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Electrocatalytic behaviour of carbon paste electrode modified with iron(II) phthalocyanine (FePc) nanoparticles towards the detection of amitrole

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Abstract

This paper describes the construction of a carbon paste electrode (CPE) impregnated with nanoparticles of iron(II) phthalocyanine (nanoFePc). The new electrode (nanoFePc-CPE) revealed interesting electrocatalytic behaviour towards amitrole; pure catalytic diffusion-controlled process, with high Tafel slope (235 mV/decade) suggesting strong binding of amitrole with nanoFePc catalyst. The effects of catalyst loading, varying pH and electrolytes were studied. The mechanism for the interaction of amitrole with the nanoFePc is proposed to involve the $\mathrm{Fe^{(III)}Pc/Fe^{(II)}Pc}$ redox process. Using chronoamperometry ($E = +0.42$ V versus Ag/AgCl) technique, the sensor was reliably employed for amitrole assay at pH 12.0 phosphate buffer (with sodium sulphate as the supporting electrolyte) for up to 12 nM amitrole with excellent sensitivity (ca. 3.44 μA/nM) and low detection limit (3.62 ± 0.11 nM, i.e. $0.305\ \mu\mathrm{g\,L^{-1}}$ using the $Y_\mathrm{B} + 3_{\sigma\mathrm{B}}$ criterion and 0.85 ± 0.03 nM, i.e. 70 ng/L with the $Y_\mathrm{B} + 2_{\sigma\mathrm{B}}$ criterion) as well as satisfactory amperometric selectivity coefficient ($K_\mathrm{amp} \approx 7.4 \times 10^{-4}$ for ammonium thiocyanate, a component of many amitrole herbicides, and 3.2×10^{-3} for asulam pesticide). The surface of the electrode can easily be regenerated by simple polishing on an alumina paper, obtaining a fresh surface ready for use in a new assay. The proposed electrode was successfully applied in the quantification of amitrole in its commercial formulation as well as in tap water samples.

Keywords: Iron(II) phthalocyanine nanoparticles; Amitrole; Electrocatalysis; Chronoamperometry

1. Introduction

The intensive use of pesticides and herbicides in recent years has increased agricultural productivity, but at the same time it has generated herbicide and pesticide residues, which exceed legal limits. Amitrole (3-amino-1,2,4-triazole) is well recognized as a non-selective herbicide used in formulations together with other chemical agents to control weeds in agriculture and along roads and railway tracks [1]. It causes alveolar damage due to inhalation [2], and is a carcinogenic agent in animals [3]. Its low volatility and high solubility in water make it a potential contaminant to ground and drinking water [4]. Unfortunately, despite the fact that amitrole should be monitored to ensure that it does not exceed the regulatory level of $0.1\ \mu\mathrm{g\,L^{-1}}$ in drinking water, set by the European Economic Commission (EEC) directive, no robust analytical procedure has been reported for its determination at this level [5]. Also, the Environmental Protection Agency (EPA) of the United States of America cancelled the use of this herbicide for food crops in 1971 [6].

In the past, several chromatographic methods were reported for the detection of amitrole in soils, tissues, ground and drinking water [7–12]. However, each of these methods requires enrichment steps to determine concentrations in the range of $0.1\ \mu\mathrm{g\,L^{-1}}$. Various electrochemical techniques have been employed for the detection of amitrole [13–16]. Different kinds of modified electrodes have been used for amitrole detection at micromolar level: cobalt phthalocyanine-modified carbon paste electrodes [17], microarray gold electrodes [18], Nafion/lead–ruthenium oxide pyrochlore chemically modified electrodes [19], and multi-walled carbon nanotube paste electrodes [20].

