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ORIGINAL PAPER

New selective modified glassy carbon electrode based on 6-furfurylaminopurine ligand for cadmium detection in real samples

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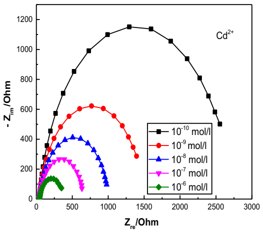
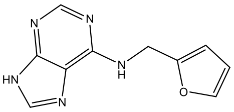
Abstract

This paper presents a simple, inexpensive, and highly sensitive electrochemical sensor based on new polymeric membrane incorporating kinetin (6-furfurylaminopurine) as a specific sensitive molecule deposited on the surface of a glassy carbon electrode for the detection of cadmium in water. The electrochemical characterization was examined using electrochemical impedance spectroscopy and cyclic voltammetry. Additive effect and selectivity for cadmium over many common cations, such as copper, lead, and zinc, at pH 4.5 are studied. We showed that the cadmium selectivity is better for membrane based on potassium tetrakis(4-chlorophenyl)borate (KTpClPB) with a significant decrease of the R_{ct} and an increase in constant phase element CPE, the sensor exhibits a LOD of 3.96×10^{-10} M with a linear response towards cadmium ions over a wide concentration range of 10^{-6} to 10^{-9} M. Finally, the proposed sensor was applied to the determination of cadmium in water and can be proposed to use successfully in real water samples.

Graphic abstract





Keywords Heavy metals · Glassy carbon electrode · 6-Furfurylaminopurine · Cyclic voltammetry · Electrochemical impedance spectroscopy

Introduction

Cadmium is non-essential metal, it is generally present in the environment at low levels; however, the human activity has greatly increased those levels to become one of the most toxic heavy metals present in the environment. It is used in auto industries, production of pigments in plastics, electronic components, and in electric batteries [1].

Various techniques have been developed for the detection of heavy metal ions like spectroscopic techniques and optical methods. However, these techniques are expensive and require specialized personnel [2]. On the other hand, electrochemical detection methods have shown some advantages over other analytical methods due to their capability of short analytical time, low cost, high sensitivity, and portability for in situ measurement [3]. Many research reported the development of electrochemical sensors for the detection

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of cadmium using organic ligands [4–8]. The interaction of these ligands and heavy metals can be explained with Pearson's hard–soft acid–base (HSAB) theory [9, 10]; it occurs through the organic functional groups of these elements that contain nitrogen, oxygen, and sulfur donor atoms considered as Lewis bases, while heavy metal ions act as Lewis acids. Pearson proposed that Lewis acids and bases can be divided into hard, soft and border line types; according to the HSAB principle, hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases to form stable complexes.

Based on this concept, we have been interested in developing an electrochemical sensor for selective recognition of cadmium using 6-furfurylaminopurine (kinetin), which is considered as the first cytokinins discovered in the 1950s by F. Skoog, C. Miller, and co-workers. For many years, it was considered to be a synthetic product, but it has been shown by several researchers that kinetin exists naturally in the DNA of almost all organisms, including human cells, and various plants [11]. The kinetin plays a role in many processes, from regulation of growth and development of plants and anti-aging properties to therapeutic utility [12].

The kinetin represents an interesting ligand for heavy metals; recently, complexes involving kinetin and its derivatives with Cu(II) and Zn(II) were studied [13, 14]. It was found that the kinetin can form stable complexes with transition metal ions through the two donor atoms of the ligand, via the O atoms from the furan ring and the N atom from the purine moiety.

In this work, we present the preparation for the first time of an electrochemical sensor-based kinetin for cadmium detection. The selectivity of the proposed sensor toward cadmium ions was improved by the addition of an anionic additive (KTpClPB) to the mixture of the membrane. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques were used for the characterization of this sensor, and applied to the determination of Cd^{2+} in real samples.

