A new continuous flow-through structured reactor for the photodegradation of aqueous contaminants

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Abstract

A flow-through photo reactor with a stainless steel mesh-supported ZnO catalytic disc has been designed in this work. The preparation method of the catalyst includes the use of Triton™ X-100 and methylene blue (MB) in order to enhance the homogeneity of the ZnO and its adhesion to the mesh. The catalysts exhibit a high surface area ($\sim 100 \text{ m}^2/\text{g}$). The photocatalytic reaction is restricted to the most external non-polar edges of the ZnO nanosheets due to the low pH of the MB solution and to the fact that the polar surfaces are hydrophobic. Despite this, the performance of the flow-through reactor is superior to that of other micro fluidic systems. The catalyst undergoes a slight deactivation during the reaction, though the activity can be restored, without causing any structural changes, by passing water through the catalyst under UV irradiation. The loss of ZnO through photocorrosion is low, especially when compared to the loss experienced by the same catalyst prepared without using methylene blue.

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Introduction

With waterborne diseases causing around two million deaths each year, water treatment is one of the challenges facing mankind in the 21st century. Water treatment technologies include Advanced Oxidation Processes (AOP) to accelerate the oxidation and destruction of a wide range of organic contaminants. Photocatalytic methods that employ AOP under UV or sunlight irradiation to obtain clean water leave only CO₂ and inorganic ions as residuals [1, 2]. However, most photocatalytic reactors employed to date operate under severe mass transfer limitations (*immobilized bulk* reactors) and/or with a low photon transfer efficiency (*slurry bulk* reactors) [3]. *Micro-reactors* or micro-fluidic reactors [4-9], based on micro-channels, micro-capillaries or planar micro-chambers, allow an optimal distribution of light and present large values of surface area per unit volume ($1 \times 10^4 - 3 \times 10^5 \text{ m}^2/\text{m}^3$), facilitating the transfer of the contaminant to the catalyst surface. However, micro-fluidic reactor chips operate under low flow rates (around 1 cm³/h) and scaling-up is a challenging task, even though lithographic techniques for fabricating micro-reactors are now readily available. Other typical drawbacks of micro-reactors, such as fouling and clogging, frequent repacking or reactivation (regeneration), leaks between channels, malfunctioning of distributors, etc., are also multiplied when scaling up the reaction system. As an alternative to standard micro-fluidic reactors, we present in this work a novel photocatalytic flow-through reactor based on a stainless steel wire micromesh (SSWM)-supported photocatalyst. This special type of supported catalyst has been developed in recent years and tested in batch reactors at lab scale for the photodegradation of organic contaminants in water [10-18]. Our research group has successfully fabricated SSWM-supported ZnO and TiO₂ porous nanosheets, with high yields of active phase on the wire mesh surface, very high values of specific surface area and a good photostability by using post-synthesis additives [14-18]. However, in recent

ultrasonic tests an insufficient adhesion of the photocatalytic particles to the SSWM was observed, together with an occasional lack of uniformity in the distribution of the particles on the mesh [17-20]. In this work we have modified the fabrication method in order to improve the adhesion, homogeneity and photostability of the catalyst, without the need for post-synthesis additives, and established a protocol to maintain the high values of the specific surface area values of the porous ZnO nanosheets.

The flow-through reactor devised in this work combines the concepts of piston flow and micro-reactor by using a SSWM-based photocatalyst with a very high irradiated surface area per unit volume ($9 \times 10^5 \text{ m}^2/\text{m}^3$) and a high photon transfer efficiency. In addition, this reactor is easily up-scalable and permits the *in situ* regeneration of the photocatalyst. The reactor has been tested for the photodegradation of methylene blue (MB) in water with catalysts synthesized under different conditions. Methylene blue is a dye that is extensively used in industrial applications and in photocatalytic studies [21, 22]. Finally, the photocatalytic results are compared with those reported in the literature for micro-fluidic systems.

Experimental

Catalyst synthesis

The standard method of synthesis of the SSWM-supported ZnO samples is described elsewhere [23] and summarized in the Supplementary Information (SI). This method was subjected to repeatability problems as a result of insufficient wetting of the mesh in the synthesis solution, due to the contact between the mesh and the autoclave or to bubbles clinging to the mesh surface during heating in the oven. This problem was solved by

adding a surfactant (Triton™ X 100, Chem Lab) to the synthesis solution (~85-100 mg/100 cm³).

The adhesion of the ZnO nanoparticles to the SSWM was improved by adding Triton and monohydrated methylene blue (Sigma Aldrich, 3 cm³ of a 5 ppm aqueous solution added to the synthesis mixture).

