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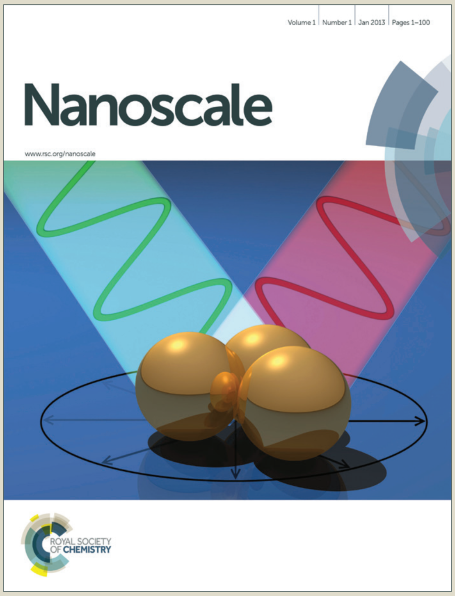

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Catalytic Nanomotors for Environmental Monitoring and Water Remediation

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Self-propelled nanomotors hold considerable promise for developing innovative environmental applications. This review highlights the recent progress in using self-propelled nanomotors for water remediation and environmental monitoring applications as well as the effect of the environmental conditions on the dynamics of nanomotors. Artificial nanomotors can sense different analytes -and therefore pollutants, or "chemical threats"-, can be used for testing the quality of water, can remove oil selectively, and alter their speed depending on the presence of some substances present in the solution where they swim. Newly introduced micromotors with double functionality to mix liquids at the microscale and enhance chemical reactions for the degradation of organic pollutants greatly broadens the range of applications to environmental applications. These "self-powered remediation systems" could be seen as a new generation of "smart devices" for cleaning water in small pipes or cavities difficult to reach with traditional methods. With constant improvement and taking into account the key challenges, we expect that artificial nanomachines could play an important role in environmental applications in the near future.

1. Introduction

Pollution of water by contaminants and chemical threats is a prevalent topic in the scientific, economic, political and consequently in the public media. The problems related to clean and safe water affect to millions of people around the world as the number of contaminants originating from human activity is increasing over the last years. Some examples are heavy metals, industrial products or chemicals such as solvents, additives or lubricants, personal consumer's products such as detergents or pharmaceuticals, or pesticides.[1] Altogether cause problems that can range from contamination of drinking water to endocrine effects, bacterial resistance and definitely human health problems.

Researchers and engineers are devoting considerable efforts to produce more efficient technological solutions to clean pollutants with lower-cost and energy consumption -sustainable-, large spectrum of detoxified chemicals, long-life activity, minimize the addition of extra contaminant/chemicals that would endanger human health by the treatment itself and ideally able to reach remote locations where standard methods are not capable to do so.[2]

The search of natural/green engineering methods for reducing the energy and chemical usage, together with clean by-products is sought after. For example, some ideal candidates for the next generation of water treatment are those able to remove pathogens, chemical threats, active transport of molecules, move ions against concentration gradients, separate compounds in complex media or deactivate chemical agents. Nanoparticles have been recently proposed as an alternative to improve or substitute standard filtration methods.[3] Unfortunately, some limitations still exist such as the recovery of the particles from the solution after water treatment, motivating the use of "smart" materials such as magnetically-responsive nanoparticles, like those named nanoscavengers.[4] Those magnetic-core nanoparticles contain antiferromagnetic core layers enabling the fast collection (less than 5 min) with a permanent magnet and enable the removal of contaminations from water. However, the transport of ions and the non-active nature of these nanoparticles may be a downside since, for high active remediation, external energy would still be needed and also those nanoparticles cannot transport ions and pollutants from one place to another.

