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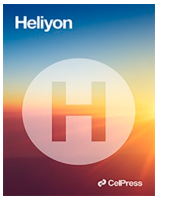

Research article

Upcycling waste derived glass into high-performance photocatalytic scaffolds by alkali activation and direct ink writing

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ABSTRACT

Novel and eco-friendly solutions are extensively needed for wastewater treatment. This work capitalizes on the combination of waste vitrification and additive manufacturing to produce an efficient photocatalyst for the specific purpose. Fine powders of waste-derived glass, containing Fe3O4 inclusions, by simple suspension (for a solid loading of 65 wt %) in alkaline solution (5 M NaOH), were transformed into pastes for direct ink writing. 3D-printed reticulated scaffolds were stabilized by the progressive hardening of a zeolite-like gel, formed by glass/solution interaction, at nearly room temperature. The printed scaffolds were successfully tested for the removal of methylene blue, realized by combining the high sorption capacity of the gel with the catalytic activity of magnetite inclusions, under UV light. A complete degradation of methylene blue is achieved by 90 min exposure, comparing favorably with other reported photocatalytic materials, requiring from 60 to 360 min. The photocatalytic activity was tested for several cycles, with no significant degradation. In other words, a waste-derived material can be reused for multiple times, to remediate wastewaters, with evident benefits on waste minimization.

1. Introduction

Waste disposal is a serious problem, especially in countries with high population density and limited landfill space. The best waste disposal method is recycling and reuse [1,2]. However, the amount of waste that can be recycled is limited to less than about 40 % of the total volume [3]. One of the major problems for the environment is, beyond municipal waste, the disposal of large amounts of industrial solid waste, as represented by red mud (residue from the refinement of Al-yielding ores) and fly ash (residue from coal combustion) [4,5].

Beyond solid waste, industrialized countries face significant problems of water pollution, demanding innovative and sustainable solutions [6]. Traditional approaches often involve the use of chemical additives or filtration processes, which may be costly and generate secondary waste streams. In this context, the integration of waste vitrification and additive manufacturing emerges as a promising strategy for developing efficient and eco-friendly photocatalysts [7,8].

In the current work, such integration is based on the definition of a waste-derived glass. Several types of non-combustible

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hazardous waste, in fact, may be safely converted into glass ('vitrification' treatment), in combination between themselves and/or with glass-forming oxides (such as silicon dioxide) [9]. The processes involves the thermal destruction of waste, in a high temperature step, forming a homogeneous liquid; glass is properly obtained if the cooling to room temperature is fast enough to prevent crystallization [10]. The approach has a significant drawback in the high costs, to be adequately compensated; in addition to savings from avoided landfilling, some revenues could derive from the valorization of waste-derived glass in useful components ('upcycling').

Hujova et al. have found out that glasses from industrial residues, composed primarily of red mud, can be applied as precursors for inorganic binders, at nearly room temperature [11], by interaction with pure water or with a highly concentrated alkaline solution. In the latter case, glass is designed to undergo a substantial dissolution, followed by condensation reactions ('polymerization') between dissolution products. A 'zeolite-like' gel is realized whenever SiO_4 and AlO_4 tetrahedral units form a three-dimensional network, according to a delicate balance of SiO_2, Al_2O_3, CaO and alkali oxides (in particular, alkali ions are fundamental to stabilize, by charge compensation, the AlO_4 units). A reference for such compositional design is represented by synthetic alumino-silicate glasses, specifically formulated as precursors for inorganic binders [12]. The control of oxide contributions is in turn possible by combining different types of inorganic waste (including glass from discarded pharmaceutical vials), as it is often done for glasses later transformed into glass-ceramics [13].

Controlling the balance of components proportions oxides in an 'engineered waste mixture', to achieve a glass with the desired proportions between SiO_2, Al_2O_3, CaO and alkali oxides, did not involve the elimination or reduction of Fe_2O_3 content. To maximize the amount of red mud, the content of this oxide was left intentionally beyond solubility limits, resulting in the formation of an alumino-silicate glass with magnetite (Fe_3O_4) inclusions. Such inclusions are interesting in the perspective of adding functionalities to the material deriving from alkali activation, as shown in our previous investigation on highly porous foams [2]. Magnetite inclusions remain embedded in the unreacted core of glass powders, bound by the above-mentioned zeolite-like gel. This composite structure, also featuring some zeolite crystals (as secondary product of polymerization reactions), may contribute positively to the degradation of organic dyes (such as methylene blue dye), by combining absorption (from the extensive formation of zeolite crystals) and photocatalysis from Fe_3O_4 [2].

