

*Full Paper*

## **Voltammetric Nanosensor for Cyfluthrin based on Graphene and Poly (3-methyl) Thiophene**

**N. Y. Sreedhar\* and M. Sunil Kumar**

*Electroanalytical Lab, Department of Chemistry, Sri Venkateswara University, Tirupati-517502, Andhra Pradesh, India*

\* Corresponding Author, Tel.: +91-9440087124; Fax: +91-857427499

E-Mail: [nyschem01@gmail.com](mailto:nyschem01@gmail.com)

*Received: 2 January 2014/ Accepted after minor revision: 2 April 2014/*

*Published online: 30 April 2014*

---

**Abstract-** Poly (3-methyl) thiophene /graphene based electrochemical sensor is developed to study the electrochemical behavior of cyfluthrin with cyclic voltammetry and differential pulse voltammetry. In comparison to bare glassy carbon electrode (GCE), enhanced peak currents and reduced peak potentials are observed for the nanocomposite electrode. Differential pulse voltammetry (DPV) signals are used to optimize experimental parameters such as pH, accumulation time and potential, pulse amplitude, step potential and rest time. A differential pulse adsorptive stripping voltammetric method is developed for the determination of cyfluthrin with linear range,  $1.0 \times 10^{-8}$ – $1.1 \times 10^{-6}$  M and detection limit of  $2.7 \times 10^{-9}$  M. The voltammetric procedure is effectively applied for well water samples with recoveries in the range of 92.40 to 98.30%.

**Keywords-** Cyfluthrin, Graphene, Poly (3-methyl) thiophene, Differential pulse voltammetry, Well waters

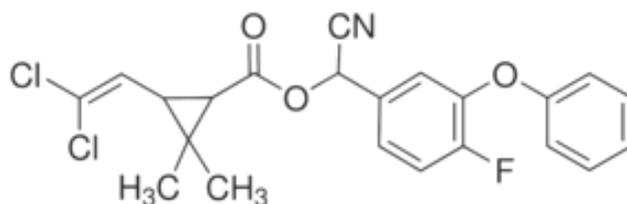
---

### **1. INTRODUCTION**

Synthetic pyrethroids represent one of the major classes of synthetic pesticides which are mainly used against a variety of crop and garden pests. They are most commonly found in household insecticides for the control of cockroaches, fleas and mosquitoes. Relative to

organophosphate (OP) pesticides, they are far less toxic because of their rapid degradation into less toxic metabolites. Nevertheless their toxicity towards non-target organisms such as fish and bees is well demonstrated. Hence it is essential to monitor the presence of these chemicals in air, water and soil. Cyfluthrin belongs to the class of synthetic pyrethroids used mainly against insect pests and fleas (Scheme1). It has high toxicity to rainbow trout and other aquatic invertebrates. Different chromatography techniques such as gas chromatography and high performance liquid chromatography are available for the determination of synthetic pyrethroids [1-3]. Based on its simplicity, sensitivity and low-cost aspects, voltammetric behavior of cyfluthrin, cypermethrin and deltamethrin are investigated using dropping mercury electrode and hanging mercury drop electrode [4-5]. Glassy carbon and mercury electrode are further employed for the electrochemical study of these compounds [6].

Graphene, a 2D nanomaterial, has fascinated the world of scientists since it possess extraordinary electrical, thermal and mechanical properties. It has wide applications in the fields of fuel cells, storage batteries, solar cells and also acts as effective adsorbent. Graphene is vibrantly used as efficient electrode material owing to its unique properties such as high surface area, good electrical conductivities and fast electron transfer kinetics. It is used for the detection of variety of analytes such as rutin, ascorbic acid, quinidine and OP pesticides [7-10]. Conjugated polymers such as polypyrrole, poly (3-methyl) thiophene also attracted the sensor world for sensitive determination of different molecules based on their microporous structures and good electrical conductivities [11-12]. Based on the above reports, the present work aims to develop sensitive voltammetric determination of cyfluthrin at poly (3-methyl) thiophene/graphene/glassy carbon electrode (P3MT/GR/GCE). Moreover, the nanocomposite sensor is demonstrated to have wide linear range, good sensitivity and selectivity for cyfluthrin. The method can be readily applied for the enhanced determination of cyfluthrin in well water samples.



