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Green carbon dots from poppy seeds with conjugated hydrogel hybrid films for detection of Fe^{3+}

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A simple, non-toxic and eco-friendly method has been developed for detection of Fe^{3+} using the beneficial plant Opium Poppy (*Papaver somniferum*) seeds as a carbon source to fabricate a hybrid film (HF). The hybrid film platform comprises of quince seed mucilage and sodium alginate to form a fluorescent hybrid film with green carbon dots derived from poppy seeds (P-CDs). All materials and methods contain non-toxic chemicals. The prepared samples have been characterized morphologically, structurally and optically by spectroscopic techniques. A hydrodynamic radius of the P-CDs is determined as an average of 4.79 nm using Dynamic Light Scattering (DLS). It has been identified that hybrid film is selective towards Fe^{3+} ions among different metal ions with one-step by the naked-eye and turn-off detection and selectivity of P-CDs to Fe^{3+} is determined by fluorescence measurement. The detection limit (LOD) of Fe^{3+} ion is found as 0.356 mM. Developments of such a hybrid material from sustainable and low-cost sources make it an interesting option as a detection material must be investigated in various fields. For the first time, quince seed mucilage combined with green carbon dots and it has been studied in the detection field as a hybrid film. This study has proven that biotechnological studies about carbon dots can also obtain efficient results by providing green, economic, energy and water saving approaches.

Keywords: Bio-sensing platform, Green carbon dots, Hybrid films, Poppy seeds, Seed mucilage, Quince

There is an urgent need to develop sustainable and green technology approaches to offer healthier life opportunities to future generations because of rapid industrialization. In green technological studies, the utilization of biomass/biowaste and non-toxic materials with biosynthesis method increase both environmental sustainability and awareness. Sustainable and eco-friendly materials derived from natural products have great potential to create alternatives to traditional materials used in various fields such as biomedical, electronics, agriculture and food[1]. Nature offers unlimited resources in studies carried out in accordance with green technology. Green carbon dots that can be derived from raw materials are popular in the domain of carbon nanomaterials because of their eco-friendly and beneficial properties, with the inclusion of bright luminescence, good photostability, low cytotoxicity, excellence biocompatibility, simple surface modification and high chemical inertness, and thereby so many researchers have interested with this advance in recent years[2–5].

Carbon dots (CDs) were discovered during the purification of single-walled carbon nanotubes by Xu *et al.*[6] in 2004 and since then CDs, a new member of the popular carbon-based nanomaterials family, with sizes of less than 10 nm, have gained enormous interest in several fields[7,8]. CDs have great potential thanks to their green and beneficial facilities to replace traditional fluorescent semiconductor quantum dots which have critical disadvantages, like high cost, toxicity with heavy metals and chemicals, crucial health and environmental risk[9]. CDs utilizations have been broadly studied in biomedical areas such as sensors[10], bioimaging[11], wound healing[12] fields so there have been reported diverse studies about carbon dots.

A lot of synthesis methods have been used as electrochemical method[13], hydrothermal method[14], pyrolysis[15], microwave method[16], arc discharge[17] and laser ablation[18]. There is always a need to improve new perspective using biomass and non-toxic ingredients from nature which are best carbon precursors for the preparation of green CDs via green synthesis and in addition, the utilization of biomass precursors is possessed of very valuable properties such as cheap cost, easy attainability, abundant precursors and good feasibility[19,20]. Accordingly, sustainable and green natural carbon precursors are an excellent option for green synthesis of the carbon dots and they have received much attention since some simple and low-cost methods have been reported. Many biomass carbon precursors (are categorized with title, for example fruit, vegetables, human derivative, waste materials etc.[21] such as aloe vera[22], pine apple peel[23],egg shell membran[24],yoghurt[25] have been used in various biomedical fields.

Biopolymers that contribute to green technology developments in terms of sustainability are becoming popular materials for multiple applications especially in the biomedical field[26,27]. Alginate is most preferred among biopolymers due to its biocompatible, water absorption, non-toxic, easy and safe usage in forming, has recently been widely used as a hydrogel, which has applications in areas such as tissue engineering, biosensing, drug delivery etc[28,29]. In addition, novel hybrid materials based on CDs retain their obvious excellent polymer properties with their unique optical properties. CDs combined with hydrogels are immensely preferred owing to their low toxicity, biocompatibility, easy fabrication, rapid sterilization and create an efficient platform for using with nanoparticles and enhancing their stability through immobilizing them[30–32].

Quince (*Cydonia oblonga*) is a fruit that has abundant nutrient value, yellow, plumy, looks like apple which is very effective in human health and mostly raised in Turkey and Iran. Each mature fruit contains about six to fifteen seeds inside[33,34]. When the seed shell of a quince encounter water, gelation, also known as mucilage, occurs due to their hydrocolloids. Also, quince seed mucilage (QSM) has three components: cellulose, water-soluble polysaccharides and amino acids[34–37]. The seeds have been utilized in food cooking and skin healing with their gel structure for years by Turkish folks. Quince seed mucilage is used on the body among the people because of its healing properties. In scientific studies, it has been proven that it heals skin wounds faster than phenytoin cream[38]. QSM has a high-water absorption capacity due to its structure. This property can serve as an auxiliary biomaterial in biomedical applications[39]. QSMs as green and renewable biomaterial, are thought as potential smart biomaterial to be used in different biomedical and other industrial applications because of their ionic strength, produced from waste food, the capacity of stabilizing agent, being low-cost, eco-friendly. They have a high swelling rate rather than other polysaccharides like guar gum, arabinoxylan etc[26].

