proportions can achieve not only a comparable performance but also reduce the cost [25, 26]. Thus the ratio of components in the mixed collector systems is of great importance for both optimizing the flotation process and reduce the collector's consumption costs [27].

Developing a new collector and taking advantage of the synergistic effect of the mixed collector for flotation of metal oxide minerals have been attempted by some researchers in the last decade. The adsorption mechanism of α-hydroxyoctylphosphonic acid (HPA) to malachite has been investigated. HPA has exhibited a superior collecting performance to the direct flotation recovery of malachite and floated out above 80% malachite at pH 5-10. FT-IR analysis confirms that HPA might react with copper species of malachite surface to form the Cu-HPA complex adsorption layers [28].

Guangyi et al. (2016) have proposed the new collector of 3-hexyl-4-amino-1, 2, 4-triazole-5-thione (HATT) for malachite flotation. Their findings show that this collector might chemisorb on the malachite surface by formation of the Cu-S and Cu-N bonds and can recover malachite with a good performance [29].

The malachite flotation behaviors have been studied in combination with sodium oleate and alcohols and octylhydroxamate by Zhili et al. (2018). The result obtained demonstrated an increase in the malachite floatability due to the co-adsorption of alcohols with sodium oleate on the malachite surface [13].

Sodium butyl xanthate (NaBX) and dodecyl amine (DDA) have been used as the combined collectors on the sulfidizing flotation of malachite. The results show that the combined use of NaBX+DDA yields a better effect than using NaBX at pH 7−11 only [30].

Jun liu et al. (2019) have reported that a novel chelating collector, 5-(2, 4, 4-trimethylpentyl)-4-amino 1, 2, 4-triazolidine-3-thione (TMATT), exhibit a stronger hydrophobization to malachite than hydroxamate [31].

The present work addresses two objectives: first, to gain an insight into PAX and hydroxamate concentration corresponding to the formation of a monolayer and proposes the optimum synergistic effects (best ratio of mixed collectors) between PAX and hydroxamate; secondly, to explore the underlying mechanism responsible for improving the flotation performance in a mixed collector

system. In order to achieve these purposes, the solubility of malachite in PAX, HXM, and a mixture of them, and the changes in the malachite surface potential, adsorption density, dynamic contact angle, and flotation performance were evaluated, and the results obtained were characterized by FT-IR analysis.

2. Materials and methods

Pure Malachite was obtained by handpicking from the mineral veins of Qaleh-Zari mine (Iran) in collaboration with the Geological Survey of Iran. The sample was crystalline and composed of slender to acicular prisms. The XRD and XRF results of the malachite sample are presented in Figure 1 and Table 1, respectively. Chemical analysis by atomic absorption show that the sample contains 68.3% CuO, 1.93% ZnO, and 0.74% PbO.

Table 1. XRF analysis of malachite.

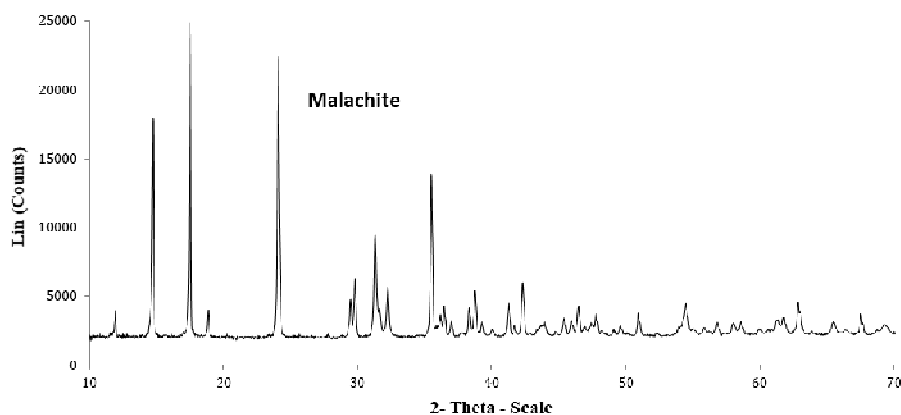| Compounds	SiO_2	Al_2O_3	Fe_2O_3	CaO	P_2O_5	CuO	ZnO	PbO	L.O.I
(%)	0.6	0.5	0.1	0.1	<0.1	67.3	2.4	0.8	28.00

