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Continuous Flow Photooxidative Degradation of Azo Dyes with Biomass-derived Carbon Dots

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Abstract: The presence of persistent organic pollutants in industrial wastewaters is becoming a problem of major concern. In the present study we explored the degradation of azo dyes, well-known common hazardous contaminants, by a green and efficient procedure using continuous flow photooxidative degradation. In particular, carbon dots synthesized from fishery waste (bass-CDs) were used as a cheap and readily available photocatalyst in combination with oxygen and UV light. Methyl orange, acid red 18, amaranth, sunset yellow and chromotrope were chosen as model substrates and their degradation was studied both in batch and in continuous flow conditions. All the azo dyes were fully degraded with both techniques highlighting the suitability of bass-CDs for the decontamination of wastewater. The main advantages are of using a “disposable” photocatalyst, in aqueous solvent and in continuous flow. In particular, continuous flow operation allowed faster decompositions: ca. 2 min versus 1-3 hours needed in batch.

Introduction

In recent years the release of toxic and persistent pollutants in the aquatic environment is becoming a topic of major concern. Synthetic dyes, in particular, form the largest group of chemicals that are produced worldwide and are among the most serious source of environmental contaminants. The global market relative to dyes and pigments is expected to rise to USD 37 billion by 2023 with an estimated annual growth rate of 5.46% (years 2018-2023).^[1] Concerning the type, volume and complexity, the textile sector occupies a major role in the dyes market.^[2] About 10,000 different dyes are used in the textile industry,^[3] with 60-70% constituted by azo dyes ^{[4],[5]} that can be toxic and nonbiodegradable. The release of these dyes into water bodies has been posing severe threats to humans and aquatic organisms due to their carcinogenic effects on liver, kidney and on the cardiovascular system.^{[3],[6]} Reactive azo dyes are characterized by one or more azo chromophores in the molecular structure.^[7] Their structure and synthetic origin make them resistant to fading on exposure to light, temperature and many chemicals. In fact, azo compounds are difficult to degrade even at low concentrations because of their resistance to light, heat,

chemicals and microbial action, making their removal by conventional wastewater treatment very difficult.^{[8],[9],[10],[11]}

In order to minimize the impact of these dyes on the environment, different approaches are currently used. These common processes include adsorption by activated carbon,^[12] precipitation,^[13] coagulation,^[14] membrane ultrafiltration ^[15] and reverse osmosis.^[16] However classical methods are inefficient because they merely transfer the dye from one phase to another producing secondary waste. Photocatalysis, on the other hand, is an advanced oxidation process (AOP), considered as an effective technique to purify wastewater by chemical degradation of the dyes.^{[17],[18]} Upon excitation, the formation of electron-hole pairs on semiconductors leads to the production of chemically active free radicals in the reaction media, in particular in water. These radicals, in particular hydroxyl ($\cdot\text{OH}$), superoxide ($\cdot\text{OO}^-$) and hydroperoxyl ($\cdot\text{OOH}$), are able to attack specific bonds of organic compounds and to decompose them, resulting in less harmful by products such as carbon dioxide, water and mineral acids.^[19] The photocatalytic activity of various semiconductor materials has been investigated over the years to degrade aqueous organic pollutants^{[20],[21],[22]} with a major attention towards titanium dioxide,^{[23],[24],[25],[26],[27],[28],[29],[30],[31],[32]} zinc oxide ^{[33],[34]} or other metal oxides.^{[35],[36],[37],[38],[39]}

As a new class of semiconductor nanomaterials, Carbon Dots (CDs) are gaining attention also in the field of wastewater treatment for the removal of dyes.^{[40],[41]} CDs are, in fact, luminescent, biodegradable and bio-based carbon material that are promising for photocatalytic applications^[42] but even with the immense progress in their synthesis, there are still few reports where bare CDs were directly used as active photocatalytic material for the degradation of dyes,^[43] and in particular azo dyes. For this application, in fact, CDs are used mainly as synthetic hybrid composites with other wide bandgap semiconductors.^{[44],[45],[46],[47]}

In one of our previous work we demonstrated the possibility to hydrothermally synthesize CDs with high ability in photoelectron transfer starting from fishery waste.^[48] These carbon nanomaterials are fully biobased and biodegradable and, in the present work, the idea to exploit their photocatalytic behaviour in order to degrade azo dyes was developed. These bass-derived

