



On-line carbon dots synthesis using flow injection analysis. Application to aluminium determination in water samples

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ABSTRACT

An on-line synthesis of CDots is proposed for the first time, using the flow injection analysis (FIA) technique, which was coupled, in a single system, to the analytical determination of aluminium in water samples. The nanoparticles were obtained from the carbonization of glucose and iron(III) in an acidic medium, and their photoluminescence increased in the presence of aluminium ions. Under optimal experimental conditions, the proposed method has shown an acceptable linearity range –between 0.04 and 3.0 mg L⁻¹ (R² = 0.999₉)– and a detection limit of 0.007 mg L⁻¹. The analysis of drinking water and groundwater samples showed good accuracy (recoveries ranged between 91 – 113%) and RSD% < 13. The on-line system exhibited a high sample throughput (36 h⁻¹), since no incubation time was required.

1. Introduction

Aluminium (Al) is an abundant element and the main component of the soil on the Earth's crust [1,2]. Al is found in virtually all natural waters, as salts, insoluble compounds, or colloid species [3]. The distribution of Al in the environment is affected by natural processes [4]. The Al present in the upper soil layers can be remobilized by environmental phenomena, such as acid rain, and can subsequently reach groundwater resources [5]. Nonetheless, the main source of Al in drinking water comes from water treatment plants, where aluminium citrate or sulphate is added as a flocculant [2]. Noticeably, human exposure to Al has been linked to the incidence of some neurodegenerative diseases, like multiple sclerosis and Alzheimer's disease, and even to certain cases of autism, in which an unusual accumulation of Al has been detected in the brain tissue of sick people [6]. Although there is no clear association between the consumption of Al and the risk of developing these diseases [2], Joint FAO/WHO Expert Committee on Food Additives (JECFA) has suggested values that apply to all Al compounds in food, including additives and drinking water [7]. Precisely, a health-based value of 0.9 mg L⁻¹ Al derives from the JECFA's recommendation [2]. Still, several countries established 0.2 mg L⁻¹ as the maximum level of residual Al in drinking water [2,8], in order to minimize the deposition of aluminium flocs in the distribution system

and the exacerbation of discoloration of water by iron [9].

The determination of Al in water samples using different analytical techniques, such as inductively microwave plasma and inductively coupled plasma (both with atomic emission spectrometry detection [10], coupled to mass spectroscopy [11]) has been reported. However, these techniques have relatively high operation costs. Conversely, fluorimetric approaches have received considerable attention due to their simplicity, low cost, and versatility [12]. However, Al determination using fluorescent probes, such as 8-hydroxyquinoline-5-sulfonic acid, chromotropic acid and morin, may have some disadvantages, e. g. lack of selectivity, low photostability, toxicity and poor water solubility [3,13]. These drawbacks can be addressed by using carbon dots (CDots), which are a new type of nanomaterials widely employed as fluorescent sensors for the determination of metals ions, inorganic anions, and biocompounds [12,14,15]. In particular, the use of CDots for the selective determination of Al in different sample matrices has been reported [13,16–18].

CDots are synthesized by applying an energy source (e.g. thermal, microwave, ultrasound, etc.) to a given amount of starting material [15, 19]. This kind of synthesis, also called bottom-up, is distinguished by its versatility in generating CDots with tunable photoluminescence, lower cost, simplicity and more sustainable processes [19,20]. However, these procedures require additional purification steps, such as centrifugation

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and wash cycles, and long-time dialysis [19]. Furthermore, CDots synthesis is normally performed ‘in batch’, and has some unresolved challenges related to long manufacturing time and low reproducibility [21]. To overcome these issues, some studies have proposed the synthesis of CDots using continuous systems, like microreactors [22,23], microfluidic arrays [24,25], and a high pressure hydrothermal reactor [21, 26]. These strategies offer a high degree of control over the synthesis variables (mass transfer, energy, etc.), and allow the synthesis of CDots with the desired characteristics, while guaranteeing the reproducibility of the process. However, none of these approaches take advantage of these strengths for the design of on-line analytical methods that couple the synthesis and determination steps in a single analytical system.

The current study proposes, for the first time, the continuous synthesis of CDots and the subsequent on-line determination of Al, using a single flow injection (FIA) system. FIA systems are recognized for extending on-line processing capabilities by simply coupling different functional units [27–29]. Thus, FIA systems make not only reproducible syntheses possible, but also its coupling to the detection step in a single system. This enables the addition of the typical advantages of on-line systems (high sampling throughput, good precision, low reagent consumption and reduced waste production, among others). The proposed CDots synthesis is based on the carbonization of a mixture of an iron(III) solution in phosphoric acid and glucose under mild heating. The enhancement of the fluorescent response of the CDots towards aluminium was used to develop a fast and simple methodology to determine this metal in drinking water samples with satisfactory results.

2. Experimental section

2.1. Reagents and solutions

Ultrapure water (Millipore, Bedford, USA) was used as a solvent for the stock solutions, as well as the carrier and dilution lines in the on-line system. Glucose monohydrate and phosphoric acid (85% w/w) were supplied by Cicarelli (Santa Fe, Argentina). Iron(III) sulphate non-hydrate was purchased from Sigma-Aldrich (Germany). The glucose solution (1.50 mol L^{-1}) was prepared daily. The iron(III) acid solution (0.20 mol L^{-1}) was prepared by dissolving the appropriate amount of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ in concentrated phosphoric acid with the aid of an ultrasonic bath. Analytical-grade reagents were used throughout this work.

2.2. Apparatus

An ultrasonic bath with an output power of 160 W (TESTLAB model TB 04 TA) was used to assist the standard preparation. TEM images for the morphologic study were obtained by transmission electron microscopy (TEM, JEOL JSM 100 CXII, Tokyo, Japan), operating at 100 kV. Infrared spectra were recorded in a Nicolet 6700, Thermo Scientific Fourier Transform IR spectrometer. The zeta potential was measured in a Malvern Zetasizer Nano Series instrument (Malvern, UK). UV-Vis spectra were acquired with an Agilent 8453 spectrophotometer. A Shimadzu RF-6000 luminescence spectrophotometer with a xenon lamp was used to carry out the fluorescence measurements. The equipment had a flow cell with an inner volume of $150 \mu\text{L}$ and a light path of 1.0 cm. The on-line system consisted of a Gilson Minipuls-3 peristaltic pump (8 channels), a Rheodyne 5041 injection valve and Tygon® tubing. All reaction coils and connections were made of PTFE tubing. A heating plate (Cole-Parmer Model 4803-02, USA) was used for the synthesis of CDots.