Nanosized materials such as carbon nanotubes, gold and metal oxide nanoparticles have been widely applied to the preparation of biosensors because of their large surface area and

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excellent biocompatibility [21–24]. However, there are only a few reports on the use of organic nanosized materials in environmental monitoring. Phthalocyanines, in particular, provide an attractive option because of their versatility, high catalytic activity, and low cost of raw materials [25]. The use of nanosized metallophthalocyanine complexes as electrode modifier has rarely been reported [26–28] and, to our knowledge, there has been no report on the application of nanosized Iron(II) phthalocyanine (nanoFePc) in the fabrication of electrochemical sensors. Iron(II) phthalocyanine and its complexes are of special interest because of their high catalytic activities in various chemical and electrochemical reactions [25,29–34].

In this study, we describe for the first time, the synthesis of nanosized iron(II) phthalocyanine and its subsequent application as a viable electrocatalyst/modifier in the construction of carbon paste electrode for the determination of amitrole (as raw material and its commercially available herbicide) at nanomolar concentrations. Chemically modified carbon paste electrodes (CM-CPEs) have been widely investigated because of their convenient preparation by mixing a modifier with the paste [35,36]. The advantages of using a CPE include (i) the availability of a wide potential range for analysis, (ii) easily renewable surface, and (iii) simplicity of fabrication.

2. Experimental

2.1. Materials

Amitrole was obtained from Sigma. The commercial amitrole herbicide employed was Illico (Sangenta, South Africa). Iron phthalocyanine (FePc) and graphite powder (1–2 μm, synthetic) were obtained from Aldrich. Mineral oil was supplied by Fluka (Buchs, Switzerland). Ultra pure water of resistivity 18.2 MΩ was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used throughout for the preparation of solutions. All electrochemical experiments with the sensor were performed in nitrogen-saturated phosphate buffer as the electrolyte. Phosphate buffer solutions (PBS) at various pHs were prepared with appropriate amounts of Na_2HPO_4 and NaH_2PO_4, and the pH adjusted with 0.1 M H_3PO_4 or NaOH. Solutions of 0.05 M of sodium salts of chloride, sulphate, chlorate, nitrate and perchlorate were used as supporting electrolytes to verify the effects of the nature of the anion. A tap water sample was collected from a public water tap in Grahamstown and was analysed on the same day using a chronoamperometric technique. The pH of the tap water was measured as 7.04; hence there was no need for a pH adjustment. All other reagents were of analytical grades and were used as received from the suppliers without further purification.

2.2. Apparatus

All electrochemical data, cyclic voltammetry (CV), square wave voltammetry (SWV) and chronoamperometry (CA) were obtained with an Autolab potentiostat PGSTAT 30 (Eco Chemie, Utretch, The Netherlands) driven by the General Purpose Electrochemical Systems data processing software (GPES, software version 4.9, Eco Chemie). The parameters for the SWV were: step potential 5 mV; amplitude 20 mV at a frequency of 25 Hz. All chronoamperograms were obtained at an applied potential 0.42 V (versus Ag|AgCl) without stirring the solution. A conventional three-electrode system was used. The working electrode was carbon paste ($d = 3$ mm) or carbon paste modified with bulk or nano-scaled FePc complex. A Ag|AgCl wire and platinum wire were used as pseudo-reference and counter electrodes, respectively. To prevent electrolyte contamination of the analyte inherent with normal reference electrodes containing high concentration of electrolyte solution, an easy-to-make solid-state reference electrode (Ag|AgCl pseudo-reference electrode) was preferred for this work. In this work, we found that at 25 ± 1 °C, the potential response of Ag|AgCl pseudo-reference in aqueous conditions was less than the normal Ag|AgCl (3 M KCl) and SCE by 0.15 ± 0.03 and -0.01 V, respectively. A Wissenschaftlick-Technishe Werkstätten (WTW) pH 330/SET-1 (Germany) pH meter was used for pH measurements. All solutions were de-aerated by bubbling pure nitrogen gas prior to each electrochemical experiment. All experiments were performed at 25 ± 1 °C. Scanning electron microscopic (SEM) pictures of the bulk and nano-scaled FePc were obtained using a JEOL JSM 840 scanning electron microscope at 5 kV accelerating voltage.

