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Designing a sensor based on carbon quantum dots for the detection of iron ions

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ABSTRACT

The Accurate detection of iron ions is of paramount importance for both environmental protection and human health. To this end, this work focused on the use of Carbon dots (CDs) obtained by hydrothermal method from grapefruit peel. These CDs were used as a sensor for detecting iron ions. Under Ultra-Violet (UV) irradiation, these CDs exhibited intense blue fluorescence. In addition, the results of pH optimization during the detection of iron ions revealed that the CDs can allow simultaneously detection of Fe^{2+} and Fe^{3+} ions at pH between 2 and 5 with detection limits of 32.631 µg/L and 36.751 µg/ L at pH 4, and selectively Fe^{3+} ions at pH 1 with a limit of 38.072 µg/L by bimodal colorimetric and UV-Vis spectroscopy detection. It should also be noted that these results were due to result in color changes in natural light and in a more pronounced quenching of fluorescence in the presence of ferric ions.

Keywords: Carbon Quantum dots (CDs); Detection, Iron ions; Synthesis of Manomaterials; Carbon Based Sensor, Hydrothermal Method.

INTRODUCTION

Environmental pollution by heavy metals constitutes a real environmental problem. Thus, the detection of these metal ions remains a major challenge in many fields such as environment, health and industry (Guo, et al., 2016; Mondal et al., 2016). Among these ions, iron ions aroused considerable interest because of their involvement in vital biological processes and their widespread presence in natural and synthetic systems. Iron is also an essential transition metal involved in various human metabolic pathways, e.g. the oxygen transport mechanism and it is acting as a cofactor (Dev S ET al., 2017). However, low level and overload of iron ions in human body can cause certain diseases such as liver damage, heart disorders, cancer, anemia and many others (Galaris et al., 2008; Sui et al., 2014). It is therefore of paramount importance to find sensitive techniques to selectively detect iron ions in biological, medical and environmental samples.

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In recent decades, a variety of optical sensors, such as functionalized metal-organic frameworks (Yang et al., 2013), noble metal quantum clusters (Zhou et al., 2017), and metal-based sensors dyes (Sui et al., 2014), has been tested to detect iron ions. Unfortunately, these optical probes often suffer from lengthy synthesis routes and/or involve toxic or expensive reagents. Therefore, developing sensitive, selective, inexpensive, environmentally friendly and rapid methods for the detection of iron ions is a major scientific and keen interest. With this in mind, carbon dots, a new class of nanoscale carbon materials consisting of quasi-spherical particles, are attracting great interest. The presence of numerous functional groups namely alcohol, carboxylic, and carbonyl functions on their surface gives high solubility in water and a bonding capacity with other chemically reactive groups (Lim et al., 2015). Furthermore, CDs possess unique properties such as high light absorption and emission efficiency, high biocompatibility, excellent free electron reservoir and electron transfer properties due to their π-conjugated structure (Luo et al., 2019). These fascinating characteristics give CDs wider application in various fields such as chemical sensing, photocatalysis, and electrocatalysis (Lim et al., 2015). These characteristics also make CDs ideal candidates for designing carbon-based sensors for iron ion detection, where their specific interactions can be exploited to fabricate highly selective detection strategies. Hence, scientists have endeavored to synthesize CDs as fluorescent probes, using lemon juice, coconut water and many others (Mondal et al., 2016; Preethi et al., 2021). Along the same lines, a sensor to detect iron ions in this study was developed. To achieve our objective, we propose to carbon quantum dots, synthesize derived from grapefruit skin juice. The optical properties of the obtained CDs were highlighted by the phenomenon of fluorescence quenching in the presence of iron ions under Ultra-Violet (UV) irradiation.

MATERIALS AND METHODS

Reagents

The reagents used in this study were grapefruit skins, obtained from the Gouro market in Adjamé (Abidjan, Ivory Coast), sodium hydroxide (NaOH, 99%, Chem-Lab), sulfuric acid (H_2SO_4, 95%, Fisher Scientific), iron II sulfate ($FeSO_4.7H_2O$, 99%), hydrogen peroxide (H_2O_2, 35%, Chem-Lab), copper II sulfate ($CuSO_4$, 99%, Jeulin), lead nitrate ($Pb(NO_3)_2$.99%, Merck), barium chloride ($BaCl_2$, 99%) and aluminum sulfate ($Al_2(SO_4)_3$, 99%) from Rectapur Prolabo. The chemicals were used without prior purification.

