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Efficient Nanoscale Gasification of Water: Perspectives for Carbon-Friendly Agriculture and Geological Sequestration

Mini Review

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Abstract

Water gasification via nano-bubbles (ultrafine bubbles <1 µm) offer a promising lever to improve foliar-spray performance by enhancing gas transfer, modifying interfacial phenomena at leaf cuticles, and acting as carriers to increase bioavailability of agrochemicals and bio-stimulants, as well as geo-sequestration (e.g., in soil). This perspective discusses emerging evidence and physical underpinnings relevant to spray applications, including

a)differential-species enrichment of nanobubble composition;

b)hypothesised routes of action in foliar and soil delivery and stomatal entry;

c)gas-transfer efficiency, and

d)implications for pesticide reduction and geo-sequestration.

We propose practical research agenda-standardised tank-stability tests with common adjuvants, droplet/nano-bubble co-characterisation at the nozzle, and field trials with outcome metrics.

Introduction

In the field of carbon- and energy-efficient gas transfer to promote agriculture and wider soil- and geo-based carbon sequestration, foliar-spray methods are perhaps more sorely in need of a rethink, as it were. More specifically, tackling the "coverage–efficacy" paradox, or trade-off, is central: small droplets off widespread cover but drift, whilst larger large droplets retain, but suffer bounce/runoff. Indeed, wider sustainability drivers around crop-spray versus irrigation are also at play in the calculus of carbon-efficient agriculture and soil-/geo-sequestration: not only energy efficiency per se of gas delivery, but also dose reduction, resistance management, and wider water stewardship [1,2]. Nano-bubble (NB)-based gasification for, inter alia, air, O2 and CO2, offers the clear potential for more energy-efficient and long-lived gas transfer [3,4] to soil and plants [5-7], and this is especially impactful in spray-droplet delivery, whether as macro-droplets or in aerosolised-spray form: there is strong evidence that nano-bubbles entrained in micro-droplets offer enhanced chemical activity [8], which is important bearing in mind the positive impact of reactive oxygen species for farming [7,9].

In order to make progress in spray-delivery applications, gas-transfer processes are central [1,2], and NBs offer an effective way to deliver gas to plants and soil more effectively, although electric-field-based generation of NBs has been shown to be more effective than traditional mechanical generation approaches [10], so we shall consider these NBs in the remainder of this perspective. However, there are several key areas underpinning progress in this domain:

a.differential-species enrichment of nanobubble composition;

b.hypothesised routes of action in foliar/soil delivery—e.g., better wetting/retention, stomatal entry;

c.gas-transfer efficiency,

d.pesticide reduction, nutrient-use efficiency, and drift mitigation when combined with nozzle/drift-control strategies, as well as geo-sequestration.

Below, we outline recent developments and challenges in each in order to provide a broader outlook for progress, as well as proposing a research agenda to drive this field forward.

Discussion

In terms of differential species enrichment, gas-chromatography experiments were performed with the GC-2010+ (Shimadzu), with helium carrier gas and the Carboxen 1010-PLOT capillary column. The Evol-Xr dispensing-system syringe (Xchange) was used to sample water containing air nano-bubbles from ref. 4. This gave a substantial species-specific enrichment of oxygen - indicating an enrichment factor of circa 3 for O_2 vis-a-vis bulk air in terms of total mass in NB form, i.e., in the “nano-dissolved” state - i.e., NB-borne O_2 composition of circa 60% [11]. Aside from NBs’ reactive oxygen species per se boosting farming [7,9], this molecular mechanism of differential and preferential O_2 delivery [11] has been found to be effective in soil-based plant germination and growth [7] - offering much for air use versus O_2 in NB-enhanced spray systems.

Considering “nano-bubbly” water delivery and enhanced carbon levels from additives [12], NBs’ hypothesised routes of action arising in foliar-and soil-delivery mechanisms are important - e.g., improved wetting/retention and stomatal entry. The mechanistic route of more facile soil penetration is based fundamentally on reduced surface tensions afforded by NBs, and it has been shown that there is a substantial tension-reduction effect for electric-field-generated NBs [13], and hard-soil penetration times were found to be accelerated circa 2.5 times with around 40% additional moisture capacity – similar to rock samples [13]. This allows such NB-treated water to then be used to improve stomatal entry and hydration of soil, with less water usage.

