

Fluorescent detection of chlorpyrifos using Mn(II)-doped ZnS quantum dots coated with a molecularly imprinted polymer

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Abstract We show that Mn(II)-doped ZnS quantum dots coated with an acrylamide-based molecularly imprinted polymer (MIP-coated QDs) can act as a fluorescent probe for the selective and sensitive detection of the insecticide chlorpyrifos (CPF). The fluorescence of the coated QDs is quenched on loading the MIP with CPF, and the effect is much stronger for the MIP than for the non-imprinted polymer. The MIP-coated QDs were characterized by fluorescence spectrophotometry, X-ray powder diffraction, and scanning electron microscopy. Under optimal conditions, the relative fluorescence intensity of the MIP-coated QDs decreases linearly with the increasing concentration of CPF in the 0.3–60 $\mu\text{mol L}^{-1}$ concentration range, and the detection limit is 17 nmol L^{-1} . The method has been used for the determination of CPF in spiked water samples and gave recoveries in the range from 87.1 to 94.5 % with relative standard deviations in the 2.9 to 6.5 % range. The method is simple, safe and inexpensive.

Keywords Molecular imprinting · Quantum dots · Fluorescent probe · Chlorpyrifos

Introduction

Chlorpyrifos [O, O-diethyl O-(3, 5, 6-trichloro-2-pyridyl) phosphorothioate] (CPF) is one of the most extensively

applied organophosphorus insecticides, which controls a broad spectrum of insects of economically important crops [1, 2]. Due to the non-polar nature of the CPF molecule, it possesses low water solubility ($\leq 2 \mu\text{g mL}^{-1}$) and readily partitions from aqueous to organic phases in the environment; therefore, the potential hazard of human exposure is high. CPF is considered a neurotoxin and endocrine disruptor [3]. CPF has been responsible for causing aquatic life toxicity in environmental water. Extensive usage of this compound leads to the accumulation of pesticide residues or their derivatives in soil, water and food.

Many methods have been described for determination of CPF including high performance liquid chromatography (HPLC) [4], gas chromatography (GC) [5, 6], liquid chromatography-mass spectrometry (LC-MS) [7], and capillary electrophoresis (CE) [8]. However, they require expensive equipment, skilled personnel and time-consuming steps of sample pretreatment [9]. Accordingly, it still remains a great challenge to develop a rapid, inexpensive and sensitive method for the detection of CPF in food and environmental analysis [10, 11].

Nowadays, quantum dots (QDs), a kind of semiconductor nanoparticles, have attracted a wide range of attention [12]. They have some unique characters, such as size tunability, narrow emission spectra but broad excitation spectra, strong signal intensity, high photo stability, and well biocompatibility [13]. The band width and maximum emission wavelength keep almost unchanged under the experimental concentration range. This is much better than the emission characteristics for typical organic dye species, which often have much broader and asymmetric emission profiles. Based on above advantages, in recent years, QDs have obtained huge development in many fields, such as biological markers [14], light-emitting diodes [15] and solar cells [16]. One major drawback that severely limits the use of common QDs (such as CdSe and

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CdTe) [17] in biomedical applications, particularly in the light of recent environmental regulations, is their toxicity [18].

In recent years, the emphasis has been shifted toward the fabrication of non-cadmium-based QDs. Cubic ZnS with a bulk band gap of 3.7 eV at room temperature is a common and attractive choice as a host semiconductor for producing QDs due to its low toxicity, low cost, and high stability [19]. A range of ZnS nanocrystals doped with different transition metals or rare-earth metal ions have been reported. Mn- and Cu-doped ZnS are two of the most well studied doped QDs because of their technologically suitable fluorescent properties [20]. Unfortunately, although those “direct” sensing approaches are very simple and highly sensitive, they lack an appropriate selectivity. Thus, improving selectivity of QDs based probes is very important.

