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Photocatalytic degradation enhancement in Pickering emulsions stabilized by solid particles of bare TiO_2

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ABSTRACT

Pickering emulsions provide a new way to enhance the efficiency of photocatalytic degradation of water-insoluble pollutants. Indeed, the semiconductor solid particles dually act as photocatalyst and stabilizer of the emulsion droplets whose size dramatically affects the photocatalytic reaction. The present work aims at the validation of this concept by using bare TiO_2 without any surface modification. Nanostructured TiO_2 has been prepared by a simple sol-gel process and characterized by X-ray diffraction, specific surface area analysis, scanning electron microscopy, and diffuse reflectance spectroscopy. The emulsions were prepared by using 1-methylnaphthalene (1-MN) as a model organic contaminant scarcely soluble in water and bare TiO_2 as photocatalyst/stabilizer. The emulsions have been characterized by electrical conductivity, optical microscopy and light scattering analyses. The photocatalytic degradation of 1-MN resulted 50 times faster in stable Pickering emulsions with respect to the case of biphasic liquid systems containing TiO_2. This finding allows to propose Pickering emulsions stabilized by TiO_2 nanoparticles as an effective and novel way to intensify the photocatalytic degradation of water insoluble organic pollutants.

Keywords: Pickering emulsion, TiO_2, 1-methylnaphthalene, photocatalysis.

Introduction

Plenty of non-biodegradable aromatic organic compounds, such as solvents, grease, oil and various hydrocarbons, exist in wastewater downstream to various industrial processes (production of cosmetics, oil refinery and petrochemicals, mechanical industry etc.) [1]. These pollutants are significant sources of environmental contamination. In fact, in addition to their possible intrinsic toxicity, they generally spread as insoluble liquid layer floating on the surface of water, decreasing atmospheric oxygen transfer to water thus dramatically affecting the natural biological processes and the quality of water. Treating this kind of wastewater is a hard task. Indeed, various factors (e.g. temperature, presence of surfactants etc.) influence the existence of these compounds as separate phases or as emulsions (oil-in-water), so the treatment process should be characterized by high flexibility and efficiency. Physical processes such as gravity separation, flotation, emulsion breaking or incineration [2,3] are commonly used to separate large amounts of oil. However, separation is a very time demanding step and the efficiency results often inadequate due to the possible formation of emulsions. Furthermore, physical treatments do not afford pollutant mineralization but only separation, thus maintaining the problem of their disposal.

TiO_2 photocatalysis has proved an extremely promising alternative for the treatment of water due to its green and sustainable features [5-7]. Formation of highly oxidizing active oxygen species through light induced redox reactions at the surface of the semiconductor allowed the degradation of almost every organic substrate with few exceptions. However, despite the large number of publications on the application of photocatalysis to degrade soluble pollutants in water [8-11], there are few reports dealing with poorly soluble organic pollutants [12-14]. In fact, hydrophobic organic pollutants poorly adsorb onto the hydrophilic surface of the photocatalyst, so the reaction results kinetically hindered. This problem has been faced by performing the treatment in non-polar green solvents such as dimethyl carbonate [15], or by coupling photocatalysis with some physical processes such as adsorption on activated carbon

[16]. The approach hereby presented consists in using the solid photocatalyst particles as emulsion stabilizers. This reduces the oily droplet sizes and increases the contact between the photocatalyst and the pollutant. In other words, the system is composed of small and stable TiO_2-surrounded hydrophobic droplets acting as microreactors in which the photocatalytic degradation can efficiently take place due to the enhanced active sites availability.

Two immiscible liquids may give rise to an emulsion if finely dispersed one into the other by means of external energy, either in the form of mechanical agitation or sonication. Emulsions stabilized by adsorbed solid particles are called “Pickering emulsions” [17, 18]. Different types of emulsions stabilized by solid particles may be obtained: (i) oil-in-water (o/w), (ii) water-in-oil (w/o), (iii) oil between two layers of water (w/o/w), or (iv) water between two layers of oil (o/w/o) [17-21].

Pickering emulsions retain the basic properties of classical emulsions stabilized by surfactants (emulsifiers), so a Pickering emulsion behaves as a classical emulsion in most of applications [17]. However, there are specific properties of Pickering emulsions. In particular, type and stability depend upon the particle wetting ability by aqueous and oil phases [22-24].

Stabilization by solid particles requires that they adsorb at the oil-water interface. For this reason, partial wetting of the solid particles by oil and water is a compulsory requirement. Hydrophilic particles can stabilize o/w emulsions whereas more hydrophobic particles can stabilize the w/o ones. The free energy of a solid particle bound to the oil-water interface is lower than the free energy of particles fully immersed in water. Therefore, the free energy related to the transfer of the particles from the aqueous phase to the interface is larger than that of thermal motion, and the binding of the particles to the interface is favored [17]. The resulting high resistance against coalescence is a major benefit of the stabilization by solid particles [25-30].

Pickering emulsions are currently investigated for their use in the fields of pharmaceutical products [31, 32], cosmetics [33], paper-making [34], and food preparation [35, 36]. Since the paper published in 2010 by Crossley at al. [37] showing the possibility of performing heterogeneous catalytic reactions in Pickering emulsions stabilized by the catalyst, several examples of catalytic reactions in Pickering emulsions have been reported [38-45]. However, there are only few reports on heterogeneous photocatalysis for the degradation of organic contaminants in Pickering emulsions [12-14]. ZnO and TiO_2 have been considered in these applications [12,46] but, to the best of our knowledge, only surface-modified semiconductors have been used so far [13, 14].

Notably, recent applications extending the concept of catalysis in Pickering emulsions are attracting interest within the scientific community. For instance, it is possible to modify the surface of the nanoparticles stabilizing the Pickering emulsions with shutter molecules covalently grafted (phase-boundary catalysis) or with supramolecular hierarchical structures (colloidal tectonics) able to tune the surface hydrophilicity and to generate porous amphiphilic architectures where organic molecules can be accommodated in reversible and predictable ways. These novel approaches offer the advantage of a more tunable and flexible system to formulate emulsions for specific applications such as the synthesis of fine chemicals [47,48]. However, complexity and time demanding research process put a strain on these systems when used for environmental larger scale applications where simple, scalable and robust systems are preferred. Furthermore, the presence of organic modifiers makes their stability questionable under irradiation, due to the presence of highly oxidizing radicals. In this paper, o/w Pickering emulsions of 1-methylnaphthalene (1-MN) in water were stabilized by bare TiO_2 without any surface modification. 1-MN is a toxic, carcinogenic, and mutagenic polycyclic aromatic hydrocarbon (PAH) [49,50] which is almost insoluble in water.

