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Use of a Schiff base-modified conducting polymer electrode for electrochemical assay of Cd(II) and Pb(II) ions by square wave voltammetry

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Abstract

The work herein describes the electrochemical detection of heavy metal ions, specifically cadmium and lead. The introduction and modification of functional groups such as Schiff bases leads to an enhanced sensitivity of the electrode to analytes. In this study, a platinum electrode has, for the first time, been modified with poly(3,4-ethylenedioxythiophene) (PEDOT/Schiff base) in CH_2Cl_2 containing Bu_4NPF_6 to detect cadmium(II) and lead(II) ions. The structures and morphologies of the polymer coatings were characterised via Fourier transform infrared spectroscopy and scanning electron microscopy, respectively. The electrochemical synthesis and redox state response in monomer-free synthesised films have been studied via cyclic voltammetry. Moreover, the effect of scan rate on the electrochemical behaviour of the modified electrodes was also studied. The voltammetric findings have been used to calculate the surface coverage required for the polymer films and the stability of polymer electrodes in the monomer-free solutions. Square wave voltammetry was applied for the determination of cadmium(II) and lead(II) ion concentrations and to assess the effects of pH on aqueous samples. The limits of detection for the modified electrode for cadmium(II) and lead(II) were found to be 0.95 μg L^{-1} and 1.84 μg L^{-1}, respectively. These findings revealed that modified films can be considered good candidates for application in electrochemical detection devices.

Keywords Square wave voltammetry · Electrochemical detection · Conducting polymers · Modified electrode poly(3,4-ethylenedioxythiophene) · Schiff base

Introduction

Globally, the pollution of the planet is one of most vital problems mankind faces because of the widespread and critical damage such pollution can cause (Intarakamhang et al. 2013; Huang et al. 2016). Heavy metal ions like Cu, Hg, Zn, Pb, Ni, and Cd are considered toxic even in extremely low concentrations (Morante-Zarcero et al. 2015). These metal ions can cause significant harm and damage in human organs such as the kidneys, liver, brain, and the lungs and respiratory system (Lu et al. 2018). Recently, contamination from heavy metals has become a significant problem as a result of the rapid development of industrial activities (Muralikrishna et al. 2017). Contamination of the environment, especially with cadmium(II) and lead(II) ions, poses a real danger to human health because these ions are toxic, non-biodegradable, and accumulate in the body over time (Yao et al. 2019). According to World Health Organisation (WHO), the maximum permitted concentrations of cadmium(II) and lead(II) in drinking water are 5 μg L^{-1} and 50 μg L^{-1}, respectively (Gumpu et al. 2015); thus, it becomes necessary to find fast, sensitive, and selective methods for the detection of cadmium and lead in various sample types. There have been several reports of electrochemical methods used to detect cadmium(II) and lead(II) (Xu et al. 2019), and these methods have many positive features compared with other techniques

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such as quick analysis times, simplicity, they use inexpensive technology, and have high sensitivities (Li et al. 2019).

The key factor in electrochemical voltammetry methods is the manufacture and usage of electrode surfaces that facilitate an electrical potential between the electrode surface and solution interfaces. Polymerisation and chemical adsorption can enhance the analytical functional performance of an electrode in areas such as the sensitivity and selectivity to analytes. A range of diverse materials, such as functionalised graphene oxide, carbon nanotubes (Salmanipour and Taher 2011), and polymer films have previously been used in voltammetric methods for the detection of metal ions.

Electroactive polymers such as polypyrrole (Yin et al. 2012; Bozzini et al. 2015), polyaniline (Alesary et al. 2018; Pillalamarri et al. 2005; Ismail et al. 2019a), poly(3,4-ethylenedioxythiophene) (PEDOT) (Michalska et al. 2004; Duan et al 2020), and their derivatives have high intrinsic conductivities and have been intensively studied to date (Bobacka 2006; Alesary et al. 2021). These materials play a key role in electrocatalysis, energy storage, and electrochemical sensors because of their unique properties such as stability, flexibility, simple synthetic processes, and low costs (Rahman et al. 2008; Ismail et al. 2019b; Abd Ali et al. 2021). In addition, these species have a good congruence with biomolecules. Therefore, these substances have come to represent effective alternatives to many materials used in, for example, batteries, chemical sensors, corrosion inhibitors, actuators, and in medical engineering. Recently, electroactive polymers have been used in the production of promising chemical sensor devices (Bidan 1992). Chemical modification, and indeed the chosen method of preparation, can often be manipulated to achieve the desired mechanical and electrochemical features of such polymers. Thus, electroactive polymers play a vital role in analytical fields and the fabrication of chemical sensors (Sun et al. 2016). A significant advantage of detection devices based on conjugated polymers is that they have the potential to show sensitive and selective properties and fast responses. In recent years, the fabrication of functionalised polymer electrodes has played a critical role in the production of a novel generation of electroanalysis systems with improved sensitivities and selectivities (Mohammed 2018). Several electrochemical tools based on polymers have been developed for use as detectors for various chemical pollutants (Barsan et al. 2015).

Modified electrodes in electroanalytical chemistry offer an easy and appropriate technology to allow for the examination of the reactions of various substrates and inorganic, organic, and biological species (Raghu et al. 2012; Han et al. 2020; Wang et al. 2012). Chemically modified polymer electrodes can be prepared and controlled using electrochemical techniques that allow for the generation of thin synthetic polymer films (Lei et al. 2014; Mohammed et al. 2020). In modern electroanalytical devices, analytical performance

in areas such as sensitivity, selectivity, and stability are dependent on electrode composition due to the straightforward working mechanism and fast responses achieved (He et al. 2018). Various modes can be used that include square wave voltammetry (SWV), which is considered a perfect candidate for sensitivity and quantification of various species such as alkaloids, phenols, vitamins, pesticides, herbicides and fungicides, benzoquinones, proteins, terpenoids, drugs, and heavy metals (Wang et al. 2012; Shervedani and Akrami 2013). A previous study has reported that a modified polyphenanthroline monohydrate/GC electrode displayed good sensitivity and reproducibility for Cd(II) ion detection via SWV (Oztekin et al. 2011). Moreover, polypyrrole films have been modified by insertion of ligand groups into the polymer film, allowing detection of metallic actions. Deshmukh and co-workers reported that an EDTA-modified py/SWNTs polymer film can be used for the detection of Pb^{2+} in aqueous solution (Deshmukh et al. 2018). Among the diverse electroactive polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is of particular interest in the area of chemical sensing due to its high conductivity and good environmental stability compared with other electroactive polymer families. Electropolymerisation of the EDOT monomer can be accomplished through its oxidation in the presence of appropriate counterions. Schiff bases have emerged as potential chemical detectors for many of the metal ions of general interest as they can selectively bind to specific cations (Vilas-Boas et al. 1998). The aim of the current research is to enhance the sensitivity and selectivity of modified polymer electrodes to be more efficient with regard to metal ion determination and with improved stability, repeatability, and conductivity of the electrodes (Etorki et al. 2007; Guadalupe and Abruna 1985). The goals of this project were: (i) to electropolymerise and modify a PEDOT/Schiff base electrode in non-aqueous medium; (ii) to examine the response of the prepared modified polymer electrode using CV; (iii) to study the effect of scan rate; and (iv) to investigate the interaction of the polymer electrode with heavy metal ions, in particular Cd(II) and Pb(II) ions, using square wave voltammetry (SWV).

Experimental

Materials and reagents

2-Aminomethyl-3,4-ethylenedioxythiophene (EDOT-MeNH$_2$) was prepared using the following procedure (Darmanin and Guittard 2013). Chloromethyl-3,4-ethylenedioxythiophene (EDOT–MeCl), salicylaldehyde (98%), potassium phthalimide, and hydrazine hydrate were obtained from Sigma Aldrich and used without further purification. Dichloromethane (DCM) (CH$_2$Cl$_2$, AR; Tianjin Damao Chemical

Reagent Factory) was purified by distillation over calcium hydride before use. Tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$, 99%; Acros Organics) was dried under vacuum at 60 °C for 24 h before use. An acetate buffer solution was prepared by adjusting 0.2 M sodium acetate (Aldrich) to the desired pH through the addition of 0.2 M glacial acetic acid. All the processes were performed in aqueous media, and the preparation of the aqueous solutions was carried out using ultrapure quality water.

