

Automated H₂O₂ monitoring during photo-Fenton processes using an Arduino self-assembled automatic system

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ARTICLE INFO

Keywords:

Arduino
Caffeine
Design of experiments
Hydrogen peroxide
Photo-Fenton
Water treatment

ABSTRACT

A cheap and easy to use Arduino self-assembled automatic system was employed to continuously monitor the hydrogen peroxide consumption during the photo-Fenton degradation of caffeine, selected as model target compound. The automatic system made it possible to measure the H₂O₂ concentration in the reaction cell via a colorimetric reaction and to take samples for HPLC analysis minimising the operator manual intervention and exposure to UV radiation. The obtained results were compared in terms of LOD and LOQ with H₂O₂ measurements manually performed using UV–Vis spectrophotometry, evidencing better analytical performance when using the automatic system; LOD and LOQ were respectively 0.032 mM and 0.106 mM for the automatic system against 0.064 mM and 0.213 mM for UV–Vis spectrophotometry. Furthermore, the photo-Fenton treatment was optimised by means of a Design of Experiments (DoE) investigating the effect of added H₂O₂ concentration, iron concentration and caffeine initial concentration on system performances. The use of the automatic device for such monitoring provided several advantages: automation (with consequent reduction of the workload), measurement increased precision, reduced reagents consumption and waste production in agreement with the principles of Green Analytical Chemistry.

1. Introduction

Analytical chemistry procedures, performed in a classical way, often require a not negligible amount of time and reagents and generate relevant amounts of wastes to be treated. Automatic systems in chemistry refer to the use of electronic devices such as sensors and actuators to control chemical processes in an accurate and reproducible way and, at the same time, reducing the operator manual intervention. One of the most widely employed electronic devices in homemade automatic systems are Arduino boards [1–3].

Arduino boards consist of a printed circuit board (PCB) equipped with a microprocessor, flash memories and pins and can be programmed using an open-source integrated development environment (IDE) that allows even users with limited knowledge in programming to write their own code [4–6]. The array of sensors and actuators commercially available for Arduino boards makes them an incredibly flexible tool not only for hobbyist projects, but for applications in the field of chemistry, including analytical chemistry as well. Some applications of

Arduino-based devices in analytical chemistry include the quantification of zinc in water [7], measuring the pH using a conductivity sensor [8,9], creating a custom-made spectrophotometer using a photoresistor coupled with wavelength selector [10], or the development of a multi-parameter probe for water analysis [11].

There are different advantages in using these types of automatic devices in analytical chemistry. Firstly, the flexibility of Arduino setups, together with their affordable prices, makes it possible to create cheap and reliable devices for the automation of repetitive and time-consuming analyses. Moreover, such automatic systems can reduce the exposure to toxic or harmful chemicals or physical hazards (e.g. exposure to UV radiation) [12]. Furthermore, laboratory measurements performed in an automated way can bring a considerable improvement in terms of accuracy and reproducibility, especially in those cases where the operator sensitivity plays an important role in outcome of the measurement (e.g. the determination of the end point of a titration) [13].

An innovative and so far unexplored research field is the use of

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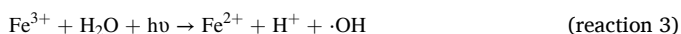
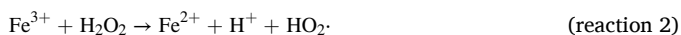
<https://doi.org/10.1016/j.talanta.2024.126195>

Received 18 September 2023; Received in revised form 26 March 2024; Accepted 30 April 2024

Available online 3 May 2024

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Arduino devices for the monitoring and control of Advanced Oxidation Processes. Advanced Oxidation Processes (AOPs) are chemical processes widely adopted for the removal of persistent organic contaminants in water [14–18]. These processes rely on the formation of highly reactive radicals (mainly hydroxyl radicals), that are non-selective and therefore are capable of oxidizing a wide variety of organic contaminants [19]. Moreover, such processes are usually performed at room temperature and pressure, avoiding extreme conditions, and making them a valid and useful tool for water treatment [20,21]. Among AOPs, the photo-Fenton process is one of the most widely used ones, and it relies on the formation of hydroxyl radicals from the reaction between hydrogen peroxide and iron(II) ions (reaction 1) [22]. In this process, iron acts as a catalyst since Fe(III) reacts again with hydrogen peroxide regenerating Fe(II) and producing hydroperoxyl radicals (reaction 2) [22]. This is however a slow reaction that strongly influences the kinetic of the whole process. The use of light has been proven to accelerate this reaction, by regenerating Fe(II), the principal species responsible for H₂O₂ decomposition yielding OH radicals formation [23–25], through reaction 3 [22].