Results and discussion

Modification of glassy carbon electrode

The glassy carbon electrode (a working electrode) was precleaned by sonication for 10 min in acetone, followed by rinsing with distilled water, then twenty CV cycles were applied to the glassy carbon electrode in a solution of 0.1 M NaOH at a potential range of – 0.8 to 0.8 V at a scan rate of 50 mV/s. The cleaned electrode was dried at room temperature; after that, the GCE was dropped into the mixture of the membrane. The surface is then dried in the open air for 15 h. All solutions were prepared with distilled water and all experiments were carried out at room temperature without removing oxygen.

Characterization of the electrode with cyclic voltammetry technique and electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a highly sensitive and informative technique ; it has been widely used as a standard technique for many electrochemical systems and applications such as corrosion, batteries, fuel cells, mechanisms, and electrical response of chemical systems. Recently, EIS was widely applied to electrochemical sensors and biosensors. This method can be used to examine the electrochemical process that influences the membrane/electrolyte systems, which makes many changes visible that other techniques cannot examine such as charge transfer resistances, double layer capacity, diffusion coefficients, electron transfer rate, adsorption on the electrode surface, etc. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to investigate the characteristics of the modified electrode. Figure 1 shows the electrochemical impedance diagram obtained before and after the deposition of the membrane on the surface of GCE in acetate buffer solution at pH 4.5. The EIS data were fitted using equivalent circuit as shown in Fig. 4; the parameters obtained after fitting the Nyquist plots demonstrate that the charge transfer resistance of the bare GCE ($R_{ct} = 4677\ \Omega$) was smaller than that of the modified bare GCE ($R_{ct} = 10{,}715\ \Omega$). The large semicircle portion exhibited by the modified bare GC electrode corresponds to a high charge transfer resistance (R_{ct}); the electrode displayed a small semicircle

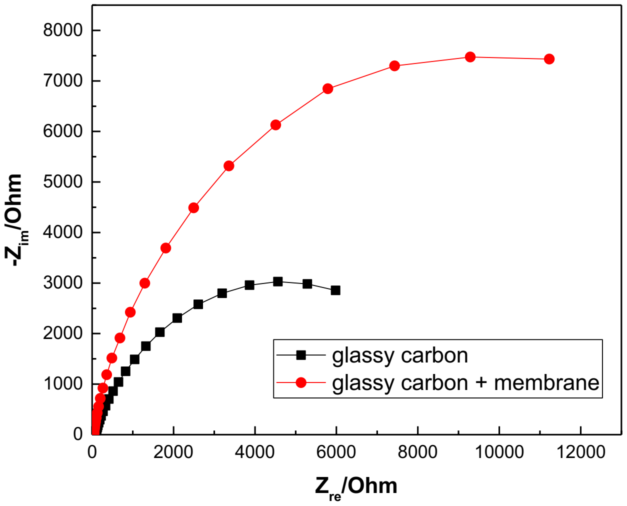

Fig. 1 Nyquist plots obtained from the 6-furfurylaminopurine functionalized glassy carbon electrode and bare electrode at frequency range 100 kHz–100 MHz, $E = -$ 1.2 V in 0.1 M acetate buffer solution, pH 4.5

with a low charge transfer resistance (R_{ct}). This suggests that the electron transfer to the electrode was slowed by the addition of the membrane [15]. This result is consistent with CV test shown in Fig. 2. After the deposition, the redox peaks have decreased, which is attributed to the decrease in the electron transfer through the polymeric membrane [16].

Sensor response

To test the response of our system, the first step was the optimization of the experimental conditions, the potential was studied in ranging from − 0.8 to − 1.3 V vs. Ag/AgCl. At − 1.2 V under a frequency range from 100 kHz to 100 MHz, with eight points per decade and 10 mV the amplitude of the excitation signal, the best arc shape was obtained, this values was used for all EIS measurements. Figure 3 shows the impedance spectra recorded towards different solutions of Cd^{2+}, Pb^{2+}, Zn^{2+}, and Cu^{2+} in acetate buffer solution, from concentrations of 10^{-10} to 10^{-6} M. As it can be seen, the curves obtained are in the form of semicircle; at high frequencies, the impedance is not modified. While at low frequencies, the semicircle diameter decreases with increasing concentrations of Cd^{2+}, Pb^{2+}, Zn^{2+}, and Cu^{2+} ions. The decrease in values of charge transfer resistance (R_{ct}) as function of the increase in ion concentrations; it can be explained by the interactions of the metal ions with the surface of 6-furfurylaminopurine membrane which affect the interfacial properties of the membrane. To obtain the best fit and to plot the calibration curve, we chose the simplified Randles equivalent circuit, shown in Fig. 4 in which a resistance, R_s (the electrolyte resistance), is in series with the parallel association of the charge transfer resistance R_{ct}, and a constant phase element (CPE). The CPE was modeled as a non-ideal capacitor, describing the charge separation at the double layer interface and the heterogeneity of the surface of the modified layer (porosity, roughness and geometry) [15, 17]. The parameters obtained by modeling the impedance spectra using the software Z-View are presented in Table 1.

