1. Introduction

It is well known that organic and industrial wastewater poses a serious threat to the environment and, if the wastewater is released untreated, it can damage aquatic life and be harmful to human health. Since the last century, significant efforts have been made to improve the efficiency of water-treatment methods. However, due to the increasing population and pollution, water cleaning has become increasingly challenging. With the advancement of nanotechnology, new catalysts and engineered nanomaterials are being developed for water treatment. One of the growing areas in nanotechnology is micro and nanorobots or motors, envisioned to carry out complex medical tasks, such as drug delivery, cancer treatment, and microsurgery. Catalytic, self-propelled micromotors use a chemical fuel, such as hydrogen peroxide, hydrazine, or acetylene, for propulsion. Amongst these, hydrogen peroxide is most widely used as a fuel in combination with the platinum catalyst for propulsion. However, due to the highly oxidative nature of hydrogen peroxide, medical applications of micromotors are limited at their current state. Nonetheless, environmental applications of motors have shown promising results. Recent advances in this area have demonstrated the degradation of organics and chemical warfare agents sensing of heavy metals, separation of organic materials, and oil removal capabilities of nano/micromotors. Iron-containing micromotors swimming in hydrogen peroxide can serve as microcleaners to degrade organic pollutants via a Fenton-like reaction. The degradation rate of organics is much higher when motile microcleaners are deployed compared to degradation using non-motile iron-containing tubes. Hydrogen peroxide is the main reagent in the Fenton reaction, which is already in use for many commercial water treatment procedures. Hydrogen peroxide is also considered as a green reagent for sustainable chemistry because it can be degraded into water and oxygen gas without producing any toxic chemicals. The classical Fenton reaction generates hydroxyl radicals when Fe$^{2+}$ reacts with hydrogen peroxide, as follows:

Fe$^{2+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{3+}$ + OH$^-$ + OH$^-$  \hspace{1cm} (1)

Fe$^{3+}$ + H$_2$O$_2$ $\rightarrow$ Fe$^{2+}$ + HO$_2^- +$ H$^+$  \hspace{1cm} (2)

During the reaction chain, Fe$^{2+}$ oxidizes to Fe$^{3+}$ and Fe$^{3+}$ is regenerated back from Fe$^{3+}$ (Equations (1) and (2)). One of the main disadvantages of the classical Fenton reaction is that at

Self-powered micromachines are promising tools for future environmental remediation technology. Waste-water treatment and water reuse is an essential part of environmental sustainability. Herein, we present reusable Fe/Pt multi-functional active microcleaners that are capable of degrading organic pollutants (malachite green and 4-nitrophenol) by generated hydroxyl radicals via a Fenton-like reaction. Various different properties of microcleaners, such as the effect of their size, short-term storage, long-term storage, reusability, continuous swimming capability, surface composition, and mechanical properties, are studied. It is found that these microcleaners can continuously swim for more than 24 hours and can be stored more than 5 weeks during multiple cleaning cycles. The produced microcleaners can also be reused, which reduces the cost of the process. During the reuse cycles the outer iron surface of the Fe/Pt microcleaners generates the in-situ, heterogeneous Fenton catalyst and releases a low concentration of iron into the treated water, while the mechanical properties also appear to be improved due to both its surface composition and structural changes. The microcleaners are characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), nanoindentation, and finite-element modeling (FEM).
the end of the treatment the iron ions need to be removed from the solution. Iron salt removal requires a high amount of chemicals for precipitation and produces a large amount of sludge. Further sludge removal is an expensive process and requires a lot of energy. In addition, the non-reusability of iron salt as a catalyst and the energy required for mixing result in extra costs for the treatment. To overcome the disadvantages of this classical homogeneous Fenton reaction, significant efforts have been made to develop heterogeneous Fenton catalysts.[43]

To develop more practical microcleaners and to overcome the limitation of the Fenton reaction, we developed microcleaners that can be reused several times for batch cleaning, swim continuously for hours, and be stored for weeks for later use, while at the same time also minimizing the iron release into the solution by generating an in-situ heterogeneous catalyst on the iron surface. The effect of different microcleaner sizes on the organic dye degradation rate, the chemical composition after the cleaning cycles, and mechanical properties of the microcleaners were studied to understand the system thoroughly. We also extended the applicability of microcleaners to another model of organic contaminant, i.e., 4-nitrophenol, demonstrating their versatile remediation functionalities.

