Hollow Polypyrrole Composite Synthesis for Detection of Trace-Level Toxic Herbicide

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ABSTRACT: In this work, we successfully demonstrated the fabrication of a chemical sensor for toxic 1,1-dimethyl-3-phenylurea (fenuron) by using a hollow polypyrrole composite film. Here, we studied the interaction between negatively charged phosphate anions enclosed in the film with positively charged nitrogen atoms present in the fenuron. The electrochemical response of the film was characterized by cyclic voltammetry in which, interestingly, we observed that the bigger alkyl aryl sulphonate ions were replaced by smaller phosphate ions with the creation of hollow/pore composite films. Confirmation for ion replacement in the film and porosity of the film were studied by elemental analysis and field emission scanning electron microscopy, respectively. The tuning of hydrophilic to hydrophobic nature of the hollow composite film was tested by the wettability test (contact angle measurement). The electrocatalytic sensing conditions such as pH and film thickness, were wisely optimized on glassy carbon (GC) electrodes for better performance. We can enhance the fenuron sensitivity by over 5 times as compared to that on the GC substrate. To our knowledge, this is the first electrochemical fenuron sensor based on a hollow polymer film by differential pulse voltammetry which can detect lower concentrations and show quick response compared to other reports. This method has potential applications in the electrochemical sensing platform with good sensitive and selective analysis in agriculture groundwater samples.

1. INTRODUCTION

Environmental pollution is of serious concern in recent times because it damages the eco system around the globe. Mainly, cultivation of plants for economical purposes is a constant challenge against losses due to pests. The most common agents are pesticides, and their different forms (insecticides, herbicides, fungicides, and other chemicals) are significantly affecting the agricultural productivity. The annual usage of active pesticide ingredients is around 2500 million tons in which large quantities of pesticides may be lost in the environment. Therefore, the knowledge of the significant factor affecting the mobility and bioavailability of pesticides is crucial. This problem is intensified in the case of highly soluble pesticides because the risk of offsite movement from the intended target area increases as the pesticide is quickly dissolved in soil and water. This process is receiving increasing attention in European countries because a high percentage of drinking water is taken from groundwater reserves. For this reason, the European Union established individual (0.1 μg L⁻¹) and total (0.5 μg L⁻¹) concentrations of pesticides in drinking water to safeguard people from harmful effects. In general, most of the urea pesticides exhibit high herbicidal activity because of the presence of heterogeneous groups such as phenyl, sulfonyl, and so forth, and urea pesticides are thermolabile with low water solubility and low volatility. Fenuron (1,1-dimethyl-3-phenylurea) is one of the known phenyl urea group herbicide. It is highly toxic with high polar nature and solubility in water; as a result, its residue has a high probability to be present in the soil and aquatic environment. Therefore, toxic fenuron detection is extremely important and because of their physicochemical characteristics, trace-level detection of fenuron is very difficult.

Previously, herbicides were detected by using colorimetric and spectrophotometric methods (with lower sensitivity). Then, the chromatography methods such as normal-phase high-performance liquid chromatography (HPLC) with photoconductivity and gas chromatography (because of their low volatility) were used for the detection of herbicides. The capillary electrophoresis method was also used for the detection of sulfonyleurea herbicides in water. The bensulfuron-methyl can be detected by HPLC with UV or photoconductivity
method. The above-mentioned methods are very expensive, time-consuming, and difficult to prepare the sample (the extraction procedure was carried out for the removal of interferences, and large quantity of the sample, skilled personnel, and costly instruments were required for analysis). However, in this work, fenuron detection is carried out by using the electrochemical method which has more advantages than other methods because this is a very simple, low-cost with high stability, minimum time consuming, highly sensitive (can detect a very low concentration of the analyte), and highly selective method.