2.3. Procedure for the synthesis of CDots and aluminium determination

Fig. 1 depicts the FIA system designed to carry out the synthesis of the CDots and the subsequent determination of aluminium. The glucose ($q_1 = 0.075 \text{ mL min}^{-1}$) and the iron(III) acid solution ($q_2 = 0.220 \text{ mL min}^{-1}$) channels converged in the reactor R_1 (0.5 mm i.d. and 6 m length), and the mixture was heated in a water bath ($98 \pm 2^\circ\text{C}$) with the aid of a heating plate. The generated nanoparticles exited reactor R_1 , and merged with a stream of water ($q_3 = 1.75 \text{ mL min}^{-1}$) in the mixing coil R_2 (i.d. = 0.5 mm, $L = 600 \text{ mm}$). The resulting flow was divided into two streams by a three-way junction. A low-flow stream ($q_4 = 0.10 \text{ mL min}^{-1}$) continued into the aluminium determination system, while the other stream was directed towards a reservoir (Res) for further use. The q_4 stream converged in a R_3 mixing coil (0.5 mm i.d. and 300 mm length) with a dilution line ($q_5 = 1.75 \text{ mL min}^{-1}$), and the resulting mixture merged with the carrier ($q_6 = 1.75 \text{ mL min}^{-1}$) in the R_4 mixing coil (0.8 mm i.d. and 1000 mm length). A $200 \mu\text{L}$ volume loop was used to inject the sample into the carrier. The fluorescence was recorded every 0.5 s at 410 and 490 nm of excitation and emission wavelengths, respectively. The analytical signal for optimization and quantification purposes was the height of the FIA peak.

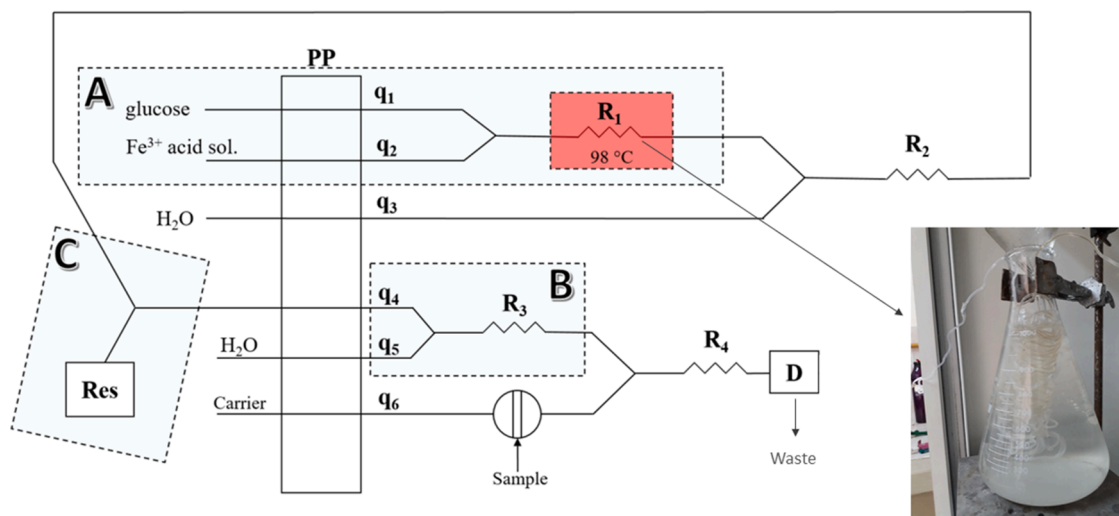


Fig. 1. Flow-injection system for the synthesis of CDots and the subsequent determination of aluminium. Peristaltic pump (PP); hot water bath (red square); channels (q_1 to q_6); reactor (R_1); mixing coils (R_2 to R_4); reservoir (Res) and spectrofluorometer (D), waste (W).

2.4. Characterization studies

For characterization studies, the synthesized CDots were submitted to dialysis using Spectra/Por® Dialysis membrane (Spectra/Por®, Biotech CE Tubing, cut off: 100–500 Da) against an acidic medium (0.1 M H₃PO₄), which was replaced every 12 h for 5 days. Characterization of the purified CDots was carried out using several analytical techniques. A drop of the CDots solution was deposited on a copper grid to obtain the TEM images. For IR measurements, the CDots were lyophilized and then grinded with KBr to obtain pellets (0.1% w/w CDots). Also, the UV-Vis spectrum of the nanoparticles was recorded. The excitation-emission fluorescence spectra and the zeta potential were recorded for a purified CDots solution in the absence and presence of 5.0 mg L⁻¹ Al.

2.5. Calibration standards and sample preparation

The stock standard solution of 1000 mg L⁻¹ Al (FUJIFILM Wako Pure Chemical Corporation, Japan Calibration Service System) was stored at room temperature. The calibration standards were prepared daily and obtained by appropriate dilution of the stock standard solution in 2 % m/v H₃PO₄.

Tap water, mineral water and underground water were collected from several locations of the Buenos Aires province, Argentina, and stored at 4°C. The samples were spiked with the aluminium stock standard solution, acidified with H₃PO₄ in such a way that the final concentration was 2% m/v, and filtered through membrane filters (0.45 µm). No further treatment was needed. All the analyzed samples and standards were measured in quadruplicate.

2.6. Selectivity study

The selectivity of the proposed method was studied by evaluating the effect of different anions and cations on the FIA signal of the CDots. For this purpose, solutions of the following ions were injected into the FIA system: sodium, potassium, calcium, sulphate, carbonate, nitrite and phosphate (up to 100 mg L⁻¹), fluoride, iron (III), zinc, copper (II) and zirconium (up to 5.0 mg L⁻¹), chromium (VI), lead (II), arsenic (V) (up to 1.0 mg L⁻¹), mercury (I and II), cadmium and aluminium (up to 0.50 mg L⁻¹).

3. Results and discussion

3.1. Characterization of CDots

The morphology and size of the as-prepared CDots were investigated by TEM. Fig. S1 shows a relatively uniform size distribution of spherical nanoparticles. The size ranged between 0.8 and 4.3 nm, with an average of 2.1 nm (Fig. S1A, inset).

The IR spectrum (Fig. S2) shows the typical wide band related to O-H stretching vibrations between 3100 and 3600 cm⁻¹ [30]. In addition, a shoulder appearing around 2916 cm⁻¹ could be assigned to the stretching vibration of C-H [31]. The peak around 1644 cm⁻¹ corresponds to the carbonyl group [31]. Bands in the region between 1000 and 1200 cm⁻¹ could be assigned to the symmetric and antisymmetric stretching of the C-O groups [32]. In addition, there is a peak at 600 cm⁻¹ that could be attributed to the Fe-O bonding [33,34].

