Floatable graphitic carbon nitride/alginate beads for the photodegradation of organic pollutants under solar light irradiation

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Abstract

Graphitic carbon nitride, both as powder and alginate floating beads, was synthesized by an easy and cheap approach using two different precursors (melamine and urea) and properly characterized by several techniques. The effect of the type of precursor on the photoactive properties of the final materials was investigated. Their activity towards the photodegradation of different pollutants (dyes, drugs, and herbicides) both in ultrapure water and simulated drinking water under solar light irradiation was investigated, reaching extraordinarily high photodegradation results (99% for diclofenac and rhodamine B and 90% for isoproturon) compared to the literature. The floating photocatalysts showed good stability during recycling maintaining high performances after 5-time usage without post-treatment. Finally, liquid chromatography equipped with mass spectrometry (UPLC/MS) was used to identify the main by-products formed during the photodegradation tests, and a plausible transformation pathway has been proposed.

Keywords: graphitic carbon nitride, floating photocatalysts, solar light, photocatalysis, organic pollutants degradation, reusability.

1. Introduction

Owing to the rapid development of modern industry and agriculture, new problems have arisen strictly related to environmental pollution and energy shortage. Several pollutants currently threaten water resources and societal well-being in different water matrices. Among these, contaminants of emerging concern (CECs) have become particularly urgent pollutants for their chemical stability, potential toxicity, and danger to human life. The awful effect of wastewater effluents containing CECs on the quality of receiving water bodies has been widely demonstrated [1, 2]. Water reuse has emerged as an important challenge, particularly in regions suffering from water scarcity. Therefore, several approaches, based on different technologies, have been developed to face this problem. Since conventional wastewater treatment processes lead to incomplete removal of CECs, the scientific community has addressed its efforts in developing highly efficient, low-cost, and low-impact treatments. These include chemical oxidation, physical adsorption, biological degradation, and other methods [3-7]. The attempts to employ microorganisms have been limited by several practical factors, such as long cultivation cycles, the necessity for nitrogen-limiting environments, slownest of the remediation process, inhibition of the microorganisms at high concentrations of toxic substances, inability to degrade recalcitrant organic pollutants completely, etc. [8, 9]. On the other hand, the use of enzymes is still too little studied to be taken into consideration. In addition to these traditional methods, from several years, advanced oxidation processes (AOPs) [10], such as

47 ozonation [11], Fenton [12], photo-Fenton [13], photolysis [14, 15], and photocatalysis [16]
48 techniques, have emerged as innovative approaches, receiving extensive attention for their benign
49 conditions, energy-saving, easy control and less secondary pollution [17]. Among all these methods,
50 photocatalysis is generally preferred for its ability to convert toxic organic compounds to CO_2 and
51 H_2O [18-20]. More recently, organic pollutants degradation by coupled techniques, i.e., ultrasound-
52 assisted photocatalysis, have emerged as alternative AOPs [21]. However, although
53 sonophotocatalysis seems to overcome the main limitations of the single techniques (enhancing the
54 active species production, guaranteeing a continuous cleaning of the photocatalyst surface, etc.)
55 current conventional configurations of batch sonoreactors (bath- and horn-type) seems to be not
56 effective at a large-scale operation, because the propagation of acoustic energy is limited, the horn
57 surface erosion due to cavitation need frequent costly maintenances or the replacement of the probe,
58 etc. [22]. Although, for photocatalytic applications, TiO_2 is still the most used semiconductor due to
59 its chemical and physical stability, good photoactivity, and low cost, researchers are willing to
60 replace it with new smart materials because of its suspected carcinogenic nature and limited activity
61 under solar light irradiation [23]. Recently, graphitic carbon nitride (g-C_3N_4) has drawn attention as
62 a metal-free visible photoactive semiconductor for water remediation. Their characteristics such as
63 mid-wide bandgap with 2.7 eV, large surface area, high mobility, high transparency, excellent
64 electrical and thermal conductivity, high mechanical strength, flexibility, chemical stability, and a
65 wide range of precursors for its preparation (dicyanamide, melamine, cyanamide, urea, thiourea or
66 ammonium thiocyanate) [24] make it an ideal material in the field of photocatalysis. g-C_3N_4 has
67 been investigated for pollutants degradation [25-27], H_2 production [28, 29], and other
68 photocatalytic reactions [30-33]. In the field of photocatalysis, crystalline semiconductors are
69 almost exclusively employed because their typical long-range atomic order is considered crucial to
70 guarantee an efficient photoexcited charge carriers' separation and diffusion.
71 Consequently, in particular, in the last years, the scientific literature has been enriched with
72 numerous papers based on exploiting the properties of graphitic carbon nitride [25-33].
73 Among them, the investigations of Vilè et al. are particularly interesting, demonstrating as
74 nanostructural modifications and elemental incorporation in carbon nitride samples lead to a new
75 class of materials, ingle-atom catalysts (SACs), characterized by very high activity towards
76 pollutants photodegradation [34, 35]. SACs consist of isolated single metals strongly confined in
77 the cavities of a porous carrier. Thanks to its N-rich structure, g-C_3N_4 represents an ideal carrier
78 able to stabilize several metal species. Ni-based heterogeneous photocatalysts, made of highly
79 dispersed Ni species over nanosheets of g-C_3N_4, showed very high performance in the
80 photodegradation of gemfibrozil, a model pharmaceutical pollutant [34]. Similarly, highly dispersed
81 Ag and Cu species on mesoporous g-C_3N_4 resulted very active in water decontamination [35].
82 Moreover, both the SACs systems were able to reduce the formation of toxic aromatic byproducts
83 during photooxidation.
84 The use of active materials in the form of dispersed powders into the reaction medium (slurry
85 configuration) indeed allows taking advantage of the whole active surface area of the catalyst.
86 However, this approach poses severe problems in large-scale industrial applications, where the
87 recovery of suspended catalyst powder is an issue. Therefore, the development of stable, highly
88 active supported catalysts, tightly binding the active phase, is certainly a significant effort towards
89 real photocatalysis applications. Recently, new materials based on immobilized photocatalysts on
90 floating substrates were employed in the photodegradation process exploiting their high surface
91 irradiation and oxygenation, ease of recovery, and reuse. Within this framework, synthetic polymers
92 are commonly used as support [36-39]. However, their low or non-degradability has raised
93 ecological concerns. Instead, an eco-friendly alternative can be represented by natural polymers
94 [40-42]. Among these, alginates are particularly interesting. They derive from brown seaweeds and

