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Correlations between optical, specific surface and photocatalytic properties of media integrated in a photo-reactor

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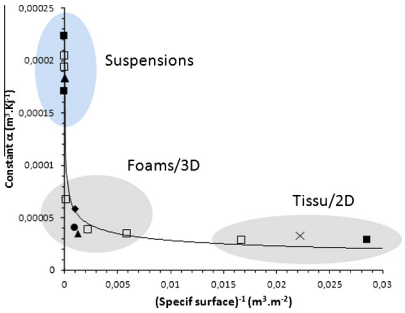
HIGHLIGHTS

- Use specific surface area as a metric to assess the performances of photocatalytic media.
- A panel of various formats proposed in the literature are studied.
- Ranked into ascending order of increasingly active specific surface area: tissue < fibers < foams < powder.

GRAPHICAL ABSTRACT



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ABSTRACT

We use specific surface area as a metric to assess the performances of photocatalytic media, where specific surface area is calculated as irradiated catalytic surface developed per unit of photoreactor volume. The photocatalytic media compared were selected to cover a wide range of specific surface areas from within a panel of various formats proposed in the literature, i.e. powder suspensions (nanometer-scale and micrometer-scale), 2D media (tissue, glass rods), macroporous media including reticular foams and bulk solids including fiber stacks. The overarching approach, where we define the configurations that deliver the best photocatalytic performances possible, is split into a two-stage phases. Stage 1 aims to correlate the media's structural properties to its transmittance. Stage 2 aims to study and rank the media in terms of their photocatalytic performances. This two-stage process, based on a panel of media, make it possible to define the configurations of photocatalytic media that make the best use of all available incident light in a given photoreactor geometry, and to adapt the media format to in-use constraints (depth, volume, light flux density). Ranked into ascending order of increasingly active specific surface area (expressed in $m^2\ m^{-3}$), the results read as follows: cellulosic tissue < metallic fibers < reticulated foams < powder suspensions.

1. Introduction

Heterogeneous photocatalysis is able to degrade organic micropollutants in a non-selective manner, and in contrast to existing tertiary processes (UVC, ozonation, membranes), solar photocatalysis drives a treatment process that, energy-wise, is clean and self-sufficient [1–5]. In the field of advanced oxidation processes based on solar radiation, heterogeneous solar catalysis, which involves exciting a photocatalyst with UV rays, runs into the major problem of optimizing use of the sunlight [1,2,5–10]. In contrast to UV lamps which provide an intense and constant beam, sunlight is particularly weak in the ultraviolet spectral region [11]. This

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region, including A–B ultraviolet, accounts for only 5% of total available solar flux at the Earth's surface, i.e. which means the maximum irradiation available for the solar-catalytic process is 50 W_{UV} m^{-2} [1–4]. In this context, efficient use of all available sunlight represents a major challenge in the design and development of this technology adapted for a sustainable water treatment. The photoreactors currently available have been configured for suspensions [2–4,9,10,12–14] and substrate media (foams and fibers) [8,9,15–18]. Their performances are assessed based on photocatalytic reaction speed or photochemical yield [1,2,15,17–22]. The media's ability to capture light is the defining factor shaping its ability to produce radical species [6–8,15,22]. The issue of making optimal use of the irradiation source is made even more crucial by the fact that the flux density available in the UV spectrum is relatively low compared to total incident solar irradiance (5–7%). This means that whatever the media format used, it is vital to define the amount of photons hitting the photocatalyst [19–24]. The literature reports a wide range of catalytic media in use, from suspensions [1,2,12–14,20–26] and fibers [8,17,18,24,27] to beads [25] and reticulated foams [15,16,28–32] and on to tissues [9,10,25] and rods [18]. These materials have been integrated into an equally wide range of photoreactors employed in different sizes, shapes and geometries and trialled in different process conditions (molecules and micropollutants, method of analysis, mass of catalyst, and so on). The sheer span of this research output complicates the task of classifying photocatalytic media according to ability to absorb light or degrade a target compound [1–3,8–10,24–32]. Research by Van Gerven et al., shows how the active catalyst surfaces developed can differ anywhere from 1 to 100 [33,34], which further highlights how active surfaces are a defining factor for photoreactor performances. Here, we use specific surface area as a metric to assess the performances of photocatalytic media, where specific surface area is calculated as irradiated catalytic surface developed per unit of photoreactor volume. The photocatalytic media compared were selected to cover a wide range of specific surface areas from within a panel of various formats proposed in the literature, i.e. powder suspensions (nanometer-scale and micrometer-scale) [10,12,14,20–24], 2D media (tissue, glass rods) [9,17,18,26], macroporous media including reticular foams [14–16,28–32] and bulk solids including fiber stacks [17,18]. The overarching approach, where we define the configurations that deliver the best photocatalytic performances possible, is split into a two-stage phases. Stage 1 aims to correlate the media's structural properties to its transmittance. Transmitted flux (absorptivity) informs on the media's ability to absorb incident light. Its properties vary with different media configurations. Looking at the literature, catalysts in powder suspensions are defined by their concentration [9,14,20–24], foams by their pore density [15,16,29–31], fibers by their bulk density [17,18], 2D media by their surface area [9,15,16], and so on. Building on Van Gerven et al., we propose a system where a media's ability to use incident light is expressed according to specific surface area [33,34]. Ultimately, the aim is to correlate specific surface area—a quantity common to the structural properties of all media—to the media's ability to absorb incident radiation, so as to determine representative optimal operational configurations for each catalyst.

