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Ultrasonic cleaning of 3D printed objects and Cleaning Challenge Devices

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ABSTRACT

We report our experiences in the evaluation of ultrasonic cleaning processes of objects made with additive manufacturing techniques, specifically three-dimensional (3D) printers. These objects need to be cleaned of support material added during the printing process. The support material can be removed by dissolution in liquids with or without ultrasonic cavitation.

Distinctive stages in the cleaning processes were found for two different liquids (water and NaOH solutions). The combination of ultrasound and high concentration of NaOH has the best results for support material dissolution in the particular conditions studied.

The sonication of cleaning processes in ultrasonic baths is typically a slow process. Here we show the advantages of using an ultrasonic horn to clean the surface of small parts and holes more effectively.

We introduce a Cleaning Challenge Device design to be used for the universal evaluation of cleaning performance of different equipment or processes, and specifically for ultrasonic baths. The results and conclusions can be of use for different cleaning situations besides 3D printed parts, such as when deciding which protocol has a better performance or comparing different equipment.

1. Introduction

Additive manufacturing techniques were invented several decades ago, but it was not until recently that three-dimensional (3D) printing has become popular and has pushed the imagination of users. The discovery of new functions and applications of relevance for many fields has been possible with the advent of 3D printing. Recently 3D printers have been used to fabricate spare parts for space missions, the printing of organs for transplantations, and novel structures and chemical reactors [1–4].

There are several different techniques for 3D printing, and also a diverse range of materials in use, each requiring dedicated post-processing procedures [5–7]. The post-processing can include polishing, brushing or painting the object; here we will refer to cleaning or removal of support material from the printed item. Support material is defined as the material that is added for stability during the printing process, and can either be a separate material or made out of the 3D printing material itself. When there are moving parts in an item, or small details that are crucial for the functioning of the object, the residues of support material or other contamination can render the object, or the whole item non-functional, leading to undesired economical losses or health problems. The cleaning of printed parts can be complex and time consuming, taking up to 30% of the total production time, as expressed by companies that the authors talked with. Typically, the cleaning involves first manual removal of bulk support material (possibly assisted by a water jet), followed by ultrasound as a 'post-treatment'. These companies would like to spend less than 4 h on cleaning.

Ultrasonic baths have been widely used to clean objects for several decades [8–10]. Ultrasonic horns are known to create even stronger mechanical effects as it focuses the ultrasonic power into a small volume [11,12]. Therefore they make possible to clean the objects faster than with ultrasonic baths. It is known that the prolonged effect of bubbles collapsing close to surfaces can lead to erosion or destruction of the surface, depending on different factors, such as the type of cavitation: inertial or stable. For this reason it is important to ensure that the duration of the cleaning process, and the applied process parameters, such as the pressure amplitude and frequency, allow for certain degree of control over the desired cleaning while avoiding the damaging behavior [13–16].

The combination of materials and contamination that can be cleaned from a substrate is so varied that it is impossible to cover all in one single study. The properties of the substrate and contamination materials (hard–hard, soft–hard, soft–soft, acoustics), or geometrical shapes (flat substrates, tubes, intricate shape objects),

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as well as chemical compatibility with a cleaning solution, are among the different variables to be taken into account [17]. This investigation focuses on the ultrasonic cleaning (post-processing) of objects printed with UV-cured material deposition (Objet printers, Stratasys) [18]. The final object comes out of the 3D printer embedded in surrounding support material, which has different properties than the object itself. The support material is actually a heterogeneous combination of construction and support material; the support material part should be removed such that the remaining scaffold of construction material collapses. Near the walls, the support material mixture is different than the bulk support material – the so-called attachment layer. When the support material sits in geometrically complex objects, it becomes difficult to remove it, since the dissolving fluid must get in contact with these surfaces difficult to reach by hand or other methods. We provide a general protocol and evaluation methods to monitor the ultrasonic cleaning, by using two models that represent cleaning challenges.

Definitions of "what is clean", and methods to quantify cleaning processes, other than the subjective inspection by eye, are two aspects to consider before it is possible to automate such processes [17]. It is important to provide quantifiable variables that can be used to compare among the different cleaning steps, different cleaning equipment, and even the individuals performing the cleaning. In the semiconductor industry these questions have been answered to a certain extent [19]. An intuitive and simple procedure is to weight the sample before and after it is cleaned; the use of microbalances to monitor contaminant removal in ultrasonic cleaning applications has been reported [20], as well as micro-pores as model systems for particle removal from high aspect ratio structures [21]. In this article we outline several methods for quantitative cleaning measurement particularly oriented to ultrasound and 3D printed objects.

The cleaned state of a given object sometimes cannot be directly checked and there may be a risk of re-contaminating it. We borrow the concept of a process challenge device from the sterilization of medical tools, which typically consists of an object emulating the item with the most challenging feature to be cleaned. As an example, gke's Batch Monitoring System [22] is a hollow spiral with a closed end that is placed in the autoclave together with the medical instruments to be sterilized. After a sterilization process, the Batch Monitoring System allows to check if the conditions for sterilizing inside the autoclave were reached, without compromising the sterility of the real instruments. Up to now we found no reference in literature of a Cleaning Challenge Device (CCD) that could be used for monitoring the efficiency of an ultrasonic cleaning method, or comparing one post-processing technique with another. We present our proposition of a CCD for the ultrasonic cleaning of 3D printed parts, which could also be used to evaluate other post-processing techniques, or to compare the efficiency of different cleaning methods.

2. Materials and methods

2.1. Sample fabrication and characterization

All the samples were fabricated with an Objet Eden 350V UV-curing material deposition 3D printer. In a pilot study, five pieces of approx. $10 \times 10 \times 8$ mm were cut from support material weighing 1.00 ± 0.01 g, and placed in ultrasonic cleaning bags (BuBble bags, BuBclean) [23].

- Sample 1, with 10 mL of demi-water.
- Sample 2, with 1.5 M NaOH (0.6 g NaOH dissolved in 10 mL of demi-water).
- Sample 3, with 1.5 M NaOH, and was kept at 30 °C.
- Sample 4, with 10 mL of demi-water, placed in an ultrasonic bath (at 30 °C) for 2×15 min with 45 min in-between.
- Sample 5, with 1.5 M NaOH and was also placed in an ultrasonic bath (at 30 °C) for 2×15 min with 45 min in-between.