Instrumental

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed using a PGSTAT20 potentiostat/galvanostat from ECO-Chemie (Utrecht, The Netherlands). The Pt (1 mm) electrode was polished using 0.3 µm alumina and then washed with pure water. The electrodeposition of the EDOT-Schiff (monomer) base on the Pt electrode was achieved via cyclic voltammetry. SWV measurements were obtained via a potentiostat device which contained three electrodes: an Ag/AgCl reference electrode, a platinum plate (2 mm^2) counter electrode, and a PEDOT-Schiff base/Pt working electrode. Fourier transform infrared (FTIR) spectra were recorded to confirm the chemical composition of the films using a Perkin Elmer FTIR Frontier spectrophotometer (Waltham, USA). Scanning electron microscopy (FEI SIRION SEM) was performed to examine the surface morphology of polymer film deposited on the Pt substrate. Cyclic voltammetry was used for the electrochemical polymerisation of EDOT/Schiff base. The voltage range was swept 10 times between −0.5 to 1.4 V at various scan rates (10, 20, 30, 50, and 100 mV s^{-1}). The formation of the

polymer layer on the surface of the electrode was evidenced by the emergence of a dark colouration on the working electrode. The polymer film coating was washed using deionised water to eliminate the excess monomer from electrode surface, which was then dried at room temperature.

Preparation of stock solutions

Standard solutions (100 ppm) of each metal ion were synthesised by dissolving the metal ion in ultrapure deionised water. The lead standard solution was prepared by dissolving 0.1598 g of Pb(NO$_3$)$_2$ (99.9%, Aldrich) in deionised water and diluting to 1 L. The cadmium solution was produced by dissolving 0.274 g of Cd(NO$_3$)$_2$.4H$_2$O (99.9%, Aldrich) in ultrapure deionised water and diluting to 1 L. These stock solutions were used to prepare a series of different concentrations from 5 to 100 ppm for each of the metal ions.

Preparation of (2,3-dihydrothieno[3,4-b][1,4] dioxin-2-yl)methanamine PEDOT/NH$_2$

The original monomer of EDOT–NH$_2$ was synthesised as illustrated in Scheme 1 according to the procedure described in the literature(Darmanin and Guittard 2013). The substitution of the chloride group by an amine group was achieved via a Gabriel reaction in the presence of potassium phthalimide and hydrazine. A mixture of 2-(chloromethyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (0.3 g, 1.6 mmol) and potassium phthalimide (0.4 g, 2.2 mmol) were dissolved in 10 ml of dimethylformamide and heated at 100 °C for 24 h. The product was then decanted into 100 ml of water and extracted with chloroform. 0.1 M sodium hydroxide and

Scheme 1 The synthesis of the monomer EDOT/ Schiff base and the polymerisation reaction
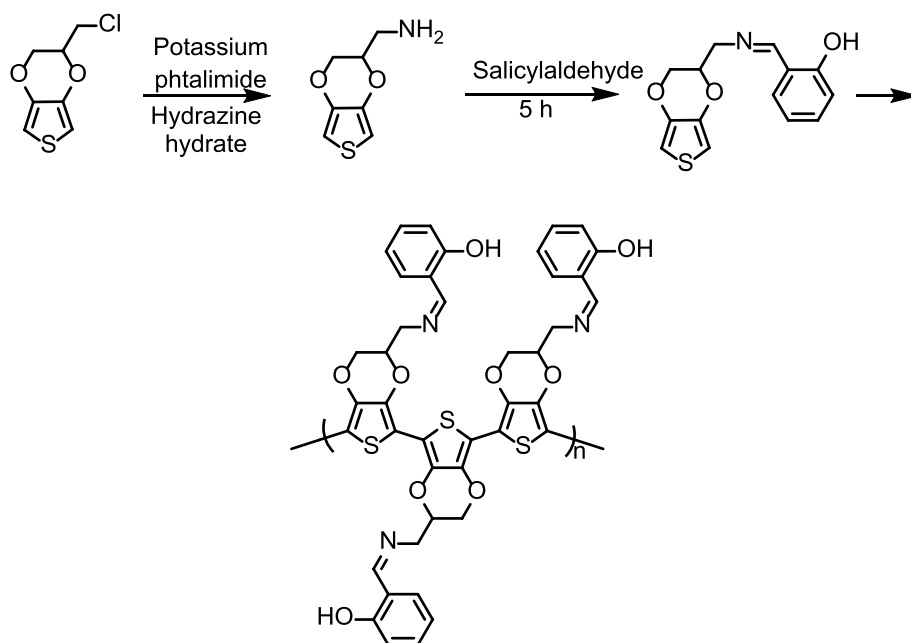
water were used to wash the organic layer and then dried with MgSO$_4$. After this step, the product was mixed with hydrazine hydrate (0.16 g, 3.2 mmol) and the mixture added to 10 ml of methanol and heated to 50 °C for 1 h. After the reaction had stopped, water was added to the mixture and the solvent was extracted under vacuum. This mixture was acidified with HCl and heated to 60 °C for 1 h. Next, the neutralisation step was accomplished for this solution using 2 M sodium hydroxide. After solvent evaporation, the amine compound was purified via column chromatography (silica gel; eluent: methanol/dichloromethane in a 1:4 ratio).

Preparation of PEDOT/Schiff ligand

2-Aminomethyl-3,4-ethylenedioxythiophene (EDOT– MeNH$_2$) (0.55 g, 2 mmol) and salicylaldehyde (0.24 g, 2 mmol) were dissolved in 20 ml of methanol with 2–3 drops of acetic acid as a catalyst under continuous stirring and then refluxed for 5 h according to the procedure described in the literature (Almashal et al. 2020). The reaction was monitored via thin-layer chromatography. At the end of the reaction, the solution obtained was filtered and washed with methanol. The crude product was dried and purified via crystallisation from ethanol. The synthesis of the monomer and polymerisation reaction steps are illustrated in Scheme 1.

Electropolymerisation of EDOT/Schiff base

The EDOT derivative was synthesised using a condensation reaction with the aldehyde EDOT-Schiff base and electropolymerised in a suitable solution to create the conducting polymer. For voltammetric deposition experiments, the EDOT/Schiff base was electropolymerised on the Pt electrode from a solution of 10 mM EDOT/Schiff base with 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in DCM using voltage cycling between −0.5 V and 1.4 V vs. the reference electrode (Ag/AgCl). The PEDOT/Schiff base film was grown on the Pt surface for 10 sequential scans with increasing anodic and cathodic peak current densities. The modified polymer electrode will hereafter be referred to as the PEDOT/Schiff base.

Electrochemical detection of metal ions

Electrochemical measurements were performed with an AUTOLAB analyser using a cell with three electrodes as described above. The working electrode was a PEDOT/Schiff base electrode, the reference electrode an Ag/AgCl/ 3 M KCl electrode, and the auxiliary electrode was a platinum electrode. Acetic acid/sodium acetate (0.2 M CH$_3$COOH + 0.2 M CH$_3$COONa) buffer solutions (pH 2–6) containing different concentrations of cadmium(II) and lead(II) ions were used as

the electrolytes for all measurements. All experiments were conducted at ambient temperature, 25 ± 2 °C. Square wave voltammetric parameters were as follows: initial potential −0.5 V, end potential 1.5 V, pulse amplitude 10 mV.