Catalytically powered micro- and nano-motors have attracted a lot of attention over the last few years in multidisciplinary fields of chemistry and physics.[5] Since the pioneering works a decade ago, synthetic nanomotors demonstrated the ability to efficiently convert chemical energy into motion like nature uses biochemistry to power biological motors.[6, 7] Not only fundamental research is being conducted in this field, but also interesting applications are opening up in several different directions, such as biomedical[8] and more recently in the environmental field.[9, 10] Several approaches have been proposed to efficiently propel and accurately control micro- and nanomotors by different mechanisms.[11-18] Self-propulsion of catalytic micromotors has been mainly demonstrated in the presence of hydrogen peroxide (H_2O_2) fuel, which decomposes into water (H_2O) and oxygen (O_2).[14, 19-26] Nevertheless, there are also a diversity of mechanisms to power micro and nanomotors, for instance photoinduced motion,[27-29] electromagnetic fields,[30-32] local electrical fields,[33] thermal gradients,[34, 35] Marangoni effect,[36] ultrasound[37, 38] or biohybrid motion.[39, 40]

Although several groups are aiming for sing the use of catalytic nanomotors in the biomedical field, up to now, the reduced biocompatibility of the fuel employed so far for locomotion (H_2O_2 and/or hydrazine) still limits their realistic use. Enzymes decomposing other chemical fuels to generate either gradient of reactants and products around the nanomotors or gas generation, may be a good option that still needs to be further developed. Alternatively, two options are proposed, either to use bio-friendly powering methods which must be compatible with biological fluids, e.g. magnetic or ultrasound propulsion, or finding applications for catalytic nanomotors where the fuel employed does not limit their use. Among the latter option, environmental applications might be an important field to explore, where the use of hydrogen peroxide in particular is not controversial, and sometimes employed as co-reagent. In this review, we summarize recent progress toward environmental applications of micro- and motors and highlight crucial challenges for opening up a variety of new applications in the field (Fig. 1).

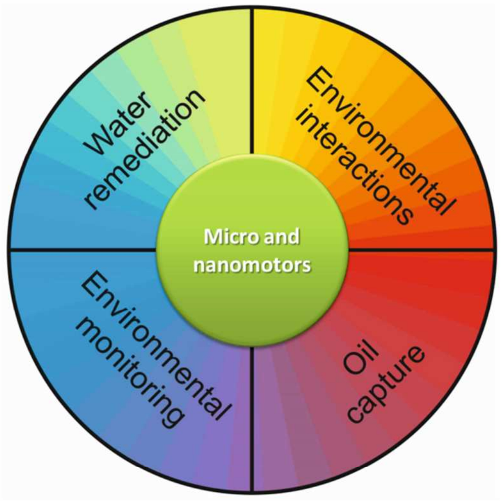

Fig. 1. Environmental applications of micro and nanomotors.

2. Environmental monitoring using nanomotors

Earlier last year, nanomotors demonstrated capabilities to detect and sense the quality of the water where they swim. For instance, Orozco et al. described artificial enzymatic micromotors for water quality testing.[41] The biocatalytic decomposition of the hydrogen peroxide fuel takes place at the inner enzymatic catalase layer of the microtube, generating oxygen bubbles as previously reported by Sanchez et al.[42] In the presence of enzyme inhibitors (heavy metals, sodium azide) the bubble frequency decreases and the change of motility of the artificial microfish is directly correlated to the concentration of pollutant (Fig. 2 A). A very recent publication from Moo et al. reported the specific response to Pb^{2+} in water compared to Cd^{2+}, using enzyme-free Cu/Pt bimetallic microtubular motors.[43] The authors take advantage of the different adsorption of those heavy metals on the catalytic Pt layer, i.e. Pb^{2+} is strongly adsorbed on platinum whereas Cd^{2+} presents weaker interaction. Consequently, Pt-based microjets are more sensitive to the poisoning with Pb^{2+} than with Cd^{2+} resulting in a different drop of the speed of the micromotors.