The UV-Vis spectrum of the nanoparticles shows an absorption band at 282 nm and a shoulder at 235 nm (Fig. S3). Those molecular absorption bands are typically assigned to π - π^* transitions of aromatic C=C and n- π^* transitions of C=O, respectively [35]. Particularly, the absorption at 282 nm can be ascribed to a π - π^* transition of the furfural moiety originated by the carbonization of carbohydrates in acidic media [36].

The excitation-emission spectra of the CDots (Fig. 2A) exhibited one single emission maximum located at $\lambda_{exc}/\lambda_{em}$ of 355/518 nm. As mentioned before, the fluorescence of the synthesized nanoparticles based on glucose and iron(III) in phosphoric acid was sensibly enhanced in the presence of aluminium. The contour plots of the CDots emission in the presence of aluminium (Fig. 2B) exhibited an overall increase in fluorescence intensity together with a new dominating emissive state at $\lambda_{exc}/\lambda_{em}$ of 410/490 nm.

The interaction between the nanoparticles and the aluminium ions was studied with two additional experiments. First, zeta potential measurements were performed to investigate the surface charge density of the system. The values obtained for a solution of CDots, in the absence and presence of Al (5.0 mg L⁻¹), were -0.79 and +0.72 mV, respectively. The negative value of the CDots surface charge could be attributed to the presence of oxygenated groups. The change of sign of the surface charge in the presence of aluminium can be explained by the coordination of these cations on the surface of the CDots. The same behaviour has been observed for CDots functionalized with quercetin [37]. On the other hand, the effect of Al on the morphology of CDots was also investigated by TEM images. The micrographs obtained show the formation of non-uniform aggregates with sizes ranging from 36 to 164 nm, and an average value of 100 nm (Fig. S1B). This aggregation phenomenon could be responsible for the fluorescence enhancement of CDots in the presence of aluminium [31,38,39].

3.2. Continuous synthesis of carbon dots and on-line detection system

The aim of the present study was to design a single analytical system for the continuous synthesis of CDots and the subsequent determination of aluminium. Therefore, it was crucial to evaluate the possibility of using the nanoparticles as they were synthesized, i.e. without the need for a previous purification step. For this purpose, a comparison between the features of the as-prepared nanoparticles and those subjected to a

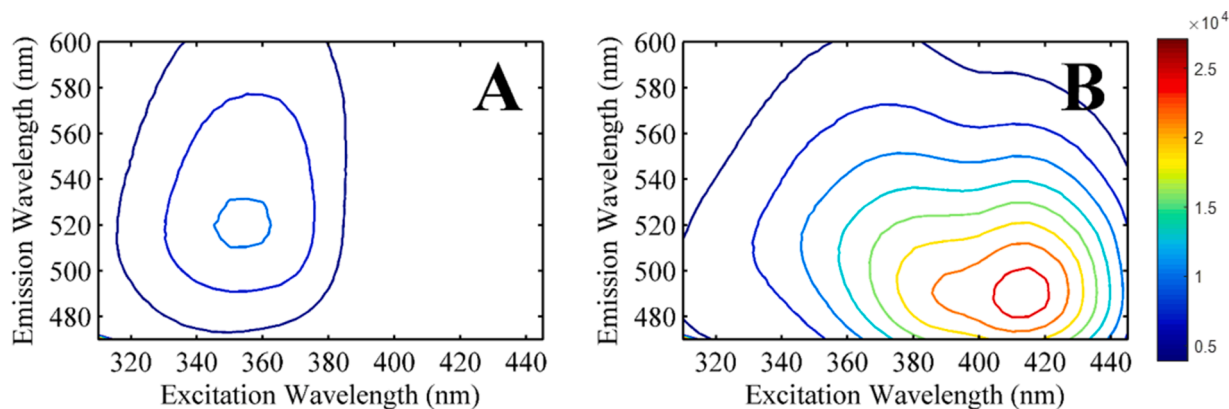


Fig. 2. Fluorescence contour plots of CDots in absence (A) and presence (B) of 5.0 mg L⁻¹ Al.

dialysis process was carried out. The fluorescence spectra of the carbon dots were recorded for both purified and non-purified CDots in the presence of aluminium. A comparison between the spectra (Fig. 3) shows that the response to aluminium is similar for nanoparticles with and without purification. Other authors have compared the typical optical properties of emission maxima between crude and dialysis-purified CDots and reported that no differences were observed [26]. Thus, it seems reasonable to use the CDots avoiding the purification step and, therefore, to couple the synthesis with the determination in a single system.

On the basis of the information obtained from the ‘in batch’ experiments (Section “Preliminary studies” in the Supplementary material), the optimization of the on-line system was performed taking into account the fluorescence signal recorded for CDots/aluminium system as the response variable. The part of the on-line system designed for the synthesis of CDots was previously described in the procedure and depicted in Fig. 1 part A. The first parameter optimized was the relationship between the concentrations of glucose and iron(III) acid solutions in accordance with the preliminary studies (Fig. S4). Taking into account this information, the flow rate relationship for glucose and iron (III) acid solution was optimized. This parameter varied in such a way that the total flow rate remained constant to ensure the same residence time in reactor R₁ throughout the experiments. The best response was obtained for the glucose/iron(III) acid solution flow rate ratio of 1:3 (Fig. S5).

Another parameter studied was the reaction time, which may be understood in terms of time of residence of the reacting mixture in the reactor R₁. In a continuous flow system, the reaction time could be controlled by both the reactor's length and the flow rate together. The flow rate was maintained at the lowest value (0.075 mL min⁻¹ for glucose and 0.220 mL min⁻¹ for phosphoric acid) to minimize the consumption of reagents and the generation of waste. Thus, the residence time varied between 9.0 and 18.0 min, which corresponds to reactor R₁ lengths of 4.0 to 8.0 metres (Fig. S6). The optimum value was obtained with the reactor of 6.0 m, which was equivalent to a residence time of 13.5 min. Shorter reactors yielded smaller analytical signals, due to a scarce or null formation of nanoparticles. When longer reactors were used, the fluorescence also decreased. A possible explanation for this fact is related to a higher formation of CDots, which was observed through a more intense colour in the resulting solution. Apparently, a high concentration of nanoparticles could absorb the radiation from the light source [40], and/or reabsorb/scatter the emitted fluorescence [41]. The CDots stream emerging from the R₁ reactor merged with a water channel (q₃) in order to reduce the temperature and dilute the reacting mixture with the aim of stopping the carbonization reaction.