The present paper is dedicated to the exploitation of the alkali activation of waste-derived glass in the field of additive manufacturing ('3D-printing'), particularly in direct ink writing (DIW). The progressive gelation of the glass suspension ('cold consolidation'), in alkaline solution, ensures that a three-dimensional structure retains its shape, directly after extrusion, without any organic additive, in analogy with geopolymer pastes [14].

DIW was originally developed in order to produce articles by the overlapping of extruded filaments, from a paste ('ink') composed ceramic particles and organic binders [15], carefully selected in order to offer a non-Newtonian behavior [16]. The pseudoplasticity allows both easy ejection from the extrusion nozzles, at low viscosity conditions (at high shear rate), and stabilization of the printed part, due to a large viscosity increase (at low shear rate) [16]. Geopolymer inks, consisting of ceramic powders embedded in alkaline solution, have recently been introduced as alternative pseudoplastic pastes for DIW. The viscosity increase, after extrusion, is a consequence of the progression of geopolymerization reactions [17]. We will show that waste-derived glass powders, suspended in alkaline solution, provide a further example of ink suitable for DIW, even in the complete absence of organic additives, thus realizing an 'inorganic DIW' process.

DIW is here exploited for the manufacturing of 3D-printed scaffolds. Compared to traditional foamed filters, they exhibit enhanced flow capacity, offering potential benefits for various applications. The utilization of 3D-printed objects offers additional advantages such as ease of separation from dye solutions. It circumvents the limitations associated with traditional separation methods like centrifugation, filtration or magnetic separation applied to powdered sorbents [18]. Also, this study investigates the photocatalytic efficiency of the developed scaffolds, focusing on the destruction of methylene blue dye in aqueous solutions [19]. The results are compared to recently reported photocatalytic materials. Finally, the recyclability of the 3D-printed objects is thoroughly examined, highlighting the sustainability aspect of this novel approach.

2. Materials and methods

Based on previous work [2,20], a glass was prepared by melting at 1550 °C a mixture of red mud, coal combustion fly ash, pharmaceutical glass, and sodium carbonate. According to the weight proportion 18:58:13:11 between constituents, the glass had a chemical composition (in wt. %) of 45.2 SiO_2, 19.5 Al_2O_3, 15.3 Fe_2O_3, 4.0 CaO, 8.5 Na_2O, 2.3 K_2O, 1.4 MgO and 4.1 others. Fast cooling was performed by pouring the melt on a steel plate. Coarse glass fragments, obtained by rapid solidification of the melt, without any annealing, underwent ball milling (Pulverisette 6, Fritsch GmbH, Idar-Oberstein, Germany), to be reduced into fine powders (<40 μm, according to manual sieving).

Waste-derived glass powders were suspended in alkaline aqueous solution (5 M NaOH), for a solid loading of 65 wt %. The suspension was mechanically stirred at 800 rpm for 2 h and then at 1600 rpm for 1 h, in order to obtain a homogeneous mixture, free of any aggregate, to be used in DIW experiments. These experiments involved the ejection of the suspension (undergoing progressive hardening) through a syringe extruder (Powerwasp Evo, Wasp, Massa Lombarda, Italy) mounted on a 'Delta' printer (Delta Wasp 206 Turbo, Massa Lombarda, Italy). The syringe comprised a conical nozzle (diameter of 810 μm, Nordson EFD, Westlake, Ohio), suitable for the extrusion of filaments with a diameter of approximately 800 μm, using compressed air at a pressure of 1 bar. The printed objects underwent drying at ambient temperature for 24 h, to realize cold consolidation.

Printed waste-derived glass samples were later subjected to optical (Carl Zeiss Microscopy, Thornwood, New York, US) and scanning electron microscopy (FEI Quanta 200 ESEM, Eindhoven, the Netherlands). The porosity was computed according to mass and volume determinations and data from helium gas pycnometry (Ultrapyc 3000, Anton Paar GmBH, Graz, Austria). The transformations

of waste-derived glass, by interaction with the alkaline solution, were studied by X-ray diffraction on powdered samples (Bruker D8 Advance, Karlsruhe, Germany; Cu Kα radiation with λ = 1.565 Å). Diffraction patterns were collected in the 2θ range of 10–70°.

