A simple and Novel Sensor for the Determination of Acetamiprid Based on its Reducing Effect on the Chemiluminescence of S, N-CQDs in CH$_3$-CN-H$_2$O$_2$ System

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A simple and novel method for the determination of acetamiprid in water samples is suggested. The method is based on the reducing effect of acetamiprid on the chemiluminescence intensity of a new sulphur and nitrogen co doped carbon dots (S, N-CQDs) in acetonitrile- hydrogen peroxide (CH$_3$-CN- H$_2$O$_2$) system.

The possible mechanism was discussed and it was found that S, N-CQDs react with $(^{1}O_2)_2^*$, produced from CH$_3$-CN-H$_2$O$_2$ reaction, leading to excited state S, N-CQDs which deactivate to ground state by photon emission. Acetamiprid diminishes the chemiluminescence (CL) intensity by competing with S, N-CQDs. The CL intensity reduction is proportional to the concentration of acetamiprid. S, N-CQDs were easily prepared by hydrothermal method. Under optimal conditions, the linear rang of 2.5-25.0 µg L$^{-1}$ with a detection limit (3σ) of 0.4 µg L$^{-1}$ were obtained. The method was successfully applied to the determination of trace amount of residual pesticide in water samples.

**Keywords:** Sulphur and Nitrogen co doped carbon dots, Chemiluminescence, acetonitrile-hydrogen peroxide, Acetamiprid
Introduction

Pesticides are widely used to prevent pests and increase the production of more crops in modern agriculture. However, there is a growing concern about the residue of these toxins in food, water and ecosystems.\textsuperscript{1,2} Direct consumption of contaminated water or food can also pose a serious threat to human health. Therefore, the residual analysis of pesticides has become a sensitive and challenging issue to ensure food quality, ecosystem protection and human health.\textsuperscript{3–12}

Neonicotinoids are among the widely used pesticides in agriculture and insect control. They not only accumulate in soil, but are soluble in water and can be washed away by water and pollute the ecosystem and a wide range of non-target species such as pollinators, soil invertebrates and aquatic organisms.\textsuperscript{13–19}

Acetamiprid is one of the newest and most efficient neonicotinoid insecticides in the world.\textsuperscript{20–24} Acetamiprid residue detection is traditionally carried out by HPLC, GC and LC-Mass.\textsuperscript{16,25–28} Although these methods are very sensitive and reliable there are disadvantage such as the need for advanced laboratory equipment and performance. Furthermore, the preparation, purification and derivation steps required to achieve high sensitivity are in most case time consuming, costly, tedious and require a skilled operator.\textsuperscript{5,7,21–23} Thus, large efforts have been made to develop alternative strategies for the analysis of pesticides. An interesting review on the recent developments of sensitive optical sensors has been published by X. Yan et al.\textsuperscript{4}

C-dots due to their excellent optical properties, good biocompatibility, water solubility, high chemical stability, low toxicity, easy and low cost synthesis have been successfully used as sensors in detecting trace amount of pesticide residues. Their
selectivity can be increased by optimizing the methods of synthesis and doping C-dots with other atoms or functional groups.\textsuperscript{29–40} Chemiluminescence (CL) techniques based on the characteristics of modified nanoparticles have been successfully applied to the determination of pesticides.\textsuperscript{23,41,42} Analytical methods based on CL of C-dots can be a powerful tool in competing with conventional methods due to the simplicity of the steps, the low detection limit, high sensitivity, wide calibration range and short time.\textsuperscript{29,31–33}

In this contribution, taking into account the consideration that the mixture of acetonitrile and hydrogen peroxide (CH\textsubscript{3}-CN-H\textsubscript{2}O\textsubscript{2}) can form singlet oxygen and hydroxyl radical \textsuperscript{43,44} and based on our observation that these species can induce CL on sulphur and nitrogen co doped carbon dots (S, N-CQDs), we introduce the new chemiluminescence S, N-CQDs/CH\textsubscript{3}-CN-H\textsubscript{2}O\textsubscript{2} system. We also found that the CL intensity of this new system is reduced in the presence of acetamiprid. Based on this fact and following our recent works on the application of CL systems to the determination of different species in real samples \textsuperscript{36,37,45} we have developed a new and simple CL system for the determination of trace amounts of acetamiprid pesticide residues. This method is based on the reduction of the CL intensity of S, N-CQDs/CH\textsubscript{3}-CN-H\textsubscript{2}O\textsubscript{2} system by traces of acetamiprid. The proposed method was successfully tested on drink, well and spring waters.