**Scheme 1.** Structure of cyfluthrin

## 2. EXPERIMENTAL

### 2.1. Reagents and chemicals

Cyfluthrin was purchased from Sigma - Aldrich, USA and graphene was procured from DropSens, Spain. Britton–Robinson buffer was prepared from 0.04 M solution each of

o-phosphoric acid, acetic acid, boric acid and the pH was adjusted using 0.2 M NaOH solution. All the chemicals and solvents used were of analytical reagent grade obtained from Merck (Mumbai, India). A stock solution of cyfluthrin (1.0 mM) was made up in methanol (AR-grade).

## 2.2. Instrumentation

All the electrochemical measurements were carried out using Autolab PGSTAT101 (Metrohm, Netherlands) controlled by Nova 1.10 software. A three electrode system consisting of glassy carbon electrode (3 mm diameter) as working electrode, a Ag/AgCl electrode as a reference electrode and a Pt wire as counter electrode were used. An Elico LI-120 pH meter was utilized to measure the pH of the buffer solution. All the measurements were carried out at a temperature of  $28 \pm 4^\circ\text{C}$ .

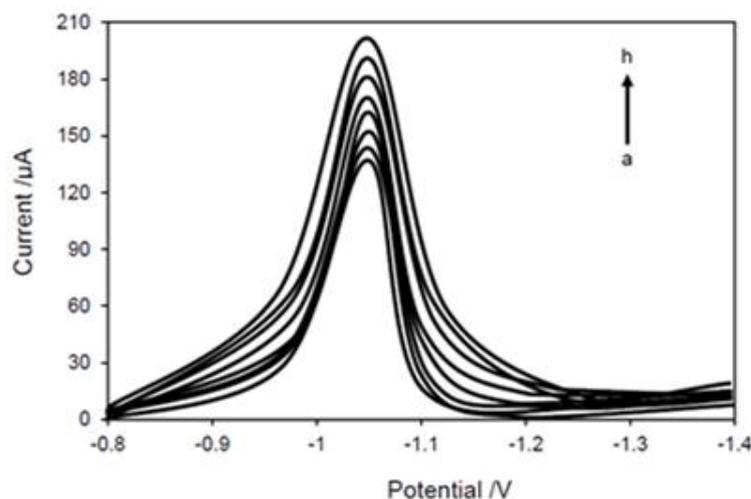
## 2.3. Fabrication of poly (3-methyl) thiophene /graphene/glassy carbon (P3MT/GR/GCE)

Prior to fabrication, the bare glassy carbon electrode (GCE) was polished with 0.3  $\mu\text{M}$  and 0.05  $\mu\text{M}$  alumina slurries, rinsed with triple distilled water and air dried. A 1 mg/mL graphene suspension was prepared by dispersing 2 mg of graphene in 2 mL of nafion (0.1%) using ultrasonication for 25 minutes. A 5  $\mu\text{L}$  homogeneous, black suspension of GR-nafion was dropped on GCE. The solvent was evaporated under room temperature to obtain graphene film modified glassy carbon electrode (GR/GCE). The electrode was rinsed with triple distilled water, dried and taken for the electrodeposition of P3MT in acetonitrile solution containing 0.04 mM of 3-methyl thiophene and 0.2 mM  $\text{NaClO}_4$ . Electropolymerisation was carried out using cyclic voltammetry by a potential sweep of 0.0 to +1.7 V vs. Ag/AgCl to GR/GCE for 4 cycles. The electrode, P3MT/GR/GCE was rinsed with triple distilled water and dried prior to voltammetric method development. Similarly P3MT/GCE and GR/GCE were fabricated for comparative studies.

## 2.4. Differential pulse voltammetric (DPV) determination of cyfluthrin

A working standard of cyfluthrin ( $1.1 \times 10^{-6}$  M) was prepared from the stock solution using double distilled water. 10 mL of test solution consists of 1.0 mL of the working standard and 9.0 mL of the BR buffer of pH 5.0 was taken into the electrolytic cell and the solution was purged with nitrogen gas for 15 minutes. The potential of the working electrode was scanned from -0.8 to -1.4 V vs. Ag/AgCl. The compound gave single, well-defined peak signal at -1.04 V. DPV signals for cyfluthrin at P3MT/GR/GCE for a series of concentrations  $1.0 \times 10^{-6}$ – $2.4 \times 10^{-6}$  M were recorded under identical conditions (Fig. 1). Enhanced peak current responses and reduced peak potentials were observed for the studied compound at

P3MT/GR/GCE compared to unmodified GCE due to the increased electrical conductivity and fast electron transfer rate of P3MT/GR/GCE.