Materials

In order to obtain juice from grapefruit skins, a crusher with a robust JS8000 C type motor with a power of 3000 W, a frequency of 50 Hz and a maximum speed of 5 rpm/min was used. It was obtained from the JIASOUNG Company. A Table top High-Speed centrifuge from the company MRCLTD Centrifuge was used. It has a capacity of up to 13000 rpm, but was set at 6000 rpm for all operations centrifugation. The UV-Vis spectra were recorded using Ocean Optics FLAME spectrophotometer (USA). The UV lamp used during the present work consisted of two wavelengths 254/365 nm. Ultrapure water obtained from deionized (DI) water system (Sichuan Zhuoyue Water Treatment Equipment Co., Ltd, Chengdu, China) with a resistivity of 18.25 MΩ.cm was used throughout all the experiments.

Synthesis and characterization of CDs

CDs were synthesized by the hydrothermal method using grapefruit skins as carbon precursors. Firstly, 285.5 g of grapefruit zest was cleaned with distilled water and ground to obtain a paste. Then 285 mL of distilled water was added to the obtained paste, followed by filtering to obtain the juice. 30 mL of this juice was then transferred into a Teflon-lined and then heated to 180°C for 5 hours in the oven. After cooling to room temperature, the resulting solution was centrifuged at 6000 rpm for 15 min followed by filtering with microfilter paper of 0.22 μm pore diameter.

Detection of Iron ions

The procedure used for the effect of metal ions on the fluorescence intensity of the CDs was as follows: different samples each containing 500 µL of the solution of the obtained CDs were mixed with 100 µL of the aqueous solutions of 50 g/L ferrous ions (Fe^{2+}) from iron II sulfate with a concentration and 50 g/L ferric ions (Fe^{3+}), obtained by the oxidation of Fe^{2+} using hydrogen peroxide with a concentration of 0.4 mol/L. The detection medium was studied by varying the pH values (1, 2, 4 and 5) of the ferrous ion solution. For that, a few drops of the sodium hydroxide or sulfuric acid solution were added to the solution containing the ferrous ions to adjust the pH of the medium. Then 100 µL of each solution containing the Fe^{2+} and Fe^{3+} ions was added separately to 500 µL to the CDs solution.

The selectivity of the synthesized CDs was also evaluated by adding 100 µL of the solutions containing Al^{3+}, Cu^{2+}, Pb^{2+}, and Ba^{2+} with a concentration of 50 g/L to 500 µL of the CDs solution, respectively.

Table 1: Limits of detection and quantification.

Ions	Detection Limit (LOD)	Quantification Limit (LOQ)	pH
Fe^{3+}	38,072 µg/L	126,906 µg/L	1
Fe^{2+}	32,631 µg/L	10,877 µg/L	4
Fe^{3+}	36,751 µg/L	122,504 µg/L	4

RESULTS

Characterization of the synthesized particles

To know the nature of the synthesized particles, we measured the absorbance of these particles (Figure 1). The results indicate a broad band [230-307 nm] consisting of two absorption peaks in the UV region and a tail that extends towards the visible domain.

Detection of iron ions

The detection of the metal ions in this work is based on the principle of quenching of fluorescence of the synthesized CDs. This principle aims to highlight the ability of metal ions to reduce the intensity of the fluorescence of our CDs sensor. In the case of Fe^{2+} and Fe^{3+} ions, it was demonstrated in this study that the addition of solutions containing respectively these two types of ions in the sensor solution considerably reduce or even extinguish the fluorescence of CDs under UV radiation (365 nm) when the oxidation state of iron ions increases (Figure 2). For separate detection, the effect of medium pH was studied. It was observed that at lower pH around pH = 1, only Fe^{3+} ions can inter act with CDs. However, for the remaining pH values, ferrous and ferric ions are detectable and this results in a change in color (Figure 3). Thus, a strongly acidic environment is only favorable for Fe^{3+} ions. From yellow, the color change to green in the presence of Fe^{2+} ions and brown for Fe^{3+} ions.

Establishment of the calibration curve and validation of the method

In order to find the detection range of ferrous and ferric ions, different concentrations ranging from 100 µg/L to 1000 µg/L at pH 1 and pH 4 of these ions were evaluated in an aqueous solution of CD_S. Figure 4 shows a decrease in the intensity of the CD_S absorption peak with the increase in the concentration of these metallic ions.