Molecularly imprinted polymers (MIPs) are highly cross-linked polymers with recognition towards target molecules [21]. The synthesis of MIPs involves the formation of the template–monomer complexes through either covalent or non-covalent interactions, followed by a copolymerization with excess cross-linking agent [22]. After polymerization, the template is removed by washing with organic solvents [23]. In recent years, MIPs have attracted much attention due to their outstanding advantages, such as predetermined recognition ability, stability, relative ease and low cost of preparation, and potential application to a wide range of target molecules [24]. Combining the high selectivity of MIPs with the fluorescent properties of QDs could develop a new method for target analyte recognition [25].

In this work, the aim was to develop a novel and rapid method for determination of CPF in water samples. An eco-friendly fluorescent probe, MIP-coated QDs, was successfully fabricated by using CPF as the template molecule. The MIP-coated QDs were characterized by Fourier transformed infrared spectroscopy (FT-IR), scanning electron microscope and X-ray diffraction. The relationship between MIP-coated QDs and CPF was investigated. Then the MIP-coated QDs were used as a fluorescence probe for detection of CPF in water samples.

Experimental

Samples and reagents

The standard of CPF and acephate were purchased from Gt. Agro (Guangxi, China, <http://www.gtagro.cn/>). The standard of chlorpyrifos-methyl (CM) was purchased from energy chemical (Shanghai, China, <http://www.energy-chemical.com/>). Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) was purchased from Shuangchuan (Tianjin, China, <http://www.shuangchuanchem.com/>). Manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) was purchased from Bodi

(Tianjin, China, <http://bdhg.company.lookchem.cn/>). Sodium Sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was purchased from Kaitong (Tianjin, China, <http://www.tjktxhsj.com/>). Oleic acid, ethanol, methanol, acrylamide (AM), azoisobutyronitrile (AIBN) and sodium hydroxide (NaOH) were obtained from Kermel (Tianjin, China, <http://www.chemreagent.com/>). Ethylene glycol dimethacrylate (EDGMA) was purchased from Aladdin (Shanghai, China, <http://www.aladdin-reagent.com/>). All chemicals employed in this study were of analytical grade. High-purity water was obtained from a Milli-Q water system (Millipore, Billerica, MA, USA, <http://www.millipore.com/>).

The standard stock solution of CPF was prepared by dissolving CPF in methanol, and the concentration was 3 mmol L^{-1} . It was stored in a refrigerator at 4 °C.

Three river water samples were collected from Harbin (China). All water samples were stored in a refrigerator at 4 °C.

Apparatus

Fourier transform infrared (FT-IR) spectrum of the MIP-coated QDs was recorded with FT-IR360 spectrometer (Nicolet, Madison, WI, USA, <http://www.artisan-scientific.com/69062.htm>) using KBr method. The X-ray diffraction (XRD) spectrum was collected on a Shimadzu XRD-600 diffractometer (Kyoto, Japan, <http://www.shimadzu.com.cn/>) with Cu $\text{K}\alpha$ radiation. The morphology of MIP-coated QDs was observed with a scanning electron microscopy (SEM, FEI Sirion, Philips, Netherlands, <http://www.philips.com.cn/>). Fluorescence intensity studies were carried out at room temperature by using Perkin-Elmer LS-55 fluorescence spectrometer (Maryland, USA, <http://www.perkinelmer.com.cn/>) which was equipped with a plotter unit and a quartz cell. A KQ5200E ultrasonic apparatus (Kunshan Instrument, Kunshan, China, <http://www.ks-csyq.com/>) was used for making samples dispersed evenly.

Synthesis of molecularly imprinted polymer coated quantum dots

The synthesis process of MIP-coated QDs involves two major steps: the first step is the synthesis of the Mn-doped ZnS QDs, and the second one is the surface imprinting of polymers onto the oleic acid modified Mn-doped ZnS QDs.

The synthesis method of Mn-doped ZnS QDs was shown as follows. At first, 25 mmol of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 2 mmol of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 80 mL of water were kept stirring for 20 min under the protection of nitrogen gas. Then, 10 mL, 25 mmol $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution was added dropwise into the mixture [26]. After being stirred for 30 min, 4 mL of oleic acid was added for modifying the Mn-doped ZnS QDs. Finally, the modified Mn-doped ZnS QDs was obtained after centrifuging and being washed with ethanol three times.