Pumera and co-workers reported the use of micromotors to sense the presence of certain molecules in the aqueous

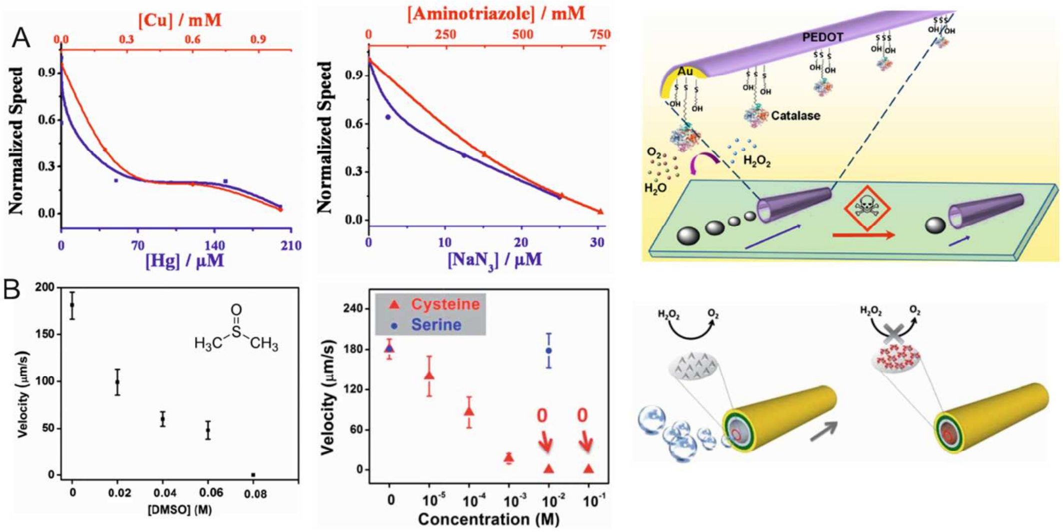

Fig. 2. Nanomotors as active self-powered sensors (A): Changes in the swimming behavior of the artificial micromotor (microfish) as a function of concentration upon 2 min exposure to Hg, Cu, sodium azide and aminotriazole. The solution contains 5% sodium cholate (NaCh), and 2% hydrogen peroxide (H_2O_2). Reprinted with permission from ref.41. Copyright 2013 American Chemical Society. (B): Influence of the concentration of DMSO, Cysteine and Serine on the velocities of the microjets. Tracking data were obtained for a timescale of 10 seconds from 5 independent running experiments in order to get the average speed. The solution contains 1% sodium dodecyl sulfate (SDS), and 9% hydrogen peroxide (H_2O_2). Both schematics on the right panels illustrate the poisoning of micromotors - either enzymatic or Pt-based- upon presence of particular analytes. Reprinted with permission from ref.44. Copyright 2013 Royal Society of Chemistry.

environment.[44] For instance, chemical quenchers of HO· radicals such as dimethyl sulfoxide (DMSO), reduce the generation of O_2 produced by microjet motors when H_2O_2 is decomposed in a disproportionation reaction via a radical pathway (Fig. 2 B). Moreover, amino acids containing thiol groups such as cysteine, methionine and peptides like glutathione can poison the Pt catalyst having a significant effect on the motility of the bubble propelled micromotors, both types rolled-up and electrochemically deposited microtubes (Fig. 2 B, right plot). Electrolytes such as Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-} and phosphates, uric acid and blood proteins such as bovine serum albumin (BSA), beta-globulin and even glucose oxidase enzyme can be detected at small concentrations in the solution by monitoring the change of speed of the nanomotors enabling the monitoring of the concentration of these compounds.[45-47] Although the speed of nanomotors is dramatically reduced in blood samples,[48] when blood samples are warmed up to physiological temperatures, nanomotors can overcome the viscosity and passivation effects.[49]

Catalytic micro/nanomotors can also be used as pH sensors taking advantage of their pH taxis capabilities. In a recent publication, Dey et al. reported a catalytic self-propelled polymeric microsphere containing randomly distributed Pd nanoparticles (NPs) that showed pH taxis behaviour.[50] Their experimental results revealed that the rate constant of the catalytic decomposition of H_2O_2 on the Pd catalytic sites increased with the pH of the medium, moving the micromotor with increasingly higher speeds from the lower pH regions in the aqueous solution towards higher pH regions (Fig. 3).