After cold consolidation, 3D printed components were applied in photodegradation tests. Small samples (weighting 0.3 g) were immersed in a 50 mL solution of methylene blue (MB), for 90 min, under UV radiation. The initial MB concentration was 50 mg/L. The decrease of dye concentration, with increasing exposure time, was inferred from changes in the absorbance of the solution at 664 nm (λ_{max}). These absorbance studies were supported by a UV–VIS spectrophotometer (Jasco V-650, USA). The photodegradation tests were repeated for five consecutive cycles, with each cycle being run four times to ensure the reproducibility of the obtained results.

3. Result and discussion

Geopolymer-yielding reactive suspensions of ceramic powders in concentrated alkaline solution do not represent the only form of organic-free, psuedoplastic slurries. Pseudoplasticity, in fact, may result from suspensions not undergoing gelation with concurrent development of a three-dimensional alumino-silicate network ('zeolite-like gel') [16,21,22]. Glass suspensions, in alkaline solutions, exhibit a quite rapid hardening, attributed to interactions between gels at the surfaces of fine glass powders. This hardening may be stimulated by a 'conditioning' step at 40–75 °C; extensive foaming of the conditioned glass slurry may be obtained by intensive shaking ('frothing'), with sudden stabilization of air bubbles operated by the progression of the same surface interactions [16,21,22].

In the present case, the use of glass powders suspended (solid loading of 65 wt%) in 5 M NaOH alkaline solution implied the effective development of a zeolite-like gel, with multiple advantages.

i) the gelation led to a stable material, according to the formation of strong bonds; hardened materials, after printing, in fact, did not undergo degradation by immersion in boiling water;
ii) the hardening was almost immediate, without any conditioning; this was due to the same glass formulation, specifically studied for extensive reaction with alkaline activators;
iii) a zeolite-like structure was promising in terms of absorption capacity [23].

As shown by Fig. 1a the slurry was easily extruded without any segregation or clogging of the nozzles, in homogeneously spaced parallel filaments. The fast setting prevented the collapse, by gravity-induced viscous flow, of overlapped filaments (see Fig. 1b; there is no evidence of sagging of horizontal filaments).

The interaction of the adopted glass with the alkaline activator is specified in Fig. 2, reporting diffraction patterns of scaffolds in different conditions. As mentioned previously, the starting material was semi-crystalline, as a result of the separation of the magnetite phase (Fe_3O_4, PDF 82–1533) directly upon cooling. Activation resulted in a 2θ-upshift of the center of the amorphous 'halo', as observed in case of formation of a sodium alumino-silicate hydrated (N–A–S–H-type) gel [2,13]; zeolite crystals appeared as a additional phases (zeolite Y, $Na_{1.84}Al_2Si_4O_{11.92}{\cdot}7H_2O$, PDF 38–0238 and cowlesite, $CaAl_2Si_3O_{10}{\cdot}6H_2O$, PDF 46–1405).

As mentioned above, the developed gel could withstand immersion (for 15 min) in boiling water. The treatment has some visible effects only on zeolite Y. The related diffraction maxima (see Fig. 2) shifted slightly to higher 2θ values and their intensity increased markedly; this finding is in contrast with the amorphization of zeolite Y in hot liquid water, related to destabilization of AlO_4 units (initially balanced by alkali ions) and disruption of Si–*O*–Al bonds [24]. In our opinion, the treatment triggered a complex interaction between zeolite crystals and the surrounding amorphous matrix, inferable from the increased background noise and some 2θ-downshift of the center of the amorphous 'halo'. However, the most important point was that the integrity of the scaffolds was preserved, despite the treatment in harsh conditions.

Scanning electron microscopy confirmed the formation of a crack-free printed lattice with no sign of viscous collapse (see Fig. 3a). The formation of highly porous struts (see Fig. 3b) was in agreement with density determinations. The geometrical density, inferred from mass/external volume ratio (external volume defined as that of the smallest parallelepiped containing regular samples, measured

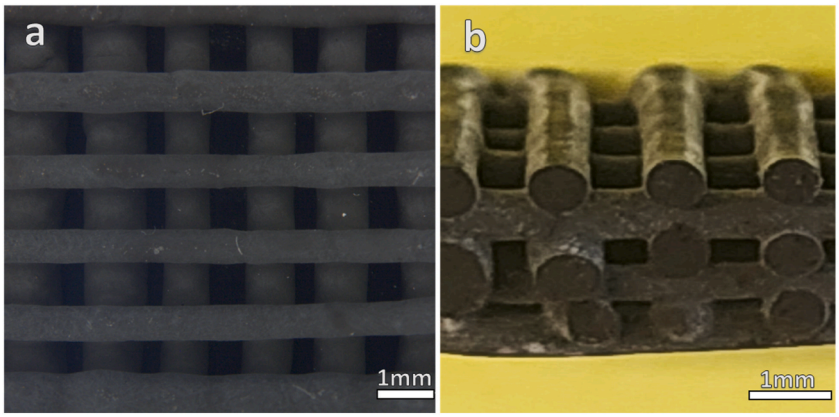

Fig. 1. Optical microscope of (a) top and (b) side view of printed waste-derived glass.