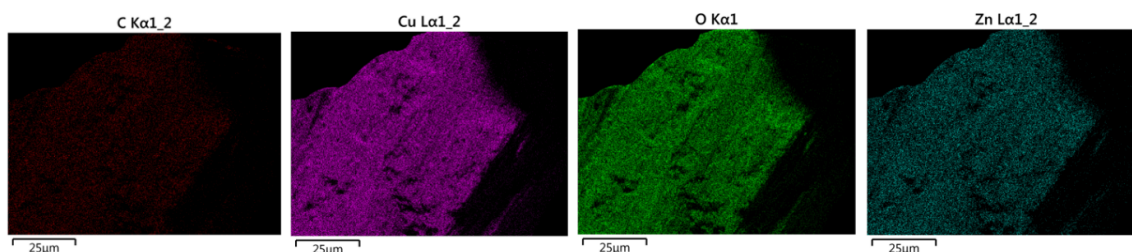**Figure 1. XRD graph of malachite sample.**

Figure 2. Element mapping of malachite surface by EDX analysis.

In Figure 2, the elemental composition of the malachite particles analyzed by EDX can be seen. The Zn distribution on the malachite particles can be a good indication that Zn atoms substitute in the malachite lattice.

The sample was crushed and ground using a porcelain mortar and wet-screened into three size fractions: +75 µm, -75 + 37 µm, and -37 µm for the collector adsorption and flotation experiments. Particles of −5 µm (separated by sedimentation) were used for the surface potential study. The ground and sieved samples were also washed in distilled water to remove the impurity ions.

In order to determine the adsorption density of the collectors on malachite, the surface area of the size fraction of (-75 +37) µm was measured by the BET adsorption method using nitrogen in a Micromeritics Orr Surface Area/Pore Volume Analyzer, and was found to be 2.1555 m^2/g.

Potassium amyl xanthate (PAX) was a product of the Cheminova Co., and potassium octylhydroxamate (HXM) was provided by the Axis House Co. (AM810). All the other reagents used in this work were of analytical grade. Double-distilled water (DDW) was used throughout this work.

Prior to zeta potential measurement, each sample was conditioned and equilibrated for 10 h in a 100-mL beaker. The concentration of the collectors was evaluated using UV spectroscopy. Flotation tests

were done using 2 g of malachite in a 250-mL "Sub-A" Denver Flotation Machine.

2.1. Zeta potential
The mineral suspensions used for the zeta potential were prepared using 0.5 g of malachite in 50 mL of DDW, and were mixed using a magnetic stirrer. Next, the suspension was given a sufficient time to sediment the particles larger than 1 µm, and then the suspension including the particles < 1 µm were decanted. The pH value of the suspension (including -1 µm particle size) was adjusted to the desired value using sodium hydroxide or sulfuric acid, and was given enough time to attain equilibrium with the atmospheric CO_2 since dissolved CO_2 could produce ions that could affect the zeta potential of malachite. After equilibrium, specified dosages of the collectors were added to the suspension and the suspension was conditioned for 10 min, and finally, the zeta potential was measured by the electrophoresis method using a Malvern DLS (dynamic light scattering) instrument.

2.2. Kinetic and adsorption expriments
The adsorption change versus the solution concentration was investigated in order to study the adsorption kinetics and adsorption densities, respectively.

Adsorption of the collector was evaluated by determining the difference in concentration of the collector in solution before and after adding the malachite sample (solution-depletion method). The experiments were conducted at the ambient temperature in a 100-mL Pyrex beaker at a solid:liquid ratio (by weight) of 1:20, the pH was adjusted by adding sodium hydroxide at 9±1, and conditioning was carried out in an orbital shaker for a predominant time (selected according to the plot of kinetic of adsorption) required for attaining equilibrium.

The mixture was filtered via a vacuum-assisted filtration system using a MN 615 filter paper. Then the filtrate was used for determination of the collector adsorption by a UV spectrophotometer. The hydroxamate concentration was evaluated by the well-known ferric hydroxamate method using the spectrophotometer, as described by Fuerestinou [32].

2.3. Contact angle measurements
The contact angle was measured by the Wilhelmy plate technique using the Lauda TE3 tensiometer. A malachite plate was used to measure the dynamic contact angle. After each measurement, the plate was polished and contacted with the new solution in 10 min. Each measurement was repeated for 5 times, and the average was considered.

2.4. FT-IR measurements
Fourier transform-infrared (FT-IR) spectra were recorded on a Thermo Scientific Nicolet spectrometer at 25 °C. The wave number of the spectra was 4000-450 cm⁻¹. The spectra of the solids were taken using KBr pellets. The grounded mineral (less than 6 µm) were used for analysis.