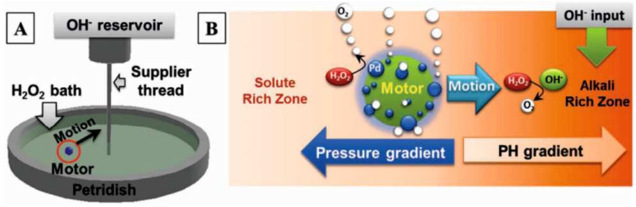

Fig. 3. pH taxis of catalytic micromotors. (A) Schematic diagram of the used experimental setup. (B) Schematic description of the depletion mechanism. The solute H_2O_2 molecules migrate from the solute rich zone (left) towards the motor surface and react with Pd NPs to produce O_2 bubbles. In the alkali rich zone (right) the solute concentration further decreases due to OH^- catalyzed volumetric reactions. Reprinted with permission from ref.50. Copyright 2013 Royal Society of Chemistry.

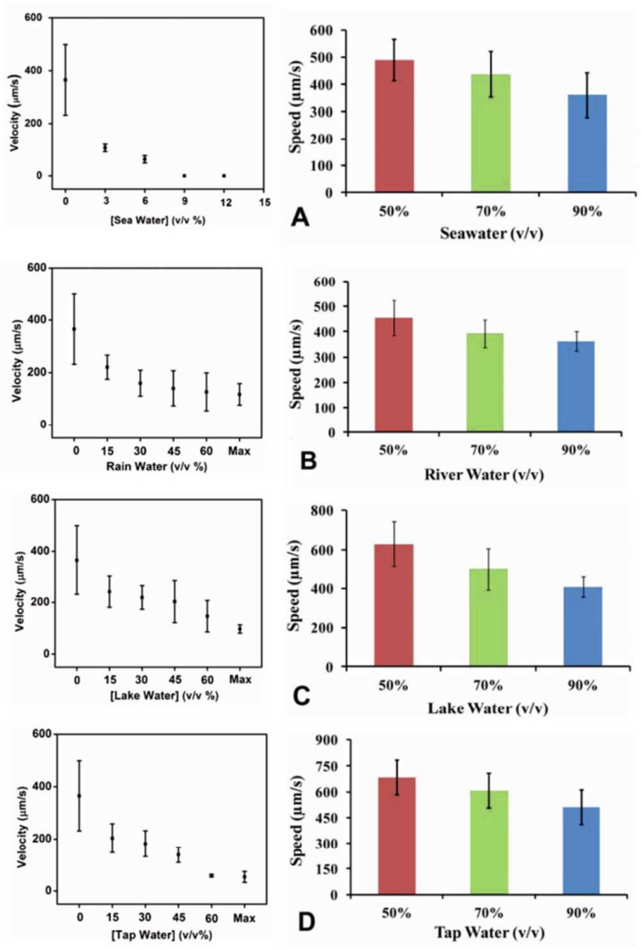

Fig. 4. Motion of the catalytic microjets (prepared by electrochemical template deposition method) in various types of waters: (A) seawater; (B) rain and river water; (C) lake water; (D) tap water. Left column: Cu/Pt catalytic microjets, temperature of 23 °C, 3% (wt.) H_2O_2 and 1 (wt.)% SDS. Right column: (PEDOT)/Pt microtubes, 3% (w/v) H_2O_2, 3% (w/v) sodium dodecyl sulfate. Temperature is not stated. Reprinted with permission from ref.51, 52. Copyright 2013 Royal Society of Chemistry.