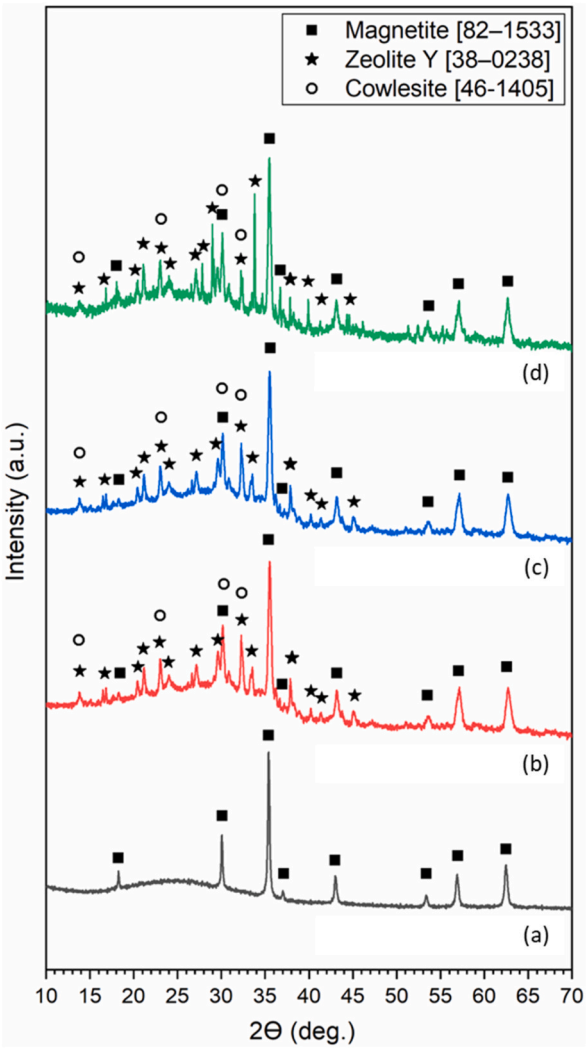

Fig. 2. Mineralogical evolution of the precursor (a), activated and printed material (b), printed material after recycling (c) and boiling test (d).

by means of a calliper) was only 0.8 ± 0.01 g/cm^3. Apparent and true densities (determined from helium pycnometry on whole or powdered samples, respectively) were 2.73 ± 0.06 and 2.86 ± 0.06 g/cm^3. This indicated an abundant porosity (70 ± 1 %), almost completely open.

The original material was used in the form of a powder sieved below 40 μm: it is interesting to note that the final microstructure comprises loosely bound, much smaller particles (see Fig. 3c) mixed with tiny fibrous structures, attributed to gel from extensive glass/activator reaction and zeolite crystals. At higher magnification, the microstructure exhibits a distinctive rough texture composed of small crystals (see Fig. 3d). Additionally, the rough texture creates a complex and irregular surface morphology, promoting better dye penetration and diffusion in the structure.

The abundant overall porosity and the presence of a multitude of pores offer highly accessible surfaces, promoting the exposure of numerous active sites and leading to excellent photocatalytic performances [25]. The wide openings, resulting from DIW, are also intended to maximize the surfaces exposed to light.

The reference absorption spectrum of a 50 mg/L methylene blue solution (in deionized water) is shown in Fig. 4a. The absorbance maximum at 664 nm provided a benchmark for the initial dye concentration (C_0); the UV degradation of the specific organic species was monitored according to the absorbance at the same wavelength (664 nm) after 60 min irradiation (C = absorption maximum of solution in the absence of 'printed glass' scaffold; C_1 = absorption maximum of solution with immersed scaffold). The absorbance exhibited a dramatic decrease in solution embedding a photocatalytic substrate (C_1/C_0 = 0.18 implied a ~82 % decrease). Fig. 4b demonstrates that an extension of the UV exposure to 90 min lead to an undetectable absorbance peak, corresponding to complete destruction of methylene blue dye.