Experimental

Synthesis of TiO_2 nanoparticles

The TiO_2 nanoparticles were synthesized using a simple sol-gel method elsewhere reported [51]. Briefly, 19 mL of titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$, > 97%, Alfa Aesar) were dissolved in 4 mL of methanol (MeOH, 99.9%, Aldrich) and the solution was sonicated in an ultrasonic bath (Elma, T460/H, 35 kHz and 170 W). The hydrolysis process was then performed by adding dropwise 74 mL of deionized water under reflux and magnetic stirring. The obtained white gel was filtered, washed several times using ethanol and deionized water, and dried at 100°C for 18 h. The obtained powder was calcined at 400°C for 4 h and finally ground.

Characterization

X-ray diffraction patterns were recorded at room temperature by an Ital Structures APD 2000 powder diffractometer using the Cu Kα radiation and a 2θ scan rate of $2°C\cdot min^{-1}$. The mean crystallite size D (nm) of the photocatalysts was estimated from the width of diffraction peaks using the Debye-Scherrer equation:

$$D = 0.9\,\lambda / \beta \cos\theta$$

where λ is the wavelength of the X-ray radiation (0.154 nm), β is the resolution-corrected width at half height and θ is the diffraction angle.

UV-vis absorption spectra of the samples were recorded in the range 200-800 nm using a Shimadzu UV-2401PC spectrophotometer. $BaSO_4$ was used as the reference.

The surface charging upon pH variation and the isoelectric point were determined by means of electrophoresis using a NanoZS instrument (Malvern, UK).

The BET specific surface area was determined by using a Micrometrics TRISTAR 3000 instrument.

The morphology of the photocatalyst was examined by scanning electron microscopy (SEM) using a Philips XL30 ESEM operating at 30 kV acceleration on samples upon which a thin layer of gold has been deposited.

The particle size was determined by transmission electron microscopy (TEM) using a JEOL JEM 12-20 operating at 120 kV acceleration. The samples were prepared by dispersing the powders in water and depositing and drying a drop of suspension onto a thin Formvar film supported on a Cu grid.

The size distribution of TiO_2 suspensions was determined by dynamic light scattering using a Zetasizer NanoZS instrument (Malvern, UK).

Droplets size measurements of o/w emulsions were carried out by means of small-angle light scattering (Mastersizer 3000 instrument, Malvern, UK). The refractive indices of the optical model used for data processing were 1.332 for water, 1.615 for 1-MN, and zero for the imaginary part of the refractive index of 1-MN.

Emulsion droplets were observed by optical microscopy using a Leica DMLM (Germany) microscope equipped with a video camera. The concentrated emulsions were diluted and spread between glass plates for microscopic observation in transmission mode and image analysis. The size distribution was determined by image analysis using the "Analysis" software.

Preparation and characterization of Pickering emulsions

Pickering emulsions were prepared with different volume fraction of 1-methylnaphtalene (1-MN: $C_{11}H_{10}$, 95% Aldrich, USA) according to the following procedure: TiO_2 was firstly dispersed in water with an Ultra-Turrax T25 rotor-stator device equipped with a S25N18G shaft (IKA, Germany) rotating at 22000 rpm during 5 minutes. The same disaggregation degree was obtained with an ultrasound disperser Sonics VibraCell at 500 W operating during 3 minutes, as described below. Thereafter, 1-MN was added and the mixture was dispersed under the same conditions. O/w emulsions of different compositions (oil and TiO_2 contents) were studied depending on the type of experiment, either physicochemical characterization or assessment of photocatalytic activity. A scan of oil contents from 10% to 80% at constant TiO_2 concentration (1%) was done in order to investigate emulsion type. The influence of TiO_2 concentration on stability and droplet size was studied for oil contents of 10% and 20%, which were higher than that of photocatalysis experiments but lower than the usual 50% oil content of most physico-chemical investigations. Such conditions kept the asymmetry of oil and water contents pertaining to photocatalysis and allowed a variation of TiO_2 concentration in a wide range. Photocatalysis experiments were performed with fairly dilute compositions (0.01 % oil and 1% TiO_2) for UV light can penetrate the medium over long enough depth.

Photocatalytic experiments

The photocatalytic experiments were carried out using a cylindrical Pyrex batch photoreactor (diameter 10 cm) equipped with a magnetic stirrer rotating at 500 rpm and containing 160 mL of 1-MN/TiO_2/water emulsion with 0.01% v/v of 1-MN and 1% w/w of TiO_2. The photoreactor was illuminated by an LLP lamp UVA (8 $mW \cdot cm^{-2}$) placed horizontally below it. A circulating water bath was used to control the temperature at 298 K. The UV irradiation and the mechanical stirring during the photocatalytic runs did not influence the stability of the emulsion. Samples were collected at pre-specified time intervals and mixed with acetonitrile/water (50% v/v) in order to break emulsions and dissolve 1-MN. Thereafter, the samples were filtered through a Millipore 0.45 μm PTFE filter before analysis.

Analytical methods

The evolution of the 1-MN concentration during the photocatalytic experiments in emulsion was followed by using a HPLC system model 1290 Infinity. This apparatus was equipped with a binary pump (Agilent Technologies, G4220B), an autosampler (Agilent Technologies, 1290 Sampler), a DAD (Agilent Technologies, G4212B) and FID detector (Agilent Technologies, G1321B). The injected sample volume was 50 μL and a HAP column (Agilent: 4.6×100 mm, 1.8 μm) was used for all of the analyses. Ultrapure water (solvent A) and acetonitrile (solvent B) were used as the mobile phase with a flow rate of 1 $mL \cdot min^{-1}$ as it follows: 0 min to 10 min 40% B, 10 min to 19 min 90% B, 19 min to 20 min 40% B. The resulting data were collected and processed using Agilent MassHunter software.

Gas chromatography coupled with mass spectrometry analyses were performed on a Hewlett Packard 6890/5973 GC-MS system, with electron impact ionization at 70 eV, He carrier gas, 30 m × 0.25 mm Zerbon ZB-Wax, 100% polyethylene glycol capillary column. Analyses were carried out in both SCAN and SIM (selective ion monitoring) modes. The starting temperature was 60 °C for 10 min; it was then linearly increased up to 220 °C at 5 $°C \cdot min^{-1}$, and held at 220 °C for 30 min.

Results

Structural and morphological characterization of bare TiO_2

The X-ray diffraction pattern of the synthesized TiO_2 is shown in Figure 1.

