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Thiadiazole-thione surfactants: Preparation, flotation performance and adsorption mechanism to malachite

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ABSTRACT

In this paper, novel thiadiazole-thione surfactants including 5-heptyl-1,3,4-thiadiazole-2-thione (HpSDT), 5-phenyl-1,3,4-thiadiazole-2-thione (PSDT) and 5-(2-hydroxyphenyl)-1,3,4-thiadiazole-2-thione (HPhSDT) were synthesized and originally introduced as collectors in froth flotation. Micro-flotation tests showed that HpSDT exhibited better flotation response to malachite than PSDT and HPhSDT, as well as excellent flotation selectivity against quartz. The contact angle results inferred that the hydrophobization intensity of these collectors toward malachite was in the order as HpSDT > PSDT > HPhSDT. ζ -potential recommended a chemisorption of HpSDT on malachite surfaces. FTIR deduced that cupric or cuprous atoms might bond with the S and N atoms of HpSDT to form a conjugated ring. XPS further gave an additional evidence that HpSDT-Cu(I) complexes were produced on malachite surfaces via combining surface Cu atoms with HpSDT's N and S atoms, with reducing surface Cu(II) to Cu (I). The tighter orientation arrangement on malachite and stronger hydrophobicity rendered HpSDT to possess better flotation affinity toward malachite than PSDT and HPhSDT.

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Introduction

As important raw materials for commercial production of copper, copper oxide ores have become increasingly significant due to the overexploitation of copper sulfide ores [1–3]. Froth flotation is an effective separation technique for upgrading and enrichment of copper oxide minerals [4–7]. In comparison with copper sulfide minerals, copper oxide minerals such as malachite, azurite or chrysocolla display weak floatability for their surface hydration. The sulfidization flotation with xanthates as collectors has become the common approach for recovery of copper oxide minerals [1–3,8]. Nevertheless, the sulfidizing agents such as Na_2S , $(\text{NH}_4)_2\text{S}$ or NaHS exhibit the differential response to various copper minerals and their dose is difficult to be precisely stoichiometric. Moreover, the sulfidizing agents tend to be oxidized into different sulfur species during the sulfidization flotation process. Although xanthates are powerful collectors for sulfide minerals, they suffer from low selectivity. All of these factors might result in unsatisfactory beneficiation of copper oxide minerals [9–16]. To improve the efficiency of sulfidization flotation technology, flotation activators

such as ethanediamine or ammonia have been studied in sulfidization flotation of copper oxide minerals [13,14].

To promote the flotation recovery of copper oxide minerals, diverse chelating-type collectors have been developed and evaluated [6,15–30]. Among them, hydroxamic acids, aldioximes, or phosphonic acids have been proved as suitable collectors for flotation enrichment of copper oxide minerals, while they might lack flotation selectivity against calcium- or iron-bearing minerals [6,9,20–24]. 2-Mercaptobenzothiazole (MBT), amino thiophenol (ATP), 2-mercaptobenzoxazole (MBO) and 2-mercaptobenzimidazole (MBI) possess powerful affinity to copper oxide/sulfide minerals [25–30], unfortunately, they suffer from the inadequate hydrophobicity owing to the benzene ring. The expensive synthesis cost to their derivatives with alkyl/alkoxyl groups linking to benzene ring restricts the flotation application of their derivatives [25,28,31,32].

Recently, the excellent flotation performances of 2-hexyl-4-amino-1,2,4-triazole-5-thione (HATT) to malachite and chalcopyrite has been proved [15,33,34]. Similar to MBT, MBO, MBI or ATP, HATT owns the S, N-donor atoms in its amino-azole-thione conjugative structure. And HATT chemisorbed on to copper mineral surfaces through formation of Cu–N or Cu–S bonds [15,34]. Unlike the hydrophobic group (i.e., benzene ring) of MBT, MBO, MBI or ATP, the hexyl group of HATT exhibited strong

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hydrophobicity, which improved the flotation recovery of copper oxide/sulfide minerals [15,33,34].

Thiadiazole-thione surfactants also contain S, N-donor atoms and own powerful coordination ability to metal atoms [35–41]. Bharati et al. [36,37] found that Cu(II) was able to combine with the S and N atoms of 5-methyl-1,3,4-thiadiazole-2-thione (MTDT) to produce Cu–S and Cu–N structures, while Pd(II) bonded with four thiolate S atoms of MTDT in the MTDT-Pd complexes. Geboes et al. [38] and Blajiev et al. [39] considered that MTDT anchored on copper metal surfaces via its S and N atoms. Matsumoto et al. [40] investigated the adsorption behavior of MTDT on Cu electrode and thought that (MTDT)₂ could be formed on Cu electrode surfaces. Varvara et al. [41] found the anticorrosive behavior of MTDT to bronze in an acidic solution. Nevertheless, using thiadiazole-thione compounds as flotation collectors has been rarely reported.

In this paper, novel thiadiazole-thione surfactants including 5-heptyl-1,3,4-thiadiazole-2-thione (HpSDT), 5-phenyl-1,3,4-thiadiazole-2-thione (PSDT) and 5-hydroxyphenyl-1,3,4-thiadiazole-2-thione (HPhSDT) were synthesized and characterized by FTIR (Fourier transform infrared) and NMR (nuclear magnetic resonance) spectra, and their collecting power toward malachite or quartz was investigated by micro-flotation experiments. Afterwards, the adsorption mechanism of thiadiazole-thione collectors to malachite was evaluated through contact angle, ζ -potential, FTIR and XPS (X-ray photoelectron spectroscopy).