Results and discussion

Electrochemical formation of PEDOT/Schiff

The poly(EDOT-Schiff base) film was prepared potentiodynamically with a voltage ranging between −0.50 V and 1.40 V over ten scans from a 0.1 M solution of monomer in CH$_2$Cl$_2$ containing Bu$_4$NPF$_6$ onto a Pt electrode at a scan rate of 10 mV s^{-1} at 25 ± 2 °C. Figure 1 illustrates the cyclic voltammograms that were recorded during the synthesis of poly(EDOT-Schiff base). As shown in Fig. 1, the onset of the oxidation potential for the PEDOT-Schiff base film was 1.22 V. During polymerisation, a black-coloured layer of polymer film formed on the Pt electrode. The current peak of the polymer film increased with increasing number of cycles, which corresponds to the systematic growth of a polymer film on the Pt electrode (Schultheiss et al. 2020). The cyclic voltammogram in Fig. 1 shows a nucleation loop in the first cycle where this anodic current related to the oxidation of the monomer and nucleation of poly(EDOT/Schiff) (Ismail et al. 2019a). The nucleation loop was not present in the following cycles because of the persistent growth of the film preventing further nucleation in the subsequent scans. The redox processes of poly(EDOT/Schiff) has led to the emergence of anodic and cathodic peaks at 0.53 V and −0.07 V, respectively, in the cyclic voltammogram. Moreover, the increase in redox peak
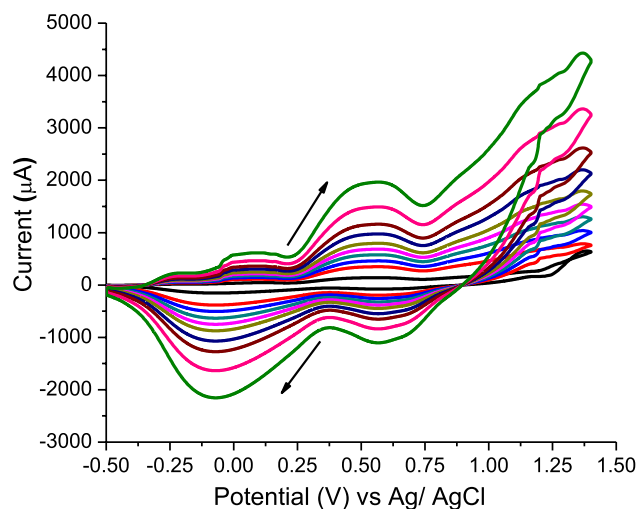

Fig. 1 Cyclic voltammogram resulting from electropolymerisation of 10 mM EDOT/Schiff base with 0.1 M Bu$_4$NPF$_6$ in DCM solution between −0.5 and 1.4 V at 10 mV s^{-1} for 10 scans. Electrode area was 0.00785 cm^2

current values in the voltammogram implied that the amount of electrodeposited PEDOT polymer on the Pt electrode had increased, which led to an increased thickness of the deposited polymer (Hillman et al. 2017). In addition, two peaks probably indicate the potential peaks of the monomers, which depended on the type and of size the anion present in the reaction medium. In other words, the emergence of redox peaks in the voltammogram can be significantly influenced by the nature and size of the ionic species present in the electrolyte.

Figure 2 shows the cyclic voltammogram (scan 10) of the electropolymerisation of the (EDOT/ Schiff) monomer at various scan rates ranging from 5 to 100 mV s^{-1} under the same polymerisation conditions used for the voltammogram in Fig. 1. The molar coverage of polymer films per unit area can be calculated from the amount of charge of the final scan in the polymer deposition using Faraday's law and Eq. (1) (Sapstead et al. 2015).
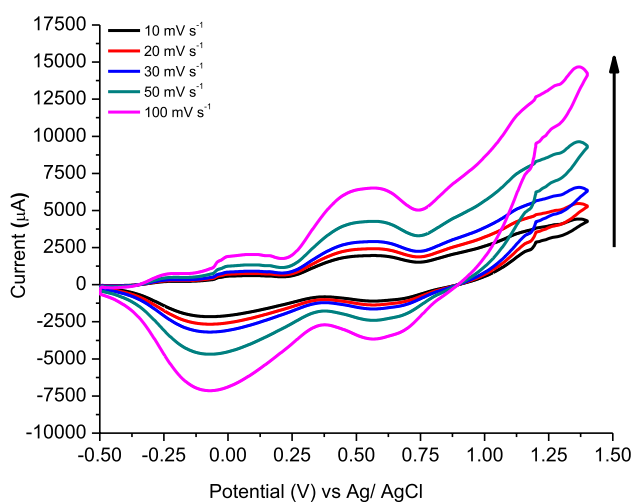
$$\Gamma = \frac{Q}{nFA} \tag{1}$$

Here, F represents the Faraday constant (C mol^{-1}), Γ is the molar coverage (mol cm^{-2}), A is the modified electrode area (cm^2), Q represents the cathodic charge, and n is the number of electrons involved in the electropolymerisation. Herein, n is equal to 2.3 (Lattach et al. 2012) and the modified electrode has a surface area of 0.00785 cm^2. The molar coverage is applied to estimate the thickness of the polymer surface (h/μm) using Eqs. (2) and (3) (Brown and Hillman 2012).

$$c = \frac{\rho}{Mr} \tag{2}$$

$$h = \frac{\Gamma}{C} \tag{3}$$

Here, c and ρ are the concentration and density of the monomer, respectively, and Mr is the molecular mass of the monomer (273.3 g/mol). h is the thickness of polymer film. The relative standard deviation (RSD%) from three consecutive experiments was calculated, as shown in Table 1, which also reports the cathodic charge, surface coverage, and thickness of prepared polymer films.

Electrochemical characterisation of polymer films

In order to obtain a greater insight into the electrochemical behaviour and stability of the polymer films, the electrochemical features were carefully analysed via cyclic voltammetry in a background electrolyte (monomer-free) of dichloromethane and aqueous solution-Bu$_4$NPF$_6$ (0.1 M) for polymer film that was prepared using a scan rate of 10 mV s^{-1} (Fig. 1), as depicted in Fig. 3A, C. Voltammetric study findings have shown broad redox current peaks that can probably be attributed to the counterions diffusing into the chain polymer film for both electrolytes (Mohammed 2018). The voltammograms of poly(EDOT/Schiff) films exhibit a broad positive peak at 0.61 V versus Ag/AgCl and a negative peak at 0.08 V versus Ag/AgCl in a DCM electrolyte. On the other hand, a broad positive peak appears at 0.52 V versus Ag/AgCl and a negative peak at 0.16 V versus Ag/AgCl in aqueous electrolyte, which are representative of the oxidation and reduction of the film produced, respectively. Herein, we observed a decrease in the
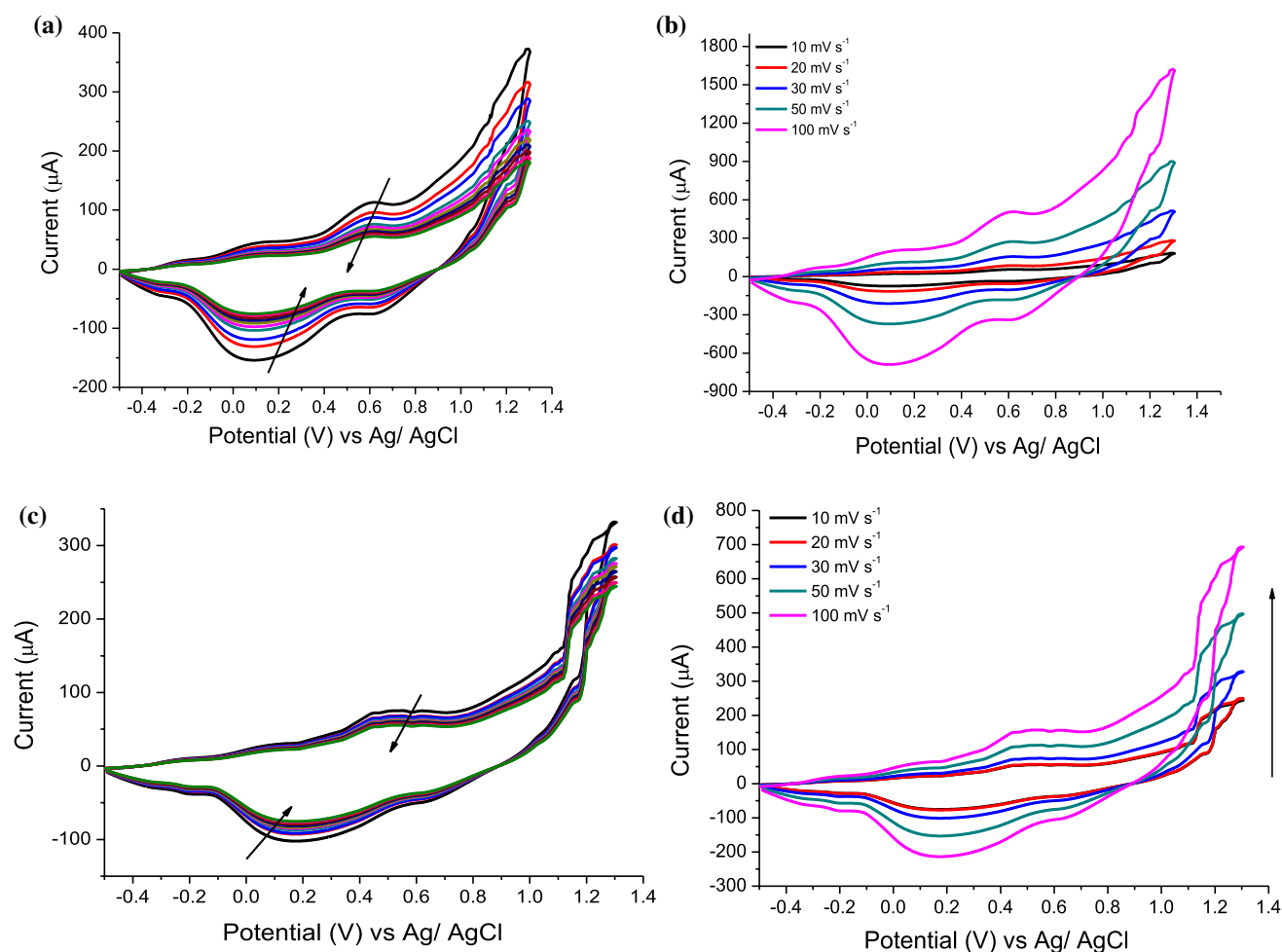