**Fig. 1.** DPV curves using P3MT/GR/GCE for cyfluthrin at concentrations, (a) 1.0, (b) 1.2, (c) 1.4, (d) 1.6, (e) 1.8, (f) 2.0, (g) 2.2 and (h)  $2.4 \times 10^{-6}$  M in BR buffer of pH 2.0

### 3. RESULT AND DISCUSSION

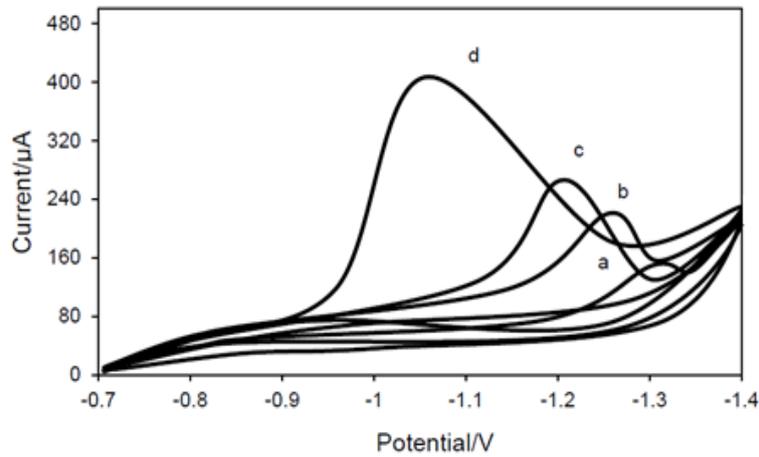
#### 3.1. Cyclic voltammetric (CV) behavior of cyfluthrin

A single, well defined reduction peak was obtained for cyfluthrin ( $1.0 \times 10^{-4}$  M) involving two electrons and two proton reduction of the carbon-carbon double bond [5]. In the reverse scan, no anodic peak was observed indicating the irreversibility of the reduction reaction (Fig. 2). Using bare GCE, P3MT/GCE and GR/GCE, the CV scan generated relatively low peak currents at higher cathodic potentials of -1.32, -1.26 and -1.20 V vs. Ag/AgCl respectively. Catalytic activity of P3MT/GR/GC electrode was demonstrated by 280 mV shift of peak potential in anodic direction relative to bare GCE. The increase in the peak current response and decrease in reduction potential demonstrates the synergistic effect on the electron transfer rate due to enhanced surface area of the electrode and the catalytic activity of the P3MT/ graphene composite.

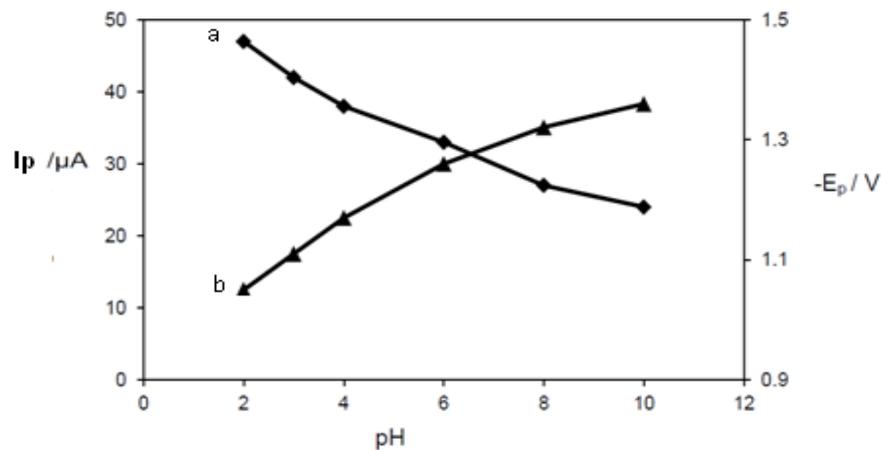
#### 3.2. Effect of pH and accumulation conditions

The availability of the protons is an important parameter in the electrochemical reduction studies. The peak current decreased when the change in pH was from 2.0 to 10.0. Hence, pH 2.0 was selected based on sharp, reproducible peak signal. As pH increases, peak potential shifted to negative values indicating proton participation in the electrochemical reduction of cyfluthrin. A plot of  $E_p$  vs. pH gives a slope of 38 mV/pH indicating proton – electron equivalence (Fig. 3). Further maximum peak signals of cyfluthrin were observed with the

nanocomposite electrode at an accumulation potential of -0.3 V and accumulation time of 120 s (not shown).