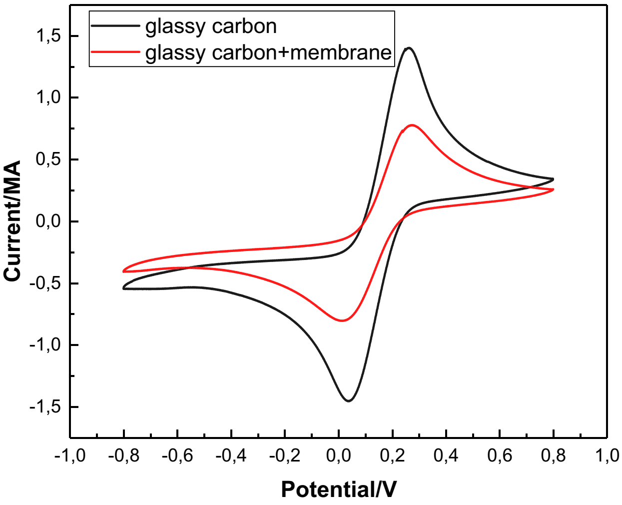

Fig. 2 Cyclic voltammogram obtained from the 6-furfurylaminopurine functionalized glassy carbon electrode and bare electrode in 2 mM mixture of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ recorded in solution of 0.1 M KCl. Deposition scan rate: 80 mV s^{-1} vs. Ag/AgCl

Analytical performances

To investigate the sensor analytical properties, including sensitivity, selectivity, linear range, detection limit, and correlation coefficient, we presented $\Delta R_{ct} = (R_{ct,0} - R_{ct})$ versus the logarithm of the metal ions concentration; the calibration curves (Fig. 5) showed a comparison between the relative slopes of heavy metals studied; and the sensor presents a linear response towards the different ions, with a good sensitivity for Cd^{2+}. The selectivity of the sensor for the detection of Cd^{2+} over the other metal ions (Cu^{2+}, Zn^{2+}, Pb^{2+}) was studied under the same experimental conditions. The results in Table 1 show that only Cd^{2+} caused a significant change in R_{ct} while other ions generated little changes, which indicated that the sensor was highly selective to detect Cd^{2+}. As it is known, the Cd^{2+} ion has a soft character, with a high degree of polarizability; the higher electrostatic interaction between this metal and the ligand can be due to the soft nucleophilic coordination with nitrogen in the purine heterocycle [18, 19].

The limit of detection was calculated by (LOD) method according to the formula: $\mathrm{LOD} = 3 \times a/s$, where a is the value of standard deviation of three blank impedance signal, and s is the slope of the related calibration curve [20]. As illustrated in Table 2, the developed sensor was characterized by a low limit of detection of 3.96×10^{-10} M toward Cd^{2+} ions with a linear dynamic range for concentrations from 10^{-9} to 10^{-6} M and a linear correlation coefficient (R^2) of 0.99284 compared with those reported in literature [21–28].