The concentration of hydrogen peroxide has been recognized to be a crucial element in photo-Fenton processes, not only because H₂O₂ can be considered the main source of cost, but also because its concentration can be rate-limiting in both direction if it is either too low or too high [26].

This highlights the need for fast and reliable H₂O₂ determination methods, as well as automatic dosage during photo-Fenton treatment. The most commonly used methods for H₂O₂ determination at laboratory scale consist of colorimetric reactions or fluorescence measurements, involving several steps of sample preparation that need to be manually performed by the operator [27,28]. On the other hand, in the perspective of the application of photo-Fenton in waste water treatment plants, other analytic approaches are needed. The lack of robust and cheap commercially available electrodes for H₂O₂ measurement, together with the need of H₂O₂ dosing during the photo-Fenton treatment, is therefore a relevant issue.

The aim of this work is the development of an automatic device employing an Arduino board, allowing to automate the online measurement of the H₂O₂ concentration during the photo-Fenton treatment of an aqueous solution of caffeine, taken as a representative emerging pollutant. The H₂O₂ measurement was performed by automating the procedure described by Minella et al. [29]. At the same time, the system periodically sampled the treated solution from the photo-reactor to perform HPLC measurements of caffeine residual concentration.

The use of the automatic device described in this work facilitates the transition to canonical analytical chemistry to Green Analytical Chemistry (GAC) [30]. Over the years, the scientific community has progressively raised greater attention to the sustainability of chemical analysis, leading to the formalisation in 2013 of the 12 principles of GAC, concise guidelines to be used for greening laboratory practices [31]. The use of low-cost devices developed in the laboratory aligns with the 12 principles of Green Analytical Chemistry, particularly emphasising principle number 5, which highlights “the selection of automated and miniaturised methods”. Principle number 12 of GAC emphasises the importance of “enhancing operator safety in the laboratory” and in the present work it is satisfied by reducing the exposure to UV-light and potentially harmful chemicals. Furthermore, the device developed in this study adhered to the GAC principle number 9 advocating “minimising energy consumption”, achieved by developing an automated system that uses an LED as the light source instead of a commonly used UV–Vis lamp for spectrophotometric determination.

Our device, in conjunction with the implementation of Design of Experiments (DoE), was employed to study the impact of experimental conditions, such as hydrogen peroxide, Fe(II), and caffeine concentrations, on the kinetics of caffeine degradation. This approach aligns with principle number 2 of GAC, which seeks to “reduce sample size and the number of samples utilised in the analysis”. Therefore, the combination of automation, the use of efficient energy sources, and the application of Design of Experiments (DoE) targets the fulfilment of several GAC principles in this study, promoting more sustainable and safer practices in chemical analyses.

2. Materials and methods

2.1. Reagents and instrumentation

Hydrogen peroxide (30 % v/v solution) was purchased from Panreac, Germany. Caffeine (ReagentPlus grade), iron(II) sulphate heptahydrate (≥99 %), sodium phosphate dibasic (98 %), sodium phosphate monobasic (≥99 %), peroxidase (from horseradish, 10000 U/vial), phenol (≥99 %), and 4-aminoantipyrine (reagent grade) were purchased from Sigma-Aldrich, Germany, and used without further purification. Sulphuric acid (95 %) was purchased from VWR Chemicals, France. Acetonitrile (HPLC reagent grade) was purchased from Merck, Germany, and all solutions were prepared using MilliQ grade water.

2.2. Electronic components

For the development of the automatic device, an Arduino ONE board has been employed. The components of the device included a Bluetooth module (DSD TECH HM-10, 25 m), two peristaltic pumps (Hyudio, ASIN: B07Q1WNHHT), a colour sensor TCS34725 (TECNOIOT, ASIN: B07YXDZVJN), a 1 W white high-intensity LED, two relay KY-019 5 V (WINGONEER, ASIN:B06XHJ2PBJ) and simple elements such as buttons, resistors, and wires. To carry out the colorimetric measure, a quartz flow cell having 1 cm of optical path (model Hellma, 178.710-0s) was employed. The colour sensor is not able to provide information at a fixed wavelength, this device works providing RGB values that correspond to the integration of a specific range of the spectrum. This information is provided in the datasheet available in the online shop page.