Opium Poppy is grown to for its opium and oil seed in Turkey, India, China and Czechoslovakia[40,41]. Opium poppy seed has been used as a plant for alternative medicine for many years by folks. It has many painkiller alkaloids (such as morphine, codeine, papaverine etc.) and has rich in protein and linoleic acid which can lower blood cholesterol. Poppy seeds contain 46.2-49.4% oil and 21.5-23.5% protein. In addition, poppy seed oil is high quality and rich in content[40–42]. In literature, studies in the biosensing field based on carbon dots with poppy seeds have not been found. All of these components are abundant with carbon, oxygen and nitrogen sources. Accordingly, poppy seeds have been determined to be quite suitable for carbon dots production. The use of this material for carbon dot synthesis has many advantages such as good water solubility, low cost, less environmental pollution, simple and easy production.

There are still requirement applications for green, basic, cheaper and movable as with the purpose of detecting heavy metal ions and in addition carbon nanomaterials are extensively utilized in these applications[43]. Iron ions are one of the most important nutrient elements encountered in drinking water, oceans, rivers and even in foods[44]. Although there are many benefits to our body system, the overage of iron causes various diseases such as kidney disease, Alzheimer's disease, liver damage etc[45]. Since people have been exposed to iron ions in recent years due to the rapid progress of the industry, it is very valuable to discover cheaper, faster, green methods instead of traditional methods. Because traditional methods involve complex equipment and long analysis steps[46], therefore, it is necessary to develop methods that can detect heavy pollutants in the water via a portable, simple, fast and low-cost way for a healthy future.

In pursuit of this aim, herein, this work demonstrates a non-toxic, low-cost, easy and simple application with green CDs derived from poppy seeds to detect Fe^{3+}. For the first time, CDs were synthesized from poppy seeds (P-CDs) *via* pyrolysis treatment and combined with alginate matrix and QSM.The purpose of the film material is to create a platform from sustainable material and a useful detection structure for CDs. We reported a new hybrid film including of P-CDs (HF/P-CDs) have great fluorescence property under UV light.

In addition, we followed a different road from the literature in the study process. In order to reduce water and energy consumption, the selectivity of the P-CDs by using 10 metal ions was examined only on HF/P-CDs with the naked-eye. Thus, the sensitivity of both P-CDs and HF/P-CDs to metal ions was discovered in one step.

Moreover, fluorescence analysis processes were carried out only with iron ions for saving water, energy and time.Briefly, a green and ecofriendly approach was developed in terms of both the synthesis of green CDs and the biopolymers used in all studies. This work was shown that the HF/P-CDs have a great potential as a naked-eye and turn-off detection film material.

Experimental Section

Materials

Opium poppy seeds and quince fruit were purchased from a local market in Pamukkale, Denizli. Alginic acid sodium salt and glycerin were purchased from Sigma-Aldrich (the United States). Glycerine was purchased from Tekkim Chemistry (Turkey). Calcium chloride ($CaCl_2$) was purchased from Merck (the Czech Republic). The deionized water was prepared in the lab. Metal ions were purchased from Sigma-Aldrich ($FeCl_3$), Tekkim Chemistry ($BaCl_2.2H_2O$, $MgCl_2.6H_2O$, $ZnCl_2$, KCl, $Pb(NO_3)_2$, $AlCl_3.6H_2O$, $CaCl_2.2H_2O$), Acros Organics ($HgCl_2$) and Merck ($CuCl_2$).

Instruments

Structural, morphological and optical properties of obtained materials were investigated by High Resolution Transmission Electron Microscope (HR-TEM), Dynamic Light Scattering (DLS), Fourier transform infrared spectroscopy (FTIR), UV–VIS Spectroscopy, Fluorescence Spectroscopy and UV-transilluminator. Fluorescence properties of nanomaterials were examined with the naked-eye in UV light by using Vilber Lourmat UV-Transilluminator (France). HR-TEM images of P-CDs were recorded on a Hitachi HT7800 (Japan). A hydrodynamic radius of P-CDs was determined using DLS measurement on Malvern ALV/CGS-3 (the United Kingdom). FTIR measurements were done using a Thermo Scientific Nicolet iS50 (Germany). The UV-VIS absorption and fluorescence spectra of the samples were recorded using the Optizen Pop Model (South Korea) and Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer (the United States), respectively.

Methods

Synthesis of carbon dots from opium poppy seeds

The pyrolysis method was preferred in the production of P-CDs.The fluorescent P-CDs were prepared with the following procedure: 40 g of poppy was washed thoroughly with distilled water. Samples were heated at 110°C for 1h in a dry oven for pre-drying and later were heated at 250 °C for 4h.After the samples were cooled at room temperature, they were powdered in a porcelain mortar. The obtained powders were centrifuged with pure water for 15 min at a speed of 13800 rpm. Then the obtained brown-yellow solution was filtered to remove precipitates by syringe filter (0.2 µm-28mm). Afterward, the final limpid solution was used for its spectroscopic characterization.

Synthesis of quince seed mucilage

The collected quince seeds were washed with distilled water and it was dried at room temperature. Then, 75 g of seeds were mixed with 50 mL of distilled water in a glass beaker. After keeping for 1 day, the mixture was stirred with a spatula and the seeds in the mucilage were picked up. Finally, the mucilage in the form of a clear gel was obtained.

Preparation of HF/P-CDs

Solvent-casting method was used for fabricating the hybrid film. This process was followed by the addition of sodium alginate solution to quince seed mucilage and P-CDs separately and respectively. Sodium alginate solution (5% (w/v)) was prepared for the film and then quince seed mucilage (40% v/v) was added to the solution. Later, glycerine (10% v/v) was added to the solution. In the final step, P-CDs (15% v/v) were added to the solution. The mixture was stirred at 10 min and 100rpm. The resulting mixture was cast into a petri dish and left at room temperature for 1 day to clear the bubbles formed on the film. And then it was dried in heating magnetic stirrers at 45°C for 4h, slowly. The dried films were then peeled off from the Petri dish. The film was stirred in 1M, 100 mL of $CaCl_2$ for 15 min. Then, the films dried at room temperature were stored in a desiccator. For the characterization steps, a pure film was prepared in the same way without the P-CDs.