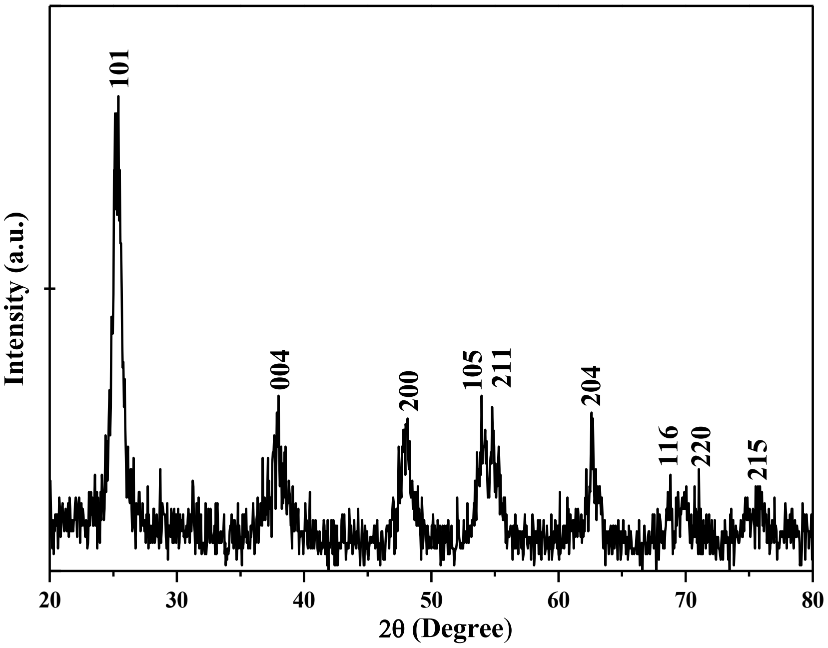

Figure 1. X-ray diffraction pattern of synthesized pristine TiO_2 nanoparticles.

The signals are characteristic of TiO_2 in the anatase form (JCPDS-ICDD card: 21-1272). In particular, the intense diffraction peaks at 25.28°, 37.81°, 47.99°, 53.95°, 55.0°, 62.9° and 75.0° correspond to the (101), (004), (200), (105), (211), (204) and (215) planes, respectively. The mean crystallite size of the TiO_2 nanoparticles, calculated using Debye-Scherrer equation, was about 10 nm.

Nitrogen adsorption and desorption isotherms (Figure 2) are of type IV, suggesting the presence of a mesoporous structure. At high relative pressures (from 0.45 to 0.80) the isotherm exhibits hysteresis of H2 type, indicating the existence of ink-bottle type pores with narrow necks and wide bodies. The specific surface area calculated by using BET method was 103 $m^2 \cdot g^{-1}$.

The pore size distribution (inset in Figure 2), calculated according to the BJH equation, is rather narrow indicating homogeneity of the material with an average pore diameter of about 5 nm.

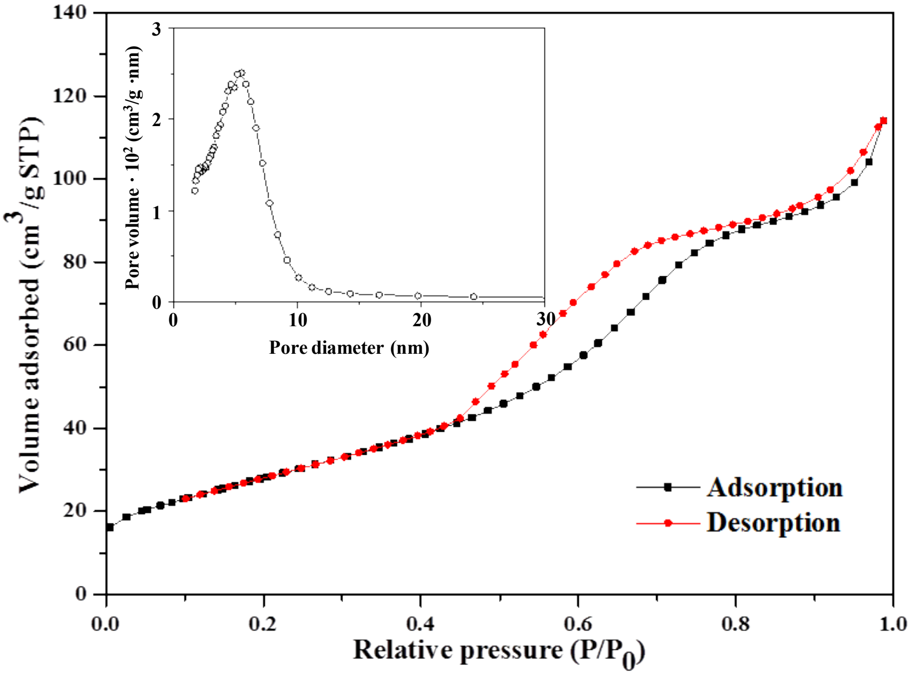

Figure 2. Nitrogen adsorption/desorption isotherms of TiO_2. Inset reports the pore size distribution.

Scanning and transmission electron microscopy images are shown in Figures 3A and 3B, respectively. The TiO_2 nanoparticles are present as aggregates of quite uniform primary spherical nanoparticles whose mean size is close to the value calculated by means of the Debye-

Scherrer equation. Notably, Figure 3A suggests that the interstices between the TiO_2 particles in the aggregates can contribute to the mesoporosity as given evidence by the physisorption measurements, although it cannot be excluded the presence of mesopores with a small neck and enlarged body in the single particles.