2.3. Procedure

2.3.1. Synthesis of nanoFePc

The nanoFePc particles were synthesized as described previously for nanoCoPc [26–28] with a slight modification. Briefly, 0.15 g FePc was dissolved in 5 ml of 98% concentrated sulphuric acid. The solution was then added drop-by-drop into a vigorously stirred 300 mL aqueous solution containing 0.45 g hexadecyltrimethyl ammonium-chloride (CTACl) ($C_{16}H_{33}N(CH_3)_3Cl$). The resulting solution was centrifugally separated. The obtained sediment was washed repeatedly with water until neutral. It was then vacuum-dried to obtain the nanoFePc powder.

2.3.2. Fabrication of the nanoFePc-CPE

Mineral oil, activated graphite powder and nanoFePc were mixed in a ratio of 20:77:3 ratio (w/w). Activation of the graphite instantaneously lead to the generation of the carboxylic and/or the hydroxyl functionalites at the graphitic carbon surface [36]. Thus, the fragments become markedly hydrophilic and repel hydrophobic molecules of the binder used to make the graphite paste. The activation method used in this work involved washing the graphite with acetone, then with a 1:3 mixture of HCl and HNO_3, and finally with pure distilled water. The paste was then dried in an oven for 4 h at 400 °C. A certain quantity of graphite paste containing nanoFePc was prepared and packed firmly into the cavity ($d = 3$ mm) of a plastic pipette tip. Electrical contact was established with a copper wire. The resulting electrode is hereby denoted as nanoFePc-CPE. The electrodes modified with the bulk FePc (FePc-CPE) and carbon paste alone (CPE) were prepared in a similar way. The surface of each electrode was wetted with distilled deionised water and polished with alumina paper (polishing strips 30144-001, Orion) before use. When not in use, the electrode was stored in a refrigerator. Current densities were calculated using the geometric surface area of a 3-mm diameter electrode.

3. Results and discussion

Electrochemical determination of amitrole is difficult using an ordinary carbon electrode due to large oxidation overpotential. One promising approach for minimizing overpotential of analytes is the use of metallophthalocyanine-modified electrodes [37–40]. For amitrole detection CoPc has been employed as a catalyst [17]. However, the limit of detection still needs to be lowered in order to detect very low concentrations of amitrole. To achieve this, we report on the use of nanoFePc-CPE. The nanoFePc was synthesized from bulk FePc as explained in Section 2. Typical scanning electron micrographs of the bulk and nanosized FePc complexes (Fig. 1) clearly confirm the change from the wood-chips-like bulk FePc structure (Fig. 1A) to its nano-sized FePc particles, clogged together possibly by the residual CTACl detergent used during the synthesis (Fig. 1B). The size of the nano-sized CoPc particles made with similar procedure as the nanoFePc was reported to be 71.8 nm [26] with diameters of approximately 10 nm [27]. Since FePc and CoPc share similar structural formulae and molecular sizes, the nanosize dimensions of the nanoFePc reported in this work can be assumed to be in the same order as the nanoCoPc.

As will be discussed later, voltammetric analysis of amitrole at optimised conditions (a 3% nanoFePc loading in CPE and pH 12.0 phosphate buffer containing Na_2SO_4 as supporting electrolyte) showed an enhanced catalytic peak current and at less positive potential (>50 mV) compared to those of the CPE or CPE modified with bulk FePc complex, clearly confirming the high catalytic effect of the nanoFePc electrode towards the detection of amitrole. Although, as a precautionary measure all solutions were de-aerated by bubbling pure nitrogen gas prior to each electrochemical measurement, we did not observe any detectable effect on the analytical response of the electrodes when solutions were not de-aerated, indicating that residual oxygen in the sample solutions has no observable effect on the electrocatalysis of amitrole.