2.3. Automatic device description

The electronic and physical assembly of the automatic device are displayed in Fig. 1 and a picture of experimental setup is reported in Fig. S1. The automatic device was programmed to perform three different tasks: “colour measure”, “colorimetric reaction”, and “take sample”. The function “colour measure” was used to obtain information from the TCS34725 sensor. This sensor provides information about the intensity of the red (R), green (G), blue (B), and white (clear) light components, colour temperature, and luminous flux (lux). The instruction, “colorimetric reaction”, turns on the pumps connected to the sample and to the colorimetric reagent, to mix the two solutions and send the mixture to the measuring cell. After 6 min, the reading from the colour sensor was automatically obtained, providing the information described for the “colour measure” function. The last instruction, “take sample”, turned on the peristaltic pump connected to the irradiated solution, allowing to withdraw samples from the irradiation cell without manual intervention from the operator. This instruction was performed three times, the first two to clean the system, the last one is to obtain the sample. These three instructions could be executed both from the device itself using dedicated buttons and remotely, thanks to the Bluetooth module, using a smartphone. To carry out this connection the “Arduino Bluetooth Controller” app, available in the play store, has been employed, and the Arduino was programmed to execute the three functions, “colour measure”, “colorimetric reaction”, and “take sample” when receiving the text characters “a”, “b” or “c” respectively (a

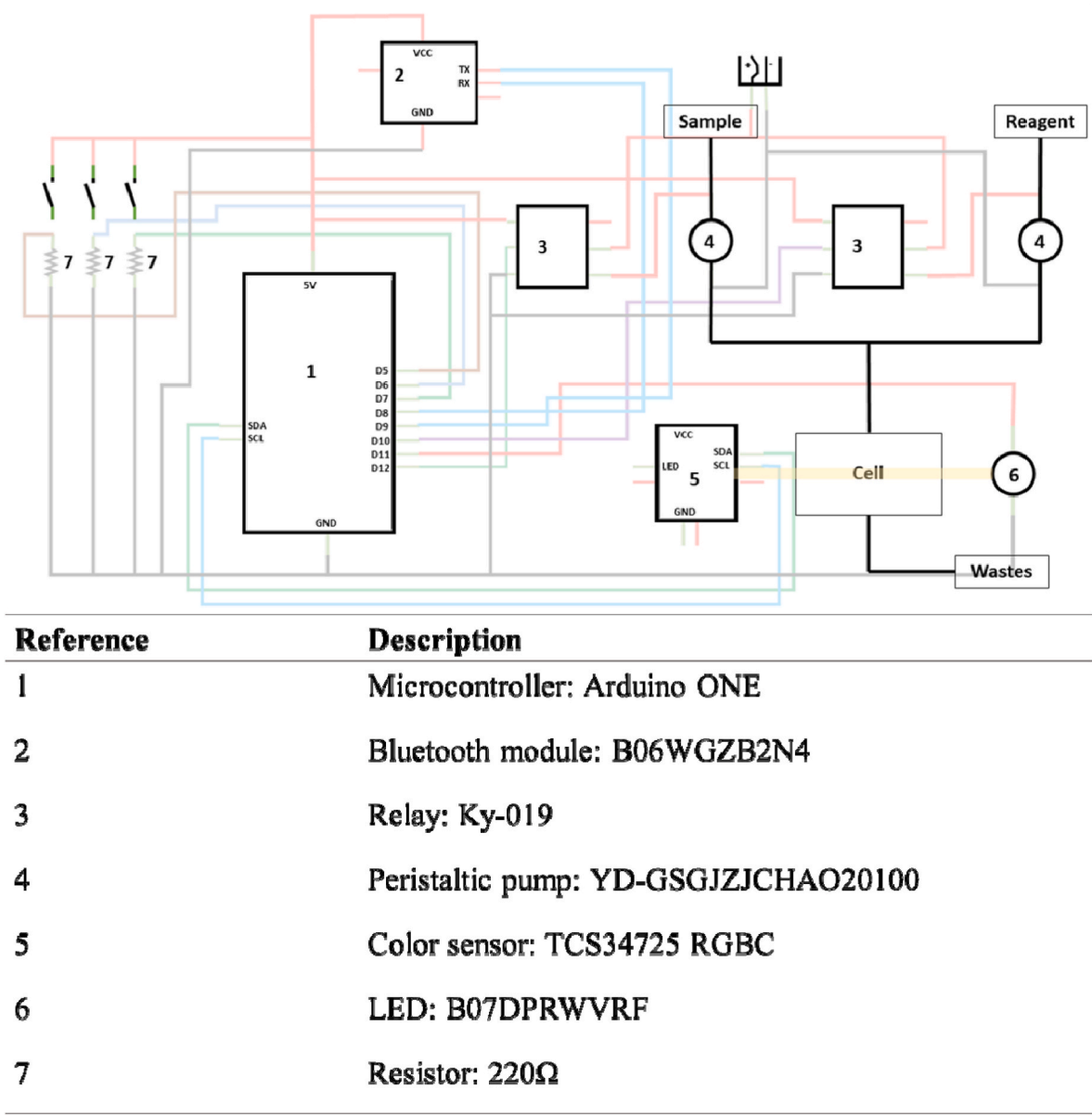


Fig. 1. Overlap of the physical and electronic scheme of the Arduino device.

screenshot of the app is reported in Fig. S2). A detailed description on flows optimization is reported in text S1.