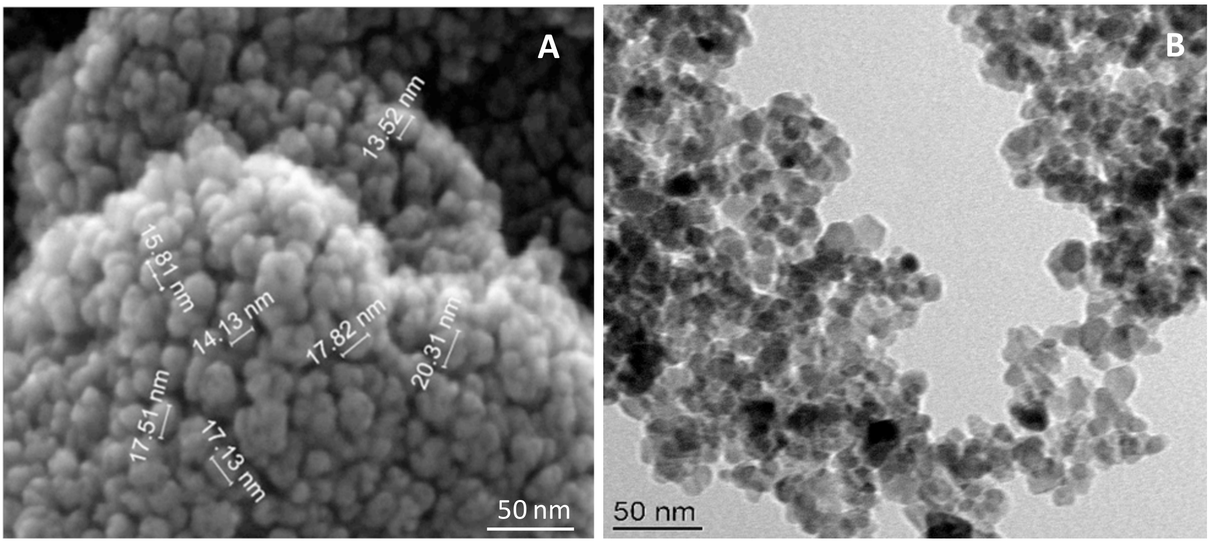

Figure 3. Scanning (A) and transmission (B) electron microscopy images of the synthesized TiO_2.

Figure 4 shows the Tauc plot along with the UV-vis absorption spectrum (inset) of the prepared TiO_2. The obtained band gap of the synthesized TiO_2 was 3.22 eV.

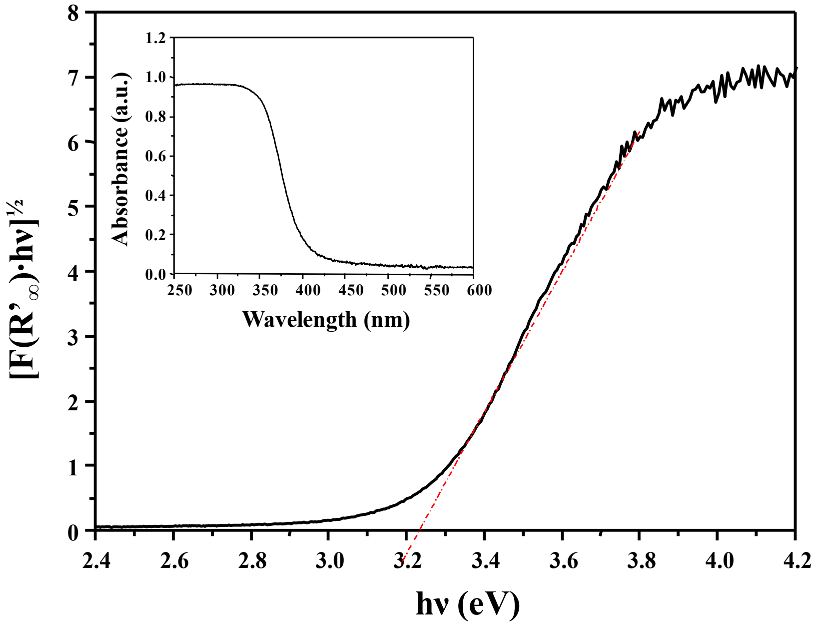

Figure 4. Tauc plot of the synthesized TiO_2 obtained by considering the sample an indirect semiconductor. Inset: diffuse reflectance spectra of TiO_2 in absorbance mode.

Zeta potential measurements (Figure 5) allowed to determine the isoelectric point of the synthesized TiO_2 and to investigate the stability of the nanoparticles as a function of pH.

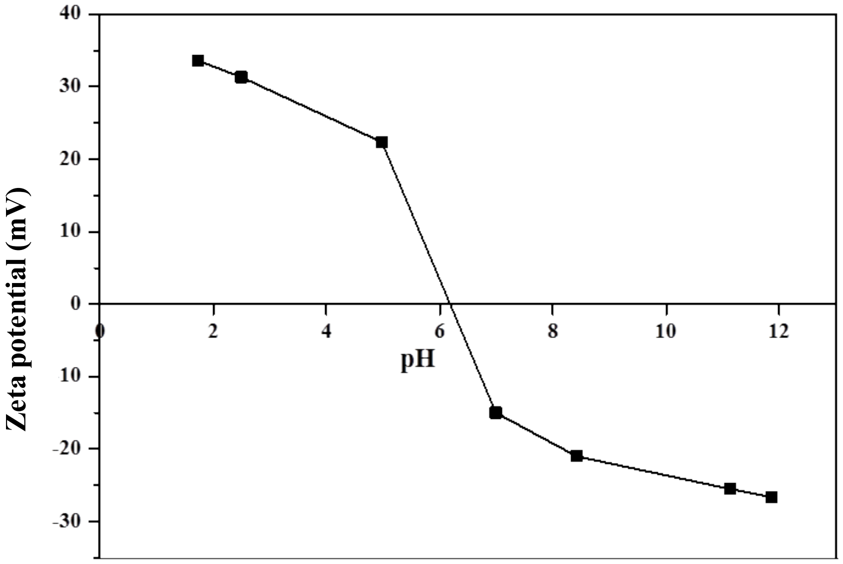

Figure 5. Zeta potential of TiO_2 in aqueous suspensions at different pH values.

The point of zero charge was at pH = 6.2. Therefore, the TiO_2 surface charge is negative at pH > 6.2 and positive at pH < 6.2 according to the protonation and deprotonation of Ti-OH surface groups given by Eqs. (1) and (2), respectively:

$$\text{Ti-OH} + H^+ \rightarrow \text{Ti-OH}_2^+ \quad (1)$$

$$\text{Ti-OH} \rightarrow \text{TiO}^- + H^+ \quad (2)$$

Characterization of 1-MN/TiO_2/water Pickering emulsions

The emulsification process is an operating parameter strongly influencing the stability and the droplets size. The objective of this study is to prepare emulsions with small droplet size having a high contact area between the organic pollutant and the photocatalyst particles used as stabilizers. The emulsification process was carried out in two steps. TiO_2 was first dispersed in water in order to allow the maximum particles disaggregation as described in the experimental part. Thereafter, 1-MN was dispersed into the TiO_2 suspension following the same procedure. The dimension of the aggregates prior to addition of 1-MN, was measured by means of dynamic light scattering both after the Ultra-Turrax dispersion and after sonication to compare the effect of the two dispersion methods. TiO_2 nanoparticles (mean diameter = 14 nm) in water aggregated in lumps whose diameter ranged from 600 nm up to 2 μm. On the other hand, sonication (3 minutes) and dispersion with Ultra-Turrax (5 minutes) reduced the aggregates diameter to ca. 300 nm, as shown in Figure 6. Similar value could be retrieved by means of optical microscopy observations (inset of Figure 6). Prolonging both the treatments for longer times did not result in further decrease of the nanoparticles aggregates size. Therefore, only dispersion by means of Ultra-Turrax has been used to formulate the emulsion in the following tests.