In total, each sample resided in the plastic bag for 2 h and was then left to dry for 1 h. Afterward, the samples were weighed again. This allowed finding the optimal conditions for the experiments in the remaining studies presented here. Following this pilot study, a more detailed experiment was set up in which the weight change after 10 min intervals was measured. The concentration of NaOH was varied from 0.5 M to 6 M.

For the cleaning of 3D printed objects two Cleaning Challenge Models were used. The first type (A) were extruded squares of $10 \times 10 \times 3$ mm, attached to an extruded polygon for handling purposes (Fig. 1A). The second model (B) had two variations. Model B.1 was a block of dimensions $65 \times 25 \times 130$ mm with two closed-end channels of diameter 5 and 1 mm and 100 mm length (Fig. 1B). Model B.2 was designed with channels of 2.5, 1 and 0.5 mm diameter, and 80 mm long holes. At the top of both model B blocks, a small chamber of $61 \times 21 \times 31$ mm allowed liquid containment. The chamber and the channels were filled with support material during the printing process. Models A and B were printed in VeroWhitePlus material (Stratasys), an acrylic compound.

The bulk support material around the printed objects was removed by hand, leaving only small remnants and a very thin (connecting) layer of support material. Finally, loose remnants were removed by low-flux flushing with water.

Infrared absorption measurements provided an indication of the chemical groups present in the support material samples. An

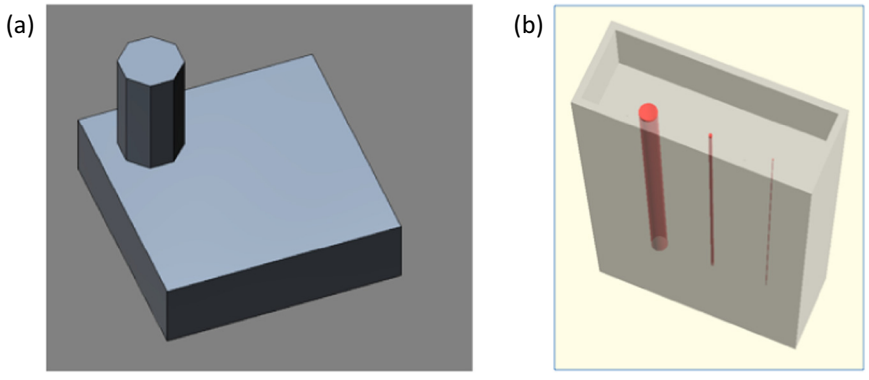

Fig. 1. (a) Test model with dimensions of the square block $10 \times 10 \times 3$ mm and (b) block with close-end channels with total dimensions of $65 \times 25 \times 130$ mm.

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infrared FT-IR Tensor (FT-IR Tensor27, Bruker) was used for these experiments. A High Resolution Scanning Electron Microscope (SEM; 1550, Zeiss) was used to visualize in detail the remaining support material on ultrasonically cleaned printed objects. A magnification of 100–1000× was used, with a voltage of 4 kV. Images were taken with a photo-camera (D900, Nikon) and macro-lens (50 mm, Sigma). A balance (APX-100, Denver Instrument) was used to weight the samples before and after each experiment, with an error margin of 0.1 mg.

2.2. Ultrasonic equipment and cleaning chemical solutions

An ultrasonic bath (USC200TH, VWR) operating at 45 kHz was used for the dissolution of support material experiments. The samples were placed in the ultrasonic bath and contained inside a 200 mL beaker supported by the lid of the bath. An ultrasonic horn (Sonopuls HD3200, Bandelin), with a tip of 2 mm diameter (MS72, Bandelin), was used to clean the printed models. This device was operated at 30% of its maximum power (200 W), and with duty cycles of 50% (i.e. pulses of 0.5 s in every 1 s) to avoid excessive heating and permanent deformation of the printed object. Stratasys advises to use a 0.5 M NaOH solution for the removal of support material and cleaning the printed parts [24]. A 2% NaOH (0.5 M) solution was prepared by dissolving 0.99 g of NaOH (Sigma Aldrich) in 50 mL of miliQ water. A 6 M NaOH solution was prepared by dissolving 11.99 g of NaOH in 50 mL of purified water, to study the effects of increased concentration.

3. Results

3.1. Dissolution of support material

The samples submerged in water alone at room temperature showed no signs of dissolving. Their final weight had increased from 1.00 ± 0.01 g to 1.13 ± 0.01 g, which suggests that they had absorbed water. All samples submerged in NaOH showed a reduction both in size and in weight, even though they also may have absorbed liquid. In NaOH at room temperature, the final weight was 0.58 g; at 30 °C, the final weight was 0.47 g. When ultrasound was also present, the final weight was 0.32 g. Each sample can be seen in Fig. 2.

Fig. 3 shows a typical graph of the sample weight percentage change ($W_{time}/W_{initial} \times 100\%$) measured every 10 min. We term the first 60 min as the active cleaning phase, in which the object is cleaned by ultrasound or another technique. In the first part of this period the weight can increase due to swelling of the sample by absorbing water. Support material is removed in this phase, but the weight loss is masked by the swelling effect. As the support material is dissolved or mechanically removed, the weight decreases up to the Post-Cleaning value, PC_a. The passive cleaning phase is the period from 60 to 1200 min, where the sample is left in a room conditions environment (25 °C, 1 atm) allowing the excess fluid to evaporate, and is weighted once more (PC_b).

Each experimental setting was repeated three times, and the weight values were averaged. The results of the percentage weight change for all three cases studied are shown in Fig. 4.

In water the ultrasound effect resulted in a final weight loss 20% larger than in silent conditions. For 0.5 M NaOH, the ultrasound increased the final weight loss with roughly 10% compared to silent conditions. The 6 M NaOH shows a final weight loss of roughly more than 20% bigger than in silent conditions. The percentage change values after the post-cleaning active (PC_a) and passive (PC_b) phases of all experiments are shown in Table 1. From these values we observe that the case of ultrasound always gives the best results, and particularly the higher concentration of NaOH removes more material.