Of all known conducting polymers, polypyrrole (PPy) is one of the most broadly studied polymers because the pyrrole can be easily oxidized and is also water soluble. In addition, PPy has been the focus of a great deal of research for sensor fabrication because of its high electrical conductivity, good redox reversibility, good environmental stability, and ease of preparation. PPy is used for many commercial applications, including secondary batteries, solid-state super capacitors, capacitive deionization process, fuel cells, and sensors. Chen et al. have tried to thicken the film of conducting polymers. However, for the conventional PPy electrode, increasing the film thickness deteriorates the electronic performance. Therefore, some attention is provided toward porous PPy. The high electrical conductivity (20.5 S cm$^{-1}$) of the nano-pore PPy thin film was reported by Li et al. Majumdar et al. have prepared a free standing PPy film and powder for the removal of anionic pollutants. PPy is of specific interest owing to its high conductivity (10–1000 S/cm) and high stability in oxidized states at room temperature for some months. The PPy/monodispersed latex sphere composite was used in large-scale Cr(VI) contaminant removal. PPy has many advantages than other conducting polymers, such as (a) PPy is thermally stable upto 250 °C compared to polyaniline (PANI), polythiophene, and so forth, degradation of PPy occurs above this temperature, (b) PPy can be easily synthesized without an acidic medium. However, PANI requires the acidic medium for preparation because the side products are produced in the polymerization step at high pH and (c) similarly, the oxidation potential of thiophene is more positive compared to pyrrole and other monomers. Therefore, a thiophene monomer is difficult to polymerize compared to the pyrrole monomer. Moreover, solubility of thiophene molecules in water is less compared to pyrrole.

To the best of our knowledge, no literature data have been so far reported for a fenuron electrochemical sensor by using a hollow PPy composite film. We reported that this is the first electrochemical pulse voltammetric sensor for fenuron with nanomolar detection. The proposed sensor showed good performance in monitoring fenuron with a very low detection limit and good sensitivity.

2. RESULTS AND DISCUSSION

2.1. Surface Morphological Studies and Electrochemical Behavior of the Film. Field emission scanning electron microscopy (FESEM) images of the PPy/alkyl aryl sulphonate (AAS) film and hollow PPy/AAS-modified film are shown in Figure 1. It is obvious that before treatment, the PPy/AAS film appeared small and spherical with smooth surface. Because negative charged AAS ions are attracted by the positive charged nitrogen atom of PPy, a large number of spherical-shaped polymer films are created.

This information is clearly indicated in the schematic diagram (Scheme 1). However, after treatment, the PPy/AAS-modified film has more number of hollow pores. Interestingly, after treatment, small sphere-shaped polymers were tuned, that is, spheres bursted out (or) sphere-like bubbles were broken down and created hollow pores and high roughness films. Therefore, after treatment, the modified film can more effectively promote the electron transfer between the target fenuron molecules and the electrode surface compared to before treatment of the film. The PPy/AAS composite film was more stable due to the presence of AAS in the film. The PPy absorption ratio was increased in the presence of AAS because of π-stacking interactions between the aryl rings of the surfactant and fenuron. The negatively charged AAS$^-$ ions were easily adsorbed on the positively charged nitrogen atom of PPy because of more electrostatic interactions between them (and interactions between cation radical intermediates with the anionic AAS$^-$). Moreover, polymerization takes place in a controlled manner in the AAS. The energy-dispersive X-ray (EDX) spectra of above-fabricated films are given in Figure 2. The respective peaks for “S” and “Na” were present in the PPy/AAS film (before treatment) with “C” and “O” peaks, which shows that the sodium salt of AAS ions have been successfully incorporated within the film, and N peaks arise due to the PPy film. (Figure 2A, Table). Remarkably, after treatment, “P” peak was present in the EDX spectra of hollow PPy/AAS films, and we also observed the decreased atomic ratio value of sulfur and carbon atoms and the increased atomic ratio value of oxygen and sodium (Figure 2B, Table). These results supported that the AAS$^-$ ions must be

Figure 1. FESEM images of (A) PPy/AAS film (before treatment) and (B) hollow PPy/AAS film (after treatment).