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CDs did not require purification because, as indicated by the silent ^1H - and ^{13}C -NMR spectra no soluble molecular species were present in the final product. A comparison of the photo-activity of dialyzed and non-purified bass-CDs, along with their full characterization, is also reported and indicates that both perform similarly. One of the main advantages is that such CDs photocatalysts are cheap, easily available and biocompatible, all features that make these materials disposable along with the treated effluent. In particular, the decomposition of five azo dyes, namely methyl orange (MO), acid red 18 (AR), amaranth (AM), sunset yellow (SY) and chromotrope (CH) (**Figure 1**), was studied in batch and with a continuous flow microfluidic reactor. Flow chemistry is, indeed, one of the top ten emerging technologies with high potential for sustainable processes.^{[49],[50],[51],[52]} The photodegradation of azo dyes in continuous flow conditions is still an underexplored topic even if inherent advantages of the microreactor system, such as the high surface-to-volume ratio, short diffusion distances, and rapid mass transfer, can improve the photocatalytic performance degrading organic contaminants.^{[53],[54],[55],[56]} Only few works reported this kind of approach by using more conventional photocatalysts such as titanium dioxide, zinc oxide, metal nanoparticles or hydrogen peroxide.^{[1],[57],[58],[59],[60],[61],[62],[63]}

We herein report an efficient and sustainable process for the degradation of azo dyes using a continuous flow microfluidic photoreactor, exploiting oxygen and fish waste-derived CDs as photocatalyst.

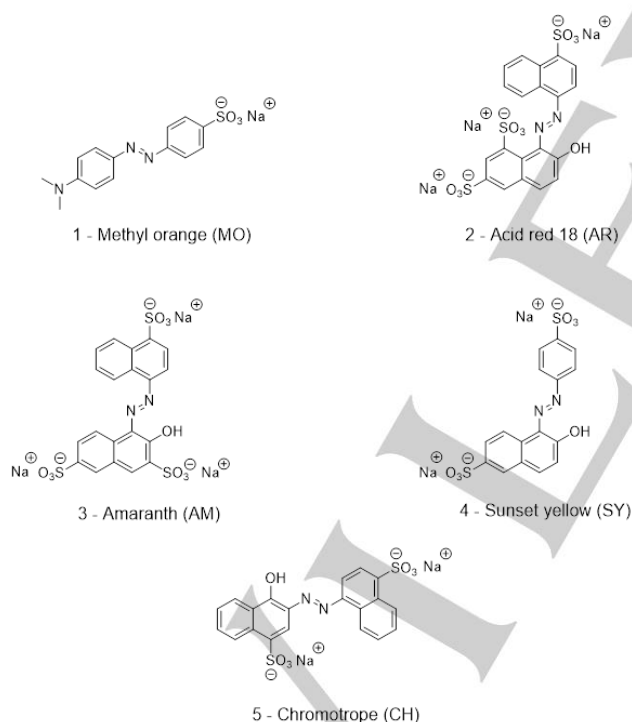


Figure 1. Azo dyes studied in the present work.

Results and Discussion

CDs derived from fish waste were selected as photocatalyst for the degradation of five azo dyes (MO, AR, AM, SY and CH).

These nanoparticles were obtained by hydrothermal synthesis using bass scales as carbon precursor resulting in nitrogen self-doped spherical dots with diameter around 10 nm. Bass-CDs exhibited two UV-Vis absorptions at 250 and 350 nm ascribable to the $\pi - \pi^*$ transition of aromatic carbons and $n - \pi^*$ transition of double bonds containing groups respectively. An excitation-dependent emission around 450 nm was observed, highlighting the role of defects in the emission mechanism.^[48]

The photooxidative degradation of dyes induced by CDs can be described as follows. When CDs absorb light at the proper wavelength, electrons in the valence band are excited to the conduction band creating holes in the valence band (equation 1). The electrons in the conduction band (e^-_{CB}) and the holes in the valence band (h^+_{VB}) can undergo recombination releasing heat (equation 2) or can react with water or oxygen dissolved in the aqueous medium. In particular, the holes in the valence band can react with water to produce hydroxyl radicals (equation 3) or can directly convert the organic dye to highly reactive intermediates leading to subsequent oxidation (equation 4). On the other hand, the electrons in the conduction band can react with oxygen to form superoxide radicals (equation 5) and, further, hydroperoxyl radicals (equation 6). All these radicals play a crucial role in degrading the organic dye, finally leading to mineralization (equations 7 and 8).^[19]

Equations 1-8. Possible degradation mechanism of azo dyes in presence of CDs and oxygen.