Naked-eye and turn-off detection of heavy metal ions on HF/P-CDs

At this stage, the aim is to explore the selectivity of the prepared hybrid film-P/CDs towards 10 metal ions and its potential as a naked eye and a turn-off detection material. Meanwhile, in this study, contrary to the literature[7,47,48], it has been tried to show that successful results can be obtained in a short way by removing some stages such as the double fluorescence analysis process of both the HF/P-CDs and liquid carbon dots with metal ions. Our point in here is to achieve efficient results in an easy-step way and to develop an environmentally friendly approach for future studies. The detection was done by placing HF/P-CDs (1×1 cm) in the respective metal ions solutions, viz., $FeCl_3$, $Pb(NO_3)_2$, $BaCl_2.2H_2O$, $HgCl_2$, $CuCl_2$, $MgCl_2.\ 6H_2O$, $ZnCl_2$, KCl, $CaCl_2.2H_2O$ of concentration 100 ppm at room temperature. The films were then removed from the metal ion solutions after 12 h and dried at room temperature.

P-CDs as sensing to Fe^{3+} ions

To investigate whether P-CDs are stable about damping effect in presence of different concentration of Fe^{3+}, on the fluorescence intensity of as-prepared P-CDs were recorded by fluorescence measurements. The P-CDs were added to Fe^{3+}ions prepared at four different concentrations (0.5 ppm, 5.0 ppm, 25.0 ppm and 50.0 ppm) at room temperature. The mixtures were stirred and then the fluorescence spectra of the mixtures were investigated via fluorescence spectroscopy.

Results and Discussion

Structural and morphological characterization

HR-TEM analysis

The size and nature of the phase of P-CDs were examined by High-Resolution Transmission Electron Microscopy (HR-TEM). Firstly, the surface morphology of P-CDs was characterized by HR-TEM. HR-TEM images showed in Fig. 1. These P-CDs were spherical and well-stand separately. The sizes of the carbon dots range from 18 nm to 200 nm (Fig. 1B and Fig. 1C). It is assumed that carbons dots have less than 18 nm when further zoom to the atomic level the size of the P-CDs at 50 nm (Fig. 1D). It is seen that carbon dots with sizes less than 10 nm can be obtained when closer.

DLS analysis

In the experimental study, the polydispersity index (PDI) and hydrodynamic radius (R_H) of the carbon dots were characterized by the DLS method[49,50]. With the experimental measurement results of the DLS method, particles R_H of P-CDs smaller than 10 nm were obtained over the PDI consistency. The particle R_H of the P-CDs was determined by DLS as an average of 4.79 nm (PDI= 0.278-0.331). In Fig. 2, the R_H of the DLS measurement results of P-CDs are given in the graph. It has also been observed that the measurement results of the particle sizes revealed in the TEM method analysis and the measurement results obtained from the DLS method are compatible with each other.

FT-IR analysis

The functional groups on the HF surface, HF/P-CDs and HF/P-CDs+Fe^{3+} were determined by the FTIR spectrum (Fig. 3). The broadening of the peak around 3300 cm^{-1} in the FTIR spectra shows hydrogen bonding

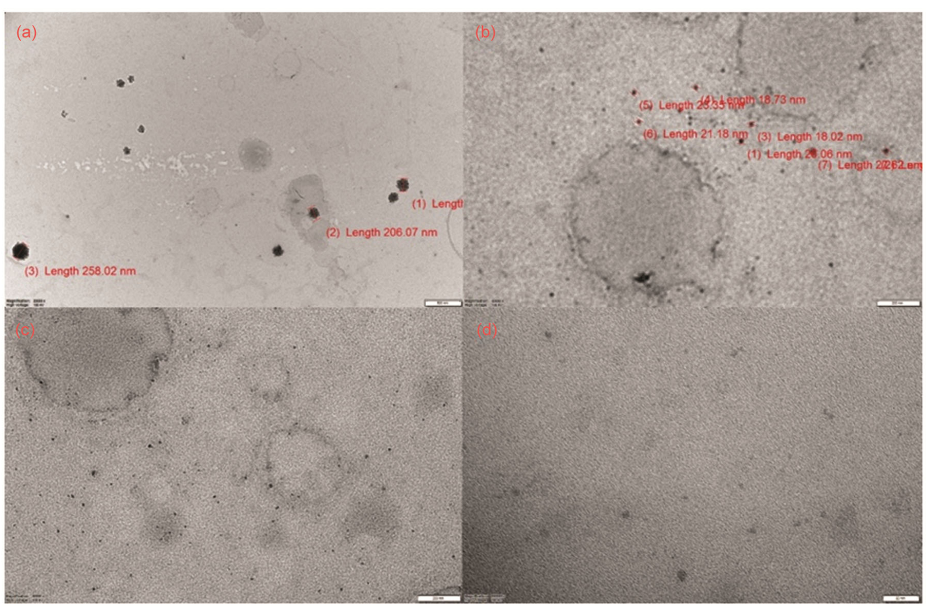

Fig. 1 — (a) 500nm,(b) and (c) 200nm,and (d) 50 nm in scales HR-TEM images of P-CDs.