The relationship between the concentration of added ferrous and ferric ions and the absorbance of CD_S via the absorbance difference (ΔA) between the peak (A0) of the

CD_S solution in absence of Fe^{2+} and Fe^{3+} and the peak (Ai) of the CDs solutions with the different concentrations of added Fe^{2+} and Fe^{3+} from 0 to 1000 µg/L was defined. From this study, we observe a linear relationship between ΔA and the concentration of ions at pH 1 for Fe^{3+} (Figure 4.B) and pH 4 for Fe^{2+} and Fe^{3+} (Figure 4.D and F) added. The calibration curves obtained between 200 and 900 µg/L, 100 and 900 µg/L and 100 and 1000 µg/L are respectively indicated by the following equations:

$\Delta A = 0{,}0001 \times C + 0{,}0025$ (1) $[Fe^{3+}]$ pH 1

$\Delta A = 0{,}1115 - 0{,}0001 \times C$ (2) $[Fe^{2+}]$ pH 4

$\Delta A = 0{,}0001 \times C - 0{,}0012$ (3) $[Fe^{3+}]$ pH 4

With C the concentration of Fe^{2+} and Fe^{3+} ions in µg/L. The determination coefficients R^2 are 0.9969 for Fe^{3+} at pH 1, 0.9984 and 0.9982 for Fe^{2+} and Fe^{3+} respectively at pH 4, confirming good linearity of the method.

In addition to the linearity deduced from the calibration curve, the limits of detection and quantification were calculated using relationships LOD = 3×s/S and LOQ = 10×s/S respectively. This made it possible to obtain the values recorded in the following table (Table 1)

Study of the selectivity of CQDs

For various applications, it would be interesting to detect other metal ions such as Al^{3+}, Cu^{2+}, Pb^{2+}, and Ba^{2+} can be found in the same media. It emerges from this study that the synthesized CQDs are not only sensitive to iron ions, but they are also sensitive to Cu^{2+} ions compared to other ions as exhibited in Figure 5.

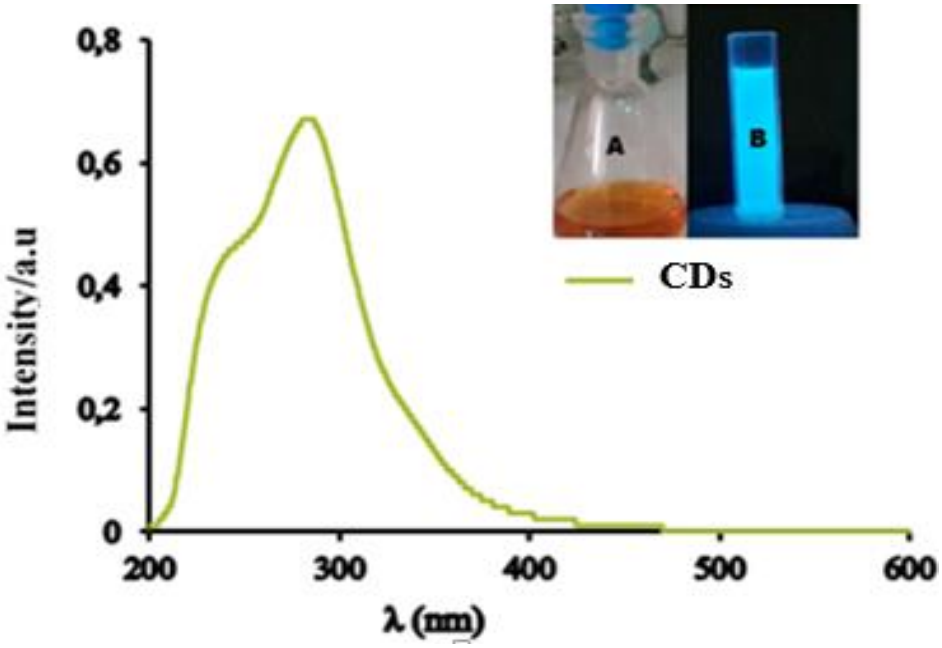

Figure 1: UV-Visible spectrum of synthesized CDs. Box: CDs solution under daylight (A) and CQDs solution under UV irradiation (B).

