Modelling of H2O2 flotation for removing microplastics from waste water

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1. Introduction

According to estimates, over 300,000 t of microplastics are emitted into the environment each year in Germany [1]. Besides the known increase in oceans and coastal areas, these particles are found in inland waters and even in drinking water. Therefore, plastics and their chemical constituents can be absorbed by the human body. The impact on health of these chemicals has not yet been researched in many areas, but it is suggested to avoid products that contain microplastics [2]. The scale of these particles (1 – 5000 µm [3]) creates new challenges for filter systems. A new filter-free separation method is therefore being developed based on a chemical flotation, which can separate microplastics in wastewater. Hydrogen peroxide (H_2O_2) is used for chemical flotation. Nanobubbles composed of oxygen are formed on the rough surface of these particles, caused by the chemical decomposition of H_2O_2 to O_2 and H_2O. The clustering of particles and bubbles decreases the effective density and they rise to the surface on due to the increased buoyancy from which they can be mechanically removed into a separate tank. Initial experiments have confirmed the functionality of this method, as shown in Figure 1. As part of this project, a numerical model was developed for the oxygen bubble formation on particles in OpenFOAM and the distribution of H_2O_2 in the process.

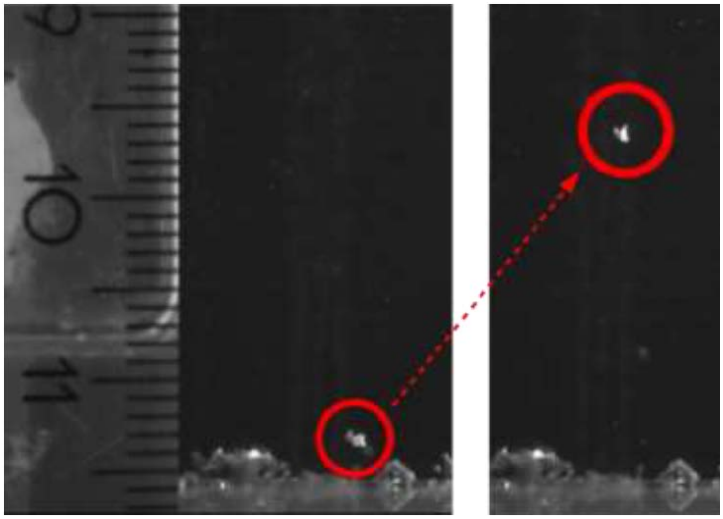

Figure 1: Functionality of the novel H_2O_2 flotation

2. Description of the solver

Based on the *pimpleFoam* solver and using the lagrangian library, a new Eulerian-Lagrangian solver for OpenFOAM-v1912 was developed with the following features:

1. Chemical reaction of H_2O_2 to H_2O and O_2.
2. Two additional transport equations for the concentration of hydrogen peroxide and oxygen in the continuous phase.
3. Initial bubble formation and growth in the Lagrangian space for the agglomeration of bubbles on the particles.
4. Particle movement.

For a better understanding of how the solver works, a detailed description of the most important implementations follows. Using the prototypical model equation, the concentration distribution of hydrogen peroxide $c_{H_2O_2}$ is modelled with a transport equation. The associated source term $S_{H_2O_2}$ describes the reaction rate of H_2O_2 as a first order chemical reaction:

$$S_{H_2O_2} = -\frac{c_{H_2O_2}}{\Delta t}\left(1 - e^{-k_c \cdot \Delta t}\right) \quad , \tag{1}$$

where k_c is the reaction rate constant dependant on temperature and, if present, catalysts. The transport of the oxygen concentration c_{O_2} is implemented in the same way. The only difference is in the source term S_{O_2}. Looking at the molar proportions of the products from the reaction, it becomes clear that the production of oxygen is only half of the reduction of hydrogen peroxide:

$$H_2O_2 \longrightarrow 0.5\,O_2 + H_2O \quad . \tag{2}$$

The first term of S_{O_2} is thus very similar to $S_{H_2O_2}$ and the second term describes the reduction of oxygen in the cell $\Delta n_{O_2,Cell}$, caused by bubble formation and growth, shown in the Eulerian phase (blue box) of Figure 2.