On gas-transfer efficiency, for a given volume of gas, the miniscule size of NBs produces a remarkably large surface-area-to-volume ratio: higher dissolved-gas levels and better mass transfer of gas into the liquid result [3,4] from their large interfacial area. For air-fed NBs from the submersible NB generator used in ref. 4, in which there was found to be a pronounced O_2 enrichment in the nano-phase, the Standard Oxygen Transfer Rate (SOTR) was around 4.3 x 10^{-4}kg O_2/l·hr, with an aeration efficiency of about 14.2kg O_2/kWhr. Bearing in mind this perspective’s consideration of recirculation-based tanks, as well as single-pass operations for NB-enhanced spray deployment, we consider recirculation based oxygenation and carbonation from air and pure CO_2 sources, respectively, from the Vulcan-500 NB generator (AquaB Nanobubble Innovations Ltd., cf. Figure 1a), with fixed gas-to-water flow ratios in a partially-open 3.5m3 recirculation tank at a flowrate of 1 m3/min of water (i.e., a residence time of 3½mins). In water where the dissolved oxygen and CO_2 had been essentially removed by scavenging chemicals, the accumulation of dissolved gases was measured using a CboxQC meter (Anton Paar), cf. Figure 1b. It can be seen readily that supersaturated conditions were reached within about 1.5 residence times (about 8.5 and 1,400mg/l), and circa 90- and 45%-supersaturation plateaux within 3 such times (to about 16.5 and 2,000mg/l, respectively). In terms of gas-transfer efficiency (i.e., percentage mass of gas dissolved in the partially-open-to-atmosphere liquid phase in the tank as a proportion of that delivered - set by mass-flow controller), this was a highly impressive 98-99.5% in the first residence time, only declining to about 90% at Henry’s-Law saturation – with little point in pursuing further NB-gas delivery beyond about 70 or 35% supersaturation, owing to lower Fick’s-Law driving force for mass transfer at these respective levels [3,4], unless desired.

In terms of pesticide reduction, it has been shown that NBs can reduce the amount to be added substantially in soil-based agriculture [7], owing to electrostatic attraction to their surfaces by these agro-chemical molecules, which boost nutrient-use efficiency substantially in an energy-efficient manner. In addition, to progress further the prospect of efficient nanoscale gasification revolutionising spray performance for carbon-friendly agriculture, there needs to be further progress in sprayer-nozzle design and delivery systems thereat of lower doses of more climate- and environmentally friendly and cost-effective chemicals. Improvements in nozzle-drift mitigation will enable more targeted geo-sequestration of the efficiently dissolved air, O_2, or CO_2 (whether pure or mixed) to be delivered from the sprayer.

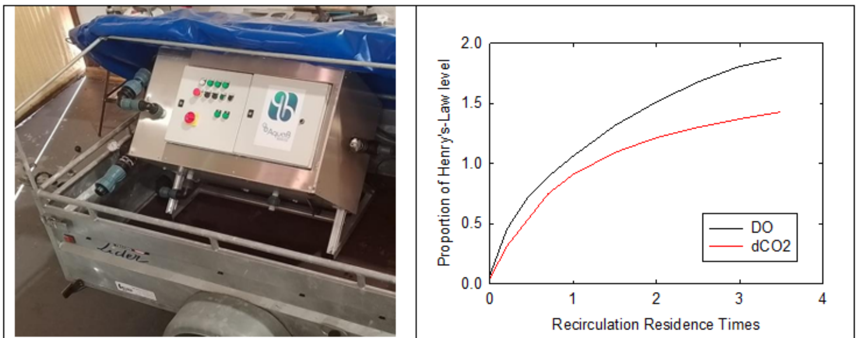

Fig. 1a: Trailer-mounted Vulcan-500 NB generator | Fig. 1b: Dissolved gas versus recirculation time

Figure 1

Outlook

We propose a practical research agenda-standardised tank-stability tests with common adjuvants, droplet/nano-bubble co-characterisation at the nozzle, and field trials with outcome metrics (e.g., dose reduction at equal efficacy, residue, and off-target drift). Here, the compatibility with adjuvants, salts, and active agents needs to be assessed; indeed, the nano-bubble size, population and charge retention will need to be assessed in spray tanks, bearing in mind highly-efficient gas transfer thereto. In so doing, with lower nozzle-mixed additive doses and a higher level of dissolved gas and reactive species, we shall be able to deliver more productive water in the form of droplets (of whatever desired size) of lower surface tension for foliar deliver, with greatly enhanced stomatal and soil penetration.

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In this research agenda, there will need to be standard protocols developed to gaugeseveral important factors, such as, inter alia:

I.tank stability under shear/pressure;

II.droplet-NB co-characterisation;

III.leaf-surface deposition imaging;

IV.soil- and geo-sequestration levels. Indeed, field metrics will also need to be developed, such as equal-efficacy dose-reduction trials, drift cards, carbon-balance accounting, as well as economics (chemicals and water usage, recirculation-gasification passes), and sensitivity to oil price/energy.

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