The synthesis method of MIP-coated QDs was carried out as follows. CPF (1 mmol), AM (4 mmol), and modified Mn-doped ZnS QDs obtained from above procedure were dispersed into 150 mL ethanol. Then AIBN (0.1 g) and the cross-linker EGDMA (10 mmol) were added. The mixture was heated at 60 °C and stirred at 300 rpm in a water bath for 24 h. Then the template was removed by Soxhlet extraction with methanol: acetic acid (19:1, v/v) until no analyte was detected. After dried in vacuum, MIP-coated QDs was obtained.

The non-molecular imprinted polymer-coated Mn-doped ZnS QDs (NIP-coated QDs) were prepared using the same procedure without addition of the template CPF.

Fluorescence analysis

Fluorescence analysis was performed on Perkin Elmer LS-55 fluorescence spectrometer. The spectra were recorded in the wavelength range of 350–750 nm upon excitation at 325 nm. Slit widths (10 nm), scan speed (200 nm min⁻¹) and excitation voltage (750 V) were kept constant within each data set and each spectrum was the average of three scans. Quartz cell (1 cm path length) was used for all measurements.

Measurements of fluorescent response to chlorpyrifos

Thirty milligram MIP-coated QDs or NIP-coated QDs was added into a centrifuge tube, and then the given concentration of CPF solution was added. The solution pH was adjusted to 9.0 with sodium hydroxide. The constant volume was 30 mL. The fluorescence intensity was measured after fully mixing.

The river water samples were applied to evaluate the practical application. The water samples were filtered by 220 nm microporous membrane. The recovery study was carried out by spiking certain volume of CPF solution into water samples.

Results and discussion

Preparation of molecularly imprinted polymer coated quantum dots

QDs with higher fluorescence efficiencies and large specific surface areas have been widely used in biological and chemical analysis. In this work, oleic acid was used to modify the surface of Mn-doped ZnS QDs. Figure 1 illustrated the preparation process of the MIP-coated QDs. CPF was used as the template molecule. The free radical polymerization was initiated using AIBN, which could form free radicals at 60 °C [27]. AM was used as the monomer in the polymerization process because polyacrylamide was a nitrogen-containing polymer which could be solvated in aqueous medium [28].

EGDMA was added as cross-linker to freeze the polymer conformation in the right shape and orientation, which would result in specific binding sites after the removal of the template molecule. Presence of sufficient cross-linker is very important for the formation of strong polymer structure which can uphold its conformation. Different MIP-coated QDs materials were prepared by changing the template/monomer ratios (1:3; 1:4; 1:5) and the template/cross-linker ratios (1:10; 1:15; 1:20). The selectivity factor, which was calculated by the dividing the fluorescence quenching value of MIP-coated QDs by that of NIP-coated QDs, was used to compare the efficiency of different MIP-coated QDs materials. At last, 1:4 molar ratio CPF/AM and 1:10 molar ratio CPF/EGDMA were selected. The characterization of MIP-coated QDs was shown in Fig. S1 (see supplementary material).

Fluorescence study

The fluorescence intensity of the MIP-coated QDs was recorded by varying the excitation wavelength from 300 to 350 nm and was shown in Fig. S2 (see supplementary material). The weak blue peak around 444 nm was generated by the defect related to the emission of the ZnS QDs. The strong orange peak around 599 nm could be attributed to the $4T^1 \rightarrow 6A^1$ transition of the Mn²⁺ impurity [20]. The maximum emission intensity at 599 nm was observed with 325 nm as the excitation wavelength. The orange fluorescence was very strong and the peak was sharp, indicating that the sizes of MIP-coated QDs were very homogeneous.

