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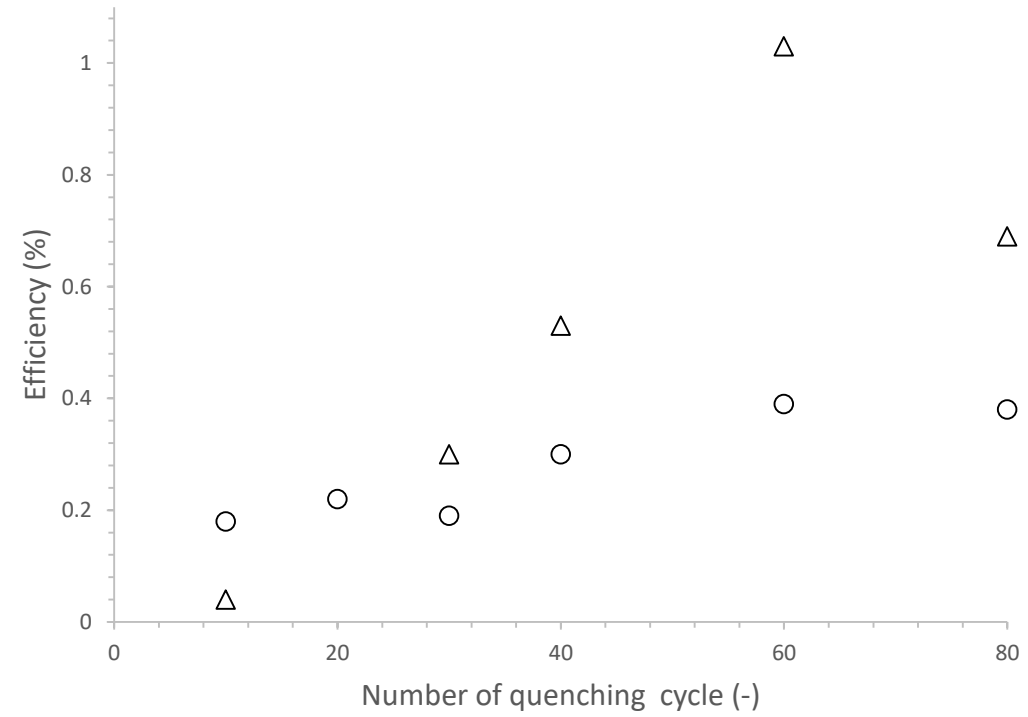
Optimizing the photocatalytic properties of macroporous geopolymer foam: influence of SILAR-technique synthesis conditions --Manuscript Draft--

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Abstract:	<p>Macroporous cross-linked materials such as 3D honeycomb foams are used as substrates for heterogeneous photocatalysis. They offer a number of interesting properties. They are highly open-porosity substrates, guaranteeing optimum mass and radiation transfer, making them ideal for photo-conversion applications such as photo-oxidation or photo-reduction, which take place in photo-reactors for pollutant degradation or solar fuel production. Many cross-linked supports such as polymeric and metallic foams studied in the literature have revealed photocatalytic capacities similar to those obtained for the catalyst nanoparticle suspensions used as a reference. To reduce the production costs of this type of material, geopolymers, widely used in civil engineering, offer a wide range of properties suitable for shaping cellular foams. In addition to their low cost and mechanical properties, it is also possible to impart porous properties and modulate their characteristics according to the synthesis operating conditions so as to elaborate macroporous cellular foams. In this study, we propose to investigate the photocatalytic properties of honeycomb geopolymer foams coated with a catalyst: ZnO. To achieve ZnO deposition, the SILAR technique was applied by modifying the key synthesis operating conditions, i.e. precursor concentration and the number of quenching cycles applied. The results obtained make it possible to define the optimum operating conditions (pH, temperature) and, above all, the number of cycles and precursor concentration required to obtain the best photocatalytic efficiency. These innovative and promising materials, little studied in the</p>

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- Functionalization of macroporous geopolymer foams
- SILAR technique for imparting photocatalytic properties
- Influence of catalyst synthesis conditions
- Key influence of precursor concentration/number of quenching cycles applied



Declaration of interests

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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Optimizing the photocatalytic properties of macroporous geopolymer foam: influence of SILAR-technique synthesis conditions

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Abstract :

Macroporous cross-linked materials such as 3D honeycomb foams are used as substrates for heterogeneous photocatalysis. They offer a number of interesting properties. They are highly open-porosity substrates, guaranteeing optimum mass and radiation transfer, making them ideal for photo-conversion applications such as photo-oxidation or photo-reduction, which take place in photo-reactors for pollutant degradation or solar fuel production. Many cross-linked supports such as polymeric and metallic foams studied in the literature have revealed photocatalytic capacities similar to those obtained for the catalyst nanoparticle suspensions used as a reference. To reduce the production costs of this type of material, geopolymers, widely used in civil engineering, offer a wide range of properties suitable for shaping cellular foams. In addition to their low cost and mechanical properties, it is also possible to impart porous properties and modulate their characteristics according to the synthesis operating conditions so as to elaborate macroporous cellular foams. In this study, we propose to investigate the photocatalytic properties of honeycomb geopolymer foams coated with a catalyst: ZnO. To achieve ZnO deposition, the SILAR technique was applied by modifying the key synthesis operating conditions, i.e. precursor concentration and the number of quenching cycles applied. The results obtained make it possible to define the optimum operating conditions (pH, temperature) and, above all, the number of cycles and precursor concentration required to obtain the best photocatalytic efficiency. These innovative and promising materials, little studied in the literature, are prime candidates for solar photo-conversion applications.

Introduction

Solar processes are widely studied for use in applications ranging from energy production in the form of heat or electricity to water treatment applications such as disinfection and detoxification [Malato 2003; Galvez 2011; Flammant 2023]. Photoreactors are systems that exploit natural solar radiation to optimize photoconversion efficiency in these process operations [Blanco 2006; Malato 2003; Cabrera Reina 2019]. The photoconversion process harnesses this radiation to produce radical species capable of reducing pollutants or producing hydrogen [Serpone 2000]. The conversion process is driven by catalysts that undergo photoexcitation processes, initiated by the absorption of photons, to produce charges that trigger oxidation-reduction reactions that enable the production of radical species. The most effective photocatalytic materials for these operations are catalyst suspensions, which develop a very large exchange surface and are homogeneously distributed in the photoreactor [Plantard 2012]. To overcome the problem of catalyst/fluid separation, catalytic supports have emerged in the form of 2D materials (tubes, cellulose fabrics), granules and pellets [Fernandez 1995]. Macroporous honeycomb supports such as foams [Ochuma 2007; Plesh 2009] have emerged as relevant candidates to meet the constraints of solar resource utilization, which mainly involves optimal exploitation of captured radiation. Unlike 2D supports, which have a very limited absorption capacity due to their geometry, cellular foams develop a very highly interconnected open porosity, which is highly conducive to radiation–matter interactions [Plesch 2013; Goetz 2023]. The porous network and rough surface conditions favor increased surface scattering and absorption processes that help ensure that all incident photons get consumed [Cassano 1995; Ribeiro 2021]. Numerical and experimental tools developed in the literature evaluate the quantity of photons absorbed by a material by factoring material in very high absorption capacity [Ribeiro 2021; Cornet 1992]. By optimizing material configuration, radiation absorption capacity can be made to rival catalyst suspensions [Plantard 2014; Van Gerven 2007], making them perfectly suited to many solar applications. These materials develop a high surface area of around $1000 \text{ m}^2/\text{m}^3$, thus promoting the reaction processes that take place on the surface of the catalyst. Studies on cellular foams have shown that their absorption and photoconversion capacity depend on their porous characteristics [Plantard 2011; Elatmani 2013; Ochuma 2007]. Most of the work carried out on metallic or polymeric foams has highlighted the importance of pore size distribution, porosity, and mean pore diameter as key levers for modulating the photocatalytic capacity of macroporous foams. These studies show that macroporous cellular foams with millimetric-scale pore diameters are the most suitable candidates for photocatalytic applications [Plantard 2014].

Inspired by developments in the civil engineering field, geopolymer foams have emerged as hugely promising materials for a wide range of applications [Davidovits 1987; Cioffi 2003; Humphreys 2002].

Studies have shown that these low-cost materials, compatible with large-scale water treatment applications, have the ability to adsorb or degrade organic or metallic pollutants [Ahmer 2019; Zhang 2012]. They are produced by alkaline activation of the aluminosilicates present in many materials (kaolin) or waste products (asbestos), using the same process route as for making cement [Tattersall 1983; Abdel-Gawwad 2020; Autef 2013; Bell 2009]. Work has shown that these materials can be made lighter by modulating their mechanical properties and porous characteristics [Allison 2015, Cioffi 2003]. Methods have been developed that process porous cement using gas production in the matrix prior to solidification, either by direct air injection or by gas-releasing chemical reaction [Deng 2014; Ducman 2016; Kocí 2022]. The aim of these methods is to impart a porous structure made up of closed or partially open pores with small (submillimetric) pore sizes. The replication method, which consists in coating the geopolymer matrix onto a support material, can serve to impart macroporous properties [Kovářík 2017; Kovářík 2021; Schelm 2019]. By selecting a substrate with the requisite pore size distribution, porosity and open cell structure, it is possible to obtain macroporous geopolymer foams with porosities in excess of 0.85 that are perfectly suited to photocatalytic applications [Hajimohammadi 2017; Henon 2012]. Recent studies have shown that it is possible to produce high-porosity geopolymer foams with millimetric-range pore [Klima 2022; Kovářík 2017], but that has been little further research into their photocatalytic properties. There are numerous processes available for coating complex surfaces with catalyst to impart photocatalytic properties to materials such as cellular foams (CVD, sol-gel) [Uricchio 2021; Plantard 2011; Rosset 2020]. Once such technique is successive ionic layer adsorption and reaction (SILAR), which enables catalyst to be deposited layer-by-layer at molecular scale, and has recently been tested on metal foams [Jellal 2021]. SILAR makes it possible to impart photocatalytic properties by depositing a nanostructured film of catalyst while preserving the porous characteristics of the support. It works by immersing the support in catalyst precursor solutions [Yergaliuly 2022].