3. Effect of the environment on the motion of nanomotors

The surrounding where the micromotors swim is a crucial parameter for the motion of catalytic nano- micromotors. Viscosity, ions and analytes contained in the solutions where nanomotors are swimming, can alter the dynamics of nanomotors, modifying their speed. Hence, the poisoning of the nanomotors is employed as indirect measurement of pollutant species by those self-propelled devices. In a recent work, Pumera and coworkers explored the influence of various types of water on the locomotion of catalytic tubular Cu/Pt micromotors, including tap water, rain water, lake water and sea water.[51] The studies were carried out fixing the concentrations of H_2O_2 and surfactant but varying the concentration of water sample, which was diluted with distilled water. In all cases, an increase of the concentration of real water samples caused a fall in the bubble ejection and motility of the microjets (Fig. 4, left plots). Determining the ionic composition of the water samples, the authors concluded that the amount of inorganic ions in aqueous solution directly correlated to the decreased locomotion of micromotors. It is important to note that no motion was observed when the Cu/Pt catalytic microjets were immersed in seawater containing 3% H_2O_2 and 1% surfactant. Further experiments with increasing concentration of sodium chloride (NaCl) in distilled water, showed a similar decrease in the performance of microjets. Contrary to previous observations,[25] the motion of catalytic bubble microjet was, in that case, highly influenced by the salt concentration in the environment. Despite the challenges found in the locomotion of Cu/Pt bimetallic microjets, Gao et al. reported propulsion of electrodeposited polymer/platinum microtubular motors, with a polymer-based outer layer composed of poly(3,4.ethylenedioxythiophene (PEDOT) even in 90% concentrated water samples, including tap water, rain water, lake water and seawater, (Fig. 4, right plots).[52] Although these micromotors self-propel in different real-life water sources, one should note that their speed compared with control experiments in deionized water (containing 3% hydrogen peroxide) is significantly reduced (980 µm s^{-1} in DI water *vs* 489 µm s^{-1} in 50% v/v DI water/seawater). Thus, the different results presented by the two research groups are not totally contradicting and may arise from the difference in materials composition of the micromotors, and perhaps caused by difference in their speeds in DI water containing H_2O_2. For example, the PEDOT/Pt bilayer micromotors have shown very high speeds (980 µm s^{-1} in 3% H_2O_2 in distilled water). This speed is about 3 times higher than the speed of bimetallic Cu/Pt micromotors in similar conditions (365 µm s^{-1} in 3% H_2O_2 and 1% sodium dodecyl sulfate as surfactant, in distilled water).

