Research Article

Ceramic-Based 3D Printed Supports for Photocatalytic Treatment of Wastewater

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3D printing technology has become a powerful tool to produce 3D structures in any type of materials. In this work, 3D printing technology is used to produce 3D porous structures in CaSO_4 which can be later activated with an appropriate photocatalyst. TiO_2 was selected as an ideal photocatalyst producing activated 3D structures which can be used to study their effectiveness in the degradation of pollutants in wastewater. Methylene blue was used as a model molecule in these studies. The photocatalytic studies showed that TiO_2 -activated 3D structures using nanoparticles of SiO_2 in the process produce more than 50% of conversion of methylene blue in just 1 h of irradiation and almost 90% in 5 h.

1. Introduction

Global warming, energy crisis, and pollution are serious concerns affecting both the human health and environment. The environmental pollution includes a wide range of hazardous chemicals which are harmful even at extremely low concentrations.

The common treatment of these pollutants involves the use of pyrolytic methods which consume large amounts of fossil fuels producing elevated levels of CO_2 and thus contributing again to climate change and energy crisis.

Another severe issue [1–3] is water pollution from emerging contaminants (ECs) such as endocrine disrupting chemicals, pharmaceuticals, and personal care products even at trace levels. Some adverse potential effects caused by ECs are water toxicity, resistance development in pathogenic bacteria, genotoxicity, and endocrine disruption [4–6].

Wastewater treatment plants are not designed to remove low concentrations of synthetic pollutants such as pharmaceuticals and hence alternatives such as the Advanced

Oxidation Technology (AOT) have been used to solve this environmental problem [7, 8].

Heterogeneous photocatalytic processes constitute one of the most important AOTs and are based on the oxidation of polluting compounds which can be found in air or water by means of a reaction occurring on a semiconductor catalytic surface activated by light with a specific wavelength.

TiO_2 is the most investigated semiconductor catalyst particularly because of its great potential in the treatment of environmental pollution [9] and it is chemically stable, nontoxic, and inexpensive [10–12]. However, TiO_2 has an important disadvantage as it is usually commercially available as powder and, therefore, a posttreatment separation stage is needed [13, 14] and hence it would be highly desirable to have the possibility of supporting the TiO_2 active phase on other structured inorganic materials.

In this sense, a new exciting approach for the production of structured materials on demand may be the use of a 3D printing (3DP) system. Until the past few years, this type of technology has been restricted to medium- and big-sized

FIGURE 1: Indirect Inkjet Print (IIP) is a layer-by-layer process of depositing liquid binder onto thin layers of powder to create a 3D object [17].

companies devoted to the fabrication of prototypes. Nowadays, they are increasingly available for small businesses (research [15]) and even for direct manufacturing. 3D micro fabrication remained a challenge until the introduction of free-forming fabrication (FFF) technology. Free-forming fabrication is any fabrication technology that fabricates 3D complex structures by assembling small elements together and usually starts with a computer aided design (CAD) model. FFF includes, but is not limited to, rapid prototyping, 3D printing, and direct writing for macro scale fabrication [16].

A digital model of the object is created in a computer. Using adequate software, the user may control several relevant parameters such as the number of layers which are piled up to generate the full item depending on the resolution required, thickness of the layers, and porosity. In the second step, each digital layer is printed in an appropriate substrate. Different 3D printing techniques can be selected depending on the material required and the way to fuse layers together. One of the 3D printing options is the Indirect Inkjet Print, where a powder is spread from a well (Figure 1), levelling it to produce a thin layer. Then the printer heads will dispense a thin layer of a binder in the required pattern of the cross section. When the layer is finished, the “build tray” will be lowered by a fraction of a millimetre, typically between 10 and 100 μ and then the process is repeated again for the next cross section. Finally, after printing the whole 3D structure, the loose powder is blown away with compressed air, revealing the full structure [16].

This type of technology has the potential to allow the fabrication of monolithic porous structures that can be covered with a layer of catalytically active material such as TiO_2 [18]. Calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) was one of the first materials to be used for IIP. It can be wetted using a commercially formulated binder (98% content water) and then forms a gypsum paste ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) by activating self-hydration [19] which can be used to produce 3D porous supporting structures.

The aim of this study is to verify that the 3D printing technology can be used to produce porous monolithic structures of calcium sulphate which can be then activated with commercial TiO_2 photocatalyst (Degussa P25) through an impregnation process. The whole 3D activated system will be tested in a fixed-bed photoreactor to verify the potential use of these heterostructures for removing wastewater contaminants using methylene blue (MB) as a model molecule.

