Metal-oxide based microjets for the simultaneous removal of organic pollutants and heavy metals

Katherine Villa†, Jemish Parmar‡†, Diana Vilela‡†, Samuel Sánchez*†, §

† Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology, Baldiri Reixac 10-12, 08028 Barcelona Spain
§ Institució Catalana de Recerca i Estudis Avancats (ICREA), Pg. Lluís Companys 23, 08010, Barcelona, Spain

ABSTRACT

Water contamination from industrial and anthropogenic activities is nowadays a major issue in many countries worldwide. To address this problem, efficient water treatment technologies are required. Recent efforts have focused on the development of self-propelled micromotors that provide enhanced micro-mixing and mass-transfer by the transportation of reactive species, resulting in higher decontamination rates. However, a real application of these micromotors is still limited due to the high cost associated to their fabrication process. Here, we present Fe$_2$O$_3$-decorated SiO$_2$/MnO$_2$ microjets for the simultaneous removal of industrial organic pollutants and heavy metals present in wastewater. These microjets were synthesised by low-cost and scalable methods. They exhibit an average speed of 485±32 µm s$^{-1}$ (~28 body length s$^{-1}$) at 7% H$_2$O$_2$, which is the highest reported for MnO$_2$-based tubular micromotors. Furthermore, the photocatalytic and adsorbent properties of the microjets enable the efficient degradation of organic pollutants such as
tetracycline and rhodamine B under visible light irradiation, as well as the removal of heavy metal ions such as Cd$^{2+}$ and Pb$^{2+}$.

KEYWORDS: micromotors; photocatalytic; water purification; Fenton; magnetic control; iron oxide; manganese oxide.

1. INTRODUCTION

Considerable research efforts are underway to develop highly efficient water treatment technologies that can mitigate water scarcity for millions of people.$^{1,2}$ These include using nanotechnology and nanomaterial-based methods to rapidly improve the water cleaning process due to their high specific surface area and excellent intrinsic properties.$^{3,4}$ Recently, self-propelled nano/micromotors have reported to speed up the removal of a wide variety of pollutants from water due to the enhanced mixing of the fluid around them.$^{5-9}$ Thus, micromotors have been employed for the removal of organic pollutants,$^{10-12}$ heavy metals,$^{13,14}$ bacterial contamination$^{15,16}$ and biological warfare agents.$^{17}$ Commonly, catalytic micro- and nanomotors use a fuel source such as hydrogen peroxide (H$_2$O$_2$) for self-propulsion, converting chemical energy into kinetic energy by decomposing the fuel catalyzed by precious metals such as platinum, silver or iridium.$^{18-22}$

Tubular micro- and nanomotors are usually fabricated by polycarbonate-template-assisted electrodeposition,$^{23}$ self-assembly of organic molecules$^{24,25}$ and rolled-up nanotechnologies.$^{26}$ These methods lead to micro- and nanomotors with a precise geometry and controlled shape. However, specialized equipment such as metal evaporators, cleanroom facilities for lithography process or electrochemical workstations is required to use these technologies.$^{27,28}$ Therefore, there is a need for the development of facile synthesis of micro- and nanomotors that involves only basic
and inexpensive equipment. Some efforts have been made to develop other simple methodologies for the synthesis of micro- and nanomotors, by using emulsions, microfluidics or by simple aggregation processes, but tubular motors cannot be obtained easily by such procedures. Our group has recently reported the fabrication of tubular mesoporous silica micromotors by sol-gel synthesis using a polycarbonate membrane as a template, which uses platinum as catalyst for the self-propulsion in H₂O₂. In order to reduce the cost associated with large-scale micromotors synthesis and solve platinum poisoning under harsh chemical environments, micromotors based on metal oxide catalysts have previously been proposed as inexpensive materials for the propulsion of micromotors, but the resulting speeds are still too low.