can be used to immobilize photocatalysts under safe and mild conditions. Sodium alginate is a biodegradable and biocompatible compound that, thanks to the presence of carboxylate ($-COO^-$) and hydroxyl functional groups ($-OH$) can electrostatically interact with various metal cations (e.g., Ca^{2+}, Ba^{2+}, etc.) by cross-link reactions to form a hydrogel structure that can be used to support or embed catalysts [40, 41, 43]. Although both g-C_3N_4 and calcium alginate are two very well-known and studied materials, alginate-based hydrogel beads have been scarcely used as carbon nitride support. The present work proposes a straightforward approach for the synthesis and characterization of g-C_3N_4/alginates floating photocatalysts. The effect of the type of precursor (melamine and urea) on the photoactive properties of the final g-C_3N_4-based materials was investigated. g-C_3N_4/alginate beads were tested for the photodegradation of three classes of pollutants (drugs, dyes, and herbicides) present individually in solution or a mixture in different water matrices (ultrapure water and simulated drinking water) under solar light irradiation. The reusability of the floating photocatalysts has been adequately investigated, showing high stability up to five runs. Finally, the main transformation products (TPs) deriving from the photodegradation processes were properly identified by UPLC/MS technique, and the principal degradation pathways are reported.

2. Materials and Methods

2.1. Materials

All chemicals of analytical grade were purchased by Sigma-Aldrich products. The pollutants mixtures were prepared in ultrapure water (UW) and in a simulated solution of drinking water (TW) as reported below. For both HPLC/UV and UPLC/MS analyses, HPLC-grade acetonitrile and water were purchased from VWR Chemicals and Carlo Erba, respectively.

2.2. g-C_3N_4 preparation

g-C_3N_4 was thermally synthetized with a one-pot polycondensation method starting from two different precursors: urea (U) and melamine (M). The desired amount of urea and melamine were placed in two different crucibles, covered with a lid. The crucibles were heated at 550°C for 2 h, according to the following temperature ramp: 135°C (5 C°/min, hold: 1h), 170°C (3°C/min, 1h), 300°C (5°C/min, 1h), 550°C (5°C/min, 2h). Then, the samples (g-C_3N_4_U and g-C_3N_4_M) were cooled to room temperature, and the obtained powders were ground and weighed.