2. Materials and Methods

The activity of the TiO_2 photocatalyst supported over a 3D printed ceramic structure was studied evaluating the photodegradation of methylene blue (Sigma-Aldrich) as a model molecule for wastewater treatments. The photocatalytically active material, TiO_2 (Degussa P25, Evonik Industries), was examined by X-ray diffraction (XRD) in order to obtain the percentage of anatase and rutile phase. Nitrogen adsorption-desorption porosimetry and mercury porosimetry techniques were used to study its specific surface area and textural properties [20]. TiO_2 (Degussa P25) was mainly composed by the photocatalytically active anatase phase, 81% (wt). The textural parameters of TiO_2 powder were 51.1 m^2/g of BET specific area, a total pore area of 63.7 m^2/g with 92.5% of porosity, and a density of 2.58 g/ml.

2.1. 3D Printing Structures. The materials used in the 3D printing process were calcium sulphate hemihydrate (Visijet PXL Core, from S.A.T.ÉLITE) and a water-based binder (Visijet Clear, from S.A.T.ÉLITE). These materials were used in a 3D printer (ProJet® 360, from S.A.T.ÉLITE), with a 300 $\times$ 450 dpi resolution and layer thickness of 0.1 mm.

First, the structure is digitally designed using free software Tinkercad [22] and the corresponding digital model is saved as a *stl* file and then sent to the 3D printer. During the three printing processes (Figures 2(a)–2(d)), a roller spread a thin powder layer from the feed area to the build area

FIGURE 2: 3DP process scheme. (a) The roller spreads a thin layer of powder from the feed area to the build area. (b) The print head injects binder droplets on the powder bed. (c) After printing a layer, the roller returns to the feed area. (d) Powder in the feed area is raised, while that in the build area is lowered. The roller then spreads another layer of powder [21].

and then the print head deposits binder droplets selectively within the build area. When the first layer is printed, the roller returns to the feed area, spreading another powder layer to the build area. This procedure is repeated until the fabrication of the whole 3D structure is completed [21].

Following this procedure, several microtubes of ceramic supporting structures were 3D printed (Figures 3(a) and 3(b)), and several small rectangular and square pieces of 2×2 cm were also 3D printed as testing samples in mechanical stability versus temperature studies (Figures 3(c) and 3(d)). 150°C was the selected pre firing temperature to give enough mechanical stability for withstanding the conditions of the impregnation process.

2.2. Improving the Mechanical Stability of the 3D Printed Structures. Two routes were followed to impregnate the 3D structures with another inorganic material enhancing the mechanical stability up to 1200°C . The 3D printed samples were previously fired at 150°C for 2 h to improve the mechanical stability in aqueous solution needed for the impregnation processes.

(i) *Route 1.* Impregnation was done with an aqueous dispersion of alumina (Al_2O_3 , Almatix GmbH) using Dolapix CE64 (Zschimmer & Schwarz) as dispersant. Several ratios of the components and impregnation times (Table 1) were considered to optimize the process. The impregnation times were also optimized ranging from 10 s up to 30 min. The so-impregnated samples were left to dry for 45 min under 70°C and then were finally fired at 1200°C for 4 h with heating and cooling rates of $5^\circ\text{C}/\text{min}$ (Figure 4(a)).

(ii) *Route 2.* Impregnation was done with an aqueous solution of Ludox® AS-30 colloidal silica (Sigma-Aldrich). As in the previous method, the printed 3D structures were initially fired at 150°C for 2 h. After that, the specimens were impregnated in Ludox (1.1 g) and then fired at 600°C for 2 h, with heating and cooling ramp rates of $5^\circ\text{C}/\text{min}$ (Figure 4(b)); this step is performed twice.

2.3. Photocatalytic Studies. The methylene blue (MB) photo-degradation process with the activated 3D printed structures (A3DS) was carried out in a fixed-bed photoreactor system

TABLE 1: Ratio of components and impregnation times used in the optimization of the impregnation process of 3D structures with Al_2O_3 .