2. Results and Discussion

2.1. Size Effect of Microcleaners on Dye Degradation and Reusability

Pre-strained nanomembranes of iron and platinum were sequentially evaporated by e-beam on photoresist in squared patterns of different sizes. The nanomembranes were selectively lifted off from the glass substrate and rolled up into micro tubular structures (Movie S1, Supporting Information), which led to the formation of the microcleaners as explained in the Experimental Section. The effect of the size of the Fe/Pt microcleaners on the degradation rate was studied using three different sizes. For all sizes, an equal area of previously designed photoresist patterns was deposited to keep the amount of catalytic material the same in each experiment even though the total number of tubes was different. Three sizes of microcleaners (200 µm, 300 µm, and 500 µm long) were fabricated by rolling up Fe/Pt nanomembranes (Figure 1A,B) and used for the degradation of the dye. The experimental parameters for dye degradation are presented in the Experimental Section.

Figure 1. Fabrication of microcleaners and their use in the degradation of malachite green (MG) dye. A) 200-µm, 300-µm, and 500-µm square photoresist patterns with e-beam evaporated Fe/Pt nanomembranes on it. B) Fe/Pt nanomembranes rolled up into 200-µm, 300-µm, and 500-µm long microcleaners with an approximate diameter of 40 to 60 µm. C) Degradation of dye over time using different sizes of microcleaners. D) Dye degradation over time normalized for single microcleaners of different sizes. E) Degradation of malachite green at different concentrations of hydrogen peroxide by 500 µm micro-cleaners in 60 minutes (insert shows the light absorbance spectrum of malachite green at different concentrations). F) Degradation of malachite green in 60 minutes, with and without the addition of H₂SO₄ by 500 µm micro-cleaners.
The classical Fenton reaction is highly oxidative in nature because of the production of hydroxyl radicals during the reaction of Fe²⁺ ions with hydrogen peroxide, which are capable of completely oxidizing organic molecules. Degradation of a model pollutant dye, malachite green, via a classical Fenton reaction has been studied in detail using iron salt (ferrous sulfate) as the source of Fe²⁺ ions. However, the external mixing needed for the degradation reaction and the removal of the sludge produced by the precipitation of Fe²⁺ ions after completion of the reaction make the process expensive. Under similar experimental conditions, the active microcleaners showed similar results but without the need for external mixing and a lower amount of iron was released from the surface into the treated water. The microcleaners thus act as multipurpose agents, whereby the platinum layers inside the microcleaner act as the engine to decompose H₂O₂ into O₂ and H₂O. The oxygen bubble trail produces a thrust that propels the microcleaner, which additionally provides micro-mixing and enhances mass transfer. The iron layer on the outside of the microcleaners reacts with the H₂O₂ to produce hydroxyl radicals via a Fenton-like reaction that degrades the organic compound. The pH was adjusted to 2.5 using sulfuric acid (the reported optimum pH is between 2–3 for the Fenton reaction catalyzed by zero valent metallic iron) and the initial concentration of malachite green was kept to 50 µg mL⁻¹ in all the experiments. During the dye degradation experiments, the dye concentration was periodically measured by UV-vis spectrometer and the microcleaners were left swimming in the contaminated dye solution until a steady-state degradation was observed after 60 minutes. Figure 1C shows the degradation curves of 200 µm, 300 µm, and 500 µm microcleaners and control experiments without microcleaners. The microcleaners degraded more than 80% of the malachite green in 60 minutes; furthermore, complete degradation was achieved over longer times (not shown). After 60 minutes of degradation, the malachite green degradation measured was for all three sizes of microcleaners. A one-way analysis of variance (ANOVA) was calculated for all measured data points for the different sizes of microcleaners to verify the statistically significant difference between them. No significant difference was found in the amount of dye degraded by the three different sizes of microcleaners at the P = 0.9850 (n = 5) level. The degradation of malachite green dye is due to the oxidation reaction facilitated by hydroxyl radicals produced while the iron containing microcleaners are swimming in wastewater containing hydrogen peroxide. Hydroxyl radicals have very strong oxidation potential (2.8 V), just below the oxidation potential of fluorine (3V); therefore, if enough time is given, hydroxyl radicals can mineralize organic molecules into carbon dioxide without leaving any toxic byproducts. Hydroxyl radicals oxidize malachite green into a final byproduct of oxalic acid, before mineralizing into carbon dioxide.