Catalyst characterization

The morphological and textural properties of the samples were studied by means of scanning electron microscopy (SEM, FEI Quanta FEG 650 model). The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance instrument operating at 20 kV and 5 mA using Cu K α radiation ($\lambda = 0.15406$ nm). The crystal size values were estimated from the (100) peak of the XRD pattern by means of Scherrer's equation. The BET specific surface area was calculated via the single-point method by means of N₂ physisorption at -196°C in a Micromeritics Autochem II chemisorption analyser. N₂ adsorption-desorption isotherms of selected samples were performed at -196°C in a Micromeritics ASAP 2020 analyser. The pore size distribution (PSD) was calculated from the N₂ adsorption isotherms by means of the Kruk-Jaroniec-Sayari method [24]. UV-VIS diffuse reflectance spectroscopy measurements were carried out to determine the band-gap energy value in a Shimadzu UV-2460 spectrophotometer equipped with an integrating sphere. Adhesion of the ZnO nanosheets to the SSWM was tested by introducing the catalyst into a polypropylene flask filled with water and immersing the flask in an ultrasonic bath for 10 min. To determine the point of zero charge (pH_{pzc}) of the catalysts and of the commercial ZnO powder employed (ChemLab, CL.002626.0250), the pH drift method was used [25]. In brief, 50-cm³ aqueous solutions of NaCl (0.01 M)

were prepared with pH values in the 4-10 range by adding either HCl (0.1 M) or NaOH (0.1 M). Samples of/with around 50 mg of zinc oxide were added to each solution at room temperature and vigorously shaken for 2 days. The initial and final pH values were measured using a GLP21 pHmeter (Crison). The intersection of the curves formed by both sets of values plotted against the initial pH served to determine the pH_{pzc} of the analysed sample. The amount of methylene blue adsorbed by the SSWM-supported catalysts at different pH values was evaluated by introducing catalyst samples in 50-cm³ aqueous solutions of MB (10 ppm) at specific pH values, adjusted by adding small amounts of HCl (0.1 M) or NaOH (0.1 M). The solutions were mechanically shaken for one day to ensure equilibrium adsorption. The concentration of MB before and after equilibrium adsorption was analysed using an UV-Vis spectrometer (Shimadzu UV-2401PC) from the absorbance at 665 nm.

Continuous operation flow-through photocatalytic reactor

The reactor was a standard polystyrene filter holder in which the filter was replaced by a disc-shaped catalyst (37 mm diameter, ~112 μ m thickness). Figures 1A-B show a photograph and a schematic representation of the reaction system. A four-channel peristaltic pump (Ismatec Ecoline VC-MS/C44-12 with Pharmed BPT tubing, 0.25 mm i.d.) is used to move a liquid stream through the reactor in two possible modes: in the *reaction mode* the peristaltic pump propels a MB solution towards the catalyst disc from the lower part of the holder, whereas in the *regeneration mode* the direction of the liquid is reversed and water is pumped towards the catalyst disc from the upper part of the holder. Two three-way valves allow the liquids to be changed from one mode to another (Figure 1). In both modes the liquid homogeneously traverses the catalyst disc through small openings (~30 μ m) in the catalytic mesh (Figure 2B), in a way similar to micro-

fluidic devices. The liquid flows in a plug-flow fashion, and enters the voids of the mesh homogeneously, the small size of the voids ensuring that external mass transfer resistance is kept to a minimum. The level of solution covering the disc is kept to a minimum (~1 mm) by using a Viton[®] O-ring between the disc and a transparent quartz disc (1 mm thickness) as a top cap (Figure 1B). Two small perforations in the polystyrene holder, at the level of the upper part of the separation O-ring, connected to small pipes (~1 mm i.d.) allow the liquid to exit. To enable the liquid to pass from the inner side of the O-ring to the outlet pipes, a small piece of SSWM (~3 mm²) is located next to each perforation, between the O-ring and the quartz disc. A perforation in the polystyrene holder, below the catalytic disc, connected to a relief pipe (shown in Figure 1A) is used to eliminate any liquid excess in case of overpressure. A second O-ring placed over the quartz disc guarantees the absence of leaks. A piece of the polystyrene filter ensures the O-ring is tightly pressed against the quartz disc (Figure 1B). An 8 mm UV light source guide (Opsytec Dr Gröbel LQ-400 model, 400W, 365nm, 88% UV-A) is used to illuminate the upper surface of the catalyst disc (33.5 mm irradiated diameter) from a controllable distance. The irradiated surface area (upper side geometric area) per unit volume of the micro-reactor is $9 \times 10^5 \text{ m}^2/\text{m}^3$. In principle, this reactor should be easy to scale up to allow large flow rates, as illustrated in Figure S1 (Supplementary Information).

Photocatalytic and regeneration tests in the flow-through reactor

Continuous operation photodegradation experiments were performed using a methylene blue (MB) aqueous solution ($C_0 = 10 \text{ ppm}$). The MB solution was magnetically stirred and air bubbled in a 2 L amber glass bottle. With the aid of the peristaltic pump (reaction mode) a constant flow of MB solution was directed into the reactor from its lower part. The liquid stream exiting the reactor was collected in test tubes at controlled time intervals

by a Frac-920 fraction collector (GE Healthcare Life Sciences). The collected samples were analysed in an UV-Vis spectrometer (Shimadzu UV-2401PC), a TOC analyser (Shimadzu TOC-V CPH + ASI-V) and an ICP-MS analyser (Agilent 7700x model) in order to evaluate the MB concentration (absorbance at 665 nm), the total organic content, and the Zn^{2+} concentration, respectively.