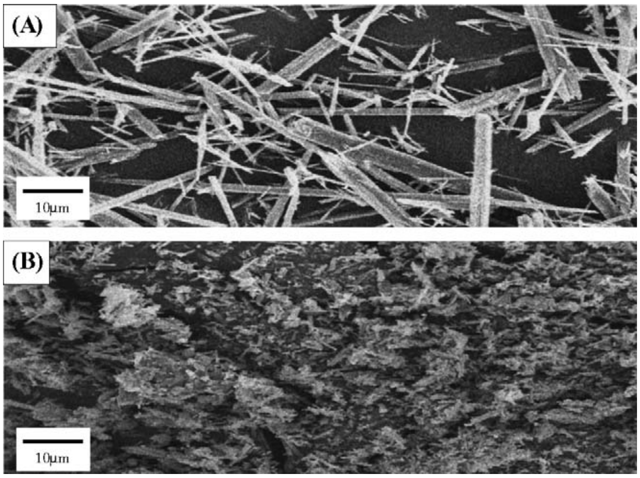


Fig. 1. Scanning electron microscopy (SEM) pictures of bulk (A) and nanoFePc (B). Magnification = 1000×.

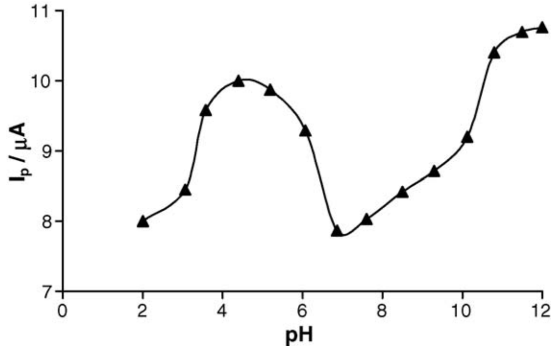
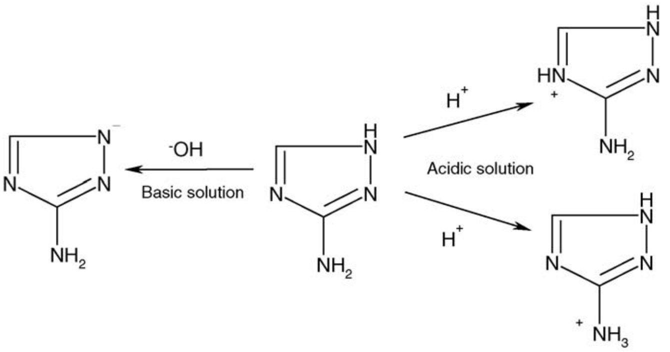


Fig. 2. Effect of pH on current response of amitrole.

3.1. Optimization of parameters

3.1.1. The pH effect

The effect of varying pH on the current response of nanoFePc-CPE at constant amitrole concentration (1 mM) is shown in Fig. 2. There are two maxima at pH 4.4 and 11.5, with the maximum at pH 11.5 higher than the one at pH 4.4. The current response decreased from the pH 4.4, but then increased from pH 7.0 until at pH 11.5 maximum where it stabilized up to pH 12.0. These observed pH maxima are in agreement with the known pK_a values of 4.2 and 10.7 for amitrole [41], indicating the presence of different forms of amitrole ions in acidic and basic media. From the known solution chemistry of the triazoles [42], the possible routes for the formation of the amitrole ions in acidic and basic media may be depicted as shown in Scheme 1. Also, the plot of peak potential (E_p) against pH (Fig. 3) shows two linear relations in acidic (pH < 7) and basic (pH > 8) media. These two linear relations would then correspond to the different forms of amitrole that exist in acidic and basic media. The magnitudes of the slopes of the lines in Fig. 3 (ca. 53 and 60 mV/pH) indicate that one-electron (accompanied by one-proton) oxidation processes takes place on the electrode surface. Since a larger current response was obtained at ≥pH 11.5 than at pH 4.4, it is expected that in alkaline conditions, all the amitrole species will be completely ionized at pH 12.0, thus all subsequent experi-



Scheme 1. Proposed mechanism for formation of amitrole ions in acidic and basic media.

