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The adsorption and configuration of octyl hydroxamic acid on pyrochlore and calcite

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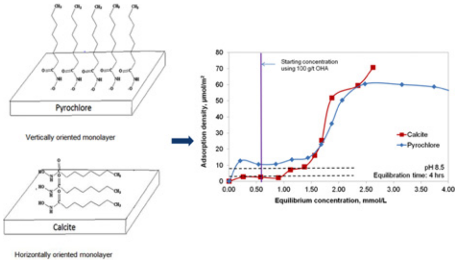
HIGHLIGHTS

- ► Hydroxamic acid chemisorbed on pyrochlore, but physically adsorbed on calcite.
- ► At low concentration, hydroxamic acid formed a vertically oriented monolayer on pyrochlore.
- ► At low concentration, hydroxamic acid formed a horizontally oriented monolayer on calcite.

GRAPHICAL ABSTRACT

At low concentrations, octyl hydroxamic acid formed a vertically oriented monolayer on pyrochlore surface, but a horizontally oriented monolayer on calcite surface.



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ABSTRACT

XPS, adsorption density and ToF-SIMS measurements were performed on pyrochlore and calcite treated with octyl hydroxamic acid (OHA). XPS results indicated a slight shift of the binding energies of the Ca 2p electrons (0.19 eV) on calcite after OHA treatment but the N 1s binding energy spectrum of OHA did not change, showing a physical adsorption mechanism. On OHA-treated pyrochlore, the binding energies of both Nb 3d and Ca 2p electrons shifted (0.24 and 0.35 eV, respectively), and the N 1s electron binding energy peak of OHA split from 400.3 eV to 400.7 and 398.5 eV, representing the neutral R—NH—OH and the ionized R—NH—O⁻ groups. The ratio of the integrated areas of the 400.7 eV peak to the 398.5 eV peak was 3.8 to 1. Therefore OHA possibly adsorbed on pyrochlore by both physisorption and chemisorption, with the number of OHA molecules involved in the adsorption at 3.8 to 1. The adsorption isotherm of OHA on pyrochlore showed two plateaus, with the first plateau corresponding to a vertically oriented monolayer of OHA. The second plateau was 4 times higher than the first plateau. Therefore, the adsorption isotherm was consistent with XPS results, in that the vertically oriented monolayer (first plateau) formed the chemisorbed layer, and the second plateau contained mostly physisorbed OHA. The adsorption isotherm of OHA on calcite showed a lower plateau which corresponded to horizontally oriented OHA. ToF-SIMS positive ion images on OHA treated mixtures of pyrochlore and calcite confirmed that OHA preferentially adsorbed on pyrochlore.

1. Introduction

Alkyl hydroxamic acid is an effective collector for many oxide minerals in froth flotation including copper [1], iron [2], tin [3], tungsten [4], and rare earth metal minerals [5,6]. It is also a selective collector for niobium oxide minerals from carbonatite ores. It has been shown previously that a commercial reagent Aero 6493,

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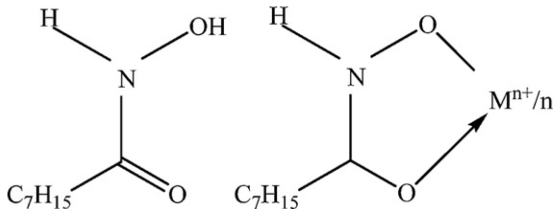

Fig. 1. Structure of octyl hydroxamic acid and its metal chelates in bulk solution.

whose major ingredient is hydroxamic acid, could recover over 85% of niobium minerals (mostly pyrochlore) from a mill feed sample taken from an operating mine in eastern Canada at less than 30% mass pull (with carbonate mineral recovery at under 30%) [7]. Its natural selectivity between niobium-bearing minerals and carbonate minerals in flotation is worth studying. Octyl hydroxamic acid (OHA) was subsequently synthesized in our labs and tested in batch flotation of the same ore sample, and similar results as the commercial collector Aero 6493 were obtained.

The hydroxamate group can form chelates with many transition metal cations in bulk solution [8–11]. More specifically, the hydroxyl groups and the carbonyl groups in the hydroxamate form a stable five-membered ring chelate with metal cations [8–11]. The carbonyl group participates in the chelation by donating its lone pair electrons [8–11] (Fig. 1). Research has also shown that they can also form chelates with metal atoms on mineral surface [3,6,12–14]. Thus hydroxamic acid are capable of bonding with mineral surface by “inner sphere adsorption” like carboxylic acid [15,16]; but the formed chelates are stronger than the coordination bonded complex of corresponding carboxylic acids [8,17,18].