The active cleaning rate (d_{active}), passive ($d_{passive}$) and, average ($d_{average}$) were calculated in g/min and are derived from the formulas:

$$d_{active} = \Delta W_{active}/T_{active} \quad (1)$$

$$d_{passive} = \Delta W_{passive}/T_{passive} \quad (2)$$

$$d_{average} = (d_{active} + d_{passive})/2 \quad (3)$$

where ΔW is the difference in weight and T_{active} and $T_{passive}$ are the time of active or passive cleaning respectively. These values are used to determine the best cleaning method for a generic object

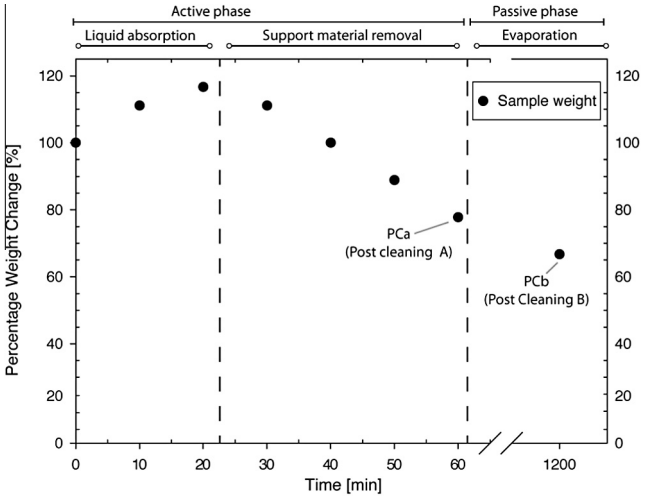

Fig. 3. Typical graph illustrating the two experiment phases of the percentage weight change: active (first 60 min) and passive (60–1200 min). The first part of the passive phase can show weight increase due to swelling. The PC_a and PC_b values are the final weights of each phase.

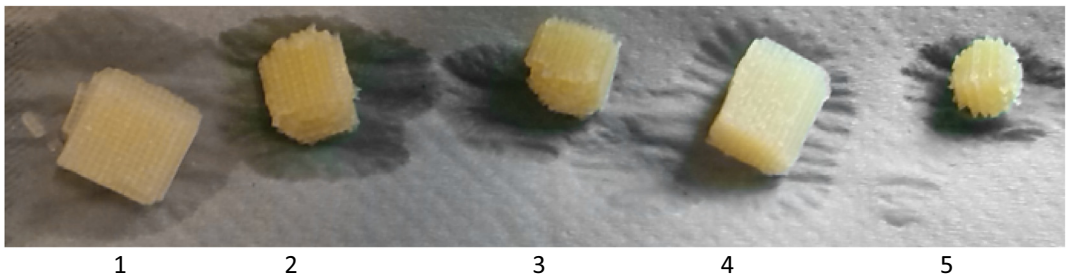

Fig. 2. Test samples of support material, after 1 h of dissolving processes. The numbers correspond to the 5 different processes outlined in Section 2.1. For samples 1 and 4 no dissolution was visible, i.e. their shape is identical to the original samples (10 × 10 × 8 mm).

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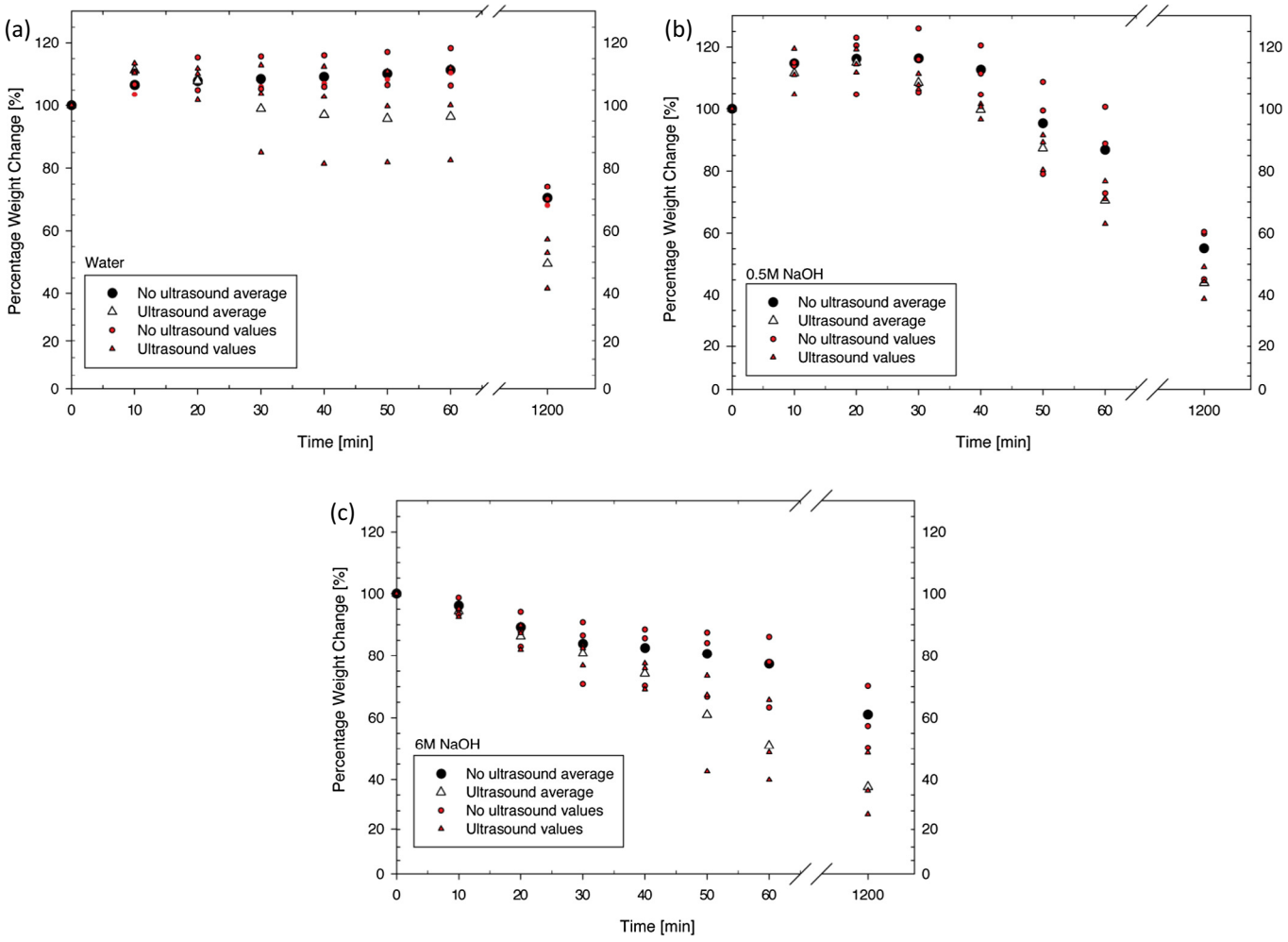

Fig. 4. Percentage weight change for the different experimental cases. (a) In water the ultrasound effect results in a final weight loss 20% larger than in silent conditions. (b) For 0.5 M NaOH, the ultrasound effect results in a final weight loss 10% larger than in silent conditions. (c) The 6 M NaOH shows a final weight loss of roughly more than 20% larger than in silent conditions.