2.5. Flotation expriments
For the flotation test, 2.0 g of ground malachite (37-75 µm) was conditioned in 50 mL of the collector solution in a beaker at pH 9 (±0.1) for 10 min. Then the solution was transferred to the glass flotation cell. The floated fraction was collected for 5 min and weighed after drying at the ambient temperature. All the experiments were conducted twice in order to ensure the reproducibility of the results.

3. Results and discussion
3.1. Malachite-water system
The crystal lattice affects the flotation performance of malachite, specially its dissolution rate, due to the release of copper ions, and also the degree of hydration of malachite affects the flotation process. Malachite, like other oxide minerals, is expected to form a hydroxylated surface when in contact with an aqueous solution. Adsorption/desorption of H^+ from the surface hydroxyls can account for the surface charge on the malachite surfaces. In addition, the potential determining ions can affect the surface charge. The effective flotation of malachite by the hydroxamate collectors lies in the pH range of 6-10 [6]. According to the Lenormand's work on the malachite-water system at the pH range of 6.6-9.4, the HCO_3^- and $CuOH^+$ ions are the predominant surface potential determining ions, and more likely, the HCO_3^- and OH^- ions on the malachite surface are displaced for each collector ion.

With increasing pH, the formation and stability of the copper hydroxide species on the malachite surface increases. The surface copper ions (pulled out of the malachite lattice) also undergo hydrolysis and form hydroxide complexes in aqueous solutions [21].

Hydrolysis occurs in the solution of various hydroxyl complexes that can be adsorbed at the interface, and thereby, assists the adsorption of the collectors on the malachite surface.

Dissolution of different species of the malachite surface lattice is the most important reason for the instability of xanthate species on the malachite surface. The electrophilicity of atoms in the outermost layer of minerals was changed due to the adsorption of the H^+ and OH^- ions. In fact, the change in electrophilisity is caused by the electron transfer due to the reduction and oxidation of atoms caused by the adsorbed ions [33]. The collector interaction must result in reducing the copper ions at the outermost layer of malachite and prevention of malachite dissolution. The dissolution of copper ions from 0.5 g malachite in 50 mL deionized water in pH values of 8, 9, and 10 according to the time in orbital shaker is shown in Figure 3. It displays that the total concentration of copper ions after 5 h is restricted to 110 ppb. Zhili (2019) has measured the solubility of malachite at different pH values. The results obtained show that the solubility of malachite decrease sharply with increase in pH from 3 to 8.2 and reaches the minimum at about pH

8.2. Above this pH value, the solubility increases. Considering the maximum floatability reported for malachite [6, 13], this is an indication that the solubility of malachite is the most important problem in the flotation system. An effective collector should minimize the solubility of malachite.
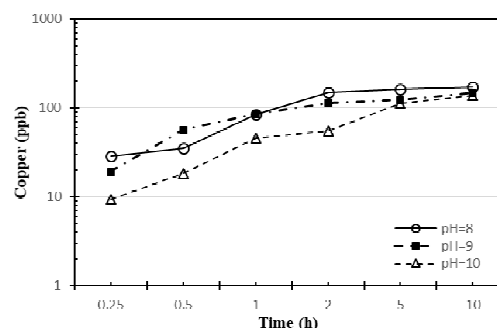

Figure 3. Solubility of malachite as a function of pH in deionized water.

Table 2. Solubility of malachite in the collector solutions.

Solution	Deionized water	PAX solution (2×10^{-4} M)	Hydroxamate solution (2×10^{-4} M)	PAX (1.3×10^{-4} M) + Hydroxamate ($.7 \times 10^{-4}$ M)
Copper conc. (ppb)	110	80	20	17

The copper concentrations in water and the collector solutions were determined by atomic absorption spectroscopy (AAS) (Table 2). The results obtained show that PAX cannot prevent malachite dissolution as much as hydroxamate. In the PAX solution, copper along with other species in malachite lattice is released from the outermost layer of malachite, resulting in the instability of xanthate on the malachite surface. It seems that the xanthate head group cannot provide sufficient charge to the copper site in the malachite surface to reduce and stabilize them.