The measuring module of the automatic system consisted in a 3D-printed PLA support holding in position the white LED light source, the flow cell, and the light sensor; a scheme of the colour measuring module is reported in Fig. S3.

2.4. Photo-Fenton reaction

Photodegradation experiments were carried out by irradiating, under continuous stirring, 100 mL of aqueous samples in a closed Pyrex® cell with a Xenon lamp (1500 W) installed in a closed solarbox (Solarbox, CO.FO.ME.GRA S.r.l., Milan, Italy) equipped with a 340 nm cut-off filter. The irradiance of the lamp, measured with a UV-Multimeter system, was 26.7 W/m².

The photo-Fenton treatment was performed using different concentrations of iron, hydrogen peroxide, and caffeine in the combinations obtained with the DoE. The three levels of concentrations tested for each component are described in section 2.7. The pH was adjusted to 3.0 using H₂SO₄. The Pyrex glass irradiation cell, covered with aluminium

foil, was placed inside the operating solarbox for 15 min before starting the irradiation to allow the solution to reach the same temperature as the solarbox. After 15 min, the aluminium foil was removed, H₂O₂ was added, and experiments started immediately after.

2.5. Caffeine measurement

To monitor the concentration of caffeine in treated water, samples were taken using the “take sample” command of the automatic system. To 1 mL of sample 0.2 mL of methanol were manually added immediately after sampling in order to stop the degradation process. Caffeine was monitored by HPLC, employing a Merck-Hitachi instrument, equipped with a Lichrospher RP-C18 column (125 mm × 4 mm i.d., particle diameter 5 µm), 1-6200 pumps and UV/Vis I-4200 detector using a measurement wavelength of 210 nm. The eluent was an 85/15 mixture of 0.1 % H₃PO₄ in ultrapure water and acetonitrile, and the flow was set to 0.8 mL/min.

2.6. H₂O₂ measurement

The colorimetric reagent was prepared dissolving 0.711 g of NaH₂PO₄·H₂O, 0.276 g of Na₂HPO₄·2H₂O, 0.234 g of phenol, 0.100 g of 4-aminoantipyrine and 0.001 g of peroxidase (VI) in 100 mL of ultra-pure water. To perform the colorimetric reaction using the automatic system, the reagent solution and the sample were automatically mixed in a 3:2 vol ratio. Due to the kinetics of the colorimetric reaction, sample measurement was performed 6 min after the mixing of the sample with the colorimetric reagent to wait for proper colour development. The automatic system was equipped with a quartz flow cell having 1 cm of optic path (model Hellma 178.710-0s) and the light source was a 1 W white LED. The measure performed with the automatic system provided the RGB values registered by the colour sensor. For comparison, the determination of H₂O₂ was also performed manually, and a spectrophotometer model Cary 100 Scan was used to measure the colour development at 505 nm using a 1 cm optic path quartz cell.

2.7. Design of experiment (DoE)

To study the behaviour of the photo-Fenton reaction depending on the concentration of the reagents and contaminant, a DoE was carried out. To obtain the DoE results, the Minitab v19.1 program was used adopting the response surface design mode. As suggested in other works, a 3-levels 3-factors Box-Behnken was performed [32–34]. The three factors studied were the concentration of the contaminant, the concentration of H₂O₂ and the concentration of Fe(II). In Table S1 are displayed the experimental conditions in which the 15 experiments of the DoE were performed. As response parameters the content of caffeine and H₂O₂, expressed as C/C₀, at 30, 60 and 90 were employed.

3. Results and discussion

3.1. Comparison between manual UV–Vis spectrophotometer and online Arduino set-up with TCS34725 sensor

The online approach was compared with a traditional, manually performed spectrophotometric determination of H₂O₂, exploiting in both cases the same colorimetric reaction, but using a different experimental set-up.