Clearly, the Fe/Pt microcleaners showed a higher degradation rate compared to the control experiments without microcleaners as shown in Figure 1C. Fe/Pt microcleaners have already been shown to outperform various controls with respect to the dye degradation rate, such as (a) Fe tubes only, (b) non-iron containing motors, i.e., Ti/Pt and (c) immobilized Fe/Pt microcleaners. Figure 1D shows the dye degradation by a single microcleaner considering that all microcleaners present in the solution contribute equally to the total degradation. The Figure reveals that a larger microcleaner of 500 µm is more effective than a 300 µm or a 200 µm microcleaner. Provided that the amount of total rolled up catalytic material present in the solution is equal, that is, 0.64 cm² in all cases, the differences in size of the microcleaners do not give an added advantage and have a limited effect on the degradation of dye in the studied size range. The total amount of catalytic material plays a more important role than the size of the microcleaners. Different experimental parameters—such as the effect of H₂O₂ concentration and the addition of H₂SO₄—were further studied by using 500 µm micro-cleaners fabricated in a new batch. Figure 1E shows the percentage of degradation of 50 µg ml⁻¹ malachite green by micro-cleaners in 60 minutes at different concentrations of H₂O₂. Above 15% H₂O₂ the degradation percentage does not increase significantly, reaching a plateau. Figure 1F shows the absorbance spectrum of malachite green after 60 minutes of degradation by microcleaners with and without the addition of sulfuric acid for 2.5 pH maintenance. Interestingly, the effect of sulfuric acid addition on the degradation percentage is almost negligible, meaning that in future applications, addition of acidic media is no longer required for the degradation of organics using microcleaners.

A reusable catalyst is important for the cost effectiveness of the Fenton-based advanced oxidative processes. The reusability performance of the microcleaners was studied, as shown in Figure 2A. All three sizes of microcleaners were tested for reusability to verify if the performance remained comparable in later cycles. In each cleaning cycle, the microcleaners were first left swimming in the malachite-dye-contaminated water for dye degradation. After this, the microcleaners were collected using a permanent magnet, cleaned with ultrapure water three times, and then reused in subsequent cleaning cycles. The time interval between two cycles was chosen to be incremental in order to capture both the short-term and long-term changes and the effect on the degradation rate. The first five cleaning cycles were performed consecutively from 1 to 5 hours, then the next cycles were performed after 18 hours and 24 hours of storage in sodium dodecyl sulfate (SDS) containing water without hydrogen peroxide to study the changes after short-term storage. The following cycles were performed after a 1-week interval between each cycle.

Degradation of the dye from 1 to 5 hours, when microcleaners were reused continuously without storing them, and at 18 hours and 24 hours after short-term storage was between 68–86%, as shown in Figure 2B. After long-term storage (one to five weeks), the degradation was slightly reduced to 56–67%, as presented in Figure 2C. The percentages of degradation were very similar for the different sizes of microcleaners for all dye degradation cycles after both short-term and long-term use, which shows that the size of the microcleaners was also of no influence in terms of reusability.

Previously, iron layers have been used for magnetic steering and guiding purposes. Here, we exploited the ferromagnetic nature of the Fe layer as an added functionality to recover the microcleaners, along with their Fenton-reaction capability. The microcleaners can be magnetically recovered and reused several times without significant changes in the dye-degradation efficiency, even after weeks of storage.
After each reusability cycle, the swimming behavior of the microcleaners was observed under an optical microscope to assess the motility and bubble-production activity. We observed that from second cycle onwards the microcleaners were producing bubbles more vigorously because of the self-cleaning and activation of platinum surface in the first cycle. The microcleaners remained active after 5 weeks (including both short-term and long-term intermediate storage, see Movie S5, Supporting Information). The structural integrity of the microcleaners was also observed to be very good during the initial cycles but in the later cycles, some of the longer microcleaners were broken into two pieces or broken layers became visible, whereas some shorter microcleaners broke into even smaller pieces without any tubular geometry. The damage in the structure could be due to i) multiple exposure of the microcleaners to the external magnetic field of a strong neodymium–iron–boron magnet during the recovery process after every cycle, and ii) internal pressure of bubbles generated while swimming. Damage in the structural integrity could be one of the reasons for the observed decrease of dye degradation percentage in the later cycles after long-term storage (Figure 2C).