3.2. PZC of malachite
The sign and magnitude of the surface charge control the adsorption of physically adsorbing collectors. In addition, a high surface charge can inhibit the chemisorption of chemically adsorbing collectors [34]. Consistently, PZC of malachite can be helpful in characterizing the ionic composition of the malachite surface, and this may provide a better understanding of the collector adsorption mechanism.
The effects of PAX and HXM on the zeta potential of malachite were measured as a function of pH, and the results obtained were presented in Figure 4. As with most oxide minerals, the zeta potential of malachite decreased as the pH increased, showing

the occurrence of ZPC at pH 8.4, which was in good agreement with that reported pH 8.2 by Zhili (2018). When malachite was conditioned with 10^{-4} M of HXM, its zeta potential changed to a more negative value, and ZPC slightly shifted from 8.4 to 8.3. Furthermore, when malachite was conditioned with 10^{-4} M of PAX, its zeta potential changed to a more negative value throughout the pH range of 6.5-10. This behavior may suggest that PAX and HXM chemisorb onto the malachite surface.
Furthermore, the effective flotation pH range of malachite by hydroxamate lies between the pH values of 6 and 10 [6, 13, 35]. As demonstrated in Figure 4, the adsorption of PAX and HXM at pH 9 cannot be a physical phenomenon because the surface of malachite is negatively charged; and PAX and HXM, as anionic collectors, cannot be physically adsorbed on a negative surface. This is the most important indication that the adsorption mechanism of PAX and HXM is not controlled by electrostatic attraction.

3.3. Kinetic of adsorption
The kinetic of the collector adsorption on the surface of minerals in the case of semi-soluble minerals is slow and depends on the solubility of minerals. It may take several hours for more

soluble minerals to as long as several days for the least soluble minerals to reach equilibrium [32]. The results of the uptake of PAX and HXM on malachite as a function of time are shown in Figure 5. The initial concentrations in each case were $5 \times$

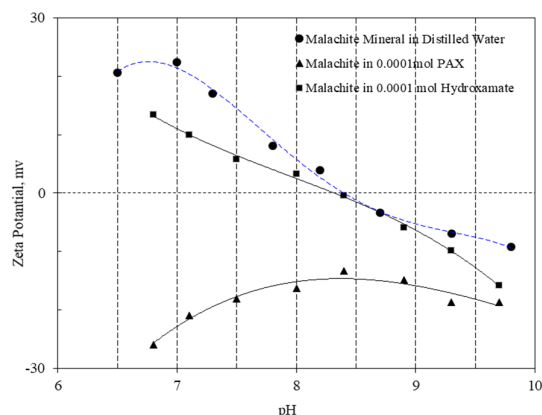10^{-4}. The equilibrium plateau values were reached after about 10 h. For the subsequent adsorption experiments, this time was used to achieve equilibrium.
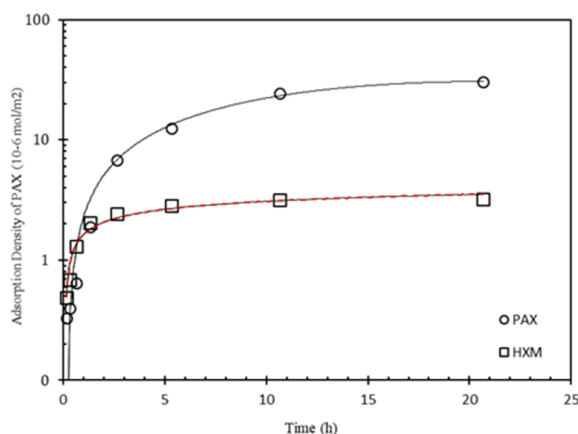

Figure 4. Zeta potential of malachite mineral in DDW, PAX solution (10^{-4} M), and HXM (10^{-4} M); the ionic strength of solution was adjusted using NaCl (0.01 M).

Figure 5. Kinetic of the PAX and HXM adsorption on malachite at 5×10^{-4} M solution concentration.

In the adsorption process, the more active sites on the malachite surface are more likely to be the copper sites, where the interaction forces are stronger. As adsorption proceeds, the less active sites (ion exchange of xanthate or hydroxamate ions with hydroxyl ion on the malachite surface) are occupied, where the sites-surfactant forces are weaker. Subsequently, H-bonding and lateral interaction between the adsorbed collectors can occur. Also in the malachite-water system, copper ions dissolved in the bulk solution can form complex with the PAX and HXM species, leading to precipitation of copper xanthate.

3.4. Adsorption isotherms

Since the direct measurement of the amount of collectors adsorbed on the mineral surface permited a physical–chemical analysis of the adsorption phenomenon, the adsorption isotherms of PAX and HXM on the malachite surface were determined. PAX is stable in neutral and weakly alkaline conditions; thus it can be assumed that the PAX decrease in the solution is due to the collector adsorption on the mineral surface.