In order to identify the useful concentration range for the automatic measure of H₂O₂, a calibration curve was prepared. Standard solutions of 0, 0.01, 0.05, 0.1, 0.2, 0.25, 0.5, 0.75, 1, 1.25, 1.5 and 2 mM of H₂O₂ were prepared. The colorimetric measure by UV–Vis spectrophotometry was initially performed at 6 and 10 min after mixing the reagent solution and the sample (Fig. S4); although a 10 min delay provided better sensitivity, a delay of 6 min allowed for a higher frequency of measurement with still sufficient color development. The same delay was therefore also adopted for H₂O₂ measurement using the automatic device.

When the colorimetric reaction was performed using the automatic device, although it was possible to obtain calibration curves with the raw data obtained from the R, G, B channels of the sensor, using ratios between colour parameters provided more stable readings, with lower coefficient of variation and larger linear calibration range. This is due to high sensitivity of the sensor to subtle changes in the received light producing high instrumental noise. However, since this noise appears in all three channels proportionally, using the ratio of the channels can compensate for the sensor noise and provide more stable measurements.

The results obtained using the R/G ratio have the same trend as the results obtained with the spectrophotometer (Figs. S5 and S6). However, using the G/B ratio for H₂O₂ quantification, provided better results and a higher linear range. For this reason, the G/B was used for H₂O₂ quantification throughout this work.

The results obtained using the automatic system were compared with those obtained with the UV–Vis spectrophotometer, in terms of limits of

detection (LOD) and quantification (LOQ). The LOD and LOQ were determined as $LOD = 3 \cdot s_y / \text{slope}$ and $LOQ = 10 \cdot s_y / \text{slope}$, where s_y is the residual deviation of the linear calibration. To determine the LOD and LOQ, a calibration set consisting of low concentration H₂O₂ standard solutions, specifically 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5 mM, was prepared. These solutions were measured using both the UV–Vis method and the automated device, following the standard procedure. The obtained data used for the calculation of LOD and LOQ, are presented in Table S2. Our results showed that the colour sensor had an LOD of 0.032 mM and an LOQ of 0.106 mM while the spectrophotometer had an LOD of 0.064 mM and an LOQ of 0.213 mM. These results suggest that the automatic measurement has a higher sensitivity for hydrogen peroxide detection than the manual measurement, that can be explained by the automatic control in the waiting time of the colorimetric reaction by the automatic system. It is important to note that as the colour development goes on over time, the delay at which the measurement is performed plays a crucial role in the results. This delay was controlled automatically when the measurement was performed using the automatic system, while it was calculated by the operator in the manual procedure.

The calibration line obtained using the TCS3425 colour sensor covered the linear range from 0.106 to 1.00 mM and is displayed in Fig. 2. An inter-day study ($n = 11$) of the calibrations has been conducted, and it has been found that the average slope between different days is $-0.513 \pm 3.4 \%$. On the other hand, an intra-day study ($n = 4$) has been conducted, and it has been found that the mean slope of the calibrations is $-0.517 \pm 3.4 \%$, which is consistent with the findings from the inter-day studies. The intra-day and inter-day RSD values obtained for the measurements of H₂O₂ standards at low, medium, and high concentration are reported in Table S3.

It is significant to note that in the RGB colour space, less chromatic and brighter values correspond to higher numeric values. As the colour of the solution becomes more intense, the colour parameters decrease at different rates, with the G value decreasing more rapidly than the B value. Consequently, when calculating the G/B ratio, the more rapid decrease of G results in a negative slope. This behaviour of the calibration curve can be attributed to the inherent properties of the colorimetric reaction and the RGB colour space representation.

3.2. Studies of the use of the new device in H₂O₂ and caffeine monitoring

To carry out the photo-Fenton process, 100 mL of the caffeine solution (20 mg/L) were used. The reaction was carried out with a concentration of 0.1 mg/L of Fe(II) and 0.8 mM of H₂O₂. The automatic system was employed to obtain a portion of the solution at 0, 10, 20, 30, 60 and 90 min, and at the same time, to determine the content of H₂O₂. Fig. 3A shows the results of the concentration of both caffeine and H₂O₂ at those times. For caffeine degradation a half-life of 65 min has been observed.

The experiment has been repeated, increasing the concentration of Fe(II) from 0.1 to 0.5 mg/L and the obtained concentration profiles are displayed in Fig. 3B. The results show that the increase of iron increases the velocity of caffeine degradation, yielding a half-life of 18 min. An additional experiment in which the concentration of added H₂O₂ was reduced to 0.4 mM while keeping a Fe(II) concentration of 0.5 mg/L, was also carried out (Fig. 3C); an increased caffeine half-life of 24 min was obtained under these conditions.