A separate continuous swimming experiment was carried out to understand if it is possible to use microcleaners for continuous longer swimming applications or many batch-wise shorter cleaning cycles. All three sizes of microcleaners were left swimming in H$_2$O$_2$ (15% v/v) solution for 24 hours and swimming was monitored periodically under the microscope (Movie S2 to S4, Supporting Information). Figure 3 shows that all 200-µm, 300-µm, and 500-µm microcleaners were swimming even after 24 hours of continuous motion. Thus, it is indeed possible to use them for long-term swimming activities. Although some microcleaners were broken into smaller pieces after a few hours of swimming, they were still active. Changes in the diameter were also observed after a few hours of swimming, as seen in Figure 3. Namely, a decrease in the diameter was visible for longer microcleaners in the images taken after 24 hours. The opposite effect was observed for the 200-µm microcleaners; some of them had opened up and broken into pieces. This difference is due to the presence of fewer windings in the microcleaners fabricated from the smaller photoresist patterns. As the same thickness of Fe/Pt nanomembranes were rolled up from different sizes of photoresist patterns, similar diameters between 40 to 60 µm (and thus, different number of
windings in the rolled-up tubular microcleaner structure) were achieved.

2.2. Heterogeneous Catalytic Shift in the Fenton Reaction and Surface Characterization

It is widely accepted that the zero-valent-iron-mediated Fenton reaction is mainly related to the ferrous ions generated from the iron surface in acidic pH. Fe$^{2+}$ ions that have leached from the surface into the solution play an important role in the reaction kinetics, whereby Fe$^{2+}$ is oxidized into Fe$^{3+}$ ions (Equation (1)). The regeneration rate of Fe$^{2+}$ ions from Fe$^{3+}$ (Equation (2)) is the rate-limiting factor for the classical Fenton reaction and the presence of a metallic surface is believed to help the reduction of the Fe$^{3+}$ ions to Fe$^{2+}$, thus maintaining the Fenton reaction rate. 

$$\text{Fe}^{2+} + \text{H}_{2}\text{O}_{2} \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH}$$

The iron released from the surface of the microcleaners in the solution was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). Measurements were performed after 60 minutes of degradation cycle for up to 8 cycles. The measured iron concentrations for the 200-µm, 300-µm, and 500-µm size microcleaners after the first cleaning cycle were around 2.10, 2.15, and 2.20 µg mL$^{-1}$, respectively. The concentration of iron in the solution after the first cycle was thus about the same for all sizes (Figure 4A), which further proves that the initial dye degradation rate for the different size motors was similar (Figure 1C). In the subsequent cycles, the concentration dropped sharply, and remained low in the subsequent cycles, as shown in Figure 4A.

The initial ferrous ion concentration in the reaction mixture greatly affects the kinetics of the Fenton reaction. As reported by Hameed et al., an iron concentration above 2 µg mL$^{-1}$ is sufficient to carry out the classical homogeneous Fenton degradation of malachite green. However, if the Fe$^{2+}$ concentration in the solution is below 1 µg mL$^{-1}$, the malachite green degradation rate will not be higher than the rate observed in the control experiment without Fe$^{2+}$. The dye degradation in the first cycle can be attributed to the released iron from the surface of the microcleaners but from the second cycle onwards, the iron concentration was below 1 µg mL$^{-1}$. In spite of having an iron concentration that was below 1 µg mL$^{-1}$, the percentage of degradation only changed marginally. This result suggests a shift in the reaction pathway towards a heterogeneous Fenton reaction. This implies the formation of an in-situ heterogeneous Fenton catalyst on the surface of the microcleaners to achieve a dye degradation efficacy as high as in the first cycle. Also, the motion of the microcleaners can keep on regenerating the active surface and thus increase the mass transfer to help maintaining the percentage of dye degradation.

To study the surface changes that occurred after the Fenton reaction, the microcleaners were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI 5500 multitechnique system spectrometer, equipped with a monochromatic X-ray source. XPS was carried out on the microcleaners before the Fenton reaction, after Fenton reaction for 5 hours, and after 5 weeks of storage. The microcleaners were washed with water and then dried in an ethanol-CO$_2$ critical point dryer before measurements (to dry them without damaging the structure). Critical point drying is necessary to avoid mechanical stresses that are generated when the surface tension changes when the solvent on and around the microcleaners is drying.