In a typical reaction experiment, a stream of MB solution at a rate of $20 \text{ cm}^3/\text{h}$ was passed through the reactor under darkness to ensure equilibrium adsorption of MB onto the catalytic disc. Then, the UV light source, with its tip positioned 26.6 mm above the catalytic mesh, was turned on to initiate the photocatalytic reaction. At this height, average irradiance in the 230-400 nm wavelength range of the catalyst disc was $10 \text{ mW}/\text{cm}^2$ (RM-12 radiometer UVBB-sensor provided by Opsytec Dr Gröbel).

In specific cases, after the reaction the reactor was operated in regeneration mode. In this mode water was pumped for about 5 hours to the reactor from the upper side of the catalytic disc by changing the position of the three way valves and reversing the flow of the peristaltic pump, while the UV light source continued to illuminate the catalyst disc.

Results and discussion

Stainless steel-wire mesh supported ZnO. characterisation

As mentioned in the experimental section the standard synthesis method needs to be improved to ensure homogeneity of the samples and adhesion to the support. The lack of homogeneity between samples can be counteracted by adding of a small amount of surfactant (TritonTMX-100), as shown in Figure 2A, where the high homogeneity of the ZnO film is clearly observed. Furthermore, the microwires of the mesh were more tightly covered by the ZnO nanosheets, as can be observed in Figures 2B-C.

The adhesion of the ZnO particles to the mesh was partially improved by adding Triton™ X-100, as can be seen in Figure 3 (ZnO losses in the ultrasonic adhesion test decreased from 19.6 ± 16.0 wt.% to 15.9 ± 14.7 wt.%), probably due to better penetration of the mesh voids by the synthesis solution. A more significant improvement to the adhesion of the ZnO particles was observed when methylene blue was added to the synthesis solution. The ZnO losses were drastically reduced in the ultrasonic test to below 5 wt.% (Figure 3). The mechanism that governs the methylene blue action in this process is currently under examination.

Modification of the synthesis method does not cause any significant changes in the morphological, structural or textural properties of the catalyst, reported in the works by Vu *et al.* [16, 23]. In the case of the sample calcined at 210°C (~20 wt.% ZnO) the XRD patterns (Figure 2D) correspond in both cases (modified and unmodified methods) to the typical hexagonal wurtzite-type ZnO (JCPDS No. 36-1451), with a crystal size of 8.8-9.4 nm, as evaluated by Scherrer's equation. The N₂ physisorption isotherms (Figure 2E) are almost coincident and typical of mesoporous materials (type IV isotherm), with a specific surface area of 105-115 m²/g, a bimodal pore size distribution (inset of Figure 2E) and a similar pore volume of around 0.3 cm³/g. In the case of samples with different ZnO yields but the same calcination temperature (210°C), there are random variations in crystal size (7.5-9.4 nm) and specific surface area (102-124 m²/g). Table 1 also shows that an increase in the calcination temperature produces the corresponding increase in the ZnO crystal size (up to 22.3 nm at 450°C) accompanied by a concomitant decrease in specific surface area (down to 24.3 m²/g at 450°C). The average band-gap energy value obtained from Tauc plots (Supplementary Information Figure S3) of the Kubelka-Munk function for samples with different ZnO yields calcined at 210°C (Table 1) was 3.31 ± 0.05 eV, as expected for pure ZnO [26]. The band-gap values of the samples calcined at higher temperatures

show a slight decrease (Table 1) contrary to the findings of some authors [27, 28] but in agreement with the results of other authors [29], who attribute the decrease in band-gap with calcination temperature to the increase in particle size, since they believe that “as the particle size increases, the number of atoms that form a particle also increases which consequently renders the valence and conduction electrons more attractive to the ion core of the particles, hence decreasing the band gap of the particles” [29].

Effect of catalyst properties on the MB photodegradation in the flow-through reactor

Figure 4 shows the results of photodegradation in the flow-through reactor of a 20 cm³/h MB solution (C₀=10 ppm) during ~17 h using catalysts with different amounts of ZnO (yield) calcined at 210°C. The MB conversion values (X_{MB}) at 3 and 17 h are presented in Table 2. A small part of these conversion values corresponds to photolysis (~4.5%, evaluated in the absence of catalyst) as it is indicated in Figure 4. From the results plotted in this figure and listed in Table 2 it can be concluded that the ZnO mass (W_{ZnO} in Table 2) has no apparent effect on the MB conversion values, which are randomly distributed among the ZnO mass values. The average conversion at 3 h is 64.6 ± 3.7%, decreasing slightly and almost linearly to 57.9 ± 4.2% at 17 h. Two reasons may explain the absence of a relation between the ZnO mass and the MB conversion; i) hardly any MB is adsorbed onto the surface of the catalyst and/or ii) the UV light only illuminates the outermost surface of the catalyst. The adsorption of an ionic dye depends on the point of zero charge (pH_{pzc}) of the adsorbent. Thus, the adsorption of MB (a cationic dye) will be favoured at pH values above the pH_{pzc}, in which case the surface of the adsorbent will be negatively charged. Conversely, in the case of pH < pH_{pzc}, the surface of the adsorbent will be positively charged, and this will hinder the adsorption of the cationic dye. Figure 5 shows the results of applying the pH drift method [25] to evaluate the pH_{pzc} values of a