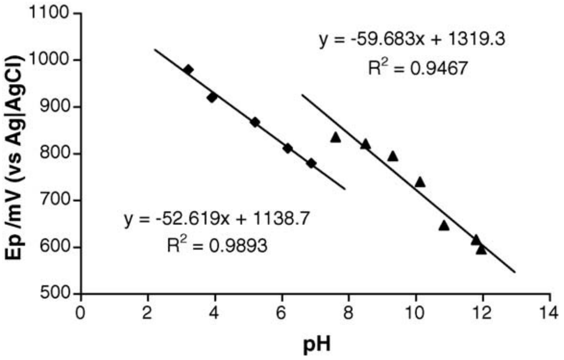


Fig. 3. Effect of pH on peak potential for the detection of 1.0 mM amitrole.

ments in this work were performed in pH 12.0 phosphate buffer solution.

3.1.2. Effect of nanoFePc loading

The dependence of anodic current response on the nanoFePc loading in the carbon paste in pH 12.0 conditions is shown in Fig. 4. The current response increases with increasing amount of nanoFePc until the mass of the modifier is about 3% of the total mass of the paste. As evident in Fig. 4, higher concentrations of nanoFePc decreased the current density significantly, the reason for which is not clear at the moment. Presumably, more nanoFePc at the electrode surface reduces the amount of conductive area of the activated graphite particle. Hence a 3% nanoFePc-modified carbon paste electrode was used throughout this work.

3.1.3. Effect of the supporting electrolytes

Supporting electrolytes have been known [43] to enhance the electrocatalytic response of MPc modified electrodes towards the detection certain analytes by increasing either the catalytic current response and/or lowering the detection potential. Table 1 presents the electrochemical response characteristics of the nanoFePc-CPE in phosphate buffer at pH 12.0, using different sodium salts as supporting electrolytes. The dependence of current response on the nature of anion used was thus examined. From the table it can be seen that the highest current response and lowest peak potential were obtained with 0.05 M sodium sulphate as the supporting electrolyte. This behaviour indicates that anions should be responsible for neutralizing the electrode surface, allowing the redox activity to occur. The anions should interact with the metal at the center of the FePc complex on the electrode, stabilizing the oxidized form according to the electron donor capacity [43]. Hence, all subsequent electrocatalytic experiments of amitrole with the proposed electrode were carried out using 0.05 M Na_2SO_4 as the supporting electrolyte.

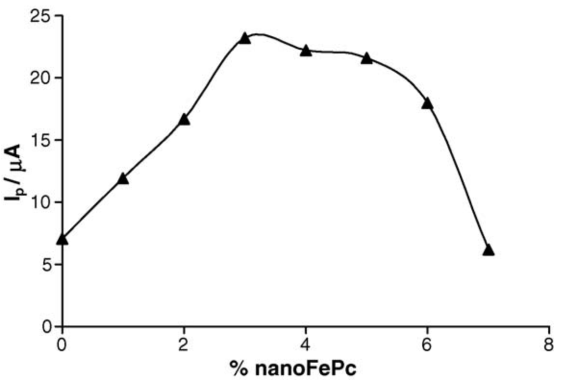


Fig. 4. Effect of nanoFePc loading on the current for detection of 1 mM amitrole in pH 12.0 phosphate buffer containing 0.05 M Na_2SO_4.