- (1) $\text{CDs} + h\nu \rightarrow \text{CDs} (e^-_{CB} + h^+_{VB})$
- (2) $e^-_{CB} + h^+_{VB} \rightarrow \text{heat}$
- (3) $h^+_{VB} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$
- (4) $h^+_{VB} + \text{organic pollutants} \rightarrow \text{degraded products}$
- (5) $e^-_{CB} + \text{O}_2 \rightarrow \cdot\text{OO}^-$
- (6) $\cdot\text{OO}^- + \text{H}^+ \rightarrow \cdot\text{OOH}$
- (7) $\cdot\text{OH} + \text{organic pollutant} \rightarrow \text{degraded products}$
- (8) $\cdot\text{OOH} + \text{organic pollutant} \rightarrow \text{degraded products}$

By looking at the mechanism the crucial role of oxygen in the degradation of organic pollutants is evident. A hypothetical mineralization pathway for methyl orange is reported in **Scheme S1**. The investigation started with batch experiments for the decomposition of the selected azo dyes to further continue with the implementation in continuous flow.

Batch experiments

The investigation started in batch, using UV light, bass-CDs as photocatalyst and by bubbling oxygen inside the reaction flask. The reactions were followed via UV-Vis spectroscopy and the spectra are reported in **Figures S13-22**.

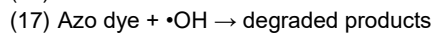
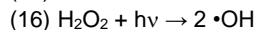
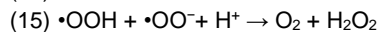
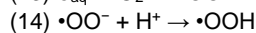
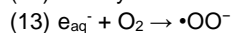
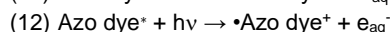
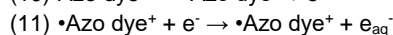
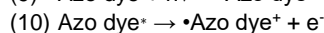
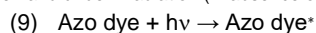
Using these conditions all the five selected azo dyes were completely degraded in 1 to 3 hours (entries 1, 4, 7, 10 and 13 **Table 1**) demonstrating the ability of CDs to produce the oxygenated radicals necessary to initiate the reaction pathway that leads to the decomposition.

To further confirm the importance of all the components, control tests without CDs or oxygen were performed. Using only the carbon nanoparticles it was possible to degrade consistent portions of the dyes (86% for MO, 73% for AR, 75% for AM, 67% for SY and 100% for CH) but in longer reaction times (24h, entries 2, 5, 8, 11 and 14 **Table 1**). This is probably due to the ability of CDs either to produce radicals directly from water (equation 3), to photoactivate the dissolved oxygen (equation 5), or to degrade directly the dye (equation 4). In any case, following these pathways, the degradation resulted to be slower confirming the need of external oxygen. On the other hand, using only oxygen it

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was possible to observe some degradation but again the degradation rate resulted to be slower than all the other cases (entries 3, 6, 9, 12 and 15 **Table 1**). In fact, degradation yields of 24% (for SY) up to a maximum of 62% (for CH) in 24 hours were reached using only oxygen in absence of bass-CDs. In these cases, probably the direct photolysis of the dyes under irradiation can result in partial mineralization. As reported from Wang et al.,^[64] indeed, the dye can be excited to produce singlet and triplet states dyes (equation 9) and it can be consequently involved in the generation of the hydrated electron (e_{aq}^-) rather than the injection of an electron in the conduction band of the semiconductor (equations 10, 11, 12). The reaction pathways described in equations 13, 14 and 15, can then take place to produce hydrogen peroxide that is easily decomposed to hydroxyl radicals by irradiation (equation 16). As already showed in equation 7, the hydroxyl radicals have a major role in the degradation of pollutants (equation 17). However, this degradation pathway resulted to be far way less efficient than the one with the addition of a semiconductor, CDs in our case.

Equations 9-17. Possible degradation mechanism of azo dyes in presence of oxygen and under irradiation (in absence of CDs).



Other control experiments in the absence of light were also performed for 24 hours: almost no degradation was observed for all the five dyes confirming the need of the combination of oxygen/CDs/irradiation (**Figure S2**).

The observed trend for MO is reported as an example in **Figure 2** (for the AR, AM, SY and CH, see **Figure S1**).