The agglomeration of a particle and a bubble is modelled in the Lagrangian phase, see the greeen box of Figure 2. First, the oxygen concentration c_{O_2} in the cell is checked. If it is higher than the oxygen saturation of water $c_{O_2,sat}$, the critical bubble diameter $d_{B,crit}$ is calculated, because smaller bubbles are not stable. Based on this diameter, the minimum amount of oxygen $n_{O_2,min}$ needed is then calculated to form a new bubble. If a bubble already exists on the surface of the particle under consideration, the mass transfer of oxygen from the cell to the volume of the bubble is modelled using two-film theory:

$$\dot{n} = \beta \cdot A\left(c_{O_2} - c_{O_2,sat}\right) \quad . \tag{3}$$

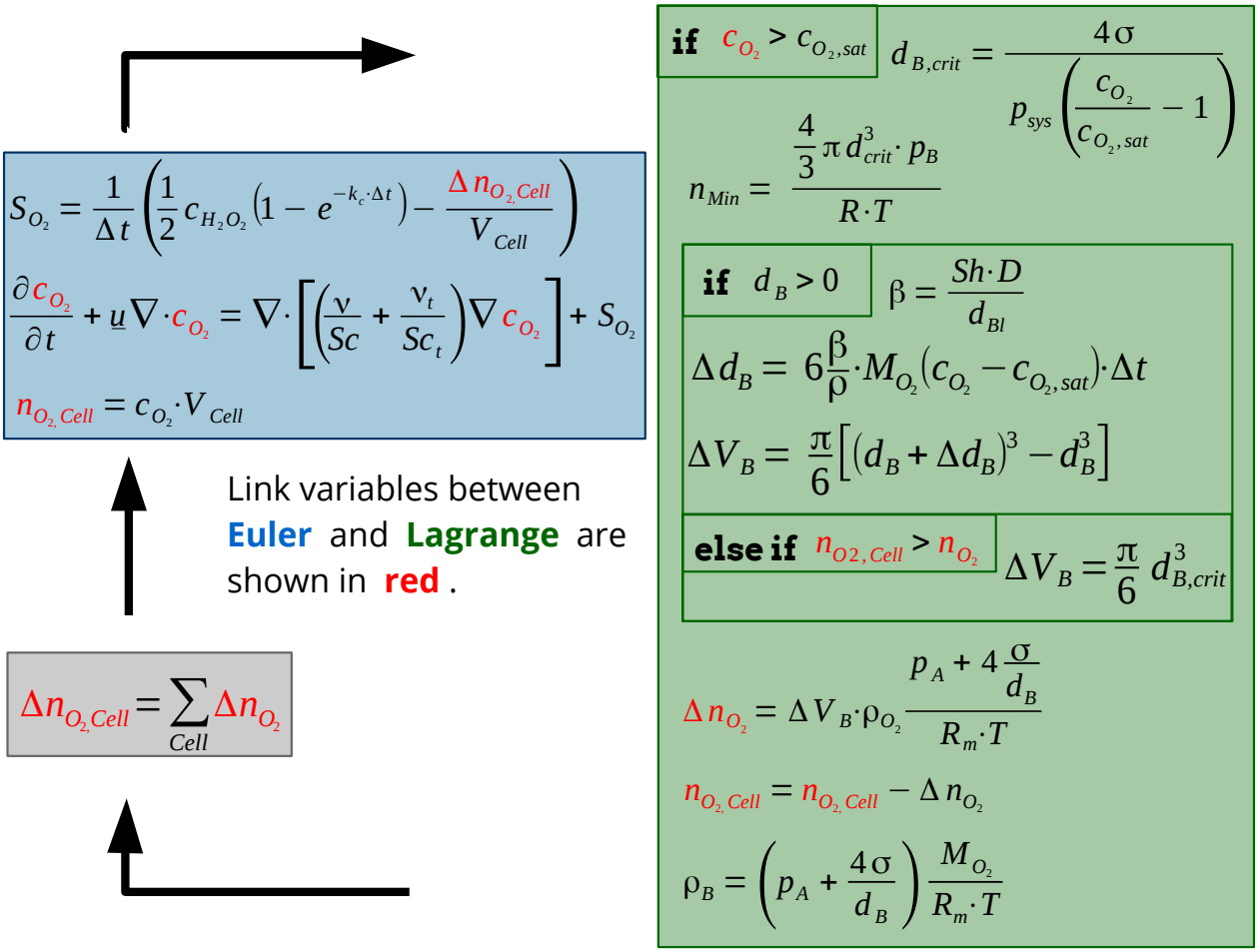

Figure 2: Scheme of implemented equations for the Eulerian phase (blue box), the Lagrangian phase (green box) and the accumulation of variables for each particle in the respective cell (grey box).

The mass transfer coefficient β can expressed by the Sherwood number Sh, the mass diffusivity from oxygen in water D_{O_2} and the diameter of the bubble d_B,

$$\beta = \frac{Sh \cdot D_{O_2}}{d_B} \quad , \tag{4}$$

and is dependent on the flow state:

$$Sh = 2 + \left(Sh_{lam}^2 + Sh_{turb}^2\right)^{1/2} \quad . \tag{5}$$

