Journal of Colloid and Interface Science 512 (2018) 701–712

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Cu(I)/Cu(II) mixed-valence surface complexes of S-[(2-hydroxyamino)-2-oxoethyl]-*N*,*N*-dibutyldithiocarbamate: Hydrophobic mechanism to malachite flotation

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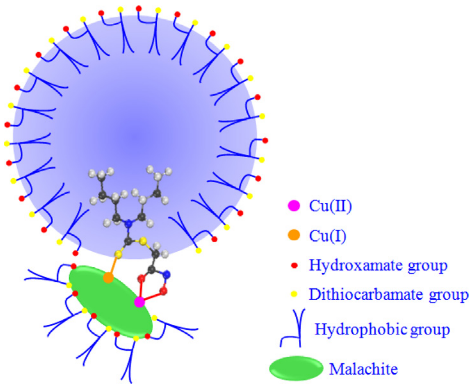
GRAPHICAL ABSTRACT

The hydrophobic mechanism of *S*-[(2-hydroxyamino)-2-oxoethyl]-*N*,*N*-dibutyl -dithiocarbamate (HABTC) to malachite ($Cu_2CO_3(OH)_2$).



ARTICLE INFO

Article history:
Received 2 July 2017
Revised 16 October 2017
Accepted 16 October 2017
Available online 17 October 2017

Keywords:
S-[(2-hydroxyamino)-2-oxoethyl]-*N*,*N*-dibutyldithiocarbamate
Malachite
Flotation mechanism
Cu(I)/Cu(II) mixed-valence surface complexes
ToF-SIMS

ABSTRACT

Hypothesis: Hydroxamate and sulfhydryl surfactants are effective collectors for flotation of copper minerals. The combination application of hydroxamate and sulfhydryl collectors has been proved to be an effective approach for improving the flotation recovery of non-sulfide copper minerals. A surfactant owing both hydroxamate and dithiocarbamate groups might exhibit strong affinity to non-sulfide copper minerals through double sites adsorption, rendering an enhanced hydrophobization to non-sulfide copper minerals flotation.

Experiments: The flotation performance of *S*-[(2-hydroxyamino)-2-oxoethyl]- *N*,*N*-dibutyldithiocarbamate (HABTC) to malachite, calcite and quartz were first evaluated through systematic micro-flotation experiments. HABTC's hydrophobic mechanism to malachite was further investigated and analyzed by zeta potential, Fourier transform infrared spectroscopy (FTIR), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS).

Findings: The micro-flotation results demonstrated HABTC was an excellent collector for malachite flotation and exhibited favorable selectivity for flotation separation of malachite from quartz or calcite under pH 8.5–10.3. Zeta potential and FTIR implied that HABTC might bond with the surface copper atoms of malachite, with releasing the H^+ ions of its hydroxamate group into pulp. ToF-SIMS provided clear evidences that the

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https://doi.org/10.1016/j.jcis.2017.10.063

Cu-hydroxamate and Cu-dithiocarbamate groups were formed on malachite surfaces after HABTC adsorption. XPS revealed that Cu(I)/Cu(II) mixed-valence surface complexes of HABTC anchored on malachite through formation of Cu(I)—S and Cu(II)—O bonds, accompanying with reduction of partial surface Cu(II) to Cu(I). The Cu(I)/Cu(II) mixed-valence double chelating character and "chair"-shape *N*,*N*-dibutyldithiocarbamate hydrophobic group, resulting in an enhanced affinity and hydrophobization of HABTC to malachite flotation.

1. Introduction

Non-sulfide copper minerals such as malachite ($Cu_2CO_3(OH)_2$), chrysocolla, azurite, cuprite and tenorite are indispensable resources for production of copper metal. Froth flotation and L-SX-EW (leaching-solvent extraction-electrowinning) are two main commercial approaches for processing non-sulfide copper minerals [1]. For non-sulfide and mixed non-sulfide plus sulfide copper ores with low copper content or high carbonate components, froth flotation becomes the preferable technology for separation and upgrading of copper minerals [1,2].