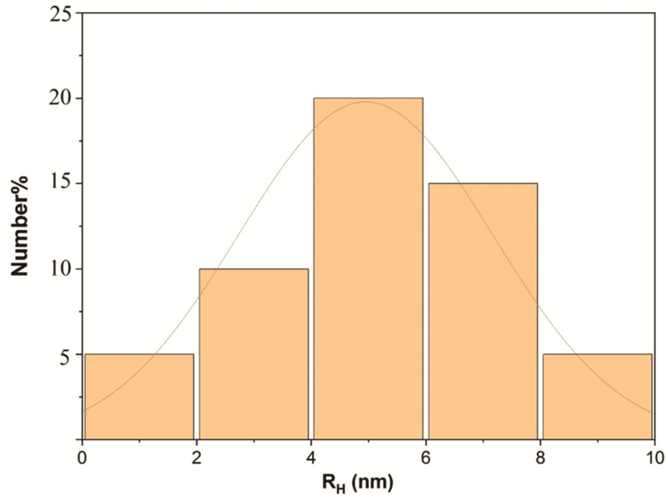

Fig. 2 — Hydrodynamic radius (RH) of P-CDs by the DLS method.

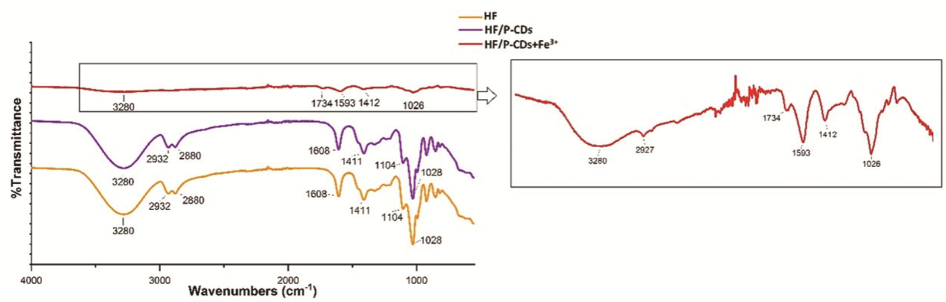

Fig. 3 — FTIR spectra of HF, HF/P-CDs and HF/P-CDs+Fe^{3+}.

among the −OH groups of alginate, glycerine, and the P-CDs system[51]. The peak bands at 2932 and 2880 cm^{-1} corresponds to C−H stretching[52,53].

The peaks at 1607 cm^{-1} and 1409 cm^{-1} are attributed to the asymmetric and symmetric stretching vibration of carboxylic acid groups[54]. The bands at 1104 and 1028 cm^{-1} belongs to the C–O and –C–O–C glycosidic linkage, respectively[55]. In all graphics, no notable differences in FTIR peaks are observed in both HF and HF/P-CDs, so that shows the presence of the same functionalities for the chemical bonds[22]. To point out, the asymmetric vibration peak of carboxylic acid group occurs at 1607, while in HF/P-CDs+Fe^{3+}, this peak shifts to a higher wave number and splits into two peaks[56]. It appears at 1734 and 1593 cm^{-1} for Fe^{3+}. This work proved that the fluorescence of P-CDs located in HF by UV light. Further, the reason for the same peaks in both HF/P-CDs and HF maybe could explain via physical interaction for interplay between the P-CDs and HF.

Optical properties of P-CDs and HF/P-CDs

P-CDs and HF/P-CDs showed excellent fluorescence properties under standard UV light with a UV transilluminator device.The appearance of the oily structure from poppy seeds when crushed after cooking is thought to help increase the fluorescence of P-CDs. Figure 4 shows the photograph of P-CDs, HF, HF/P-CDs under daylight and UV light.

UV-VIS Spectroscopy

The formed materials were examined for optical analysis. The photograph of P-CDs, HF/P-CDs, HF under daylight and UV light is exhibited in Fig.4. The color of P-CDs is yellow under daylight and bluish under the UV light. Blue fluorescent outlook under UV light verifies the fluorescence offered by the P-CDs system. The UV-VIS spectrum disclosed broad absorbance from 200 to 600 nm (Fig. 5). In Fig.5, for yellow line, the broad weak absorption peak from 280 nm was observed which is contributed to the π-π* transition of C=C bonds for aromatic sp^2 hybridization and a shoulder low peak came out at 380 nm which is contributed to n-π* energy transition of C=O bond, respectively. In addition, the peak at nearly 260 to 280 nm and a shoulder Fig. 5 out at nearly 300–380 nm corresponding to n-π* transition in graph suggest

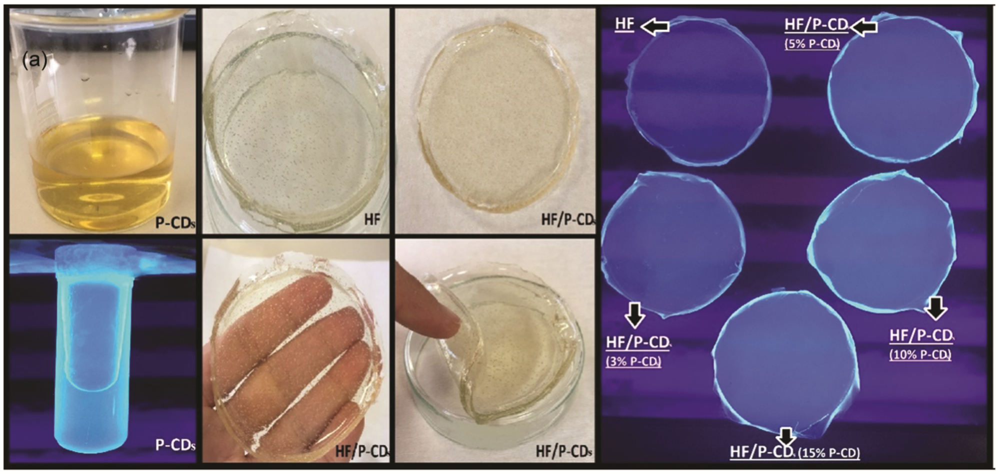

Fig. 4 —Photograph of P-CDs, HF and HF/P-CDs under daylight and UV light.