The equilibrium adsorption density of PAX on malachite as a function of PAX concentration is shown in Figures 6. In addition, the surface potential and flotation yield of malachite in accordance with the relevant concentrations are represented.

Figure 6 exhibits the adsorption isotherm of PAX on malachite at pH 9, showing that with increase in the concentration of PAX, the adsorption amount increases steadily, reaching a plateau at the initial PAX concentration of about 10^{-4} M. The isotherm belongs to the Langmuir isotherm behavior (regarding the initial slope), suggesting that PAX is chemically adsorbed on the malachite surface.

Multi-layer adsorption in most cases causes a reduction in the mineral surface hydrophobizing, while the non-selective precipitation of collector salts or hemi-micelles reduce the selectivity of flotation. Therefore, determining the concentration of the collector corresponding to monolayer formation is of particular importance. The primary curvature of adsorption density of PAX on malachite in Figure 6 shows that more sites are available on the malachite surface for xanthate adsorption so the adsorption of xanthate species will continue to form a monolayer. With regard to the sudden decrease in the gradient of adsorption, it can be an indication of the complete monolayer formation, and one can say that a monolayer of PAX molecules cover most of the malachite surface. In addition, the surface potential and flotation yield curves are well-correlated with the adsorption density and show a change in slope at the PAX concentration of about 10^{-4} M.

This phenomenon could be explained by a simple description. The cross-section area of the PAX

functional group is 29 A^2 [21]. If the entire malachite surface is covered by the PAX molecules, then 1.24 mg PAX is required to cover the entire surface of 0.5 g of ground malachite in the size fraction range of 37-75 microns with a specific surface area of 2.1555 m^2/g. In the present work, at a PAX concentration of 10^{-4} M, 0.92 mg of PAX was adsorbed onto 0.5 g of malachite.

It is important to consider that the inert gas molecules (in this case, nitrogen) are used for the measurement of surface area by the BET method. The PAX and HXM molecules are much larger than nitrogen so measurement of the surface area (2.1555 m^2/g), and consequently 1.24 mg PAX, could be overestimated. Therefore, for a complete monolayer adsorption, the concentration of 10^{-4} M can be confirmed by these computations.

3.5. Contact angle and flotation yeild

The advancing contact angle of the malachite surfaces modified by PAX and HXM and flotation yield of malachite as a function of the collector concentration are shown in Figure 7. The total collector concentration (PAX+HXM) in all tests was 1×10^{-4} M. The hydrophobicity of the malachite surface changed according to modification with different ratios of the PAX and HXM solution. Figure 7 demonstrates that at concentrations of 6.6×10^{-4} M PAX and 3.3×10^{-4} M HXM, the biggest advancing contact angle of malachite and high malachite recovery is achieved. Therefore, a PAX:HXM mole ratio of 2:1 was selected as a favorable collector solution for the following studies.
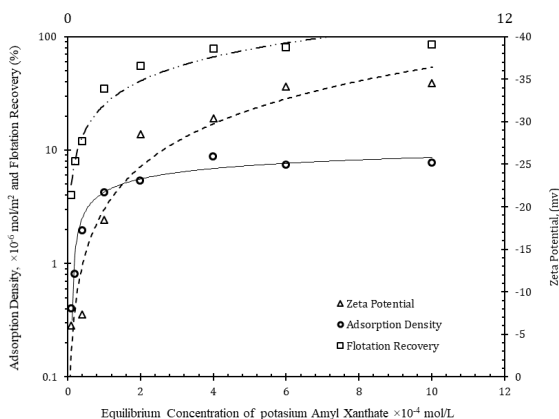

Figure 6. Adsorption density of PAX on malachite, flotation recovery, and zeta potential of malachite as a function of the PAX concentration at pH 9.
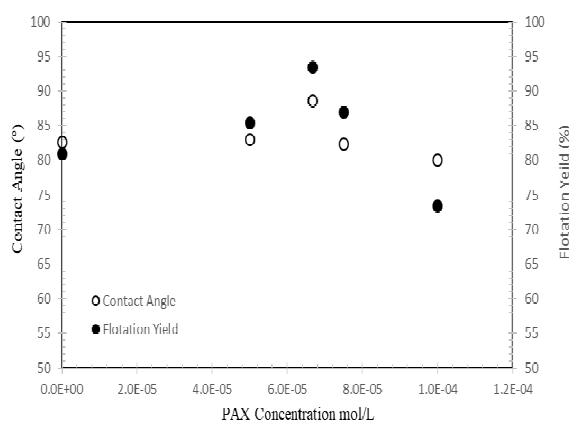

Figure 7. The advancing contact angle and flotation yield of malachite treated by the PAX and HXM solution at pH 9; the total collector (PAX+HXM) concentration was 1×10^{-4} mol/L.