The effect of the dilution on the response of the CDots/aluminium system was also studied. It was observed that the higher the dilution, the better the fluorescent signal. However, high dilutions would require a large number of successive diluting lines (involving or not extra peristaltic pumps), due to limitations in the internal diameter of the

commercially available tubing. Thus, to avoid an increase in the complexity of the system, the CDots stream was split into two channels: a small one (q₄), which was subject to subsequent dilutions within the system (Fig. 1 part B), and a second stream that was collected in a reservoir (Res, Fig. 1 part C). In order to take advantage of the accumulated CDots production, the synthesis system (channels q₁ to q₃) could eventually be disabled, and the aluminium determination could be continued using the CDots stored in Res.

The effect of different dilutions of the CDots channel (q₄) was evaluated, and the maximum fluorescence was achieved for high dilutions. (Fig. S7). Further dilutions were not possible due to the aforementioned limitations of the Tygon® tubes. Thus, this strategy made it possible to achieve dilution values of up to 18.5-fold.

Finally, the sample loop and the reactors R₂ to R₄ were also optimized. The values chosen correspond to the ones that provided the highest fluorescence signals. Table 1 summarizes the studied range and the optimum values of the complete FIA system.

With all the variables optimized, the reproducibility of the CDots on-line synthesis was checked. As it can be seen in Fig. S8, the fluorescence recorded throughout the time using the optimized continuous system gave a stable and almost constant baseline, which indicates that a reproducible synthesis of CDots is achieved.

3.3. Selectivity study

At this point, it is important to clarify why iron was used in the synthesis of carbon dots. Some authors have observed that carbon dots obtained from mineral acids and carbohydrates suffer a marked quenching effect of the luminescent emission due to the presence of iron ions [42,43]. The same behaviour was confirmed in our preliminary studies, when the CDots were synthesized using only glucose and phosphoric acid. In these studies, iron was found to produce a decrease in the fluorescent signal in the same band where aluminium increased the measured fluorescence.

Since iron is an abundant element in natural water samples, strategies were sought to avoid this interference. Hence, as previously reported in the literature, iron was included as a precursor in the synthesis [31,44]. The nanoparticles obtained using 0.20 mol L⁻¹ Fe³⁺ presented

Table 1
Summary of the optimized FIA variables.

Variable	Studied range	Optimum value
Flow rate ratio (glucose: H ₃ PO ₄)	1:1 – 1:9	1:3
R ₁ reactor length (m)	4.0 – 8.0	6.0
Dilution ratio (q ₄ channel)	1.0 – 18.5	18.5
R ₂ reactor length (mm)	300 – 1000	600
R ₃ reactor length (mm)	100– 600	300
R ₄ reactor length (mm)	200 – 1500	1000
Sample volume (μL)	50 – 600	200
Carrier flow rate (mL min ⁻¹)	0.30 – 0.55	0.45

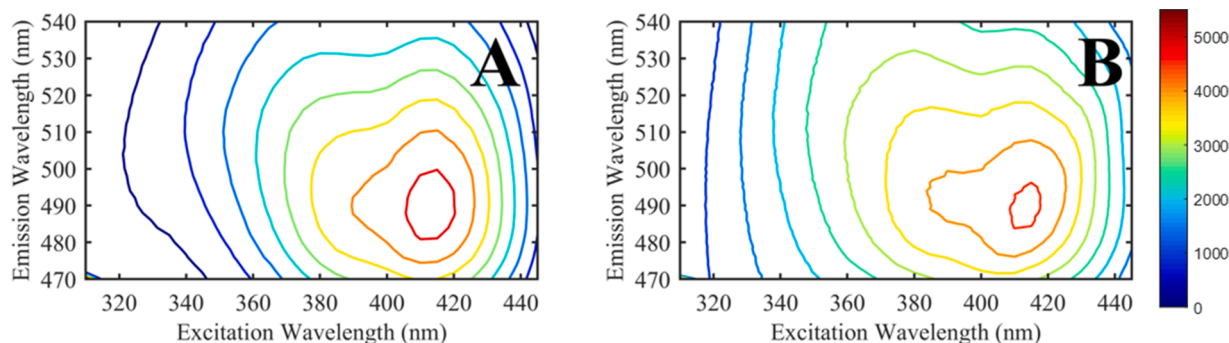


Fig. 3. Fluorescence contour plot of the purified CDots (A) and as-prepared in the on-line system (B) in the presence of 5.0 mg L⁻¹ Al.

the same fluorescence enhancement in the presence of aluminium, but showed no significant signal change when iron was added.

The selectivity was evaluated by testing the fluorescence response of the CDots towards different ions. As it can be seen in Fig. S9, most compounds cause neither enhancement nor quenching of the CDots fluorescence, except for aluminium, which gives rise to a substantial signal increase.

On the other hand, the possible interfering effect was assessed by measuring the fluorescence emission of the CDots-Al system in the presence of different ions commonly occurring in natural waters (Table 2). Among the tested ions, fluoride caused a pronounced quenching on the fluorescence of the CDots-Al system, probably due to the complex formation of fluoride with aluminium [45].

The effect of fluoride could be significantly lowered with the addition of H_3PO_4 in such a way that the final concentration was 2% m/v. In this sense, Baumann demonstrated that the addition of phosphoric acid effectively decomposes the complex formed between fluoride and aluminium [46]. Table 2 presents the concentration values at which the ions generated a change of 5 % in the signal. According to this, the proposed method has an appropriate selectivity to be applied for the determination of aluminium in water samples.

3.4. Analytical figures of merit

The calibration line was linear between 0.04 and 3.0 $mg L^{-1}$, and the regression equation can be expressed as $y = (53.5 \pm 0.265)x + (33.3 \pm 0.406)$, with a determination coefficient of 0.9996. No trends on residuals were observed, and the ANOVA test applied to the regression indicated that there was no lack of fit ($\alpha = 0.05$). The detection and quantification limits for aluminium ions were 0.007 and 0.023 $mg L^{-1}$, respectively, which were calculated considering a signal/noise ratio (S/N) = 3 [47]. The percentage relative standard deviation was 0.24 % (at a concentration level of 0.50 $mg L^{-1}$, $n = 5$), and the sample throughput was 36 h^{-1} .