Experiments

Materials

HpSDT, PSDT and HPhSDT were synthesized in our laboratory and their purity was over 98.5% after recrystallization [42,43]. Other chemicals were bought via commercial channels. Pure malachite and quartz samples were separately obtained from Daye, Hubei Province and Guilin, Guangxi Province (China). Their X-ray fluorescence (XRF) and X-ray diffraction (XRD) were presented in Table 1 and Fig. 1. The mineral samples were artificially crushed, ground and screened [15,18]. The powder samples with a diameter of 38–76 μm were selected for micro-flotation experiments, and those with a diameter less than 38 μm were further ground to pass 5 μm , and used in ζ -potential, FTIR and XPS measurements.

Micro-flotation, contact angle and ζ -potential experiments

A modified 220 mL Hallimond tube was adopted for the micro-flotation tests which were conducted according to our previous operation procedures as listed in Fig. 2 [15,18]. The reported flotation recovery was computed according to the mass of the concentrates (floated products) and tailings (underflow products). The detailed description for the micro-flotation experiments was presented in Supporting information.

The wettability of new-polished malachite surfaces before and after HpSDT, PSDT or HPhSDT adsorption was detected on the JC2000C device (Zhongchen Digital, China) [15,34]. For each measurement, the new-polished malachite flake was separately immersed in 50 mL HpSDT, PSDT or HPhSDT solutions with the designed concentration and pH value. After stirring the collector solutions for a given time, the malachite flake was taken out,

soaked in distilled water for a very short time, dried by pure N₂, and then employed for contact angle measurement. The presented result was the average value of three independent measurements.

The ζ -potential of malachite particles with or without HpSDT, PSDT or HPhSDT treatment was detected under $1 \times 10^{-2} \text{ mol L}^{-1}$ KCl on the ZetaPlus analyzer (Brookhaven, USA). 0.05 g of $-5 \mu\text{m}$ malachite particles and 40 mL KCl solutions (20% ethanol, v/v) were mixed, and then dilute KOH or HCl solutions were dropwise fetched into the suspension to obtain the required pH value. Afterwards, a desired amount of HpSDT, PSDT or HPhSDT solutions (20% ethanol, v/v) and extra KCl solutions (20% ethanol, v/v) were sequentially added to a total volume of 50 mL. The dilute pulp was stirred for 5 min, and its ζ -potential and pH value were recorded. The reported ζ -potential value was the average of ten independent measurements with a representative deviation of $\pm 5 \text{ mV}$.

FTIR and XPS spectra measurement

The FTIR spectra of HpSDT, its reaction products with Cu²⁺ or Cu⁺ ions, and malachite particles before and after HpSDT adsorption were recorded with an infrared spectrometer (Nicolet FTIR-740, USA) via KBr disk pellets at room temperature.

During HpSDT interaction with Cu²⁺ or Cu⁺ ions, the yellow-green or brown-gray sediments respectively appeared in their mixed solutions, accompanying with the decrease of solution pH values as shown in Table 2.

The XPS spectra for HpSDT, HpSDT-Cu²⁺/Cu⁺ sediments, and malachite before and after HpSDT adsorption were recorded on Thermo Scientific ESCALAB 250Xi (using Al K α radiation with $h\nu = 1486.71 \text{ eV}$). The XPS bands were fitted via Gaussian and Lorentzian functions through Thermo Avantage software. The C 1s spectrum at 284.6 eV were selected as an internal standard to calibrate the binding energy. The detailed measurement procedures were shown in Supporting information.

Results and discussion

Synthesis of HpSDT, PSDT and HPhSDT

The synthetic route of HpSDT, PSDT and HPhSDT was shown in Scheme 1.

Synthesis of dithiocarbazate salt (2a–2c)

Hydrazine compounds (1a–1c, 0.2 mol), potassium hydroxide (0.24 mol) and 80 mL ethanol were mixed in a reaction flask equipped with a thermometer and a mechanical stirrer. Afterwards, carbon disulfide (0.3 mol) was dropwise fetched into under 10 °C. The reactive mixture was stirred at 20 °C for 3 h, and the resultant dithiocarbazate salt (2a–2c) was filtered, dried and used for the next reaction.

Preparation of 5-substituted-1,3,4-thiadiazole-2-thione (3a–3c)

The dithiocarbazate intermediates (2a–2c, 0.1 mol) were blended with appropriate amount of concentrated sulfuric acid (thrice to the mass of dithiocarbazate salts), and stirred 3 h at -3 to 3°C . Then, the crushed ice was dumped into the mixture. Some solid appeared, which was filtered and washed with distilled water until the filtrate became neutral. After sequential treatment by

Table 1
The XRF results of malachite and quartz.

Element, weight/%	Cu	Fe	C	Co	Al	Mn	Si	O	Pb	P
Malachite	55.84	0.02	8.74	0.02	0.05	0.01	0.14	34.98	0.02	0.18
Quartz	–	–	–	–	0.20	–	46.57	53.23	–	–

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