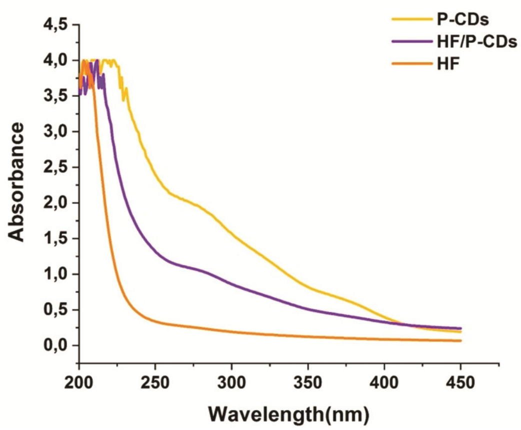

Fig. 5 — UV–VIS absorption spectrums of P-CDs, HF/P-CDs and HF.

the occurrence of CDs at sometimes, and these results are in suit with the data provided in the previous articles[57–60].

The color of HF/P-CDs is amber under daylight and bluish under the UV light. Additionally, it was observed that the fluorescence of HF increased as the amount of P-CDs in the mixture increased under UV light (Fig. 4). In Fig. 5, for purple line, the same as like P-CDs, there is a broad weak peak at 280 nm except the second peak at 380 nm. And last, in Fig. 5, for orange line, there is no peak in the graph. By comparison with HF and HF/P-CDs for this analysis, a peak raise and enhancement are observed when P-CDs are located in the film. Also, the HF has gained fluorescent properties with the addition of P-CDs in under UV light. On the other hand, P-CDs have been observed to have better optical properties compared to others, but a nano-hybrid films like HF/P-CDs should be improved for the optical research. Moreover, there is no absorbance in the visible region and so P-CDs and HF/P-CDs could be used as a UV blocking material[22].

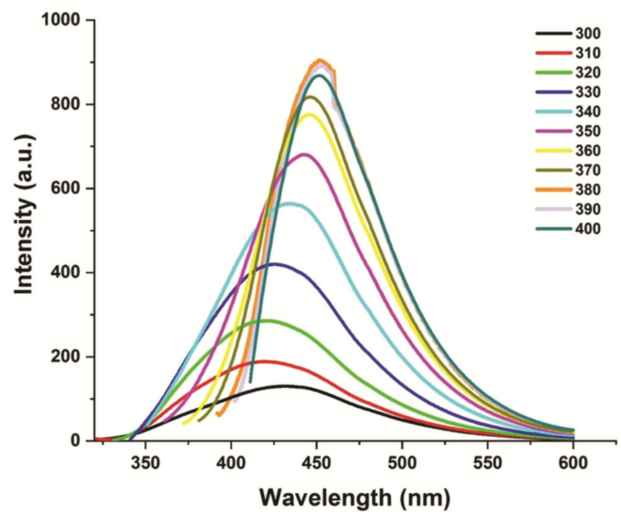

Fig. 6 — Fluorescence spectra of P-CDs at various excitation wavelengths in the range from 300 nm to 400 nm with 10 nm increment.

Fluorescence spectroscopy

The fluorescence intensity of as-prepared P-CDs depended on the excitation wavelength was shown in Fig. 6. Normalized emission spectra of P-CDs were recorded using the range of 300–400 nm excitation wavelengths. The intensity was increased gradually with increasing excitation wavelength from 300 to 400 nm at 10 nm increments. The P-CDs showed the maximum fluorescence intensity at 450 nm with an excitation wavelength of 380 nm. The fluorescence intensity and emission wavelengths of the P-CDs depend on the excitation wavelengths and by the way this is prevalent information about fluorescence

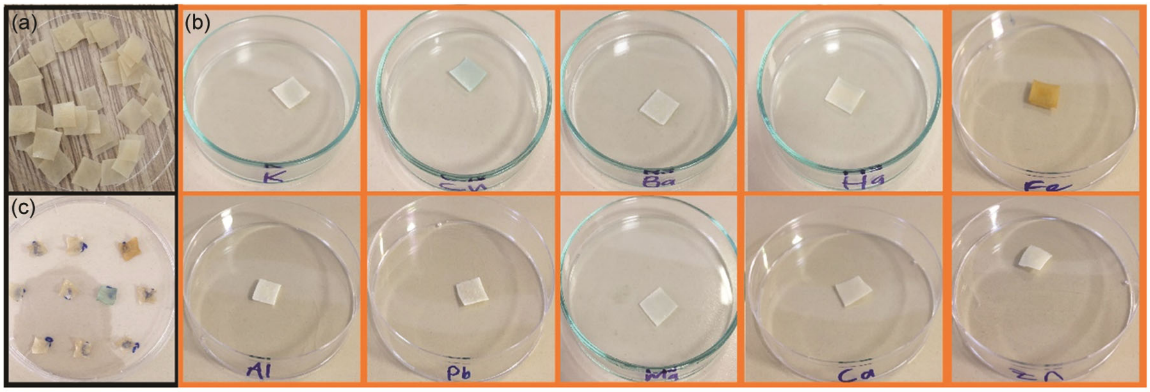

Fig. 7 — (a) The photograph of HF/P-CDs (1x1cm) under daylight; (b) Colour changes of HF/P-CDs after immersed in 10 metal ions with naked-eye, separately and (c) Dried after 12 h at room temperature.