Effect of addition of anionic additive

According to the literature, the addition of lipophilic anionic additive in cation-selective membranes is in the role of decrease the ohmic resistance, reduce anion interference and response time, enhance the behavior and selectivity, improve electrical properties, and increase the sensitivity of membrane electrodes [29, 30]. To investigate the effect of the addition of the anionic additive on the response of the membrane, we plotted R_{ct} versus the logarithm of concentration of Cd^{+2} with and without addition of KTpClPB. As shown in Fig. 6, the R_{ct} slope of the membrane with KTpClPB is higher than that without KTpClPB. Table 3 shows that the charge-transfer resistance R_{ct} decreases with the increase of the different detected Cd^{2+} ions

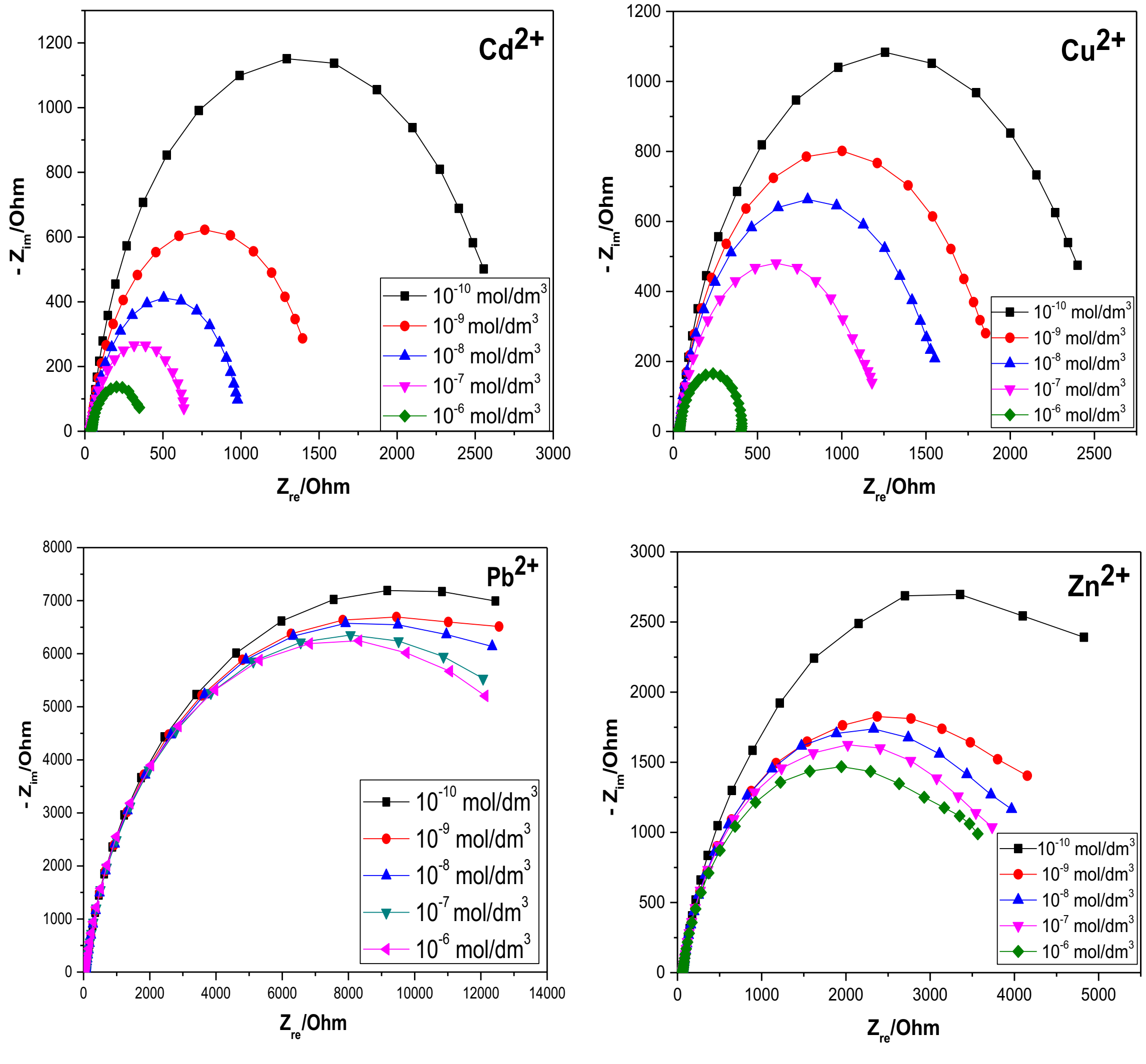

Fig. 3 Nyquist diagrams for different Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} concentrations of glassy carbon electrode after thin film deposition. Frequency range 100 kHz–100 MHz, $E = -1.2$ V in 0.1 M acetate buffer solution, pH 4.5