Table 1
Percentage change values for the experimental conditions studied at post-cleaning points PC_a and PC_b.

Solution time (min)	No ultrasound			Ultrasound		
	H_2O	0.5 M NaOH	6 M NaOH	H_2O	0.5 M NaOH	6 M NaOH
PC_a (after 1 h)	111.32	86.85	77.33	96.41	70.46	50.99
PC_b (after 20 h)	70.42	55.15	60.97	49.59	44.26	37.65

or support material. The calculated cleaning rate values given in Eqs. (1)–(3) (d_{active}, $d_{passive}$ and $d_{average}$) are plotted in Fig. 5. The highest dissolution rate is achieved with 0.5 M NaOH when using ultrasound, which has comparable values to the 6 M NaOH, that shows the best removal values for the type of material and ultrasonic bath used in this study.

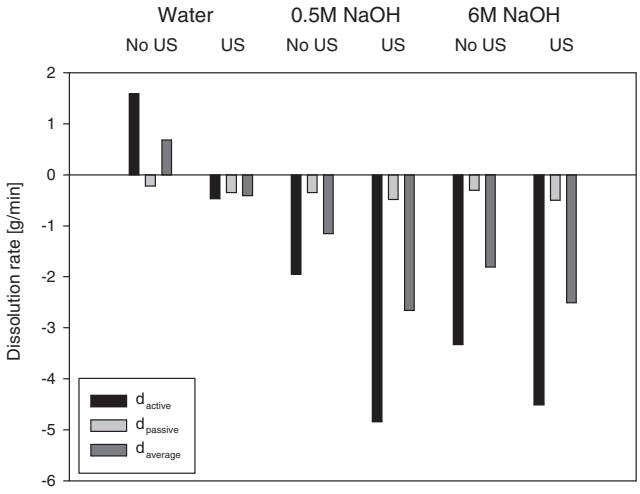

Fig. 5. Dissolution rate values as calculated with Eqs. (1)–(3). Only in the case of water without ultrasound an increase in weight is seen due to swelling by water absorption. The 0.5 M and 6 M NaOH solutions show comparable d_{active}.

3.2. Infrared spectroscopy

The support material surface composition was analyzed with infrared spectroscopy, and the results are shown in Fig. 6. The region near 3500 cm^{-1} (marked 1) indicates the presence of —OH or N—H bonds. The peak at 1550 cm^{-1} (2) corresponds to C=O or N—H bonds. The peaks around 1000 cm^{-1} (3) are attributed to C—O or C—N bonds. These results indicate that the sample contains a compound in ester form, as stated in the material ingredient database in which, besides the acrylic monomer (<30%), it has

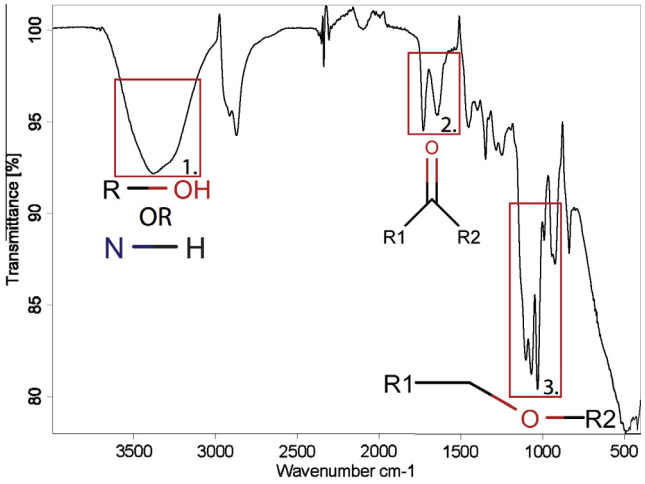

Fig. 6. Transmittance values of infrared measurements with distinctive features: (1) the region near 3500 cm^{-1} indicate the presence of —OH or N—H groups. (2) The peak around 1550 cm^{-1} corresponds to C=O or N—H bonds. (3) The peaks around 1000 cm^{-1} are attributed to C—O or C—N groups.

acrylic acid ester (<0.3%) [25]. These compounds when reacting with water form an alcohol and an acid.

No change in the in the apparent material composition was observed visually. More detailed studies can be carried out in future work to support this observation.

3.3. Evaluation of cleaning printed objects

The printer used in this study adds distinct support material as the print material is deposited, which can largely but not completely be removed manually. Especially challenging are sharp corners, small features and internal spaces. Different techniques were used to analyze the surface of the objects and identify the support and print material, hence providing an indication of "cleanliness".

3.3.1. Microscopy

SEM images allowed for observing the layered structure of the printed models. The support material can be recognized as it shows a different texture than the construction material (Fig. 7).

A disadvantage of SEM imaging is that it is time consuming and offers a limited field of view, which is not practical for the typical sample sizes used in 3D printing activity. For this reason we also performed optical microscopy (BX-FM, Olympus) as shown in Fig. 8, which shows remnants of support material as observed under 10× magnification.

3.3.2. Image processing

Macroscopically, the support material can be recognized as areas of light reflection, since the support material reflects light better than the construction material. We built a setup for photographing 3D printed objects, and perform image-processing analysis (color change, contrast enhancement, frequency filters), such that cleaning can be quantified. Figs. 9 and 10 show images used for the quantification process.

3.4. Ultrasonic cleaning

When operating standard ultrasonic baths, such as used in Section 3.1, the cleaning time can last longer than if a high-power device such as an ultrasonic horn is used. For this reason, the ultrasonic horn tip was positioned within 1 mm of the Cleaning Challenge Models and moved in steps across the surface. Ultrasound was applied at each position for a few seconds. Photographs of the surface were taken after each line across the surface to evaluate the removal process.

