



The action of cellulose-based and conventional flotation reagents under dry and wet conditions correlating inverse gas chromatography to microflotation studies



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ABSTRACT

The fundamental formation of the three phase contact in flotation is an intensively and controversially discussed phenomenon and the contact angle method is usually employed to characterise the wettability of solid surfaces. A more recent technique to explore the hydrophobicity of solid particulate phases is inverse gas chromatography (iGC) which is used to quantify the wettability of solid surfaces through thermodynamic parameters. In this article, the recently introduced net free energy of interaction between particles and bubbles immersed in water ΔG_{pwb} is derived from the surface free energy analysis and its correlation to the flotability of solid phases is evaluated. At the same time, a more detailed analysis on the action of flotation reagents is presented performing iGC measurements under dry and flotation experiments under aqueous conditions. In general, flotation reagents have to satisfy required features to adsorb selectively, render the solid surface wetting property sufficiently, and comply current regulations concerning the preservation of the environment. Consequently, many conventional reagents are increasingly subjected to restrictions. One potential alternative candidate is nanocellulose due to the versatile chemical composition and functionality. The synthesis of cellulose nanocrystals (CNCs) includes different mechanical and chemical modification routes to lower the crystal sizes and integrate specific functional groups and organic components into the cellulose structure. This study is concentrated on the investigation of aminated CNCs for the flotation of quartz in comparison to conventional reagents. The employment of CNCs as a renewable and sustainable alternative to conventional chemicals is challenging due to the more complex structure of cellulose crystals and leads to new perspectives regarding the action of flotation reagents at the interface of a mineral under dry and wet environments.

1. Introduction

The various composition of processed ores requires specific properties of the flotation reagents to selectively adsorb on a mineral surface, render the wetting property of the mineral surface to a more hydrophobic behaviour and, more and more important nowadays, being uncritical in terms of environmental impact (Zouboulis et al., 2003). Cellulose nanocrystals (CNCs) are considered to be a potential, environmental-friendly candidate to replace synthetic chemicals or other biological substances derived from vegetable oils or animal fats in mineral processes (Kümmerer et al., 2011). The chemical composition of CNCs is versatile dependent on applied synthesis routes (Klemm et al., 2005). In theory, modified CNCs can be produced consisting of specific functional groups and organic components resulting in various physical properties, such as size and size distributions, specific surface charge

distributions and wetting properties leading to an efficient reagent system in ore dressing (Hartmann et al., 2016).

The increased processing of mineral resources urges the economically viable exploitation of ore deposits (Trubetskoy et al., 2012; Mariano and Evans, 2015). Finely disseminated ores are as well more and more exploited with the need of fine grinding for liberation leading to particle sizes well below 100 μm (Trahar, 1981). For this particle size fraction, flotation is an efficient separation process which is based on different wetting properties of mineral surfaces (Crawford and Ralston, 1988). The fundamental physicochemical property of solid surfaces determining the wetting behaviour of liquids on solid surfaces is the specific surface free energy (Balard et al., 1996; Girifalco and Good, 1957). Inverse gas chromatography (iGC) is a versatile technique to determine the specific surface free energy distribution of particulates under well-defined conditions (Ylä-Mäihänen, 2008; Nowak and

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Pacek, 2015; Smith et al., 2014; Ferguson et al., 2017). The knowledge of the distribution of the specific surface free energy of mineral particles, and its change due to the adsorption of flotation reagents, is expected to correlate to the flotability of the minerals by quantifying the maximum specific surface free energy of the mineral at which orthokinetic heterocoagulation takes place (Mohammadi-Jam et al., 2014; Mohammadi-Jam and Waters, 2016; Ralston et al., 2002). Consequently, the rupture of the interfacial water film is prevented when the free energy of a sufficient fraction of the mineral surface surpasses a certain level due to strong attractive interactions with water molecules.

In this study, the iGC technique is used to investigate the effect of physisorbed aminated CNCs with various alkyl chain lengths and conventional reagents on the specific surface free energy distribution of quartz (Vidyadhar and Hanumantha Rao, 2007). Moreover, the net free energy of interaction between solid surfaces and gas bubbles immersed in aqueous solution (ΔG_{pwb}) is further investigated as a thermodynamic parameter to characterise the action of flotation reagents under dry atmosphere. The net free energy of interaction relates the work of water adhesion to the mineral surface, W_{adh} , to the work of water cohesion, W_{coh} , given by:

$$\Delta G = W_{\text{adh}} - W_{\text{coh}} \quad (1)$$

In regard to the flotation process, the particle-bubble attachments are efficient when the change of the net free energy of interaction is negative (Holysz and Chibowski, 1992). Recently, a first article was published showing a correlation between the reduction of the net free energy of interaction and the flotability of minerals after adsorption of collector molecules (Rudolph and Hartmann, 2017). This correlation between the change of the net free energy of interaction and flotability of a mineral after reagent adsorption is challenged to be applicable for CNCs.