Previous research has demonstrated the potential of combining the self-propulsion of micromotors with advanced oxidation processes (AOPs) such as Fenton reactions and photocatalysis for environmental remediation. Photocatalytic processes are environmentally-friendly and offer the possibility of using solar radiation as the main energy source, which significantly decreases the cost of water treatments. Considering that the visible region is one of the major components of solar irradiation, the development of photocatalytic and Fenton-like micromotors that can harvest solar irradiation to remove different kind of pollutants has the potential to advance micromotors-based water cleaning methods.

Here, we present multifunctional mesoporous silica-based microjets with MnO₂ immobilized on the inner surface and decorated with γ-Fe₂O₃ nanoparticles (NPs) (band gap of ~2.0 eV) as magnetic photocatalyst on the outer surface, hereafter called FeSiMnOₓ microjets (Fe₂O₃/SiO₂-MnO₂ microjets). FeSiMnOₓ microjets are fabricated by growing silica tubes on a polycarbonate template by sol-gel method. The immobilized MnO₂ and Fe₂O₃ catalysts act as functional materials for both propulsion and removal of pollutants. Furthermore, the FeSiMnOₓ microjets are
magnetically steered and guided in a controlled manner, facilitating their recovery and further reuse.

2. EXPERIMENTAL SECTION

2.1. Synthesis of microjets

Mesoporous silica (SiO$_2$) microtubes were obtained using a polycarbonate membrane (Whatman, conical-shaped micropores with 2 μm diameter) as the template, and a mixture of tetraethyl orthosilicate (TEOS, ≥99.0% (GC), Sigma-Aldrich), hexadecyltrimethylammonium bromide (CTAB, BioUltra ≥99.0%, Sigma-Aldrich), 3-aminopropyltriethoxysilane (APTES, 99.0%, Sigma-Aldrich) and triethanolamine (TEOA, ≥99.0 %, Sigma-Aldrich), as described in a previous work reported by our group.$^{34}$ These SiO$_2$ microtubes were used as the scaffold for the micromotors. Once the mesoporous silica tubes were grown inside the membrane, it was placed in 30 mL of 10mM KMnO$_4$ (ACS reagent ≥99.0%, Sigma-Aldrich) and transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 9 h. Afterwards, the black resulting membrane was polished with water to remove the excess of MnO$_2$. The SiO$_2$-MnO$_2$ microtubes were released by dissolving the membrane template in CH$_2$Cl$_2$ (GPR RECTAPUR, VWR) for 15 min and then washing them twice for 3 min with CH$_2$Cl$_2$, ethanol and water, respectively.

To optimize the MnO$_2$ filling inside the silica tubes, different KMnO$_4$ loadings of 10, 20 and 30 mM were tested. The best swimming behavior was observed in MnO$_2$-based microtubes synthesized with 10 mM of KMnO$_4$, thus being this concentration of KMnO$_4$ selected as the optimal concentration for our fabrication protocol.
Finally, the surface of SiO$_2$-MnO$_2$ microtubes was functionalized with $\gamma$-Fe$_2$O$_3$ (Maghemite, nanopowder <50 nm, Sigma-Aldrich) by mixing them with 1 mL of an ethanolic suspension containing 0.001 g of $\gamma$-Fe$_2$O$_3$ nanoparticles (NPs) for 6 h. After this, the Fe$_2$O$_3$/SiO$_2$-MnO$_2$ microtubes were separated from the NPs by filtering the suspension with a 2 μm pore size membrane (Whatman), and then they were washed several times with ethanol and water, respectively.

For the sake of simplicity, the Fe$_2$O$_3$/SiO$_2$-MnO$_2$-based microtubes have been labelled as FeSiMnO$_x$ microjets, SiMnO$_x$ microjets (without Fe$_2$O$_3$) or FeSiO$_x$ microtubes (without MnO$_2$).