3.5. Determination of aluminium in water samples

The practical application of the proposed method was evaluated in water samples. As an example, Fig. S10 shows the time trace of the analytical signal obtained in the determination of some of the samples (raw and spiked samples), to better appreciate the peak shape, precision and sample throughput. Standard recovery experiments were performed for aluminium detection in tap water, mineral water and spring water. The samples were spiked with a stock standard solution of Al at two different concentration levels (0.11 and 0.22 $mg L^{-1}$). Then, the fortified samples were filtered to remove suspended material, acidified with phosphoric acid, and injected into the system. Table 3 shows the results of the analysis of the samples. The recovery values ranged between 95 and 113 %, and the precision was satisfactory (% RSD < 13). Some of the samples contained Al levels slightly above the values recommended by the WHO. However, as stated in the introduction, these limits are based

Table 2

Tolerance study of different ions at the concentration normally found in the studied samples on the CDots-Al system (1.0 $mg L^{-1}$ Al).

Ion	Concentration ($mg L^{-1}$)
Cl^-	> 100
F^-	> 2*
SO_4^{2-}	> 100
NO_3^-	> 50
PO_4^{3-}	> 70
CO_3^{2-}	> 100
K^+	> 10
Na^+	> 100

* Obtained after addition of 2% H_3PO_4

Table 3

Recovery values and precision for the determination of aluminium in water samples.

Samples	Al^{3+} added ($mg L^{-1}$)	Al^{3+} found ($mg L^{-1}$)	Recovery (%)	RSD (%)
Bahía Blanca, Tap water	0.00	0.29	—	—
	0.11	0.41	109	13
	0.22	0.50	95	3.9
Mineral water	0.00	0.20	—	—
	0.11	0.32	109	2.2
	0.22	0.44	109	1.6
Tap water, Ingeniero White	0.00	0.16	—	—
	0.11	0.27	100	8.0
	0.22	0.41	113	10
Tap water, Jacinto Arauz	0.00	0.27	—	—
	0.11	0.39	109	0.8
	0.22	0.48	95	3.9
Spring water, Ingeniero White	0.00	0.17	—	—
	0.11	0.28	100	2.7
	0.22	0.39	98	3.0

mainly on organoleptic requirements, and do not pose a threat to the health of the population.

With respect to conventional methods [48], the proposed method achieves similar detection limits compared to the alternative UV-Vis method based on eriochrome cyanine R (standard method 3500-Al B), which reported detection levels around 6 $\mu g L^{-1}$. In addition, the spectroscopic method requires large amounts of reagents and a longer analysis time than the FIA method, since it requires about 5-10 min before measurements [49]. On the other hand, methods based on atomic absorption spectroscopy (standard method 3111D) reported instrumental detection levels about one order of magnitude higher than the FIA method (0.10 $mg L^{-1}$). In addition, for low aluminium concentrations, an extraction with methyl isobutyl ketone and 8-hydroxyquinoline (standard method 3111E) is necessary. Electrothermal atomic absorption spectroscopy (standard method 3113B) also reported detection levels in the same range as the FIA method (about 3 $\mu g L^{-1}$), but the method normally operates with argon to minimize furnace oxidation and prevent the formation of metal oxides, which increases operating costs. In addition, inductively coupled plasma-based methods have lower detection limits (40 $\mu g L^{-1}$ for standard method 3120 A and 0.03 $\mu g L^{-1}$ for standard method 3125). However, the large costs linked to these methodologies are daunting. In addition, when using mass spectrometry as a detection technique, high purity reagents and a clean environment are required for sample preparation, and it is important to have a clean room to minimize potential contamination artifacts.

3.6. Comparison with other continuous methods of CDots synthesis

A comparison was made with other procedures, described to date in the literature, for the continuous synthesis of CDots (Table 4).

Regarding the application of the CDots obtained in continuous, most of them present analytical determinations of different metals or their application as pH sensors. However, some of the continuous analytical systems were also designed to study the optimum conditions for different CDot syntheses. It should be noted that none of the continuous synthesis methods have coupled the on-line determination step in a single system.

The first difference between the proposed system and the systems found in the literature is related to the use of a lower temperature in the synthesis, due to the use of a high concentration of phosphoric acid, which allows obtaining structural changes in shorter times [52]. This feature of the synthesis method allows the output stream not to be segmented as in other continuous systems [25,51], or to require supplementary cooling processes [21], which makes it possible for the output stream to be compatible with an on-line determination system based on flow injection analysis (FIA). Another disadvantage of high

Table 4
Comparison of several reported methods for the continuous synthesis of CDots.

Starting solutions	Reaction temperature (°C)	Flow rate [Reaction time]	Features	Application	Ref.
Citric acid + ammonia + supercritical water (450°C)	450	10 – 20 mLmin ⁻¹ [NS]	<ul style="list-style-type: none"> - Three feed (including a supercritical water feed). - high pressure -Heater. - Back-pressure regulator. - Cooler. - Filtration unit (1kDa membrane). - ½ concentration 	Scalable preparation of CDots. Off-line fluorimetric detection of Cr(VI).	[21]
Citric acid solution (CA) with Ethylenediamine (EDA) slowly dropped into CA solution (stirring)	160	16 mLmin ⁻¹ [4.56 min]	<ul style="list-style-type: none"> - Microreactor (temperature controller) - Flowmeter. PTFE (2 mm i.d.) and stainless-steel tubes. - Pressure valves. - No purification 	Off-line fluorimetric detection of Fe(III).	[22]
Solution of glucose in formamide (previously prepared)	180	[NS] [2 min]	<ul style="list-style-type: none"> - Two SPs - Oil bath - PTFE capillary (1 mm i.d.) - atmospheric pressure - No purification 	Screening of CDots reaction conditions	[23]
Ascorbic acid in DMSO (previously prepared)	190	0.010 mLmin ⁻¹ [NS]	<ul style="list-style-type: none"> - One SP - Heating platform - PID temperature microcontroller - PTFE tubes (between SP and microfluidic reactor, 0.9 mm i.d.) 	Off-line 2 mL of CDots solutions + HCl or NaOH pH fluorescence and colorimetric (imaging) sensing.	[24]
Citric acid + urea	250	[NS] [20 min]	<ul style="list-style-type: none"> - 2 advection pumps. - Microreactor 	Off-line fluorimetric detection of Fe(III)	[25]
			Oil bath and condensation section (water bath)		
Citric acid + different N-sources (polyethyleneimine (PEI) or EDA)	190	0.010 mLmin ⁻¹ [NS]	<ul style="list-style-type: none"> - segmented output flow - Three SPs - PID temperature microcontroller - Back pressure 	Off-line fluorimetric detection of 0.5 mL of Carbon dots solution + Cu(II) or Hg(II) (when using PEI and EDA as N-sources).	[50]
			Regulator (17 bar)		
			<ul style="list-style-type: none"> - PTFE tubes (between SP and microfluidic reactor, 0.8 mm i.d.) - Dialysis (1kDa) 		
CA with EDA slowly dropped into CA solution (stirring)	190	[NS] [> 8 min]	<ul style="list-style-type: none"> - Flowmeter -Foamy copper microreactor -Stainless tube -Check valve -Digital temperature controller - Dialysis bag (1 kDa) - intermittent outflow 	Off-line fluorimetric detection of Hg(II)	[51]
Glucose and iron acid solution	98	0.30 mL min ⁻¹ [13.5 min]	<ul style="list-style-type: none"> - One PP. - Water bath - PTFE & Tygon tubing 	On-line fluorimetric detection of Al(III)	This work