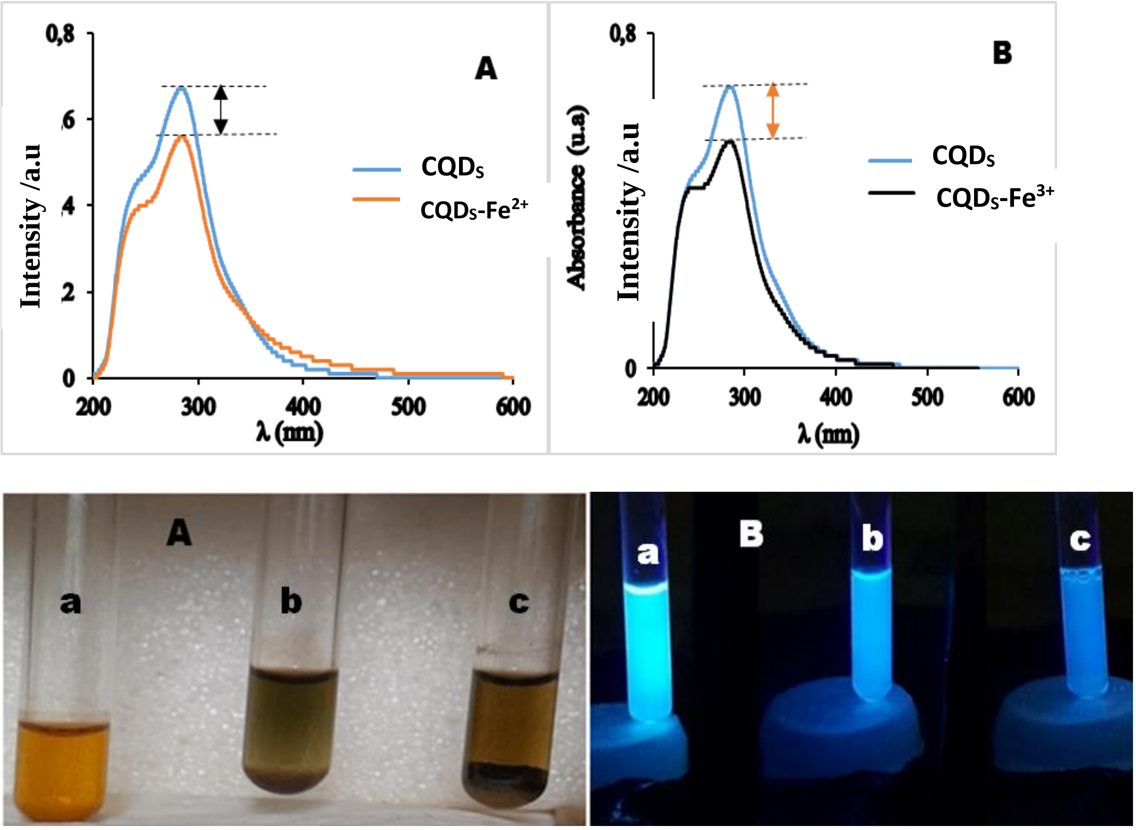

Figure 2: (1) UV-Vis spectra A) in the presence of Fe^{2+} and B) in the presence of Fe^{3+}. (2) Solution of (a) CD_S, (b) CD_S -Fe^{2+} and (c) CD_S-Fe^{3+} A) with daylight and B) under radiation using wavelength λ = 365 nm

