Oil-contaminated Surface Cleaning using Oxygen and Nitrogen Nanobubbles

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Abstract. Surface cleaning is extremely important topic in various industrial and laboratorial applications. Cleaning agents should fulfil numerous requirements, including effectiveness, leaving minimal amount of residue as well as being able to clean different surfaces and contaminants. In this work, the nanobubble dispersions were tested for cleaning of two different contaminants: vegetable oil and UV color protective oil. Both contaminants were applied onto glass slides and stainless steel plates. Nanobubble dispersions were generated in distilled water. Outflow from nanobubble generator was set tangentially to the contaminated surface during nanobubble generation. The effectiveness of cleaning was assessed visually and by contact angle analysis. Results have shown that the effectiveness of cleaning is higher for oxygen nanodispersion compared to nitrogen nanodispersion. However this process requires further fine-tuning to increase its effectiveness.

1. Introduction

Nanobubbles have numerous characteristics which distinguish them from their macroscale counterparts [1,2]. Nanodispersions of gas are used in solid-liquid separation in wastewater treatment plants both with and without frother addition [3–6]. Recently, the interest in fine cleaning of different surfaces is increasing. However, cleaning agents should fulfill numerous requirements, including effectiveness, leaving minimal amount of residue as well as being able to clean different surfaces and contaminants. The nanobubbles proved to be able to clean BSA (Bovine Serum Albumin) from different surfaces [7,8]. The investigation of cleaning off different contaminations are yet to be made. Nanobubbles have potential to be the future of the cleaning process due to absence of surfactants or dangerous chemical agents involved in the cleaning process.

This paper tackles the problem of reducing the amount of oily contaminations from glass and stainless steel surface what may be important in both industrial cleaning and daily basis cleaning at home.

2. Materials and methods

2.1. Contaminated sample preparation

Two kinds of surfaces were chosen to be contaminated: glass slides (Thermofisher Scientific) and stainless steel plate. Surfaces were pre-cleaned using ethanol 99.8% (Poch Basic) and distilled water. Two kinds of contamination were chosen – UV-color-protective oil (OSMO) and vegetable oil. Four contamination solutions were prepared and presented in Table 1 – three for UV-color-protective oil (Contamination 1-3) and one for vegetable oil (Contamination 4).
Table 1. Contamination compositions

| Description                                           |
|-------------------------------------------------------|
| Contamination 1 Pure UV-color-protective oil (without dilution) |
| Contamination 2 0.2%w solution of UV-color-protective oil in acetone |
| Contamination 3 1.0%w solution of UV-color-protective oil in acetone |
| Contamination 4 4.0%w solution of vegetable oil in acetone |

Contamination solutions were applied to the surfaces in the following way. For Contamination 1, droplet of substance was applied to the centre of the surface and second plate or slide was used to spread the contamination homogenously upon the surface and leave only the thin layer of contamination. Surface was left for drying. For Contaminations 2-4, 15 μl of contamination solution was applied on the centre of the surface and left for evaporation of acetone.

2.2. Generation of nanobubble dispersion and nanobubble cleaning

Scheme of the generation setup is shown in Figure 1. The water storage tank had capacity of 6 dm³. 5 dm³ of distilled water was used. Submersible pump DEP 400 (HSBAO) and membrane module was submerged in the water. The gas was pressurised through the cylindrical membrane which was filled with flowing liquid. Shear stress caused bubbles to be cut off from the surface of the membrane earlier than they would detach in still liquid. Two gases were used in this study: oxygen and nitrogen. The generation of the dispersion was carried out for 1 h. The pressure of the gas was controlled and set on the value of 0.6 bar.

For cleaning with nanobubble dispersions, the same process parameters were set on the nanobubble generation system. The contaminated sample was immobilised using clamp in front of the outflow of the membrane unit so the generated nanodispersion would flow tangentially to the contaminated surface. The cleaning lasted for 1 h. The cleaning with nanodispersion was performed thrice. Additionally, the reference check for sample contaminated in the same way was performed without the gas flow to check the cleaning potential of distilled water alone. Surfaces after cleaning were left for evaporation of water and then measured for the contact angle. After generation of bubbles and after each cleaning of each sample the liquid was sampled for nanoobject size distribution density measurement.