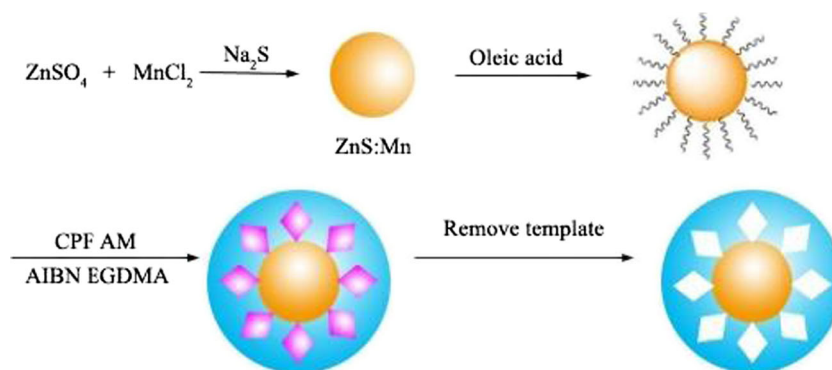
In the current work, the template CPF was entrapped in the polymer matrixes through noncovalent binding. To further elucidate the high selectivity of the MIP-coated QDs in aqueous media, the NIP-coated QDs were prepared. As shown in Fig. 2, the fluorescence intensity of MIP-coated QDs was relatively weak (spectrum c) before the removal of templates. While after Soxhlet extraction with methanol: acetic acid (19:1, v/v), the fluorescence intensity of the MIP-coated QDs was restored dramatically. However, no difference in the shape and position of the emission spectrum was observed (spectrum b). The fluorescence intensity was restored almost to that of the NIP-coated QDs (spectrum a), which indicated that the templates were removed completely from the recognition cavities in the MIP-coated QDs. It suggests that the MIP-coated QDs actually facilitate the application for the rapid and simple quantification of analytes in aqueous media.

The influences of pH and incubation time on the fluorescence intensity were investigated and the results were shown in Fig. S3 (see supplementary material).

Adsorption capacity of the composite particles

In order to investigate the binding performance of the MIP-coated QDs and NIP-coated QDs, a binding

Fig. 1 The preparation process of MIP-coated QDs



analysis was carried out using the different concentrations of CPF. The remarkable advantage of the synthesized material is a larger mass-transfer speed, where the optimal CPF adsorption time of MIP-coated QDs and NIP-coated QDs were 40 min. As shown in Fig. 3a and b, the changes in fluorescence intensity of MIP-coated QDs were much more significant than those of NIP-coated QDs, which indicated that during the MIP-coated QDs preparation process, binding sites and cavities were formed.

Selective adsorption on molecularly imprinted polymer coated quantum dots

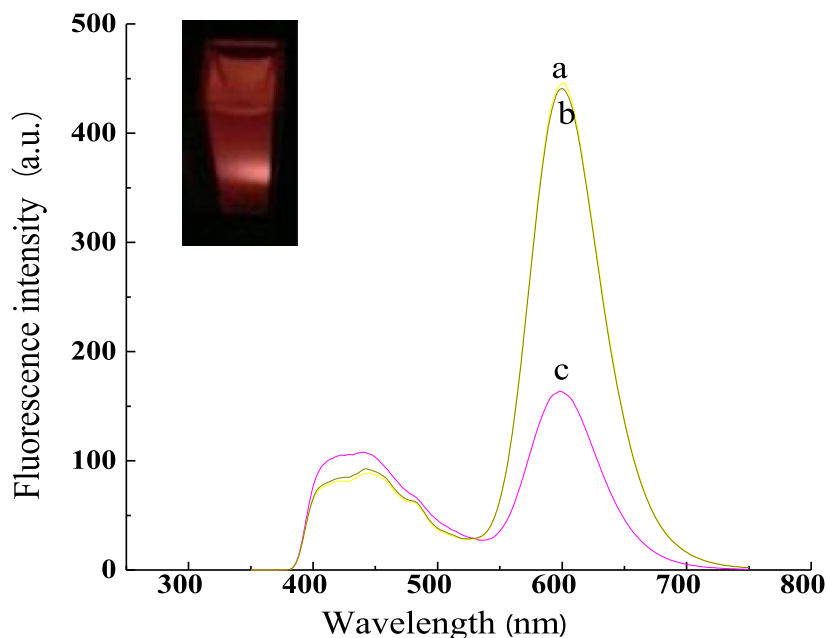
In this work, we evaluated the effects of template molecule CPF, interference molecule acephate and analogue molecule