2.3. Floating g-C_3N_4/alginate (FCNA) beads preparation

The FCNA beads were prepared by dispersing 0.1g of catalyst (g-C_3N_4_U or g-C_3N_4_M) in 20 mL of sodium alginate 3 % solution. The dispersion was sonicated for 1h and stirred for 24 h; in the end, 1 g of $CaCO_3$ was added, and the solution was stirred again for 1 h (Solution A). In 50 mL of $CaCl_2$ 3 % solution, 5 mL of acetic acid were added and stirred for 30 min (Solution B). Solution A was slowly dropped into solution B, obtaining 5 mm diameter floating spheres. The spheres were stirred for 24 h and were abundantly rinsed in water (Figure 1).

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156 **Figure 1:** Schematic illustration for the FCNA beads preparation.
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158 The percentage of g-C_3N_4 in alginate beads was determined by weighing and was 0.6%.
159 Any attempt to increase the g-C_3N_4 load (0.2 g/L and 0.3 g/L of catalyst) within the polysaccharide
160 matrix failed, leading to beads that were difficult to handle and disperse in water due to their
161 fragility. In those conditions, the excess of g-C_3N_4 inhibits the cross-link reaction and,
162 consequently, the hydrogel formation.
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164 **2.4. Characterization**
165 g-C_3N_4 powders were properly characterized by several analytical techniques. The corresponding
166 FCNA beads have not been characterized due to their high-water content, which limits the
167 possibility of using the most common characterization techniques
168 Concerning the morphological aspects, g-C_3N_4 was characterized by scanning electron microscopy
169 (SEM) using a Zeiss LEO 1525 field emission microscope without any pretreatment of the samples.
170 Fourier Transform infrared (FTIR) spectra were performed using a Jasco FT-IR 410
171 spectrophotometer dispersing a few milligrams of each material in anhydrous KBr and pressing it to
172 obtain a thin pellet. The spectra were recorded in the range 400-4000 cm-1 with a resolution of 0.5
173 cm^{-1}.
174 X-ray powder diffraction investigations were executed using a PANanalytical X'Pert PRO
175 diffractometer with Cu Kα radiation and at 40 kV × 40 mA nominal X-ray power.
176 Specific surface area and porosity distribution were determined by processing N_2
177 adsorption/desorption isotherms at 77 K (Micromeritics Tristar II 3020 (Micromeritics)) with
178 Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda analyses. Before the analysis,
179 samples were heat-treated (T = 150 °C, 4 h, N_2) to remove adsorbed foreign species.
180 An M-Probe (SSI) XPS instrument was used to analyze the sample surfaces detecting in particular
181 O1s, C1s, and N1s regions. The instrument is equipped with a monochromatic Alkα anode and is
182 calibrated using C1s at 284.6 eV.
183 The light absorbance properties were investigated by UV-vis diffuse reflectance spectroscopy of
184 powder samples using a Perkin Elmer Lambda 35 UV VIS Spectrophotometer.
185
186 **2.5 Pollutant mixture abatement tests**
187 The photoactivity of the samples, both as powders and floating beads, were tested for the absorption
188 and photodegradation of three different pollutants diclofenac (DCF), isoproturon (ISO), and

189 rhodamine B (RhB). Proper solutions of each pollutant (10 mg·L^{-1}) were prepared using both
190 ultrapure water (UW) and simulated drinking water (DW) as the matrices. Simulated DW was
191 prepared according to Annex B2 of the second protocol of the French Norm NF P41-650 regarding
192 the specification for water filter pitchers (Tab.1).
193 **Table 1:** Ionic species and relative concentration for the preparation of simulated drinking water.
194

Species	Concentration (mg·L^{-1})
Ca^{2+}	44.5
Na^+	45.7
Mg^{2+}	9.3
Cl^-	78.7
SO_4^{2-}	36.5
HCO_3^{2-}	121.2