In flotation recovery of non-sulfide copper minerals, one crucial requirement is to selectively hydrophobize their surfaces by surfactant (known as collector in froth flotation) adsorption so that the air (or nitrogen) bubbles can selectively attach to the hydrophobized mineral particles and carry them to the pulp/air interfaces [3,4]. Non-sulfide copper minerals tend to hydroxylate their surfaces in aqueous pulps and exhibit strong hydrophilic [5], they are more difficult to be hydrophobized than copper sulfide minerals (the hydrophobicity of sulfur atom is stronger than that of oxygen atom). Commonly, direct flotation is applied to recover copper sulfide minerals by using sulfhydryl collectors [4,6,7]. For recovery of non-sulfide copper minerals, there are two popular approaches, direct flotation using long-hydrophobic-chain collectors such as fatty acids, petroleum sulphonates or oxime derivatives, and sulfidization flotation using xanthates or other sulfhydryl collectors [8–12]. For the sulfidization flotation, it suffered from inevitable defects including the discrepant response of non-sulfide copper minerals to sulfidizing agents such as NaHS, NH_4HS or Na_2S, their hypercritical dose and rapid decomposition with processing time [1,13–15]. While for direct flotation, oximido collectors such as hydroxamic acids have been considered to be effective chelating collectors for selective flotation of non-sulfide copper minerals including malachite, chrysocolla and azurite from calcium-bearing carbonate minerals and quartz [9,10,16–18]. Hope et al. investigated the flotation response of mixed chrysocolla–malachite–quartz particle samples using *n*-octanohydroxamate collector, and achieved excellent copper recovery [9]. The copper-hydroxamate surface complexes were observed after *n*-octanohydroxamate adsorption on non-sulfide copper minerals [19,20]. Ni and Liu found that octyl hydroxamic acid physisorbed on calcite surfaces at pH 8.5 [21]. Marion et al. [18] mentioned the complexes of acetohydroxamic acid, salicylhydroxamic acid, and benzohydroxamic acid with cupric ions were far more stable than those with alkaline-earth metal cations. And they concluded benzo- and octylhydroxamic acids were effective collectors for selective flotation separation of malachite from quartz.

Furthermore, sulfhydryl surfactants have been directly applied in non-sulfide copper minerals flotation [5,16,22]. Barbaro et al. suggested aminothiophenol chemisorbed on chrysocolla to form copper-aminothiophenol surface complexes and performed selective flotation separation of chrysocolla from quartz [5]. Fuerstenau et al. observed the copper-dithiocarbamate complexes on malachite surfaces after sodium diethyldithiocarbamate treatment [16]. Buckley et al. found the copper-dithiophosphate surface complexes on cuprite after dialkyl dithiophosphates adsorption [22]. Recently, the combination application of sulfhydryl and oximido collectors in flotation of mixed nonsulfide-sulfide copper ores has been proved to be an effective approach for improving the flotation recovery of copper minerals [13,14,23]. A surfactant owning both sulfhydryl and oximido groups might exhibit unique hydrometallurgical performances for flotation recovery of copper non-sulfide and sulfide minerals. Nevertheless, such oximido-sulfhydryl surfactants have been rarely reported as flotation collectors.

In this paper, a novel surfactant, *S*-[(2-hydroxyamino)-2-oxoethyl]-*N*,*N*-dibutyldithiocarbamate (HABTC) was introduced as a collector for flotation separation of malachite from calcite or quartz. HABTC's hydrophobic mechanism to malachite was evaluated by micro-flotation, zeta potential, FTIR, ToF-SIMS and XPS. Understanding the role of oximido, sulfhydryl and hydrophobic groups in a collector molecule to malachite flotation would be helpful to promote the flotation recovery of non-sulfide copper minerals and to develop more efficient flotation surfactants.

2. Materials and methods

2.1. Materials

Pure malachite samples originated from Congo were purchased from Daye Non-ferrous Metals Company (China). Pure calcite and quartz were obtained from Guilin, Guangxi Province. The X-ray diffraction (XRD) and X-ray fluorescence (XRF) results of the three minerals were listed in Fig. S1 and Table S1 in the supporting information, respectively. The purity of malachite, quartz or calcite samples was greater than 98.5%. The massive mineral samples were artificially crushed and ground in an agate mortar with a pestle. The fraction with particle size ranging from 76 to 38 μm or from 149 to 76 μm was screened and used for micro-flotation tests. The specific surface areas of the 38–76 μm fraction were 0.458 $m^2 \cdot g^{-1}$ for malachite, 0.111 $m^2 \cdot g^{-1}$ for calcite and 0.120 $m^2 \cdot g^{-1}$ for quartz determined by Brunauer-Emmett-Teller (B.E.T) method through liquid N_2 sorption tests on a Nova-1000 surface area analyzer (Quantachrome Instruments, USA). The fraction with diameter less than 5 μm was used for FTIR, XPS and zeta potential measurements.

HABTC used in this study was prepared and recrystallized from ethanol-water solvent in our laboratory with a purity greater than 99.0% [24]. The molecular structure of HABTC was shown in Fig. S2 in the supporting information. Other chemicals used in the present study were purchased from commercial suppliers with Analytical Reagent (AR) grade. High purity nitrogen was used as the flotation gas. Distilled water was used throughout all experiments unless otherwise stated.

2.2. Micro-flotation tests

Micro-flotation tests were conducted in a 225 mL modified Hallimond tube. In each test, 2 g of pure mineral samples or artificially mixed minerals were introduced into 180 mL water in a beaker.