SSWM-supported catalyst ($T_C = 210^\circ\text{C}$, ZnO yield = ~20 wt.%) and a commercial ZnO powder (ChemLab, CL.002626.0250). The points of intersection in Figure 5 indicate the pH_{pzc} values: 7.5 for the SSWM-supported catalyst and 8 for the commercial powder. The pH of the 10 ppm MB solution used in the photodegradation experiments is 6.1, similar to that of the deionized water. Specific adsorption experiments confirmed the insignificant MB adsorption at the pH of the MB solution (0.6 mg/g at pH = 6.5). Only when the pH of the solution was increased to values above the pH_{pzc} of the SSWM-supported catalyst, was the adsorption of MB apparent (2.4 mg/g at pH = 9.5). It is interesting to note that the pH_{pzc} of the SSWM-supported catalyst is somewhat lower than the values reported in the literature for ZnO nanoparticles, between 8.5 and 9.5 [25, 30-32]. SSWM-supported ZnO nanosheets are polar, but the non-polar edges of the nanosheets are preferentially exposed due to the alignment of the nanosheets (see Figure 2C and discussion in [19]). Assuming that water is not adsorbed on the polar planes (this hypothesis is supported by our previous work [20] and widely justified in the supplementary information), then MB would only react on the most external non polar edges of the sheets. Therefore, almost no MB (at $\text{pH} < \text{pH}_{\text{pzc}}$) is adsorbed on the surface of the catalyst, even on the external surface of the nanosheets, but only on their most external edges. This would explain why the MB conversion is only randomly affected by the ZnO yield. In spite of the low utilisation of the catalyst surface, its photoactivity in the flow-through reactor is exceedingly high, as is borne out by a comparison with other micro-reaction systems, which opens the door to a future investigation of the photodegradation of anionic dyes, for which a significant adsorption might be expected.

Figure 6 shows the evolution of MB conversion with time for the ~20 wt.% ZnO catalysts calcined at different temperatures (210-450°C). The conversion values at short reaction times decrease when T_C increases from 210 to 250°C, and then show a significant increase

for higher calcination temperatures (Table 2). The inset in Figure 6 shows the slope of the line that fits the curves from the point of maximum conversion until the end of the reaction (minimum conversion), a value equivalent to the rate of deactivation during the reaction ($-dX_{MB}/dt$). It can be seen that the deactivation rate clearly increases with the calcination temperature. A more crystalline ZnO seems to enhance the deactivation. Deactivation takes place via the accumulation of volatile compounds on the surface of the material that turn the catalyst blackish (left photograph in Figure 7). These compounds are volatilized under an inert atmosphere at temperatures below 600°C without leaving carbonaceous residues.

MB mineralization and ZnO losses during the reaction in the flow-through reactor

The values of total organic carbon conversion (X_{TOC} , %) obtained by TOC analysis with samples acquired at reaction times of around 17 h are presented in Table 2. The average ratio of TOC conversion to MB conversion (at 17 h) is 0.45 ± 0.08 for all the experiments listed in Table 2. This value is similar to that obtained for batch photocatalytic systems based on TiO₂ [33] and better than that reported for other reaction systems such as the dielectric barrier discharge non-thermal plasma reactor [34].

Table 2 also shows the losses of ZnO during the reaction (L_{ZnO} , wt.%) as a consequence of photocorrosion [35-37], as determined from the evolution of the Zn²⁺ concentration in the exit stream (analysed by ICP-MS). In a previous work [16], a SSWM-supported ZnO catalyst ($T_C = 210^\circ\text{C}$, ZnO yield = ~20 wt.%) prepared without the use of Triton™ X-100 and/or MB in the synthesis solution was subjected to batch experiments of MB photodegradation under UV irradiation. After one hour of reaction the sample had lost almost 60 wt.% of its initial ZnO content [16]. Table 2 shows that the maximum loss of