**Experimental**

**Apparatus**

CL signals and fluorescence spectra were recorded by Sirius L Luminometer (Titertek Berthold, Germany) and RF-540 spectrofluorimeter (Shimadzu, Japan), respectively. To
characterize the size and shape of S, N CQDs, Transmission Electron Microscopy (TEM, Leo906, Zeiss, Germany) was used. The FT-IR spectra were obtained by FTIR spectrophotometer (Tensor 27 Bruker). EDS spectrum and UV-vis spectra were recorded by using Energy dispersion X-ray spectrometry device (EDX, MIR AIII, France, [www.tescan.com](http://www.tescan.com)) and Cary-100 spectrophotometer (Varian; [www.varianinc.com](http://www.varianinc.com)).

Reagents

Analytical grade reagents and double distilled deionized water (product of Kasra, Tabriz, Iran) were used throughout. Acetonitrile, sodium carbonate, hydrogen peroxide, citric acid, sodium hydroxide and L-cysteine were from Merck (Darmstadt, Germany). The pesticides were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

Preparation of the S, N-CQDs

The rapid and easy hydrothermal method was used to synthesize S, N-CQDs as described in articles. Briefly 0.2g of citric acid and 0.1 g of L- cysteine were gently mixed, powdered and the solid mixture was placed in an autoclave at 200 °C for 3 hours. The pH of the solution was adjusted to 7 by sodium hydroxide solution after it was cooled to room temperature. Then, the solution was diluted to 100 mL with deionized water.

General procedure for CL monitoring

CL measurements were performed on a 3 mm tube with a length of 15 mm and a diameter of 12 mm with a static injection mode. Typically, a routine test consisted of
100 µL of sodium carbonate (0.05 M), 20 µL of hydrogen peroxide (0.5 M), 300 µL of
diluted S, N-CQDs and a suitable amount of acetamiprid standard solution or 200 µL of
water solution as prepared according to the Procedure for the preparation of real water
samples section. The volume of solution in the cell was diluted to 1 mL with deionized
water. Eventually, the CL reaction was triggered by automatic injection of 60 µL of
\(\text{CH}_3\text{-CN (55%)}\) and the maximum CL response was recorded as the analysis signal.

Procedure for the preparation of real water samples

All kinds of waters (tap, spring and well), without any preparation, were spiked with
known amounts of acetamiprid standard solution and 200 µL of spiked water solutions
were proceeded as general procedure.

Results and Discussion

Specific features of S, N-CQDs

The TEM image of S, N-CQDs shows that nanoparticles are almost uniformly spherical
in the range of 3-5 nm, Fig. 1. In the FT-IR spectrum study, Fig. 2 (a), the stretching
vibrations of \(\text{C} = \text{O}, \text{C} = \text{C}\) and C-N are shown at 1701, 1608 and 1396 cm\(^{-1}\) respectively.
The peaks around 1220 and 2555 cm\(^{-1}\) are attributed to the stretching vibration of C=S
and S-H. Finally, the broad band in 3400 cm\(^{-1}\) represents the stretching vibrations of
O-H and N-H. According to the EDS spectrum, Fig.2 (b), of the synthesized
nanoparticles, the weight percentages of nitrogen and sulfur are 11.47 and 7.35,
respectively and based on these results, it can be concluded that nitrogen and sulfur
atoms have been doped to the synthesized CQDs.
The two peaks at 209 and 346 nm on the UV-Vis absorption spectrum represent the $\pi$-$\pi^*$ transfers from C=C and n-$\pi^*$ transfer from C=O, respectively, Fig. 3 (a). The fluorescence behavior of the synthetic S, N-CQDs is shown in Fig. 3 (b). This figure indicates that the wavelength of the emission spectrum does not depend on the wavelength of the excitation. At an excitation wavelength of 350 nm, a maximum emission of 419 nm.