Equating the mass transfer between two phases with the oxygen transfer by bubble growth in cell leads to a simple equation for the increase in bubble diameter Δd_B. If the required amount of oxygen in the cell is not sufficient, the bubble grows only by the amount of supersaturated oxygen present. However, if no bubble had formed on the microplastics until now and if the amount of oxygen in the cell is sufficient to reach the critical bubble diameter, a new bubble will form. From the density of the bubble a new effective density of the cluster ρ_{eff} can be determined:

$$\rho_{eff} = \frac{\rho_B \cdot V_B + m_P}{V_B + V_P} \quad . \tag{6}$$

The amount of oxygen consumed Δn_{O_2} is calculated by the ideal gas equation. The increased pressure in the bubble due to the surface tension σ is described by the Young-Laplace equation. The decrease in the amount of oxygen is summed up for all particles in the cell $\Delta n_{O_2 Cell}$ and then transferred to the Euler phase as total decrease per cell and is used again as an updated variable for transport equation in the Euler phase.

Test case

The geometry selected is a cuvette with the dimensions 0.069 m by 0.078 m by 0.02 m (x, y, z). 5 µm large particles are injected as a homogeneous suspension in the entire volume with same material properties. The oxygen content at the beginning is uniformly 0.005 kg/m^3. To simulate a local injection, a non-uniform initial condition for the hydrogenperoxide concentration is used. Figure 3 shows the results for four time steps. At the start the particles are evenly distributed and their effective density is the density of the plastic of $\rho_P = 1016$ kg/m^3. The concentration of oxygen continues to