**Fig. 2.** CV curves for cyfluthrin ( $1.0 \times 10^{-4}$  M) at (a) bare GCE, (b) P3MT/GCE, (c) GR/GCE and (d) P3MT/GR/GCE with scan rate of 0.1 V/s



**Fig. 3.** Dependence of peak currents (a) and peak potentials (b) on pH in presence of cyfluthrin ( $1.0 \times 10^{-7}$  M)

### 3.3. Effect of instrument parameters

Cyclic voltammetry was used to study the variation of peak current with the scan rate. The peak signal increased linearly with the scan rate over the range 50-250 mV/s. A plot of  $I_p$  vs.  $V$  led to straight line  $I_p = 0.24V + 396.6$  with  $R^2 = 0.984$  (not shown). This indicates that the electrochemical reaction under study is adsorption controlled and irreversible. The effect of pulse amplitude on peak current was studied from 10–100 mV. Maximum peak current was obtained at 25 mV and was selected. Based on high peak currents, the optimum step potential

and rest period were 5 mV and 10 s respectively. An optimum stirring rate of 2500 rpm is employed for the efficient adsorption of cyfluthrin on the electrode surface.

### 3.4. Calibration curve

A calibration line was plotted between reduction peak currents and concentration of cyfluthrin over wide range of  $1.0 \times 10^{-8}$ – $1.1 \times 10^{-6}$  M. The linear regression equations were given by  $I_p = 75.90C + 33.40$  with  $R^2 = 0.997$ . The limits of detection ( $LOD = 3s/m$ ) of cyfluthrin are  $2.7 \times 10^{-9}$  M where 's' is the standard deviation of intercept and 'm' is the slope of the plot.

### 3.5. Stability and reproducibility of the electrode

The electrode was stored in nitrogen atmosphere at room temperature for 30 days after which the change in peak signal was found to be less than 10%. Fabrication reproducibility of the electrode was determined using six different electrodes prepared by identical procedure with RSD of 3.53%. The inter-day and intra-day reproducibility of the electrodes was determined by using the same electrode for the detection of cyfluthrin ( $1.1 \times 10^{-6}$  M) on six successive days and for six consecutive determinations on single day produced RSD values of 2.87% and 3.14% respectively. Hence the developed electrode has good stability and reproducibility.

### 3.6. Interference studies

The influence of commonly used pesticides as well as inorganic ions on the peak current of cyfluthrin ( $1.1 \times 10^{-6}$  M) was studied. It was found that 300 ppm excess of methyl parathion, chlorpyrifos and 200 ppm excess of cypermethrin had little effect on the peak signal. Moreover 500 ppm of  $Cl^-$ ,  $SO_4^{2-}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$  and  $Pb^{2+}$  ions not interfered with peak signals. These studies revealed that P3MT/GR/GC electrode has good selectivity for selected pesticides and inorganic ions in the determination of cyfluthrin.

### 3.7. Application to spiked well water samples

The proposed method was directly applied for the determination of cyfluthrin in spiked well water samples using standard addition method. Well water samples collected were filtered with Whatman No.41 filter paper and stored at 4°C. The water samples were then spiked with cyfluthrin with concentration range 5-25 µg/L. An aliquot of the spiked sample solution was transferred into the electrolytic cell containing 9.0 mL of BR buffer of pH 2.0 and determined using differential pulse adsorptive stripping voltammetric method. The validity of analytical method was tested by using recovery studies. The maximum recoveries

and corresponding relative standard deviation were 98.30% and 4.58% respectively for cyfluthrin (Table 1). The present method was found to be comparable in analytical performance with the previous methods reported for the sensitive determination of cyfluthrin except for [1] which gave low detection limits but involves sophisticated Hollow fibre-based liquid phase microextraction followed by GC-MS (Table 2).