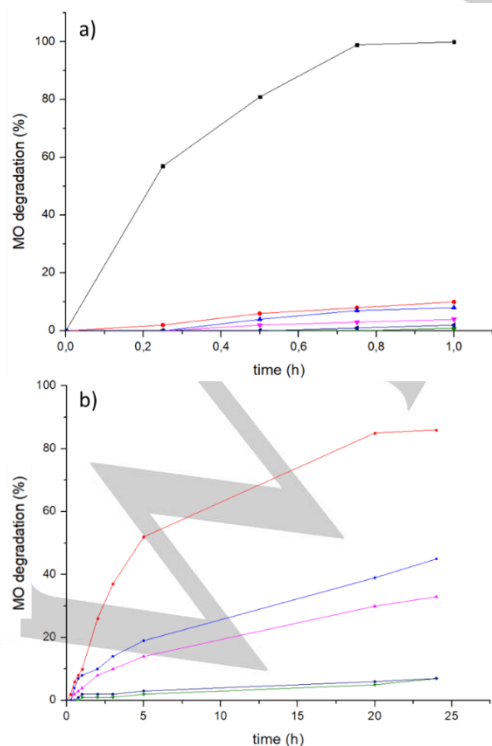


Figure 2. Observed trend for the photooxidative degradation of methyl orange in batch conditions. a) trends in 1 hour, b) trends in 24 hours. Black = using CDs and Oxygen, red = no oxygen, blue = no CDs, pink = no CDs no oxygen, green = no oxygen no light, dark blue = no CDs no light.

As can be seen in **Table 1** and in **Figure S1** the trend is similar for all the azo dyes except for CH. In that case, in fact, also the test performed using CDs without oxygen was effective and managed to reach 100% of degradation in 24 h. The chemical structure is similar for all the dyes but, reasonably, in CH the hydroxyl group in *para* to the sulfonic group allows an easier oxidation leading to a quinone intermediate.

Table 1. Best degradation percentage reached for MO, AR, AM, SY and CH in batch conditions.

Entry	Azo dye	Conditions	Degradation (%), (time)	k (M·min ⁻¹)
1		Oxygen + CDs	quant. (1 h)	1.4·10 ⁻⁴
2	MO	Only CDs	86 (24 h)	2.7·10 ⁻⁵
3		Only Oxygen	45 (24 h)	2.5·10 ⁻⁵
4		Oxygen + CDs	quant. (1 h)	1.4·10 ⁻⁴
5	AR	Only CDs	73 (24 h)	8.0·10 ⁻⁶
6		Only Oxygen	59 (24 h)	3.3·10 ⁻⁶
7		Oxygen + CDs	quant. (2.5 h)	6.1·10 ⁻⁵
8	AM	Only CDs	75 (24 h)	7.1·10 ⁻⁶
9		Only Oxygen	30 (24 h)	6.9·10 ⁻⁶
10		Oxygen + CDs	quant. (2 h)	1.5·10 ⁻⁴
11	SY	Only CDs	67 (24 h)	1.3·10 ⁻⁵
12		Only Oxygen	24 (24 h)	1.4·10 ⁻⁵
13		Oxygen + CDs	quant. (3 h)	5.5·10 ⁻⁵
14	CH	Only CDs	quant. (24 h)	3.4·10 ⁻⁵
15		Only Oxygen	62 (24 h)	6.7·10 ⁻⁶

To further confirm the complete mineralization of the dyes ¹H NMR experiment were conducted on the reaction mixtures. As can be seen in the spectra reported in **Figures S3-12**, all the peaks related to the azo dye molecules disappeared and silent NMR spectra were recorded. This evidence highlights the absence of organic molecules: the starting materials disappeared, and no other organic compounds were detected.

As already observed in the literature,^{[65],[66],[67]} all the degradation plots can be approximated to a straight line suggesting a zero-order reaction kinetic (see **Figures S23-37**). The rate constants (see **Table 1**) were obtained by the slope of the degradation plots and calculated using equation 18, where [dye] is the molar concentration of the dye, t is the time (min), r is the degradation rate and k the rate constant (M·min⁻¹).^[68]

Equation 18. Zero-order kinetic model.

$$-\frac{d[\text{dye}]}{dt} = r = k$$

Analysis of the rate constants confirmed the higher degradation rate in the tests performed using CDs and oxygen together: for all the five dyes tested, k was one or two orders of magnitude higher respect to the experiments with only the CDs or only oxygen. It must be noted that for SY the calculations were performed disregarding the first three experimental points indicative of an induction period. In addition, for SY the rate constants with only CDs or with only oxygen were comparable in the first 2 h, while

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the final degradation percentage (after 24 h of irradiation) resulted to be higher when using the CDs.