NS: Not stated. SP: Syringe pump. PP: Peristaltic pump. PTFE: Polytetrafluoroethylene PEI: Polyethyleneimine. EDA: Ethylenediamine. DMSO: Dimethylsulfoxide.

temperatures in the synthesis has to do with the high pressures generated in the system. In several of the reported continuous syntheses, it is necessary to use control valves for possible backflows that may arise due to the high pressures generated in the microreactors [21,22,50].

Two very interesting options were presented by Gomez de Pedro et al. [24] and Berenguel-Alonso et al. [50], who propose microfluidic systems for the continuous synthesis of CDots. The disadvantage of these systems, however, has to do with the markedly low flow rates, which require long synthesis times (about 50 min) to achieve volumes as small as 500 µL.

Another advantage of the developed method, shared with other reported methods, is that the reaction mixture is carried out completely within the system, unlike others in which the pre-mixing must be performed before being introduced into the system [21–24,51]. Finally, the most important characteristics of the proposed system are related to its completely on-line development, from synthesis to analytical determination, using a single continuous flow system, simple, with few components, at relatively low temperatures, and without the need for pressure controllers. The continuous synthesis of carbon dots has a

number of advantages compared to batch synthesis. The synthesis is fast, cleaner and with less waste production, which has a lower impact on the environment, as other authors have also pointed out [21]. Moreover, the possibility to fully couple the synthesis with on-line determination is an additional advantage.

4. Conclusions

The current study reports a novel strategy for the continuous synthesis of CDots coupled, for the first time, with a quantitative determination in the same flow injection analysis system. The CDots prepared from glucose in an acidic medium showed excitation-independent emission and selective fluorescent enhancement toward aluminium ions. The simplicity of the system and the short synthesis times, together with the particular fluorescent properties of the CDots, allowed the development of a new analytical method for Al ions determination in water samples. Notably, purification of the CDots was not necessary for the proper determination of aluminium.

The proposed method was selective to aluminium ions, and showed

satisfactory figures of merit, with a wide linear range, low detection limits and good precision. The determination of aluminium in drinking and underground waters showed good recoveries and satisfactory precision, demonstrating the applicability of the proposed methodology.

Declaration of Competing Interest

There are no conflicts to declare.

Data availability

Data will be made available on request.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.talo.2023.100192](https://doi.org/10.1016/j.talo.2023.100192).