*Acetamiprid detection by new luminescence system*

In order to investigate the CL behavior of the newly developed system and the influence of acetamiprid on this system, the kinetic profiles of $\text{H}_2\text{O}_2$, $\text{Na}_2\text{CO}_3$, $\text{CH}_3\text{-CN}$ and $\text{H}_2\text{O}_2$, $\text{Na}_2\text{CO}_3$, $\text{CH}_3\text{-CN}$, S, N-CQDs (S, N-CQDs/ $\text{CH}_3\text{-CN-}$H$_2$O$_2$ system) in the absence and presence of acetamiprid were recorded. The results are shown in Fig. 4. According to the profile (a) in Fig. 4, very weak and long persistent CL is observed for $\text{H}_2\text{O}_2$, $\text{Na}_2\text{CO}_3$, and $\text{CH}_3\text{-CN}$. However, the CL of S, N-CQDs was increased considerably in the presence of $\text{H}_2\text{O}_2$, $\text{Na}_2\text{CO}_3$, $\text{CH}_3\text{-CN}$, Fig. 4 b. By adding a trace amount of acetamiprid pesticides, a significant reduction is observed in the CL of the last system, Fig. 4 c. Due to the linear relationship between pesticide concentration and the rate of decrease, a method was proposed and used to measure acetamiprid pesticide.

*Possible mechanism for CL reaction*

The reaction mechanism was investigated using color filters. The results showed that the emitted wavelength is in the range of 400-500 nm, which is consistent with the CQDs emission wavelength. Therefore, it can be concluded that the emitting species should be the excited S, N-CQDs. As suggested by Lu et al.$^{43}$ singlet oxygen and hydroxyl radical are first formed by reaction between $\text{H}_2\text{O}_2$ and $\text{CH}_3\text{-CN}$. The resulting
(1^1O_2)_2^* then reacts with S, N-CQDs leading to excited S, N-CQDs which emit light.\textsuperscript{37,46} A possible mechanism is shown in scheme 1. The decreasing effect of the acetamiprid can probably be due to the competition of this pesticide, even at trace amounts, with S,N-CQDs for H_2O_2-CH_3-CN resulting in the decrease of the amount of excited S,N-CQDs and hence the intensity of the CL emission.

\[
\begin{align*}
O \\
H_3C-C &\equiv N + 2H_2O_2 \rightarrow H_3C-C-NH_2 + O_2 + H_2O \\
^1O_2 + H_2O_2 \xrightarrow{OH^-} & 2\cdot OH + O_2 \\
^1O_2 + O_2 \rightarrow & (O_2)_{2^*} \\
(O_2)_{2^*} + S, N-CQDs & \rightarrow S, N-CQDs^* \\
S, N-CQDs^* \rightarrow & S, N-CQDs + h\nu
\end{align*}
\]

**Scheme 1.** Proposed mechanism for S, N-CQDs /H_2O_2-CH_3-CN system.

*Optimization of reaction conditions*

The influences of acetonitrile in the range of 0.064 to 0.898 mol L\(^{-1}\), peroxide in the range of 0.002 to 0.02 mol L\(^{-1}\), sodium carbonate in the range of 0.001 to 0.04 mol L\(^{-1}\), and S, N-CQDs in the range of 50 to 400 µL on the CL response were studied to obtain the maximum sensitivity for the detection of acetamiprid. The results are shown in Figs 5-8 respectively. The maximum response as the optimal value for acetonitrile, hydrogen peroxide, sodium carbonate and S, NCQDs were 0.70 mol L\(^{-1}\), 0.01 mol L\(^{-1}\), 0.005 mol
L$^{-1}$ and 300 µL, respectively, which were used in subsequent experiments.