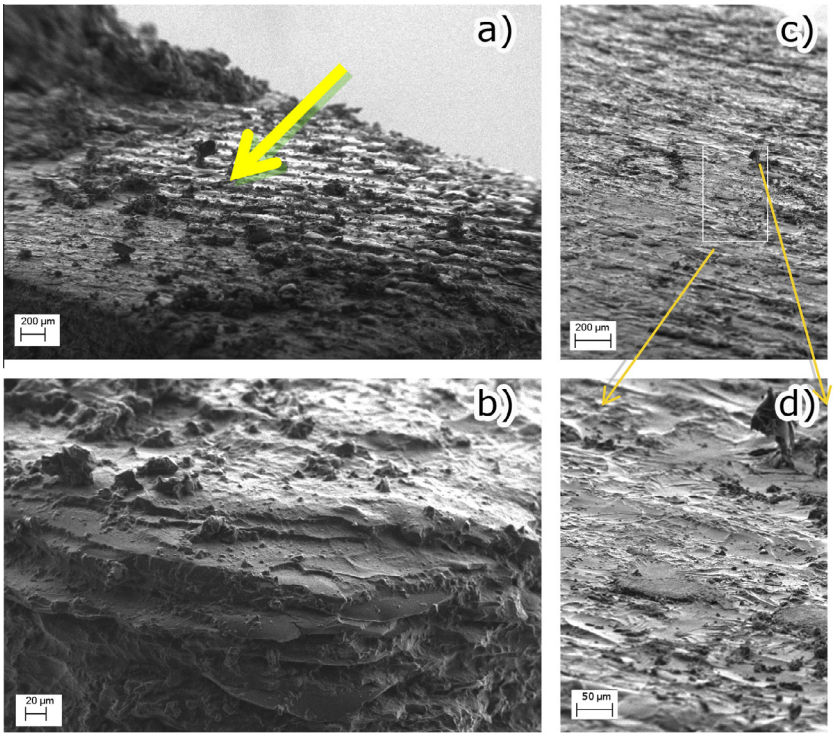

Fig. 7. (a) SEM image of the top surface of a Challenge Model type A. In (a) the support material is seen to the right part (indicated by an arrow) with a more roughed texture than the cleaned part to the left. In the (b) image the layered structure of the object is seen in the corner of the model. Image (c) shows a cleaned part and the inset (zoomed in d) shows the smoother surface of the print material that was visually clean.

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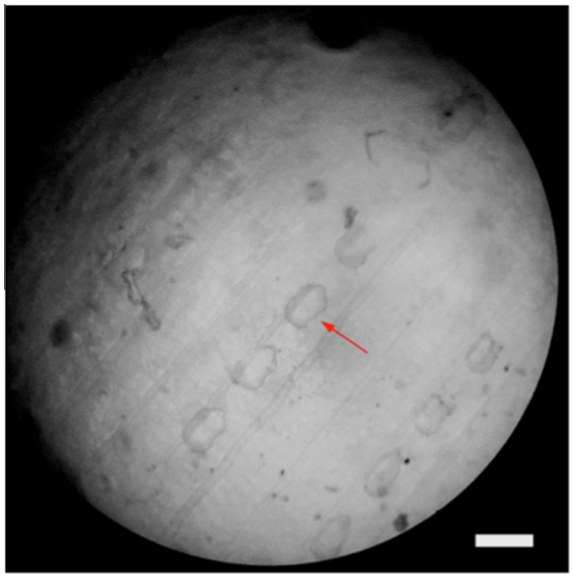

Fig. 8. 10× magnification of remaining support material after manual removal. The red arrow indicates a piece of support material. The white bar represents 50 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.4.1. Cleaning Challenge Model A

In Fig. 11, the top surface of a model A shows remnant support material (the attachment layer) as more light reflecting areas.

The total time to achieve 100% support material removal was less than 5 min. The rate of cleaning was calculated from the tip exposure area (7 mm^2), achieved within one ultrasound pulse (i.e. one second). The cleaning rate was therefore 7 mm^2/s. The duty cycle and tip movement speed and pattern can be varied to optimize this process.

3.4.2. Cleaning Challenge Model B

The majority of the bulk material in Model B was first removed by hand as shown in Fig. 12. Each model was placed inside a 5L glass beaker filled with tap water or a 0.5 M NaOH solution, at room temperature. The ultrasonic horn was used for cleaning the holes inside of the model, while the model was moved manually underneath the horn tip. In the Model B.1, the channels with diameters of 5 and 1 mm were cleaned with the ultrasonic power setting at 70%, using only demi-water.

Fig. 13a shows the progression of the cleaned depth as a function of time. The first 20 mm of the 5 mm-channel was cleaned 'remotely', i.e. by placing the ultrasonic horn tip just above the entrance of the channel. The removal rate was 2.8 mm/min. Beyond 20 mm, the ultrasonic horn tip was allowed to make contact with the support material, and the cleaning rate increased to 7.5 mm/min. At 49 mm depth, the tapered horn tip binds in the channel (the place where the tip cannot be further pushed inside the channel); the removal rate beyond this point was 2.5 mm/min. The 5 mm channel was cleaned to a final depth of 69 mm. This was 20 mm further than the point where the horn tip bound in the channel.

The cleaned depth as a function of time in the case of Model B.2 is presented in Fig. 13b. This model was treated by the ultrasonic horn at 50% power. Two copies of this model were printed; one was cleaned using demi-water and the other using 0.5 M NaOH solution. The cleaning rate for the 2.5 mm channel was 2.9 mm/min with water, and 3.3 mm/min with NaOH. The final cleaned depth was 3.5 mm deeper with NaOH than with water. The cleaning rate for the 1 mm channel was 2.4 mm/min, both for water and NaOH. With water, the removal process stopped at 6 mm, whereas with NaOH the removal continued during the studied time. Note that the removal rate was initially approximately the same as for the 1 mm channel in model B.1, but since the ultrasound power is lower (50% versus 70%), the final depth is only 6 mm. The cleaning rate for the 0.5 mm channel was 1.1 mm/min; the final depth was 4.5 mm (with water) or 6.7 mm (with NaOH).