Here we propose to investigate the photocatalytic properties of geopolymer foams functionalized with a catalyst (ZnO). We chose to test foams elaborated by replication as the operating conditions had been optimized in a previous study [Benkhirat 2023]. The selected geopolymer foam is a macroporous honeycomb structure with millimetric-size pores. Photocatalytic properties are obtained by depositing ZnO on the surface using the SILAR method. This article focuses on optimizing the ZnO synthesis conditions to obtain the best possible photocatalytic efficiency, and testing key operating conditions (pH and temperature of the precursor solution). Moving forward, we then focus on the influence of the two key operating parameters of the SILAR technique, i.e. catalyst precursor concentration and number of quenching cycles. The performance of the materials is assessed by measuring photocatalytic

efficiency, which expresses photoconversion of target molecules in relation to quantity of photons received.

I] Elaboration of ZnO-coated geopolymer foams

For this study, a geopolymer foam was created using the replication method, then functionalized with ZnO using the Silar method.

I.1 Replication method for geopolymer foams

The production of geopolymer foam proceeds in two steps.

The first step is to synthesize a geopolymer paste, which involves preparing a homogeneous gel from metakaolin [Juenger 2011]. The most widespread method used is alkaline activation of aluminosilicates to form a Na-Al-Si-H (hydrated alkaline aluminosilicate) gel with a high Al content [Fernández-Jiménez 2009]. The geopolymer gel processing protocol used in this study, widely described in the literature, is illustrated in Figure 1, and involves the preparation of an alkaline solution composed of a mixture of NaOH and Na₂SiO₃ at a concentration of 8M [Fernandez-Jimenez 2005]. The alkaline solution is first prepared and stirred for 24 hours, then mixed with the metakaolin in a molar ratio of 1 to 1. The mixture is then stirred manually with a spatula for two minutes until it becomes a smooth, homogeneous paste.

The second step aims to impart a porous structure to the geopolymer material during the solidification process [Henon 2013]. Foams used in this work were elaborated using the replication method, which consists in impregnating an alveolar-structure support with the geopolymer gel [Schelm 2019; Henon 2012]. In this study, Polyethylene foams (PEFs) were selected for their macroporous honeycomb structure. These foams have a porosity of 87% with a pore size distribution ranging from 0.5 to 2mm. Further details on their porous characteristics can be found elsewhere [Benkhirat 2023]. Parallelepipedic foam samples with a cross-section of 5 cm and a thickness of 1 cm were prepared as a support for the geopolymer gel. To obtain geopolymer foam, five quenching cycles are applied with the geopolymer paste to coat the PEFs, where each cycle involves immersing the PEF in the paste for 30 seconds, squeezing the foam to remove excess paste, and then cleaning the sample with a jet of compressed air. These steps are designed to ensure that the PEF is homogeneously coated and that the paste does not plug the porous structure. The foams produced are then dried at 40°C for 24 hours, then calcined at 800°C for two hours. These steps serve to remove water and excess PEF and impart mechanical properties to the geopolymer foam. The resulting materials have an open macroporous alveolar structure (Figure 4).

I.2 SILAR method

The SILAR method is a technique for producing multilayer films at nanometric scale. The growth of nanostructures is influenced by various parameters, such as precursor concentration, pH and temperature of the cationic solution, and number of cycles, which affects the duration of adsorption [Prabath Ratnayake 2021].

The photocatalyst selected for this work is zinc oxide, which has been widely studied in the literature in the form of nanopowders [Rosset 2017] for photocatalysis applications. In this study, the SILAR method illustrated in Figure 2, was applied to fabricate ZnO nanostructures on the surface of geopolymer foams. The principle of a quenching cycle, as detailed in previous studies [Jellal 2021; Raidou 2014], consists in successively immersing the geopolymer foam in three solutions. The first 30-second quench is performed in a 0.08 M cationic solution prepared by dissolving $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in deionized water. The addition of complexing agents stabilizes the cations until ZnO is deposited on the surface. The Zn^{2+} cations act as seeds for the growth of ZnO nuclei, which will increase as a function of the number of cycles. The second 30-second quench takes place in an anionic ammonia solution (Deionized water) heated to 80°C. Zn^{2+} cations from the zinc-ammonium complex react with hydroxyls from the zinc-ammonium complex to produce a stable $\text{Zn}(\text{OH})_2$ zinc hydroxide complex. The final 15-second quench involves rinsing in pure water to remove excess or incompletely-reacted ions. Successive cycles using this methodology lead to the formation of a nanostructured film on the surface of the substrate. To impart crystalline properties, samples are dried in an oven at room temperature for 24 hours and then annealed in an oven at 500°C for two hours (4).

In this study, geopolymer foams developed by replication are functionalized to impart photocatalytic properties from ZnO. Different ZnO synthesis conditions were tested, such as zinc precursor concentration (0.08M to 1M), number of quenching cycles (10 to 80), temperature of the cationic solution (25°C to 90°C) and pH (9 to 11.5). Table 1 reports all the synthesis conditions applied to functionalize 30 geopolymer foams.

II] Properties of the geopolymer foams

II.1. Analysis of surface states and porosity

Samples of geopolymer foams ZnO-functionalized under different synthesis conditions were observed by SEM. Figure 3 shows SEM images of functionalized foam surfaces for two concentrations of zinc precursor at different magnifications. The high-magnification images show that the surface is mainly covered with hierarchical structures in the form of nanosheets and nanoflowers, represented by a core

surrounded by 6 'petals'. The architectures are tens of micrometers long. The formation of these structures is linked to the presence of NH_4OH in the cationic solution, which stabilizes the Zn^{2+} cations. The zinc-ammonia complex precipitates to the surface of the support through nucleation of the ZnO nuclei. The size of the ZnO nanostructures increases with successive cycles, leading to the formation of ZnO nanosheets. Yergaliuly et al. and Cheng et Al. also obtained similar ZnO nanostructures [Yergaliuly 2022, Cheng 2008] and showed that the transition from nanoflowers to nanosheets is modulated by the variation in precursor concentration. This allows the Zn^{2+} cation content to be increased, leading to the formation of ZnO nanostructures with varied morphologies. If we look at the surface at lower magnification, we see that the layered network covers the entire cellular structure of the foam. At higher concentrations, both coverage and thickness are significantly greater. As the precursor concentration increases, the ZnO structure reorganizes into the form of several layers of sheets on the surface of the geopolymer foam.

The functionalized geopolymer foams were also observed using an optical microscope (Keyence VHX-7000 Digital microscope), which serves to more comprehensively visualize the surface of the foams, and in particular their porous structure. Foams were prepared by varying the concentration of zinc precursor from 0.2 to 1M (Figure 4a). At low concentrations, the ZnO homogeneously coats the surface of the geopolymer foam while preserving its porous structure. As precursor concentration increases, the deposited layer partially clogs the macropores by reducing their diameter, and ultimately even obstructs certain macropores in the geopolymer foam when precursor concentration is very high ($C=1\text{M}$). Figure 4B illustrates the influence of number of quenching cycles, showing that the coating increases markedly, with the number of cycles, on the surface of the geopolymer foam. When the number of cycles applied is low, the foam is covered with a thin film that is evenly distributed over the cells and branches of the macroporous structure. As the number of quenching cycles becomes important, the layer increases in thickness, leading to partial pore closure or even total obstruction of certain macropores when the number of cycles exceeds 60.

II.2 Microstructural investigation of the ZnO-functionalized geopolymer foams

XRD analyses were performed at room temperature using a PANalytical XPert Pro diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$). X-ray diffraction measurements of θ - θ symmetrical scans were made over an angular range of 10 to 70°. The step size and the time per step were fixed at 0.017° and 100 s, respectively. The X-ray diffractograms were recorded and studied using PANalytical softwares (Datacollector and HighScorePlus). The contribution from $\text{AlK}\alpha_2$ was removed [Rachinger method, Rachinger 1948]. The instrumental function was determined using a reference material (SRM 660, lanthanum hexaboride, LaB_6 polycrystalline sample) and can be expressed by a polynomial function.

For XRD analysis, two crystalline phases were clearly detected (figure 5). The main diffraction peaks (diamond, ◆) collected at $2\theta=31.78, 34.46, 36.23, 47.55, 56.65, \text{ and } 62.93^\circ$ are attributed to a zinc oxide compound (ZnO, ICDD-JCPDS card N°70-8072). (Yoshio 2001). A ZnO layer was deposited on the geopolymer foam. The main diffraction peaks (square, ■) collected at $2\theta=10.24, 17.76, 20.54, 21.28, 23.19, 27.39, 29.75, 31.03, 34.81, 38.41, 39.03, 42.58, 43.37, 47.12, 59.22, 65.23 \text{ and } 67.63^\circ$ are assigned to a sodium alumino silicate compound (NaAlSiO₄, Nepheline ICDD-JCPDS card N°75-2933) [Dimitrijevic 2004]. A minor crystalline phase could be assigned to an aluminium silicon oxide compound (Al₂(Al_{2.588}Si_{1.412})O_{9.706}, ICDD-JCPDS card N°74-8549). The main diffraction peaks (circle, ●) are located at about $2\theta=16.41, 26.22, 30.92, 33.17 \text{ and } 40.85^\circ$ [Tkalcec 2005].

Micro-Raman experiments were performed using a HORIBA LabRAM HR Evolution Raman spectrometer equipped with an optical microscope (Olympus K.K. BX 41, x50 (long working distance, LWD), a charge coupled device detector (1024 x 256 pixels, 26 x 26 μm^2 by pixel) and a laser beam (laser diode with a wavelength of 532 nm, laser power of 39 mW). The Raman shift was calibrated using a Si standard sample. Raman spectra were recorded in the wavenumber range (spectral region) from 70 to 1100 cm^{-1} . The laser power was reduced to about 20 mW (50% filter strength) in order to avoid laser-induced effects (e.g. surface heating). No temperature effects (such as a shifting of the peaks or differences in the intensity ratios compared with reference spectra) were observed. The Raman spectra were collected at the focal point of the x50 objective lens (with a numerical aperture (NA) of 0.75) with a spectral resolution close to 1 cm^{-1} /pixel. The 600 grooves/mm grating and the confocal pinhole value of 100 μm were selected. The acquisition time and the number of acquisitions per spectra were fixed to 10 s and 2, respectively. The Raman spectra were collected using the software delivered by HORIBA LabSpec 6.0. The spectra background was removed.