**Analytical figures of merit**

Under the above selected optimized experimental conditions the calibration graph was designed for the measurement of acetamiprid pesticide. A good linear correlation was observed between the amount of acetamiprid and the decrease in CL intensity in the range of 2.50 to 25.00 µg L$^{-1}$, Fig. 9. The regression equation was $\Delta I = 30014C + 22.823$, $R^2 = 0.9992$ where $\Delta I$ is the difference between the CL intensity in the absence and presence of the acetamiprid with a detection limit of 0.4 µg L$^{-1}$. The relative standard deviation was 1.5% for 3 replicate determination of 0.01 mg L$^{-1}$ of acetamiprid.

Table 1 shows the comparison between the proposed method and some other reported methods for the determination of acetamiprid. As can be seen the analytical performance of this method is comparable with the most of other reported methods. Furthermore our proposed measurement method is faster, simpler and less expensive than the other methods.

**The effect of interferences on the acetamiprid determination**

In order to confirm the selectivity of the proposed method for the determination of acetamiprid, different amounts of coexisting species were added to the test solution containing 0.01 mg L$^{-1}$ of acetamiprid and tested according to the general procedure, the results are given in Table 2. A species was considered to interfere when its presence produced a variation of more than 5% in the change of CL intensity of the sample.
Analysis of real samples

The propose method was successfully used to determine the pesticide residue in three real water samples (spring, well and tap waters). The results are given in Table 3. Student’s t-test indicated that there are no significant differences between added and found values.

Conclusions

Due to the increasing use of acetamiprid pesticide in agriculture and the possibility of contamination of various waters with the residue of this toxin, a new S, N-CQDs/CH$_3$-CN-H$_2$O$_2$ system is introduced and used for the determination of this toxin in water samples. The proposed method is new, fast and easy with good selectivity and sensitivity. The chemicals used are readily available for any researcher and could be easily used in any laboratory for the analysis of acetamiprid in real water samples.
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Table 1 Comparison of the proposed method with other reported methods for determination of acetamiprid

| Method                          | Linear range/µg L\(^{-1}\) | Limit of detection/µg L\(^{-1}\) | Reference |
|---------------------------------|-----------------------------|----------------------------------|-----------|
| GC/ECD                          | 2-1000                      | 0.32                             | 26        |
| RatiometricFlourescence         | 25-5×10\(^3\)              | 16.8                             | 47        |
| MSPE-HPLC                       | 0.5-100.0                   | 0.1                              | 28        |
| Colorimetric                    | 10-50                       | 1.02                             | 21        |
| MSPE-HPLC                       | 10-500                      | 1.0                              | 18        |
| HPLC-MS                         | 10-500                      | 0.4                              | 48        |
| LC                              | 0.0125-0.15                 | -                                | 20        |
| MSPE-HPLC (UV detection)        | 0.10-30                     | 0.02-0.05                        | 19        |
| The enzyme inhibition           | 10-10\(^6\)                | 2.66                             | 3         |
| Fluorescence                    | 20-800                      | 8.3                              | 49        |
| of UCNP@ MIP                    |                             |                                  |           |
| Developed method                | 2.5-25                      | 0.4                              | This work |
Table 2  Tolerance limits of some species in the determination of 0.01 mg L$^{-1}$ acetamiprid

| Species               | Interferent to analyte ratio |
|-----------------------|------------------------------|
| NO$_3^-$              | 2000                         |
| PO$_4^{3-}$           | 1500                         |
| Glucose, Mn$^{2+}$, Na$^+$, K$^+$, Cl$^-$ | 1000                         |
| SO$_4^{2-}$, Zn$^{2+}$, Al$^{3+}$, Ba$^{2+}$, F$^-$, Ni$^{2+}$, As(V), Metalaxyl, Deltamethrin, Clodinafop, propargyl | 500                         |
| Fe$^{2+}$, Pb$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Malathion, Hexaconazole | 250                         |
| Ag$^+$, NH$_4^+$      | 125                          |
Table 3  Determination of acetamiprid in real water samples.