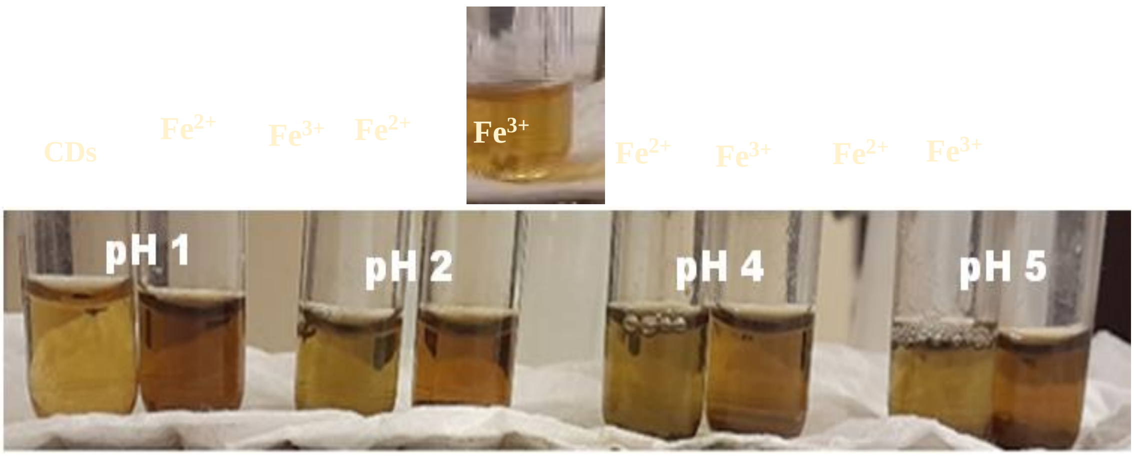

Figure 3: Detection of Fe^{2+} and Fe^{3+} ions at different pH.

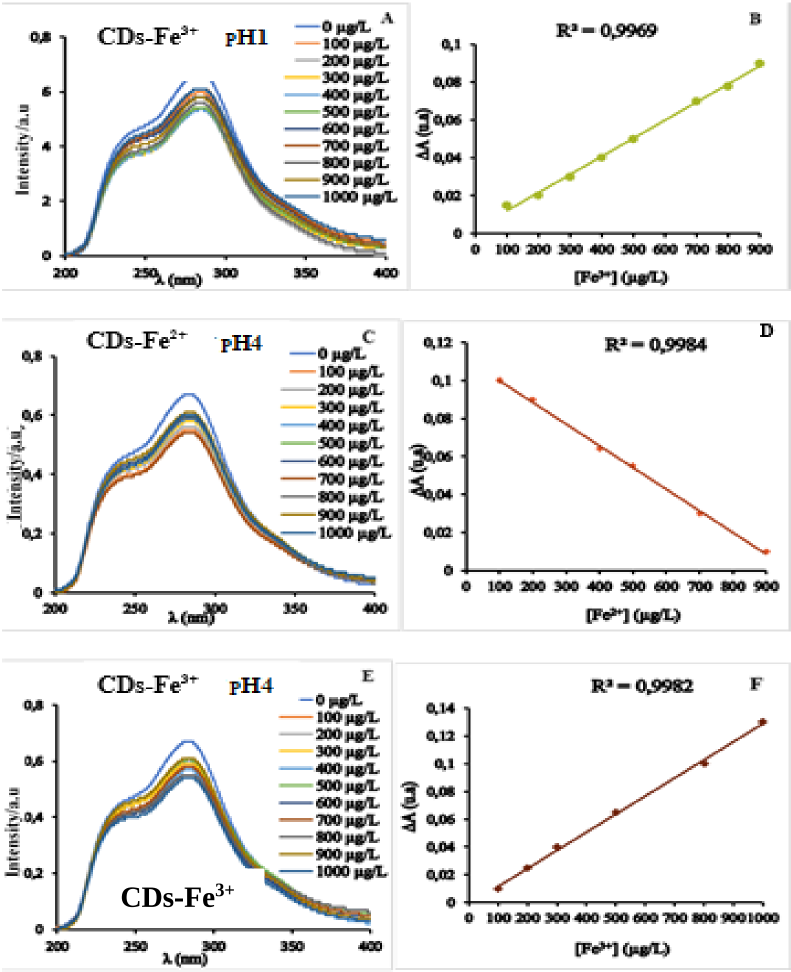

Figure 4: A), C) and E) Absorption spectra of CDs in the absence and presence of Fe^{3+} pH1 Fe^{2+} and Fe^{3+} pH 4 at different concentrations. B), D) and F) graphs corresponding to $\Delta A = A_0 - A_i$ as a function of the concentration of iron ions.