3.3. Design of Experiments (DoE)

The most relevant results obtained with the DoE emerge when analysing the rate of caffeine consumption with respect to the H₂O₂ and Fe(II) initial content. Figs. S7 and S9 clearly demonstrate that the Fe(II) parameter exhibits a pronounced influence on the velocity of caffeine degradation. At short irradiation times, the concentration of H₂O₂ does not appear to exert a significant impact on caffeine degradation. However, as the irradiation time increases, the concentration of H₂O₂

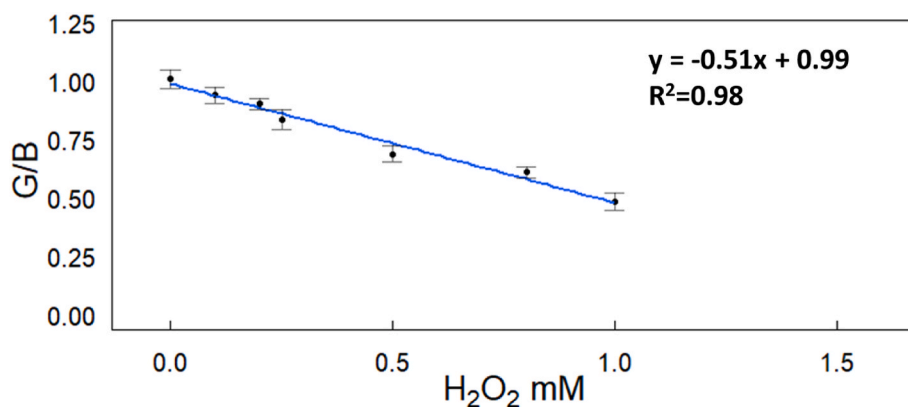


Fig. 2. Calibration line for the H₂O₂ measured using the colour sensor (G/B ratio) with the standard deviation from different days (n = 11).