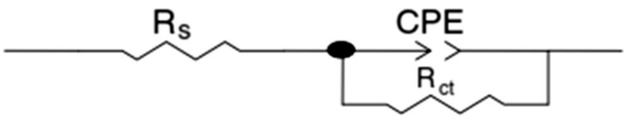

Fig. 4 Equivalent circuit used for fitting of the impedance

concentrations. However, the presence of the lipophilic anion additive in the membrane provides a significant decrease of the R_{ct} and an increase in constant phase element CPE. When the concentration of cadmium increases, the ionic transfer at the interface becomes larger, which implies a reduction in the charge-transfer resistance R_{ct}. This is due to fact that KTpClPB acts as a charge compensating counter ion in the membrane and, thus, facilitates the process of ion charge transduction [31, 32].

Stability and repeatability of the prepared sensor

To investigate the stability and repeatability of the proposed sensor, a membrane (PVC/6-furfurylaminopurine-KTpClPB/GCE) was prepared and used to detect 10^{-9} M cadmium in 0.1 M acetate buffer solution (pH 4.5) at a regular interval (7 days) over 28 days; the R_{ct} values show a relative standard deviation (RSD) of 4.1%; and the sensor retained 89.7% of the initial response after storage for 4 weeks in room temperature. The above results indicated the good stability and repeatability of the proposed sensor for potential applications.

Analytical performances in real samples

To illustrate the application of our sensor in real samples, a membrane (PVC/6-furfurylaminopurine- KTpClPB) was

Table 1 Fitting data for 6-furfurylaminopurine-KTpClPB-based impedimetric sensor for different Cd^{+2}, Cu^{+2}, Pb^{+2}, Zn^{+2} concentrations

	[Ion]/M	CPE (Q) × 10^{-6}/F	R_s/Ω	R_{ct}/Ω	ΔR_{ct}/Ω
$[Cd^{2+}]$	00	44.49	40.35	10,715	–
	10^{-10}	28.11	42.70	3261	7454
	10^{-9}	26.69	40.22	1274	9441
	10^{-8}	24.10	43.58	870.1	9844.9
	10^{-7}	22.86	38.27	572	10,143
	10^{-6}	22.35	43.19	284.6	10,430.4
$[Cu^{2+}]$	00	35.43	42.83	5405	–
	10^{-10}	28.63	40.74	2282	3123
	10^{-9}	26.64	37.29	1724	3681
	10^{-8}	25.50	34.48	1434	3971
	10^{-7}	25.39	40.11	1067	4338
	10^{-6}	23.28	36.43	354.2	5050.8
$[Pb^{2+}]$	00	33.62	47.61	14,947	–
	10^{-10}	29.90	58.35	12,591	2356
	10^{-9}	28.80	57.81	12,178	2769
	10^{-8}	27.94	54.40	12,290	2657
	10^{-7}	27.20	57.67	11,698	3249
	10^{-6}	26.60	58.65	11,750	3197
$[Zn^{2+}]$	00	33.08	59.57	5398	–
	10^{-10}	27.59	67.50	4669	729
	10^{-9}	23.83	60.47	3391	2007
	10^{-8}	22.01	63.86	3233	2165
	10^{-7}	22.14	60.72	3036	2362
	10^{-6}	20.75	58.25	2644	2754