To be inexpensive and viable, catalysts for pilot-scale remediation systems must be easily recovered and reused. To verify the stability and reproducibility of photocatalytic performance, scaffold were tested several times; after every catalytic run, the support

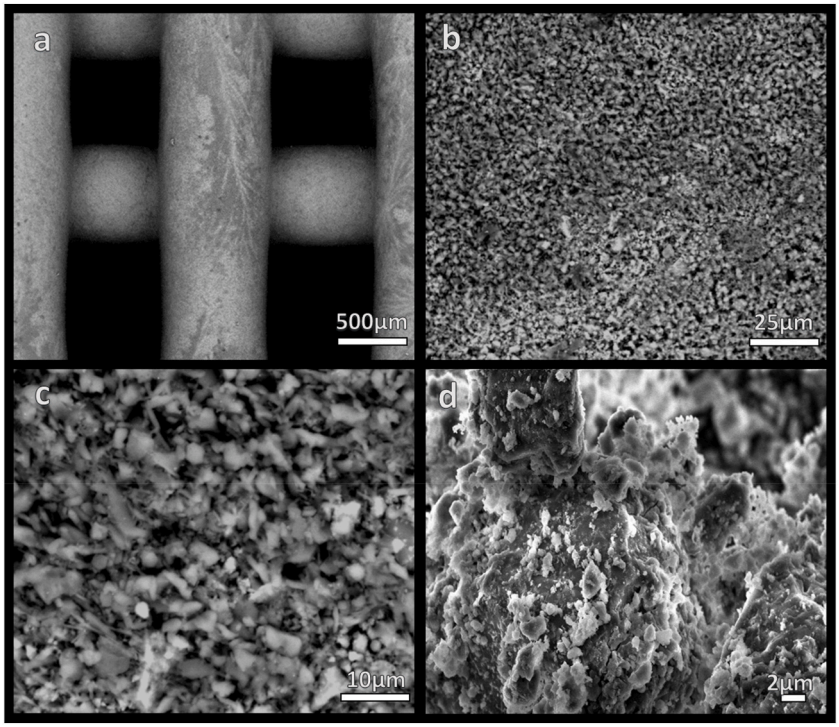

Fig. 3. a) Scanning electron microscopy images of printed lattice from activated waste-derived glass; b,c,d) high magnification images of the microstructures of printed struts.

was removed from the solution and 'cleaned' by exposition to UV light, for 30 min. The efficiency (E) was inferred by studying again the absorbance maximum at 664 nm, as follows:

$$E = \frac{C_o - C_i}{C_0 - C_1} \bullet 100\%, with\ i \geq 1 \quad \text{(Eq. 1)}$$

where C_i is the concentration of MB after cycle 'i' (i = 1,2,3,4,5) and C_1 is the concentration of MB after the first cycle. As shown in Fig. 4c, the catalytic performance of the printed, activated waste-derived glass was had only a modest decrease (8 %) after the fifth cycle. The powder diffraction analysis of the recycled material (Fig. 2) demonstrated the stability of phase assemblage and indicated the reproducibility of the photocatalytic scaffold and its potential for practical applications.

A final evaluation concerned the comparison with other iron oxide-based photocatalytic supports, as reported in Table 1. The degradation efficiency of the newly developed material from waste-derived glass is superior to that of materials based on α-Fe_2O_3 nano spindles, Fe_2O_3/TiO_2 composite, Fe_2O_3–TiO_2 loaded fluid catalyst and Fe_3O_4/activated carbon (AC)/TiO_2 nano-catalyst [26–30]. Titania-embedding polymer substrates offer a comparable degradation efficiency, but they are derived from primary raw materials, not from a waste-recovery approach, as in our case. It should be noted that both sample dose and initial dye concentration, in the literature, have a significant variability (from 0.05 to 2 g and from 4 to 100 mg/L, respectively). Our photocatalyst compares favorably with studies requiring a moderate sample dose.

4. Conclusions

An iron-rich waste-derived glass containing magnetite inclusions has been successfully applied in the photocatalytic destruction of methylene blue (from solutions representing an example of contaminated wastewater). The glass led to a structured photocatalyst simply by direct ink writing of a concentrated glass suspension. DIW exploits the activation of the glass matrix through its reaction with NaOH. The photocatalytic activity is attributed to magnetite inclusions, embedded in a highly porous zeolite-like gel. DIW enables facile manufacturing of reticulated scaffolds with wide openings, enhancing the irradiated surface. Despite its simplicity, the developed technology facilitates the fabrication of stable and recyclable devices. Devices with more complex topologies, to maximize exposure to UV light, are envisaged.