2.2. Microjets characterization

A JEOL JEM-2100 LaB$_6$ microscope operating at 200 kV accelerating voltage and equipped with an Oxford Instruments INCA x-sight (Si(Li) detector) and a Zeiss SESAM microscope (200kV) equipped with an EDS System from ThermoFisher were used to perform transmission electron microscopy (TEM) and Energy-dispersive X-ray (EDX) analysis. Scanning Electron Microscopy (SEM) images were taken on a FEI NOVA NanoSEM 230 microscope. Surface charge of $\gamma$-Fe$_2$O$_3$ NPs was examined by Dynamic Light Scattering (DLS, Wyatt Möbius coupled with an Atlas cell pressurization system). The motion of microjets was observed and recorded by using an inverted optical Microscope (Leica DMI 3000 B) equipped with a camera (Leica DFC 3000 G) with LAS V4.5 software. For recording of the videos, 10 μl of microjets suspension was placed onto a glass slide and 0.2 wt% of sodium dodecyl sulfate (SDS, ACS reagent ≥99.0%, Sigma-Aldrich) was added in the presence of different concentrations of H$_2$O$_2$. The speed and tracking of microjets was calculated from the recorded videos and analyzed using openCV libraries and Python-based software.
The magnetic control setup consists of two pairs of coils in Helmholtz configuration, which create a magnetic field gradient in, respectively, the X and Y directions. Cylindrical steel rods are put inside the coils to increase the strength field. The intensity of the gradient is controlled remotely through an Arduino microcontroller, whose current is amplified using a TS250 Wave Amplifier. A Python script with an user interface is used to send orders to the Arduino in real time, allowing total control of the magnetic field from a PC. The gradient per unit of electric current created by the coils for each pair is 18 G (A·mm)$^{-1}$. During the magnetic control experiments, a maximum current of 2.5 A was used.

2.3 Photocatalytic set-up

The photocatalytic degradation of aqueous solutions of rhodamine (RB) and tetracycline (TC) was carried out in a 5 mL cylindrical glass vessel. For the photocatalytic experiments, a 300 W high pressure UV-visible lamp (Ultravitalux Osram, 280-780 nm) was used as light source. A polyester UV filter sheet (Edmund Optics) was used to remove wavelengths radiation below 400 nm and to ensure only visible irradiation. In all degradation experiments, 1 mL of RB (10 ppm) or TC (50 ppm) solution containing 0.3 mg of microjets was placed in the vessel with 0.2 wt% SDS as surfactant. No acidic or basic pH adjustments were performed during the photocatalytic tests.

Prior to illumination, the microjets were kept in the dark for 30 min to reach adsorption-desorption equilibrium on their surface. In this way, the decrease in the absorbance signal of the pollutants due to adsorption can be ruled out in the degradation experiments. After that, the lamp was turned on and 5 wt% H$_2$O$_2$ was added to initiate the reaction. Liquid aliquots were periodically taken out during the reaction (before the absorbance measurements, the solids were removed by centrifugation in the case of SiMnO$_x$ microjets or by a magnet in the case of FeSiMnO$_x$ and FeSiO$_x$
microjets). They were then immediately analyzed by measuring their absorbance at 555 nm and 358 nm for RB and TC respectively, using a UV-Vis spectrophotometer (Specord 50 plus).

Control experiments without microjets (only H$_2$O or H$_2$O$_2$ + light irradiation) were also performed to evaluate the contribution of the photolysis of H$_2$O$_2$ on the oxidation of our target pollutants. Additionally, a test with non-filled FeSiO$_x$ microtubes (without MnO$_2$) in the presence of H$_2$O$_2$ under light irradiation was also carried out to investigate the influence of the motion of microjets on the resulting photocatalytic performance.