The Raman peak positions are collected for several relevant points on the samples surface. The deposited ZnO layer and the geopolymer foam substrate were detected, both. The main bands (figure 6, ◆ marker) located at about 95 cm^{-1} (E₂(low) vibration mode), 431 cm^{-1} (E₂ high) vibration mode) and 578 cm^{-1} (A₁(LO) vibration mode) are assigned to a ZnO compound [Decremps 2018, Thyr 2021]. The main bands (figure 6, ■ marker) observed at about 270 and 389 cm^{-1} (T-O-T bending modes region) and 966 cm^{-1} (T-O stretching vibrations modes, mainly Si-O-Al bonds) are characteristic of a NaAlSiO₄ compound, close to nepheline [Matson 1986, Ferraris 2014, Le Losq 2017]. In the range of 570 to 650 cm^{-1} , the broadened feature may contain Raman band contributions of ZnO (E₁(LO) vibration mode) and NaAlSiO₄ (nepheline) compound, both. The wide band, observed by other authors [Matson 1986, McCloy 2015] may be also due to the presence of a small amount of a disordered structure of nepheline.

III. Assessment of photocatalytic properties

The aim here is to identify the photocatalytic efficiencies of geopolymer foams functionalized with ZnO, which involves determining the photoconversion capacity of the materials developed, expressed as quantity of photoconverted molecules per quantity of photons received [Serpone 2000; Rosset 2018]. This indicator makes it possible to evaluate and compare the influence of ZnO functionalization conditions on the surface of geopolymer foams and thus go on to define optimal conditions. All foams functionalized with zinc precursor were tested under different SILAR deposition conditions (Table 1), i.e. pH and temperature of the cationic solution, precursor concentration, and number of quenching cycles.

III.1. Assessment tools

III.1.1 Photocatalytic set-up

The approach adopted to determine the photocatalytic efficiencies of the materials was to measure photocatalysis kinetics under perfectly-controlled conditions for all samples. Phenol was chosen as the indicator of photocatalytic activity. Phenol is a chemical substance widely used in the chemical, petrochemical and plastics industries and has also been used as a reference in numerous studies [Jordan 2002]. It is toxic to living organisms [Canadian 1999] and is regularly screened in groundwater and surfacewater [Pinto 2005].

A standard protocol used in the literature was applied [Rosset 2018]. The bench consists of a series of 25-cm² beakers filled with a 200 ml solution of phenol. An illumination system consisting of a 31.4 cm² UV lamp produces irradiation centered on 365 nm with a flux density varying from 0-110 w.m⁻². Photocatalytic tests were carried out with a flux density set at 104 w.m⁻² and a phenol solution at 10 mg.l⁻¹. In terms of methodology, the functionalized foams are fixed in the beaker using a support to hold the foam. The solution is stirred beforehand to ensure it is perfect homogeneous. The lamp is switched on 30 min before the experiments in order to stabilize the radiance delivered. The beaker is then placed under the lamp. Phenol concentration is monitored in 15-minute steps for 1 hour, then every 30 minutes for 4 hours.

III.1.2 Photocatalytic efficiency

In the literature, photodegradation kinetics is widely used to evaluate material performances, define catalyst synthesis conditions, or optimize experimental conditions [Minero 1999]. This approach leads to a very wide range of responses, as photocatalytic activity depends on the nature and concentration

of the catalyst but also mainly on the flux density. It is therefore imperative to set the operating parameters to limit the influences of pH, temperature and pollutant concentration [Chen 2017]. To free ourselves from the influence of flux density and light production system, authors have proposed using photon yield to evaluate the capabilities of photocatalytic materials [Plantard 2014]. Photocatalytic efficiency is defined by the ratio between the number of molecules photoconverted and the number of photons received (Eq. 1). The number of molecules photoconverted is determined from photocatalytic experiments by quantifying the variation in indicator concentration in the solution during photodegradation. The number of photons received is deduced from the energy received, which is calculated from the emission spectrum and flux density applied. Numerous works have relied on this quantity to assess the light absorption capacity of photocatalysts in different forms, i.e. nanopowders, foams, composites, and thin films deposited on glass or 3D media [Davydov 1999, Marugan 2006, Plantard 2014]. Photocatalytic efficiency is expressed using equation 1 :

$$\varphi = \frac{(C_0 - C_t) \cdot V \cdot N}{N \cdot \frac{S}{E_\lambda} \int_0^t I \cdot dt} \quad \text{Eq. 1}$$

where C_t is concentration of the molecules at time t , V is volume of the measuring cell (m^3), N is the Avogadro number (mol^{-1}), M is the molar mass of phenol ($g \cdot mol^{-1}$), S is the irradiated surface (m^2) and I is the flux density in ($w \cdot m^{-2}$). The number of photons is deduced from the flux density based on the energy of a photon at the average wavelength.

III.2] Photocatalytic performance results

III.2.1 Preliminary study

The aim of this study is to control the conditions under which catalysts are synthesized on the surface of cellular geopolymer foams, in order to optimize their photocatalytic performance. The study of secondary operating parameters, such as temperature and pH, was carried out in order to define the best operating conditions for synthesis.

The foams were coated with catalyst at a concentration of 0.08M and at a fixed 30 quenching cycles but varying the temperature of the synthesis solution, i.e. 25°C, 60°C or 90°C. Photocatalytic kinetics were measured using a bench-test instrument for the defined experimental conditions, i.e. a 200 ml volume of phenol solution concentrated to 10 $mg \cdot L^{-1}$. The results were used to calculate the number of photoconverted molecules and number of incident photons according to equation 1. Figure 7 shows the variation in efficiency as a function of the temperature of the synthesis solution. Photocatalytic activity changes significantly with temperature. Photocatalytic efficiency, which peaks at 90°C, reached

a value of 0.25%. It has been shown in the literature that the temperature of the cationic solution influences the morphology (crystal orientation and size) and crystalline properties of the catalyst. For example, Heinonen et al. synthesized zinc oxides hydrothermally at different temperatures (30°C to 90°C) and showed that nanorods obtained at 90°C gave the strongest catalytic performance [Heinonen 2016].

A series of geopolymer foams were functionalized while varying the pH of the cationic solution (i.e. pH9, pH10.5 or pH11.5). Photocatalytic measurements were carried to determine photocatalytic efficiency. Figure 8 shows the variation in efficiency as a function of pH of the cationic solution. Photocatalytic efficiency decreases significantly with increasing pH of the cationic solution. It tends to decrease more than two-fold when the pH of the solution goes from 9 to 11.5. This trend is in line with previous literature showing that this parameter modifies the optical and crystallinity properties of the catalyst [Yergaliuly 2022; Cheng 2008]. Indeed, the addition of a complexing agent during the preparation of the cationic solution helps to homogenize nanostructure formation by multiplying the number of nucleation points.

We also addressed the durability of the photocatalytic materials to assess how photocatalytic activity would age over cycles of use. The aging test involved repeating a photocatalysis experiment several times with the same foam. The geopolymer foam was functionalized with ZnO at a precursor concentration of 0.2M and applying 20 quenching cycles. Beakers containing phenol solution and foam were irradiated for two hours with the UV lamp applying a flux density of $104 \text{ W}\cdot\text{m}^{-2}$. Between each cycle, the phenol solution was renewed and the foam was rinsed with water. Kinetics were recorded to calculate photocatalytic efficiency, and are plotted in Figure 9. Photocatalytic activity remained relatively stable over the 4 cycles, indicating that the properties of ZnO-functionalized foams were not significantly altered during use. In the literature, most photocatalytic materials are reported to undergo partial alteration of their structural and photocatalytic properties, mainly due to mechanical alteration induced by agitation or fouling of the materials [El atmani 2013]. Aging can also be induced by molecules or by-products formed during degradation that irreversibly bind to the catalyst surface by sorption chemistry [Chekem 2020]. These results show that SILAR-functionalized geopolymer foams can be used over several cycles.

III.2.2 Effect of precursor concentration

The aim here is to evaluate the influence of precursor concentration on photocatalytic activity. To this end, we measured the kinetics of geopolymer foams functionalized at 6 different ZnO concentrations (0.08M, 0.2M, 0.4M, 0.6M, 0.8M, 1M) per the above procedure.

Figure 10 plots the photocatalytic efficiencies of functionalized foams as a function of precursor concentration. The plots represent the variation in quantities of photoconverted molecules (in moles) as a function of quantity of incident photons captured by the foams (in moles). The photocatalytic activity of geopolymer foams is highly dependent on precursor concentration. Efficiency values varied from 0.05 to 0.18%, which is around the same order of magnitude as obtained in the literature for metallic foams or 2D supports [Plantard 2011].

Photocatalytic efficiency decreased significantly with increasing precursor concentration before stabilizing at concentrations above 0.6M. SEM images show that syntheses carried out at low precursor concentrations tend to form flower-like nanostructures. As reported in the literature, this crystalline structure offers interesting photocatalytic properties [Yergaliuly 2022]. The nanostructures are perfectly homogeneously distributed and evenly cover the surface of the alveolar structure at a constant thickness. Conversely, when precursor concentration is higher, sheet-like nanostructures form on the walls of the geopolymer foams (Figure 3). Some areas are perfectly coated with a layer of ZnO whereas some cells appear to be partially covered by catalyst clusters. Optical microscope images of foams coated with a high concentration of precursor also tend to show a heterogeneous catalyst distribution, with more substantial clusters forming in certain areas. More material gets deposited on the cells than on the meshes. The quench-cycle synthesis methodology leads to the solution accumulating in certain zones, as the geopolymer foam is not fully dried between two immersions. These results are also supported by the literature. Heinonen et al. showed that precursor concentration has an effect on the morphology, adhesion quality and optical properties of the catalyst coating [Heinonen 2016]. Similarly, Rodriguez et al. functionalized various 2D and 3D supports with TiO₂ and highlighted the influence of synthesis conditions on the photocatalytic and optical properties of the materials developed [Rodriguez 2009]. Inappropriate synthesis conditions, and in particular an excess of precursor, lead to a deterioration in coating quality and, in particular, in optical and adhesion properties.

The marked decrease in photocatalytic efficiency with increasing precursor concentration thus appears to be explained by the quality of the coating. Syntheses carried out with low precursor concentrations (and a low number of quenching cycles) provide optimum optical and photocatalytic properties.

III.2.3 Effect of quenching cycles

To further optimize the synthesis conditions, we also studied the influence of number of quenching cycles on photocatalytic properties. A series of 5 foams prepared at a precursor concentration of 0.08M were coated and between 10 and 80 quenching cycles were applied, and we again measured the

kinetics of photocatalytic degradation to deduce the variation in photoconverted molecules as a function of number of photons received. Figure 11 plots the efficiency of ZnO-coated geopolymer foams as a function of number of quenching cycles.