Consequently, an attempt to explain the action of different types of reagents under dry and wet conditions is given and the efficacy of cellulose-based and conventional reagents compared. Basically, the exclusive characterisation of the components of the surface free energies of solid states does not explain the nature of interactions under aqueous conditions (Ali et al., 2013). In general, the term “hydrophobic” is a misnomer which is derived from the experience of attracting apolar surfaces immersed in water and even partially prevents an unprejudiced confrontation with the fundamental questions concerning the origin of particle-bubble attractions (Hildebrand, 1979; Schubert, 2005). In fact, so called hydrophobic materials, such as Teflon or alkanes, immersed in water attract water molecules with a free energy of 40–50 mJ/m² whereupon the expression to “fear water” is inappropriate (van Oss, 2003). Therefore, the analysis of iGC experiments considering the interaction of gaseous molecules with a solid surface under dry conditions and the relation to the results to particle-bubble attachments under aqueous conditions represents a methodology to contemplate a new perspective approaching the mechanism of hydrophobicity.

2. Material and methods

2.1. Synthesis of cellulose nanocrystals and quartz

Three aminated CNCs with different alkyl chain lengths were synthesized, namely methyl-amine- (MAC), butyl-amine- (BAC), and hexyl-

amine- (HAC) cellulose nanocrystals. A well-known process for the preparation of CNCs was used which is explained in more detail elsewhere (Visanko et al., 2014). In brief, the cellulose raw material, bleached kraft pulp (*Betula pendula*), was converted to 2,3-dialdehyde cellulose through lithium chloride, LiCl (> 98.0%, Sigma-Aldrich) assisted sodium periodate, NaIO₄ (> 99.09%, Sigma-Aldrich) oxidation at 75 °C under moderate agitation for three hours. Consequently, cellulose with an aldehyde concentration of 3.86 mmol/g was obtained. For the reductive amination, a 10-fold excess of methyl-amine (> 98%; TCI), n-butyl-amine (> 98%; TCI), or n-hexyl-amine hydrochloride (> 98%; TCI), in relation to the aldehyde groups of the cellulose, was suspended in 300 ml demineralized water and the pH value was adjusted to 4.5 using a diluted HCl solution (Merck). Simultaneously, a 2-fold excess of 2-picoline borane (95%, Sigma-Aldrich), in relation to the aldehyde groups of the cellulose, was dissolved in 100 ml demineralized water. The cellulose pulp (absolute 4 g) and 2-picoline borane solution were added to the amine suspension and stirred for 72 h in a closed container under ambient conditions. Subsequently, the extant chemicals were removed from the solution via vacuum filtration and the obtained product purified through three washing steps. At first, the residual reaction chemicals were removed washing the filtered pulp with 200 ml demineralized water. The filter cake was removed and re-suspended in 300 ml ethanol (95%, VWR) for five minutes. Finally, the pulp was filtered through vacuum filtration and, subsequently, purified through washing with 600 ml demineralized water. The pulp was diluted to a solid concentration of 0.2% by weight related to the absolute mass of the suspension. The individualisation of the pulp to nanocrystals was realized using a Microfluidics two-chamber high shear homogenizer (M-110EH-30 Microfluidizer, Microfluidics). The purified fibre suspension passed through the 400 µm – 200 µm, 400 µm – 100 µm, and 200 µm – 87 µm chambers three times corresponding to pressures of 1300 bar and twice 2000 bar, respectively. Consequently, a clear, non-viscous CNC suspension was obtained and stored in a closed container at 4 °C. The lengths and widths of CNCs were detected using TEM images (see Table 1). The number of amine groups present in the CNCs was analysed by the determination of the nitrogen content using a PerkinElmer CHNS/ = 2400 Series II elemental analyzer. The chemical composition of CNCs is given in Table 1.

Quartz (Sibelco Europe, Nilsä Finland) was ground in a ball mill (Retsch PM 200, Germany) and classified by an air jet sieve (Hosokawa Alpine e200 LS, Germany) to obtain a particle size fraction between 45 and 56 µm. This quartz fraction was placed on a sieve with 45 µm mesh size and a batch of 10 g of the fraction was washed with demineralized water to remove smaller particles. Finally, the quartz fraction was dried at 105 °C overnight. The specific surface area was determined using the Brunauer-Emmet-Teller (BET) method (micromeritics, Gemini VII) before the sample was packed in the iGC glass tube and after the iGC measurements (SEA, Surface Measurement Systems UK Ltd.). The conventional reagents used were ethyl-ether-amine (EDA, Clariant), alkoxypropane-amine (AP, LilaFlot 810, Akzo Nobel), and dodecyl-amine (DDA, OneMed).

2.2. Microflotation

For the estimation of the applicability of CNCs to be used as flotation reagents compared to conventional collectors, the particular sample was removed from the glass tube after the iGC measurement and

Table 1
Physiological dimensions, nitrogen content and specific number of amine groups of the CNCs (Hartmann et al., 2016).

Name	Abbreviation	Length in nm	Width in nm	N-content in wt%	Degree of substitution in mmol/g
Methyl-amine CNC	MAC	142 ± 11	6.0 ± 0.3	1.48	1.06
Butyl-amine CNC	BAC	125 ± 7	3.3 ± 0.2	0.76	0.54
Hexyl-amine CNC	HAC	144 ± 14	4.6 ± 0.3	1.14	0.81

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