Continuous-Flow experiments

The encouraging results obtained investigating the degradation of azo dyes in batch mode prompted us to extend the protocol under continuous flow (CF) conditions to have faster and more efficient processes.

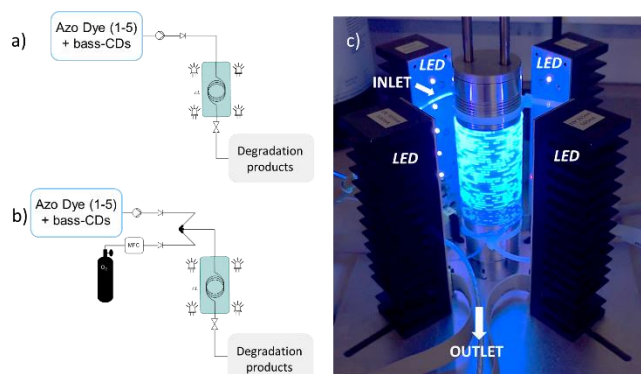


Figure 3. Simplified flowchart of a) continuous flow set up for the degradation of azo dyes without oxygen and b) continuous flow set up for the degradation of azo dyes with oxygen. c) photograph of the photoreactor.

First, the CF experiments were conducted without the addition of oxygen; the setup (**Figure 3a**) was composed of an HPLC pump to convey the feed (5 ppm azo dye and 2 mg/mL of bass-CDs in D.I. water) to a PFA reactor (internal volume 2.6 mL, **Figure 3c**). The reactor was homogeneously irradiated using four LEDs pillars at a wavelength of 365 nm and the pressure of the system was controlled downstream using a backpressure regulator at 7 bar. To determine the best conditions in term of flow rate (Φ), and consequently of residence/irradiation time (R_t), MO was chosen as a model substrate and some preliminary tests were conducted (see **Table 2**). As expected, decreasing the flow from 1.5 to 0.5 mL/min (and therefore increasing the R_t) the degradation percentage increased. To avoid excessively long residence times, a flow equal to 0.5 mL/min was selected. With these conditions, the degradation percentage reached a satisfactory 49% of degradation in 5.2 min, while in batch conditions without oxygen almost 5 hours were necessary to reach the same result (see **Figure 2b**).

Table 2. Flow conditions tests performed on MO and relative MO degradation percentages. Feed: [MO] = 5ppm, [bass-CDs] = 2 mg/mL; $\lambda=365$ nm.

Entry	Φ (mL/min)	R_t (min)	MO degradation (%)
1	1.5	1.7	34
2	1.0	2.6	39
3	0.5	5.2	49

The same conditions were then applied to the other four azo dyes. For AR, 37% degradation was reached in 5.2 min (entry 3, **Table 3**) compared to 7h in batch; for AM 23% (entry 5, **Table 3**) compared to 2 hours in batch. For SY, 5.2 min allowed to reach 59% degradation percentage compared to 17 hours in batch (entry 7, **Table 3**); while for CH, 66% was obtained (entry 9, **Table 3**), same as in the batch experiment in 5 hours.

Control experiments without CDs were also performed demonstrating the need to use a photocatalyst for the

decomposition of these type of pollutants. As can be seen in **Table 3** (entries 2, 4, 6, 8 and 10) without the addition of bass-CDs the degradation hardly proceeded reaching a maximum value of only 4% in the case of CH.

Table 3. Dye degradation percentages for continuous flow experiments performed without oxygen. Feed: [dye] = 5ppm, [bass-CDs] = 2 mg/mL; $\lambda = 365$ nm; $\Phi = 0.5$ mL/min; $R_t = 5.2$ min.

Entry	Azo dye	CDs	Dye degradation (%)
1		Yes	49
2	MO	No	0
3		Yes	37
4	AR	No	0
5		Yes	23
6	AM	No	0
7		Yes	59
8	SY	No	1
9		Yes	66
10	CH	No	4

The continuous-flow investigation continued then with the addition of oxygen. A new continuous flow setup was then assembled using an oxygen supply and a mass flow controller to regulate the oxygen flow rate (**Figure 3b**). The feed and the oxygen were conveyed through an arrowhead mixer and successively to the same reactor used for the experiments without oxygen (**Figure 3c**). The residence times calculations were done following equations S1, S2 and S3.