Fig. 2 Cyclic voltammogram (scan 10) for deposition of 10 mM EDOT/Schiff base with 0.1 M Bu$_4$NPF$_6$ in DCM solution at various scan rates, ν, 5–100 mV s^{-1}. Electrode area is 0.00785 cm^2

Table 1 Charge of poly(EDOT/Schiff) reduction peak at various scan rates (5–100 mV s^{-1}). Electrode area was 0.00785 cm^{-2}

Polymer films	Scan rate (mV s^{-1})	Charge of reduction peak Q (C)	RSD% $n=3$	Coverage Γ (mol cm^{-2})	Thickness h (μm)
Poly(EDOT/Schiff)	10	1.30×10^{-2}	1.32	7.46×10^{-6}	14
	20	1.12×10^{-2}	2.45	6.42×10^{-6}	12
	30	9.15×10^{-3}	1.85	5.25×10^{-6}	10.5
	50	8.02×10^{-3}	2.06	4.60×10^{-6}	9.22
	100	6.11×10^{-3}	1.47	3.50×10^{-6}	7.01

Fig. 3 Voltammetric response of poly(EDOT/Schiff) electrodes prepared at 10 mV s^{-1} (Fig. 1) and acquired in **A** 0.1 M Bu$_4$NPF$_6$ in DCM, and **C** 0.1 M Bu$_4$NPF$_6$ in the aqueous electrolyte (monomer-free) at −0.5 to 1.3 V. Voltammetric responses of the same polymer film at various scan rates in the range 10–100 mV s^{-1} **B** DCM and **D** aqueous electrolyte

peak currents as a function of increasing scan number; thus, there is decay in the peak potentials and the associated CV shapes were changed. This could be attributed to degradation of the film when switching to the overoxidation potential, which led to poor stability during redox cycling. In order to study the degradation of poly(EDOT/Schiff) and it can be proposed in any practical application of their sensor system, the long-term of electrochemical stability of the prepared poly(EDOT/Schiff) electrode (Fig. 1) was studied in aqueous electrolyte (monomer-free) for 200 scans. The results showed that poly(EDOT/Schiff) has a high electrochemical stability; thus, there is no shift in the peak potentials and the associated CV shapes were not changed (see supplementary information Fig. S1).

In this work, the effect of scan rate on electrochemical response has been studied in a background electrolyte (monomer-free) of dichloromethane and aqueous solution-Bu$_4$NPF$_6$ (0.1 M), as shown in Fig. 3B, D. From

these two curves, we can observe that the current of the peak was proportional to the scan rate (Ouyang et al. 2017); this supports the assumption of good electroactivity and stability of the polymer film. This finding indicates that redox current peaks are proportional to the scan rates for the same polymer electrode (Deshmukh et al. 2018). Further, both oxidation and reduction peaks have a linear relationship with scan rate, which is indicative of surface-confined control, as revealed in Fig. 4A, B. Tables 2 and 3 show the charges for the electrochemical response of polymer growth in Fig. 1 as cycled in the background electrolyte (monomer-free) at different scan rates, as presented in Fig. 3B, D. The charge was calculated from the CV curves in Fig. 3B, D by integration of the current of the redox peaks with respect to time. The charges found for cycles 1 and 10 are shown in Tables 2 and 3. Tables 2 and 3 show the cathodic charge values and a study of the electro-stability of the prepared films
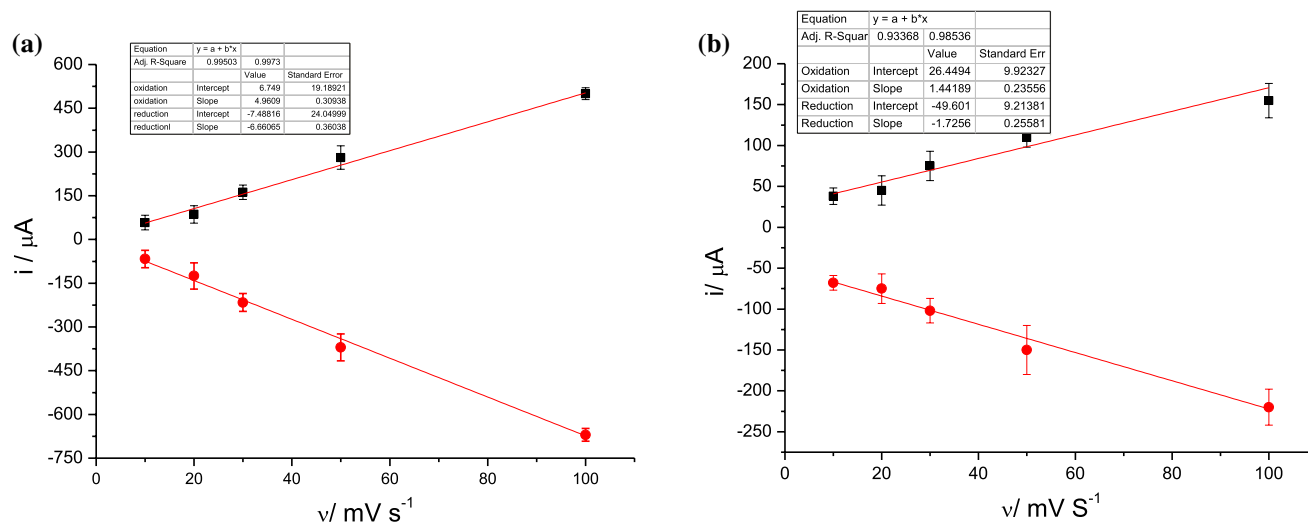
(a)

Equation	y = a + b*x	
Adj. R-Square	0.99503	0.9973
	Value	Standard Error
oxidation Intercept	6.749	19.18921
oxidation Slope	4.9609	0.30938
reduction Intercept	-7.48816	24.04999
reductionl Slope	-6.66065	0.36038

(b)

Equation	y = a + b*x	
Adj. R-Squar	0.93368	0.98536
	Value	Standard Err
Oxidation Intercept	26.4494	9.92327
Oxidation Slope	1.44189	0.23556
Reduction Intercept	-49.601	9.21381
Reduction Slope	-1.7256	0.25581

Fig. 4 Variation of redox peak current **A** from Fig. 3B and **B** from Fig. 3D with scan rate (in the range 10–100 mV s^{-1})

Table 2 Cathodic charges of PEDOT/Schiff panels in Fig. 1 exposed to 0.1 M Bu$_4$NPF$_6$ in DCM electrolyte (monomer-free) at various scan rates

Scan rate mV s^{-1}	Q red, 1st cycle C	Q red, 10th cycle C	% Q red 10th/Q red 1st retention
10	8.45×10^{-3}	6.12×10^{-3}	72
20	5.89×10^{-3}	4.78×10^{-3}	81
30	4.78×10^{-3}	3.96×10^{-3}	82
50	4.08×10^{-3}	3.08×10^{-3}	75
100	2.64×10^{-3}	2.25×10^{-3}	85

Table 3 Cathodic charges of PEDOT/Schiff panels in Fig. 1 exposed to 0.1 M Bu$_4$NPF$_6$ in aqueous electrolyte (monomer-free) at various scan rates

Scan rate	Q red, 1st cycle C	Q red, 10th cycle C	% Q red 10th/Q red 1st retention
10	8.19×10^{-3}	6.12×10^{-3}	77
20	3.71×10^{-3}	3.08×10^{-3}	83
30	2.97×10^{-3}	2.68×10^{-3}	90
50	2.13×10^{-3}	2.45×10^{-3}	87
100	1.86×10^{-3}	1.70×10^{-3}	91

(at various scan rates in the range 10–100 mV s^{-1}). The electro-stability was calculated via cyclic voltammetry from the difference between the tenth and first cycles in two monomer-free electrolytes. The results show that increasing the scan rate for PEDOT/Schiff growth results in a decrease in the charge (i.e. 1st and 10th cycles) for the polymer film exposed to 0.1 M Bu$_4$NPF$_6$ in DCM and aqueous electrolytes (monomer-free).