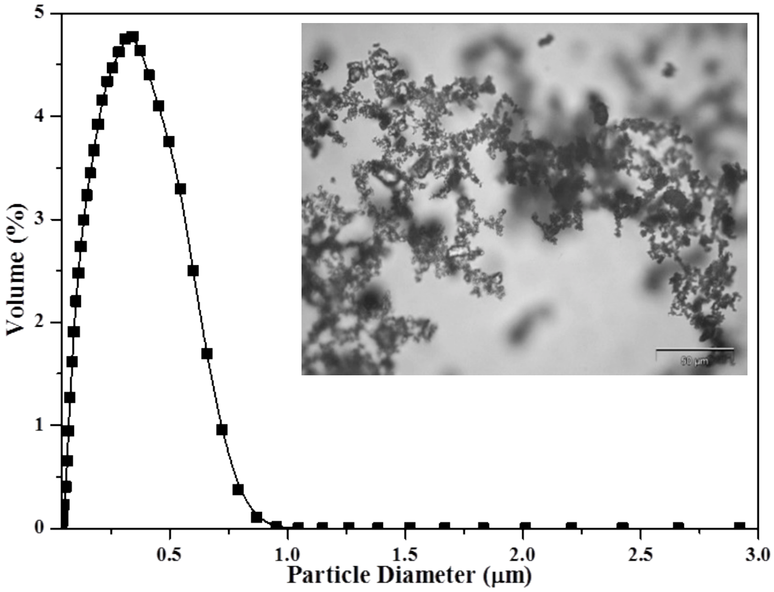

Figure 6. Particle size distribution and transmission optical microscopy image (inset) of TiO_2 nanoparticles dispersed in water by using the Ultra-Turrax disperser.

Thereafter, the emulsification process was carried out by dropwise adding 20% v/v 1-MN to the above described 1% w/w TiO_2 dispersion, by using the Ultra-Turrax disperser for further 5 minutes at the same conditions. The resulting system (Figure 7A) was comprised of a clear aqueous solution supernatant over a stable Pickering emulsion layer. This sedimentation of the emulsion phase is ascribable to the higher density of 1-MN (1.029 $g\cdot cm^{-3}$) with respect to water. Notably, it would be possible to take advantage of the higher density of the emulsion droplets with respect to the aqueous phase. In principle, in fact, a continuous treatment process on large scale can be proposed where the photodegradation reaction of settled droplets would take place at the bottom of the reactor, while the supernatant aqueous phase would be continuously separated by floatation.

The emulsion was stable for at least three months and the droplets size of 1-MN in water stabilized by TiO_2 nanoparticles did not change significantly. These results were confirmed by optical microscopy observation of the emulsion layer which showed that droplets of 1-MN were well dispersed and stabilized in the continuous water phase (Figure 7B).

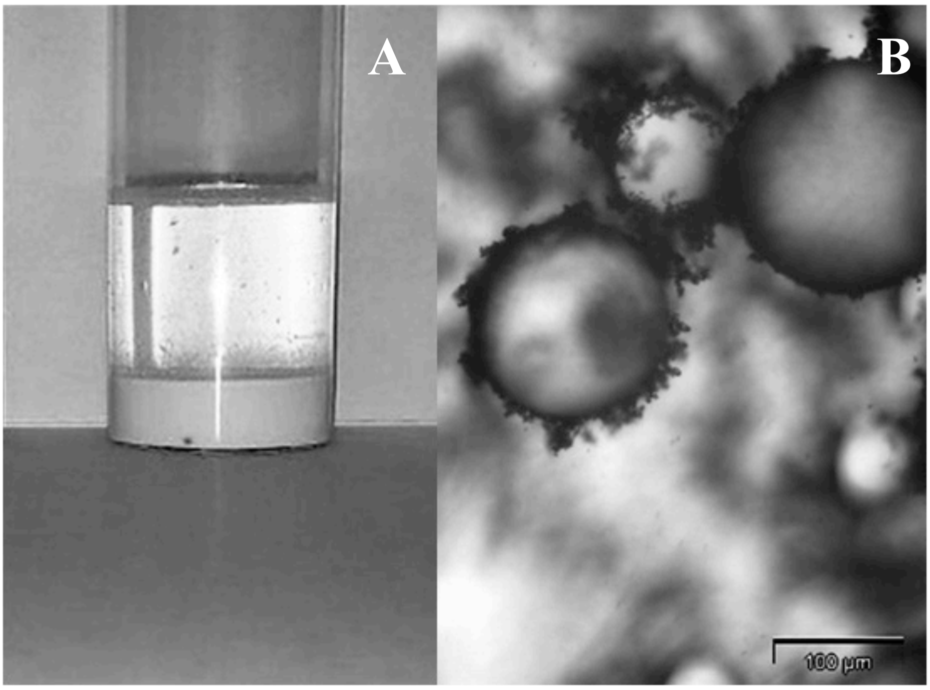

Figure 7. (A) Image of the system obtained after preparation procedure of the emulsion described in the experimental part: aqueous solution (supernatant), Pickering emulsion (underlying layer). (B) Optical microscopy image of the Pickering emulsion.

These results give evidence that unmodified TiO_2 nanoparticles can stabilize Pickering emulsions. The amounts of pollutant (1-MN) and TiO_2 nanoparticles are the two crucial factors influencing the emulsion type and the droplet size as discussed below.

Identification of the emulsion type

Figure 8 reports conductivity measurements of a sequence of emulsions containing different volume fractions of 1-MN as the oil phase (ϕ_{oil}) stabilized by 1% w/w TiO_2.

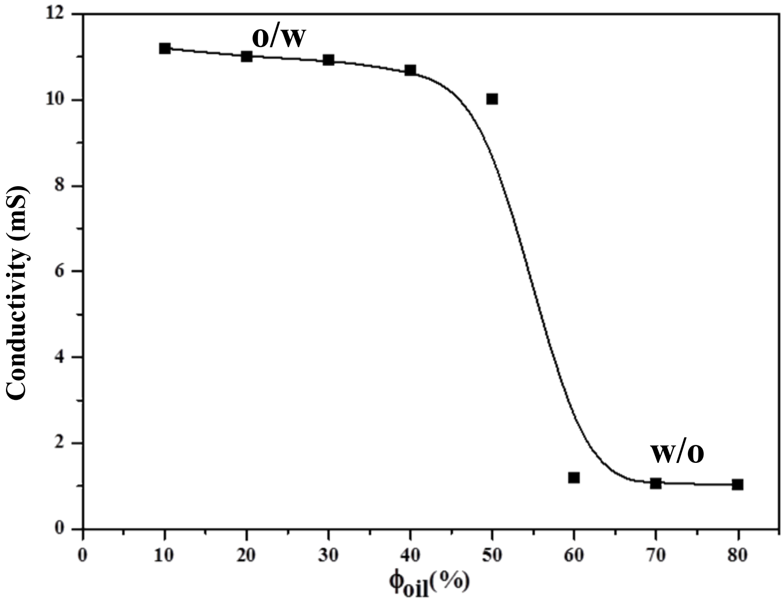

Figure 8. Phase inversion of 1-MN in water emulsions stabilized by TiO_2 nanoparticles.