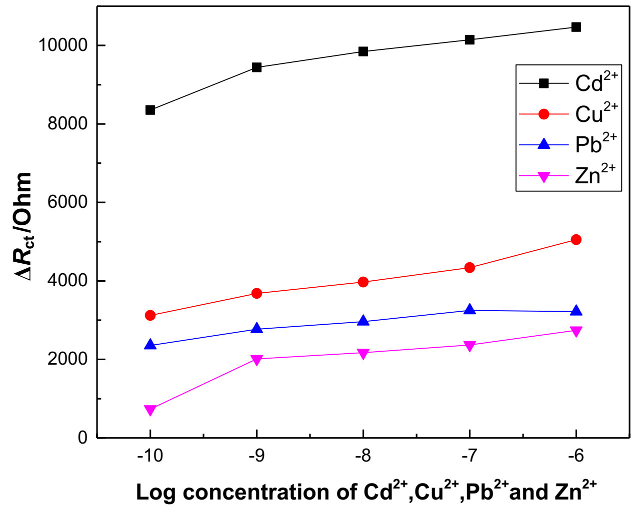

Fig. 5 Variation of the charge transfer resistance (ΔR_{ct}) as function of the four metals concentration logarithm

applied to detect Cd^{2+} in real water from the river of Hammam Salhine in Khenchela-Algeria. The performance of the sensor was evaluated by the standard addition method combined with EIS. The concentration of Cd^{2+} obtained by the developed sensor was validated against ICP-MS as a reference method on the same water samples. The results (Table 4) obtained from the developed sensor show agreement with those obtained by the ICP-MS method.

Conclusion

In this work, a glassy carbon electrode functionalized with PVC-6-furfurylaminopurine membrane was used for the detection of cadmium by electrochemical impedance spectroscopy technique. The impedance analysis was performed with an equivalent circuit model. This study has shown that the proposed sensor was highly selective to Cd^{2+} over other metal ions and exhibits a low limit of detection (LOD) of 3.96×10^{-10} M with a linear range from 10^{-9} to 10^{-6} M. In addition, the developed electrode displayed a good stability and repeatability. Moreover, the functionalized sensor described in this research will facilitate the determination of cadmium in real water samples. Finally, the new sensor can be considered as green with good analytical performance and environment-friendly characteristics.

Experimental

All chemical reagents used in this work were obtained from sigma Aldrich and employed without further purification. Stock solutions of $Cd(NO_3)_2$. H_2O, $Pb(NO_3)_2$•H_2O, $Zn(NO_3)_2$•H_2O, and $Cu(NO_3)_2$•H_2O diluted as required, dioctyl sebacate (DOS), polyvinyl chloride (PVC), tetrahydrofuran (THF), 6-furfurylaminopurine, potassium tetrakis(4-chlorophenyl)borate (KTpClPB). The supporting electrolyte was 0.1 M acetate buffer solution (pH 4.5). All solutions were prepared with distilled water and all experiments were carried out at room temperature without removing oxygen.

Apparatus

Electrochemical measurements were carried out using SP-300 EC-Lab potentiostat (Bio-Logic Science Instruments) controlled by EC-Lab software (version 10.40). A conventional three-electrode cell containing glassy carbon electrode (GCE) as the working electrode with a diameter of 2.0 mm, a counter electrode made of platinum, and a

Table 2 The limit of detection (LOD) and linear range of the sensor compared with published Cd^{2+} electrochemical sensors

Electrochemical platform	Technique	Detection limit /M	Linear range /M	References
$[Ru(bpy)_3]^{2+}$-GO nanocomposite modified AuE	DPV	2.8×10^{-9}	0.02×10^{-6}–0.9×10^{-6}	[21]
AuNPs/CNFs	SWASV	10^{-7}	0.1×10^{-6}–1.0×10^{-6}	[22]
Fe_3O_4–chitosan/GCE	SWASV	3.92×10^{-8}	1.2×10^{-6}–1.7×10^{-6}	[23]
PET-SPE	EIS	10^{-9}	0–50×10^{-6}	[24]
MWCNT tower-based GCE	SWASV	2.5×10^{-8}	2×10^{-6}–8×10^{-6}	[25]
Complexing polymer films	SWASV	5×10^{-7}	10^{-7}–10^{-5}	[26]
AuNPs/GC by laser ablation in liquid	DPASV	3×10^{-7}	0–1.4×10^{-6}	[27]
Carbon nanotube thread	SWASV	1.9×10^{-6}	2×10^{-6}–4.5×10^{-6}	[28]
PVC/6-furfurylaminopurine- KTpClPB	EIS	3.96×10^{-10}	10^{-9}–10^{-6}	This work