References

- X. Mei, D. Wang, L. Zhang, J. Li, C. Dong, Synthesis of carbon dots for Al³⁺ sensing in water by fluorescence assay, *Luminescence* 36 (2021) 1469–1475, <https://doi.org/10.1002/bio.4088>.
- World Health Organization, Guidelines for Drinking-water Quality: Fourth edition incorporating the first addendum, Forth, 2017. <http://apps.who.int/iris>.
- A. Alonso-Mateos, M.J. Almendral-Parra, Y. Curto-Serrano, F.J. Rodríguez-Martín, Online monitoring of aluminium in drinking water with fluorimetric detection, *J. Fluoresc.* 18 (2008) 183–192, <https://doi.org/10.1007/s10895-007-0262-5>.
- J. Nie, Exposure to Aluminium in Daily Life and Alzheimer's Disease, *Adv. Exp. Med. Biol.* 1091 (2018) 99–111, https://doi.org/10.1007/978-981-13-1370-7_6.
- R. Nawaz, M. Arshad, H. Garivait, A.A. Adnan, Mobilization and Leaching of Trace Elements (Fe, Al and Mn) in Agricultural Soils as Affected by Simulated Acid Rain Mobilization and Leaching of Trace Elements (Fe, Al and Mn) in, (2013). [10.14233/ajchem.2013.15560](https://doi.org/10.14233/ajchem.2013.15560).
- C. Exley, E. Clarkson, Aluminium in human brain tissue from donors without neurodegenerative disease: A comparison with Alzheimer's disease, multiple sclerosis and autism, *Sci. Rep.* 10 (2020) 1–7, <https://doi.org/10.1038/s41598-020-64734-6>.
- Joint, F. A. O., World Health Organization, & WHO Expert Committee on Food Additives, Evaluation of certain food additives and contaminants: seventy-fourth [74th] report of the Joint FAO/WHO Expert Committee on Food Additives, World Health Organization, 2011.
- Norwegian Scientific Committee for Food Safety, Risk assessment of the exposure to aluminium through food and the use of cosmetic products in the Norwegian population, 2013. <http://www.english.vkm.no/>.
- J.L.J. Hallal, A.M.S. Lucho, R.S. Gonçalves, Electrochemical polymerization of furfural on a platinum electrode in aqueous solutions of potassium biphthalate, *Mater. Res.* 8 (2004) 23–29, <https://doi.org/10.1590/S1516-14392005000100006>.
- T.O. Samarina, D.S. Volkov, I.V. Mikheev, M.A. Proskurnin, High-sensitivity and high-performance determination of trace aluminium in water for pharmaceutical purposes by microwave plasma and inductively coupled plasma–atomic emission spectrometry, *Anal. Lett.* 51 (2018) 659–672, <https://doi.org/10.1080/00032719.2017.1348510>.
- B.S. Wang, C.P. Lee, T.Y. Ho, Trace metal determination in natural waters by automated solid phase extraction system and ICP-MS: The influence of low level Mg and Ca, *Talanta* 128 (2014) 337–344, <https://doi.org/10.1016/j.talanta.2014.04.077>.
- D. Kong, F. Yan, D. Shi, Q. Ye, Z. Han, L. Chen, L. Wang, Carbon dots: Synthetic methods and applications as fluorescent probes for the detection of metal ions, inorganic anions and organic molecules, *J. Iran. Chem. Soc.* 12 (2015) 1841–1857, <https://doi.org/10.1007/s13738-015-0659-z>.
- B. Wang, X. Liu, W. Duan, S. Dai, H. Lu, Visual and ratiometric fluorescent determination of Al³⁺ by a red-emission carbon dot-queretin system, *Microchem. J.* 156 (2020), 104807, <https://doi.org/10.1016/j.microc.2020.104807>.
- M.L. Liu, B. Bin Chen, C.M. Li, C.Z. Huang, Carbon dots: Synthesis, formation mechanism, fluorescence origin and sensing applications, *Green Chem* 21 (2019) 449–471, <https://doi.org/10.1039/c8gc02736f>.
- C. Ji, Y. Zhou, R.M. Leblanc, Z. Peng, Recent Developments of Carbon Dots in Biosensing: A Review, *ACS Sensors* 5 (2020) 2724–2741, <https://doi.org/10.1021/acssensors.0c01556>.
- S. Sooksin, V. Promarak, S. Ittisanronnachai, W. Ngeontae, A highly selective fluorescent enhancement sensor for Al³⁺ based nitrogen-doped carbon dots catalyzed by Fe³⁺, *Sensors Actuators B Chem.* 262 (2018) 720–732, <https://doi.org/10.1016/j.snb.2018.01.239>.
- B.-Y. Fang, C. Li, Y.-Y. Song, F. Tan, Y.-C. Cao, Y.-D. Zhao, Nitrogen-doped graphene quantum dot for direct fluorescence detection of Al³⁺ in aqueous media and living cells, *Biosens. Bioelectron.* 100 (2018) 41–48, <https://doi.org/10.1016/j.bios.2017.08.057>.
- J.R. Bhamore, S. Jha, R.K. Singhal, T.J. Park, S.K. Kailasa, Facile green synthesis of carbon dots from *Pyrus pyrifolia* fruit for assaying of Al³⁺ ion via chelation enhanced fluorescence mechanism, *J. Mol. Liq.* 264 (2018) 9–16, <https://doi.org/10.1016/j.molliq.2018.05.041>.
- D. Xu, Q. Lin, H.T. Chang, Recent advances and sensing applications of carbon dots, *Small Methods* 4 (2020) 1–17, <https://doi.org/10.1002/smt.201900387>.
- T. Feng, S. Tao, D. Yue, Q. Zeng, W. Chen, B. Yang, Recent advances in energy conversion applications of carbon dots: From optoelectronic devices to electrocatalysis, *Small* 16 (2020), 2001295, <https://doi.org/10.1002/sml.202001295>.
- I.A. Baragau, N.P. Power, D.J. Morgan, T. Heil, R.A. Lobo, C.S. Roberts, M. M. Titirici, S. Dunn, S. Kellici, Continuous hydrothermal flow synthesis of blue-luminescent, excitation-independent nitrogen-doped carbon quantum dots as nanosensors, *J. Mater. Chem. A* 8 (2020) 3270–3279, <https://doi.org/10.1039/c9ta11781d>.
- L. Rao, Y. Tang, Z. Li, X. Ding, G. Liang, H. Lu, C. Yan, K. Tang, B. Yu, Efficient synthesis of highly fluorescent carbon dots by microreactor method and their application in Fe³⁺ ion detection, *Mater. Sci. Eng. C* 81 (2017) 213–223, <https://doi.org/10.1016/j.msec.2017.07.046>.
- Y. Lu, L. Zhang, H. Lin, The use of a microreactor for rapid screening of the reaction conditions and investigation of the photoluminescence mechanism of carbon dots, *Chem. - A Eur. J.* 20 (2014) 4246–4250, <https://doi.org/10.1002/chem.201304358>.
- S.G. Pedro, A. Salinas-Castillo, M. Ariza-Avidad, A. Lapresta-Fernández, C. Sánchez-González, C.S. Martínez-Cisneros, M. Puyol, L.F. Capitan-Vallvey, J. Alonso-Chamarro, Microsystem-assisted synthesis of carbon dots with fluorescent and colorimetric properties for pH detection, *Nanoscale* 6 (2014) 6018–6024, <https://doi.org/10.1039/C4NR00573B>.
- M. Shao, Q. Yu, N. Jing, Y. Cheng, D. Wang, Y.D. Wang, J.H. Xu, Continuous synthesis of carbon dots with full spectrum fluorescence and the mechanism of their multiple color emission, *Lab Chip* 19 (2019) 3974–3978, <https://doi.org/10.1039/c9lc00683d>.
- Y. Cheng, Z. Chen, Y. Wang, J. Xu, Continuous synthesis of N,S co-coped carbon dots for selective detection of Cd(II) ions, *J. Photochem. Photobiol. A Chem.* 429 (2022), 113910, <https://doi.org/10.1016/j.jphotochem.2022.113910>.
- J. Qiao, Dynamic flow approaches for automated radiochemical analysis in environmental, nuclear and medical applications, *Molecules* 25 (2020) 1462, <https://doi.org/10.3390/molecules25061462>.
- M. Trojanowicz, M. Pyszynska, Flow-Injection Methods in Water Analysis—Recent Developments, *Molecules* 27 (2022) 1410, <https://doi.org/10.1002/sml.201402648>.
- S.O. Souza, D.V.L. Ávila, V. Cerdá, R.G.O. Araujo, Selenium inorganic speciation in beers using MSFIA-HG-AFS system after multivariate optimization, *Food Chemistry* 367 (2022), 130673, <https://doi.org/10.1016/j.foodchem.2021.130673>.
- Z. Huang, F. Lin, M. Hu, C. Li, T. Xu, C. Chen, X. Guo, Carbon dots with tunable emission, controllable size and their application for sensing hypochlorous acid, *J. Lumin.* 151 (2014) 100–105, <https://doi.org/10.1016/j.jlumin.2014.02.013>.
- S. Sooksin, V. Promarak, S. Ittisanronnachai, W. Ngeontae, A highly selective fluorescent enhancement sensor for Al³⁺ based nitrogen-doped carbon dots catalyzed by Fe³⁺, *Sensors Actuators B Chem* 262 (2018) 720–732, <https://doi.org/10.1016/j.snb.2018.01.239>.
- Z. Yang, M. Xu, Y. Liu, F. He, F. Gao, Y. Su, H. Wei, Y. Zhang, Nitrogen-doped, carbon-rich, highly photoluminescent carbon dots from ammonium citrate, *Nanoscale* 6 (2014) 1890–1895, <https://doi.org/10.1039/C3NR05380F>.
- X. Su, C. Chan, J. Shi, M.K. Tsang, Y. Pan, C. Cheng, O. Gerile, M. Yang, A graphene quantum dot@Fe₃O₄@SiO₂ based nanoprobe for drug delivery sensing and dual-modal fluorescence and MRI imaging in cancer cells, *Biosens. Bioelectron.* 92 (2017) 489–495, <https://doi.org/10.1016/j.bios.2016.10.076>.
- T. Luo, Y. Nie, J. Lu, Q. Bi, Z. Cai, X. Song, H. Ai, R. Jin, Iron doped carbon dots based nanohybrids as a tetramodal imaging agent for gene delivery promotion and photothermal-chemodynamic cancer synergistic theranostics, *Mater. Des.* 208 (2021), 109878, <https://doi.org/10.1016/j.matdes.2021.109878>.
- X.T. Zheng, A. Ananthanarayanan, K.Q. Luo, P. Chen, Glowing graphene quantum dots and carbon dots: Properties, syntheses, and biological applications, *Small* 11 (2015) 1620–1636, <https://doi.org/10.1002/sml.201402648>.
- V. Gude, A. Das, T. Chatterjee, P.K. Mandal, Molecular origin of photoluminescence of carbon dots: aggregation-induced orange-red emission, *Phys. Chem. Chem. Phys.* 18 (2016) 28274–28280, <https://doi.org/10.1039/C6CP05321A>.
- Y. Zou, F. Yan, L. Dai, Y. Luo, Y. Fu, N. Yang, J. Wun, L. Chen, High photoluminescent carbon nanodots and quercetin-Al³⁺ construct a ratiometric