2.4 Heavy metals removal

In order to prove the capability of FeSiMnO$_x$ microjets to capture heavy metals, 0.3 mg of the microjets was added to 1 mL of a water solution, which contained 1 ppm of lead (Pb$^{2+}$) and cadmium (Cd$^{2+}$), in the presence of another contaminant (10 ppm of RB). After allowing the FeSiMnO$_x$ microjets to swim for 7 and 15 min in the previously prepared solution, the concentration of both heavy metals was determined at both time intervals by square wave voltammetry using a mercury-coated glassy carbon electrode (GCE)$^{46}$ as working electrode. Prior to the measurements, any trace of H$_2$O$_2$ was removed by adding an excess of 1 M sodium bisulfite solution to avoid any interference in the electrochemical signals. First, the mercury film was pre-plated at the beginning from a non-deaerated 80 mg L$^{-1}$ mercury solution (in 0.02 M HCl), by holding the carbon strip electrode at $-1.15$ V for 15 min. Then, the potential was switched to $-0.20$ V for a 2 min cleaning period. The subsequent cycles involved the Pb$^{2+}$ and Cd$^{2+}$ deposition (3 min of preconcentration at $-1.15$ V) and stripping steps (from -1.15V to -0.2V). Before the next measurement, the electrode is maintained for 60 s at -0.2 V to ensure that Pb and Cd do not remain on the working electrode surface. After finishing the measurement of heavy metals, the mercury
film is removed from the GCE by holding it at +0.4 V for 5 min. An acetate buffer 0.02 M solution (pH 4.8) was used as electrolyte during the sensing of the heavy metals, the intermediate steps and the removal of the mercury film from the GCE.

The linear range was between 0.01–0.1 ppm for Pb$^{2+}$ ($A_{\text{peak}}=1.086+0.027[\text{Pb}^{2+}]$, $r=0.980$) and Cd$^{2+}$ ($A_{\text{peak}}=0.04255+0.01405[\text{Cd}^{2+}]$, $r=0.990$), respectively. To measure the concentration of Pb$^{2+}$ and Cd$^{2+}$ ions from the assay solution, a dilution 1:10 (total volume 5 mL, 0.02 acetate buffer solution) was carried out, before and after the removal of both ions by the FeSiMnO$_x$ microjets.

3. RESULTS AND DISCUSSION

FeSiMnO$_x$ microjets were synthesized by facile and scalable procedures as shown in Figure 1. The tubular structure was achieved by using a polycarbonate (PC) membrane as template and a mixture of SiO$_2$ precursors at 80 ºC. Then, 10 mM KMnO$_4$ was reduced to MnO$_2$ inside the pores of the membrane by a hydrothermal reaction. After releasing the tubes from the PC membrane, $\gamma$-Fe$_2$O$_3$ NPs were mixed with SiO$_2$-MnO$_2$-based microtubes and attached to their outer surface. The final tubular structure consists of a biconical mesoporous silica tube with MnO$_2$ inner layer and $\gamma$-Fe$_2$O$_3$ NPs on the outer surface (Figure 1).
Figure 1. Chemical fabrication of mesoporous Fe$_2$O$_3$/SiO$_2$-MnO$_2$ (FeSiMnO$_x$) microjets for the photocatalytic degradation of organic pollutants and removal of heavy metals.

The structural and morphological characterization of the microjets was carried out by TEM-EDX-mapping and SEM, respectively (Figure 2). The SEM images show that the microjets have a tubular biconical structure (see blue inset) with a length of about 17 µm (Figure 2A). The length of the microjet is co-related with the thickness of the PC membrane (20 µm) used for the synthesis process. The TEM image in Figure 2B shows a color contrast along the SiMnO$_x$ tube due to the non-homogeneous dispersion of MnO$_2$ on the inner surface (as evidenced by the TEM mapping of several tubes, see SI Figure S1). This heterogeneity in the inner surface of the microjets may result in several nucleation points for bubble growth, which can be beneficial for the microjets motion. After the modification of the outer surface of the SiMnO$_x$ microjets with γ-Fe$_2$O$_3$ NPs, it is observed that the γ-Fe$_2$O$_3$ NPs are distributed along the surface (Figure 2C and red dotted inset) and on the edges of the cavity of the FeSiMnO$_x$ microjets (see blue square inset in Figure 2C). Figure 2D displays the rough outer surface of the FeSiMnO$_x$ microjets. This results from the
adherence of $\gamma$-Fe$_2$O$_3$ NPs to the silica surface, due to the electrostatic interaction between the external $-\text{NH}_2$ groups from the SiO$_2$ tubes surface and the negative charge of $\gamma$-Fe$_2$O$_3$ NPs ($-7.43 \pm 1.53$ mV, average $\pm$ standard error of mean, $n = 6$) measured by DLS. As observed in Figure 2E, these $\gamma$-Fe$_2$O$_3$ NPs have a diameter size ranging from 20-50 nm. The TEM-EDX spectrum confirms the presence of Si, Fe and Mn in FeSiMnO$_x$ microjets (Figure 2F). Furthermore, EDX mapping and the profile analysis of the tubes for the different elements show the distribution of Mn in the tubes and the dispersion of Fe$_2$O$_3$ NPs along their surface (Figure 2G and 2H).