195
196 The experiments were performed by stirring the proper amount of photocatalyst in a 250 mL batch
197 glass reactor filled with 100 mL of pollutant solution maintained at spontaneous pH (about 5 for
198 UW and about 7 for DW). The suspension was kept in the dark for 30 min, then it was irradiated for
199 180 min with a solar lamp (ULTRA VITALUX 300W-OSRAM) placed above the reactor. The
200 solar lamp used for the experiments had an effective power density of irradiation of 35 W·m^{-2}. The
201 pollutants abatement was monitored for 210 min, sampling aliquots every 15 min in the first half-
202 hour and every 30 min in the subsequent 3 h. The samples were quantitatively analysed by
203 HPLC/UV. Chromatographic analysis was performed with an isocratic elution of a mobile phase
204 composed of water (65%), acetonitrile (35%), and formic acid (0.1%), at 1.00 mL·min^{-1} flow. The
205 HPLC instrument (Agilent 1100 Series) was equipped with a C18 Supelco column (25 cm x 4 mm,
206 5 µm), a 20 µL injection loop, and a UV detector. The DCF, ISO, and RhB disappearance was
207 monitored at 278 nm, 240 nm, and 554 nm, respectively.
208 The transformation products of the three analytes were recognized through UPLC/MS technique
209 using the same chromatographic conditions. The MS interface parameters for sample acquisition
210 were the following: heater temperature 150 °C, sheath gas flow rate (arb) 20, auxiliary gas flow rate
211 (arb) 10, sweep gas flow rate (arb) 10, spray voltage negative mode 3.50 kV, capillary temperature
212 275 °C, capillary voltage -10 V, tube lens -10 V, m/z range 50-500 Da.
213 The same procedure was also used to degrade solutions containing a mixture of the pollutants (10
214 mg·L^{-1}) both in UW and DW.
215 The alginate shell of floating beads causes a slight release of organic material in solution, which
216 compromises the results of TOC (Total Organic Carbon) analyses to verify the mineralization
217 capacity of the FCNA.
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219 **2.6 Reusability tests**
220 FCNA beads from urea and melamine were tested for RhB degradation for five consecutive tests.
221 After each run, the floating beads were recovered using a small colander, washed three times with
222 deionized water, and immediately reused.
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224 **3.   Results and discussion**
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226 **3.1.   Materials characterization**
227 Figure 2 (left) shows the FT-IR spectra of the synthesized g-C$_3$N$_4$ powders.
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Figure 2: FT-IR spectra (left) and XRD diffraction patterns (right) of both g-C$_3$N$_4$_M and g-C$_3$N$_4$_U, respectively.

Both the synthesized materials show the typical IR patterns of carbon nitride. The characteristic peaks located 1000-1800 cm^{-1} can be attributed to the bending and stretching vibration modes of C–N and C=N, whereas the broad bands between 3000-3500 cm^{-1} are due to tensile vibrations of N–H bonds [33]. The peaks located in the region from 900 to 1800 cm^{-1} correspond to the characteristic stretching modes of CN heterocycles. According to the literature [33], the peaks at ca. 1410 and 1060 cm^{-1} are assigned to the C-O vibrations in C-OH, and C-O-C functional groups, respectively, associated with a slight O-doping during the thermal treatment carried out in the air.

Both the materials show similar XRPD patterns, indicating that the synthesized g-C$_3$N$_4$ maintains the same crystalline structure.

More in detail, the two main peaks at 27.5° and 12.9° can be assigned to (002) diffraction plane and (100) plane of g-C$_3$N$_4$, due to the interlayer stacking of conjugated aromatic system and to in-plane repeated tri-s-triazine units, respectively. Moreover, the peak at 14.16° is ascribed to the (100) reflection, whereas reflections corresponding to the (300) and (004) planes provide a possible explanation for the two broad peaks at 44.4° and at 57.4°, respectively. In addition, a large percentage of an amorphous phase is evidenced in both the materials, as confirmed by the broadband at around 25°. This is more pronounced for g-C$_3$N$_4$_U than for g-C$_3$N$_4$_M. In fact, urea lacks proper s-triazine structure, and during the thermal condensation process, several intermediates (biuret, cyanuric acid, ammeline, and ammelide) can be involved making hard the formation of uniform and well connected heptazine-based g-C$_3$N$_4$ and causing structure defects in the final product inevitably [44].

Moreover, according to Sun and coworkers [45], the weak peaks at ~18°, ~22°, ~44°, and ~56° can be assigned to (100), (101), (111), (103), and (004) planes, respectively of g-C$_3$N$_4$, although most part of the scientific literature report contradictory assignment.

The surface element composition and chemical state of the samples were investigated by XPS. As shown in Figure S1 A B, both the survey XPS spectra display three peaks associated to C1s (31.5% for g-C$_3$N4_U and 33.3% for g-C$_3$N4_M), N1s (52.1% for g-C$_3$N4_U and 59.7% for g-C$_3$N4_M), and O1s (4.7% for g-C$_3$N4_U and 4.6% for g-C$_3$N4_M). The oxygen peak can be easily attributed to the O$_2$ absorbed from the atmosphere during the calcination process. The atomic carbon-nitrogen ratio C/N for g-C$_3$N4_U and g-C$_3$N4_M was 0.87 and 0.94, respectively. If compared to the stoichiometric value (0.75), the C/N obtained from the synthesized materials can be interpreted as the formation of carbon vacancies in O-doped g-C$_3$N$_4$ structure. As reported in the scientific literature [20], defect engineering, such as carbon or nitrogen vacancies, is an important strategy for designing efficient photocatalysts.