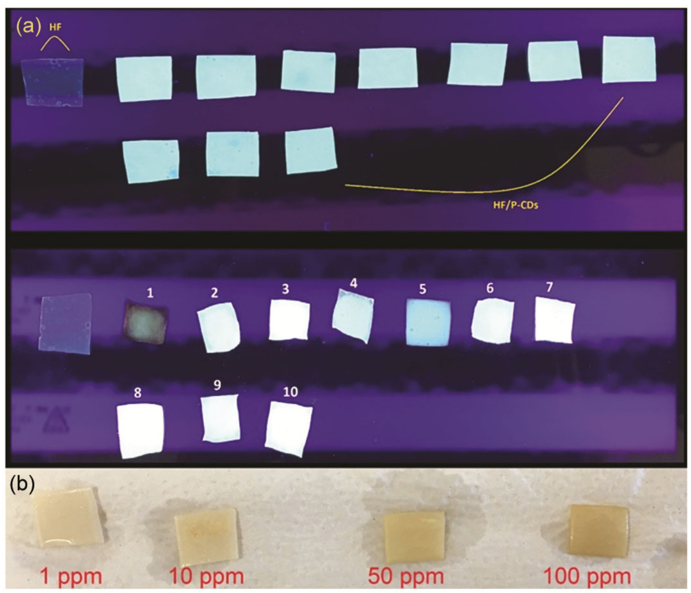

Fig. 8 — (a) The photograph of HF, HF/P-CDs without metal ions and color changes of HF/P-CDs after immersed in 10 metal ions under UV-light and (b) Colour changes of HF/P-CDs (1×1cm) with different concentration of Fe^{3+}.

properties of CDs. The fluorescence intensity and emission wavelengths of the P-CDs depend on the excitation wavelengths and by the way this is prevalent information regarding to fluorescence properties of CDs which is depend on to different sizes of the CDs and the distribution of different surface defects of CDs[61–65].

Fe^{3+} detection of P-CDs

As described in the method, the interaction between the HF/P-CDs film (1×1) and 10 metal ions (100 ppm) was observed with the naked eye. The result is shown visually in Fig. 7.

In the films, was observed intense yellow color change to Fe^{3+} ion and little bluish color change to Cu^{2+}. Later, in order to observe the fluorescence change against metal ions, the fluorescence of the films was examined by the UV transilluminator Fig. 8 (a). As visually detected, the fluorescence of the film was quenched with Fe^{3+} ion. Thus, the sensitivity of both P-CDs and HF/P-CDs film to Fe^{3+} ion was discovered in one-step. So, HF/P-CDs film is a highly potential practical platform for a naked-eye and turn-off detection material. Fig. 8 (b) shows, the color of the hybrid film increased towards a more intense yellow-brown color with increments of the Fe^{3+} ion concentration (1, 10, 50 & 100 ppm).

Fluorescence measurements were made with only P-CDs for better results because the P-CDs have higher absorbance data than other HF or HF/P-CDs. In the study, fluorescence measurements were made with P-CDs in order to obtain a more efficient and

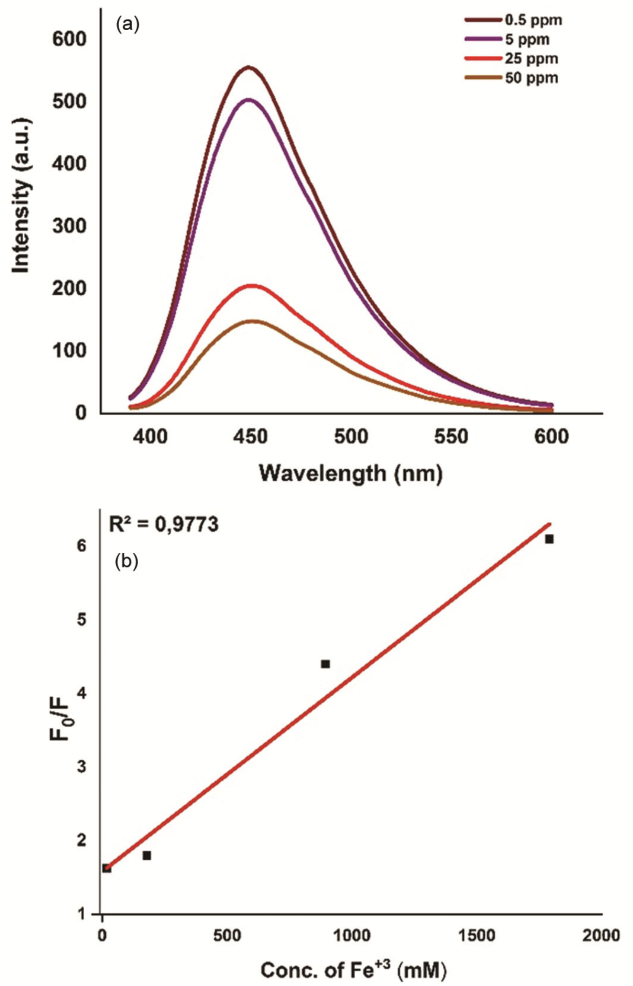

Fig. 9 — (a) The fluorescence intensity of P-CDs at different concentrations of Fe^{3+} ions and (b) Plot of F_0/F with the concentration of Fe^{3+}.

direct result. Finally, fluorescence intensity between the P-CDs and different concentrations of Fe^{3+} ions (0.5 ppm, 5 ppm, 25 ppm, 50 ppm) were analyzed at room temperature at an excitation wavelength of 380 nm. Here, concentrations of Fe^{3+} ions were lowered to find a lower detection range. The fluorescence intensity of P-CDs decreased with increasing Fe^{3+} concentration In Fig. 9 (a).This change showed and proved the sensitivity of P-CDs to Fe^{3+} ions. This result also confirmed the experimental results between HF/P-CDs and metal ions. The quenching efficiency was analyzed with the Stern-Volmer equation. This equation;

$$F_0/F=1+K_{SV}[Q] \quad \ldots (1)$$

where K_{SV} is the Stern-Volmer quenching constant, $[Q]$ is the concentration of Fe^{3+}, F_0 and F are the fluorescence intensities at 450 nm in the absence and presence of Fe^{3+} ions, respectively. Mostly, fluorescence quenching can be described via dynamic or static quenching[66]. Fig. 9 (b) showed good linearity in the range of 9×10^{-6} mM-9×10^{-4} mM (R^2=0.9773).The detection limit (LOD) gives information about a sensor because it supplies data on the lowest analyte concentration that a sensor can determine[67,68]. The detection limit includes mathematical calculation in different ways, such as the standard deviation of the blank or standard deviation of the net signal. The detection limit (LOD) was determined from 3.3×s/k equation, where s was the standard deviation from the response and k was the slope of Fig. 9 (b)[69]. The LOD was determined 0.356 mM.