As in the previous case, MO was chosen as a model dye to define the best conditions. As can be seen in **Table 4**, the flow rate of the feed was kept constant (0.5 mL/min) while the oxygen flow was changed to obtain the best degradation percentage. With MO, using an oxygen flow of 5.5 mL_N/min, and a residence time of ca. 2 min, complete degradation was observed. The complete decomposition of this azo dye was obtained in batch conditions bubbling oxygen for 1 hour, demonstrating the major effectiveness of continuous flow for this type of wastewater treatment.

Table 4. Oxygen flow conditions tests performed on MO and relative MO degradation percentages. Feed: [MO] = 5ppm, [bass-CDs] = 2 mg/mL; $\lambda=365$ nm; Φ feed = 0.5 mL/min.

Entry	Φ oxygen on MFC (mL _N /min)	Φ oxygen real (mL/min)	Φ_{TOT} (mL/min)	R_t (min)	MO degradation (%)
1	5.5	0.78	1.28	2.03	quant.
2	7.5	1.07	1.57	1.65	51
3	10.0	1.43	1.93	1.35	46

For these tests the feed was always composed by an aqueous solution containing 5 ppm of the dye and 2 mg/mL of bass-CDs. Considering the high efficiency of the continuous flow degradation using oxygen, the amount of CDs in the feed was decreased to see if it was possible to obtain the same result with lower amounts of photocatalyst. However, using 1 mg/mL of CDs, lower degradation percentages were observed: with a total residence time of 2.03 min ($\Phi_{feed} = 0.5$ min, $\Phi_{oxygen\ on\ MFC} = 5.5$ mL_N/min) only 29% of MO was decomposed, and increasing the residence time to 2.71 min ($\Phi_{feed} = 0.5$ min, $\Phi_{oxygen\ on\ MFC} = 3.5$ mL_N/min) only 31% (see **Figure S14**).

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The optimal conditions for the decomposition tests of the other four azo dyes were set as follows: 2 mg/mL of bass-CDs, $\Phi_{\text{feed}} = 0.5$ mL/min, $\Phi_{\text{oxygen on MFC}} = 5.5$ mL_N/min and $R_t = 2.03$ min. AR, AM, SY and CH were fully degraded under these conditions (Table 5, entries 3, 5, 7 and 9) highlighting the high efficiency of this process. In control experiments performed without the bass-CDs, none or very low degradation percentages were observed reaching a maximum of 9% with CH (entry 10, Table 5).

Table 5. Dye degradation percentages for continuous flow experiments performed with oxygen. Feed: [dye] = 5ppm, [bass-CDs] = 2 mg/mL; $\lambda = 365$ nm; $\Phi_{\text{feed}} = 0.5$ mL/min, $\Phi_{\text{oxygen}} = 5.5$ mL_N/min, $\Phi_{\text{oxygen real}} = 0.78$ mL/min, $\Phi_{\text{tot}} = 1.28$ mL/min, $R_t = 2.03$ min.

Entry	Azo dye	CDs	Dye degradation (%)
1	MO	Yes	quant.
2		No	0
3	AR	Yes	quant.
4		No	5
5	AM	Yes	quant.
6		No	0
7	SY	Yes	quant.
8		No	1
9	CH	Yes	quant.
10		No	9

From these experiments the importance of both oxygen and carbon dots for the degradation process of azo dyes was highlighted. It was demonstrated that bass-CDs acted like an efficient photocatalyst for the formation of oxygenated radicals responsible for the decomposition of water pollutants, and that the addition of oxygen increased the degradation rate both in batch and in continuous flow. Using the batch setup bubbling oxygen with a frit it was possible to completely degrade the pollutant in times varying from 1 to 3 hours depending on the azo dye. In continuous flow, on the other hand, in only 2 minutes of residence time all the five selected azo dyes reached 100% degradation (Table 6).

Table 6. Comparison of the time necessary to have complete degradation of the five azo dyes in batch or in continuous flow.