CRediT authorship contribution statement

Mokhtar Mahmoud: Writing – original draft, Investigation, Formal analysis, Data curation. **Jozef Kraxner:** Writing – review &

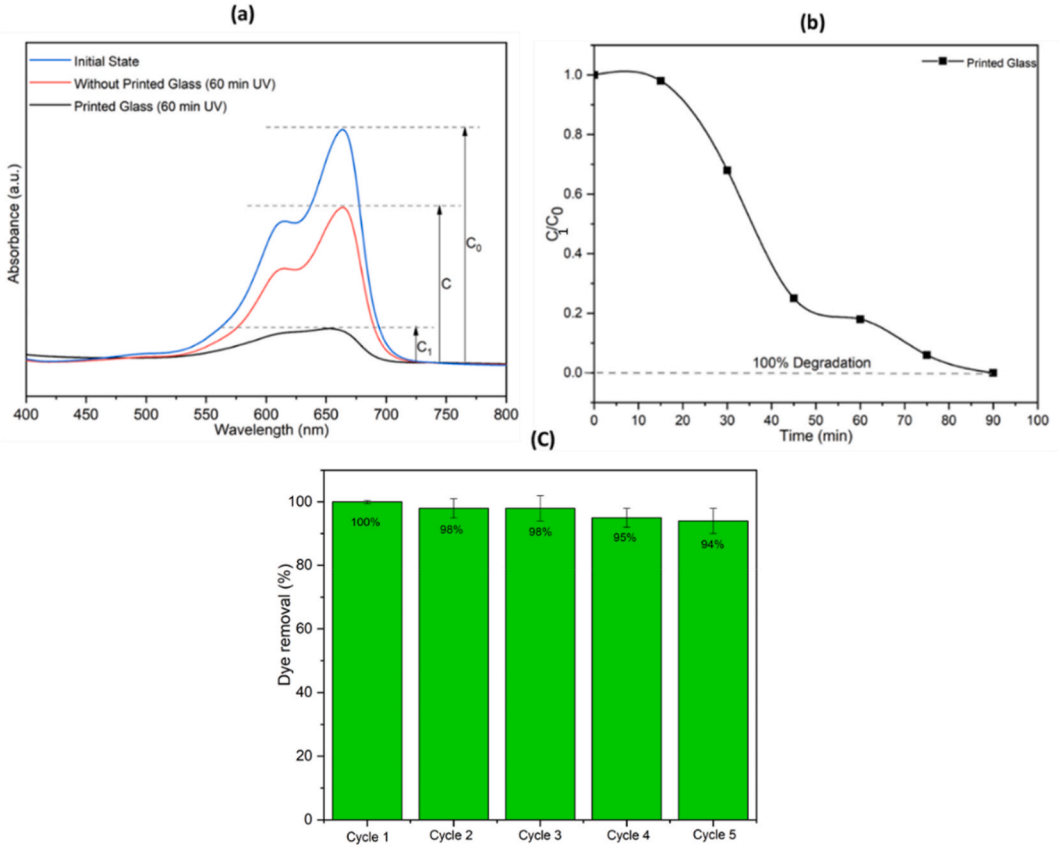

Fig. 4. (a) Absorbance spectra of methylene blue solutions in the initial state and after UV exposure (with or without immersed scaffold); (b) relative methylene blue concentration with increasing UV exposition time; (c) evolution of methylene blue (MB) change of the degradation efficiency (%) with the number of immersion cycles.

Table 1
A comparison of degradation efficiency of methylene blue dye of various photocatalytic materials.

Materials	Sample Dose (g)	Initial Dye Concentration (mg/L)	Degradation efficiency (%)	Rate of degradation (min)	Ref
α-Fe_2O_3 nano spindles	0.05	10	78	360	[26]
Fe_2O_3/TiO_2 composite ceramic	2	25	83	240	[27]
Fluid catalyst loaded with Fe_2O_3 and TiO_2	0.2	10	94.2	120	[28]
Fe_3O_4/AC/TiO_2 Nano-Catalyst	0.1	100	98	60	[30]
TiO_2-Polymeric Substrates	0.1	4	100	110	[29]
This work	**0.3**	**50**	**100**	**90**	

editing, Supervision, Funding acquisition. **Akansha Mehta:** Methodology, Formal analysis, Data curation. **Hamada Elsayed:** Writing – review & editing, Validation, Data curation, Conceptualization. **Dušan Galusek:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Enrico Bernardo:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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