Conclusion

There is a need to greener and low-cost materials used in scientific studies to reduce energy and water consumption because of rapid globalization. In this work, we fabricated a fluorescent hybrid film that is composed of quince seed mucilage, alginate and CDs from poppy seeds. Carbon dots were synthesized from poppy seeds and it was combined with quince seed mucilage and alginate for the first time. The nano size of the P-CDs was determined with the HR-TEM and the hydrodynamic radius was found 4.79 nm with the DLS. A new hybrid film for the determination of Fe^{3+} ions was successfully developed based on fluorescence quenching by the naked-eye and turn-off detection. The LOD was determined 0.356 mM and the linearity was found R^2 = 0.9773. Along with the good linearity obtained, a linear fluorescence quenching is predicted to occur at lower Fe^{3+} concentration ranges. Obtaining the same peaks for both HF and HF/P-CDs by FTIR is interpreted as the carbon dots being positioned by physical interaction within the hybrid material. To point out, both the green prepared P-CDs and HF/P-CDs are environmentally friendly and the preparation method is simple, green, cheaper showing that the P-CDs and the HF/P-CDs have a good potential detection material as fluorescent sensors. Also, this study proved that efficient results can be obtained from short and green routes by saving time, energy and water. Additionally, the obtained hybrid material has a multifunctional form used in similar studies such as drug release and tissue engineering, apart from the detection material.