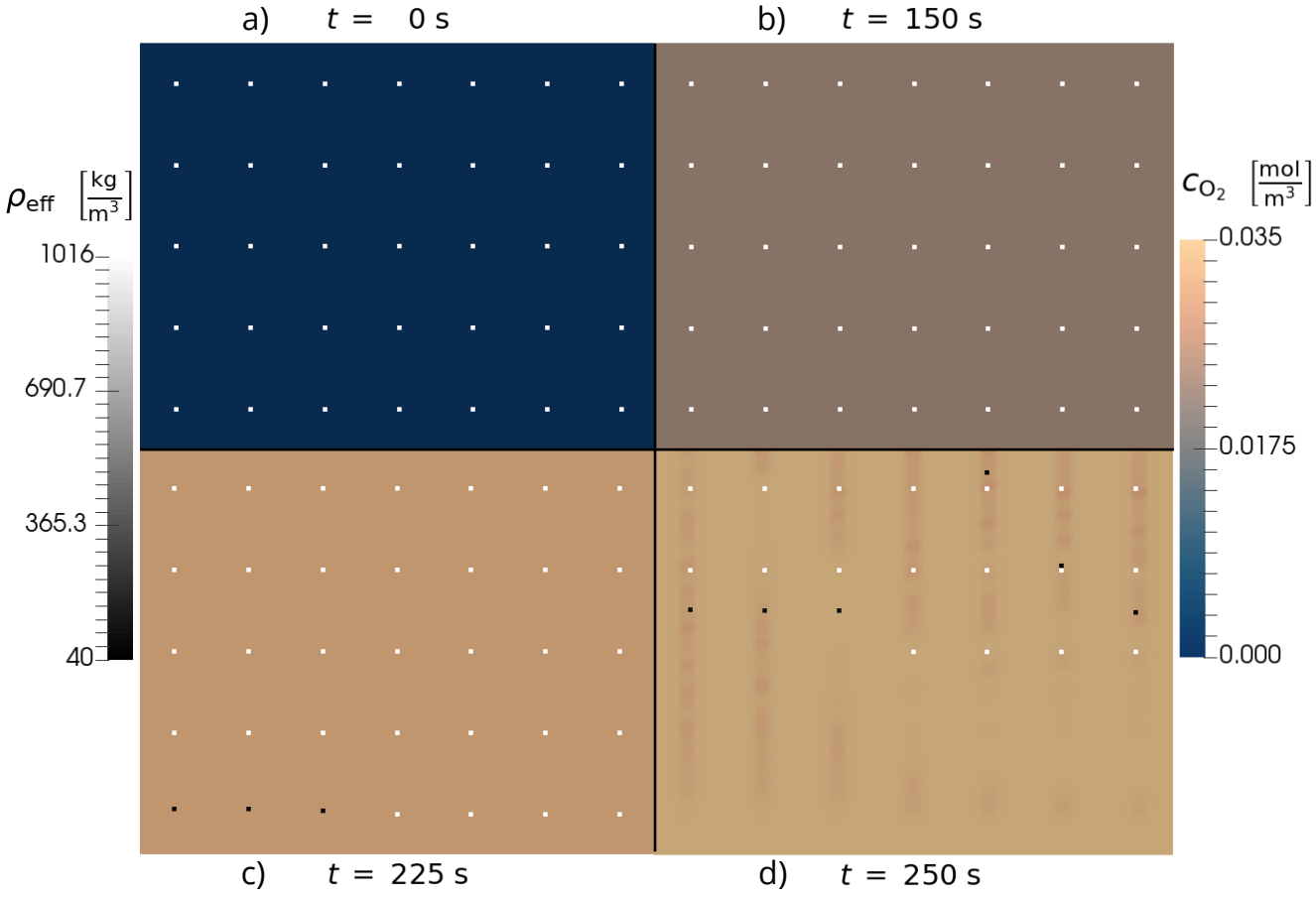

Figure 3: Simulation of the flotation of microplastics in a cuvette, a) at time zero, b) after 150 s, c) after 225 s and d) after 250 s.

rise over the course of time and eventually exceeds the oxygen saturation in the water. As soon as an oxygen bubble is formed, the density of the agglomerate changes and the particle rises to the surface where it is removed from the system, see Figure 3 c) and d).

Outlook

A validation based on the first experiments will be carried out so that the solver can also be used for more complex studies. The aim of the project is to develop a continuous plant that can float up to 1000 L/h of wastewater. The solver should help to determine the best possible process parameters and thus make a strong contribution to the success of this pre-competitive plant.

References

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