Two types of emulsions were found: (i) w/o type, where the continuous phase is oil (low conductivity) at ϕ_{oil} > 50-60% v/v, and (ii) o/w type, where the continuous phase is water (higher conductivity) at ϕ_{oil} < 50-60% v/v.

This change, known as “phase inversion”, is usually accompanied by large changes of emulsion properties, such as viscosity, droplet size, and conductivity. A layer of pure oil was slowly released to the bottom of the emulsions containing ϕ_{oil} > 60 % v/v. Therefore, 1-MN/TiO_2/water Pickering emulsions formulated with ϕ_{oil} higher than 60 % v/v were not stable. Notably, only o/w emulsions can be efficiently stabilized due to the hydrophilic nature of the surface of TiO_2 nanoparticles.

Size of emulsion droplets

Droplets size is an important parameter for the characterization of emulsions. Furthermore, it should also affect the photocatalytic reaction rate, since small droplets have a large contact area between the photocatalyst, oil and water phases. The droplets size is influenced by factors such as the fractions of solid particles and the amount of oil.

The amount of the photocatalyst in Pickering emulsions plays a crucial role in determining the droplets size and the stability against coalescence. Figure 9 shows the dependence of the droplets size on the amount of TiO_2 used as the emulsion stabilizer.

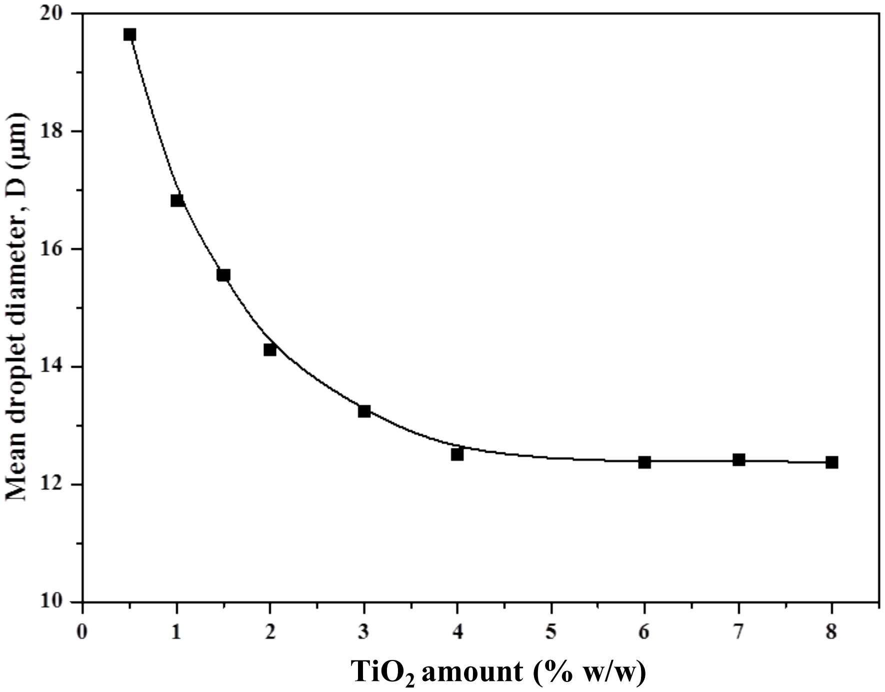

Figure 9. Mean droplet diameter of the 1-MN/TiO_2/water Pickering emulsion (10 % v/v 1-MN) as a function of the TiO_2 amount.

In the presence of 0.1-0.4% TiO_2, emulsions were not stable and coalesced immediately after preparation (results not shown). Efficient stabilization of Pickering emulsions was obtained above a minimum content of TiO_2 particles equal to 0.5% w/w. By increasing the TiO_2 amount from 0.5 up to 8% w/w, the droplets size firstly decreased and then reached a “plateau” at ca. 12.5 μm for TiO_2 amounts higher than ca. 3% w/w. This “plateau” may be explained by a lack of efficiency in the emulsification process. In fact, the emulsification with Ultra-Turrax disperser was unable to decrease the droplets size of the pollutant down to the value which would be obtained by extrapolation of the trend in the decreasing part. For this reason, in the “plateau” regime an excess of TiO_2 nanoparticles dispersed in the aqueous phase could be observed.

The decrease of droplets size with respect to the concentration of TiO_2 corresponds to the increase of the interfacial area. Indeed, larger TiO_2 content allowed the stabilization of larger contact areas (smaller droplets). This is in qualitative accordance with the geometrical relationship [13] $R = A/m$, where R is the droplet radius, m is the mass of solid particles and A is a constant that depends on the volume of the dispersed phase.

Also, the amount of oil is a crucial parameter. Larger oil contents require larger amount of particles to ensure the full coverage of droplets keeping constant their size. The effect of the oil-to-water ratio on the droplets size of Pickering emulsions was studied for a range of volume fractions of 1-MN up to 20% v/v. Results are shown in Figure 10.