**Figure 2.** Characterization of FeSiMnO$_x$ microjets. A) SEM image of the SiMnO$_x$ microjet, inset
corresponding to the cavity of the tube, B) TEM image of the SiMnO₅ microjet, C) SEM image of the FeSiMnO₅ microjet, blue solid inset corresponding to the tube cavity and red dotted inset corresponding to γ-Fe₂O₃ NPs on the outer surface, D) TEM image of the FeSiMnO₅ microjet, E) Magnification of the red dotted lines in Figure 2D, F) EDX spectrum of the FeSiMnO₅ microjet, G) EDX mapping of the FeSiMnO₅ microjet and H) element profile of the FeSiMnO₅ (represented by a red dotted line).

The mechanism of propulsion of FeSiMnO₅ microjets is based on the catalytic decomposition of H₂O₂ into water and oxygen gas by MnO₂, leading to the generation of microbubbles in their cavity. The motion capabilities of FeSiMnO₅ and SiMnO₅ microjets were examined using an optical microscope. To find out the relation between MnO₂ loading and motion of SiMnO₅ microjets, different concentrations of KMnO₄ (10-30 mM) were studied. As shown in Figure S2, an increase of KMnO₄ concentration (>10 mM) resulted in a total blockage of the internal holes of the microjets (Figure S2B-C) and/or rupture of the tubular structure in half (Figure S2C). As a result, not all the microtubes were swimming (Video S1), and if they were their speed was very low (Video S2). Therefore, 10 mM KMnO₄ was selected as the optimal concentration for the synthesis of SiMnO₅ and FeSiMnO₅ microjets.

Figure 3A shows the motion behavior of SiMnO₅ and FeSiMnO₅ microjets in 5 wt% H₂O₂ and 0.2 wt% of SDS (Video S3 and S4, respectively). Both microjets display directional trajectories, but FeSiMnO₅ microjets show a faster speed than SiMnO₅. This improvement in the speed of FeSiMnO₅ microjets is related to the presence of γ-Fe₂O₃ NPs, which can also catalyze the decomposition of H₂O₂ into O₂ gas through a series of complex reactions. Recently, we found that free iron-based NPs do not exhibit bubble propulsion in the presence of H₂O₂, but once they become a cluster they can self-propel by releasing bubbles from the cavities of the cluster and the
rough surface. Therefore, the agglomeration of γ-Fe₂O₃ NPs on the tubes surface might be beneficial for the enhancement of the propulsion of FeSiMnOₓ microjets.

**Figure 3B** illustrates the speed of SiMnOₓ and FeSiMnOₓ microjets at different H₂O₂ concentrations (1, 3, 5 and 7 wt%). The speed of the jets increases by increasing the fuel concentration, reaching the highest values at 7 wt% H₂O₂ of 165±13 µm s⁻¹ and 485±32 µm s⁻¹ for SiMnOₓ and FeSiMnOₓ microjets respectively. FeSiMnOₓ microjets are almost 3 times faster than the bare SiMnOₓ, swimming at approximately 28 body length s⁻¹ at 7 wt% H₂O₂. As depicted in **Table 1**, the speed showed by FeSiMnOₓ microjets is the highest reported so far for tubular micromotors propelled by non-metallic catalysts. The trajectories of the SiMnOₓ and FeSiMnOₓ microjets are shown in **Figure 3C**. It was observed that FeSiMnOₓ and SiMnOₓ microjets move randomly following helical or straight paths.
**Figure 3.** Motion characterization of FeSiMnO₉ microjets. A) Optical images of the trajectories of SiMnOₓ and FeSiMnOₓ microjets swimming for 2 s at 5 wt% H₂O₂, B) speed of the SiMnOₓ and FeSiMnOₓ microjets at different H₂O₂ concentrations (n=5, error bars represent the standard error of the mean) and C) Swimming trajectories of SiMnOₓ and FeSiMnOₓ microjets at 5 wt% H₂O₂.