FTIR characterisation of EDOT/NH$_2$ and PEDOT/Schiff base structures

Figure 5 illustrates the FTIR spectra of EDOT/NH$_2$ and electrochemically prepared poly(EDOT/Schiff base) structures. An FTIR spectrum of PEDOT/NH$_2$ has the distinctive features of PEDOT and the amino group. The bands of the NH$_2$ group vibrations were observed in the range 3380–3240 cm^{-1}. The peaks at 3090 cm^{-1} and 2975 cm^{-1} cm were assigned to C–H aromatic and C–H aliphatic stretches, respectively. The vibrations for the C–O–C and C-S groups in EDOT were observed at 1100 cm^{-1}, 940 cm^{-1}, and 615 cm^{-1}, respectively. The bands at 1641, 1535 and 1362 cm^{-1} were attributed to the C=C and C–C stretches in the thiophene cycle (Ouyang et al. 2017). The FTIR spectrum of the prepared polymer Schiff base had characteristics peaks at 1645 cm^{-1} and 3365 cm^{-1} that could be attributed to imine (C=N) and OH groups, respectively. The band at 2939 cm^{-1} was assigned to the C–H aromatic and dioxyethylene bridge stretching modes of the EDOT molecule. Further, the bands at 1128 cm^{-1} and 975 cm^{-1} were noted for EDOT/Schiff (Deshmukh et al. 2018).

Morphological characterisation of PEDOT/Schiff base

The surface morphology of the PEDOT-Schiff film electrodeposited on the Pt electrode before and after adsorption of metal ions (Cd(II) and Pb(II)) was analysed by scanning electron microscopy (SEM) to characterise the morphology and surface structure of the film (Fig. 6). The polymer film was preformed potentiodynamically by applying a potential in the range −0.5 to 1.5 V versus Ag/AgCl at a scan rate of 10 mV s^{-1} for 10 cycles. Figure 6A
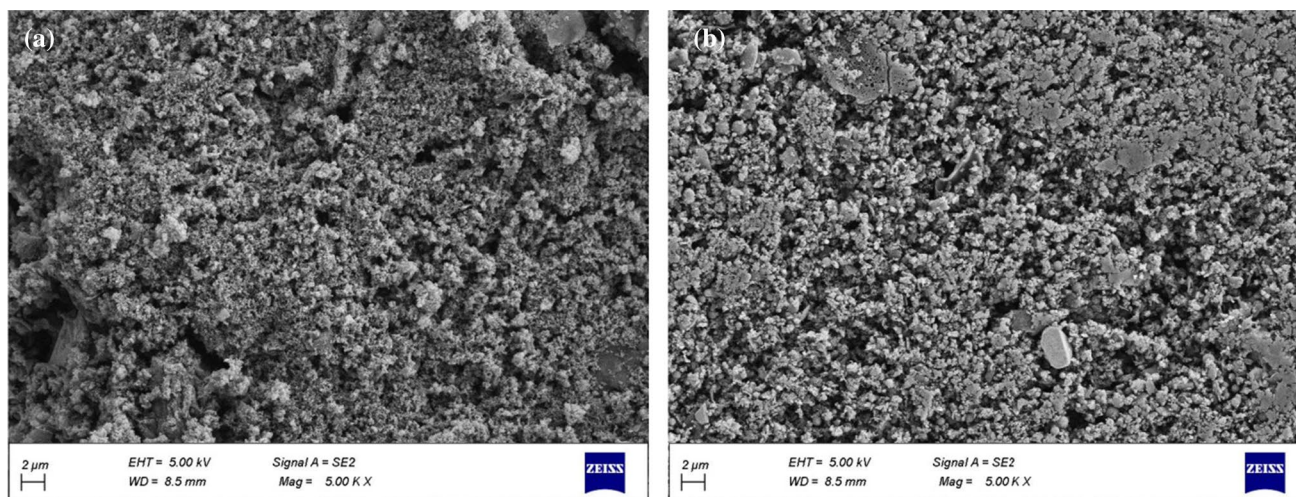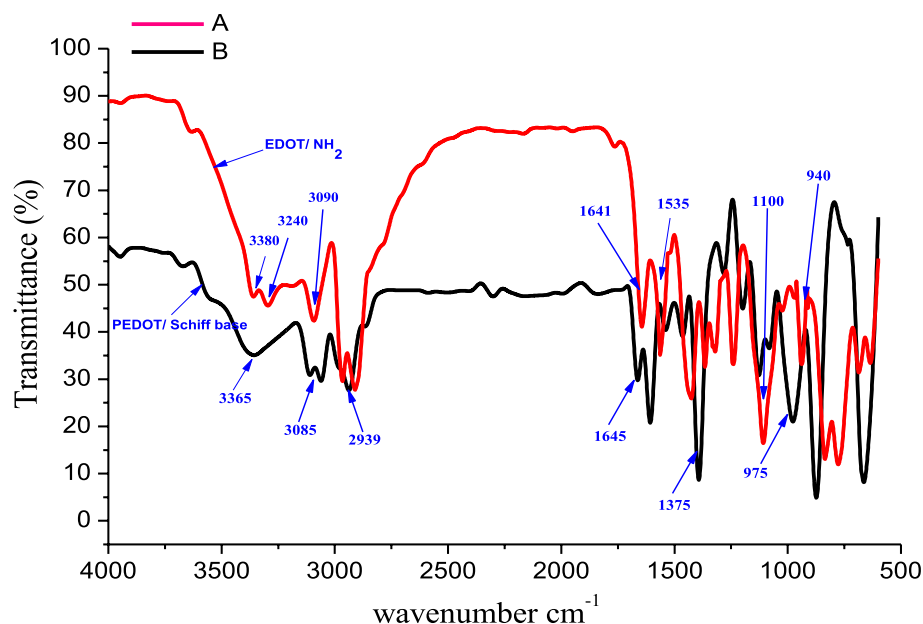
Fig. 6 SEM images of **A** poly(EDOT/Schiff) formed using electropolymerisation at a scan rate 10 mV s^{-1} before adsorption, and **B** poly(EDOT/ Schiff) after adsorption of metal ions (see the conditions in Fig. 11)

shows that the PEDOT-Schiff film has uniform particles with a globular morphology before adsorption. Further, the SEM image (Fig. 6A) clearly exhibits particles of different grain sizes in the nanometre range, confirming the nanostructure of the prepared polymer composite. However, the morphological surface of the polymer composite changed after adsorption (Fig. 6B), indicating the presence of lead and cadmium ions on the surface electrode of the polymer composite. The variation in morphology of the polymer occurs due to the dissolution of ions from the prepared polymer composite and deposition of lead and cadmium metal ions on the surface of the polymer composite.

Therefore, these variations in the surface morphology can be attributed to the interaction of the PEDOT-Schiff composite with Cd(II) and Pb(II) solutions through coordinative bonding and electrostatic interactions between the Cd(II) and Pb(II) ions and the polymer (as sorbent). In general, the morphology of the polymer surface is significantly affected by the experimental conditions, such as the pH, temperature, solvent type, ions present, and scan rates used (Niu et al. 2001). Energy-dispersive X-ray (EDX) spectra, as shown in Fig. 12, confirmed the presence of Pb(II) and Cd(II) ions on the composite surface following exposure to these ions in solution.