Scheme 1. Schematic Diagram of the Synthesis Procedure of Hollow PPy/AAS
expelled by phosphate ions and sodium insertion in the film for compensation of ion exchange during treatment in phosphate buffer solution (PBS).

The incorporation of the sodium ions and phosphate ions while replacing AAS ions into the polymer matrix was achieved by the cyclic voltammetric (CV) method. The ion exchange of the PPy/AAS film can be switched from anion exchanger to cation exchanger by the applied potential. The CV responses during the treatment of the fabricated polymer film in PBS are given in Figure 3. We can observe extreme changes in the voltammogram and size of the curve during treatment. Here, cyclic voltammogram was divided into four regions, as denoted by “a,” “b,” “c,” and “d” for understanding the ion-exchange process. The variations in region “a” and “b” were corresponding to the cations replacement/sodium ions insertion for the compensation of AAS anions in the film, and variations in the region of “c” and “d” indicate the replacement of AAS ions by phosphate ions. Based on the doctoral thesis of Zhao, it is reported that the presence of aryl sulphonic acid anions in the composite film created a spherical growth on the surface, and also indicated that movement of anions are less when the sizes of anions are bigger in the film so that anions incorporate into the composite matrix irreversibly during polymerization. Therefore, it creates permanent negative charge inside the polymer matrix. The movements of anions are highly reversible while the sizes of anions are smaller in the film. Based upon the above concept, larger pores are created by the removal of large-sized anions in the composite film during the process. The electro-neutrality of the film was maintained by compensates the negatively charged phosphate ions and sodium ions from the electrolyte are doped during the treatment. At the same time, spherical-shaped micelle of AAS anions created pores while leaving the matrix. Thus, the creation of hollow porous films was achieved by this process. Moreover, we have used higher concentrations of AAS anions than critical micelle concentration. AAS anions will form spherical-shaped micelle because of the presence of aryl groups. In the process, amount of permanent negative charges in the polymer matrix suddenly decreased. Hence, in the presence of doubly charged anions, the sharp cation-doped peak in region “b” was not present after the first cycle, indicating that cation responses can be influenced by anions employed. Hence, the cation exchange property in the region “a” and “b” was greatly

Figure 2. (A) EDX spectra and table for the PPy/AAS film (before treatment). (B) EDX spectra and table for the hollow PPy/AAS film (after treatment).

Figure 3. Electrochemical cycling of the PPy/AAS-modified electrode by CV in 0.1 M PBS (pH = 7). Potential range: 0.80 to −1.30 V, scan rate: 50 mV s⁻¹.
Figure 4. (A) CV curve of the PPy/AAS-modified electrode in 0.1 M PBS (pH = 7) at the first cycle (before treatment), potential range from 0.80 to −1.30 V, scan rate: 50 mV s⁻¹ (before treatment), (B) CV curve of the PPy/AAS-modified electrode in 0.1 M PBS (pH = 7) at the last cycle (after treatment), potential range from 0.80 to −1.30 V, scan rate: 50 mV s⁻¹ (after treatment, the hollow PPy/AAS film was prepared).

decreased in the presence of phosphate solution. Therefore, the total charge inside the film was decreased in the presence of phosphate ions. After 70 cycles (last cycle), the modified PPy/AAS film exhibited smaller capacitance in its oxidized (PPy) form than before treatment (first cycle). Similarly, some of the groups described that bigger anions are replaced by the smaller anions.⁵⁰−⁵⁴ We have calculated capacitance of the film before and after electrochemical treatment by the CV method (Figure 4). The PPy/AAS film exhibited higher capacitance current due to the presence of AAS anions inside the film (capacitance = ~0.22 mF) than the hollow PPy/AAS film (capacitance = ~0.006 mF). This difference in capacitance of PPy/AAS and hollow PPy/AAS film formation is mainly due to the replacement of AAS anions by phosphate anions in the film during the ion-exchange process. The electrode capacitance was calculated by the following equation,⁵⁵ \[ C_CV = \frac{Q_{CV}}{U}, \] where \( U \) is the potential range from −0.1 to 0.5 V and \( Q_{CV} \) is the area enclosed in the rectangular CV.