Figures 8 and 9 show the measured adsorption isotherms for the collectors alone and from the mixture solutions adsorbed on malachite as a function of the equilibrium concentration. In Figure 9, in the mixture solution, in the presence of PAX, the adsorption amount of HXM on malachite slightly increased when the concentration of HXM was lower than 3×10^{-4} M.

In Figure 8, in the presence of mixed PAX/HXM, the adsorbed amount of PAX on the malachite surface significantly increased in the PAX concentrations more than 10^{-4} M. This increase can be explained by the co-adsorption, PAX can be adsorbed between the molecules of HXM through hydrogen bonding and hydrophobic interactions. This synergistic effect led to a considerably stronger hydrophobisity on the malachite surface and a better surface activity compared to single PAX or HXM.
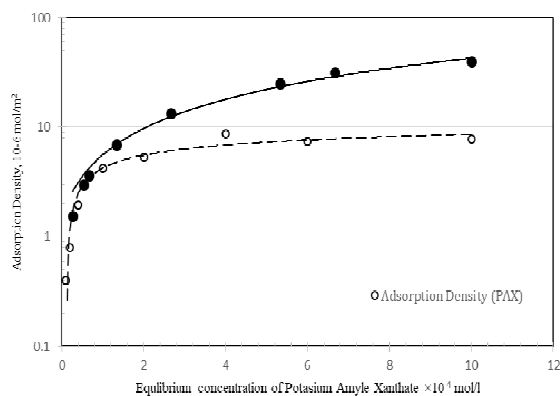
Figure 8. Adsorption density of PAX on malachite as a function of solution concentration of PAX with and without HXM at pH 9 (PAX/HXM = 2:1).
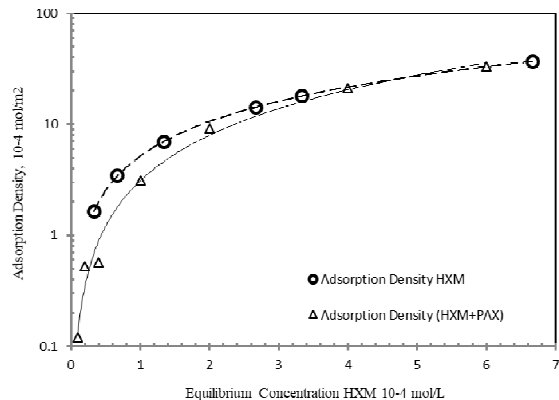

Figure 9. Adsorption density of HXM on malachite as a function of solution concentration of HXM with and without PAX at pH 9 (PAX/HXM = 2:1).

4. FT-IR Spectral results

The FT-IR spectra of pure malachite and malachite treated with PAX, HXM, and a mixture of PAX and HXM are displayed in Figure 10. In nature, malachite is rarely encountered as a chemically pure compound. Usually it includes zinc ions in a wide concentration range (up to a Zn/Cu ratio = 1) known as the mineral rosasite. The bands below $600\ cm^{-1}$ can be assigned to the Cu-O bonds (strong Cu-O interactions) [34]. The C=O bond of copper octylhydroxamate was found at $1520\ cm^{-1}$