The XPS spectra of both g-C$_3$N$_4$_M and g-C$_3$N$_4$_U (Figure 3) show a slight difference in particular in O1s high resolution (HR) spectra.

Figure 3: A) C1s of g-C$_3$N$_4$_M, B) C1s of g-C$_3$N$_4$_U, C) N1s of g-C$_3$N$_4$_M, D) N1s of g-C$_3$N$_4$_U, E) O1s of g-C$_3$N$_4$_M, F) O1s of g-C$_3$N$_4$_U.

The binding energies of C1s and N1s core electrons are similar for both the materials, suggesting a very similar chemical environment for carbon and nitrogen.
In the C1s spectrum (Figure 3 A and B), the peaks at 284.6 eV, 288.0 eV, and 289.3 eV are assigned to impurity carbon, sp2 bonded carbon in the aromatic ring N=CN and sp2 carbon of the – NH$_2$ group on the aromatic ring, respectively [45]. For both the two g-C$_3$N$_4$ the N1s spectrum can be splitted into three different peaks at 398.3 eV, 399.3 eV, and 400.6 eV associated with the sp2

hybrid nitrogen CN=C, tertiary nitrogen (N-(C)$_3$) and terminal amino group (CNH) respectively [46].

Finally, the O1s peak at 531.6 eV is related to C=O and N-C-O groups, whereas the peak at 533.1 eV can be attributed to water adsorbed on the surface [47]. The third peak at 534.0 eV in the O1s spectrum of g-C$_3$N$_4$_U can be reasonably attributed to C−O−C bonds in the heterocyclic rings of the graphitic structure [48].

As reported in the scientific literature [49], bulk g-C$_3$N$_4$ produced by thermal polymerization of N-rich compounds as precursors are generally characterized by low specific surface area and compact structures that limit their application in photocatalytic reactions.

However, morphology investigation on the synthesized samples (Figure 4) revealed a rough surface characterized by plates of different dimensions. In particular, if on the one hand, g-C$_3$N$_4$_M seems characterized by irregular staked sheets, on the other hand, g-C$_3$N$_4$_U is mainly smooth, exhibiting minor areas where a more porous and rougher surface is exposed.

Figure 4: SEM images of g-C$_3$N$_4$_M (left) and g-C$_3$N$_4$_U (right).

According to IUPAC classification, nitrogen adsorption-desorption isotherms reported in Figure 5 are classified as type IV with H3 hysteresis loop [50].

Figure 5: Nitrogen adsorption-desorption isotherms for the two powdered samples.

This type of isotherm is typical of mesoporous materials with a hierarchical pores structure, and H3 hysteresis loop shows that these materials are formed by non-rigid aggregates of plate-like particles [50]. This is in accordance with SEM images reported in Figure 4.

In Table 2, surface area and porosity distribution are reported, determined by analyzing the adsorption nitrogen isotherm branch [51].

Table 2: surface area and porosity distribution percentage of both g-C_3N_4_U and g-C_3N_4_M as powders.

		g-C_3N_4_U	g-C_3N_4_M
Specific Surface Area (m²·g⁻¹)		180 ± 2	10.29 ± 0.08
Porosity Distribution (%)	d<2 nm	-	4.0
	2<d<10 nm	66.4	52.7
	10<d<20 nm	10.7	13.3
	20<d<50 nm	11.2	17.6
	d>50 nm	11.7	12.4

The specific surface area of g-C_3N_4_U powder is one order of magnitude larger than that of powdered g-C_3N_4_M, and for both the samples, this area is preferentially distributed in small mesopores (2 <d <10 nm). However, the highest percentage (about 66%) characterizes g-C_3N_4_U. The extraordinary high value of the surface area for g-C_3N_4_U can be easily attributed to the production of a large amount of products (NH_3, H_2O, and CO_2) generated during the thermal condensation reaction that can act as soft templates producing more porous structures [44].

Figure 6 A and B shows the UV-Vis absorbance and bandgap spectra of g-C_3N_4_U and g-C_3N_4_M powders.

Figure 6: Absorbance spectra (A for g-C$_3$N$_4$_U and B for g-C$_3$N$_4$_M) and plot of (αhv)^2 versus photon energy (hv) (C for g-C$_3$N$_4$_U and D for g-C$_3$N$_4$_M).