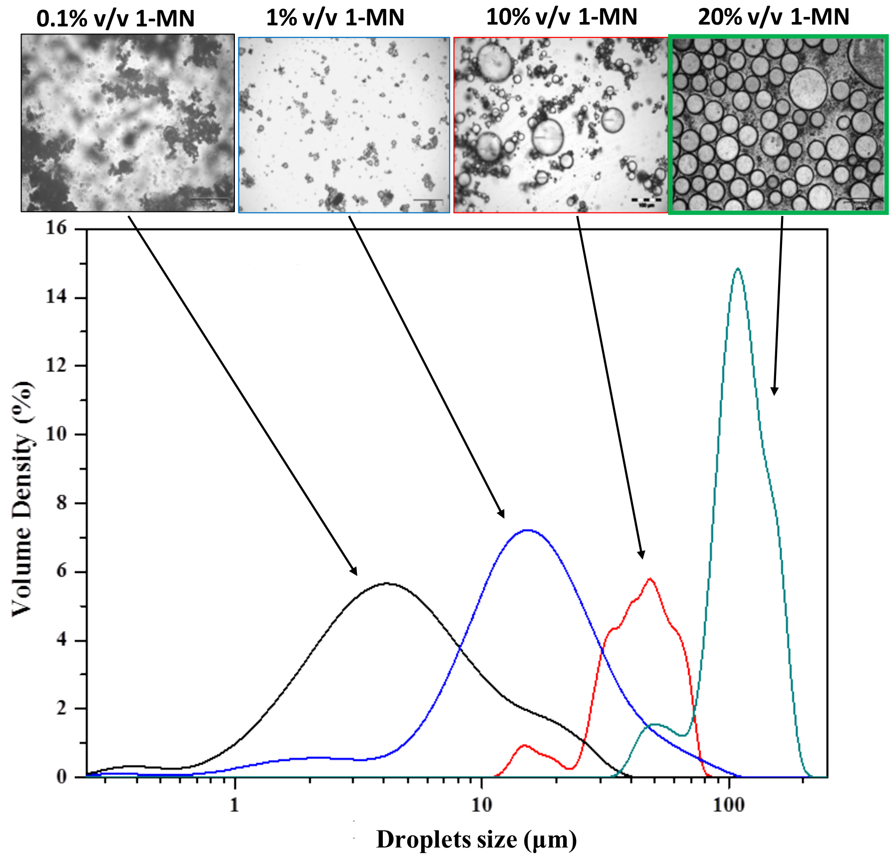

Figure 10. Size distribution of emulsion droplets prepared with different volume fractions of 1-MN in the presence of 1% w/w TiO_2, along with the corresponding optical microscopy images.

By keeping constant the amount of TiO_2 dispersed (1% w/w), the droplets size increased upon increasing the oil fraction.

It has been stated that increasing the oil content and decreasing the particles concentration had similar effects on droplet size because the area-to-volume ratio of a spherical droplet is $A/V = 3/R$ [52, 53]. This geometry-based relationship was not followed in the present case since the droplet sizes at low 1-MN contents were lower than the limiting size reached for 10% 1-MN (Figure 9). For a volume fraction of 1-MN equal to 0.1% v/v, the mean droplet size was quite small (5 µm) and Pickering emulsions were stable. This size is close to the smallest size dispersion with an Ultra-Turrax can achieve. Therefore, this amount was selected for the photocatalytic degradation experiments.

Photocatalytic degradation of 1-MN

The objective of this study was the intensification of the photocatalytic degradation of 1-MN in Pickering emulsions. The small pollutant droplets surrounded by the photocatalyst nanoparticles and dispersed in the emulsion act as microreactors in which the degradation reaction is intensified due to the larger oil-water interfacial area and the maximized contact between the photocatalyst and the pollutant. Notably, the emulsion was stable during the photocatalytic run as no 1-MN phase separation was noted under UV light irradiation. As a proof of concept, two irradiated systems have been considered: (i) 1-MN/water emulsion stabilized by TiO_2 nanoparticles and (ii) not emulsified 1-MN/water mixture in the presence of TiO_2. Results are shown in Figure 11.

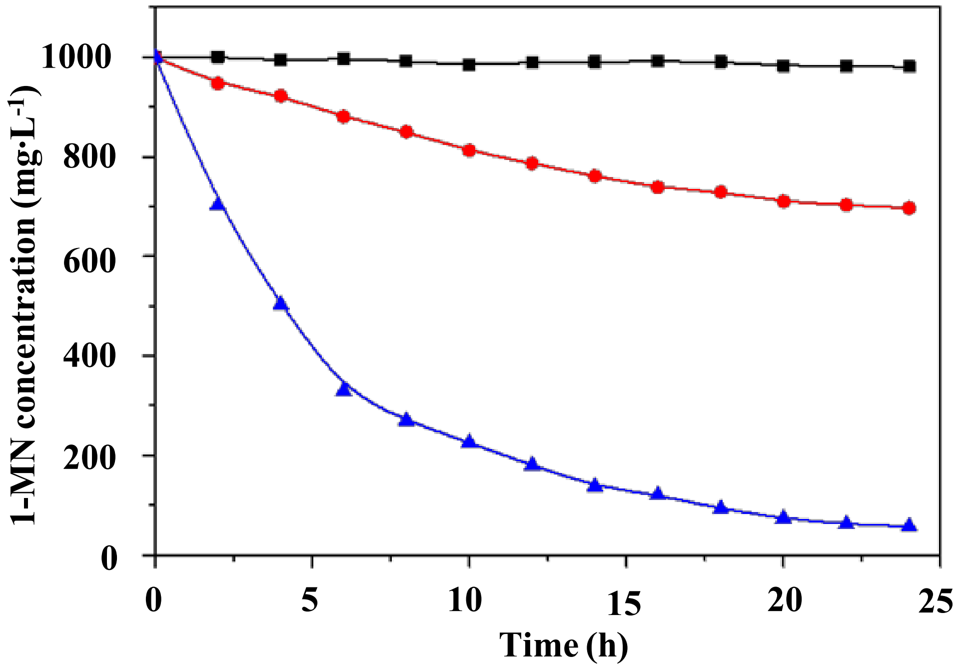

Figure 11. Photocatalytic degradation of 0.1 % v/v 1-MN. (black line) Blank test in the absence of catalyst; (red line) non-emulsified system in presence of 1% w/w TiO_2; (blue line) Pickering emulsion system stabilized by 1% w/w TiO_2.

The overall concentration of 1-MN progressively decreased during the photodegradation process for the two systems. However, the photocatalytic degradation in the emulsified system was significantly faster and reached 95% after 24 h of UV irradiation, whilst only 25% of the initial 1-MN could be degraded after the same time in the non-emulsified system. By taking into account the photoreactor volume $V = 160$ mL, the volume fraction of 1-MN $\phi_{\text{oil}} = 0.1\%$ v/v, and the 1-MN droplet size $D = 5$ µm, the total 1-MN/water interfacial area in the emulsified system is:

$$A = \frac{6\,V\,\phi_{\text{oil}}}{D} \approx 0.02 \text{ m}^2 \quad (3)$$

On the other hand, the droplets size in the non-emulsified system (only gently stirred) is of the order 1-2 mm, giving A values ranging between 5×10^{-5} and 10^{-4} m^2, which is 50 to 100 times lower than the value obtained in the Pickering emulsion. In the non-emulsified system, 1-MN photodegradation takes place within the aqueous phase saturated with 1-MN (solubility of 1-MN in water at 20°C is 25 ppm), while the large drops of 1-MN act as reservoirs slowly releasing the pollutant to the aqueous phase in which, therefore, the 1-MN concentration can be considered constant. For this reason, the rate of the photodegradation reaction is also constant, thus justifying the linear decay observed in the initial part of Figure 11 for the non-emulsified system.