CM on MIP-coated QDs and NIP-coated QDs. The structure of CPF, acephate and CM were shown in Fig. S4 (see supplementary material). CPF, acephate and CM are organophosphorous pesticides. The evolutions of fluorescence spectra of MIP-coated QDs or NIP-coated QDs interacted with different amounts of acephate or CM were shown in Fig. 3.

There was no obvious difference of fluorescence intensity change between the MIP-coated QDs and NIP-coated QDs for acephate. Both MIP-coated QDs and NIP-coated QDs fluorescence intensity changed by acephate are non-specific. The reason was that there was no tailor-made recognition sites formed in both MIP-coated QDs and NIP-coated QDs for acephate, so there was no significant difference on the binding capacity of the acephate.

The imprinting factors (IF) of different molecules were shown in Table S1 (see supplementary material). It indicated

Fig. 2 The fluorescence spectra of NIP-coated QDs (spectrum a), MIP-coated QDs after (spectrum b) and before (spectrum c) the removal of templates from the recognition sites



- a. QDs@NIP
- b. QDs@MIP after removing the templates
- c. QDs@MIP before removing the templates

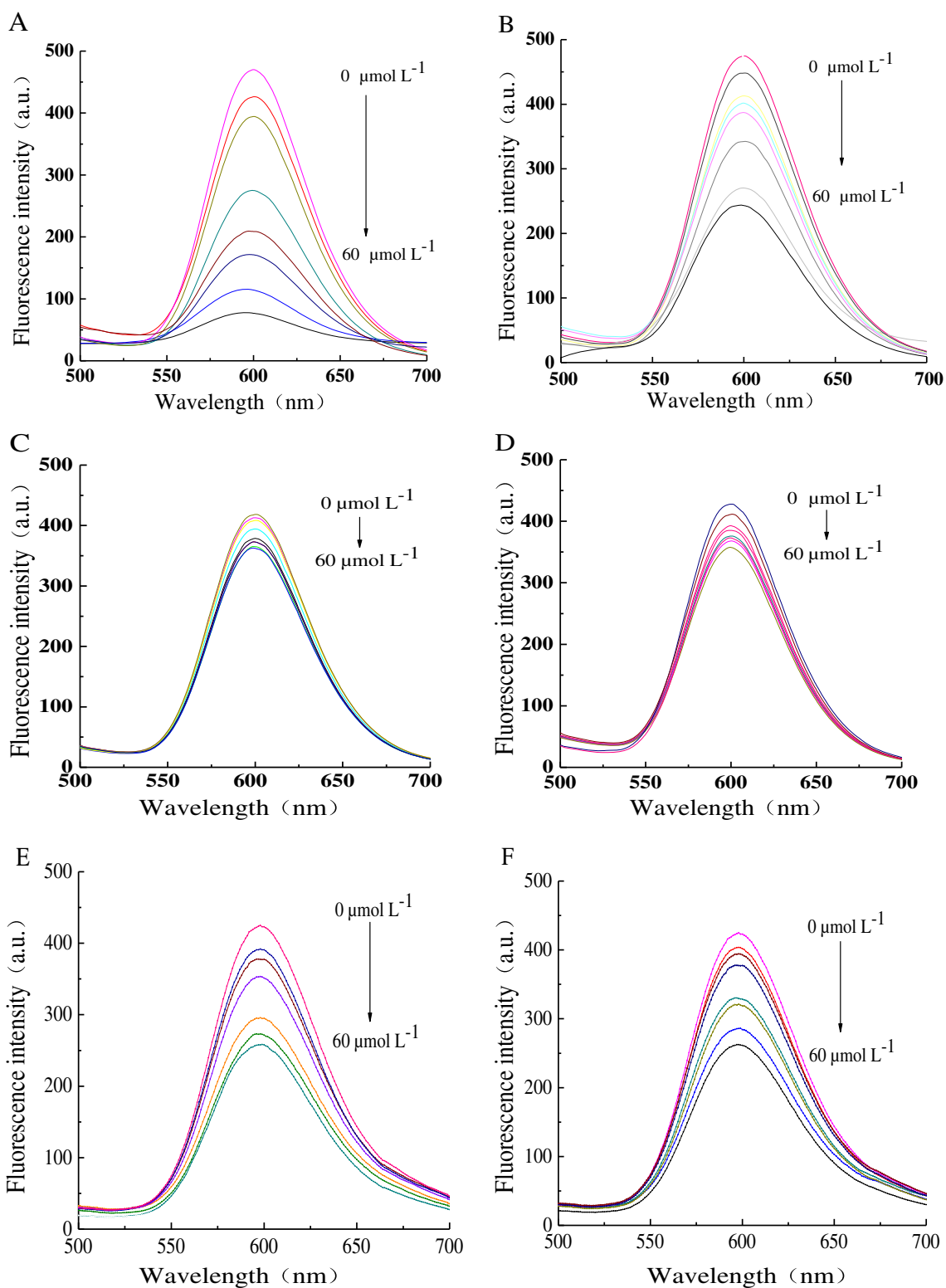


Fig. 3 The evolutions of fluorescence spectra of MIP-coated QDs or NIP-coated QDs interacted with different amounts of CPF, acephate or CM

that the MIP-coated QDs had provided selectivity to CPF and its analogue molecule CM, which has very similar structure with the template CPF (Fig. S4). However, MIP-coated QDs provided higher selectivity to CPF (3.0) than that of CM (1.4).

Fluorescence quenching analysis

Typical fluorescence quenching of the MIP-coated QDs composites from 0.3 to 60.0 $\mu\text{mol L}^{-1}$ CPF was

Table 1 Figures of merit of sensitive and selective methods for determination of chlorpyrifos

| Methods | Materials | Samples | Analytical ranges (nmol L ⁻¹) | LODs (nmol L ⁻¹) | Advantages | Disadvantages | Recovery (%) | RSD (%) | Ref. |
|--|---|------------------|--|---------------------------------|--|---|-----------------|------------|-------------|
| Ultrasound assisted extraction-HPLC-UV detector | Magnetic molecularly imprinted polymer | Rice | 1.4×10^1 – 5.7×10^2 | 4.11 | High selectivity and low cost | Tedious sample preparation process | 81.2–92.1 | 2.4–7.3 | [4] |
