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Flotation performance and adsorption mechanism of malachite with *tert*-butylsalicylaldoxime

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ABSTRACT

In this research, the flotation performance and adsorption mechanism of *tert*-butylsalicylaldoxime (TBSA) to malachite were studied by micro-flotation, contact angle, zeta potential, FTIR and XPS analysis. The result of micro-flotation tests indicated TBSA yielded high malachite recovery and satisfied selectivity against calcite or silica at pH 9.0–10.5. The contact angle results inferred that the hydrophobicity of malachite surfaces was improved after TBSA modification. The results of zeta potential suggested that TBSA might chemisorb on malachite surfaces. XPS and IR spectrum analysis confirmed that the O atoms in C═N─OH group and benzene ring fixed with Cu species on malachite surfaces through C─O─Cu, N─O─Cu and d-pπ bond respectively.

1. Introduction

As the high grade and easy-to-process copper sulfide ores are being depleted at faster rates than ever, the utilization of low grade, complex and highly copper oxide minerals is facing serious challenges. Malachite is a typical kind of copper oxide mineral which is becoming more important and must be exploited to ensure copper availability for future [1].

Flotation has been proved a useful way for recovering valuable minerals from complex ores [2]. In nearly a hundred years of mineral-processing history, the flotation process got great development due to better flotation collector. Surfactant (known as collector in mineral processing) plays a key part in flotation through modifying hydrophobicity of targeted minerals [3]. Xanthanes, dithiophosphates and thiourea are utilized as collectors in the flotation of malachite at the early stages [4,5]. Later on, fatty acids and petroleum sulfonate have been proved to be the powerful collectors for copper oxide minerals flotation. Unfortunately, the employment of those collectors revel poor selectivity [6].

In last decade, numerous chelating collectors are designed and developed to deal with complex ores. Phosphonate compounds have been reported as powerful collectors for flotation of metal oxide minerals, while show poor selectivity to calcite [7,8]. 3-hexyl-4-amino-1,2,4-triazole-5-thione have been investigated as a useful collector for malachite flotation [9]. Thiadiazole-thione surfactants show powerful affinity to malachite and satisfied selectivity against quartz [10].

Hydroxamic acids, such as benzohydroxamic acid and octyl hydroxamic acid, have been proved to be useful collectors for copper oxide minerals [1]. Furthermore, several novel collectors which possess a same metal binding group, has been synthesized based on varying chain length and aryl substitution. Deng investigated the performance of N-(6-(hydroxyamino)-6-oxohexyl) octanamide (NHOO) for wolframite. The flotation results show that NHOO can recover 90.7% wolframite without $Pb(NO_3)_2$ activity. It inferred NHOO give better performance than conventional hydroxamic acid collectors through molecular structural optimization [11]. Zhao found cyclohexyl hydroxamic acid (CHA) is an excellent collector for scheelite flotation [12]. Yin thought p-*tert*-butyl-benzohydroxamic acid has more collecting ability than BHA acid as the *tert*-butyl group introduced into benzene ring [13].

Similiar to hydroxamic acid surfactants, oximes also have characteristic group of ─C═N─OH, and most are recognized as extraction agents in mineral processing. Fedor Vasilyev found 2-hydroxy-5-nonylsalicylaldoxime is selective extractant for separating copper from

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concentrated aqueous sulfate solutions in an aliphatic diluent, who exhibit great adaptability in a wide range of copper and extractant dosage [14]. According to Rafighi's work, 2-hydroxy-1-naphthaldoxime and 1-hydroxy-2- naphthaldoxime exhibited satisfied extractive properties toward cobalt in sodium chloride aqueous system [15].

In addition, oximes also can be used in mineral flotation as collectors. Octanaldoxime exhibited powerful collecting ability to malachite [16]. 8-hydroxyquinoline and salicylaldoxime had been proved an effective mixied collector for the copper recovery from the synthetic mixtures malachite-quartz and malachite-calcite [17]. 2-ethyl-2-hexenal oxime showed good flotation efficiency for recovery of malachite and chalcopyrite. According to author's opinion, the π–π conjugated structure of 2-ethyl-2-hexenal oxime may share electron to Cu species and help itself fixing on mineral surface [18].

These studies led us to initiate structural modifications of the hydrophobic groups while retaining the −C=N−OH group. Those methods of molecular modification include alkylation, acetylation and amidation reaction [1,19]. In this research, *tert*-butylsalicylaldoxime (TBSA) was exploited as a chelating collector for malachite flotation, who contained reasonable hydrophobic chains, π–π conjugated system and oxime terminal group. Moreover, the adsorption mechanism of TBSA on malachite was investigated by contact angle, zeta potential, FTIR and XPS measurements.

2. Materials and methods

2.1. Materials

Single mineral of malachite, quartz and calcite used in this research were purchased from Chengmenshan copper ore, Jiangxi province.