The kinetics of photodegradation in the case of Pickering emulsion was 50 times faster than in the non-emulsified system. This order of magnitude reflects the difference in the dimension of droplets between the two systems, thus confirming that droplets size is the main parameter affecting the photocatalytic degradation in Pickering emulsion. The toxicity of oxidation products and intermediates is also a matter of concern. Consequently, understanding chemical transformations during the photocatalytic degradation of 1-MN and identifying the resulting products are extremely important points. Notably, the TiO_2 induced photodegradation of naphthalene [54] and its substituted derivatives [55] in diluted systems has been thoroughly investigated in the relevant literature. For this reason, a deep mechanistic discussion is unnecessary and out of the aims of the present report. On the other hand, some findings specifically related to the peculiar system under investigation are worth to be mentioned.

The photo-oxidation products were detected by GC-MS analysis and identified by computer-assisted comparison with a mass spectral database. As previously reported, 1-MN first undergoes oxidation of the methyl group, yielding successive oxidation products, such as the corresponding alcohol (1-naphthalenemethanol) and aldehyde (1-naphthalenecarboxaldehyde). Further OH radical mediated oxidation affords cleavage of carbon-carbon bonds in the naphthalene structure, yielding light by-products containing only one variously substituted aromatic ring. On the other hand, heavier compounds obtained by addition of radical intermediates could be also detected in the present system. In particular, non-negligible amounts of 4-(1,3-dimethyl-2-naphthyl)-1,2-benzenediol and naphthalene-1-carboxylic acid 4-formyl-phenyl ester (Figures 12A and B, respectively) were identified.

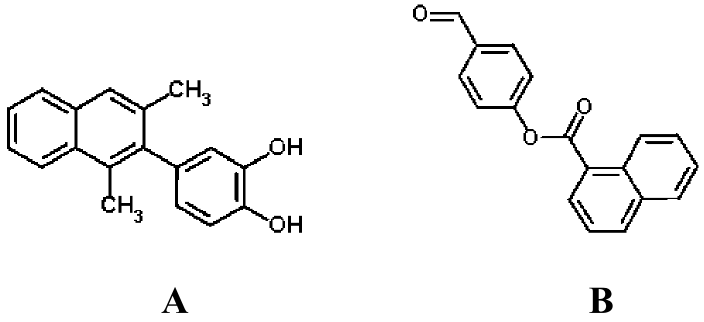

Figure 12. Structures of two addition products identified by means of GC-MS analysis during photocatalytic degradation of 1-MN in Pickering emulsion: (A) 4-(1,3-dimethyl-2-naphthyl)-1,2-benzenediol; (B) naphthalene-1-carboxylic acid 4-formyl-phenyl ester.

The presence of these compounds may be justified by considering that the photocatalytic degradation takes place at the surface of the 1-MN droplets acting as microreactors. Therefore, the probability of addition of the produced intermediate radicals is higher in the present system than in previously reported cases where 1-MN degradation occurred in acetonitrile or in low concentrated aqueous solutions.

Conclusions

Unmodified TiO_2 nanoparticles were prepared by a simple sol-gel method and used for the first time as stabilizers for 1-MN/water Pickering emulsions. Operational parameters affecting the emulsion droplets size, such as the fraction of solid particles, the amount of 1-MN, and the emulsification process were studied and discussed. In particular, the emulsion showed phase inversion from oil in water to water in oil at 1-MN fractions higher than 40% v/v, and the stabilization of the emulsion occurred above a minimum content of TiO_2 particles of 0.5% w/w. Small drop size improved the contact area between the organic contaminant and the photocatalyst thus intensifying 50 times the photocatalytic degradation of 1-MN with respect to the non-emulsified system. Degradation of 1-MN in Pickering emulsion produced non-negligible amounts of addition compounds which were never reported before for the same reaction carried out in diluted naphthalene solutions.

Pickering emulsions can effectively be proposed for the treatment of wastewater containing non-soluble organic contaminants, due to the high efficiency of the process and to the advantages deriving from the use of stable, cheap and abundant unmodified TiO_2 nanoparticles.

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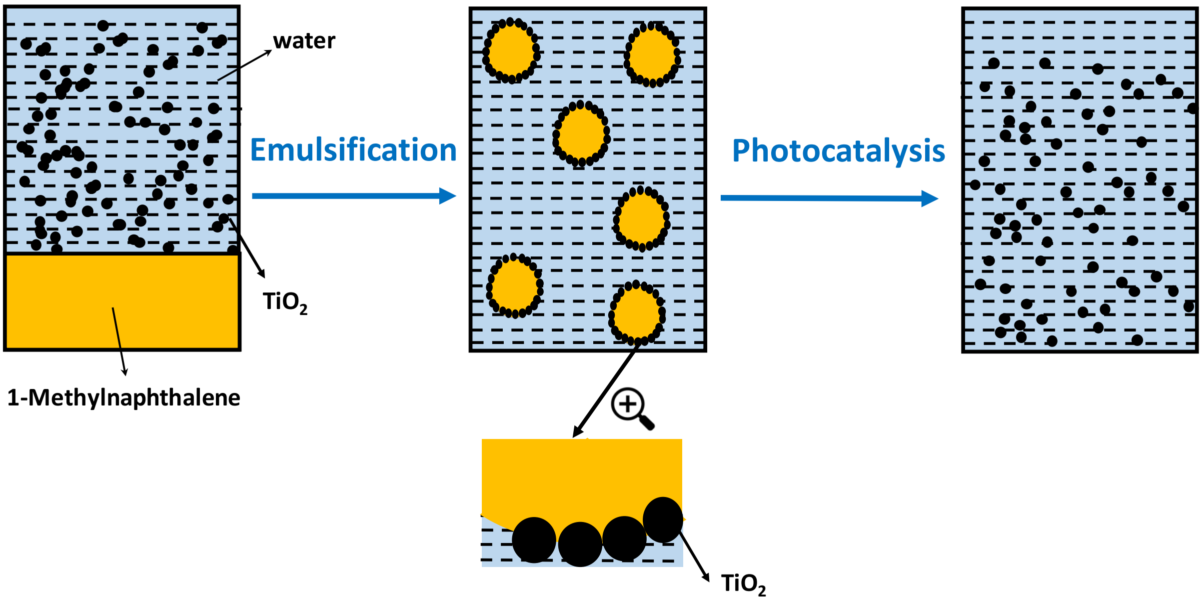
water
TiO$_2$
1-Methylnaphthalene
Emulsification
Photocatalysis
TiO$_2$