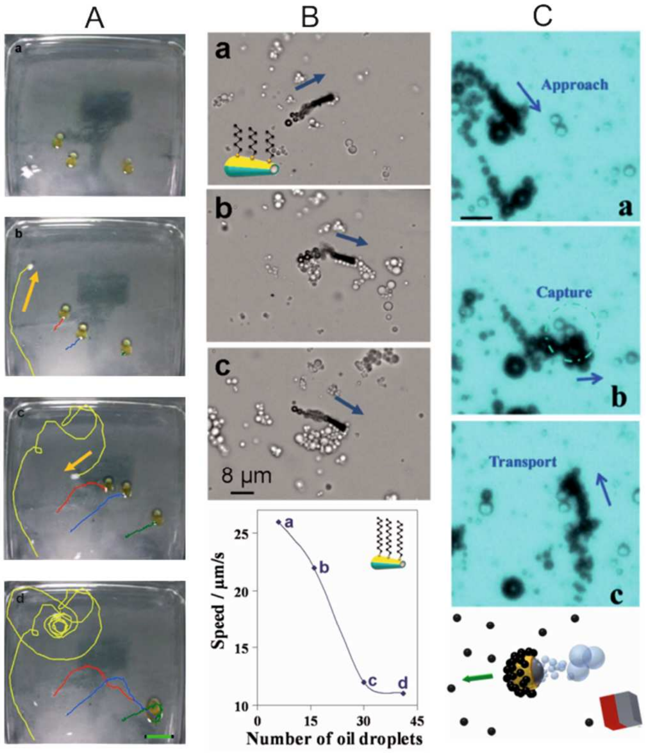

Fig. 5. Oil capture and dispersion using micro- and nanomotors. (A) SDS/PSf capsule inducing movement onto oil droplets. Images taken at a) t=0, b) 0.8, c) 3.5 and d) 7.0 s. The three oil droplets merge in 7.0 s. Scale bar 2.24cm. Reprinted with permision from ref.36 Copyright 2011 Wiley-VCH. (B) Catalytic microjets with hexanethiol-modified hydrophobic walls capturing oil droplets and transporting them. Plot shows the reduction of dodecanethiol-modified microjet speed with the number of oil droplets transported. Reprinted with permision from ref.54 Copyright 2012 American Chemical Society. (C) Janus micromotor driven by Mg in water solutions. Similarly to (B), the micromotors contain hydrophobic cap for oil capture. Reprinted with permision from ref.55 Copyright 2013 American Chemical Society.

4. Towards removal of oil from water

The surface modification of some types of nanomotors allows them to capture oil from contaminated waters. Work from Pumera and co-workers described a sodium dodecyl sulfate (SDS)-loaded polysulfone (PSf) capsule that was used to shepherd several oil droplets and to merge them, cleaning the surface of the water.[36] The driving force of self-propulsion is based in the Marangoni effect. The PSf capsule was casted by dropping 5 µL of a solution of PSf in N,N'-dimethylformamide (DMF) onto the surface of an aqueous solution, creating a millimiter-sized PSf porous capsule. The DMF in the capsule was released slowly and asymmetrically through its pores, leading to self-propulsion. When the SDS/PSf capsule was exposed to the water surface where several oil droplets were previously placed, the collective motion of the oil droplets induced by the SDS/PSf capsule was observed (Fig. 5 A). Further improvements of the same group, explored the incorporation of different surfactants to the PSf capsule, in order to induce motion of oil droplets.[53] An increase of the concentration of surfactant in the capsule, causes a rise on the velocity of the repulsed oil droplet, being SDS the one producing the fastest propulsion speed.

At smaller sizes, the first example of using functionalized catalytic micromotors for removing oil from water was reported by Wang's group.[54] For this application, catalytic microtubular Au/Ni/PEDOT/Pt motors were fabricated by electrochemical deposition and further functionalized with alkanethiols to form a hydrophobic monolayer on the outer gold surface of the microtube. Capture of oil droplets was observed when these micromotors were added in aqueous samples containing microdroplets of olive oil, due to the strong interaction between the alkanethiol on the surface of the micromotor and the oil phase (Fig. 5 B). The influence of the alkanethiol length was examined by functionalizing the micromotor with self-assembled monolayers (SAMs) of different alkanethiol lengths (C6, C12 and C18). The experimental observations illustrated a weak interaction of the micromotor with the oil droplet using C6 but a stronger interaction when C12 was utilized. However, further modification of micromotors with C18 hardly displayed motion due to blocking of the inner catalytic Pt layer. As expected, the polarity of the head functional group influenced the interaction between the micromotor and the oil droplet. Another approach to capture oil from water, also based on SAMs modification, was the use of self-propelled magnesium Janus particles in seawater samples.[55] The magnesium particles were coated by nanometric layers of Ti, Ni and Au and further functionalized with octadecanethiol (Fig. 5 C). The driving force of self-propulsion is based on the redox reaction of magnesium and water, to produce hydrogen bubbles and magnesium hydroxide as a byproduct. Although an oxide passivation layer can be rapidly formed on the Mg surface and, consequently, hamper the self-propulsion mechanism, Gao et al. found that the presence of the gold layer (Au plays a crucial role in the H_2 generation due to macro-galvanic corrosion mechanism, i.e. one metal corrodes preferentially to another when two metals are in contact) and chloride ions allows the hydrogen generation reaction to proceed. In this particular case, the formation of hydrogen bubbles will stop as soon as the Mg-based body of the motor will be fully consumed. Since chloride-rich environments are required for a proper performance of this motor, seawater appears as a suitable media where this particular type of micromotor can actuate. However, the lifetime of Mg-based micromotors appears as a drawback for developing practical applications for these microdevices.