Over the study area, photocatalytic efficiency increases almost linearly with number of cycles, and appears to reach an optimum when more than 60 cycles are applied, as photocatalytic efficiency was two-fold higher at 60 cycles (0.4%) than at 10 cycles (0.18%). Note that these results are in line with the photocatalytic efficiency values reported in the literature for photocatalytic substrates. In work carried out on 2D supports, alveolar foams and suspended catalysts, Plantard et. Al. reported photocatalytic efficiencies ranging from 0.3% to 3%, depending mainly on the specific surface area developed by the support [Plantard 2011; Plantard 2014]. The highest photocatalytic efficiencies are obtained for nanometric catalyst suspensions, due to their perfectly homogeneous distribution and the high exchange surface area they develop.

At low precursor concentration ($c=0.08M$), the nanostructured ZnO deposit forms layer-by-layer as the quenching cycles progress, thus gradually covering the entire foam cell structure. As shown in the SEM images (Figure 3), the catalyst coating obtained at low cycle counts is highly homogeneous. The pore network is preserved, with a macroporous alveolar structure of open pores. However, as further quenching cycles progress, the ZnO film tends to partially close the pores. As the thickness of the film increases, membranes start to form in the cells and clog part of the pore structure, as evidenced in observations made with a confocal optical microscope (KEYENCE VHX-7000 Digital) (Figure 4). The macroporous structure is initially made up of totally open pores when only 10 cycles have been applied, but then both the thickness and volume of the structure increase significantly with each further cycle, until a proportion of the macropores progressively begin to close.

These experimental results show that increasing the quenching cycles improves the photocatalytic properties of geopolymer foams. Here we find that photocatalytic efficiency appears to peak at 60 quenching cycles, suggesting that coating thickness and distribution reach an optimum configuration and that the pore structure is partially altered by the ZnO coating, which clogs the macropores.

IV] Discussion and analysis

The ZnO synthesis parameters (pH, temperature, precursor concentration) were optimized to define the operating conditions that afford the best photocatalytic efficiencies. Our results also showed that the combination of precursor concentration and number of quenching cycles applied is a key interdependent factor. These two parameters need to be selected to achieve the highest photocatalytic efficiency without altering the properties of the catalyst or the pore structure of the

geopolymer foam. Indeed, too much deposition will lead to the formation of a pore-clogging coating. The aim is therefore to ensure a homogeneous coating on the surface of the porous structure.

To address this issue, geopolymer foams were ZnO-functionalized while varying the precursor concentration and number of quenching cycles. Two precursor concentrations were selected (0.08 and 0.8M). For each of these concentrations, we tested from 10 to 80 quenching cycles. Figure 11 plots the variation in photocatalytic efficiency of the functionalized foams as a function of number of quenching cycles.

Whatever the precursor concentration, photocatalytic efficiency increased significantly with number of quenching cycles successively applied. The highest efficiency was achieved with a functionalized foam fabricated at a precursor concentration of 0.8M and 60 quenching cycles, which achieved 1.1% efficiency whereas the same number of quenching cycles on a foam fabricated at a concentration of 0.08M achieved only 0.4% efficiency. These results are similar to those obtained in the literature for TiO₂ catalyst suspensions in nanometric or micrometric powders [Plantard 2012], which achieved efficiencies that reached a few percent and that increased with decreasing particle size. This is due to the distribution of the diffusers (catalyst particle) in the solution, which develops a large surface area. It has been established that catalyst suspensions make optimum use of incident radiation [Ribeiro 2021; Santarelli 1982]. Studies carried out on materials such as suspensions, powders, functionalized foams and 2D materials converge to show that photocatalytic performance is directly linked to the surface area developed by the material [Plantard 2014]. Suspensions with a specific surface area of around 10,000 m².m⁻³ have the highest activity, whereas foams with a specific surface area of around 1,000 m².m⁻³ have 50% less activity. These results confirm that surface area is the key parameter for maximizing photocatalytic performance.

For the same reasons, macroporous cross-linked materials such as 3D foams exhibit better mass and photon transfer than 2D support materials [Plantard 2014]. Plesch et al. showed that cell size plays a key role in photocatalytic performance [Fernandez 1995; Plesh 2009]. They studied several alveolar foams with average pore sizes of 3000 μm, 1100 μm and 800 μm, and found that photocatalytic efficiency is directly dependent on pore size and that the best performance is obtained for foams with pores larger than 3000 μm. Thus, the photocatalytic activity of cellular foams decreases with decreasing average pore size. Kouamé et al. worked on a panel of substrates including β-SiC honeycomb foams and found the same trend, with the highest photocatalytic performance obtained with foams with the largest pores (> 4500 μm) [Kouamé 2012]. Shan et al. recently compiled work on supported photocatalysts [Shan 2010] and concluded that the ideal photocatalytic support would be a

material organized on two scales: a macroporous alveolar structure enabling radiative transfers and flows, and a specifically-engineered photosensitive surface facilitating photoreaction processes.

Turning now to the influence of precursor concentration, foams functionalized at 0.08M precursor concentration had a higher photocatalytic efficiency at low numbers of quenching cycles. This pattern is due to the quality of the nanostructured ZnO coating on the foam surface. As discussed, at low precursor concentrations, the ZnO layers deposit homogeneously in the form of flower-like nanostructures. As the number of cycles increases, the photocatalytic efficiency of functionalized foams at 0.8M precursor concentration increases significantly and ultimately surpasses the photocatalytic efficiency obtained with a 0.08M precursor concentration at beyond 30 quenching cycles. SEM and microscope images (Figures 3 and 4) show that the coating on the surface of the foams covers the entire surface of the substrate. These favorable functionalization conditions offer the best photocatalytic performance. SEM images of foams produced at different numbers of quenching cycles show the progressive formation of ZnO membranes that start to partially obstruct the initially open macropores as the numbers of cycles increases. This, excess ZnO leads to progressive pore closure. This trend could explain why photocatalytic efficiency stabilizes when the number of cycles reaches 60. Indeed, it is well established in the literature that macroporous foams are good candidates for photocatalysis thanks to their porous network and, above all, their alveolar structure made up of interconnected open macropores. It is these properties that intensify the transfer of radiation and matter within the material. When the overlap becomes too great, it alters the pore network, limiting pore size and pore volume. These results show that beyond a certain number of cycles, the benefit of increasing the ZnO coating does not compensate for the modification of the pore network and the reduction in macropore sizes. Here, the most favorable conditions for functionalizing alveolar foams are a precursor concentration of 0.8M with 60 quenching cycles.

This study highlighted two key parameters that modulate photocatalytic performance: the first is the variation in precursor concentration used to synthesize ZnO nanostructures using the SILAR method, and the second is the number of quenching cycles. For the implementation of functionalized foams, it is essential to find the best trade-off between these operating parameters in order to obtain the best photocatalytic performance.

Conclusion

This work focused on the catalyst-driven functionalization of geopolymer foams in order to develop high-performance photocatalytic materials for solar photoreactors. The macroporous geopolymeric foams used as photocatalytic supports have porous characteristics that are perfectly suited to optimizing transfers of radiation and matter, thereby maximizing their photocatalytic capacity. We defined the key conditions for synthesizing ZnO (temperature and pH of the precursor solution) on the foam surface, and we characterized the surface conditions and crystalline structure required to ensure that the coating is homogeneously distributed on the surface of the supports. These properties were shown to be dependent on synthesis conditions and to confer photocatalytic properties. This first step demonstrated the feasibility of using the SILAR technique on a new geopolymer support.

Our work focused on the influence of precursor concentration and number of quenching cycles on the photocatalytic properties of the geopolymer foams. This investigation, which has never before been carried out on geopolymeric supports, highlighted the significant influences of that these two parameters have a significant influence on both photocatalytic efficiency and quality and distribution of the nanostructured catalyst film on the macroporous structure of geopolymeric foams. Different combinations of precursor concentration and number of cycles were tested in an effort to achieve the best photocatalytic performance. Based on photocatalytic efficiency, defined as the ratio of quantity of photoconverted molecules to quantity of incident photons, we find that a precursor concentration of 0.8M and 60 quenching cycles confer the highest photocatalytic activity.

This work demonstrated the value of the SILAR technique for functionalizing novel substrates with complex structures. This promising approach, which makes it possible to control deposition characteristics at molecular scale, could be applied to other substrates conventionally functionalized by sol-gel methods.

Conclusion

In the context of the development of high-performance photocatalytic materials for solar photoreactors, this work focused on the functionalization of geopolymer foams with a catalyst. The macroporous geopolymeric foams used as photocatalytic supports have porous characteristics that are perfectly suited to optimizing radiation and matter transfer, thereby maximizing their photocatalytic capacity. The conditions for synthesizing ZnO (temperature and pH of the precursor solution) on the foam surface were defined. Surface conditions and crystalline structure were characterized to ensure that the coating was homogeneously distributed on the surface of the supports. These properties were shown to be dependent on synthesis conditions and to confer photocatalytic properties. This first step demonstrated the feasibility of the SILAR technique on a new geopolymer support.

Our work focused on the influence of concentration and the number of quenching cycles applied on the photocatalytic properties of foams. This study, which had never before been carried out on geopolymeric supports, highlighted the significant influences of these two parameters on both photocatalytic efficiency and the quality and distribution of the nanostructured catalyst film on the macroporous structure of geopolymeric foams. To achieve the best photocatalytic performance, different combinations of precursor concentration and number of cycles were tested. Based on efficiency, defined as the ratio of the quantity of photoconverted molecules to the quantity of incident photons, a precursor concentration of 0.8M and 60 quenching cycles were found to confer the highest photocatalytic activity.

This work has demonstrated the value of the SILAR technique for functionalizing original substrates with complex structures. This promising approach, which makes it possible to control deposition characteristics on a molecular scale, could be applied to other substrates conventionally functionalized by Sol-gel methods.

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Captions

Table n°1: SILAR synthesis conditions for the functionalization of geopolymer foams.

Figure n°1: Description of the processing steps for geopolymer foams using the replication method

Figure n°2: Description of the SILAR processing steps for ZnO photocatalysts on geopolymer foams

Figure n°3: SEM photographs of ZnO-coated geopolymer foams under different synthesis conditions: synthesis applied in 30 quench cycles with a precursor concentration of 0.08M (shots A, B and C) and 0.8M (D, E and F).

Figure n°4: Photographs of geopolymer foams functionalized during 30 quenching cycles with a precursor concentration of 0,2M (A), 0,6M (B), 1M (C) and geopolymers functionalized with a precursor concentration of 0.2M at quenching cycles of 10 (D) , 40 (E) and 60 (F).