Fe is mostly present in an oxidized form on the outermost surface already before the Fenton reaction takes place, as evidenced by the existence of a Fe 2p doublet located at 709.8 and 723.9 eV, which can be assigned to Fe$^{3+}$ (Figure 4C). It is plausible that the in situ generation of a Fe$_x$O$_y$ heterogeneous catalyst at the surface of the microcleaners reacts with hydrogen peroxide to yield a reactive oxidative species in the Fenton-like reaction after first use. In fact, the Fe 2p doublet is slightly shifted toward higher binding energies after 5 weeks of storage, indicating the presence of Fe$^{3+}$. According to the literature, the peak positions of Fe shift towards higher binding energies as the oxidation state of Fe increases. Although the difference in binding energy between the Fe$^{2+}$ and Fe$^{3+}$ oxidation states is very small (therefore, it is difficult to determine the relative amount of Fe$^{2+}$ and Fe$^{3+}$ in the microcleaners), it is clear that the surface becomes more oxidized as time passes. It should be noted that the shoulder observed at around 706 eV both before and after 5 hours of Fenton reaction, which can be attributed to metallic Fe (2p$_{3/2}$) weakens after 5 weeks. Hence, a complex mixture of iron oxides (FeOOH, Fe$_2$O$_3$, or Fe$_3$O$_4$) is probably present at the surface of the microcleaners after 5 weeks. Also, a slight shift in the Pt 4f doublet is observed after 5 weeks of Fenton reaction (Figure 4B). This might indicate oxidation of metallic Pt, but to a much lesser extent than Fe owing to the noble nature of Pt. Regarding the O 1s core-level spectra, a complex, broad signal with several maxima is observed (Figure 4D). After 5 hours of Fenton reaction the contribution from lattice O$_{2-}$ (529 eV) relatively increases, indicating again that the surface is more oxidized. Likewise, the peak at 530.7 eV has been attributed to non-stoichiometric oxides in the surface region (oxygen deficiencies). After 5 weeks, the O 1s signal was dominated by the contributions from hydroxyl groups. Moreover, the Fe/Pt ratio markedly
diminished after Fenton reaction: 1.51 before Fenton; 1.37 after Fenton for 1 h; 0.90 after Fenton for 5 weeks, indicating that Fe undergoes a leaching process, which is in agreement with the ICP analyses.

### 2.3. Mechanical Behavior of Fe/Pt Microcleaners

In order to assess the mechanical robustness and integrity of the microcleaners, nanoindentation experiments were performed on the rolled tubular microcleaners obtained from the 500 µm × 500 µm Fe/Pt films. Experiments were carried out i) before the Fenton reaction, ii) after 5 hours of Fenton reaction, and iii) after 5 weeks of storage.

**Figure 5A** (left panel) shows the applied load \( (P) \) versus penetration depth \( (h) \) curve of a microcleaner before the Fenton reaction (i.e., an unused microcleaner). The test revealed a smooth loading behavior up to a load of about 0.1 mN, where a pronounced pop-in (i.e., sudden displacement burst) could be observed. This displacement was associated with a cracking event of the material, which could further be verified through optical microscopy. The center panel of Figure 5A shows the image of the tubular microcleaner before indentation, whereas the right panel shows the same microcleaner after indentation. The arrows in the right panel indicate a layer of microcleaner that was chipped away during indentation and, most likely, corresponds to the cracking event shown in the left panel of Figure 5A. All other investigated microcleaners showed a similar behavior before Fenton reaction, accompanied by a certain barreling of the microcleaners.

A representative nanoindentation curve of the microcleaners after 5 hours of Fenton reaction is shown in Figure 5B (left panel). The maximum penetration depth attained after the Fenton reaction is smaller than before Fenton. Namely, \( h \) decreased from around 35 µm (before Fenton) to around 23 µm (after 5 hours), respectively. This means that the Fenton reaction induced an increase in strength of the microcleaners. Cracking events and exfoliation of the microcleaners were also seen to take place during the indentation tests performed after Fenton reaction, although only at loads close to 0.2 mN (see Figure 5B (center and right panel)). In summary, before Fenton reaction the microcleaners appear to be more ductile, with a higher attained penetration depth than after Fenton reaction for a given value of maximum applied load (compare Figure 5A and B). Both, before and after 5 hours of Fenton reaction, indentation tends to cause a certain barreling of the tubes (particularly before Fenton reaction), which in the end induces cracking and exfoliation of the outer shells of the tubes. As aforementioned, after 5 hours of Fenton reaction the microcleaners appear to be mechanically stiffer mainly because: i) tightening up, reducing the diameter of the microcleaner and increasing the number of layers (i.e., their thickness) and ii) the formation of iron oxides on the outer surface of the microcleaners as seen in the XPS analysis in Figure 4C.