Procedure	Al_2O_3 (g)	Water (g)	Dolapix (g)	Impregnation times (s)
1	30,0	8,39	0,161	10, 20, 30, 60, 300, 600, and 1800
2	30,0	16,2	0,423	
3	30,0	33,8	0,644

FIGURE 3: ((a) and (b)) 3D printed supporting structures in CaSO_4 . (c) 3D printed square testing pieces in the green state and (d) after firing at 250°C for 3 h. FIGURE 4: Schemes for improving the mechanical stability of 3D printed supporting structures using two alternative impregnation routes: (a) route 1 with Al_2O_3 and (b) route 2 with Ludox dispersions.

(Figure 5(a)). A3DS were placed in the photocatalytic reactor (18 cm length and 0.6 cm internal diameter) (Figure 5(b)), and a solar radiation sodium vapor lamp (Philips, model 400-WG/92/2), placed at a distance of 50 cm from the fixed-bed reactor, was used as light source (total radiation flux measured on the fixed-bed surface was $160 \text{ mW}/\text{cm}^2$). MB solution in water (20 ppm) was introduced in a 250 ml wastewater photoreactor tank (Figure 5(c)), keeping the temperature constant at 25°C . The MB solution was recirculated

along the system using a peristaltic pump (Watson-Marlow, model 302S). Several samples were taken during several hours of irradiation time and they were analyzed by UV-Vis spectrophotometry in order to follow the evolution of MB concentration into the reactor. Moreover, MB photolysis (with light source and without photocatalyst) and MB adsorption onto A3DS (with photocatalyst and without light source) experiments were developed in order to evaluate its contribution to the global wastewater decontamination process.

FIGURE 5: (a) Fixed-bed photoreactor scheme. (b) Fixed-bed reactor. (c) Wastewater photoreactor tank.

FIGURE 6: Optical images of impregnated 3D structures with dispersions of Al_2O_3 , using an Al_2O_3 concentration of (a) 0.77 g/ml, (b) 0.65 g/ml, and (c) 0.47 g/ml.

2.4. Microstructural Characterization. The morphologies of the 3D structured samples in the green and sintered states were examined using a stereomicroscope Leica Zoom 2000 (Leica Microsystems, Inc.) and a scanning electron microscope (SEM) (model Jeol LTD, JSM-6300) combined with energy dispersive spectroscopy (EDS). For SEM studies, all samples were covered with a thin film of sputtered silver to avoid charging problems and to obtain better image definition.

3. Results and Discussion

As commented in the text, before the activation of the 3D supporting structures, the mechanical stability of the structures must be improved and we can use two routes.

3.1. Route 1: Impregnation with Alumina. Several impregnation studies (Table 1) with alumina dispersions were tested. The impregnation time was also optimized and it was concluded that no significant differences were observed between samples impregnated for 30 s or 5 min and, hence, 30 s was the time used in all the procedures tested. Procedure 1 (Table 1) produces a 0.8 mm thick external covering layer of Al_2O_3 over the 3D structure; however, the porous 3D structure seems to be alumina-free (Figure 6(a)), and hence the inner structure will collapse at high temperature.

Procedure 2 (Table 1) produces two types of covering: an external layer of Al_2O_3 , as in the first case, and an additional inner impregnated layer covering about 70% of the 3D porous structure (Figure 6(b)). The combination of both layers is ideal for improved mechanical stability.

And finally in procedure 3 (Table 1) with a more diluted dispersion, only the internal layer was observed (Figure 6(c)), which is not enough to provide mechanical stability at high temperatures and hence procedure 2 was used to test all the 3D printed structures.

From the SEM images, it is possible to observe a good distribution of $1\ \mu\text{m}$ Al_2O_3 particles in the surface of the covered 3D structure (Figure 7(a)) and also a good distribution inside of the porous structure (Figures 7(b) and 7(c)). The presence of Al_2O_3 is negligible in the inner part of the 3D porous structure (Figure 7(d)), with a value of 0.6% (wt) of Al shown in the EDX studies compared to 25.1% (wt) of Al obtained in the structures impregnated shown in Figures 7(b) and 7(c).

Once the 3D printed structures (Figures 3(a) and 3(b)) have been impregnated with Al_2O_3 and fired at 1200°C , an activation process with the photocatalytic material must be performed. A cement-based material was used to fix the TiO_2 powder to the 3D structure producing an A3DS and then 3 photocatalytic experiments were carried to analyze the photocatalytic behavior of the 3D- TiO_2 structure under UV light.