Amphiphilic molecules which form chemical bonds (surface anchoring) with atoms or moieties on solid substrate can result in a self-assembled closed packing monolayer significantly increasing the substrate’s hydrophobicity. Chelating reaction formed between polydentate ligand and metal atoms on substrate surface can lead to a closed packed monolayer [19–21]. Saturated alkyl chain in surfactant is more flexible than chains with unsaturated bonds, and they tend to form linear conformation due to the hydrophobic interaction between hydrophobic chains nearby if in a close packed self-assembled monolayer [22]. With increasing surfactant concentration in the solution, the adsorbed molecules’ orientations would gradually change to parallel to each other until the monolayer is formed [23].

It is suggested that hydroxamic acid can also form such a monolayer on the metal oxide surface through aforementioned chelating reaction [24–26]. However, the reported work concerned the adsorption of alkyl hydroxamic acid on calcium-bearing minerals such as fluorite or phosphate [26,27]. It is interesting to note that hydroxamic acid could adsorb on different mineral surfaces but the resultant imparted hydrophobicity and floatability could be very different, such as on pyrochlore and calcite [7]. This work reports results of a study on the adsorption mechanism of octyl hydroxamic acid (OHA) on the surfaces of pyrochlore and calcite, more importantly, the configuration of the adsorbed molecules on the surfaces and the resultant hydrophobicity of the mineral surface after adsorption.

2. Materials and methods

2.1. Materials

n-Octyl hydroxamic acid (OHA) was used in this work, and it was synthesized in our lab from the corresponding ester following the procedures of Devlin et al. and Pirrung and Chau [28,29]. The synthesized octyl hydroxamic acid was precipitated in acidic deionized water (pH = 2), washed with acetone/water mixture and dried in a vacuum desiccator. The dried hydroxamic acid was a white and feather like powder, which was kept in a refrigerator. Sodium hexametaphosphate, sodium hydroxide and hydrochloric acid were all purchased from Fisher Scientific. Distilled water was used in all tests.

Two high purity mineral samples, pyrochlore and calcite, were employed in this study to represent the niobium containing value mineral and the carbonatite gangue. High purity mineral samples of pyrochlore, in a powder form, was obtained from COREM, Quebec, Canada, which assayed 59.8% Nb_2O_5, 10.5% CaO and 2.73% SiO_2. Since the theoretical Nb_2O_5 content in pure pyrochlore is 66.55%, this sample contained approximately 91% pyrochlore. Calcite (58.34% CaO) sample were purchased from Ward’s Scientific Establishment, Ontario, Canada.

All the mineral samples were crushed, ground in a mechanical agate mortar/pestle grinder and screened to collect the −25 μm fraction for adsorption isotherm measurements. The specific surface areas of the −25 μm pyrochlore and calcite samples were determined on Quantachrome Autosorb 1MP (Quantachrome Instruments, USA) using nitrogen as adsorbate based on the BET theory, and the results are 0.88 and 1.27 m^2/g, respectively. For XPS measurements the −25 μm fraction was further ground to approximately 2 μm.

2.2. X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) characterization of samples was carried out on a Kratos Axis 165 spectrometer with monochromatized Al $K\alpha_{1,2}$ radiation as an excitation source ($h\nu = 1486.6$ eV). The analysis area was about 400 μm × 700 μm. Survey scans were conducted using an electron analyzer with a pass energy of 160 eV and a step size of 0.35 eV, and then high resolution scans were carried out within specific binding energy ranges at a constant pass energy of 20 eV and a step size of 0.1 eV. All measurements were carried out at pressures below 10^{-8} Pa. All the spectra obtained were calibrated using C 1s at 284.8 eV. Sample powders were loaded into the sample holder by creating a surface as smooth as possible by unaided eyes. The integral areas of selective peaks on the full survey scan of minerals were divided by relative sensitivity factors (RSFs) and normalized, from which relative atomic concentrations was obtained.

The OHA treated mineral samples were prepared as follows: first, 50 mL 0.5 wt% (31 mmol/L) OHA was prepared in a 100 mL beaker at pH 8.5, which was the natural pH in batch flotation. Then 1.5 g of the mineral sample was added to the beaker and the mixture was stirred with a magnetic stir bar for 1 h under room temperature. The conditioned pulp was subsequently centrifuged and decanted. The mineral particle sediments were washed five times by five aliquots of 50 mL deionized water at pH 8.5 (adjusted by sodium hydroxide) and dried in a vacuum desiccator until analysis.

2.3. Adsorption isotherm determination

Adsorption densities of the OHA on the pyrochlore and calcite minerals were measured at pH 8.5 and room temperature (20 °C). One gram of the −25 μm mineral (pyrochlore or calcite) was added to a conical flask, then 150 mL solution with different OHA concentrations was added. Control blank was run using 150 mL 5 mmol/L OHA but no mineral was added. Natarajan et al. [13] have shown that usually 30 min is sufficient for adsorption/desorption of hydroxamic acid to attain equilibrium on mineral surfaces. We used a 4 h equilibration time to ensure that the adsorption has reached equilibrium. The control blank test indicated that the OHA solution concentration did not detectably change after 4 h shaking at pH 8.5,