**Figure 5C** shows the results of nanoindentation on a microcleaner after 5 weeks in storage. In this case, the penetration...
depth attained for an applied load of 0.2 mN was around 10 µm and no cracking events were observed for this maximum applied load. In order to assess whether exfoliation of the microcleaners took place at higher loads, we also performed nanindentation experiments with $P_{\text{Max}} = 1$ mN. As can be observed in Figure 5C (left panel), in this case a clear cracking event occurred around $P = 0.6$ mN. This critical load for cracking was therefore higher than the ones observed in Figure 5A and B, suggesting an increase in the mechanical resistance of the microcleaners with usage. Typical optical microscopy images of these tubes before and after indentation with $P_{\text{Max}} = 1$ mN are shown in Figures 5C (center and right panel, respectively).

Table 1 shows the energy analyses performed during indentation of the microcleaners for the three investigated conditions. Remarkably, the elastic recovery (i.e., the ratio between the elastic energy, $U_{\text{el}}$, and the total energy, $U_{\text{tot}}$) after 5 weeks of storage was clearly larger than before Fenton or after 5 hours of usage. Hence, from a mechanical point of view, the tubes were stronger after Fenton than before, as fracturing was clearly delayed and the elastic recovery was enhanced by more than a factor of 2 with respect to the as-prepared microcleaners before Fenton.

Additionally, nanoindentation finite-element simulations were performed using commercial software (ABAQUS) in order to shed further light on the mechanical performance of the microcleaners. The chosen geometry for the simulations was a cylinder with a wall-to-diameter aspect ratio similar to the investigated microcleaners before and after 5 hours of Fenton reaction. The mesh used during the simulations consisted of

Table 1. Summary of the elastic ($U_{\text{el}}$), plastic ($U_{\text{pl}}$), and total ($U_{\text{tot}}$) indentation energies for the microcleaners. The ratio $U_{\text{el}}/U_{\text{tot}}$ corresponds to the elastic recovery of the indented microcleaners.

| Tube                | Elastic energy $U_{\text{el}}$ [nJ] | Plastic energy $U_{\text{pl}}$ [nJ] | Total energy $U_{\text{tot}}$ [nJ] | $U_{\text{el}}/U_{\text{tot}}$ |
|---------------------|-------------------------------------|-------------------------------------|-----------------------------------|-------------------------------|
| Before Fenton       | 0.97                                | 2.71                                | 3.68                              | 0.26                          |
| After Fenton 5 h    | 0.46                                | 1.83                                | 2.29                              | 0.20                          |
| After Fenton 5 weeks| 2.13                                | 1.67                                | 3.80                              | 0.56                          |
fully integrated brick-shape elements, the Berkovich indenter was considered to be a perfectly rigid body, and the cylinders were perfectly elastic with a Young’s modulus equal to 200 GPa. The boundary conditions were chosen such as to prevent the vertical displacement of the cylinder during indentation. The von Mises yield criterion was used to study the differences in the mechanical performance of the microcleaners before and after 5 hours of Fenton reaction. The diameter of the microcleaners decreased after the reaction (Figure 6A,C) due to the tightening of the layers, likely because the pressure pulses generated during bubble development and release promoted the release of residual strain from the layers. The simulations revealed that the tube after Fenton reaction (Figure 6D) accumulated a higher stress directly beneath the indenter tip for a given applied load than the tube before Fenton reaction (Figure 6B), indicating that it is mechanically harder. Concomitantly, for a certain applied load, the overall deformation of the tube before Fenton reaction was higher than in the simulated tube after Fenton. The results of this simple simulation (which does not take into account the multiwalled structure of the microtubes) agreed qualitatively well with the experimental observations.

2.4. Degradation of Phenolic Compound

In order to demonstrate the remediation capabilities of microcleaners to other organic pollutants, we performed a degradation experiment for a phenolic compound (4-nitrophenol) using 500 µm microcleaners. 4-nitrophenol is one of the most common organic pollutant molecules present in industrial wastewater. Degradation of 4-nitrophenol is challenging using bacteria, yet hydroxyl radicals are capable of completely mineralizing it into carbon dioxide [57–59].