The bandgap edges were estimated to be 436 nm and 454 nm for g-C$_3$N$_4$_U and g-C$_3$N$_4$_M, respectively. In contrast, the bandgap values, determined by plotting (αhv)^n versus hv (Figure 6 C and D), were 2.9 eV for g-C$_3$N$_4$_U and 2.7 eV for g-C$_3$N$_4$_M, according to the literature [26].

3.2 Photocatalityc activity

All the synthesized g-C$_3$N$_4$-based materials, both as powders and floating alginate beads, were tested for the photodegradation of different organic pollutants (DCF, ISO, and RhB) both in UW and in DW under solar light irradiation.

It is known that photocatalysis is a catalyst mass-dependent reaction [52]. However, if on the one hand, large amounts of photocatalyst lead to a high amount of active species in solutions (hydroxyl radicals and/or electrons by absorbing more photons), on the other hand, an excess could increase the turbidity of the solution reducing the absorption of the energy from light radiation, thereby decreasing the degradation efficiency. Therefore, starting from RhB as a model pollutant and UW as an ideal matrix, at first, the effect of photocatalyst mass, both as powder and FCNA beads, was adequately investigated, as shown in Figure 7.

Figure 7: Effect of phocatalyst amount on the RhB photodegradation by A) g-C$_3$N$_4$_U powder, B) g-C$_3$N$_4$_M powder, C) FCNA(U) beads, D) FCNA(M) beads.

The adsorption properties of photocatalysts play a key role in their photocatalytic activity. As shown in Figure 7 A and B, g-C$_3$N$_4$_U exhibits higher adsorption capacity than g-C$_3$N$_4$_M, according to the BET results. The high adsorption of RhB on the surface of g-C$_3$N$_4$ is due to the electrostatic interactions between the positive charges of the ethylamine groups of the dye and the more negatively charged surface of the semiconductor. In the case of g-C$_3$N$_4$ embedded in calcium alginate beads, the adsorption capability of the materials is strongly reduced owing to the prevailing positive charges of the calcium alginate shell at the working pH values [53].

All the materials synthesized by urea show higher photoactivity towards RhB degradation than those from melamine. More in detail, thanks to its structural characteristics, g-C$_3$N$_4$_U powder reaches a percentage of RhB photodegradation higher than 99% within the first hour of light irradiation even if the photocatalyst concentration is reduced from 0.5 g·L^{-1} to 0.4 g·L^{-1}. Although by further reducing the amount of catalyst in solution, the RhB photodegradation process becomes slower, however, the pollutant is almost completely degraded within 3 hours of irradiation (Figure 7 A and S2A). The organic shell of the alginate beads can hinder the interaction of the pollutant with the active surface of the photocatalyst, slowing down the photodegradation process that, in any case, permits the degradation of about 90% of RhB within 3 hours of solar light irradiation when an appropriate amount of catalyst is used (Figure 7 C and S2B). g-C$_3$N$_4$_M-based materials are generally less active than the corresponding ones synthesized by urea (Figure 7 B and D and S2C

and D). Their poorer performances can be again easily justified by the low surface area value (an order of magnitude smaller than that from urea) of the photocatalyst.

The results obtained here are far superior to those reported up to now in the literature for this type of material. Recently Hao *et al*. demonstrated that floating calcium alginates beads loaded with 25% of g-C$_3$N$_4$ were able to degrade methylene blue up to 80.94% within 42 h [54], whereas Zhang *et al*. removed 94% of reactive brilliant red X-3b using g-C$_3$N$_4$-TiO$_2$ P25 encapsulated in calcium alginate beads within 1 h of light irradiation [55]. In the present work, despite being the photocatalyst load in calcium alginate beads more than 40 times lower than in the materials proposed by Hao, a complete quote degradation of the dye was achieved after just of light irradiation without any TiO$_2$ addition.

Based on these promising results, both the FCNA beads were applied to the photodegradation of two other types of pollutants (DCF and ISO as a model molecule for drugs and herbicides, respectively). The photodegradation tests were c conducted in UW and DW (Figure 8).

Figure 8: Photodegradation of RhB (A), DCF (B) and ISO (C) by FCNA beads both in UW and DW.

The results reported in Figure 8 clearly show that the photodegradation capability of both the FCNA beads is strictly related both to the type of pollutant and to the environment.