5. Water remediation mediated by nanomotors

Despite recent advances in environmental studies with micromotors that combine motion and water treatments, there continues to be a need for reusable and multifunctional micro- and nanomotors with long lifetimes that can degrade efficiently a variety of pollutants. In a recent work, Sanchez and co-workers illustrated for the first time the ability of self-propelled micromotors to oxidize organic pollutants in aqueous solutions.[9] The novelty of the work lies on the synergy between internal and external functionality of the micromotors. In particular, these multifunctional microtubular motors use hydrogen peroxide as a fuel for locomotion, given by the generation of O_2-bubbles in the internal Pt layer, while actively degrading organic pollutants in solution due to the useful function of the external Fe wall as active material that enables the water remediation (Fig. 6 A). The mechanism of degradation is based on Fenton reactions relying on spontaneous acidic corrosion of the iron metal surface of the micromotors in the presence of H_2O_2, which acts both as a reagent for the Fenton reaction and as a fuel to propel the micromotors. These findings have proven that the advantage of the new designed micromotors based on their capacity to provide, owing to their motion, enhancement of catalytic reactions. The importance of these findings opens up the way to fabricate autonomous microscopic cleaning systems that can work without external energy input and in a much faster way than static counterparts. The micromotors offer this ability to move the catalyst (ions) around without external actuation or addition of catalyst (iron salts) to achieve water remediation, removal of organic dyes, etc. Remarkably, oxidation is achieved even in the absence of surfactant, due to the double functionality of the Fe/Pt microtubular motors. Micromotors can still self-propel without surfactants although at slower speeds. Their active motion, yet, boosts the degradation of model pollutants such as Rhodamine 6G.

Almost at the same time, parallel efforts by Wang et al. reported the use of PEDOT/Pt micromotors to aid in the oxidation chemical threats.[10] In that work, the oxidative decontamination of organophospate (OP) nerve agent in the presence of hydrogen peroxide was accelerated by the presence of the self-propelled micromotors that contributed to an efficient fluid mixing without the need of external mechanical stirring (Fig. 6 B). Similarly to the work described above, hydrogen peroxide has double functionality acting as a fuel to propel the micromotors and as an oxidizing reagent for decontaminating the aqueous solution. The authors also studied the ability of employing these micromotors to accelerate the decontamination of several OP pesticides with analogous molecular structures, including methyl paraxon (MP), ethyl paraxon (EP) and bis(4-nitrophenyl) phosphate (b-NPP). In all cases the oxidation was not observed when the same mixture with OP pollutants and H_2O_2 reacted for the same duration without the presence of micromotors in the aqueous solution. Interestingly, no oxidation signals were detected when surfactant was not added in the solution, but in the presence of