Figure 7 shows that using H₂O₂ as oxidant alone cannot degrade 4-nitrophenol, while micro-cleaners can degrade around 30% in 60 minutes. The difference in the percentage of degradation for malachite green and 4-nitrophenol is due to the different reaction kinetics of hydroxyl radicals for different organic molecules. Microcleaners degraded ≈18 µg of 4-nitrophenol in 10 minutes and ≈41 µg in 60 minutes from 3 mL of contaminated water containing 150 µg of initial amount (50µg mL⁻¹). A longer duration is required to achieve complete degradation, but the addition of larger amounts of microcleaners could achieve faster oxidation and even total degradation.

3. Conclusions

We demonstrated reusable, self-propelled Fe/Pt microcleaners that can carry out a Fenton-like reaction with high activity and without the need for external mixing. We found that the variation in the length of microcleaners does not affect the performance if the amount of catalytic material used is kept constant. The reusability results showed that the microcleaners can be recovered using magnets and reused for multiple times within a short duration of less than a week without any decrease in their organic-degradation performance. Even longer term storage for several weeks is possible without sacrificing much of the activity. The microcleaners can also be used for continuous swimming applications for at least 24 hours. Although the iron released into the treated water from the second cycle onwards was much less compared to that from the first cycle, the activity of the microcleaners remained constant. We observed that the surface of the microcleaners oxidized to produce in situ iron oxides that act as a heterogeneous catalyst. The formation of iron oxides along with the tightening of the rolled-up layers increased the mechanical strength of the microcleaners after the Fenton reaction. Degradation experiments of 4-nitrophenol
and malachite green proved the possibility of using microcleaners for wide range of organic pollutants. The experiments presented here evidence the long-term reusability of very active microcleaners, which will be beneficial towards lowering the cost of the water treatment using this advanced technology. Further experiments should be driven towards the remediation of other pollutants in real wastewater samples and in confined pipes or places difficult to reach by traditional methods.

4. Experimental Section

Fabrication of the Microcleaners: Microcleaners were fabricated by rolling up nanomembranes of iron and platinum metal deposited on square patterns of photoresist. Positive photoresist patterns (200 µm, 300 µm, and 500 µm) were developed using standard photolithography techniques. For this a positive photoresist (ARP 3510) was spin-coated (3500 rpm for 35 s) on previously cleaned glass wafers (18 mm × 18 mm) to make a layer with uniform thickness (2.4 µm) and exposed to UV light under a chromium mask with the respective sizes of the patterns confined in a 1 cm² area by a mask aligner. The photolithographic patterns on the glass substrates were developed (using 1:1 water/DMSO) and dried by blowing nitrogen before depositing the metal nanomembranes. A custom-built e-beam evaporator was used for the deposition. Two layers of iron (100 nm) were evaporated at different deposition rates (at 0.30 nm s⁻¹ and 0.06 nm s⁻¹ respectively); a third layer, this time of platinum (5 nm), was evaporated (at 0.02 nm s⁻¹) to make a layer with uniform thickness (2.4 µm) and exposed to UV light under a chromium mask with the respective sizes of the patterns confined in a 1 cm² area by a mask aligner. The photolithographic patterns on the glass substrates were developed (using 1:1 water/AR 300) and dried by blowing nitrogen before depositing the metal nanomembranes. A custom-built e-beam evaporator was used for the deposition. Two layers of iron (100 nm) were evaporated at different deposition rates (at 0.30 nm s⁻¹ and 0.06 nm s⁻¹ respectively); a third layer, this time of platinum (5 nm), was evaporated (at 0.02 nm s⁻¹). All three layers were deposited at a glancing angle (65°), which led to a non-deposited window in each pattern. The photoresist wall adjacent to the non-deposited window remained exposed which was required for the controlled directional rolling of the nanomembranes. A mixture of dimethyl sulfoxide (DMSO) and acetone (1:1) was used to selectively etch the photoresist from the exposed wall. The nanomembranes were rolled up from the side of the exposed wall to the unexposed wall in the shape of tubular microcleaners.