Figure n°5: Diffraction pattern (10-70°) collected for geopolymer ZnO-coated foam composed by ZnO (◆), NaAlSiO₄ (■) and Al₂(Al_{2.588}Si_{1.412})O_{9.706} (●)

Figure n°6: Raman spectrum (70-1100 cm⁻¹) collected for geopolymer ZnO-coated foam composed by ZnO (◆) and NaAlSiO₄ (■)

Figure n°7: A) Kinetics of phenol degradation by variation of cationic solution temperature deposited on geopolymer foam, B) Variation of photocatalytic efficiency of ZnO-coated geopolymer foams as a function of cationic solution temperature.

Figure n°8: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams as a function of pH cationic solution.

Figure n°9: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams with a precursor concentration of 0.2M at 20 quenching cycles, as a function of photocatalytic aging tests.

Figure n°10: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams as a function photocatalytic of precursor concentration (quenching cycle equal to 10) .

Figure n°11: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams with a precursor concentration of 0.08M, as a function photocatalytic of quenching cycles applied.

Figure n°12: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams as a function of quenching cycle with a precursor concentration of 0.08M(o) et 0.8M (Δ).

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Samples	Apparent volumic mass (Kg/m ³)	Precursor concentration (M)	Number of quenching cycle (-)	pH (-)	Temperature (°C)
Foam(0,08)	80	0,08	30	10,5	25°C
Foam(0,2)	140	0,2	30	10,5	25°C
Foam(0,4)	160	0,4	30	10,5	25°C
Foam(0,6)	190	0,6	30	10,5	25°C
Foam (0,8)	190	0,8	30	10,5	25°C
Foam (1)	210	1	30	10,5	25°C
Foam 7 (0,08M) 10C	80	0,08	10	10,5	25°C
Foam 8 (20C)	160	0,08	20	10,5	25°C
Foam 9 (40C)	190	0,08	40	10,5	25°C
Foam 10 (60C)	190	0,08	60	10,5	25°C
Foam 11 (80C)	210	0,08	80	10,5	25°C
Foam 12 (0,2M) 10C	80	0,2	10	10,5	25°C
Foam 13 (20C)	180	0,2	20	10,5	25°C
Foam 14 (40C)	180	0,2	40	10,5	25°C
Foam 15 (60C)	230	0,2	60	10,5	25°C
Foam 16 (80C)	430	0,2	80	10,5	25°C
Foam 17 (0,8M) 10C	70	0,8	10	10,5	25°C
Foam 18 (40C)	200	0,8	40	10,5	25°C
Foam 19 (60C)	280	0,8	60	10,5	25°C
Foam 20 (80C)	480	0,8	80	10,5	25°C
Foam 21 (pH)= 9,02	240	0,08	30	9,02	25°C
Foam 22 (10,5)	220	0,08	30	10,5	25°C
Foam 23 (11,48)	80	0,08	30	11,48	25°C
Foam 24 (25°C)	80	0,08	30	10,5	25°C
Foam 25 (60°C)	130	0,08	30	10,5	60°C
Foam 26 (90°C)	260	0,08	30	10,5	90°C

Table n°1: SILAR synthesis conditions for the functionalization of geopolymer foams.

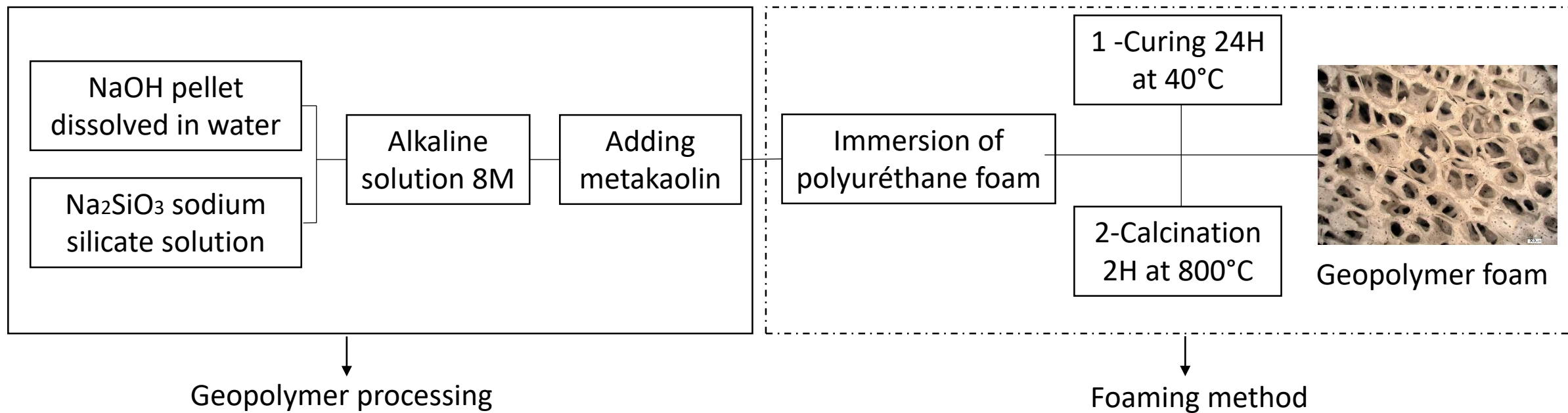


Figure n°1: Description of the processing steps for geopolymer foams using the replication method

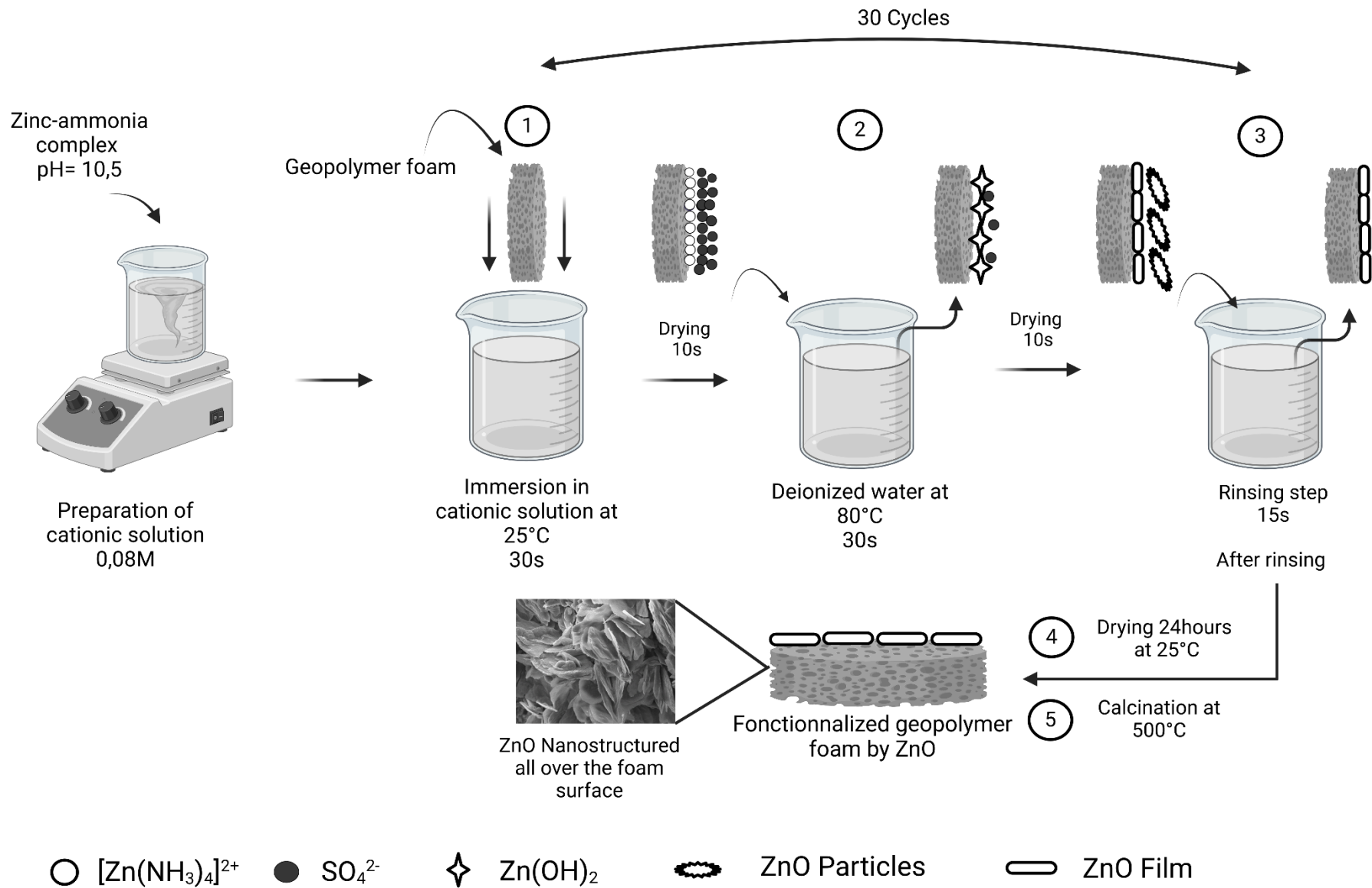


Figure n°2: Description of the SILAR processing steps for ZnO photocatalysts on geopolymer foams