![Figure 1. Scheme of the experimental setup for nanodispersion generation](image)

2.3. Contact angle measurements

Drop Shape Analyser 100 (KRÜSS) along with the Advance software was used for contact angle measurements by sitting droplet method. Deionised water was used as the liquid phase which was applied on the surface. 10 droplets were sited onto the surface for each technical replication. Contact angle was measured for pre-cleaned samples, contaminated samples and samples after nanobubble cleaning.
2.4. **Nanobubble size distribution density measurement**

Zetasizer Nano ZS (Malvern Instruments) using DLS technique was used for determination of nanobubble size distribution density. Based on the distribution densities Sauter diameter of bubbles in each sample was calculated.

3. **Results and discussion**

3.1. **Contact angle results**

For surfaces after pre-cleaning the averaged contact angles for glass slide and stainless steel plate were 46.52° ± 3.60° and 71.78° ± 3.20°, respectively.

![Figures showing contact angle measurements for glass slides after cleaning](image)

**Figure 2.** Contact angle measurements for glass slides after cleaning with distilled water and nitrogen nanobubble dispersion (a) Contamination 1 (b) Contamination 2 (c) Contamination 3 (d) Contamination 4

In Figure 2 one can see the results for cleaning of the contaminated glass slides using nitrogen nanobubble dispersions. It is visible that for colour-protective oil (Figure 2 a-c) the contact angle after one cleaning with nanodispersion is lower than in case of cleaning without the nanobubble addition to the flow. In case of vegetable oil (Figure 2d), the contact angle after evaporation of acetone is lower than in case of colour-protective oil. However, after evaporation vegetable oil formed numerous small contaminated regions in contrary to visibly homogenous spread of contamination of color-protective oil. After cleaning with water or nanobubble dispersion with water, the oily contaminant formed homogenous layer, possibly due to higher hydrophobicity of the contaminant. Also, there is no decrease in the contact angle after the subsequent cleanings.
Figure 3. Contact angle measurements for stainless steel plate after cleaning with distilled water and nitrogen nanobubble dispersion (a) Contamination 1 (b) Contamination 2 (c) Contamination 3 (d) Contamination 4

In Figure 3 one can see the effects of cleaning stainless steel plate using nanobubbles of nitrogen. Obtained cleaning effectiveness is not as good as in case of the glass slide what may correspond to higher roughness of the steel plate surface. Also, the effectiveness is decreasing along with decrease of contamination concentration. What is interesting, for Contamination 4 (Figure 3d) the contact angle is nearly constant.

![Figure 3](image)

Figure 4. Contact angle measurements for glass slides after cleaning with distilled water and oxygen nanobubble dispersion (a) Contamination 1 (b) Contamination 2 (c) Contamination 3 (d) Contamination 4

The results of cleaning effectiveness of oxygen nanodispersions are presented in Figures 4 and 5. For Contaminations 1-3 on the glass slide (Figure 4a-c) the effects of cleaning are similar to ones obtained for nitrogen nanodispersion but the nitrogen nanodispersion displays slightly better effectiveness (contact angles closer to the value of clean slide). Also similarly to the glass slides cleaned by nitrogen nanodispersion, the contact angle after cleaning increased in value for Contamination 4 (Figure 4d).

However, for cleaning of stainless steel with oxygen nanodispersion (Figure 5) the difference between nitrogen and oxygen nanobubbles is much more visible. For oxygen nanodispersion cleaning, the contact angles have decreased for Contaminations 1 and 3 (Figure 5 a and c), what shows that this gas is much more effective in cleaning metallic surfaces than nitrogen. It is worth noting that no visible rust or damage to the metal was seen during or after the process.

![Figure 4](image)
Figure 5. Contact angle measurements for stainless steel plate after cleaning with distilled water and oxygen nanobubble dispersion (a) Contamination 1 (b) Contamination 2 (c) Contamination 3 (d) Contamination 4

3.2. Sauter diameter of nanobubbles before and after cleaning
Sauter diameter of generated bubbles was about 400 nm and 250 nm for nitrogen and oxygen nanobubbles, respectively, what is in line with our previous research results [2,9]. After cleaning the Sauter diameter remained similar, without significant change in standard deviation.

4. Conclusions
In this work, nanodispersions of two gases were used to clean glass and stainless steel surfaces of the oily contaminations. The main advantage of this type of cleaning is no addition of frothers or surfactants to the cleaning medium. Results have shown that both surfaces can be cleaned of UV-color-protection oil, but the cleaning of vegetable oil proved to be more challenging and requires further studies. There is also room for increasing the effectiveness of cleaning off UV-color-protective oil due to the fact that the contact angles on both surfaces were still far from the contact angle on the precleaned surface.

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