ZnO with the catalyst synthesized using the modified procedure, as described in the present work, is ~13.7 wt.% for the catalyst with the lowest ZnO yield, decreasing with the increase in ZnO yield down to its lowest value of ~1.0 wt.%. This inverse relationship between the ZnO yield and the *fractional* ZnO losses during the reaction results in a similar *absolute* ZnO loss for all catalysts which, at the end of reaction (~17h), leaves an average Zn²⁺ concentration in all the treated water samples of 3.1 ± 1.0 ppm, an average which includes the values obtained with the catalysts calcined at different temperatures. The Zn²⁺ concentration diminishes over longer reaction times, since the photocorrosion reaction rate follows a descending trend similar to that of the MB photodegradation rate. Although one of the purposes of future works will be to eliminate any loss of catalyst, it is worth noting that drinking water with 3 ppm of zinc is far from being a risk to the human health according to the World Health Organization [38]. As can be seen in Table 2, the ZnO losses from photocorrosion decrease with the calcination temperature (from 3.6 wt.% at 210°C to 1.2 wt.% at 450°C). This may be due to the progressive annealing of reactive photocorrosion centres as the calcination temperature increases.

The fact that the *absolute* amount of Zn²⁺ released into the water is independent of the ZnO mass in the catalyst is further proof of the hydrophobic behaviour of the polar faces of the ZnO nanosheets. As with MB photodegradation, photocorrosion only takes place on the surface of the most external edges of the nanosheets, where water can exert its photocorrosive activity according to the reactions [35-37]:

where h⁺ are the positive holes created by the action of UV irradiation. It seems that all significant reactions [photodegradation, deactivation and photocorrosion] take place at

the external non-polar edges of the nanosheets, to which water and methylene blue have access.

Regeneration of the SSWM-supported ZnO catalyst

Due to the slight deactivation experienced by the catalysts during the reaction (Figures 4 and 6), a SSWM-supported catalyst with a ~20 wt.% ZnO yield and calcined at 250°C was used to explore the regeneration of the catalyst between successive cycles of reaction in the flow-through reactor. The regeneration stage consisted in setting the reactor to regeneration mode and passing water through the catalyst under UV irradiation for about 5 hours. The methylene blue conversion curves for each cycle are plotted in Figure 7. The photographs included in the figure show the catalyst disc at the end of the first reaction cycle (left) and after the first regeneration stage (right). As can be clearly observed, the black spots formed during the reaction on the surface of the material have been eliminated by the combined action of water and light during the regeneration stage. The second reaction stage shows a clear reactivation of the catalyst, which is less pronounced in the third reaction stage. Successive cycles show a stable reactivation. The losses of ZnO during the successive reaction cycles (Figure 7) remain more or less stable in the 1.4-1.9 wt.% range. The specific surface area of the catalyst was measured before reaction, at the end of the first reaction cycle and after the first regeneration stage, yielding values of 74.5, 75.9 and 76.4 m²/g, respectively. No structural changes were detected in these samples by XRD analysis. This is conclusive proof that the reaction is restricted to the surface of the most external edges of the nanosheets, where the volatile compounds are neither a source of additional surface area nor a material blocking the porosity of the catalyst.

Comparison of the flow-through reactor with micro-fluidic reactors

Finally, if the catalytic disc is considered as a micro-reactor itself, it might be worthwhile to make a comparison between the performance of the flow-through reactor and other micro-fluidic systems used for the photodegradation of methylene blue [39-41]. Table 3 shows the main characteristics of systems we have compared, including the type of catalyst, UV lamp, irradiance, reactor volume and reaction parameters. On the basis of the maximum conversion values reported by the different authors the activity expressed as the amount of MB photodegraded per micro-reactor volume and time can be evaluated. It can be seen that, even with a value of irradiance generally lower than that used in the other reactor systems and a more *modest* catalyst (ZnO vs TiO₂ or BiVO₄) the flow-through reactor yields a superior activity.

It is important to note that the reactor described in the present work shows a low pressure drop and no obstruction problems. To employ solar radiation, the catalyst formulation can be easily changed by doping of ZnO or by synthesizing other oxides (TiO₂, Fe₂O₃, etc.) from the SSWM-supported ZnO by means of sacrificial template accelerated hydrolysis [15, 23, 42]. Low cost, high availability, easy handling, flexibility, mechanical stability and scalability are other advantages that favour this kind of reactor.

Conclusions

A flow-through reactor has been designed for the continuous degradation of contaminants in water. It employs a catalytic disc, stainless steel wire micromesh-supported ZnO nanosheets, whose preparation method has been improved with respect to previous works by adding Triton™ X-100 and methylene blue to the synthesis solution. This modification

yields a catalyst with a homogeneous distribution and an enhanced adhesion of the ZnO particles on/to the mesh and a high specific surface area ($>100 \text{ m}^2/\text{g}$). However, in the photodegradation of MB performed under UV irradiation it has been proved that most of the surface of the catalyst particles is not in contact with the MB solution, and that the reaction is restricted to the most external non-polar edges of the ZnO nanosheets. This is a consequence of the hydrophobicity of the polar faces of the nanosheets and the low pH of the MB solution, i.e. below the ZnO point of zero charge. Nevertheless, the performance of this reactor is exceedingly high and superior to that of other micro-fluidic systems described in the literature. The catalyst undergoes a slight deactivation during reaction due to the accumulation of black volatile compounds on its surface. Its activity can be restored by passing water through the catalyst under UV irradiation. The loss of ZnO through photocorrosion is very low, especially when compared to the loss experienced by the catalyst when prepared without the addition of methylene blue to the synthesis solution. The reactor described in the present work shows a low pressure drop and no obstruction problems.