4. Discussion

4.1. Support material dissolution

From the initial experiment of support material dissolution it could be seen that the combination of ultrasound and NaOH had

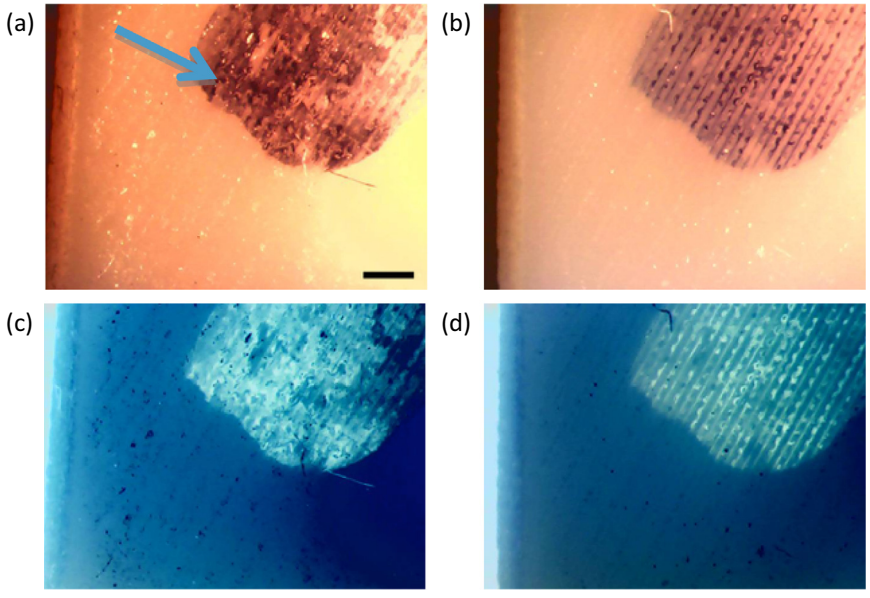

Fig. 9. Non-processed detail images of the surface of a 3D printed object (a) before, and after manual cleaning treatment (b). In (c and d), the same surface is shown after image processing of (a and b) respectively. The dark dots correspond to remaining support material and allow a qualitative representation of the amount of support material remaining, i.e. cleanliness. The black bar in (a) represents 1 mm, and the darker spot (pointed with the blue arrow) was made with a permanent marker for comparison purposes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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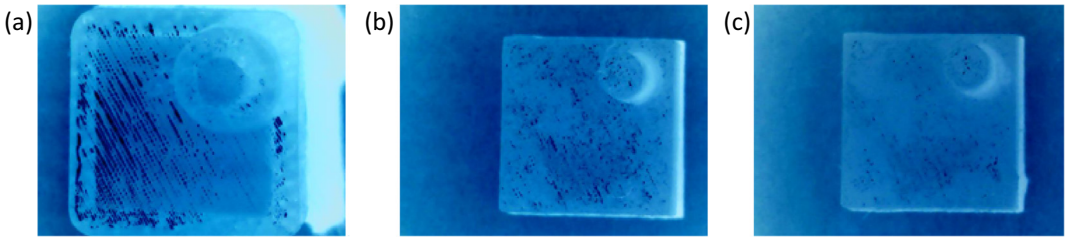

Fig. 10. Overview images of the surface of a 3D printed object, after image processing. The black dots correspond to remaining support material. Image (a) shows the object before manual cleaning; the object in (b) has gone through a first manual cleaning step, resulting in 81% cleaning; the object in (c) has gone through additional manual rubbing and was 95% cleaned; see Fig. 1 for dimensions.

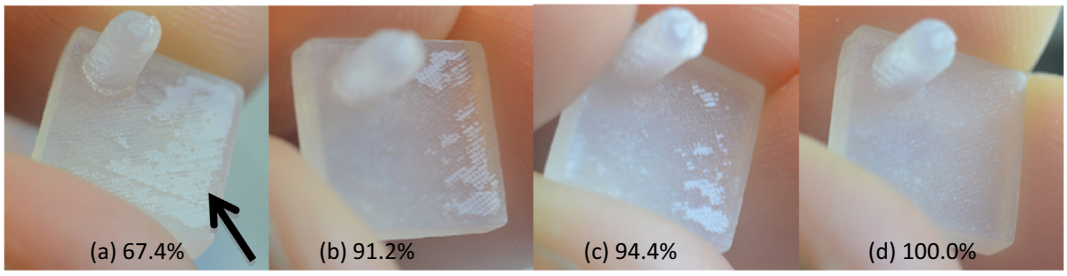

Fig. 11. Consecutive stages of cleaning with an ultrasonic horn, starting after manual removal of the bulk support material (a) to the final cleaned state (d). The percentages of the cleaned surface is indicated, the arrow points at support material; see Fig. 1 for dimensions.

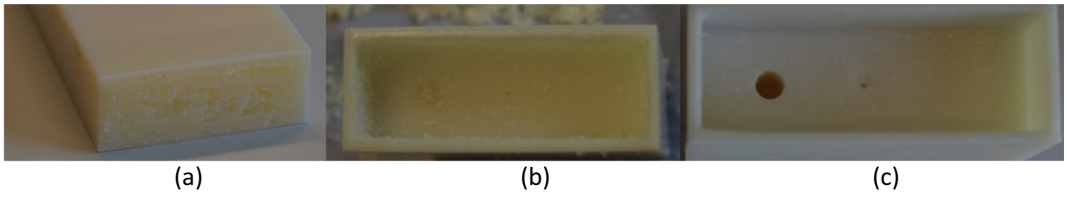

Fig. 12. Bulk support material in the chamber of Model B.1, before (a) and after (b) manual removal and (c) ultrasonic horn removal.

the best cleaning effect (see Fig. 4). NaOH is more effective in dissolving the support material than water. The material provider advises the use of NaOH solutions as cleaning medium, though acidic or surfactant solutions could be employed as well. In selecting other cleaning solutions, one should take into account the negative effects it might have on the polymer used to print the 3D objects.

The effect of heating is also demonstrated, since the amount of dissolved support material at 30 °C increased from 42% to 53% compared to room temperature (not taking into account any absorbed liquid). Agitation by ultrasound yielded the most dissolved support material: 68% after 2 h. The rate of dissolution was roughly 0.25 g/h. This rate will be strongly dependent on the surface area of each printed object, and may be enhanced at other concentrations of NaOH or temperature, or more effective ultrasonic agitation.