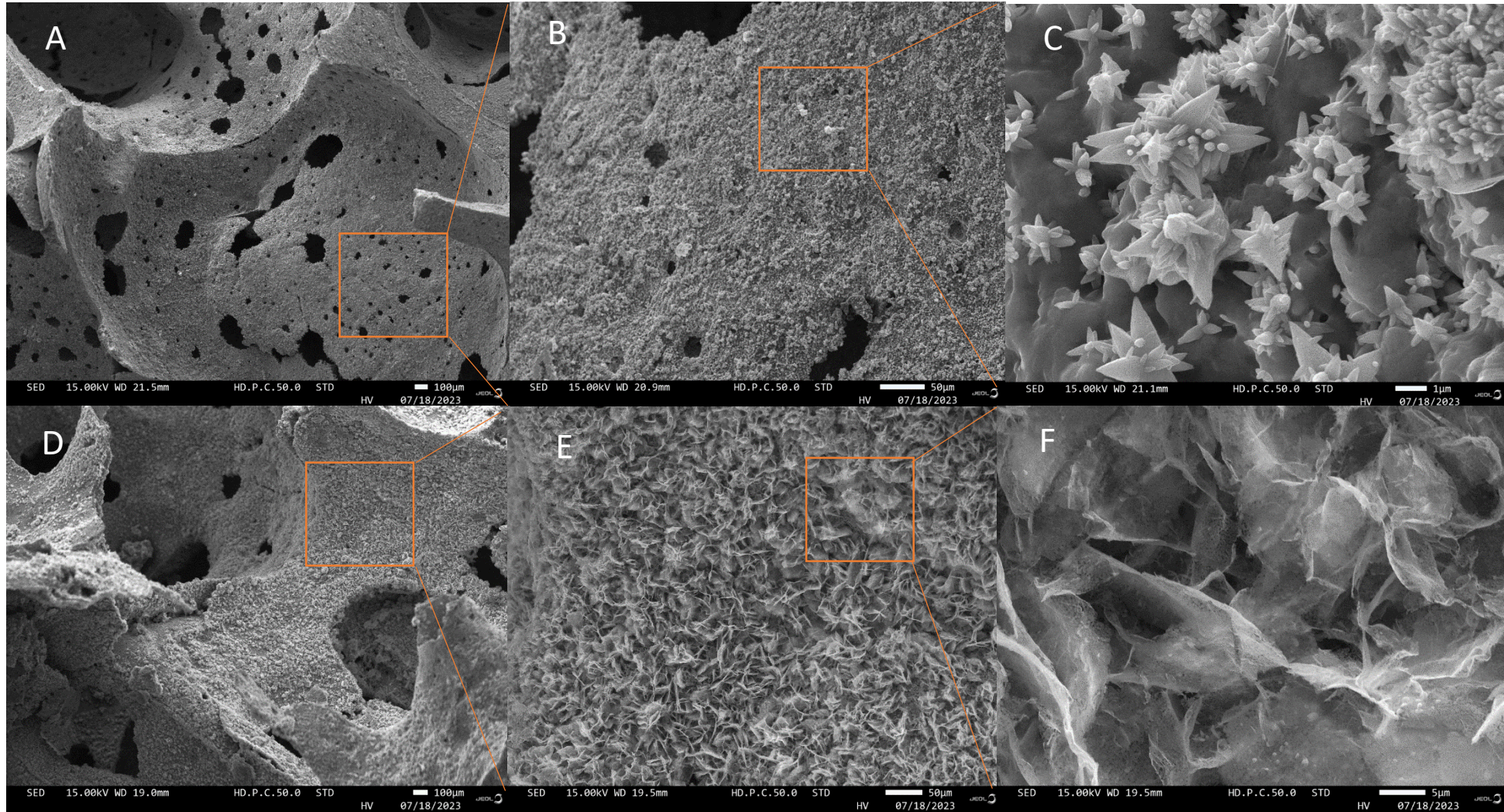


Figure n°3: SEM photographs of ZnO-coated geopolymer foams under different synthesis conditions: synthesis applied in 30 quench cycles with a precursor concentration of 0.08M (shots A, B and C) and 0.8M (D, E and F).

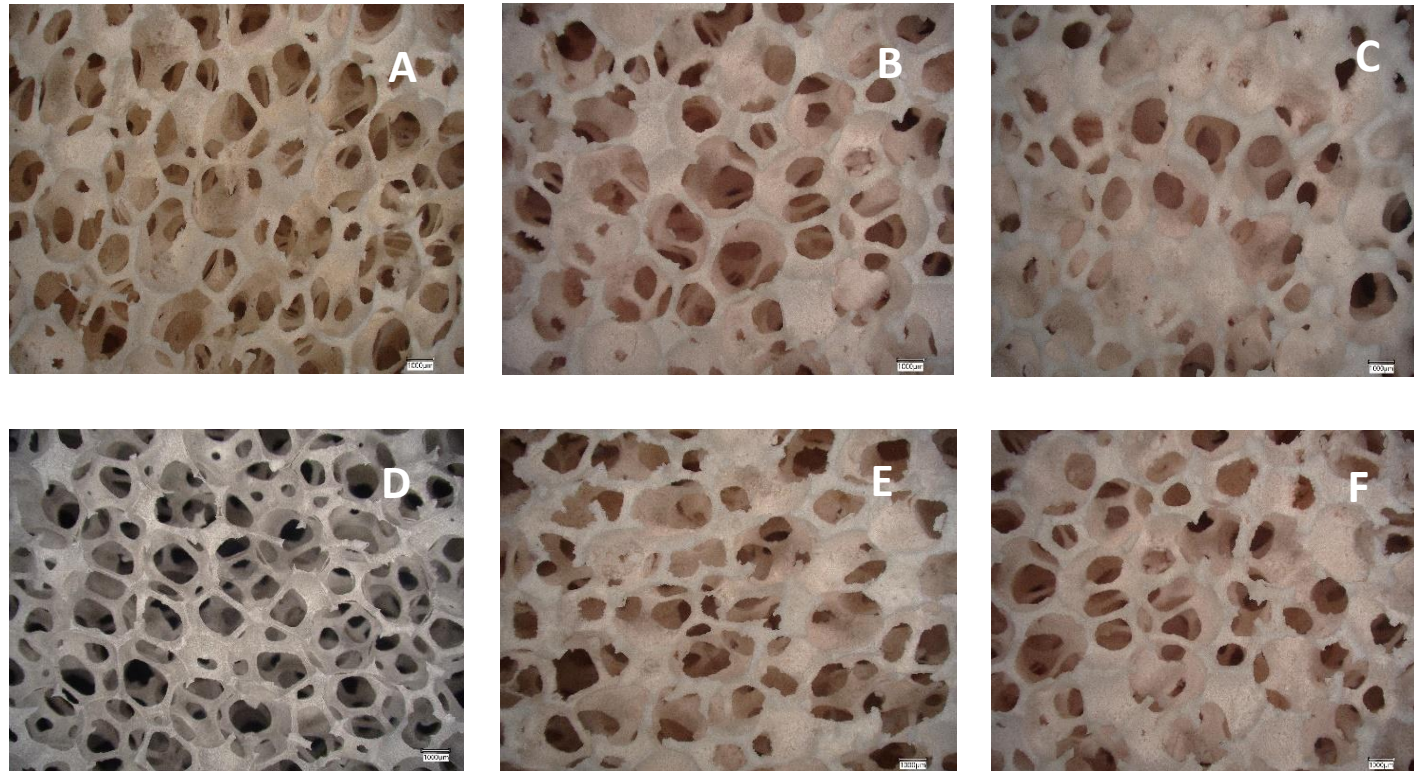


Figure n°4: Photographs of geopolymer foams fonctionalized during 30 quenching cycles with a precursor concentration of 0,2M (A), 0,6M (B), 1M (C) and geopolymers fonctionalized with a precursor concentration of 0.2M at quenching cycles of 10 (D) , 40 (E) and 60 (F).

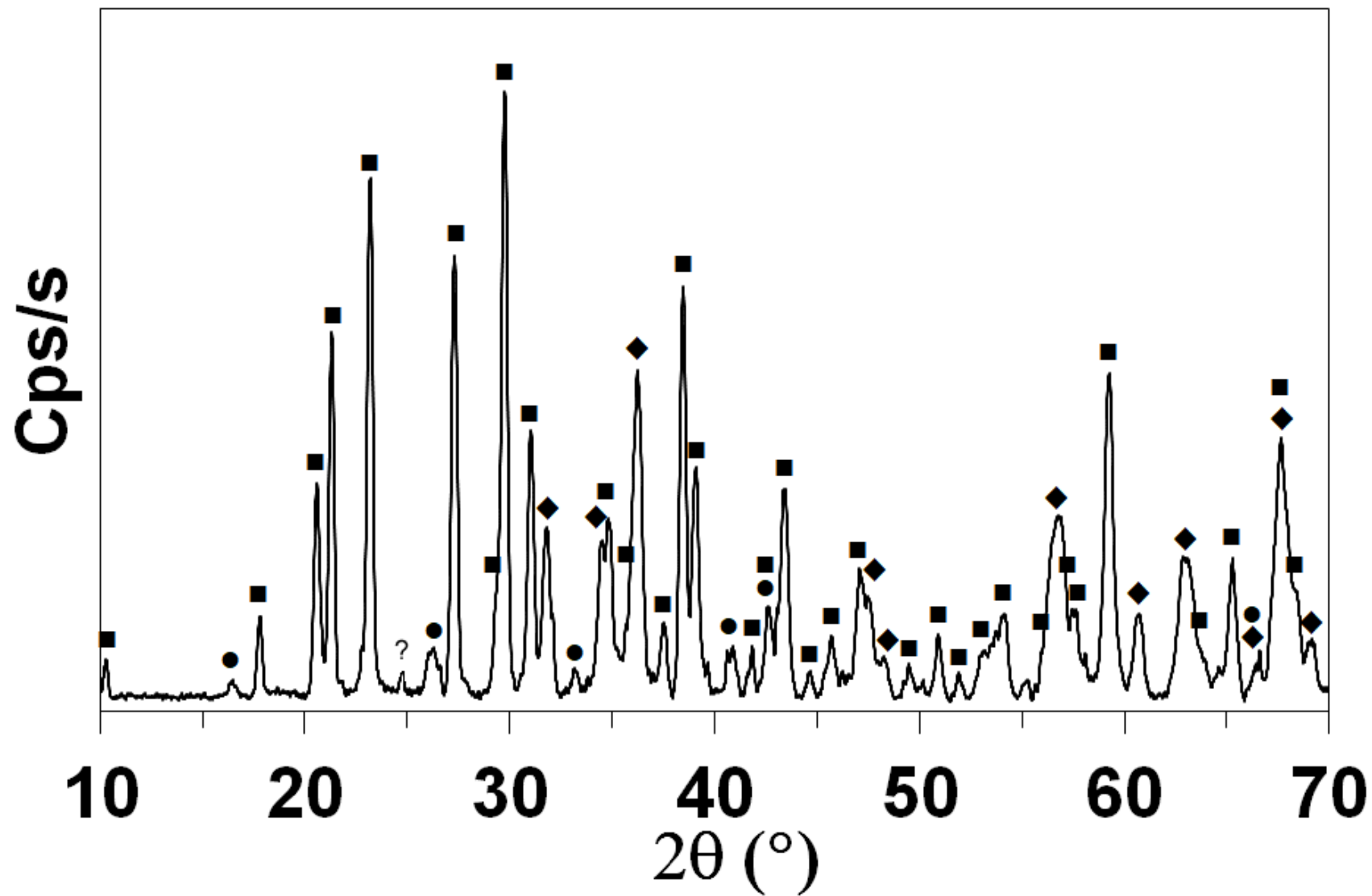


Figure n°5: Diffraction pattern (10-70°) collected for geopolymer ZnO-coated foam composed by ZnO (◆), NaAlSiO₄ (■) and Al₂(Al_{2.588}Si_{1.412})O_{9.706} (●)