Table 1
Effect of different supporting electrolytes (0.05 M) on the current and potential response of the nanoFePc-CPE at fixed amitrole concentration (1 mM) at pH 12.0 phosphate buffer solution (PBS, 0.1 M); scan rate = 25 mV/s

Electrolyte	Current density, *J* ($\times 10^4$ A/cm^2)	Peak potential, E_p/V (vs. Ag|AgCl)
PBS alone	3.5	0.61
CH_3COONa	5.7	0.46
$NaNO_3$	7.1	0.46
Na_2SO_4	9.2	0.45
NaCl	2.8	0.51
$NaClO_4$	4.6	0.48

All values are averages from 10 measurements performed during 2 months (R.S.D. < 2%).

3.2. Electrocatalytic behaviour towards amitrole

Amitrole was analysed using the optimised conditions (pH 12.0 phosphate buffer containing a 0.05 M Na_2SO_4 as supporting electrolyte). For comparative response of the three electrodes (CPE, bulk FePc and nanoFePc) SWV was employed since it is well recognised [44] to be a more sensitive voltammetric technique than the normal CV. It is evident from Fig. 5, that while CPE showed a broad anodic peak due to amitrole around 0.44 V (versus Ag|AgCl), the same CPE modified with FePc and nanoFePc exhibited well-defined oxidation peaks at approximately the same potential (0.42 V versus Ag/AgCl). The waves exhibited by the electrode modified with the FePc complexes indicate that these electrodes can be used to enhance electronic communication between the electrodes and amitrole. Compared

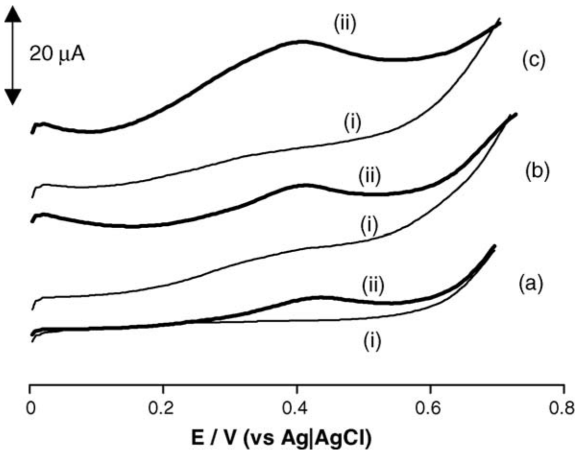


Fig. 5. Typical square wave voltammograms of (a) CPE (b) FePc-CPE and (c) nanoFePc-CPE in pH 12.0, phosphate buffer solution (containing 0.05 M Na_2SO_4) without (i) and with (ii) 0.1 mM amitrole.

to the CPE and FePc, the nanoFePc (Fig. 5c) clearly shows higher electrocatalytic activity towards amitrole in terms of an enhanced current density.

Using normal CV technique (not shown), the effect of different scan rates (0.025–1.20 V s^{-1}) at constant amitrole concentration (1.0 mM) revealed some important information. First, anodic peak current (I_{pa}) is directly proportional to square root of the scan rate ($\nu^{1/2}$), indicating a diffusion-controlled reaction. Second, a plot of $I_{pa}/\nu^{1/2}$ versus ν resulted in the characteristic shape that is typical for a catalytic process. Finally, using the usual equation (Eq. (1)) for a totally irreversible, diffusion-controlled process such as amitrole oxidation [45–47]:

$$E_p = \frac{b}{2}\log \nu + \text{constant} \tag{1}$$

The plot of E_p versus (1/2) log ν gave a linear relationship, with a Tafel slope ($b = 2.303RT/\alpha nF$) of approximately 235 mV/decade, suggesting that the rate-determining step for the electrocatalysis is a one-electron transfer process assuming a transfer coefficient of $\alpha < 0.5$ at 298 K. The Tafel slope obtained in this work is comparable (within the limits of experimental errors) to the −239 mV/decade recently reported by Zen et al. [19] for amitrole oxidation using a Nafion/lead–ruthenium oxide pyrochlore chemically modified electrode. Tafel slopes greater than the normal 30–120 mV/decade are known [19,48,49] to be due to the substrate–catalyst interactions, where the substrate binds very strongly to the catalyst during the interaction as the reaction intermediate step. The Tafel slope obtained in this work may also be rationalised as strong binding of the amitrole–nanoFePc in the intermediate step.