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References

1 Li Y C E, ACS *Biomater Sci Eng*, 5 (2019) 2079.
2 De B & Karak N, *J Mater Chem A*, 5 (2017) 1826.
3 Liu J, Li R & Yang B, *ACS Cent Sci*, 6 (2020) 2179.
4 Kour R, Arya S, Young S J, Gupta V, Bandhoria P & Khosla A, *J Electrochem Soc*, 167 (2020) 037555.
5 Kang C, Huang Y, Yang H, Yan X F & Chen Z P, *Nanomater*, 10 (2020) 1.
6 Xu X, Ray R, Gu Y, Ploehn H J, Gearheart L, Raker K & Scrivens W A, *J Am Chem Soc*, 126 (2004) 12736.
7 Carvalho J, Santos L R,Germino J C,Terezo A J, Moreto J A, Quites F J & Freitas R G, *Mater Res*, 22 (2019) 12736.
8 Li Y, Xu X, Wu Y, Zhuang, J, Zhang X, Zhang H, Lei B, Hu C & Liu Y, *Mater Chem Front*, 4 (2020) 437.
9 Chu K W, Lee S L, Chang C J & Liu L, *Polymers*, 11 (2019) 689.
10 Qu Y, Yu L, Zhu B, Chai F & Su Z, *New J Chem*, 44 (2020) 1500.
11 Yang X, Zhuo Y, Zhu S, Luo Y, Feng Y & Dou Y, *Biosens Bioelectron*, 60 (2014) 292.
12 Kandra R & Bajpai S, *Arab J Chem*, 13 (2020) 4882.
13 Wang C I, Wu W C, Periasamy A P & Chang H T, *Green Chem*, 16 (2014) 2509.
14 Xu J, Lai T, Feng Z, Weng X & Huang C, *Luminescence*, 30 (2014) 420.
15 Hu Y, Wang Y, Wang C, Ye Y, Zhao H, Li J, Lu X, Mao C, Chen S, Mao J, Wang L & Xue Q, *Carbon NY*, 152 (2019) 511.
16 Gul U, Kanwal S, Tabassum S, Gilani M A & Rahim A, *Microchim Acta*, 187 (2020) 135.
17 Naik G G, Alam M B, Pandey V, Mohapatra D, Dubey P K, Parmar A S & Sahu A N, *J Fluoresc*, 30 (2020) 407.
18 Nguyen V, Zhao N, Yan L, Zhong P, Nguyen V C & Le P H, *Mater Res Express*, 7 (2020) 015606.
19 Meng W, Bai X, Wang B, Liu Z, Lu S & Yang B, *Energy Environ Mater*, 2 (2019) 172.
20 Wang M, Wan Y, Zhang K, Fu Q, Wang L, Zeng J, Xia Z & Gao D, *Anal Bioanal Chem*, 411 (2019) 2715.
21 Sharma V, Tiwari P & Mobin S M, *J Mater Chem B*, 5 (2017) 8904.
22 Deb A, Saikia R & Chowdhury D, *ACS Omega*, 4 (2019) 20394.
23 Vandarkuzhali S A A, Natarajan S, Jeyabalan S, Sivaraman G, Singaravadivel S, Muthusubramanian S & Viswanathan B, *ACS Omega*, 3 (2018) 12584.
24 Ye Z, Zhang Y, Li G & Li B, *Anal Lett*, 53 (2020) 2841.
25 Dinc S, Kara M, Demirel Kars M, Aykul F, Cicekci H & Akkus M, *Appl Phys A Mater Sci Process*, 123 (2017) 1.
26 Hussain M A, Muhammad G, Haseeb M T & Tahir M N, *Quince Seed Mucilage: A Stimuli-Responsive/Smart Biopolymer*(Springer, Cham), (2019) 127.
27 Kumar Gupta G, De S, Franco A, Balu A M & Luque R, *Molecules*, 21 (2015) 48.
28 Şimşek T & Keyf S, *Karaelmas Sci Eng J*, 8 (2018) 482.
29 He Y, Zhang N, Gong Q, Qiu H, Wang W, Liu Y & Gao J, *Carbohydr Polym*, 88 (2012) 1100.
30 Ganguly S, Das P, Banerjee S & Das N C, *Funct Compos Struct*, 1 (2019) 022001.
31 Naik V M, Gunjal D B, Gore A H, Anbhule P V, Sohn D, Bhosale S V & Kolekar G B, *Anal Bioanal Chem*, 412 (2020) 2993.
32 Suntornnond R, Tan E Y S, An J & Chua C K A, *Sci Rep*, 7 (2017) 1.
33 Silva B M, Andrade P B, Ferreres F, Seabra R M, Oliveira M B P P & Ferreira M A, *Nat Prod Res*,19 (2005) 275.
34 Kozlu A & Elmacı Y, *J Food Process Preserv*, 44 (2020) 1.
35 Ghafourian M, Tamri P & Hemmati A, *Jundishapur J Nat Pharm Prod*, 10 (2015) 10.
36 Ashraf M U, Muhammad G, Hussain M A & Bukhari S N A, *Front Pharmacol*, 7 (2016) 1.
37 Kirtil E & Oztop M H, *Food Res Int*, 85 (2016) 84.
38 Hemmati A A & Mohammadian F, *J Herbs Spices Med Plants*, 7 (2000) 41.
39 Tamri P, Hemmati A & Boroujerdnia M G, *Int J Surg*, 12 (2014) 843.
40 Özcan M M & Atalay Ç, *Grasasy Aceites*, 57 (2006) 169.
41 Sharma A, Parul S & Singh N, *Int J Food Nutr Sci*, 4 (2015) 84.
42 Sethi K L, Sapra R L, Gupta R, Dhindsa K S & Sangwan N K, *J Sci Food Agric*, 52 (1990) 309.
43 Afreen S, Talreja N, Chauhan D & Ashfaq M, *Multifunctional Hybrid Nanomaterials Sustainable Agri-Food Ecosystems* (Elsevier, Amsterdam), (2020) 335.
44 Zhang S, Li J, Zeng M, Xu J, Wang X & Hu W, *Nanoscale*, 6 (2014) 4157.
45 Que E L, Domaille D W & Chang C J, *Chem Rev*, 108 (2008) 1517.
46 Liu J, Ren X, Meng X, Fang Z & Tang F, *Nanoscale*, 5 (2013) 10022.
47 Wu Q, Wang X, Rasaki S A, Thomas T, Wang C, Zhang C & Yang M, *J Mater Chem C*, 6 (2018) 4508.
48 Gogoi N, Barooah M, Majumdar G & Chowdhury D, *ACS Appl Mater Interf*, 7 (2015) 3058.
49 Özcan Y, İde S, Jeng U, Bütün V, Lai Y H & Su C H, *Mater Chem Phys*,138 (2013) 559.
50 Özcan Y, Orujalipoor I, Huang Y C, Bütün V & Jeng U S, *Anal Lett*, 48 (2015) 2693.
51 Konwar A, Gogoi N, Majumdar G & Chowdhury D, *Carbohydr Polym*, 115 (2015) 238.
52 Majumdar S, Krishnatreya G ,Gogoi N, Thakur D & Chowdhury D, *ACS Appl Mater Interf*, 8 (2016) 34179.
53 Guo Z, Li Q, Li Z, Liu C, Liu X, Liu Y, Dong G, Lan T & Wei Y, *J Colloid Interf Sci*, 562 (2020) 224.
54 Choi Y, Ryu G H, Min S H, Lee B R, Song M H, Lee Z & Kim B S, *ACS Nano*, 8 (2014) 11377.
55 Davachi S M, Pottackal N, Torabi H & Abbaspourrad A, *Sci Rep*, 11 (2021) 1.
56 Konwar A & Chowdhury D, *RSC Adv*, 5 (2015) 62864.
57 Hoan B T, Tam P D & Pham V H, *J Nanotechnol*, 2019 (2019) 9.
58 Eda G, Lin Y Y, Mattevi C, Yamaguchi H, Chen H A, Chen I S, Chen C W & Chhowalla M, *Adv Mater*, 22 (2010) 505.
59 Ansi V A & Renuka N K, *Sens Actuat B Chem*, 264 (2018) 67.
60 Zulfajri M, Liu K C, Pu Y H, Rasool A, Dayalan S & Huang G G, *Chemosensors*, 8 (2020) 47.
61 Liu M L, Chen B B, Li C M & Huang C Z, *Green Chem*, 21 (2019) 449.

62 Liang Q, Wang Y, Lin F, Jiang M, Li P & Huang B, *Anal Methods*, 9 (2017) 3675.
63 Edison T N J I, Atchudan R, Shim J J, Kalimuthu S, Ahn B C & Lee Y R, *J Photochem Photobiol B Biol*, 158 (2016) 235.
64 Hola K, Bourlinos A B, Kozak O, Berka K, Siskova K M, Havrdova M, Tucek J, Safarova K, Otyepka M, Giannelis E P & Zboril R, *Carbon N Y*, 70 (2014) 279.
65 Li X, Zhang S, Kulinich S A, Liu Y & Zeng H, *Sci Rep*,4 (2014) 1.
66 Wang T, Wang A, Wang R, Liu Z, Sun Y, Shan G, Chen Y & Liu Y, *Sci Rep,* 9 (2019) 1.
67 Kellner R, Mermet J M, Otto M & Cases M V, *Analytical Chemistry: A Modern Approach to Analytical Science* (Wiley-VCH, Weinheim) (2004) 1209.
68 Demchenko A P & Dekaliuk M O, *Nanoscale*, 8 (2016) 14057.
69 ICH Q2 (R1): *Validation of Analytical Procedures: Text and Methodology* (Europian Medicines Agency, London) (2005).