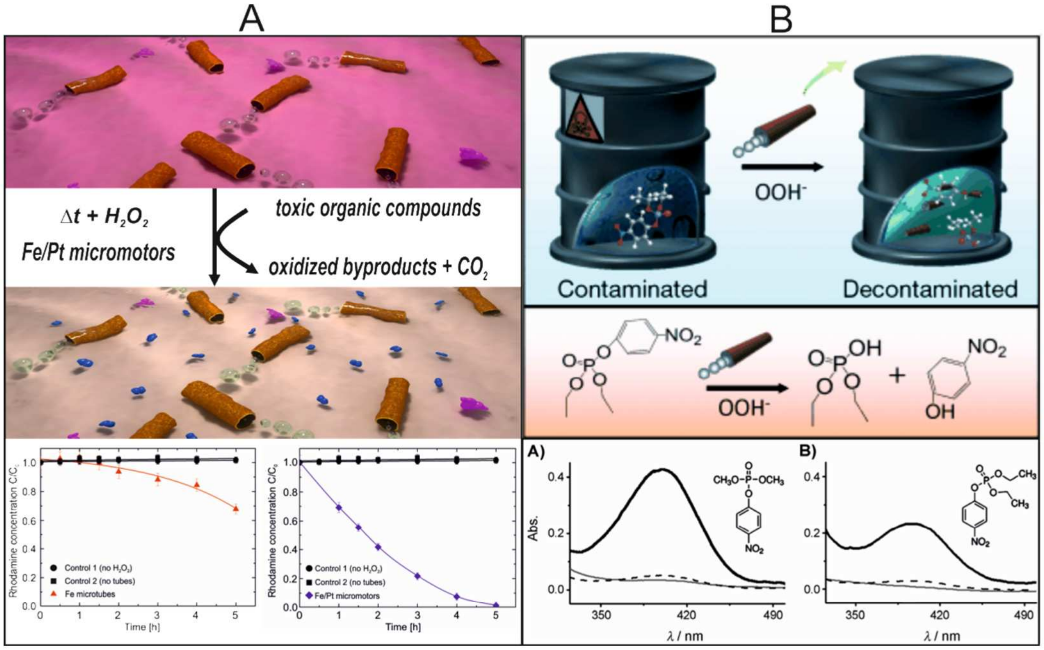

Fig 6. Micro-motors employed for water remediation. (A): Removal of toxic organic compounds from aqueous solutions with Fe/Pt micromotors in H_2O_2 solutions. Pink molecules represent rhodamine 6G (Rh6G); the small blue molecules represent oxidized compounds and carbon dioxide as reaction products. Plots show a quantitative comparison of Rh6G degradation by pure iron (Fe) tubes (red triangles) and by catalytically active Fe/Pt tubes (blue diamonds) over 5 h. Reprinted with permision from ref.9 Copyright 2013 American Chemical Society. (B): Illustration of a micromotor-based accelerated oxidative detoxification of OP nerve agents. The micromotor-based strategy allows rapid detoxification of chemical threats under mild conditions, and involves the in situ generation of OOH^- nucleophiles. Plots show the efficiency of the decontamination process, by measuring the absorbance of the p-NP reaction product obtained in the presence (black line) and absence (grey line) of the micromotors, and with the motors not moving (dashed line). Reprinted with permision from ref.10 Copyright 2013 Wiley-VCH.

micromotors. The authors observed that increasing the number of micromotors immersed in the treated solution a 100% of decontamination can be achieved using significantly shorter reaction times and lower peroxide concentrations compared to common neutralization processes of chemical warfare agents that require mechanical agitation.

6. Conclusions and future challenges

The recent progress on artificial nanomotors is opening up initial proof-of-concept environmental applications. This review has highlighted prospects and challenges in transferring recent advances in micro and nanomotors toward practical environmental applications. While great advances have been made over the past decade towards demonstrating initial proof-of-concept environmental studies, the achievement of practical environmental applications requires further innovation. Up to now, the current technologies are far of scaling up the processes reported for remediating large amounts of polluted water and much more work is required. Several issues need to be solved before scaling one step to practical applications. For instance, the lifetime of the multifunctional micromotors is limited to the remaining materials at the micromotor's body that involved/consumed in oxidation or locomotion reactions (Fe, Mg). Other drawbacks could be the poisoning of the platinum layer due to the presence of compounds in the wastewater that can bond chemically to the active surface sites of the catalyst, or a high viscosity of the treated wastewater that could hamper the motion of the micromotors.

An expected increasing innovation on this research field and a predictable further development of new abilities introduced in self-propelled micro- nanomotors will provide a myriad of environmental possibilities to perform more complex and demanding operations. We envision future nanomotors to deal especially at the microscale and environments hard to reach to. As other types of nanomotorss such as DNA nanomachines can already detect pH changes inside living cells,[56] future research could be envisioned integrating those DNA sensors to artificial self-propelled nanomotors. These foreseeable new micro/nanomotors would eventually revolutionize environmental monitoring and water remediation technologies, hoping to improving quality of life.

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