| sample       | Added/ µg L⁻¹ | Found/ µg L⁻¹ | Recovery (%) |
|--------------|---------------|---------------|--------------|
| Well water   | 0.00 -        | 25.50 ± 0.50  | 102.00       |
|              | 25.00         | 25.00 ± 0.50  | 98.96        |
|              | 50.00         | 49.67 ± 0.76  | 99.34        |
|              | 100.00        | 99.31 ± 1.40  | 99.31        |
| Spring water | 0.00 -        | 24.74 ± 0.50  | 101.34       |
|              | 25.00         | 25.40 ± 0.58  | 101.60       |
|              | 50.00         | 50.89 ± 0.82  | 101.78       |
|              | 100.00        | 100.26 ± 1.10 | 100.26       |
| Tap Water    | 0.00 -        | 24.74 ± 0.50  | 101.34       |
|              | 25.00         | 25.40 ± 0.58  | 101.60       |
|              | 50.00         | 50.89 ± 0.82  | 101.78       |
|              | 100.00        | 100.26 ± 1.10 | 100.26       |
Figure Captions

Fig 1   TEM image of S, N-CQDs

Fig. 2   (a) FT-IR spectrum and (b) EDS spectrum of S, N-CQDs

Fig. 3   (a) UV-visible absorption spectrum of S, N-CQDs and (b) Fluorescence spectra for S, N-CQDs excited at wavelengths of 275, 300, 325, 350 and 375 nm, (a-e, respectively).

Fig. 4   Kinetic profile of (a) H₂O₂, Na₂CO₃ and CH₃-CN; (b) H₂O₂, Na₂CO₃, CH₃-CN and S, N-CQDs (S, N-CQDs/CH₃-CN-H₂O₂ system) and (c) S, N-CQDs/CH₃-CN-H₂O₂ system in the presence of acetamiprid, Conditions: S, N-CQDs, 300 µL; CH₃-CN, 0.7 mol L⁻¹; H₂O₂, 0.01 mol L⁻¹; Na₂CO₃, 0.005 mol L⁻¹; acetamiprid, 0.008 mg L⁻¹.

Fig. 5   The effect of different concentrations of CH₃-CN. Conditions: S, N-CQDs, 100 µL; H₂O₂, 0.01 mol L⁻¹ and of Na₂CO₃, 0.01 mol L⁻¹.

Fig. 6   The effect of different concentrations of H₂O₂. Conditions: S, N-CQDs, 100 µL; Na₂CO₃; 0.01 mol L⁻¹; CH₃-CN, 0.7 mol L⁻¹

Fig. 7   The effect of different concentrations of Na₂CO₃. Conditions: S, N-CQDs, 100 µL; CH₃-CN, 0.7 mol L⁻¹; H₂O₂, 0.01 mol L⁻¹.
Fig. 8  The effect of different volumes of S, N-CQD (50, 100, 150, 200, 250, 300, 350 and 400) µL, Conditions: CH$_3$CN, 0.7 mol L$^{-1}$; H$_2$O$_2$, 0.01 mol L$^{-1}$; Na$_2$CO$_3$, 0.005 mol L$^{-1}$.

Fig. 9 Acetamiprid calibration graph under optimum conditions (CH$_3$CN, 0.7 mol L$^{-1}$; H$_2$O$_2$, 0.01 mol L$^{-1}$; Na$_2$CO$_3$, 0.005 mol L$^{-1}$ and S, N-CQDs, 300 µL$^{-1}$).
Fig. 1
Fig. 2
Fig. 3
Fig. 4

Fig. 5
Fig. 6

Fig. 7
Fig. 8

Fig. 9

\[ y = 30014x + 22.823 \]

\[ R^2 = 0.9992 \]