Entry	Azo dye	Conditions	Time to have 100% degradation
1	MO	Batch ^[a]	1 h
2		Continuous flow ^[b]	2 min
3	AR	Batch ^[a]	1 h
4		Continuous flow ^[b]	2 min
5	AM	Batch ^[a]	2.5 h
6		Continuous flow ^[b]	2 min
7	SY	Batch ^[a]	2 h
8		Continuous flow ^[b]	2 min
9	CH	Batch ^[a]	3 h
10		Continuous flow ^[b]	2 min

[a] Feed: [dye] = 5ppm, [bass-CDs] = 2 mg/mL; $\lambda = 365$ nm; oxygen bubbled with a frit. [b] Feed: [dye] = 5ppm, [bass-CDs] = 2 mg/mL; $\lambda = 365$ nm; $\Phi_{\text{feed}} = 0.5$ mL/min, $\Phi_{\text{oxygen}} = 5.5$ mL_N/min, $\Phi_{\text{oxygen real}} = 0.78$ mL/min, $\Phi_{\text{tot}} = 1.28$ mL/min, $R_t = 2.03$ min.

Conclusions

In the present work, a method for the complete degradation of azo-dye pollutants in a fast and eco-sustainable way is reported. A continuous flow photoreactor was used with carbon dots as photocatalysts to perform the photooxidations of the azo contaminants. The employed CDs were synthesized easily and in large amounts from fish waste, thereby fitting in the idea of Circular Economy. These nanoparticles are readily available, biodegradable and biocompatible, as opposed to the majority of common semiconductor photocatalyst, leading to a green, sustainable and non-harmful photocatalytic process. Thanks to the advantages of flow chemistry, such as high surface-to-volume ratio, short diffusion distances, and rapid mass transfer, it was possible to fully degrade five different azo dyes (methyl orange, acid red 18, amaranth, sunset yellow and chromotrope) in only 2 minutes. Using the combination of bass-CDs, oxygen and UV irradiation ($\lambda = 365$ nm), it was possible to totally decompose the dyes also in batch conditions, but longer reaction times were needed (from 1 to 3 hours depending on the azo dye). The tested flow methodology should be easy to apply to the purification of industrial wastewaters in a continuous, cheap and affordable way. The bass-derived CDs did not require dialysis because they were free from other soluble molecular species, making the photoactivity of the dialyzed bass-CDs identical to the non-dialyzed CDs. We wish to stress that one of the advantages of our system is that it uses CDs without the need for purification. A second advantage is that the simple synthesis, wide availability, full biodegradability and biocompatibility of these CDs eliminates the need to recover them after the reaction and allows to use them as “disposable” catalysts that can be discarded together with the dye decomposition products without creating new harmful contaminants.

In conclusion, the photocatalytic application of fish waste derived CDs, in combination with the benefits of flow chemistry, for the degradation of pollutant and resistant azo dyes is reported.

Experimental Section

General. All the reagents were purchased from Merck Life Science S.r.l. (Milano, Italy). Oxygen was industrial grade (99.99%, ALPHAGAZ 1, Air Liquide). UV-Vis absorbance spectra were recorded with an AvaSpec-ULS2048XL EV spectrometer using a deuterium-halogen light source. The absorbances were measured at the characteristic absorption wavelength for every azo dye: 464 nm for MO, 506 nm for AR, 520 nm for AM, 482 nm for SY and 516 nm for CH. The degradation percentage was calculated using equation 19, where C_0 is the initial concentration of the dye and C_i is the dye concentration at the selected time. The concentrations were calculated by calibration curve at UV-Vis.

$$\text{degradation\%} = \frac{C_0 - C_i}{C_0} \times 100$$

Equation 19. Calculation for the azo dyes degradation percentage.

¹H NMR spectra were collected at 25°C on a Bruker Ascend 400 operating at 400 MHz using D₂O as solvent; The chemical shifts (δ) have been reported in parts per million (ppm) relative to the residual non-deuterated solvent as an internal reference and are given in δ values downfield from TMS.

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Synthesis of Fish-derived Carbon Dots (bass-CDs). Bass-CDs were synthesized and characterized according to our previously reported work.^[46] Briefly 2 g of dried and grounded sea bass (*Dicentrarchus labrax*) scales were put in a Teflon-lined autoclave with 20 mL of MilliQ water. The system was heated at 200 °C for 24 h. The obtained brownish suspension was filtered, and the water was removed by rotary evaporation to obtain a brown solid with 30–50% yield.