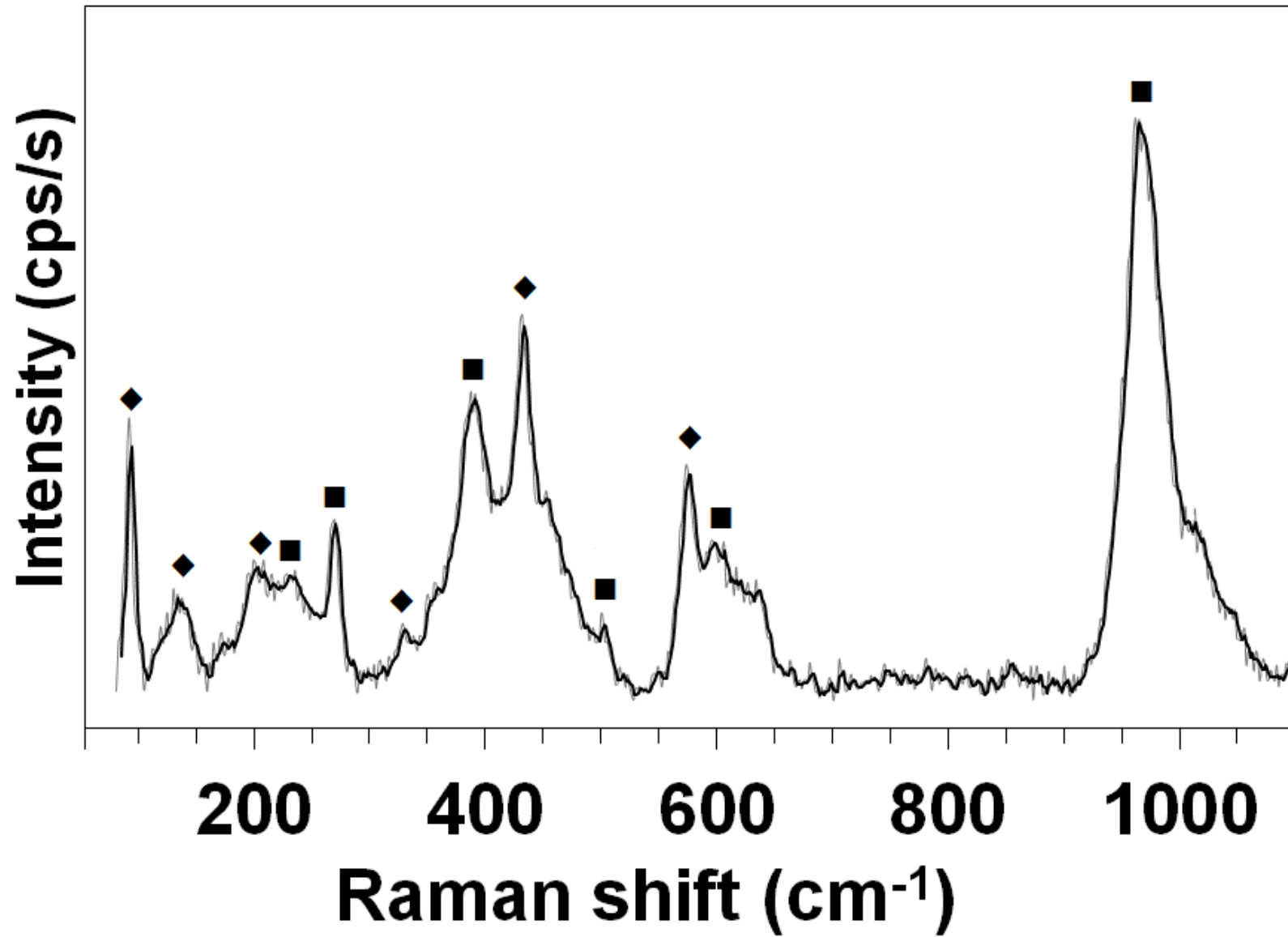


Figure n°6: Raman spectrum (70-1100 cm⁻¹) collected for geopolymer ZnO-coated foam composed by ZnO (◆) and NaAlSiO₄

(■)

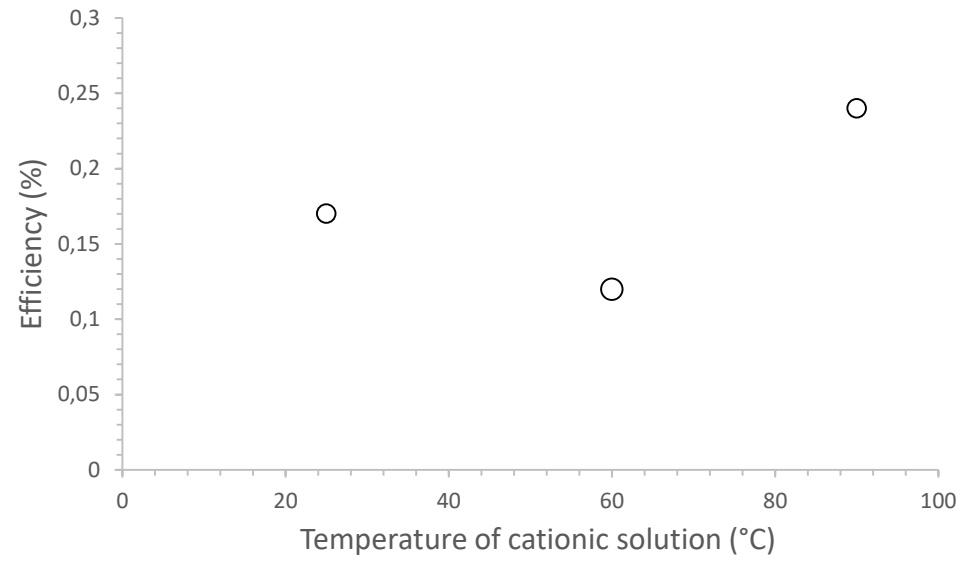


Figure n°7: A) Kinetics of phenol degradation by variation of cationic solution temperature deposited on geopolymer foam, B) Variation of photocatalytic efficiency of ZnO-coated geopolymer foams as a function of cationic solution temperature.

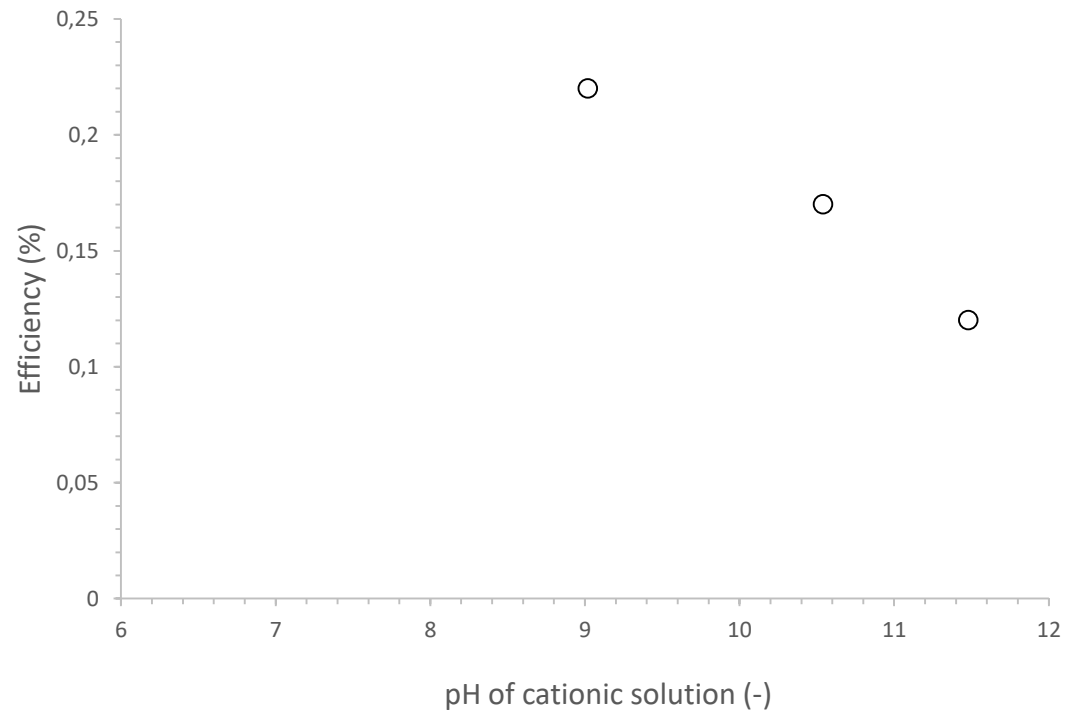


Figure n°8: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams as a function of pH cationic solution.

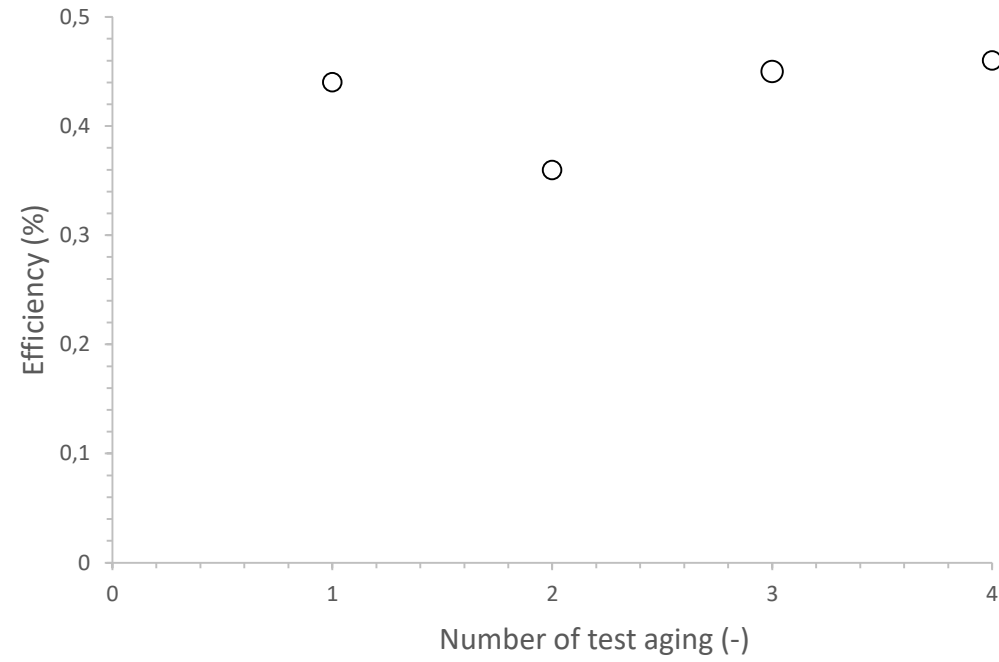


Figure n°9: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams with a precursor concentration of 0.2M at 20 quenching cycles, as a function of photocatalytic aging tests.