Previous report on the interaction of CoPc with amitrole [17] proposed the involvement of the Co$^{(III)}$/Co$^{(II)}$ redox processes. The Fe$^{(III)}$/Fe$^{(II)}$ redox processes are evident as deeps or broad peaks in Fig. 5 (curves (i) of (b) and (c) for FePc and nanoFePc, respectively) around 0.30 V (versus Ag|AgCl), but not observed for the CPE SW voltammogram (Fig. 5a, curve (i)). The Fe$^{(III)}$/Fe$^{(II)}$ redox potential is very close to the oxidation potential (0.42 V versus Ag|AgCl) of the amitrole. Thus, the mechanism through which electrocatalytic oxidation of amitrole operates at the nanoFePc-CPE may be represented (for basic media where amitrole is an anion) as shown by Eqs. (2)–(4):

$$\text{Fe}^{2+}\text{Pc} \rightarrow \text{Fe}^{3+}\text{Pc} + \text{e}^- \tag{2}$$

$$\text{Fe}^{3+}\text{Pc} + \text{amitrole}^- \rightarrow [\text{Fe}^{3+}\text{Pc(amitrole}^-)] \tag{3}$$

$$[\text{Fe}^{3+}\text{Pc(amitrole}^-)] \rightarrow \text{Fe}^{2+}\text{Pc} + \text{amitrole}_{\text{(oxidized)}} \tag{4}$$

That is, initial oxidation of the Fe$^{(II)}$ to Fe$^{(III)}$ followed by the oxidation of the amitrole anion to its products via Fe$^{(III)}$ and subsequent regeneration of the Fe$^{(II)}$ species.

Electrochemical detection of amitrole was performed using chronoamperometry because of the excellent sensitivity of this technique. There was a steady increase in current response following addition of increasing concentrations of amitrole in pH 12.0 phosphate buffer solution with nanoFePc-CPE. A plot of amperometric response (I_p) versus amitrole concentration was linear from 1 to 12 nM, stabilising at concentrations >12 nM due to a possible decrease in the conductive area of the catalyst. The regression equation of the linear plot for was

$$I_p(\mu\text{A}) = 3.4379\,[\text{amitrole}] + 10.4258, \quad \text{with } r^2 = 0.9990$$

where amitrole concentration [amitrole] is in nM. From the slope, the sensitivity is ∼3.44 μA/nM. Using the $Y_B + 3_{\sigma B}$ criterion [50] (i.e., the intercept plus three times the standard deviation of the blank), the detection limit was determined as 3.62 ± 0.11 nM (0.305 μg L^{-1}). We should mention that a much lower detection limit (0.85 nM, i.e. 0.07 μg L^{-1}) was also obtained using $Y_B + 2_{\sigma B}$ criterion, which is reasonable given the satisfactory reproducibility of this electrode. Detection limits ranging from 0.4–0.6 μM with sensitivities in the μA/μM order have been obtained previously using carbon paste modified with cobalt phthalocyanine complex [17] or with lead–ruthenium oxide pyrochlore chemically modified electrode [19]. It is interesting to note that although our detection potential of 0.42 V versus (Ag|AgCl) is similar to literature report [17] of 0.55 V versus Ag|AgCl (sat'd KCl) for the detection of amitrole in alkaline conditions with CoPc-based electrode using chronoamperometric technique coupled to flow injection analysis (FIA-Amp), the sensitivity and detection limit shown by our proposed nanoFePc-based electrode are approximately three orders of magnitude better than these previous reports [17,19] for the electrocatalytic detection of amitrole. These results further indicate that the proposed nanoFePc electrode would improve the sensitivity and detection limits of amitrole if a more sensitive analytical technique such as the FIA-Amp is employed.