First of all, in contrast with the scientific literature [25], it is possible to observe that when embedded in alginate beads, the two types of g-C$_3$N$_4$ are highly active in the photodegradation of DCF thanks to the favorable electrostatic interactions between the negatively charged drug molecules and the positively charged alginate surface, reaching over 90% of pollutant abatement

within 90 min both in UW and DW (Figure 8 B). Moreover, as reported below, the UPLC/MS analyses (carried out on the final solutions containing the pollutants as a mixture) did not show degradation products attributable to DCF that were probably absorbed by the alginate shell and/or deposited on the surface of the photocatalyst.

Concerning the other pollutants, the two floating materials exhibit slightly different behavior. Regarding the photodegradation ability of the two FCNA beads towards RhB degradation, the effect of the matrix type is evident here. Both the materials in DW show a higher degradation rate than that achieved in UW, probably related to the presence of chloride ions, as reported in the literature [56, 57]. On the contrary, an increase in the ionic strength value seems to have a negative effect on the ISO degradation, probably related to the non-ionic nature of the pollutant molecule. However, even in DW, the greater surface area of FCNA(U) leads to a higher RhB, and ISO abatement compared to FCNA(M).

Finally, the floating photocatalysts were tested for the photodegradation of a mixture of the three pollutants both in UW and DW, as displayed in Figure 9.

Figure 9: Photodegradation of a mixture of RhB, DCF and ISO by FCNA(U) (A) and FCNA(M) beads (B) both in UW and DW.

Surprisingly, when used for the photodegradation of a mixture of the three pollutants, the two types of floating materials show very similar behavior both in UW and DW. However, while DCF is completely degraded within 90 min in both the different environments, the photodegradation of RhB and particularly of ISO is inhibited. Since several factors, such as pH, pollutant concentration, etc., concur, an exhaustive explanation of these results is challenging to provide. Nevertheless, the absence of DCF transformation products (TPs), observed in UPLC/MS analyses, in contrast with literature results for g-C_3N_4 photocatalyst [25], might indicate that DCF TPs are adsorbed so strongly onto semiconductors surface that their active sites are blocked lowering the photoactivity of these materials towards RhB and ISO. To confirm this hypothesis, the photodegradation test was repeated by using FCNA(M) beads in a mixture containing only RhB and ISO in DW (Figure S3). Indeed, in the absence of DCF, the photocatalyst recovers the same degradative efficiency demonstrated in the tests performed on the degradation of the single pollutants (Figure 8 A and C).

3.3 Proposed photocatalytic process for RhB degradation

As reported in the literature [58, 59], the first step of heterogeneous photocatalysis consists of the organic molecules adsorption onto the catalyst surface, quickly followed by the reaction with the photoexcited charge carriers (e^- and h^+) or free radicals (e.g., ·OH). Depending on the

characteristics of the organic molecules adsorbed onto the photocatalyst surface and the characteristic of the photocatalysts, different kinetics of photodegradation can occur [60-63].

Although over the years, g-C_3N_4 and its composites have been thoroughly investigated, the adsorption step, that represents a critical point in heterogeneous photocatalysis, has been poorly studied. In this regard, Song *et al.* have recently compared the efficiency of g-C_3N_4 nanosheets and conventional g-C_3N_4 towards RhB degradation by a synergistic adsorption/photodegradation process, demonstrating the extraordinary activity of nanosheets due to their tremendous high surface area that guarantees higher percentage of adsorption and subsequent fast photodegradation [64].

Similarly, as shown in Figure 7 (A and B), the adsorption capability of g-C_3N_4_U powder towards RhB is almost ten times higher than that of g-C_3N_4_M powder (30% and 4% for g-C_3N_4_U powder and g-C_3N_4_M powder, respectively). The increased surface area of g-C_3N_4_U powder leads to high rates of adsorption. The adsorbed RhB molecules are rapidly degraded by more than 90% within 30 min under solar light irradiation, thanks to a large number of active sites available onto the photocatalyst surface able to produce active species, such as holes (h^+), superoxide radicals ($O_2^-\cdot$), and hydroxyl radicals ($\cdot OH$) during the photocatalytic processes (Figure 10).

Figure 10: a schematic of adsorption/photocatalytic degradation processes on g-C_3N_4 powder.

When g-C_3N_4_U powder is embedded in the alginate beads, the adsorption process on the surface of the semiconductor is strongly reduced (Figure 7 C), owing to the polysaccharide shell. However, also in this case, the extraordinary high surface area of the material is still able to produce active species in large amounts, guaranteeing a fast photodegradation process.