fluorescent sensing system, Carbon N. Y. 77 (2014) 1148–1156, <https://doi.org/10.1016/j.carbon.2014.06.056>.

- [38] B. Bin Chen, R.S. Li, M.L. Liu, H.Z. Zhang, C.Z. Huang, Self-exothermic reaction prompted synthesis of single-layered graphene quantum dots at room temperature, Chem. Commun. 53 (2017) 4958–4961, <https://doi.org/10.1039/c7cc00546f>.
- [39] B. Bin Chen, R. Sheng Li, M. Li Liu, H. Yan Zou, H. Liu, C.Z. Huang, Highly selective detection of phosphate ion based on a single-layered graphene quantum dots- Al^{3+} strategy, Talanta 178 (2018) 172–177, <https://doi.org/10.1016/j.talanta.2017.09.007>.
- [40] J.R. Lakowicz, Principles of fluorescence spectroscopy, Third, Springer, 2010, <https://doi.org/10.1006/abio.2000.4850>.
- [41] C. Wang, Z. Xu, C. Zhang, Polyethyleneimine-functionalized fluorescent carbon dots: water stability, pH sensing, and cellular imaging, ChemNanoMat 1 (2015) 122–127, <https://doi.org/10.1002/cnma.201500009>.
- [42] A.Q. Hassan, R.K. Barzani, K.M. Omer, B.R. Al-Hashimi, S. Mohammadi, A. Salimi, Dual-emitter polymer carbon dots with spectral selection towards nanomolar detection of iron and aluminum ions, Arab. J. Chem. 14 (2021), 103452, <https://doi.org/10.1016/j.arabj.2021.103452>.
- [43] Z. Xu, C. Wang, K. Jiang, H. Lin, Y. Huang, C. Zhang, Microwave-assisted rapid synthesis of amphibious yellow fluorescent carbon dots as a colorimetric nanosensor for Cr(VI), Part. Part. Syst. Charact. 32 (2015) 1058–1062, <https://doi.org/10.1002/ppsc.201500172>.
- [44] R. Hu, L. Li, W.J. Jin, Controlling speciation of nitrogen in nitrogen-doped carbon dots by ferric ion catalysis for enhancing fluorescence, Carbon N. Y. 111 (2017) 133–141, <https://doi.org/10.1016/j.carbon.2016.09.038>.
- [45] G. Crisponi, V.M. Nurchi, G. Faa, M. Remelli, Human diseases related to aluminium overload, Monatshefte Fur Chemie 142 (2011) 331–340, <https://doi.org/10.1007/s00706-011-0474-x>.
- [46] E.W. Baumann, Trace fluoride determination with specific ion electrode, Anal. Chim. Acta. 42 (1968) 127–132, [https://doi.org/10.1016/S0003-2670\(01\)80277-4](https://doi.org/10.1016/S0003-2670(01)80277-4).
- [47] D.L. S.-V.J. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. De Jong, P.J. Lewi, Handbook of chemometrics and qualimetrics: Part A, Elsevier Science B.V., 1997, [https://doi.org/10.1016/S0922-3487\(98\)80057-9](https://doi.org/10.1016/S0922-3487(98)80057-9).
- [48] E. Rice, R. Baird, A. Eaton, Standard Methods for the Examination of Water and Wastewater ed-23rd, American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington DC, 2017.
- [49] R.B. Mesquita, A.O. Rangel, Development of sequential injection methodologies for the spectrophotometric direct and kinetic determination of aluminium in natural and waste waters, J. Brazilian Chem. Soc. 19 (2008) 1171–1179, <https://doi.org/10.1590/S0103-50532008000600018>.
- [50] M. Berenguel-Alonso, I. Ortiz-Gómez, B. Fernández, P. Couceiro, J. Alonso-Chamarro, L.F. Capitán-Vallvey, A. Salinas-Castillo, M. Puyol, An LTCC monolithic microreactor for the synthesis of carbon dots with photoluminescence imaging of the reaction progress, Sensors Actuators B Chem. 296 (2019), 126613, <https://doi.org/10.1016/j.snb.2019.05.090>.
- [51] Y. Tang, L. Rao, Z. Li, H. Lu, C. Yan, S. Yu, X. Ding, B. Yu, Rapid synthesis of highly photoluminescent nitrogen-doped carbon quantum dots via a microreactor with foamy copper for the detection of Hg^{2+} ions, Sensors Actuators B Chem. 258 (2018) 637–647, <https://doi.org/10.1016/j.snb.2017.11.140>.
- [52] H. Teng, T.-S. Yeh, L.-Y. Hsu, Preparation of activated carbon from bituminous coal with phosphoric acid activation, Carbon N. Y. 36 (1998) 1387–1395, [https://doi.org/10.1016/S0008-6223\(98\)00127-4](https://doi.org/10.1016/S0008-6223(98)00127-4).



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