| Vortex extraction- multiplexed bead assay | Hapten-BSA coupling fluorescent beads | Vegetables | 2.85 – 2.85×10^3 | 4.79 | High sensitivity | Complex preparation | 70.2–112.8 | 13.8 | [11] |
| Solid-phase extraction-GC-FPD detector | Molecularly imprinted polymer | Water | 1.43×10^2 – 8.56×10^3 | 0.29 | High selectivity | Tedious sample preparation process | 99–105 | 4.6–7.9 | [23] |
| Stirring extraction-solid phase extraction-HPLC-UV detector | Molecularly imprinted polymer | Vegetables | 1×10^5 – 1×10^7 | 2.9×10^3 | High selectivity | Time-consuming | 76.1–93.5 | 3.6–9.7 | [22] |
| Immersion extraction-online solid-phase extraction-chemiluminescence detection | Molecularly imprinted polymer | Vegetables | 2–1,000 | 0.92 | Fast analysis speed | Complicated online system | 93–106 | 3.6 | [9] |
| Acetylcholinesterase-based biosensor | Gold nanoparticles-carbon spheres | Aqueous solution | 1×10^{-4} – 1×10^4 | 1.29×10^{-4} | High sensitivity | High cost of preparation | 82.4–91.2 | 4.9 | [29] |
| Stirring extraction- visible light photoelectrochemical sensor | Au nanoparticles and molecularly Imprinted Poly(o-phenylenediamine)-modified TiO ₂ nanotubes | Vegetables | 50–10,000 | 0.96 | Good reproducibility, stability and selectivity | High cost | 95.5–106.8 | <5.0 | [30] |
| Amperometric biosensor | Acetylcholinesterase | Water | 1.0×10^3 – 5.0×10^7 | 5×10^3 | High selectivity | Anti-interference ability and poor sensitivity | 91.3–93.9 | 4.9–8.2 | [31] |
| Cloud-point extraction - LC-UV detector | Genapol X-80 | Water | 1.43×10^2 – 7.13×10^3 | 8.02 | Simply step | Surfactant impact LC detection | 62.6–84.5 | 2.2 | [32] |
| Online-solid phase extraction-LC-MS detection | C8 | Cord blood | 0.29 – 2.9×10^2 | 0.03 | Reduce manual operation | Complicated online system and expensive mass spectrometer | 92.4–102.0 | 4.8 | [33] |
| Fluorescence detector | Molecularly imprinted polymer coated quantum dots | Water | 3×10^2 – 6×10^4 | 17 | High sensitivity and selectivity, less toxic, low cost and save time | Maybe unsuitable for solid samples | 87.1–94.5 | 2.9–6.5 | This method |