Influence of pH

It is unquestionable that pH directly influences the shapes of the voltammograms, and it is thus important to consider the effect of pH on electrochemical processes (Hassan et al. 2018). The pH of the solution notably affects the type of metal ions and the functional groups on the electrode surface. For example, in an acidic electrolyte, the functional groups at the polymer surface will be converted to the protonated form, while in the basic electrolyte metal ions may form hydroxides and precipitate out of solution. Therefore, the chemical bonding of imine groups with metal ions will be significantly affected by the pH of the electrolyte. Low pH will deactivate the imine group, whereas high pH will lead to the formation of metal hydroxides and inhibit the accumulation of metals. According to Panday et al., it is important to achieve the highest peak current possible during experimentation (Pandey et al. 2019).
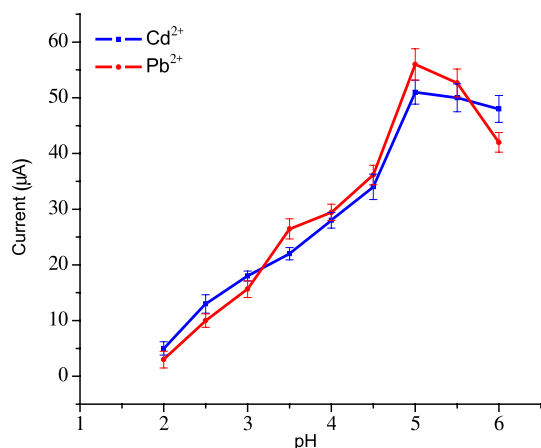

Fig. 7 Plot of SWV peak currents for Cd and Pb ions as a function of pH as obtained on PEDOT/Schiff electrodes
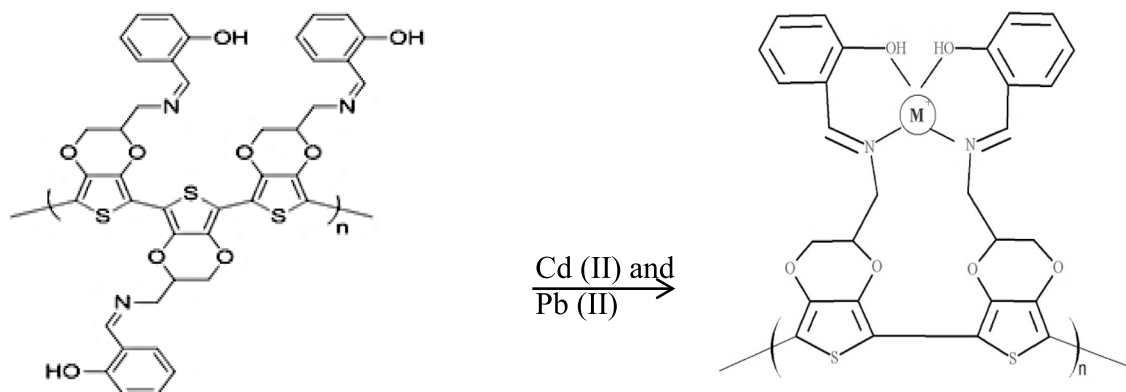
Analyte solutions containing 5 µg L^{-1} of Cd(II) and Pb(II) ions in media with different pHs were used for the voltammetric investigation. The square wave voltammograms exhibited clear peaks for metal ions in media with diverse pH values. It was found that the peak current shapes and heights in a solution of pH 5 were well-defined and higher compared to those recorded at other pHs. Thus, pH 5 was considered the most suitable for the determination of ion concentrations in solution. The findings obtained are graphically depicted in Fig. 7 where, as shown, the modified electrodes have low current peaks in highly acidic solution (pH 2), after which the current peak increases with increasing pH until reaching pH 5, which was subsequently used for the analysis of cadmium and lead cation concentrations.

Measurement of Cd(II) and Pb(II) using SWV

The procedure for the electroanalytical determination of cadmium and lead concentrations in aqueous solution was divided into two steps. Firstly, the modified electrode was immersed in a sample solution containing the analyte (Cd(II) or Pb(II)) at a known pH of 5 and a selected concentration (5–100 µg L^{-1}), where metal ions were binding chemically to the ligands at the surface of the electrode; and, secondly, the polymer electrode was removed from the metal ion solution and rinsed with deionised water and then transferred to a voltammetric cell containing only a supporting electrolyte (acetate buffer solution). The square wave voltammograms were performed using various cadmium and lead concentrations. Figure 8 shows the proposed interaction between the polymer ligand and metal ions.

The determination of Cd(II) and Pb(II) ions

Optimal practical conditions for the determination of Cd(II) and Pb(II) ions by the PEDOT/Schiff electrode using the
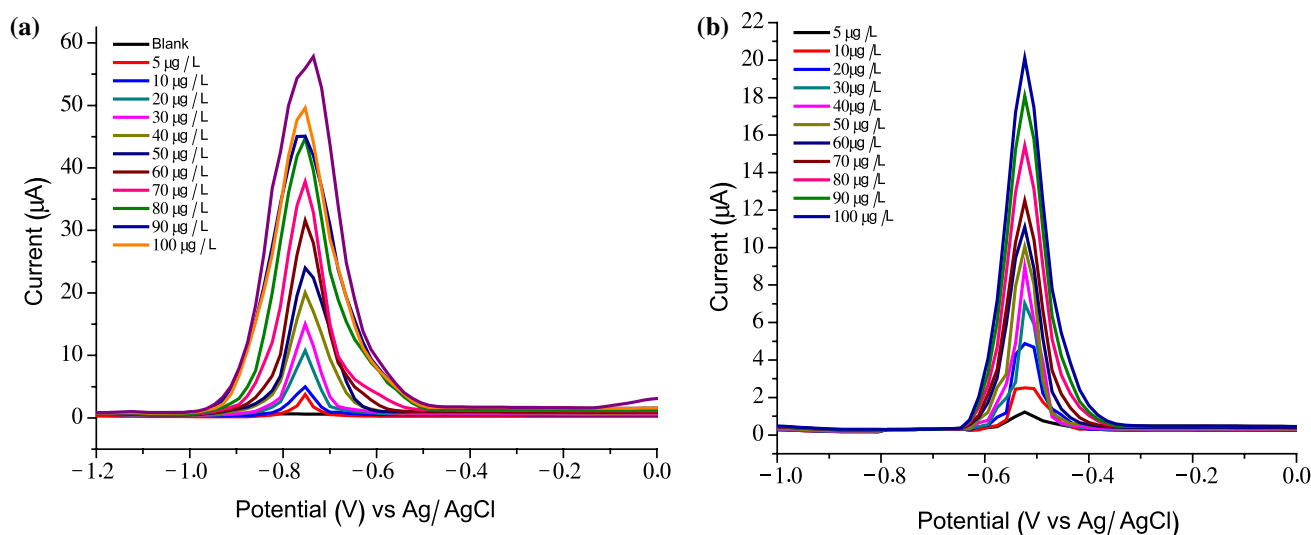

Fig. 8 Assumed schematic for the formation of the PEDOT/Schiff-metal ion complexes

Fig. 9 SWV curves for different concentrations of **A** Cd(II) and **B** Pb(II) from lower to higher concentration (5–100 μg L^{-1}) using a poly(EDOT/Schiff) electrode

SWV technique were separately assessed for each electrode. Initially, the current responses were recorded for the polymer electrodes using a blank solution without metal ions. The blank solution responses did not have any current signals in the voltage range from −1.2 to 0 V, as illustrated in Fig. 9 (black line). Accumulation of the Cd(II) and Pb(II) ions occurred by immersion of the modified electrode in buffer solution at pH 5 containing Cd(II) and Pb(II) ions. This process led to complex formation between the metal ions and the PEDOT/Schiff base layer. The chemical accumulation process which occurred for Cd(II) and Pb(II) ions probably affected the accumulation of other reducible species at the voltage used during the preconcentration processes. After the immersion of metal ions in the PEDOT/Schiff electrode, they were washed with pure water. After that, the modified electrode was moved to the electrochemical cell, which contained buffer solution. The SWV response was registered for each metal ion, i.e. Cd(II) and Pb(II) (Fourou et al. 2016; Zhang et al. 2020).

The square wave voltammograms of modified electrodes, after 15 min of immersion in buffer solution, at pH 5 with 5 μg L^{-1} of Cd(II) and Pb(II) ions, are shown in Fig. 9. The determination of Cd(II) and Pb(II) ion concentrations was investigated between −1.2 to 0.0 V (vs. Ag/AgCl). As can be noted in Fig. 9, the interaction of the Cd(II) and Pb(II) ions with the modified electrode surface leads to the alteration of the electrochemical properties of the electrode. Clearly, the anodic peak has increased due to Cd(II) and Pb(II) ions, which formed a complex on the modified electrode (Fig. 9) compared with the peak current recorded after immersion of the same electrode in solution without metal ions (Fig. 9A, B).