2.2. Wettability Test of the Modified Films. The wettability of the hollow PPy/AAS film was measured (Figure 5) by the contact angle test which is very much useful to confirm the hydrophobic behavior of the film.⁵⁶ The contact angle of water on the PPy/AAS film was less than 5° which indicated super hydrophilic nature of the film. However, the contact angle value of the hollow PPy/AAS film increased (47.8°), which indicated that the modified film became slightly hydrophobic film due to the replacement of AAS⁻ ions by the phosphate ions and sodium ions insertion in the polymer backbone, and large number of pores were also created on the surface of film after treatment. The SEM and EDX results are in agreement with the above phenomenon.

2.3. Optimization Studies. 2.3.1. Effect of Different Anionic Surfactants. The electrochemical responses of fenuron were studied by using fabricated hollow PPy/AAS, hollow PPy/sodium dodecyl sulfate (SDS), and hollow PPy/p-toluene sulphonic acid (p-TSA)-modified electrodes (the film had different anionic surfactants, namely, AAS, SDS, and p-TSA.). Figure 6 shows the CV responses of fenuron with the potential range of −0.2 to 1.3 V in pH 4 buffers by using different modified electrodes. Particularly, the hollow PPy/AAS film gives a sharp and well-defined oxidation peak when the higher current appeared at 1.06 V compared to responses of hollow PPy/SDS and hollow PPy/p-TSA films for fenuron. Similarly, a small reduction peak of fenuron appeared at 0.1 V. The oxidation peaks for fenuron by hollow PPy/SDS and hollow PPy/p-TSA were present at 0.94 and 0.92 V, respectively. Here, the micelles size of the anionic surfactant plays a major role in the fenuron response. Because of the incorporation of the anionic surfactant into the PPy, the micelles size increases from p-TSA < SDS < AAS, which is related to the fenuron peak current response. The hollow PPy/AAS film has given higher response for fenuron than other films such as hollow PPy/SDS and hollow PPy/p-TSA films due to the following reasons: (1) the hollow PPy/AAS film has more hydrophobic interactions with the aromatic part of fenuron than other fabricated films, (2) the more electrostatic interaction arises between the AAS⁻ ions in the polymer matrix with nitrogen atoms of the fenuron molecule.⁵⁷ Finally, (3) acceleration of fenuron molecule easy diffusion through the porous structure of the hollow PPy/AAS film.
2.3.2. Effect of pH and Thickness. The voltammetric response of 100 μM fenuron by the hollow PPy/AAS film was investigated in the presence of different pH mediums (2.0–10.0). As shown in Figure 7, higher response current appeared for 100 μM fenuron by using pH 4 buffer. However, fenuron response was decreased while using a high pH range up to 10. At the same time, fenuron oxidation peak potential was shifted to more negative potential when pH was increased from 2 to 10 due to the intervention of protons in fenuron oxidation.

The thickness of the hollow PPy/AAS film was controlled by the number of polymerization cycles. The electropolymerization of pyrrole in the presence of AAS− with the potential range from −0.40 to 0.67 V was carried out by the CV method. The effect of film thickness was studied for enhancing the sensor performance of fenuron. Initially, the different thickness film was prepared by varying the number of polymerization cycles (2–14). Then, these films were treated with PBS solution. As shown in Figure 8, fenuron response was increased with increasing the thickness of the fabricated film (or) increasing the polymerization cycles (2–12). This is related to enhancement of the total electroactive transport area of the modified film. Hence, oxidation and reduction peaks of fenuron were increased. The rate is then diffusion controlled through the polymer matrix. When increasing the film thickness (14 cycle), fenuron response was decreased due to hindered electron transport through the polymer matrix. Hence, the 12-cycle film was used with optimum thickness.