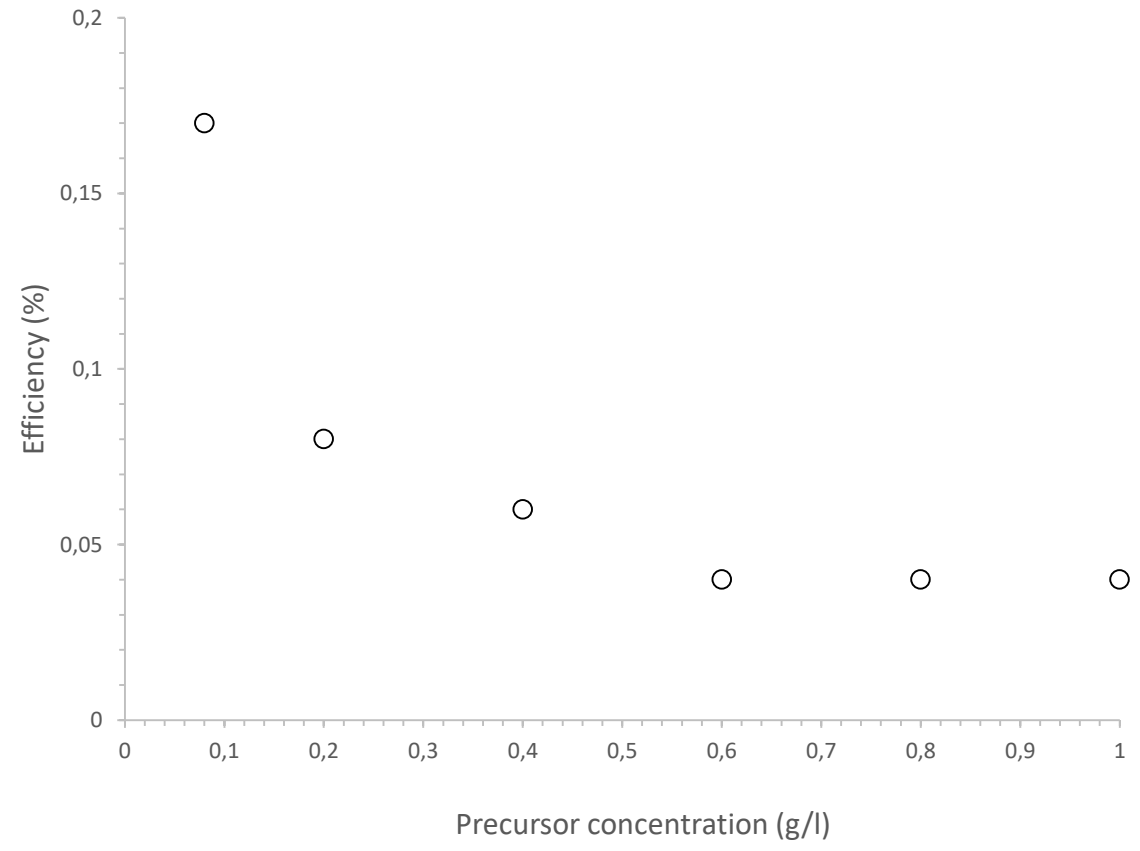


Figure n°10: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams as a function photocatalytic of precursor concentration (quenching cycle equal to 10) .

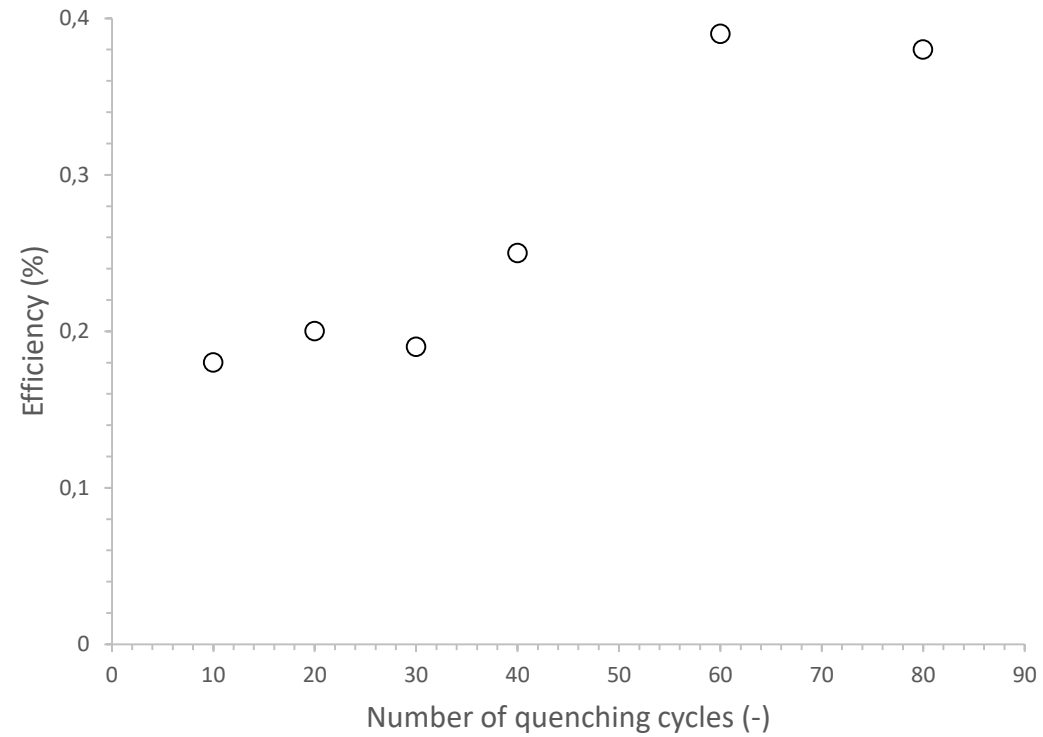


Figure n°11: Variation of photocatalytic efficiency of ZnO-coated geopolymer foams with a precursor concentration of 0.08M, as a function photocatalytic of quenching cycles applied.

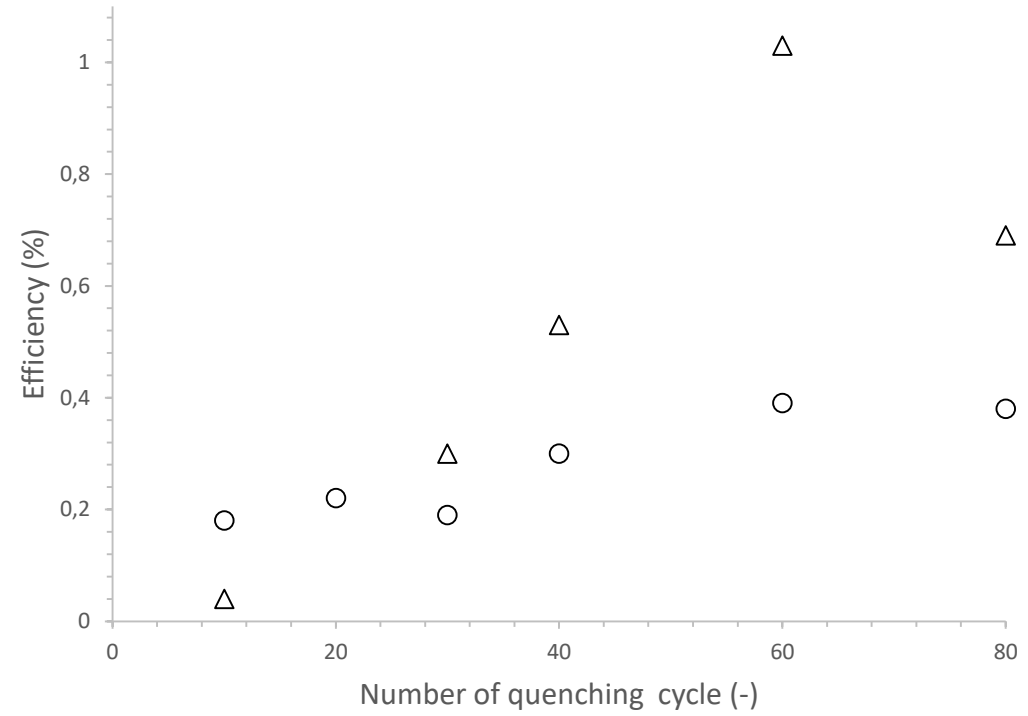


Figure n°12: Variation of photocatalytic efficiency of ZnO-coated geopolymers foams as a function of quenching cycle with a precursor concentration of 0.08M(○) et 0.8M (Δ).

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Dear Editor,

We are pleased to submit “Optimizing the photocatalytic properties of ultra-macroporous geopolymer foams : influence of synthesis conditions of SILAR technique” by Benkhirat.S, Nouneh.K, E. Ribeiro, S.Eichendorff, E. Beche and Plantard G. for publication as an original research article in *results in chemistry*.

In this paper, we propose to develop and optimize the conditions for synthesizing a catalyst on a macroporous alveolar geopolymer foam. The aim is to impart photocatalytic properties to the geopolymer material, and then to control and optimize the synthesis conditions so as to achieve the highest photocatalytic capacities. The SILAR technique was used to coat the ZnO catalyst. The synthesis conditions studied included pH, precursor solution temperature, precursor concentration and number of quenching cycles. To our knowledge, this study of the functionalization of geopolymer foams for photocatalytic applications is totally original. It highlights the importance of the combination of precursor concentration and number of quenching cycles on photocatalytic properties. Interconnected macroporous foams have been identified as perfectly suited to enhancing photocatalytic performance. Macroporous geopolymer foams offer promising prospects for water treatment applications.

Therefore, we think it should be published in a highly recognized journal with a wide readership such as *results in chemistry*.

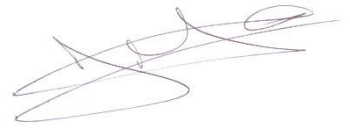
You will find the manuscript with lines numbers, abstract, keywords, figures, tables, acknowledgment and references.

All authors mutually agree for submitting their manuscript of their original work. None of the material has been published or is under consideration elsewhere.

We look forward to learning of your decision and appreciate your consideration.

Best regards,

Gael Plantard



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