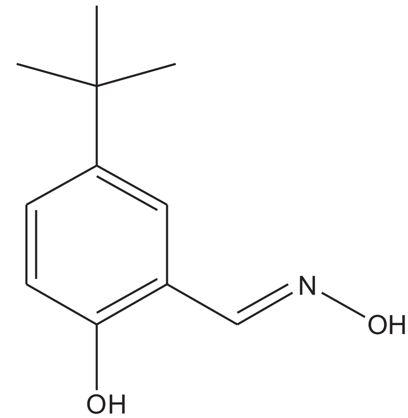

Fig. 2. Chemical structure of *tert*-butylsalicylaldoxime TBSA.

Each samples were analysed by X-ray diffraction, which indicated that most of the grains were pure according to result of Fig. 1. The single mineral samples were ground in porcelain, then collected −75 + 38 μm fractions which were investigated in flotation tests, and the artificial mixture ore was prepared by mixing malachite, quartz and calcite samples at a weight ratio of 1:1:1. The −38 μm fractions were further ground to −5 μm for adsorption mechanism research. TBSA was synthesized based on our previous literature [20]. The chemical structure of TBSA was shown in Fig. 2. Before flotation, collectors were purified by recrystallization in ethanol-water solvent and dispersed by 2% ethanol aqueous solution in ultrasound. Experiments in this paper were all carried out with de-ionized water and analytical grade chemicals.

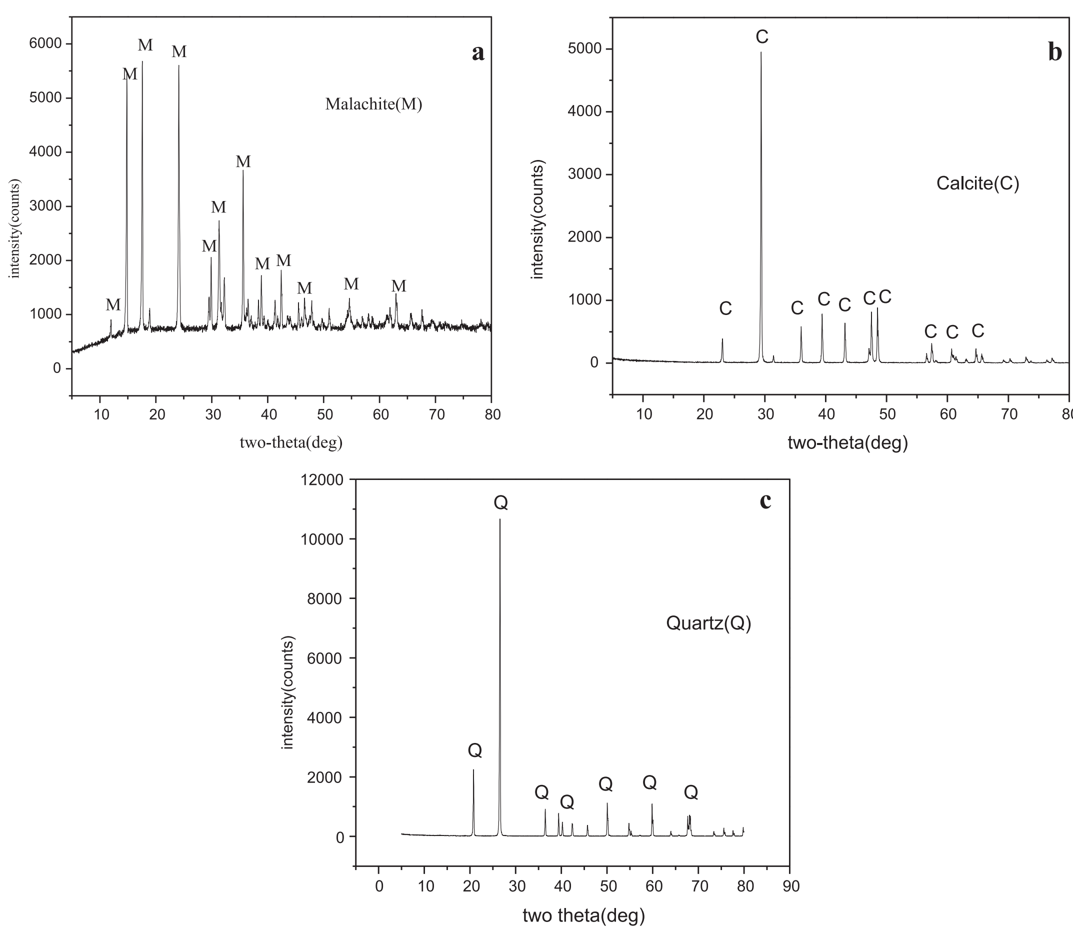

Fig. 1. X-ray diffraction of the malachite (a), calcite (b) and quartz (c) samples.