**Table 1.** Recovery test for cyfluthrin in spiked well water sample

Sample	Added Concentration	Observed Concentration* ( $\mu\text{g/L}$ )	Recovery (%)	RSD (%)
Well water	5	4.62	92.40	3.67
	10	9.83	98.30	4.58
	15	14.67	97.80	5.12
	20	19.38	96.90	2.98
	25	24.21	96.84	3.92

\*No. of determinations = 5

**Table 2.** Comparison of analytical merits of different methods for cyfluthrin determination

S.No.	Technique/Method	Linearity	Detection limits	Reference
1	Hollow fibre-based liquid phase microextraction-GC-MS	10- 400 $\mu\text{g/L}$	0.002 -0.012 $\mu\text{g/L}$	1
2	HPLC-Chemiluminiscence	0.2 -12.60 $\mu\text{g/mL}$	0.017 $\mu\text{g/mL}$	3
3	Differential pulse polarography-HMDE	$6.0 \times 10^{-8}$ - $1.15 \times 10^{-8}$ $\text{mol/dm}^3$	$2.4 \times 10^{-8}$ $\text{mol/dm}^3$	5
4	Differential pulse adsorptive stripping voltammetry P3MT/GCE	$1 \times 10^{-8}$ - $1.1 \times 10^{-6}$ M	$2.7 \times 10^{-9}$ M	Present work

#### 4. CONCLUSION

P3MT and graphene modified glassy carbon electrode was successfully employed for the determination of cyfluthrin. Due to the synergistic combination of the individual components

of the nanocomposite, increased peak current and decreased peak potentials were obtained for cyfluthrin at the nanocomposite. The electrode further exhibited increased sensitivity, selectivity, good stability and reproducibility. Wide linear range was observed between peak currents and concentration of cyfluthrin over the range  $1.0 \times 10^{-8}$ – $1.1 \times 10^{-6}$  M with detection limit  $2.7 \times 10^{-9}$  M. The proposed method was successfully applied for well water samples with good recoveries. It is envisaged that the analytical protocol can be applied for well waters since it is quite simple, low-cost and highly sensitive for cyfluthrin. Further the nanocomposite sensor is implicated as an ideal device for the detection of electroactive pesticides which is currently underway at our laboratory.

### Acknowledgements

One of the authors acknowledges the financial support of the present work by University Grants Commission (UGC), New Delhi, India.

### REFERENCES

- [1] I. San Romána, M. L. Alonso, L. Bartolomé, and R. M. Alonso, *Talanta* 100 (2012) 246.
- [2] A. Ramesh, and P. Elumalai Ravi, *J. Chromatogr. B* 802 (2004) 371.
- [3] M. Martínez Galera, M. D. Gil García, and R. Santiago Valverde, *J. Chromatogr. A* 1113 (2006) 191.
- [4] H. Chaaieri Oudou, R. M. Alonso, and R. M. Jiménez, *Electroanalysis* 13 (2001) 72.
- [5] M. Sreedhar, M. T. Reddy, K. Balaji, and J. S. Reddy, *Intern. J. Environ. Anal. Chem.* 86 (2006) 757.
- [6] D. C. Coomber, D. J. Tucker, and A. M. Bond, *J. Electroanal. Chem.* 452 (1998) 5.
- [7] Huanshun Yin, Yunlei Zhou, Lin Cui, Tao Liu, Peng Ju, Lusheng Zhu and Shiyun Ai, *Microchim. Acta* 173 (2011) 337.
- [8] F. Li, J. Li, Y. Feng, L. Yang, and Z. Du, *Sens. Actuators B* 157 (2011) 110.
- [9] R. J. Dhanjai, *Colloids Surf. B* 105 (2013) 278.
- [10] J. Gong, X. Miao, T. Zhou, and L. Zhang, *Talanta* 85 (2011) 1344.
- [11] J. B. Raoof, R. Ojani, and S. Rashid-Nadimi, *Electrochim. Acta* 50 (2005) 4694.
- [12] P. Manisankar, P. L. Abirami Sundari, R. Sasikumar, and D. Jestin Roy, *Electroanalysis* 20 (2008) 2076.