The calibration equations and correlation coefficients (R^2) were calculated for the Cd(II) and Pb(II) ions as $y = 1.639 + 0.434x$ (x: μg L^{-1}, y: μA), R^2 = 0.9989 for Cd(II) and $y = 0.492 + 0.159x$, R^2 = 0.9961 for Pb(II), respectively, as shown in Fig. 10. The limits of detection (LOD) were determined to be 0.95 μg L^{-1} and 1.84 μg L^{-1} for the Cd(II) and Pb(II) ions, respectively, which demonstrates the high sensitivity of the modified polymer electrode towards heavy metal ion detection. The separation in peaks locations for metal ions offer an accurate strategy to detect Cd(II) and Pb(II) ions, significantly reducing interfering effects from other heavy metal ions (Dang et al. 2018; Zhai et al. 2018). Calibration was performed to allow for the determination of metal ions at pH 5 in buffer solution. Figure 10 shows square wave voltammograms recorded using consecutive additions of ion metals over the 5–100 μg L^{-1} concentration range at the EDOT/Schiff modified electrode. Peak currents appeared at −0.77 V and −0.50 V for the various concentrations of Cd(II) and Pb(II), respectively (Fig. 9). A linear relationship between the concentration of ion metals and current peaks was evident from the experimental findings.

Simultaneous electrochemical determination of Cd(II) and Pb(II) in a binary mixture

The analytical signal of various concentrations of Cd(II) and Pb(II) ions is illustrated in Fig. 9A, B, respectively. Subsequently, the simultaneous determination of Cd(II) and Pb(II) ions with the PEDOT/Schiff electrode was carried out to detect Cd(II) and Pb(II) ions in the same solution (Hassan et al. 2019). SWV voltammograms of the PEDOT/Schiff electrode after sequential additions from different
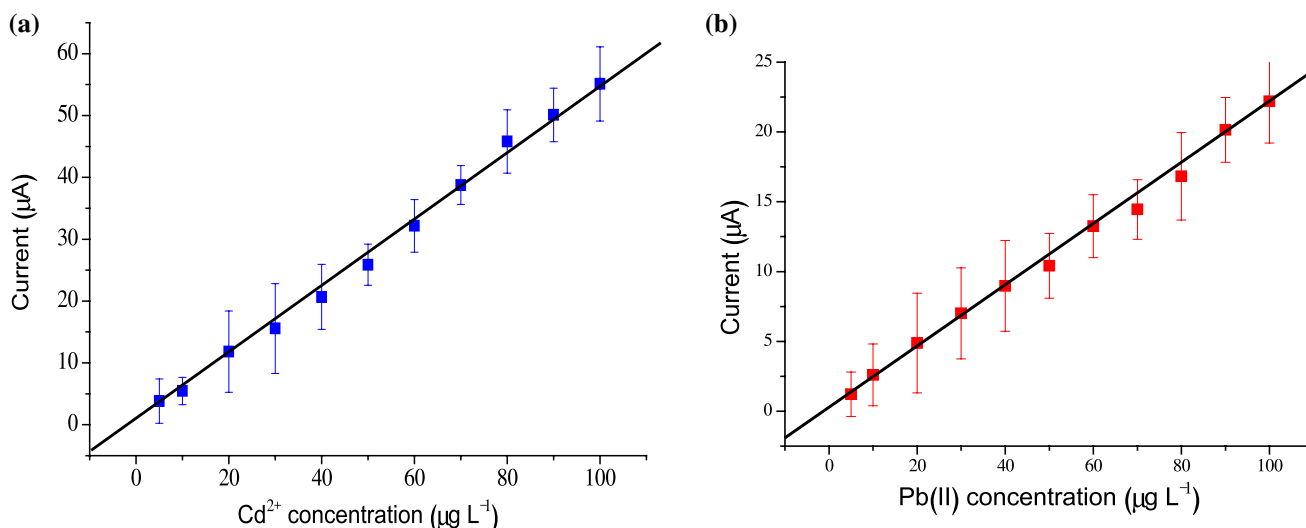
(a)

(b)

Fig. 10 Calibration plot for measurement of different concentrations (5–100 µg L^{-1}) of **A** Cd(II) and **B** Pb(II) taken from Fig. 9 using a poly(EDOT/ Schiff) electrode
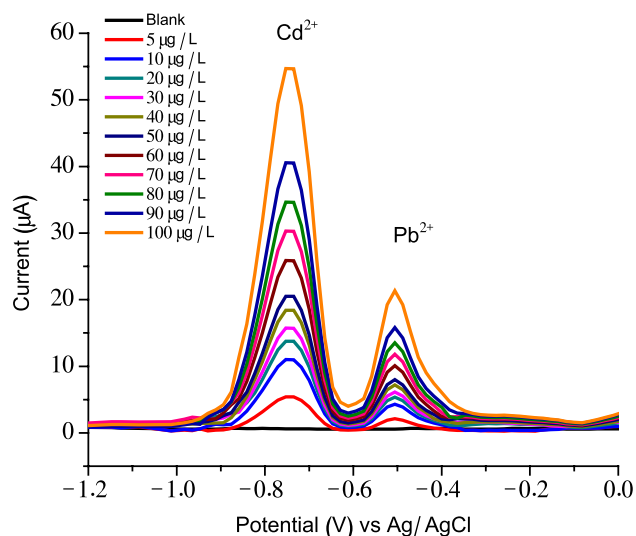

Fig. 11 SWV response of poly(EDOT/Schiff) electrode for the simultaneous analysis of Cd(II) and Pb(II)

concentrations of Cd(II) and Pb(II) are shown in Fig. 11. The characteristic peaks of Cd(II) and Pb(II) were seen at -0.77 and -0.50 V, respectively. These findings were in agreement with the individual species' characteristics (Fig. 9). The effects of ion concentrations were examined under optimum conditions. Metal ion concentrations were examined between -1.2 to 0.0 V (vs. Ag/AgCl) at various concentrations in the range 5 µg L^{-1} to 100 µg L^{-1} for Cd(II) and Pb(II), respectively. Figure 11 represents the square voltammograms recorded at the PEDOT/Schiff electrode at a scan rate of 5 mV s^{-1}. From this figure, it can be seen that

the individual peak currents increased linearly with increasing concentrations of the individual metal ions in the binary solutions (Deshmukh et al. 2018).

The findings of the study confirmed that the modified electrode shows the appropriate reliability and efficiency to be used for detecting Cd(II) and Pb(II) ions. Furthermore, the analytical performance of the PEDOT/Schiff electrode in this project was compared with previous work in the literature for Cd(II) and Pb(II) detection, as shown in Table 4.

EDX measurements

In order to study the structure of polymer and show the presence of metal ions within the polymer surface, the elemental analysis of polymer electrode before and after adsorption of metal ions was accomplished via EDX analysis. Figure 12A illustrates the EDX spectra of the poly(EDTA/Schiff base) composite with C, N, O, and S as the major elements of the composite before adsorption of metal ions (Cd and Pb). After adsorption of metal ions (Cd and Pb), additional peaks attributable to Cd(II) and Pb(II) were observed in the EDX spectra (Fig. 12B), indicating binding between these ions and ligand groups on the polymer surface.