Size Effect, Reusability, and 4-Nitrophenol Degradation Experiments: Three different sizes of microcleaners (200 µm, 300 µm, and 500 µm long with a diameter ranging from 40–60 µm) were fabricated from the nanomembranes that were deposited on the photoresist patterns confined in the 1 cm² area on the glass substrate. The number of microcleaners rolled up from a constant amount of catalytic material present in a 0.64 cm² area (including all square patterns) was different for the different pattern sizes (around 1600, 729, and 256, respectively, for the different sizes in increasing order). After being rolled up, the microcleaners were first transferred into sodium dodecyl sulfate (SDS) water (0.5% w/v) and then used for the degradation experiments, carried out in a beaker containing a total of 3 mL of polluted water consisting of malachite green (50 µg mL⁻¹), hydrogen peroxide (15% v/v), and SDS (0.5% w/v) at an acidic pH (2.5). The dye concentration was measured using a spectrophotometer (Specord 250, Analytical Jena) at 0, 10, 30, and 60 minutes during the experiments to study the size effect. New batches of 500 µm micro-cleaners were fabricated and used to study the effect of hydrogen peroxide concentration (5%, 10%, 15%, 20% and 25%) on the degradation of malachite green in 60 minutes. Degradation of 4-nitrophenol (50 µg mL⁻¹) was carried out using 500 µm micro-cleaners in the same experimental condition used for malachite green degradation.

A different batch of microcleaners of all sizes was fabricated, using the same parameters that were used for the size-effect experiments, to study the reusability. All three sizes of microcleaners were reused both after short- and long-term storage. The short-term experiments were carried out at varying time intervals; first five cycles were carried out out at 1 to 5 hours continuously changing polluted water after the end of the 60 minutes of a degradation cycle. After the end of each cycle, the microcleaners were confined in a corner of the beaker using a strong neodymium-iron-boron hard magnet and the treated water was replaced with pure water (Millipore water) to clean the surfaces of the microcleaners, the cleaning step was repeated twice and then a new batch of polluted water solution was added for the next cycle. The composition of the polluted water was kept constant as in the size-effect experiments. After 5 hours, the microcleaners were cleaned and stored in SDS water (0.5% w/v) before using in the next cycles at 18 hours and 24 hours from the first cycle. In a similar way, long-term storage experiments were carried out using the same microcleaners after 1 week of intermediate storage between two cycles, and up to 5 weeks from the first cycle. The dye concentration after each cycle was measured using a UV–vis spectrophotometer. After each cycle, the treated water was collected and further analyzed by ion coupled plasma optical emission spectroscopy (ICP-OES) to measure the iron concentration that had leached out from the surface of the microcleaners.

Continuous Swimming and Video Recording: An upright microscope (Leica DFC300GC camera) was used to record the videos of the rolling-up of different sizes of microcleaners whereas an inverted microscope (Leica DMI300B) was used to study the swimming behavior of the microcleaners after each cleaning cycle. A custom-designed 3D-printed microscope stage was fabricated to record the swimming of the microcleaners directly in the beaker where the degradation experiment was going on. During the continuous swimming experiment, the microcleaners were observed under the inverted microscope at 1, 5, and 24 hours.

Surface Characterization: X-ray photoelectron spectroscopy (XPS) analyses were carried out on a PHI 5500 Multitechnique System (from Physical Electronics) spectrometer, equipped with a monochromatic X-ray source (KrAl line with an energy of 1486.6 eV and power of 350 W), placed perpendicular to the analyzer axis and calibrated using the 3d11/2 line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The analyzed area was a 0.8 mm diameter disk surface for each sample. All charging effects were corrected for by referencing the binding energies to that of the adventitious C 1s line at 284.5 eV.

Mechanical Properties: The microcleaners were dried using an ethanol–CO₂ critical point dryer before doing the nano-indentation experiments. Typical load-displacement measurements were conducted on the microcleaners before Fenton reaction, after 5 h of Fenton reaction and after 5 weeks. For the sake of simplicity, microcleaners obtained from the 500 µm × 500 µm Fe/PT layers were selected for the mechanical tests. These experiments were performed in a load-control mode, using a UMIS instrument from Fischer-Cripps Laboratories equipped with a Berkovich pyramid-shaped diamond tip. The maximum applied load values ranged between 0.2 mN and 1 mN. To ensure statistically meaningful results, at least 10 indentations were performed for each type of microcleaners and the representative average behavior is reported. The elastic (Uₑ) and plastic (Uₚ) energies during indentation were assessed from the areas enclosed between the unloading segment and the displacement axis (Uₑ) and between the loading and unloading segments (Uₑ). The total indentation energy is then Uₑ = Uₑ + Uₚ and corresponds to the area enclosed between the loading segment and the displacement axis. The ratio Uₑ/Uₑtot is related to the elastic recovery of the tubes after having been indented.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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