3.3. Application to real sample analysis

To assess the applicability of the developed electrode for the proposed direct amperometric procedure, a commercially available amitrole herbicide Illico, was analysed by the standard addition method. A fresh tap water sample containing 1.9 nM of commercial amitrole (in Illico) was spiked with 3.0 nM aliquots of amitrole. Six replicate determinations showed recovery of 99.61 ± 0.12% of the spike. A similar experiment in pH 12.0 phosphate buffer gave a recovery of 98.46 ± 0.24% amitrole, which is about the same value as the manufacturer's cited values. These results thus demonstrate the suitability of the proposed nanoFePc-CPE to real sample analysis.

3.4. Selectivity of the electrode

The selectivity of the electrode was investigated using the mixed solution method [51]. The concentration of the interfering species and amitrole were 10^{-6} and 10^{-7} M, respectively. The selectivity was checked against NH_4SCN (a common component of many amitrole-based herbicide formulations) and asulam. The values of K_{amp} (where K_{amp} = the amperometric selectivity coefficient) were determined from Eq. (5) [51] for analysis in the presence of NH_4SCN (a similar equation will apply for analysis in the presence of other interfering ions):

$$K_{\text{amp}} = \left(\frac{\Delta I_{\text{mixture}}}{\Delta I_{\text{amitrole}}} - 1\right)\frac{[\text{Amitrole}]}{[\text{NH}_4\text{SCN}]} \tag{5}$$

where $\Delta I_{\text{mixture}}$ and $\Delta I_{\text{amitrole}}$ are respectively, the changes in current for the mixture containing amitrole and the interfering ion, and amitrole alone. The K_{amp} values are $(7.41 \pm 0.14) \times 10^{-4}$ for NH_4SCN but $(3.16 \pm 0.10) \times 10^{-3}$ for asulam. According to Stefan et al. [51], a K_{amp} value less than 10^{-3} (as obtained for NH_4SCN) clearly indicates non-interference. On the other hand, if the K_{amp} value falls within the magnitude order of 10^{-3} (as obtained for asulam) suggests that the species is an interferent but not a strong one. Thus, the proposed electrode can be reliably used in the detection of amitrole in the presence of these species, particularly the NH_4SCN, under the conditions employed in this work.

3.5. Stability and reproducibility

The effect of continuous scanning (20 scans) on the catalytic peak currents using cyclic voltammetry (at $25\,\text{mV}\,\text{s}^{-1}$) was investigated at a fixed concentration of amitrole (1×10^{-5} M). A dramatic decrease in peak currents (>70%) was observed after the first scan, which is an indication of a poisoned electrode possibly due to strong co-ordination of the oxidation product(s) of the amitrole with the nanoFePc catalyst. However, upon renewal of the electrode by simply polishing on an alumina paper the initial catalytic current was obtained. Electrode fouling is less significant at low (nanomolar range) than at much higher amitrole concentration, meaning less polishing during the analysis of amitrole at low concentrations. The nanoFePc used in the fabrication of this electrode has been repeatedly used for the CPE for up to 8 months for the fabrication of this carbon paste electrode without detectable change in its response towards the detection of amitrole.

4. Conclusion

This study shows that a combination of the well-known catalytic properties of iron(II) phthalocyanine with the unique properties of nanoparticles (such as a larger surface area) in a carbon paste environment has made it possible to quantify amitrole concentrations at nanomolar level. This nanoFePc sensor shows catalytic effects on the oxidation of amitrole, as shown by the enhancement of oxidation peak of amitrole. Therefore, a more sensitive electrochemical method for the determination of amitrole in its raw material form and its commercial formulations in tap water samples has been developed. This type of electrode offers certain advantages over conventional electrodes in its ease of fabrication, excellent catalytic activity, sensitivity and simplicity. Thus, the nanoFePc-CPE shows great promise for potential sensing applications, such as in amperometric sensors for flow-injection analysis.

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