Reactivation of PEDOT/Schiff electrode

Repeated usage of the modified electrode in the determination of the concentrations of metal ions necessitates the regeneration of the PEDOT/Schiff electrode. Reactivation of PEDOT/Schiff electrode was achieved by immersing in 0.1 M EDTA solution for 15 min and then washing with ultrapure water. A voltammogram recorded for PEDOT/

Table 4 Comparison of the analytical performance of the PEDOT/Schiff electrode with other modified electrodes

Electrodes	Methods	Analytes	Detection limit	References
5-Br-PADAP	ASV	Pb(II)	0.1 µg L^{-1}	Salmanipour and Taher (2011)
P1,2-DAAQ	SWASV	Cd(II)	0.3 µg L^{-1}	Hassan et al. (2018)
		Pb(II)	0.58 µg L^{-1}	
GC/p-1,8-DAN	SWV	Cd(II)	19 ng L^{-1}	Hassan et al. (2019)
		Pb(II)	30 ng L^{-1}	
CNFs	ASV	Cd(II)	0.38 µg L^{-1}	Qin et al. (2017)
		Pb(II)	0.33 µg L^{-1}	
polyamide 6/Chitosan	SWV	Cd(II)	0.88 µg L^{-1}	Migliorini et al. (2017)
PMTB	DPV	Cd(II)	0.35 µg L^{-1}	Manikandan and Narayanan (2019)
		Pb(II)	0.18 µg L^{-1}	
Polyaniline	SWASV	Cd(II)	4.43 µg L^{-1}	Promphet et al. (2015)
		Pb(II)	3.30 µg L^{-1}	
Poly(1,5-DAN)/MWCNTs	SWASV	Cd(II)	3.2 µg L^{-1}	Vu et al. (2015)
		Pb(II)	2.1 µg L^{-1}	
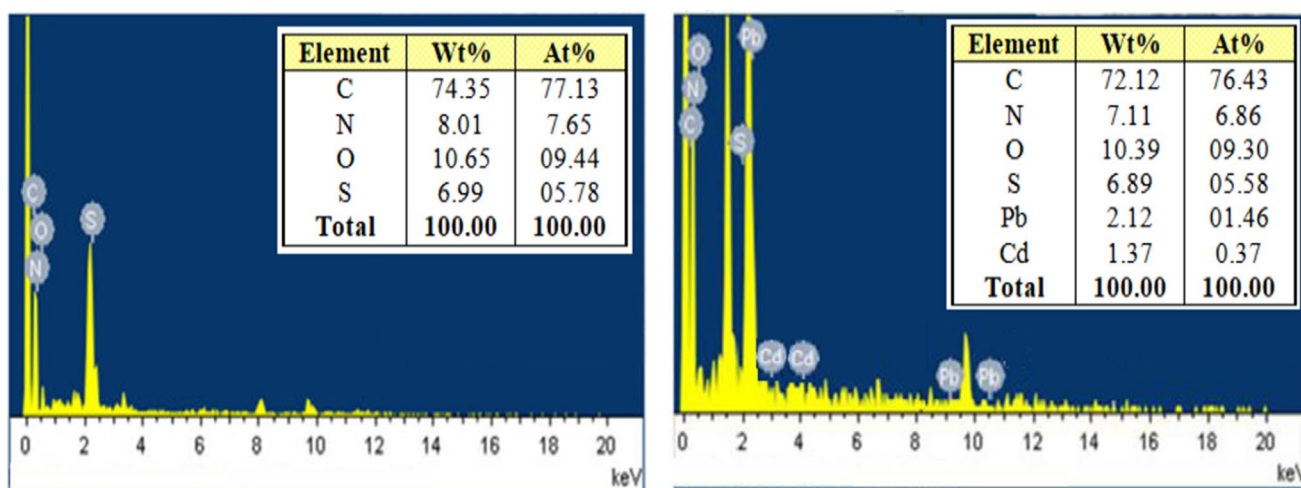
Fig. 12 EDX spectra showing elemental analysis of poly(EDTA/Schiff base) **A** before and **B** after adsorption of metal ions

Schiff electrode after reactivation was essentially congruous with the voltammogram of the PEDOT/Schiff electrode when reacted with metal ions, as shown in Fig. 13 (red curve). This indicates that the incorporated metal ions had been totally removed from the PEDOT/Schiff electrode. Therefore, the reactivated PEDOT/Schiff electrode could be used for the detection of metal ions without any appreciable effect on the electro-activity.

Repeatability and reproducibility study

The repeatability of the PEDOT/Schiff electrode was determined under the optimised conditions using 20 µg L^{-1} Cd(II) and Pb(II), respectively. Five consecutive measurements were taken using the same polymer electrode; the estimated relative standard deviations (RSD) were 3.4% and 2.8% for

Cd(II) and Pb(II), respectively. Moreover, the reproducibility of the PEDOT/Schiff electrode was examined. This process required the preparation of five modified electrodes that were then used in the detection of 20 µg L^{-1} Cd(II) and Pb(II), respectively. The RSD of the PEDOT/Schiff electrode was 3.8% and 3.1% for Cd(II) and Pb(II), respectively, which indicated that the PEDOT/Schiff electrode prepared has good repeatability and reproducibility.

Interference study

To assess the selectivity of the modified electrode in the detection of metal ions, the effect of other ions on the response to Cd(II) and Pb(II) was investigated. In this study, various ions were chosen to act as interfering ions to investigate the selectivity of the PEDOT/Schiff electrode. Various
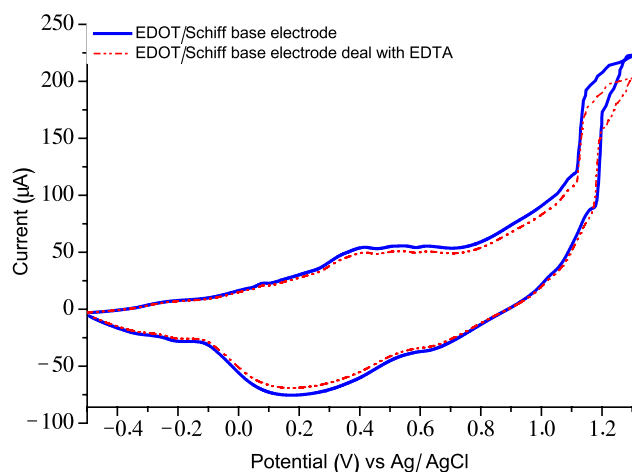
Fig. 13 Cyclic voltammetric of PEDOT/Schiff modified electrode (blue curve) in Bu_4NPF_6 aqueous electrolyte (red curve) after treating with 0.1 M EDTA

Table 5 Three interference analyses for various metal ions on the current responses of Cd(II) and Pb(II)

Interfering ions	Relative current change (%)	
	Cd(II)	Pb(II)
Na	0.19	0.25
K	0.36	0.42
Ca	−0.92	−0.85
Mg	1.17	1.09
Ba	1.67	1.35
Cu	6.34	5.92
Hg	−4.93	−5.62
Al	−0.56	−0.54
Fe	5.21	4.12
NO_3	0.47	0.85
Cl	0.78	0.23

ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Hg^{2+}, Al^{3+}, Fe^{3+}, NO_3^-, and Cl^-) were added to a solution containing 20 μg L^{-1} Cd(II) and Pb(II). The addition of interfering ions did not lead to any perceptible difference in measurements, and these findings demonstrated that the electrochemical responses for Cd(II) and Pb(II) were not influenced by the interfering ions in any apparent way (Table 5).

The interference experiments proved that additive ions have no perceptible interference effect to detection of target ions even when their concentrations exceed those of the ion of interest in the solution, at 20 μg L^{-1} for Cd(II) and Pb(II), by 50-fold. However, 30-fold concentrations of Fe^{3+}, Cu^{2+} and Hg^{2+} were found to have a slight influence on the determination of Cd(II) and Pb(II) concentrations. The intermetallic compounds that can form between metal ions is a general

problem in voltammetric methods, though this small change could be due to competition between iron and the target metal ions for active sites on the surface modified electrode. Further interference experiments of Cd(II) and Pb(II) with other earth-abundant toxic metals (e.g. Ni^{2+} and Co^{2+} ions) were carried out, the data for which are given in the supplementary information (Table S1).

Conclusions

The goal of this study was to modify functionalised polymer films for application in the electrochemical detection of metal ions in solution. The preparation of polymer films and overall operational performance was monitored using electrochemical ("iVt") techniques. All modified electrodes were characterised using electrochemical (CV) and spectroscopic (FTIR) techniques. The findings indicated the successful formation of polymer films via cyclic voltammetry. Following the electropolymerisation, films were investigated using various scan rates (10–100 mV s^{-1}) to examine electrochemical stability, demonstrating that redox peak currents are linearly dependent on scan rate. Further, the voltammetric data were used to estimate the surface coverage of the polymer films via Faraday's law. A novel electrochemical tool for the quantification of metal ions, using an electroactive polymer, was developed. PEDOT functionalised with a Schiff base was electrodeposited on a Pt surface electrode by electrochemical techniques (CV) and then used for the detection of Cd(II) and Pb(II) ions in solution. The poly(EDOT/Schiff) electrode exhibited good sensitivity during electrodetermination of trace amounts of metal ions (Cd(II) and Pb(II)), showing low limits of detection of 0.95 μg L^{-1} for Cd(II) and 1.84 μg L^{-1} for Pb(II). Cd(II) and Pb(II) ions were detected both individually and simultaneously using square wave voltammetry using the new poly(EDOT/Schiff) moieties.

Declarations

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