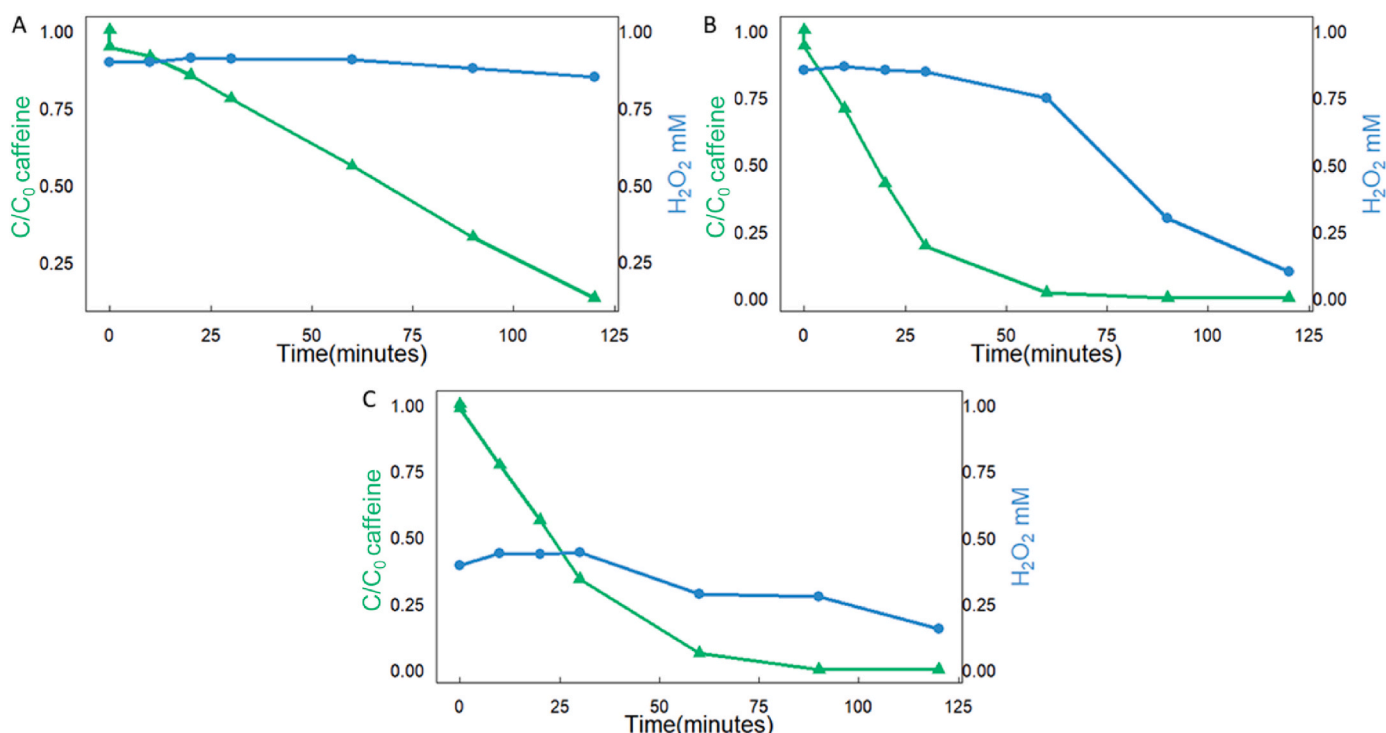


Fig. 3. Results obtained for monitoring of H₂O₂ (blue dots) and caffeine (C/C₀) (green triangles) in a photo-Fenton process at conditions of: A) 20 mg/L of caffeine, 0.8 mM of H₂O₂ and 0.1 mg/L of Fe(II); B) 20 mg/L of caffeine, 0.8 mM of H₂O₂ and 0.5 mg/L of Fe(II); C) 20 mg/L of caffeine, 0.4 mM of H₂O₂ and 0.5 mg/L of iron.

assumes a more relevant effect. Notably, at later stages, an association between H₂O₂ and Fe(II) can be observed, facilitating enhanced degradation kinetics (Fig. S7). Evaluation of the consumed H₂O₂, based on the same parameters, suggests that Fe(II) wields the most influential role in hydrogen peroxide consumption (Fig. S8). Conversely, higher initial concentrations of H₂O₂ correspond to a more rapid H₂O₂ consumption.

Additional data analyses also investigated the consumption of H₂O₂ as a function of the initial concentration of H₂O₂, caffeine, and Fe(II) (Fig. S10, S11n and S12). As it can be seen in Fig. S10, iron concentration and initial H₂O₂ are both influential in H₂O₂ depletion rate. Conversely, higher initial concentrations of H₂O₂ led to a more rapid H₂O₂ consumption. As for the role of the contaminant initial concentration, lower and higher concentrations of the contaminant led to an increased H₂O₂ consumption. As evidenced by the preliminary studies (Section 3.2), it is apparent that H₂O₂ is not rapidly consumed as initially presumed.

Overall, the results of this DoE made it possible to identify the optimal conditions allowing to achieve the higher caffeine degradation using the lowest amount of reagents in the range of concentrations

studied. Fig. 4 shows the surface graph obtained for H₂O₂ consumption (Fig. 4A), caffeine degradation (Fig. 4B), and the overlapping of both at 90 min (Fig. 4C). The overlap shows that to achieve the higher caffeine degradation, different combinations of the reagents are possible. It is important bearing in mind that it would be preferable to minimise the amount of added H₂O₂ rather than Fe(II) as iron is a catalytic reagent and that it is also better not to have residual H₂O₂ at the end of the treatment process to avoid reagent wasting. According to these requirements, the best conditions identified with the DoE to carry out the degradation of caffeine 20 mg/L were initial concentrations of 0.85 mg/L for Fe(II) and 0.5 mM for H₂O₂.

4. Conclusions

In conclusion, we have successfully demonstrated the effectiveness of a low-cost Arduino system to perform the quantification of hydrogen peroxide during photo-Fenton process for caffeine degradation in an automatic online way. The benefits of employing such device includes