2.4. Fenuron Responses of Hollow PPy Composite Films by CV and Differential Pulse Voltammetry. A comparison of electrochemical responses of PPy/AAS and hollow PPy/AAS films by CV toward fenuron in pH 4 buffer is shown in Figure 9. We can see that the hollow PPy/AAS film gives a well-defined sharp oxidation peak for fenuron. However, the PPy/AAS film has highly capacitive curve, which showed a lower current signal attributable to the nonspecific binding of fenuron on the surface of the film. Because of electrochemical treatment, the hollow PPy/AAS film creates a large number of pores and also increases the active sites on its electrode surface. So that fenuron can easily diffuse through porous films with more interactions with electrodes. Particularly, the interaction arises between the negatively charged phosphate anion-enclosed film and the positively charged nitrogen atom of the fenuron. Similarly, a weak reduction peak for fenuron has appeared at more negative potential. Figure 9 shows that the possible oxidation mechanism of fenuron is followed by one electron and one proton transfer; initially, it creates a radical, then, dimerization by interaction of another radical of the monomer.

Figure 7. (A) CV response curves of the hollow PPy/AAS film-modified GCE in the presence of 100 μM fenuron in various pH buffer solutions at the scan rate of 50 mV s⁻¹ and (B) calibration plot for various pH vs anodic peak currents.

Figure 8. CV response curves of the hollow PPy/AAS film-modified GCE obtained from different polymerization cycles (2–14 cycles) in the presence of 100 μM fenuron at the scan rate of 50 mV s⁻¹ in pH 4 buffer solution (inset curve is the maximized image).

Figure 9. Possible oxidation mechanism of fenuron and the comparison of CV responses for fenuron in pH 4.0 buffer at hollow PPy/AAS film-modified GCE and PPy/AAS film-modified GCE.
hollow PPy/AAS film-modified glassy carbon electrode (GCE) are given in Figure 10. The corresponding oxidation peak for fenuron was increased with increasing the concentrations of fenuron from 4 to 100 μM with a lower detection limit of 1 μM (at S/N = 3). The linear regression equation can be expressed as $I_p (\mu A) = (1.5580) + 0.2030c (\mu M)$, with a correlation coefficient $R^2 = 0.9717$, and sensitivity value is 0.2030 $\mu A \mu M^{-1}$.

Differential pulse voltammetry (DPV) is a pulse voltammetric technique that offers the advantage of quickness and superb sensitivity connected with effective discrimination against the capacitive current. This technique has been applied for determination of trace amounts of numerous electroactive organic compounds in the environment. DPV studies of fenuron were performed on the fabricated hollow PPy/AAS film as the working electrode. The trace-level DPV responses of fenuron in pH 4.0 are displayed in Figure 11. Under the optimized conditions, oxidation peak current of fenuron increases with the addition of fenuron concentrations from 10 nM to 110 μM. The calibration curve was drawn between peak current versus fenuron concentrations. The obtained linear regression equation, correlation coefficient, and sensitivity are $I_p (\mu A) = 0.1437c (\mu M) + 1.0580$, and 0.1437 $\mu A \mu M^{-1}$, respectively. The linear detection range of fenuron is from 10 nM to 110 μM, and the lowest detection is 5 nM (as per S/N ratio). This is very close to the standard concentration level of pesticides in drinking water. However, this value is lower than the maximum residue levels of phenyl urea herbicides (0.02–0.1 mg/kg) established by Europe. Comparison of the proposed sensor for the determination of fenuron with other techniques is shown in Table 1. From the table, the detection limit of our proposed sensor is 5 nM which is comparable to other techniques. However, advantage of our proposed sensor is the wide linear detection limit compared to the other techniques such as the HPLC method,62 HPLC–DAD method (liquid chromatography with UV diode array detection),63 and matrix solid phase dispersion (MSPD) method–RP-LC.67 Similarly, the detection time or response time is very low (40 s) compared to other techniques (several minutes).