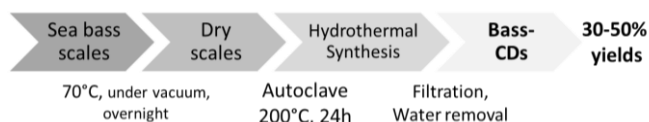


Figure 4. Simplified flowchart of the synthetic procedure for the preparation of carbon dots from bass scales.

Feed Preparation. The feed solutions were composed of azo-dyes 1-5 (Figure 1) 5 ppm and 2 mg/mL of bass-CDs in D.I. water.

Batch Experiments. The solution of the selected dye (5 ppm) and bass-CDs was irradiated with four LEDs pillars each containing 6 high power LEDs ($\lambda = 365$ nm, 1100 mW) while oxygen was bubbled inside using a frit. For the experiments without oxygen the solution was continuously stirred. Samplings were performed at different time intervals and analysed via UV-Vis spectroscopy. Control experiments in absence of light and of photocatalyst were also performed.

CONTINUOUS-FLOW EXPERIMENTS

Continuous-Flow Setup for experiments without oxygen. The continuous-flow setup for the experiments without oxygen involved an HPLC pump (Knauer Azura P41S equipped with a 10 mL stainless steel head) conveying the feed to the reactor that consisted in a perfluoroalkoxyalkane (PFA) tubing (1/16", internal volume = 2.6 mL) coiled on a stainless-steel cylinder and irradiated with four LEDs pillars each containing 6 high power LEDs ($\lambda = 365$ nm, 1100 mW). The pressure of the system was controlled with a Zaiput dome-type back pressure regulator (BPR) inserted downstream (set point: 7 bar). Further details on the continuous flow setup are reported in the Supporting Information and in Figure 3a.

Typical Run. The HPLC pump used to deliver the aqueous solution of the selected azo dye (5 ppm) and CDs (2 mg/mL) was set to 0.5 mL/min. The feed was conveyed to the photoreactor through PFA tubing (1/16"). Irradiation occurred along the entire reaction channel (2.6 mL internal volume, 5.2 min residence time) under 7 bar of pressure. Control experiments in absence of light and of photocatalyst were also performed.

Continuous Flow setup for experiments with oxygen. The continuous-flow setup for the experiments with oxygen involved an HPLC pump (Knauer Azura P41S equipped with a 10 mL stainless steel head) connected to an arrowhead mixer with PFA tubing (1/16"). The oxygen flow rate was controlled through a Bronkhorst mass flow controller (MFC) and conveyed to the arrow head mixer using a 1/16" PFA tubing too. The reactor consisted in a PFA tubing (1/16", internal volume = 2.6 mL) coiled on a metal cylinder and irradiated with four LEDs pillars each containing 6 high power LEDs ($\lambda = 365$ nm, 1100 mW). The pressure of the system was controlled with a Zaiput dome-type back pressure regulator (BPR) inserted downstream (set point: 7 bar). Further details on the continuous flow setup are reported in the Supporting Information and in Figure 3b.

Typical run. The HPLC pump used to deliver the aqueous solution of the selected azo dye (5 ppm) and CDs (2 mg/mL) was set to 0.5 mL/min and the oxygen flow was set to 5.5 mL/min with MFC. Both fluids were conveyed to the photoreactor through PFA tubing (1/16"). Irradiation occurred along the entire reaction channel (2.6 mL internal volume, 5.2 min residence time) under 7 bar of counterpressure. Control experiments in absence of light and of photocatalyst were also performed.

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Keywords: Azo compounds • Carbon Dots • Continuous flow • Photooxidation • Waste prevention

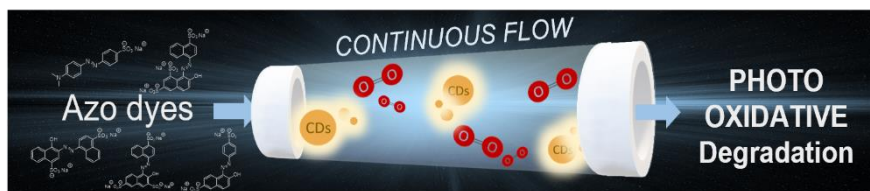
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Entry for the Table of Contents



We herein report a fast and efficient protocol for the complete mineralization of pollutants, in particular azo dyes. Exploiting the advantages of continuous flow technique with biobased carbon dots, oxygen and UV irradiation it was possible to degrade completely the dyes in 2 min, paving the way toward more sustainable wastewater treatment.