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Reference list

[1] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: A review, *Water Research*, 44 (2010) 2997-3027.

- [2] S. Parsons, Advanced oxidation processes for water and wastewater treatment, *Water Intelligence Online*, 4 (2005) 9781780403076.
- [3] N. Wang, X. Zhang, Y. Wang, W. Yu, H.L. Chan, Microfluidic reactors for photocatalytic water purification, *Lab on a Chip*, 14 (2014) 1074-1082.
- [4] X. Li, H. Wang, K. Inoue, M. Uehara, H. Nakamura, M. Miyazaki, E. Abe, H. Maeda, Modified micro-space using self-organized nanoparticles for reduction of methylene blue, *Chemical Communications*, (2003) 964-965.
- [5] Z. Zhang, H. Wu, Y. Yuan, Y. Fang, L. Jin, Development of a novel capillary array photocatalytic reactor and application for degradation of azo dye, *Chemical Engineering Journal*, 184 (2012) 9-15.
- [6] Y. Matsushita, N. Ohba, S. Kumada, K. Sakeda, T. Suzuki, T. Ichimura, Photocatalytic reactions in microreactors, *Chemical Engineering Journal*, 135, Supplement 1 (2008) S303-S308.
- [7] H. Lindstrom, R. Wootton, A. Iles, High surface area titania photocatalytic microfluidic reactors, *AIChE Journal*, 53 (2007) 695-702.
- [8] L. Lei, N. Wang, X.M. Zhang, Q. Tai, D.P. Tsai, H.L.W. Chan, Optofluidic planar reactors for photocatalytic water treatment using solar energy, *Biomicrofluidics*, 4 (2010) 043004.
- [9] S. Das, V.C. Srivastava, Recent Advances in Fabrication of Photocatalytic Micro-Reactor, in: *Materials Science Forum*, Trans Tech Publ, 2016, pp. 156-167.
- [10] M.-H. Hsu, C.-J. Chang, Ag-doped ZnO nanorods coated metal wire meshes as hierarchical photocatalysts with high visible-light driven photoactivity and photostability, *Journal of Hazardous Materials*, 278 (2014) 444-453.
- [11] S. Jung, K. Yong, Fabrication of CuO-ZnO nanowires on a stainless steel mesh for highly efficient photocatalytic applications, *Chemical Communications*, 47 (2011) 2643-2645.
- [12] M. Bestetti, D. Sacco, M.F. Brunella, S. Franz, R. Amadelli, L. Samiolo, Photocatalytic degradation activity of titanium dioxide sol-gel coatings on stainless steel wire meshes, *Materials Chemistry and Physics*, 124 (2010) 1225-1231.
- [13] S. Yanagida, A. Nakajima, Y. Kameshima, K. Okada, Photocatalytic Destruction of 1,4-Dioxane in Aqueous System by Surface-Roughened TiO₂ Coating on Stainless Mesh, *Key engineering materials*, 412 (2009) 137-141.
- [14] T.T. Vu, A.B. Rodil, G. Marbán, T. Valdés-Solís, Nanostructured stainless steel wire mesh-supported Cd_xZn_{1-x}O: A stable photocatalyst under visible and ultraviolet irradiation, *Journal of Environmental Chemical Engineering*, 2 (2014) 1612-1620.
- [15] T.T. Vu, T. Valdés-Solís, G. Marbán, High surface area stainless steel wire mesh-supported TiO₂ prepared by sacrificial template accelerated hydrolysis. A monolithic photocatalyst superior to P25 TiO₂, *Journal of Environmental Chemical Engineering*, 2 (2014) 2229-2235.