**Table 1.** Speed comparison of different micromotors propelled by non-metallic catalysts.

<table>
<thead>
<tr>
<th>Materials in micromotors</th>
<th>Shape</th>
<th>[H₂O₂] (% wt)</th>
<th>Speed (μm s⁻¹)</th>
<th>Approximate body length (μm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT/MnO₂</td>
<td>Tube</td>
<td>5</td>
<td>200±80</td>
<td>16</td>
<td>35</td>
</tr>
<tr>
<td>Fullerene-MnO₂</td>
<td>Tube</td>
<td>5</td>
<td>39±5</td>
<td>---</td>
<td>49</td>
</tr>
<tr>
<td>MnO₂</td>
<td>Amorphous</td>
<td>12</td>
<td>~50</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>Graphene/MnO₂</td>
<td>Tube</td>
<td>5</td>
<td>210.4±80.4</td>
<td>21</td>
<td>51</td>
</tr>
<tr>
<td>Graphene/MnO₂</td>
<td>Alveolate</td>
<td>2.5</td>
<td>47.92</td>
<td>7.4</td>
<td>52</td>
</tr>
<tr>
<td>PEDOT/MnO₂</td>
<td>tube</td>
<td>6</td>
<td>~125</td>
<td>15.6</td>
<td>53</td>
</tr>
<tr>
<td>MOF/Co</td>
<td>Amorphous</td>
<td>5</td>
<td>~25</td>
<td>5</td>
<td>54</td>
</tr>
<tr>
<td>MOF/Mn</td>
<td>Amorphous</td>
<td>5</td>
<td>~12</td>
<td>2.4</td>
<td>55</td>
</tr>
<tr>
<td>MnFe₂O₄</td>
<td>Hollow sphere</td>
<td>2</td>
<td>~260</td>
<td>11</td>
<td>30</td>
</tr>
<tr>
<td>Fe₂O₃/SiO₂/MnO₂</td>
<td>Tube</td>
<td>5</td>
<td>380.8±38.7</td>
<td>22.4</td>
<td>This work</td>
</tr>
</tbody>
</table>

The presence of γ-Fe₂O₃ NPs provides magnetic properties to the FeSiMnOₓ microjets. Taking into account the intended use of microjets for water cleaning, magnetic properties add beneficial functionality for guiding their swimming direction and for their removal by an external magnet after the cleaning treatment,¹³,⁵⁶ avoiding further water contamination by the catalyst itself, which is one the key issues in water treatment.⁸ Moreover, the magnetic properties of FeSiMnOₓ would
allow to magnetically guide them towards polluted areas that are difficult to access. More importantly, once the different kind of pollutants are removed, the microjets could be guided\textsuperscript{13} or transferred\textsuperscript{56} to another container for further decontamination processes. Figure 4A-B displays the snapshots of the microjets without and with magnetic control, respectively. The orientation of the microjets was randomly distributed in the absence of a magnetic field (Figure 4C). After applying the magnetic field, most of the microjets were aligned and following the instructed direction (downward), even in the presence of massive bubbling (Figure 4D, Video S5). As can be seen from Figures 4E, after applying the magnetic field, the direction of FeSiMnO\textsubscript{x} microjets can be also changed instantly from left to right (Figure 4E, Video S6).
Figure 4. Magnetic control of FeSiMnO\textsubscript{x} microjets. A) A snapshot from a video of FeSiMnO\textsubscript{x} microjets swimming with random orientation, B) A snapshot from a video of FeSiMnO\textsubscript{x} microjets with their orientation controlled by magnetic guidance (downward), C) Distribution of orientation of micromotors without magnetic field (n=100), D) Distribution of orientation of micromotors in the presence of magnetic field along Y axis (n=100) and E) Optical snapshot from a video of FeSiMnO\textsubscript{x} microjets controlled by magnetic guidance (left and right).