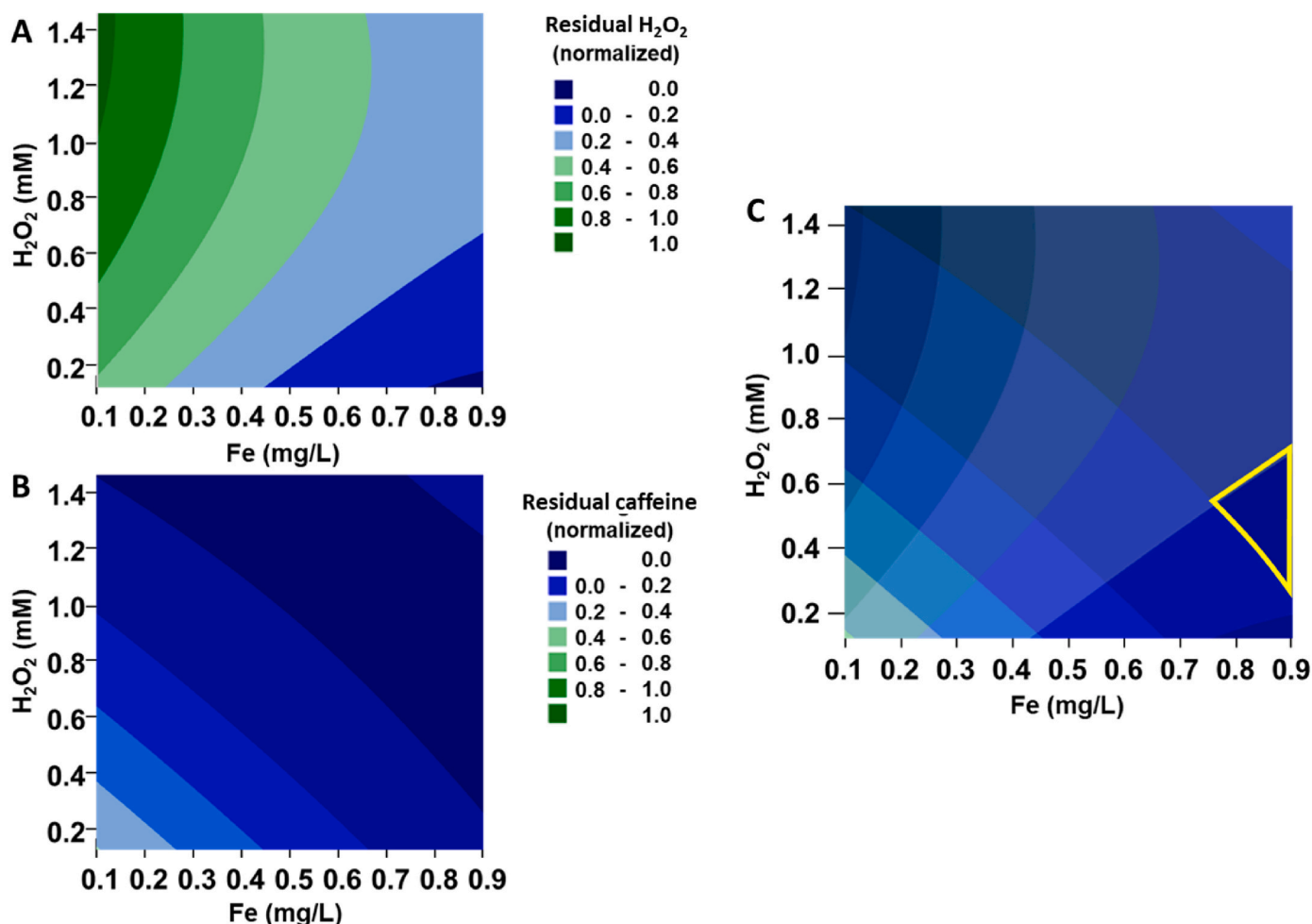


Fig. 4. Overlapping of the contour graph obtained for caffeine degradation and peroxide consumption obtained with $[\text{H}_2\text{O}_2]$ vs $[\text{Fe}]$ for a fixed content of caffeine (20 mg/L) at 90 min.

reduced manual labour for the operator and reduced exposure to hazardous UV radiation. Furthermore, the results revealed that this automatic system was more sensitive than traditional manual procedure, allowing to obtain an LOD and a LOQ of 0.03 and 0.11 mM respectively with a linear range of 0.11–1.00 mM. Moreover, the use of the Arduino device facilitated the monitoring of the performances of a photo-Fenton reaction when the initial concentration of caffeine, H_2O_2 , and Fe(II) were varied.

For this purpose, the use of the automatic system in combination with a Design of Experiments (DoE), allowed to reduce the number of experiments and generated wastes and led to the identification of the optimal concentrations of H_2O_2 , and Fe(II) to be added to achieve efficient caffeine degradation.

Our findings highlight the significant potential of automatic systems, to streamline laboratory processes while enhancing efficiency, accuracy, and operator safety. Therefore, the exploration and integration of such automatic devices in laboratory settings enables more efficient and sustainable scientific research. Beyond chemical measurements, this technology can be applied across multiple scientific fields, potentially transforming the way in which experiments are conducted and improving scientific progress.

CRedit authorship contribution statement

Kevin U. Antela: Investigation, Methodology, Software. **Davide Palma:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing. **Angel Morales-Rubio:** Data curation,

Resources, Writing – review & editing. **M. Luisa Cervera:** Validation, Writing – review & editing. **Alessandra Bianco Prevot:** Conceptualization, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgements

Authors acknowledge support from the Project CH4.0 under the MUR program “Dipartimenti di Eccellenza 2023–2027” (CUP: D13C22003520001).

University of Torino is kindly acknowledged for financial support to local research (RILO funds).

Kevin U. Antela acknowledges the Generalitat Valenciana for the financial support (CIBEP/2021/07) during his predoctoral stay in a research institution outside the Valencian Community.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2024.126195>.

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