studied. It demonstrated that the probe showed obvious responses to different concentration of CPF, which was very effective and suitable for practical application. The quenching in this system follows the Stern-Volmer equation:

$$F_0/F = 1 + K_{sv}c_q$$

Where the F_0 and F are the fluorescence intensities in the absence and presence of the quencher respectively, c_q is the concentration of the quencher, and K_{sv} is the Stern-Volmer constant. The quenching materials MIP-coated QDs with CPF satisfied the following equation: $F_0/F=0.0817c_q+1.0277$, the correlation coefficient is 0.9992. The linear range of the calibration curve is obtained from 0.3 to 60.0 $\mu\text{mol L}^{-1}$ with a detection limit of 17 nmol L^{-1} and the limit of quantification is 50 nmol L^{-1} . When the concentration is more than 60 $\mu\text{mol L}^{-1}$, the fluorescence quenches seriously. At this point, the fluorescence intensity of the measured value is small; the repeatability of measurement is not satisfactory.

Different analytical methods [4, 9, 11, 22, 23, 29–33] for determination of CPF were summarized briefly in Table 1. As can be seen, the recovery, precision and LOD of this method were comparable to other methods. When compared with chromatographic methods, the analytical time of this work was saved because we used fluorescence technology instead of tedious chromatographic separation process. Moreover, our method is simple, rapid and low cost when compared with other sensor methods. Furthermore, the material that we used in this method has high selectivity because of using molecularly imprinting technique.

Application to real sample analysis

In order to evaluate the feasibility of the method, three river water samples collected from Harbin (China) were analyzed. No response corresponding to CPF was observed in these water samples. Different amount of CPF with three concentrations (0.3, 3.0 and 30.0 $\mu\text{mol L}^{-1}$) were added into the water samples. Then the water samples were processed according to the procedures described in section [Measurements of fluorescent response to chlorpyrifos](#). The quantitative recoveries ranged from 87.1 to 94.5 %, the relative standard deviation (RSD) ranged from 2.9 to 6.5 % were obtained. The results showed that the fluorescent probe based on MIP-coated QDs has the potential applicability for CPF detection in real samples.

Conclusion

In this work, we have developed a facile strategy to fabricate the QDs-based MIP by using CPF as template and it has been successfully characterized and optimized for use as a fluorescent probe. In comparison with the antibody-or aptamer-based analytical methods, this approach is still in its infancy, and the MIP-coated QDs probe has not been widely employed. The results indicated that the MIP-coated QDs provided selectivity to CPF, which was based on the interactions of the size, shape, and functionality of the template. Furthermore, the potential advantages of this approach including simple preparation, high stability and low cost will attract more investigators for its wide applications in the near future. It is disappointing that the LOD provided by this method is inferior to some other methods. We will focus on the improvement of the sensitivity of this technique in the future.

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