Ultrasonic agitation will be most effective when the ultrasonic bath is used optimally, i.e. when parameters such as the temperature, gas content, filling height, ultrasound frequency and pulsing as well as sample positioning, are chosen correctly [26]. The effect of ultrasound leads to an increase of weight loss of 20% compared to the samples left in water without any agitation in one hour, while in our pilot experiments it was even 68% difference after 2 h. In the case of only water (Fig. 4a), for both the silent and US conditions the curve is flat for most of the experiment. The weight increase in the "active phase" of non-sonicated samples comes from swelling due to liquid absorbed in the material. The dissolution of the support material in the ultrasonic treated samples is increased by 20%. The graphs for 6 M NaOH show a change in the curve shape during the first 30 min, with an apparent decrease in swelling when compared with 0.5 M NaOH and water. When using NaOH solution of different concentrations the shape of the curve changes as can be seen in Fig. 4b and c, with the more concentrated solution (6 M) showing a steeper slope of dissolution rate.

Among the sonication effects that can speed up the removal of support material we can mention acoustic streaming, bubble cavitation effects such as jetting and shockwaves, and chemical reactions as a result of radical generation. Radicals can degrade the polymers present in the printed and support material, and undergo base-hydrolysis to generate acrylic acid and acrylamide. The acrylic acid ester present in the support material (Fig. 6, Section 3.2) can react with water (hydrolysis) and form an acid and an alcohol, both soluble in water [27]. When a base solution (such as NaOH) is added, saponification will occur, which results in an alcohol, a sodium ion, and a conjugated base of the acid forming the ester. If the solution pH is lowered at the final stage of a saponification reaction, the reversibility of the reaction is reduced, which could be beneficial for removing the support material permanently. In our case, since the concentration of NaOH used is high, the small decrease in pH that can occur due to nitric acid produced in the $N_2 + O_2$ reaction will be negligible.

It is known that at low ultrasonic frequencies such as used in this study (45 kHz) the mechanical effects of ultrasound (jets, streaming and shockwaves) are more significant than radical production; yet, since the support material might be composed of poly-ester, the radical generation as a result of ultrasonic

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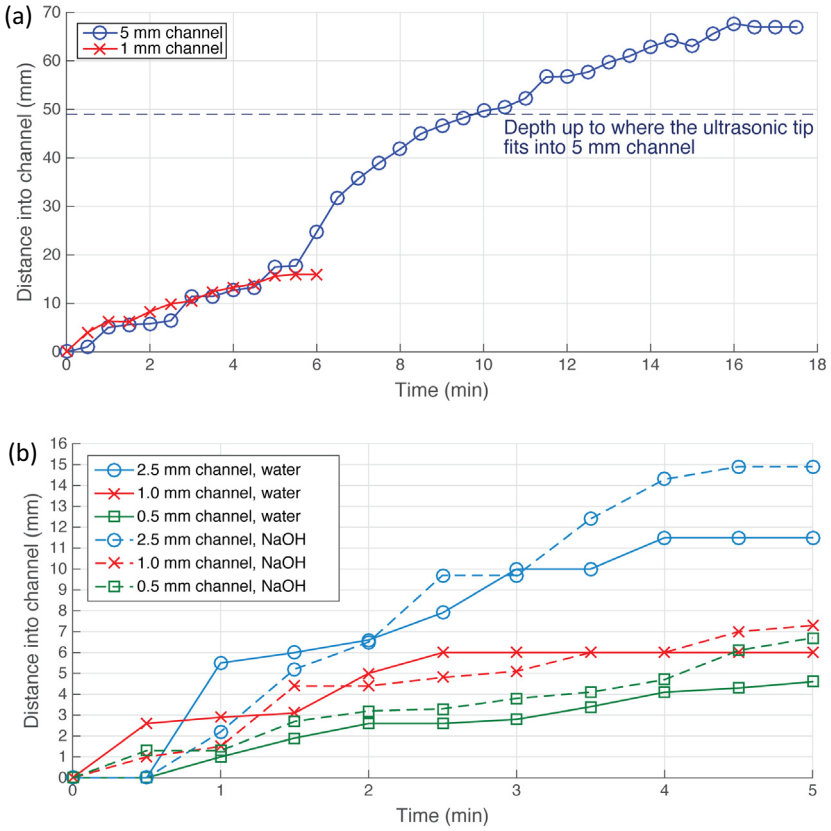

Fig. 13. (a) Cleaned depth in the channels of Cleaning Challenge Model B.1, as a function of time. (b) Time evolution of the depth cleaned inside the channels of Cleaning Challenge Model B.2 for water and 0.5 M NaOH solution.

cavitation could contribute to the hydrolysis reactions [13,28]. We speculate that the radical generation ($H^{\cdot}$ and $OH^{\cdot}$) known to occur in ultrasonic cavitation could contribute to an accelerated dissolution of the support material. Both radicals can attack the ester group at different bonds, accelerating the reaction. Further studies are needed to quantify this effect [29,30].

In practical situations a protocol that uses the least amount of chemicals and energy consumption is always desirable. However, the higher concentration of NaOH, even though it has a better removal effect, has a lower pH that can result in negative effects such as material corrosion. Handling such basic solutions increases the complexity of the cleaning processes, and has a non-negligible environmental impact when disposing the remaining solution after treatment. Additionally, the 0.5 M NaOH solution showed a higher active dissolution rate, which might be useful for processes where a shorter post-processing time is required, such as with fragile structures. Even though we did not look at the traces of NaOH in the cleaned surfaces, an additional cleaning step to neutralise NaOH should be performed to ensure the durability of the printed object.

4.2. Ultrasonic cleaning of 3D printed models

In Section 3.4.1 we demonstrated how the use of an ultrasonic horn accelerates the removal of remnant support material layers from the Cleaning Challenge Model A. This is relevant for the cleaning of small features or fragile objects requiring refined post-processing. Optical quantification is a suitable method for measuring remaining support material on outer surfaces, although it cannot be used for quantification of cleaning inside channels printed in opaque materials.