The photocatalytic performance of the FeSiMnO\textsubscript{x} microjets was evaluated upon the degradation of TC and RB (chosen as model pollutants from the pharmaceutical and dye industries, respectively). These kinds of pollutants are known as refractory organic compounds, being very difficult to remove by the classical wastewater treatments. Thus, the design of novel catalytic systems is essential for the efficient degradation of these refractory pollutants.

Firstly, to evaluate the photocatalytic performance of FeSiMnO\textsubscript{x} microjets, control experiments without microjets were carried out. To this end, the contribution of H\textsubscript{2}O\textsubscript{2} (in the dark) and H\textsubscript{2}O\textsubscript{2} plus visible irradiation was studied in the degradation of the above-mentioned pollutants. As can be seen in Figures 5A-B, both controls are only degrading 10% and 30% of TC and RB, respectively, after 15 min of treatment. In addition, enhanced degradation rates of both pollutants were not observed after visible irradiation in the presence of H\textsubscript{2}O\textsubscript{2} and without micromotors.

The photocatalytic experiments were then performed in the presence of microjets. As it is observed in Figure 5A and 5B, the degradation rates were markedly improved in comparison with the control tests, following an increasing trend: FeSiMnO\textsubscript{x} > SiMnO\textsubscript{x} > FeSiMnO\textsubscript{x} (in the dark) > FeSiO\textsubscript{x} microtubes. Since FeSiO\textsubscript{x} microtubes (without MnO\textsubscript{2}) do not present self-propulsion, the slight degradation performance was due to the photocatalytic properties of Fe\textsubscript{2}O\textsubscript{3} NPs on the
surface of FeSiOₓ microtubes. In the case of SiMnOₓ microjets, MnO₂ can act as a dual catalyst for the decomposition of H₂O₂ to generate O₂ bubbles for the motion but also for the degradation of organic pollutants via Fenton-like reaction. However, as shown in Figure 5A and 5B, the resulting performance is much slower than the one obtained with the FeSiMnOₓ microjets.
Figure 5. Removal of contaminants in wastewater over FeSiMnO$_x$ microjets after 15 min of reaction. A) C/C$_0$ kinetics of photocatalytic degradation of TC, B) C/C$_0$ kinetics of photocatalytic degradation of RB, C) Removal of lead and cadmium by adsorption on FeSiMnO$_x$ microjets in presence of 10 ppm RB at 0 min (black) after 7 min (blue) and 15 min (red) of reaction.

The fast degradation activity shown by FeSiMnO$_x$ microjets is mainly due to the efficient photocatalytic performance exhibited by $\gamma$-Fe$_2$O$_3$ NPs on the surface of the microjets, along with the catalytic properties of MnO$_2$ on the inner surface. When the degradation reactions were carried out in the presence of FeSiMnO$_x$ microjets and H$_2$O$_2$ under dark conditions (Figures 5A and 5B), the removal yield was much lower than FeSiMnO$_x$ microjets under visible light irradiation.

The mechanism of the photocatalytic degradation of RB and TC involves the activation of $\gamma$-Fe$_2$O$_3$ photocatalyst with visible irradiation to generate electron-hole pairs. These photogenerated pairs can migrate to the catalyst surface and react with the adsorbed molecules to produce hydroxyl (HO$^*$) and superoxide (O$_2^{-}$) radicals.$^{59-61}$ Given the high oxidation potential of these radicals,$^{62}$ they can perform the total degradation of the organic matter (pollutants) to non-harmful molecules (CO$_2$ and water). At the same time, MnO$_2$ can also produce additional HO$^*$ radicals through the Fenton-like reaction in the presence of H$_2$O$_2$,$^{57,63-66}$ resulting in an enhancement of the total oxidation of the organic pollutants.