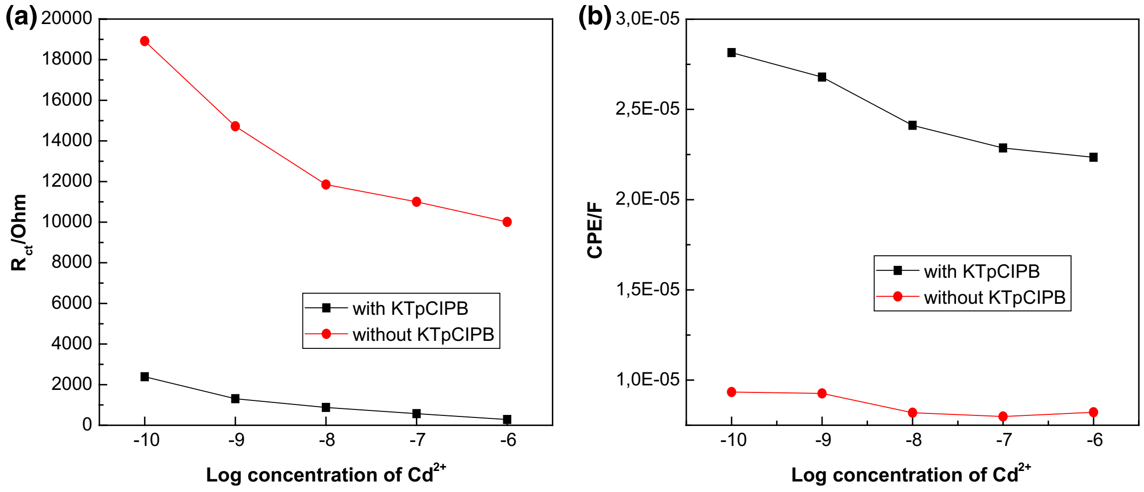

Fig. 6 Variation of **a** the resistance and **b** the capacitance of 6-furfurylaminopurine membrane against Cd^{2+} concentration with and without addition of KTpClPB

Table 3 Fitting data for the functionalized glassy carbon electrode for different Cd^{2+} concentrations (R_{ct}: charge transfer resistance, *CPE* constant phase element) with and without addition of KTpClPB

Membrane composition	$[Cd^{+2}]$/M	R_{ct}/kΩ	CPE (Q)$\times10^{-6}$/F
Membrane without KTpClPB	10^{-10}	18.913	9.34
	10^{-9}	14.720	9.26
	10^{-8}	11.853	8.20
	10^{-7}	11.000	7.98
	10^{-6}	10.011	8.22
Membrane with KTpClPB	10^{-10}	3.261	28.11
	10^{-9}	1.274	26.69
	10^{-8}	0.870	24.10
	10^{-7}	0.572	22.86
	10^{-6}	0.285	22.35

reference electrode based on Ag/AgCl. All electrochemical measurements were carried out in a 20 cm^3 cell.

Table 4 Comparison of cadmium concentrations (µg/dm^3) in water samples detected using ICP-MS and the proposed EIS method ($n=4$)

Sample	ICP-MS	EIS	
		Found	RSD/%*
River water	0.02 ± 0.39	0.015 ± 0.09	6.15

*RSD relative standard deviation

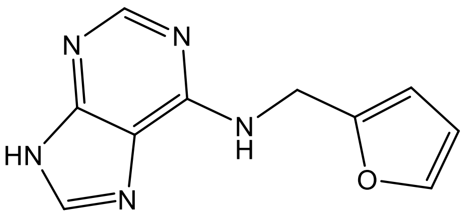

Fig. 7 Structure of 6-furfurylaminopurine

Membrane preparation

The polymeric membrane was obtained from dissolving: 6 mg of 6-furfurylaminopurine Fig. 7, 32 mg of PVC, 4 mg of additive (KTpClPB), and 58 mg of plasticizer (DOS) in 7 cm^3 of tetrahydrofuran at room temperature [31, 33, 34].

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