The results for the Cleaning Challenge Models B.1 and B.2 show that channels of diameter 0.5–5 mm could be cleaned with an ultrasonic horn up to a certain depth that depends on the diameter of the channel, the ultrasound power setting, and the liquid used. This is confirmed by the fact that the removal rates for the first (non-contact) 20 mm and the final 20 mm (also non-contact) are similar. Streaming and/or cavitation lead to cleaning up to 2 cm in front of the tip. Large channels were cleaned better than small channels, especially when the ultrasonic horn tip could enter the channel, with a cleaning rate of 7.5 mm/min; the largest depth reached was 7 cm. However, when the ultrasonic horn tip enters the channel, it is very likely to touch the walls and channel entrance. This leads to damage of both the printed model and the ultrasonic horn tip, and should be avoided. When the tip could not enter the channel (any further), then the cleaning rate was reduced by approximately 3 times, and the final depth was limited to 20 mm (large channel, 70% power setting) down to 5 mm (smallest channel, 50% power setting). This suggests that the cavitation bubbles and the streaming induced by the ultrasonic horn are capable of removing support material, but only in the vicinity of the ultrasonic horn tip; thinner and curved channels may have even less penetration depth. The speed of sound of the support material is unknown, but assuming it is similar to that of water (1500 m/s), the wavelength at 30 kHz would be on the order of a few cm. While this suggests that standing waves fit inside the channel, it is likely that the support material dampens the ultrasound significantly (as with many soft materials). Therefore acoustic reflections are expected to play a minor role.

While ultrasonic baths have a much larger working area (or volume), the cavitation process inside baths is a random, unfocused process and consequently, the cleaning is much slower than with an ultrasonic horn. For practical situations, there is a trade-off

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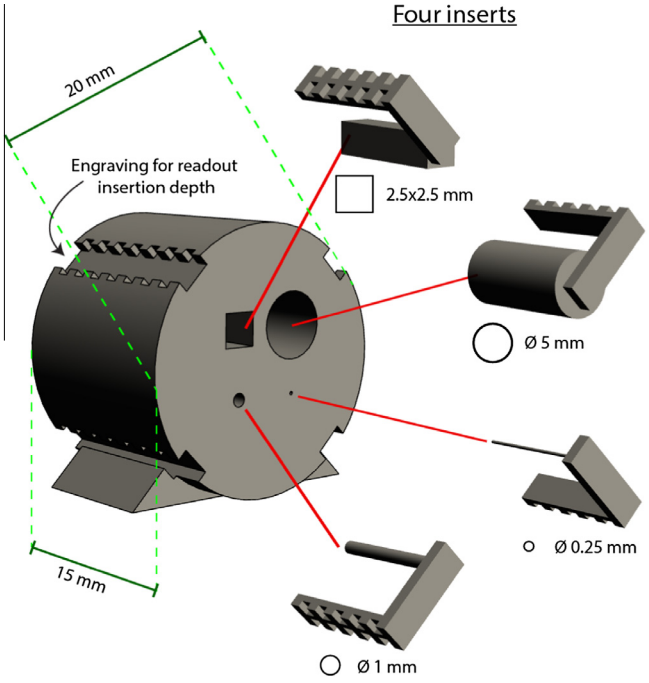

Fig. 14. Schematics of the CCD benchmark model with inserts rods. The corresponding shaped rods are inserted in the holes and a scale can be used to measure the penetration depth. The quality of the cleaning protocol can be assessed in a simple way.

between fast, local cleaning with an ultrasonic horn, and slower cleaning of entire objects with an ultrasonic bath. A combination, in which an ultrasonic horn is used to clean the remaining small details not removed by an ultrasonic bath may also be useful. Commercially available equipment for contact-less cleaning can also be used as an alternative; for example, a nozzle generates a megasonic wave (600 kHz) through a flowing liquid to a small area of ca. 4 mm on a substrate [31].

Based on our observations, the contribution of chemical dissolution by NaOH is minor when using the ultrasonic horn. Fig. 13b shows that most of the cleaning is done by mechanical forces, with only a small increase in removal rate or depth when NaOH is used instead of water. We consider that the time scale of chemical dissolution effects is slower than that of the mechanical removal forces. These results may not be statistically significant since there is a variation in the results from the manual operation of the ultrasonic horn, which is difficult to account for.

4.3. Cleaning Challenge Device (CCD) design proposition

As discussed in the introduction, the evaluation of "what is clean" needs to be further investigated. The answer is application dependent, since e.g. mechanical models have less stringent cleanliness requirements than medical implants. For each application a robust evaluation of the cleaning techniques is required. For this reason we have designed a special Cleaning Challenge Device (CCD) that we make freely available online [32] so that, in conjunction with the experimental results presented in this article, scientists and users of 3D printing tools can use and share their experiences.

Inspired by the Cleaning Challenge Models used in this study, our CCD (shown in Fig. 14) was designed to include, in a simple geometrical object, the most important and challenging features to be cleaned: small close-end holes with different cross sections, ridges, etc. The model consists of a cylindrical body (20 mm in radius, 15 mm in length), with a total volume of 4.43 cm^3. The diameter of each hole in the body was chosen to represent different resolutions of the most common printers currently on the market; the 0.25 mm diameter rod and circle correspond to only a few layers in high-resolution printers. The depth of insertion of a rod in a corresponding hole printed in the main body of the model can be used to evaluate if the support material was removed inside. Additionally, the friction due to the rotation of a (cylindrical) rod inside the hole gives a secondary indication of the quality of the cleaning.

We have used this CCD to test different ultrasonic cleaning protocols in our lab. This has reduced our typical cleaning procedures for 3D printed objects in an ultrasonic bath from 8 min to 1 min. We encourage other researchers or 3D printing enthusiasts to incorporate such protocol and CCD in their post-processing routines. We aim at making this CCD a benchmark model for investigating the capabilities of cleaning techniques, but also to compare different cleaning procedures. It can serve as a periodic quality control tool as well, since it can evidence whether the cleaning procedures and devices still function properly with the passing of time.

5. Conclusions

The use of ultrasonic cavitation has been demonstrated to have a positive effect in the removal of support material with relevance for the 3D printing objects, specifically Objet Eden 350V. The use of sodium hydroxide (NaOH) solutions showed also an improved removal rate at the two concentrations studied (0.5 and 6 M). The optimal conditions found for the removal were those using 6 M NaOH in combination with ultrasound, but for some applications the 0.5 M offers milder basic conditions with good cleaning effect. Additionally, the liquid could be warmed up to ~30 °C in order to enhance the chemical dissolution. It remains to be seen, e.g. with SEM or other analysis methods, if the NaOH solutions have no effect on the printed material surface properties after the cleaning procedure.

We introduce and make available a Cleaning Challenge Device (CCD) that can help in the assessing of post-processing of 3D printed materials. This device can also be used in the monitoring of other processes, or characterization of equipment effectiveness in the removal of different contaminants.

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