### Table 1. Comparison of the Proposed Sensor for the Determination of Fenuron with Other Techniques

| methods | linear range, μM | detection limit, μM | references |
|---------|------------------|---------------------|------------|
| amperometry | 1–47 | 0.35 | 61 |
| HPLC | 0.01–0.89 | 0.001 | 62 |
| HPLC | 4–6990 | 4.00 | 63 |
| LC–MS | 0.01–0.03 | 0.006 | 64 |
| HPLC–DAD method [liquid chromatography with UV diode array detection] | | 0.001 | 65 |
| low-temperature phosphorimetric methods | 0.61–121.8 | 0.122 | 66 |
| MSPD–RP-LC | 0.20–3.04 | 0.002 | 67 |
| direct laser photo-induced fluorescence method | 0.12–60.9 | 0.009 | 68 |
| DPV | 0.01–110 | 0.005 | present work |

2.5. Interferences, Stability, and Real Sample Analysis. Some of the inorganic metal ions and some anions may be present in real samples. So that effects of various interferences in pH = 4 buffer were analyzed by the addition of interferences (such as 1.5 mM of Na⁺, Cu²⁺, Zn²⁺, Mg²⁺, Fe²⁺, Fe³⁺, Ca²⁺, SO₄²⁻, Cl⁻, PO₄³⁻, and CO₃²⁻, and 1 mM of urea, carbaryl,
Figure 12. (A) DPV response of the hollow PPy/AAS film-modified GCE to the addition of various interferences. (B) Reproducibility of the hollow PPy/AAS-modified electrode.

In addition, reproducibility of the hollow PPy/AAS-modified electrode was checked by DPV. Figure 12B exposes that the relative standard deviation of fenuron is 1.95%, indicating superb reproducibility. Then, the modified electrode was kept at room temperature for one week. This electrode was used for the fenuron measurement. The obtained results were close to the initial response up to 93.5%, which clearly show that the sensor had good storage stability.

3. CONCLUSIONS

In summary, we developed an efficient sensing platform based on the hollow PPy/AAS film for the detection of toxic fenuron. The effects of pH and thickness of the films on the performance of the proposed sensor were studied. This is the first electrochemical sensor for fenuron using pulse voltammetric technique with nanomolar detection without significant interference. The proposed sensor matrix demonstrates a high selectivity, good reproducibility, a low detection limit (5 nM), and wide linear range from 10 nM to 110 μM of fenuron by the DPV method. The present investigations reveal that the performance of the proposed sensor exhibits its suitability for enhanced as well as sensitive determination of toxic fenuron in the agriculture groundwater sample with good recovery.
0.67 V (scan rate: 50 mV s\(^{-1}\)). Then, the PPy/SDS film was treated in 0.1 M PBS solution and in the potential range of 0.80 and −1.30 V by several cycles. The prepared film was named as the hollow PPy/SDS film. Similarly, the PPy/p-TSA film was synthesized by the electrochemical polymerization method in 0.025 M LiClO\(_4\) solution containing 0.1 M pyrrole and 0.05 M p-TSA in the potential range between −0.40 and 0.67 V at a scan rate of 50 mV s\(^{-1}\). Hereafter, the PPy/p-TSA film was electrochemically treated in 0.1 M PBS in the potential range of 0.80 and −1.30 V by several cycles. The obtained hollow PPy/p-TSA film was used for further analysis.

4.4. Electrochemical Measurements. Electrochemical measurements were carried out in a three-electrode system using CV and DPV techniques. Initially, the hollow PPy/AAS film was kept into the electrochemical cell containing 25 mL of pH 4.0 buffer, and electrochemical responses of fenuron was studied by CV in the potential range of −0.2 to +1.3 V at a scan rate of 50 mV. DPV was also performed in the potential range between 0.3 and +1.3 V. The peak current values for the corresponding concentration of fenuron were recorded by CV and DPV.

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Notes

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