- [16] T.T. Vu, L. del Río, T. Valdés-Solís, G. Marbán, Fabrication of wire mesh-supported ZnO photocatalysts protected against photocorrosion, *Applied Catalysis B: Environmental*, 140-141 (2013) 189-198.
- [17] T.T. Vu, L. del Río, T. Valdés-Solís, G. Marbán, Stainless steel wire mesh-supported ZnO for the catalytic photodegradation of methylene blue under ultraviolet irradiation, *Journal of Hazardous Materials*, 246-247 (2013) 126-134.
- [18] T.T. Vu, L. Del Río, T. Valdés-Solís, G. Marbán, Tailoring the synthesis of stainless steel wire mesh-supported ZnO, *Materials Research Bulletin*, 47 (2012) 1577-1586.
- [19] A. Fernández-Pérez, V. Rodríguez-Casado, T. Valdés-Solís, G. Marbán, Room temperature sintering of polar ZnO nanosheets: I-evidence, *Physical Chemistry Chemical Physics*, 19 (2017) 16406-16412.
- [20] A. Fernández-Pérez, V. Rodríguez-Casado, T. Valdés-Solís, G. Marbán, Room temperature sintering of polar ZnO nanosheets: II-mechanism, *Physical Chemistry Chemical Physics*, 19 (2017) 16413-16425.
- [21] A. Di Mauro, M.E. Fragalà, V. Privitera, G. Impellizzeri, ZnO for application in photocatalysis: From thin films to nanostructures, *Materials Science in Semiconductor Processing*, 69 (2017) 44-51.
- [22] A. Mills, An overview of the methylene blue ISO test for assessing the activities of photocatalytic films, *Applied Catalysis B: Environmental*, 128 (2012) 144-149.
- [23] T.T. Vu, G. Marbán, Sacrificial template synthesis of high surface area metal oxides. Example: An excellent structured Fenton-like catalyst, *Applied Catalysis B: Environmental*, 152-153 (2014) 51-58.
- [24] M. Kruk, M. Jaroniec, A. Sayari, Application of large pore MCM-41 molecular sieves to improve pore size analysis using nitrogen adsorption measurements, *Langmuir*, 13 (1997) 6267-6273.
- [25] H. Benhebal, M. Chaib, T. Salmon, J. Geens, A. Leonard, S.D. Lambert, M. Crine, B. Heinrichs, Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol-gel process, *Alexandria Engineering Journal*, 52 (2013) 517-523.
- [26] A. Mang, K. Reimann, S. Rübenacke, Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure, *Solid State Communications*, 94 (1995) 251-254.
- [27] Z.N. Kayani, F. Saleemi, I. Batool, Effect of calcination temperature on the properties of ZnO nanoparticles, *Applied Physics A*, 119 (2015) 713-720.
- [28] E. Mornani, P. Mosayebian, D. Dorrnian, K. Behzad, Effect of calcination temperature on the size and optical properties of synthesized ZnO nanoparticles, *Journal of Ovonic Research Vol*, 12 (2016) 75-80.

- [29] N.M. Al-Hada, E. Saion, A. Shaari, M. Kamarudin, S.A. Gene, The influence of calcination temperature on the formation of zinc oxide nanoparticles by thermal-treatment, in: *Applied Mechanics and Materials*, Trans Tech Publ, 2014, pp. 181-184.
- [30] S.R. Kanel, S.R. Al-Abed, Influence of pH on the transport of nanoscale zinc oxide in saturated porous media, *Journal of Nanoparticle Research*, 13 (2011) 4035-4047.
- [31] D. Collins, T. Luxton, N. Kumar, S. Shah, V.K. Walker, V. Shah, Assessing the impact of copper and zinc oxide nanoparticles on soil: a field study, *PLoS One*, 7 (2012) e42663.
- [32] E.H. Jones, C. Su, Transport and retention of zinc oxide nanoparticles in porous media: Effects of natural organic matter versus natural organic ligands at circumneutral pH, *Journal of Hazardous Materials*, 275 (2014) 79-88.
- [33] Y. Wang, R. Shi, J. Lin, Y. Zhu, Significant photocatalytic enhancement in methylene blue degradation of TiO₂ photocatalysts via graphene-like carbon in situ hybridization, *Applied Catalysis B: Environmental*, 100 (2010) 179-183.
- [34] P. Manoj Kumar Reddy, B. Rama Raju, J. Karuppiah, E. Linga Reddy, C. Subrahmanyam, Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor, *Chemical Engineering Journal*, 217 (2013) 41-47.
- [35] H. Fu, T. Xu, S. Zhu, Y. Zhu, Photocorrosion Inhibition and Enhancement of Photocatalytic Activity for ZnO via Hybridization with C60 *Environmental Science and Technology*, 42 (2008) 8064-8069.
- [36] A.L. Rudd, Photo-induced dissolution of zinc in alkaline solutions, *Electrochimica Acta*, 45 (2000) 1571-1579.
- [37] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar/UV-induced photocatalytic degradation of three commercial textile dyes, *Journal of Hazardous Materials*, 89 (2002) 303-317.
- [38] J.M. Donohue, C.O. Abernathy, P. Lassooszy, G. Hallberg, Rolling Revision of the WHO Guidelines for Drinking-Water Quality, *World Health*, (2004).
- [39] Z. Meng, X. Zhang, J. Qin, A high efficiency microfluidic-based photocatalytic microreactor using electrospun nanofibrous TiO₂ as a photocatalyst, *Nanoscale*, 5 (2013) 4687-4690.
- [40] N. Padoin, L. Andrade, J. Ângelo, A. Mendes, R.d.F.P.M. Moreira, C. Soares, Intensification of photocatalytic pollutant abatement in microchannel reactor using TiO₂ and TiO₂-graphene, *AIChE Journal*, 62 (2016) 2794-2802.
- [41] X. Wang, Z. Liu, N.Y. Chan, H.W. Chan, X. Zhang, Photocatalytic microfluidic reactor with a novel compound catalyst film using solar energy, in: *Proceedings of the 16th International Conference on Miniaturized Systems for Chemistry and Life Sciences, MicroTAS 2012*, 2012, pp. 1993-1995.