3.4 Recycling Tests

The possibility of reusing photocatalytic materials is fundamental for reducing waste production and process costs. Therefore, the stability of the two types of photocatalytic beads was investigated towards RhB degradation for 210 min for five runs times with the same photocatalyst without any regeneration test. At the end of each cycle, the floating beads were quickly recovered from the solution by using a small colander and reused for the next run after washing with deionized water.

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655 **Figure 11:** Recycle of FCNA beads (left from U) and right (from M) towards RhB
656 photodegradation.
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658 As shown in Figure 11, after five successive runs, no noticeable change was observed in the
659 degradation percentage of the RhB dye for both the floating photocatalysts.
660 Moreover, after the last cycle the g-C$_3$N$_4$_U photocatalyst was recovered by centrifugation, washed
661 by ultrapure water and characterized by FT-IR and XRD techniques.
662 A comparison of the XRD patterns and FT-IR spectra of the fresh and used photocatalyst (Figure
663 12) indicates the stability and retention of structure of the materials after five cycles.

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674 **Figure 12:** Comparison of the XRD patterns and FT-IR spectra of fresh and used g-C$_3$N$_4$_U
675 photocatalyst.

676 As reported by Habibi-Yangjeh *et al*. [65], for real applications the photocatalyst recovery could be
677 made easier by adding a magnetic component to the material. In this regards, several efforts have
678 been devoted to the fabrication of sorbent and/or photocatalytic powders [66-68]. However, the
679 engineering of non-powdery materials is still an open and unsolved question that is worth
680 addressing to make photocatalysts not materials niche but compounds of wide application.
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3.4 Identification of transformation products

The identification of TPs, resulting from the analysis of the solutions of pollutants mixture treated by both the floating materials, was carried out by UPLC/MS in positive mode polarity. As reported above, no TPs deriving from DCF degradation have been identified. Complete mineralization of this pollutant is unlikely based on other studies reported in the literature [25]. Therefore, a strong absorption on the surface of the alginate shell and/or of the photocatalyst is conceivable.

Figure 13 (up) proposes the photodegradation reaction pathway for RhB.

Figure 13: Identified TPs and photodegradation pathway for RhB (up) and ISO (down).

RhB photodegradation under solar light irradiation can occur by two simultaneous competitive processes: *N*-deethylation and destruction of dye chromophore structure [36]. The mass peaks at m/z 443, 415, 387, 359, and 331 are attributable to RhB and its *N*-deethylated intermediates, respectively. However, this does not exclude that the other process may also take place but simply that the analytical technique used does not allow the detection of the TPs deriving from the destruction of dye chromophore structure because of the low dimensions and high polarity of these metabolites.

Figure 13 (down) shows the identified TPs from ISO photodegradation and the proposed photodegradation reaction pathway. The molecular structure of ISO allows OH radicals to attack at different sites, leading to four monohydroxylated compounds having 223 m/z. The TP at 193 m/z can be readily interpreted as demethylation of the ISO molecule, whereas the TP at 136 m/z can be assigned to the presence of isopropylaniline [69].

Conclusions

In the present study, efficient, reusable floating-C_3N_4/alginate beads were successfully synthesized using two different precursors (urea and melamine) and applied for the photodegradation of different classes of organic pollutants (dyes, drugs, and herbicides). Thanks to its tremendous high surface area, alginate pearls synthesized by urea as g-C_3N_4 precursor showed higher activity than melamine, despite the low load of photocatalyst (0.6%). The effect of the ionic strength on the photoactivity of the floating photocatalysts was investigated, demonstrating that it affects the electrostatic interactions between the photocatalyst surface and the organic molecule in solution. When used for the degradation of mixtures of pollutants, the abundant hydroxyl groups on the surface of calcium alginate lead to a strong adsorption of TPs of diclofenac, reducing the photodegradation efficiency of the active sites towards rhodamine B and isoproturon. More importantly, floating-C_3N_4/alginate beads exhibited good cycle stability after 5-run recycling. The preparation of low cost, environmentally friendly, and reusable metal-free photocatalysts active in the photodegradation of a mixture of pollutants under solar light irradiation opens the way to the application as substitutes for traditional materials.

CRediT authorship contribution statement

Ermelinda Falletta: Conceptualization, Methodology, Validation, Formal analysis, Supervision, Writing - original draft, Writing - review & editing.

Mariangela Longhi: Investigation, Data curation.

Alessandro di Michele: Investigation, Data curation.

Daria C. Boffito: Investigation, Data curation.

Claudia L. Bianchi: Conceptualization, Supervision, Writing, Funding acquisition.

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