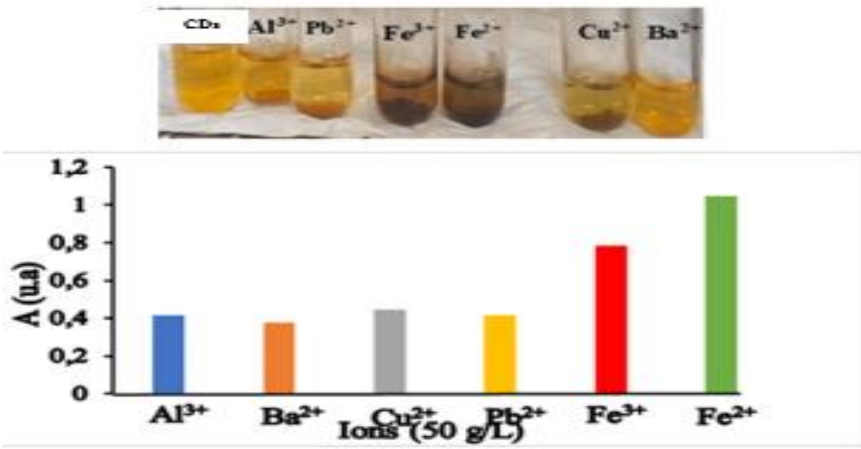

Figure 5: Selectivity of CDs.

DISCUSSION

Characterization of the synthesized particles

The first peak, considered as a shoulder, is around 240 nm and can be attributed to the π-π* transition of the C=C bond, sp^2 carbon of the graphitic core. The second, with maximum intensity around 287 nm, can be attributed to the n-π* transition of the C=O or C-O bond (Emam et al., 2017; Nawal et al., 2018). From these different observed peaks which are in accordance with the literature, we can affirm that the synthesized particles are carbon dots.

Detection of iron ions

This reduction finds its meaning in the fact that there is formation of a stable complex between the iron ions and the functions present on the surface of the CDs. During excitation, the electrons coming from the CDs are transferred into the 3 d subshell of the ions. This transfer thus leaves holes in the CDs, thus the recombination of the hole-electron pair is non-radiative. (Jiang et al., 2015). With daylight, an immediate color change is observed for ferric ions while ferrous ions take time before having a stable color (Figure 3). These color changes may be due to the aggregation of the CDs, thus resulting on the UV-vis spectra by a decrease in the maximum intensity of the absorbance which is slightly accentuated on the B spectrum by a few centimeters compared to spectrum A. This would justify the strong interaction of Fe^{3+} ions with the CDs surface which is visualized so well under UV radiation by a very pronounced reduction in fluorescence, which would mean that the synthesized CDs are more sensitive to ferric ions than to ferrous ions.

Establishment of the calibration curve and validation of the method

This result confirms the aggregation phenomenon by as seen in the solution under daylight. The results are in good agreement with the literature (Riaz et al., 2014). These results show a sensitivity of the colorimetric technique coupled with UV-Vis, thus suggesting the possibility of evaluating Fe^{2+} and Fe^{3+} ions. These results show a sensitivity of the colorimetric technique coupled with UV-Vis, thus suggesting the possibility of evaluating Fe^{2+} and Fe^{3+} ions.

Study of the selectivity of CQDs

The results of the selectivity study confirm that, the hydroxyl and carboxylic groups present on the surface of the synthesized CDs are notably sensitive to iron ions than to other metal ions (Monisha et al., 2022).

Conclusion

In the present work, carbon quantum dots were used as a sensor for the detection of iron ions in an aqueous medium. They were synthesized by the hydrothermal method which is a simple, rapid and efficient synthesis technique, using grapefruit skin juice as a carbon source. The prepared CDs showed high solubility and fluorescence intensity under UV irradiation without any surface modification. In daylight a change in color and under UV irradiation could be seen, the intensity of CDs fluorescence decreases in the presence of Fe^{2+} and Fe^{3+} ions. Furthermore, the results of the influence of pH show that the CDs are capable of separately detecting iron ions, in this case Fe^{3+} ions at pH 1 with a detection limit of 38.072 µg/L and a simultaneously detection of the two types of ions (pH 2 to 5) with detection limits ranging from 32.631 µg/L for Fe^{2+} to 36.751 µg/L for Fe^{3+} when using the UV-Vis spectroscopy technique. In addition, except Cu^{2+}, these CDs showed good selective activity against other metal ions. From this study, it appears that this technique can be used for monitoring iron ions. This work, which is part of the protection of the environment and the preservation of human health, aims to study the detection of iron ions in an aqueous environment.

COMPETING INTERESTS

The authors declare that they have no competing interests.

AUTHORS' CONTRIBUTIONS

MLK carried out the experiments; MAA wrote the first draft of the manuscript; MAA and JCM suggested the project about this work, applied for funding, followed the execution of this work, and deeply checked the manuscript writing process; WIBI, NBBP, SKKK and SKK collected the samples and prepared the method of extraction.

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