FIGURE 7: SEM images and EDX data of Al_2O_3 -impregnated samples following procedure 2 (Table 1) with 30 s of impregnation time. (a) SEM image of surface of the covered 3D structure. ((b) and (c)) SEM image showing a good distribution of Al_2O_3 inside the porous structure. (d) SEM image of the inner part of the supporting CaSO_4 porous structure.

FIGURE 8: Temporal evolution of MB removal during photocatalytic experiments under UV light irradiation using 3DAS fabricated with the first route (Section 2.2).

Figure 8 shows the result of the photocatalytic performance under UV light radiation. The temporal evolution of the concentration of the MB as contaminant model showed that MB achieves 46.6% of conversion with the irradiation time after 4 h. This value proves that the 3D supporting structure can be effectively used as a support for photocatalytic materials; however, the degree of conversion can be considered relatively low and hence a more optimized structure, possibly with geometries maximizing illumination

of the active area and/or improvement of the active area, should be fabricated.

Indeed, just modifying the geometrical surface from plain surface to twisted one produces an enhancement of more than 6% in the conversion of MB (Figure 9), that is, from 46.6 to 52.6%, after 4 h.

3.2. Route 2: Impregnation with Silica Nanoparticles (Ludox). Another way to improve the efficiency is to minimize the

FIGURE 9: Simple 3D models of two types of geometrical surfaces printed to verify how the surface design can modify the photocatalytic experiments.

FIGURE 10: Several 3D printed square pieces of CaSO_4 were used to optimize the infiltration process with Ludox. All the samples were infiltrated with a solution of Ludox: water with a ratio of 1:5 (wt) for 30 s and then dried for 10 min at 70°C and finally they were fired at the temperatures shown in the images for 2 h.

distortion of the surface of the 3D printed structures by the impregnated particles. The deposition of micro-sized Al_2O_3 solid particles, previously described, may decrease the available surface area to be covered with the photocatalyst and hence an alternative way to improve the mechanical stability of the 3D printed structures with a minimal distortion of the 3D surface is required. This can be achieved by using a solution of silica nanoparticles (Ludox) which can be easily infiltrated through the whole porous structure as described in the experimental section, Section 2.2, route 2.

Several tests were performed to optimize the Ludox: water ratio, drying steps, and firing temperature. For example, Figure 10 shows 3D impregnated samples exhibiting a good distribution of micro/nanoparticles of silica when the final firing temperature was maintained below 600°C . At higher temperatures, the 3D porous CaSO_4 structure disappears as well as the silica agglomerates; thus the final temperature was kept at 600°C .

The 3D structures were printed following the second route described in Section 2.2 and then they were activated

producing A3DS. In this case, a dispersion of TiO_2 was prepared using a Ludox solution in a 1:1 (TiO_2 : SiO_2) ratio (weight). The sample was left to dry for 1 h at 70°C and finally fired at 300°C for 2 h.

The photoreactor tube was filled with A3DS (Figure 11) and then the photocatalytic performance under UV light radiation was studied. The temporal evolution of the concentration of the MB showed that it achieves 50% of conversion with the irradiation time in just 1 h, which is more than the conversion obtained with the first route after 4 h. A value close to the 90% of conversion was obtained after 5 h. This proves again that the 3D supporting structure can be used as a support of photocatalysts materials and that the optimization of the previous impregnation process can be critical to enhance the activity of the optimized A3DS.

4. Conclusion

3D printing technology has been successfully used to create 3D supporting structures of CaSO_4 which can be activated with TiO_2 showing photocatalytic activity.

FIGURE 11: Temporal evolution of MB removal during photocatalytic experiments under UV light irradiation using 3D printed supports fabricated with the second route (Section 2.2). The inset image shows (a) the 3D printed support covered with the photocatalyst TiO_2 and (b) the photoreactor filled with the 3D structures and recirculating MB.

Two approaches have been proposed and optimized to enhance the mechanical stability of the 3D supports up to 1200°C . In one of them, Al_2O_3 is used as a binder of the whole 3D structure; in the other method, a dispersion of nanoparticles of SiO_2 (Ludox) acts as a binder.

In both cases, the A3DS show photocatalytic activity for the MB removal from wastewater, reaching more than 50% of conversion in just 1 h of irradiation when using Ludox in the activation process. This approach reaches a high photodegradation rate of about 90% after 5 h.

The A3DS offer clear advantages for the industrial treatment of wastewater given that the photocatalytic materials remain confined to the packed bed avoiding the need of separating the catalyst from the decontaminated water effluent.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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