[6]. The formation of copper octylhydroxamate affects the 1517 band and shifts it to $1510\ cm^{-1}$. Furthermore, the bands below $600\ cm^{-1}$ belong to Cu-O shifted to other levels, which shows that new bonds are formed by copper atoms on the malachite surface. These may be other indications that HXM is adsorbed on the malachite surface via a chemical reaction. In addition, similar observations can be seen in malachite treated by a mixture solution of PAX and HXM.
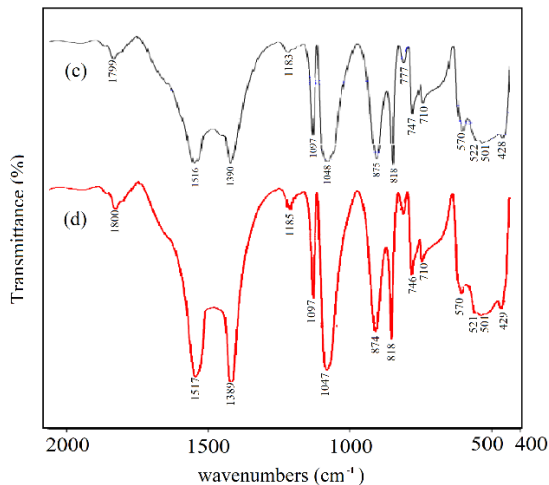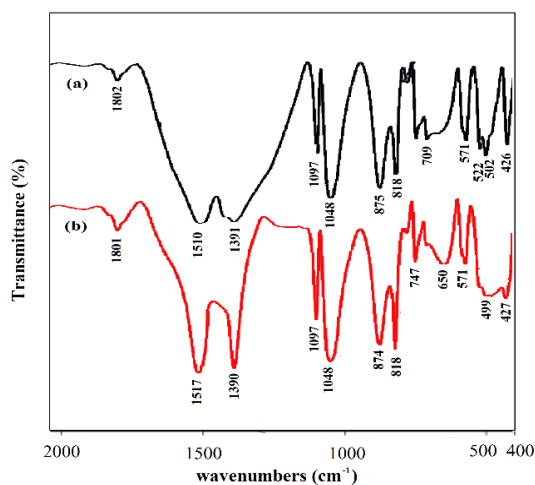

Figure10. Infrared spectra of malachite contacted with HXM (a), pure malachite (b), malachite contacted with a mixture of PAX and HXM (c), and malachite contacted with PAX solution (d) at pH 9.0.

The malachite sample contacted with the PAX and PAX+HXM solutions shows the new 1185 and $1183\ cm^{-1}$ bands, respectively (Figures 10c, 10d). The peak for C-O-C asymmetric stretching vibration of copper butyl xanthate was found at about $1204\ cm^{-1}$ [13]. Therefore, these peaks may be attributed to the formation of copper xanthate,

which is an indication that PAX is chemisorbed on the malachite surface. According to the given explanations, it can be concluded that PAX and HXM are both chemically co-adsorbed on the malachite surface .

The formation of monolayer starts by adsorption of xanthate and hydroxamate via charge transfer

chemisorptions in which the xanthate and hydroxamate ions are discharge on the copper sites on the malachite surface. Strong chelation force of hydroxamate adsorption (the nature of bi-functional hydroxamate ligand and adsorption at two sites) leads to the adsorption with a higher mechanical strength on the malachite surface. According to Chowdhury and Antolasic (2012), the hydroxamate ions form multi-layers by hydrogen bonding. Xanthate has an oxygen atom in its functional group that can react with hydroxamate by hydrogen bonding and contribute to the formation of a special multi-layer that increases hydrophobicity of malachite, and consequently, increases PAX adsorption.
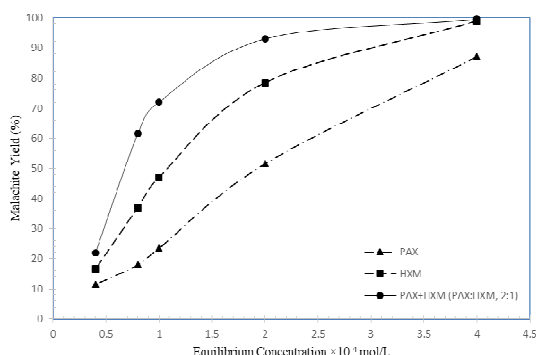

Figure 11. Flotation yield of malachite by PAX, HXM, and a combination of them as a function of concentration.

As a comparison of the flotation experiments for the PAX and HXM and a combination of them on malachite, a series of flotation tests were carried out in different concentrations of the collectors. Figure 11 shows the flotation of malachite as a function of the collector concentration at pH 9.

The yield of malachite increased with increase in the concentration of PAX, HXM, and mixed PAX/HXM. Using PAX as a collector in direct flotation of malachite, the malachite yield increased to 51.5% and 87% as the PAX concentration was increased to 2×10^{-4} and 4×10^{-4} M, respectively. In the case of HXM, the malachite yield increased to 78.5% and 99% as the HXM concentration was increased to 2×10^{-4} and 4×10^{-4} M, respectively. HXM exhibited more potential to float malachite than that of PAX.