Stage 2 aims to study and rank the media in terms of their photocatalytic performances. Active catalytic surface per unit of photoreactor volume is again the common denominator borrowed for this stage [33]. Photocatalytic media performances are assessed in their optimal configuration ensuring minimal transmittance of light flux, i.e. using virtually all incident irradiation [6,15]. This two-stage process, based on a panel of media, should make it possible to define the configurations of photocatalytic media that make the best use of all available incident light in a given photoreactor geometry, and to adapt the media format to in-use constraints (depth, volume, light flux density). The ultimate goal is to be able to select the media that delivers the most effective and efficient media integrated photoreactor.

2. Experimental protocol

2.1. Photocatalytic media

The media tested here have been studied in earlier research [12–17] and were selected based on their structural characteristics and photocatalytic performances (Table 1) to cover the full panel of mobile and immobilized media reported in the literature, i.e. nanoparticle catalysts, sheet or rod-based 2D media, and the more complex formats such as reticulated foams and fiber stacks.

TiO_2 powder is widely recognized within the science community as the benchmark, largely due to its outstanding efficiency. Produced as a combination of two mineral crystals, anatase (70%) and rutile (30%), it is sourced as a nanocrystallite aggregate centered around a 25 nm grain size. VP Aeroperl P-25/20 is a larger-grained TiO_2 centered around a 20 μm grain size that facilitates the final separation step [12]. The characteristics of these two powders are taken from earlier research and recapped in Table 1 [9,10,12].

Alhstrom 1048-grade (Alhstrom) tissue is an industrially-manufactured 2D media for wastewater treatment applications. The tissue is a fabric weave of cellulosic fibers mechanically impregnated with TiO_2 by a silica gel binder [2,3,15,22,24]. The catalyst covers 20% of the total 2D tissue surface [9]. This industrially-sourceable media is employed here as the benchmark 2D media substrate.

Reticular foams are a set of recently-developed media offering an exceptionally macroporous (85–90%) mesh that shows great promise for the applications targeted [34–38]. The chaotic and disordered architecture of reticular foams makes them outstandingly good diffusers of irradiance inside the reaction volume-space [33–38]. Integrated into the photoreactor system, they develop 10–100-fold greater active surfaces than flat 2D media [31–36]. Their structural properties also make them geometrically remodelable, making it possible to adjust factors such as depth or pore size distribution within the mesh, and thus to structurally handle and control flux density gradient inside the media. Their active specific surface area (m^2 m^{-3}) is dependent on pore size [37,38].

$$S_{spe} = \frac{3.03}{D_{por}} \quad (1)$$

The basic volume sizes available for engineered reticular foams range from 10 μm up to 10 mm. The characteristics of the foams selected for analysis are taken earlier research and recapped in Table 1 [9,15–18].

Metal swarf (debris from metal parts machining) carries very low production costs. These divided solids come as disorderedly-arranged metallic fibers (Fig. 1) that bulk into a highly macroporous framework. This original structural framework offers a large

Table 1
Optical, structural and photocatalytic characteristics of the media used.

	Exposent m (–)	Absorption coefficient ε (–)	Specific surface S^p (m^2 g^{-1})	Energetic constant $a \times 10^{-3}$ (m^3 kJ^{-1})
Tissu (2D)				0.029
Rod (2D)				0.034
Suspension (P25)	0.54	0.0027	50–90	0.205
Suspension (VP)	0.53	0.0037	30–50	0.193
Foam (3D)	0.51	0.014	4–40	0.671
Fiber (3D)	0.7	0.013	2.5	0.039