Finally, to prove that FeSiMnO$_x$ microjets are capable of removing other types of contaminants, we selected Cd$^{2+}$ and Pb$^{2+}$ as model pollutants of toxic heavy metals. Taking advantage of the interactions between Fe$_2$O$_3$ NPs and heavy metals$^{67,68}$, we used FeSiMnO$_x$ microjets for the removal of Cd$^{2+}$ and Pb$^{2+}$ in the presence of another pollutant, such as RB. Figure 5C illustrates the results corresponding to the capture of both heavy metals after 7 and 15 min of treatment with
0.3 mg FeSiMnO₃ microjets in 5% H₂O₂. It was observed that FeSiMnO₃ microjets were able to remove more than 98% and 94% (n=3) of Cd²⁺ and Pb²⁺, respectively, from a contaminated water with 1 ppm of each metal. Thus, we demonstrated that FeSiMnO₃ microjets can be used for the efficient remediation of several classes of contaminants, such as antibiotics, dyes and heavy metals in wastewater.

4. CONCLUSIONS

In conclusion, we have developed highly efficient FeSiMnO₃ microjets for multifunctional environmental applications, such as the degradation of persistent organic pollutants under visible irradiation and the removal of heavy metals from wastewater. The microjets can be easily guided and extracted using a magnetic field. Remarkably, FeSiMnO₃ microjets exhibited the highest speed (485±32 µm s⁻¹) that has been obtained so far for tubular micromotors powered by non-noble metals such as MnO₂. The synthesis of microjets was carried out using only chemical methods and simple apparatus, which is an advantage for their eventual mass-production. The strategy of combining two metal oxides (Fe₂O₃/MnO₂) that are able to decompose H₂O₂ with simultaneous generation of hydroxyl radicals resulted in a significant improvement in the photocatalytic performance of the microjets. This approach opens up new inexpensive alternative methods to fabricate other types of metal-oxide based microjets and microtubular structures for different applications in the environmental field.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Figure S1. TEM EDX-Mapping images of different SiMnO₃ microjets (file type, Word)
Figure S2. SEM characterization of SiMnO\textsubscript{x} microjets synthesized with different KMnO\textsubscript{4} concentrations (file type, Word)

Video S1. Motion of SiMnO\textsubscript{x} microjets (20 mM KMnO\textsubscript{4}).
Video S2. Motion of SiMnO\textsubscript{x} microjets (30 mM KMnO\textsubscript{4}).
Video S3. Motion of SiMnO\textsubscript{x} microjets.
Video S4. Motion of FeSiMnO\textsubscript{x} microjets.
Video S5. Magnetic control (downward direction).
Video S6. Magnetic control (left and right direction).

AUTHOR INFORMATION

Corresponding Author

* Phone: +34 934 020 558; email: ssanchez@ibecbarcelona.eu

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

£ These authors contributed equally.

Acknowledgments

The research leading to these results has received funding from the European Research Council under the European Union’s Seventh Framework Program (FP7/20072013)/ERC grant agreement no. 311529 (LT-NRBS) and ERC-2015-PoC/Project ID: 713608 (MICROCLEANERS). S.S. thanks the Spanish MINECO for grants CTQ2015-68879-R (MICRODIA). D. V. acknowledges
financial support provided by the European Commission under Horizon 2020’s Marie Skłodowska-Curie Actions COFUND scheme [Grant Agreement No. 712754] and by the Severo Ochoa programme of the Spanish Ministry of Economy and Competitiveness [Grant SEV-2014-0425 (2015–2019)]. IBEC group thanks the CERCA Programme / Generalitat de Catalunya. The authors thank the Stuttgart Center for Electron Microscopy (StEM) and the support of Mr. Kersten Hahn in the TEM and EELS investigations. The authors thank A. Miguel-López for the development of the magnetic control setup and the Python-based software for the tracking of micromotors.

REFERENCES