In the case of PAX/HXM (the mole ratio of PAX/PYHM = 2:1), the yield of malachite rapidly increased, particularly at low collector concentrations. For example, at a collector concentration of 2×10^{-4} M, the flotation yield of malachite in the presence of the mixed surfactant

was approximately 93%, whereas it was only approximately 51.5% for PAX and 78.5% for HXM. The results obtained are in good agreement with the adsorption of PAX and HXM alone and from mixture solutions on malachite in Figures 8 and 9. The PAX/HXM mixtures thus showed a positive effect on flotation of malachite. This mixture of collectors exhibited a superior collecting performance compared to only xanthate or hydroxamate.

5. Conclusions

In this work, two anionic collectors, potassium amyl xanthate (PAX) and potassium alkyl hydroxamate (HXM), were found to exhibit a synergistic effect on the flotation of malachite. The following conclusions could therefore be drawn. The results show that PAX cannot prevent malachite dissolution as much as hydroxamate. In the PAX solution, copper along with other species in the malachite lattice are released from the outermost layer of malachite and result in the instability of xanthate on the malachite surface.

The mixed surfactants PAX/HXM exhibit a stronger collecting ability than that of the individual PAX or HXM, and the best flotation performance of malachite occurs in the PAX: HXM mole ratio of 2:1.

The results obtained from the adsorption densities further confirmed the synergistic effects of the mixed PAX/HXM on the adsorption of PAX on the malachite surface, and the adsorbed amounts of PAX were distinctly enhanced due to the co-adsorption of PAX and HXM on the malachite surface in the presence of the mixture. FT-IR analysis confirmed the chemical co-adsorption of PAX and HXM on the malachite surface.

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بررسی مکانیزم جذب گزنتات و هیدروکسامات در سطح مالاکیت

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چکیده:

قابلیت شناوری کانی‌های اکسیدی مس مانند مالاکیت با استفاده از کلکتورهای مرسوم فلوتاسیون کانی‌های سولفیدی مس، پایین بوده و فلوتاسیون آنها نیازمند استفاده از کلکتورها و طرح‌های فلوتاسیون جدید است. در بسیاری از معادن مس، مقدار قابل توجهی کانی‌های اکسیدی مس به ویژه مالاکیت کانی‌های سولفیدی مس را همراهی می‌کنند. با توجه به این که گزنتات‌ها پرکاربردترین کلکتورهای مورد استفاده در فلوتاسیون کانی‌های سولفیدی و بویژه کانی‌های سولفیدی مس هستند و فلوتاسیون موفق کانی‌های اکسیدی مس توسط هیدروکسامات‌ها نیز انجام شده است. استفاده از اثر هم‌افزایی کلکتورهای گزنتات و هیدروکسامات می تواند یک روش مؤثر در افزایش کارایی فلوتاسیون کانی‌های اکسید مس به همراه کانی‌های سولفیدی باشد. در این تحقیق، اندرکنش‌های آمیل گزنتات پتاسیم و آلکیل هیدروکسامات پتاسیم بصورت منفرد با مالاکیت طبیعی، و اثرات هم‌افزایی آنها در شناورسازی مالاکیت بررسی شده است. داده‌های بدست آمده از حلالیت مالاکیت در محلول‌های کلکتوری، تغییرات در پتانسیل سطح مالاکیت، سینتیک‌ها و دانسیته‌های جذب کلکتورها، تغییرات زاویه تماس دینامیکی، تجزیه و تحلیل‌های FT-IR و آزمایش‌های فلوتاسیون، مورد تجزیه و تحلیل قرار گرفته است. نتایج به دست آمده نشان می‌دهد گزنتات و هیدروکسامات به صورت همزمان با مکانیزم شیمیایی روی سطح مالاکیت جذب می‌شوند. مقدار گزنتات جذب شده در سطح مالاکیت در محلول مخلوط کلکتوری گزنتات- هیدروکسامات به دلیل جذب همزمان به طور قابل توجهی افزایش می‌یابد. نتایج فلوتاسیون، افزایش قابلیت شناوری مالاکیت را در محلول مخلوط گزنتات- هیدروکسامات را نسبت به محلول‌های منفرد گزنتات و هیدروکسامات تأیید می‌کند. بر اساس نتایج، مخلوط گزنتات- هیدروکسامات اثر هم افزایی قابل توجهی در آب‌گریزی سطح مالاکیت نشان می‌دهد.

کلمات کلیدی: مالاکیت، پتانسیل سطح، جذب سطحی، هم‌افزایی، فلوتاسیون کفی.