[42] T.T. Vu, T. Valdés-Solís, G. Marbán, Novel high surface area stainless steel wire mesh supported $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{O}$ solid solution prepared by room temperature sacrificial template accelerated hydrolysis. Application in the production of hydrogen from methanol, *Applied Catalysis B: Environmental*, 160–161 (2014) 57–66.

Captions to figures

Figure 1. Flow-through reactor. A) Photograph of the reaction system, B) Schematic representation.

Figure 2. Properties of SSWM-supported photocatalysts ($T_C = 210^\circ\text{C}$, ZnO yield = ~20 wt.%) prepared by the unmodified or modified synthesis methods. A) Photograph; B and C) SEM images; D) XRD patterns of the ZnO catalysts and a commercial ZnO powder; E) N_2 physisorption isotherms (inset: pore size distributions).

Figure 3. Adhesion test results for SSWM-supported ZnO samples prepared in the presence or absence of TritonTM X-100 and/or Methylene blue.

Figure 4. Evolution of methylene blue conversion with time for the SSWM-supported catalysts with different ZnO yields.

Figure 5. Evaluation of pH_{pzc} for SSWM-supported ZnO ($T_C = 210^\circ\text{C}$, ZnO yield = ~20 wt.%) and a commercial ZnO powder.

Figure 6. Evolution of methylene blue conversion with time for the SSWM-supported catalysts prepared at different calcination temperatures.

Figure 7. Consecutive reaction cycles intercalated by regeneration steps for SSWM-supported ZnO ($T_C = 250^\circ\text{C}$, ZnO yield = ~23 wt.%).

Tables

Table 1. Structural, textural and optical parameters of the SSWM-supported ZnO materials

ZnO yield (wt.%)	T _C = calcination temperature (°C)	Crystal size (nm)	BET specific surface area (m ² /g)	Band-gap (eV)
8.0	210	8.0	103	3.33
15.7	210	9.1	111	3.36
18.5	210	9.4	115	3.34
31.0	210	7.5	124	3.28
33.5	210	8.3	103	3.33
25.9	250	8.7	92.8	3.22
19.3	350	14.2	26.5	3.18
16.5	450	22.3	24.3	3.18

Table 2. Results of MB photodegradation in the flow-through reactor

T _C (°C)	ZnO yield (wt.%)	W _{ZnO} (mg)	X _{MB} at t=3 h (%)	X _{MB} at t=17 h (%)	X _{TOC} at t=17 h (%)	L _{ZnO} * (wt.%)
210	5.1	11.4	68.9	54.9	21.6	13.7
210	8.4	19.6	65.2	60.6	22.2	8.7
210	16.6	42.3	63.6	56.7	21.0	4.5
210	19.9	55.4	66.5	58.1	26.6	3.6
210	28.5	80.3	60.5	59.1	26.0	2.1
210	33.4	113.7	59.2	51.4	31.4	1.0
210	42.9	153.2	68.5	64.5	-	1.5
250	22.7	62.0	54.6	43.0	19.4	1.7
350	21.6	58.4	64.4	47.7	-	1.7
450	19.4	51.5	71.8	52.2	27.2	1.2

* ZnO loss at the end of reaction due to photocorrosion

Table 3. Comparison of micro-reactor systems for MB photodegradation

Reference	This work	Meng <i>et al.</i> [39]	Padoin <i>et al.</i> [40]	Wang <i>et al.</i> [41]
Reactor	Flow-through	Micro-fluidic-based	Micro-fluidic-based	Micro-fluidic-based
Catalyst	SSWM-supported ZnO	Nanofibrous TiO ₂	TiO ₂ P25	BiVO ₄ thin porous film
Lamp	Dr Gröbel UV LQ400	UV-LED 365 nm	UV-A-365 nm	Low-cost blue-light panel LED
Irradiance (mW/cm²)	9.9	50	0.6	140
Reactor volume (m³)	9.9×10 ⁻⁸ *	1.2×10 ⁻⁶	1.3×10 ⁻⁸	1.0×10 ⁻⁸
Reactant	Methylene blue	Methylene blue	Methylene blue	Methylene blue
C₀ (ppm)	10	10	10	9.6
Flow (cm³/h)	20	6	5.4	2.3
Residence Time (s)	17.8	12.4	8.6	16.0
Maximum conversion (%)	64.6**	56.9	18.3	39.0
Activity [mg/(m³h)]	1.3×10 ⁶	2.8×10 ⁴	7.7×10 ⁵	8.4×10 ⁵

*Volume of the irradiated photocatalytic disc; **Averaged for all catalysts in Figure 4 at t=10⁴ s

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7