Int. J. Environ. Sci. Technol. (2014) 11:1115–1126
DOI 10.1007/s13762-013-0296-y

ORIGINAL PAPER

Cadmium (II)-selective electrode based on palm shell activated carbon modified with task-specific ionic liquid: kinetics and analytical applications

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Received: 23 January 2012 / Revised: 30 May 2012 / Accepted: 23 April 2013 / Published online: 17 May 2013

Abstract In this study, palm shell activated carbon modified with task-specific ionic liquid was used as a novel electrode component for the potentiometric determination of cadmium ions in water samples. The proposed potentiometric sensor has good operating characteristics, including relatively high selectivity towards the Cd (II) ion, a Nernstian response to Cd (II) ions in a working concentration range of 1.0×10^{-9}–1.0×10^{-2} M, with a reasonable detection limit of 1×10^{-10} M and a slope of 30.90 ± 1.0 mV/decade. No significant changes in electrode potential were observed when the pH was varied over the range of 4–9. A direct technique based on the use of ion-selective electrode potentiometry has been developed in our laboratory for the study of reaction kinetics and kinetic methods of analysis by continuous monitoring of the rate of production or consumption of an ion. The apparent adsorption rate constant was estimated assuming pseudo-second-order kinetics. Additionally, the proposed electrode has been successfully used for the determination of the cadmium content in real samples without a significant interaction from other cationic or anionic species.

Keywords Heavy metals · Ion-selective electrode · Potentiometric sensor · Trioctylmethylammonium salicylate

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Introduction

Major sources of cadmium are industrial processes, such as the production of cadmium-pigmented plastics, nickel–cadmium batteries and paints. According to the World Health Organization (WHO) guidelines, the permissible concentration of cadmium in drinking water is less than 0.005 mg L^{-1}. Cadmium can accumulate in the human body, especially in the kidneys, and can cause dysfunction of the kidney; therefore, there is increasing interest in the determination of the amount of cadmium ions in drinking water due to its toxicity to human health. The most commonly used techniques for the determination of the amount of cadmium ions in aqueous solution include the following: flame atomic absorption spectrometry (FAAS) (Afkhami et al. 2006), electrothermal atomic absorption spectrometry (ETAAS) (Li et al. 2009), inductively coupled plasma mass spectrometry (ICP-MS) (Balarama Krishna et al. 2000; Guo et al. 2010; Beiraghi et al. 2012), atomic fluorescence spectrometry (AFS) (Wen et al. 2009) and high-performance liquid chromatography (HPLC) (Yang et al. 2005). Although these techniques provide accurate results, they have several disadvantages, such as the requirement of expensive apparatus, complicated operation, high costs of operation and maintenance, and the requirement of well-controlled experimental conditions. For these reasons, the potentiometric method for the determination of the amount of cadmium ions is one of the most favourable techniques. Some of the advantages of potentiometry for trace analysis include high sensitivity, high selectivity, low instrumentation and the possibility of sample analysis without the need of a prior separation. Carbon paste electrodes are known to be useful materials for potentiometric sensors and have been extensively employed in various electrochemical detection schemes due to their simple and fast preparation, surface renewal, eco-friendly techniques and non-toxic character. Carbon is a very important electrode material that is widely used due to its low cost, easy functionalisation, high versatility, broad potential window and chemical inertness. Different forms of carbon, such as glassy carbon, impregnated graphite, carbon fibre, carbon film, carbon nanotube and activated carbon, can be used as electrode materials (Švancara et al. 2009a). Carbon electrodes can be modified with different chemical compounds for the determination of heavy metal in real samples (Švancara et al. 2009b). Palm shell activated carbon is a waste produced during palm oil production and represents an important group of carbonaceous materials with unique mechanical, physical and electrochemical properties (Onundi et al. 2010).

Similar to activated carbon, room temperature ionic liquids (RTILs) have also recently received a great deal of attention. Ionic liquids are salts that have very low melting temperatures (close to room temperature). Ionic liquids have become an extremely popular item in recent separation and purification research due to their unique properties. The physical and chemical properties of ionic liquids (ILs) depend on the nature and the size of their cationic and anionic species. Davis and co-workers first introduced the concept of task-specific ionic liquids to describe ILs that incorporate functional groups designed to impart particular properties to them. Task-specific ionic liquids are a unique subclass of ionic liquids that possess a potential spectrum of utility extending far beyond that likely for more conventional IL (James 2004). The physical and chemical properties (e.g. high polarity, conductivity, viscosity, acidity and hydrophobicity) of task-specific ionic liquids can be tuned by varying the structure of the component ions to obtain the desired properties. Ionic liquids, as well as task-specific ionic liquids (TSILs), are finding an increasing number of applications in synthesis, separations and electrochemistry. Recently, new ion-selective sensors based on room temperature ionic liquids have been developed (Peng et al. 2008; Wei and Ivaska 2008; Faridbod et al. 2009; Khani et al. 2010). Room temperature ionic liquids have become an extremely popular theme in recent electrochemical sensing research due to their large electrochemical window, high conductivity, non-volatility, low toxicity and good electrochemical stability.

In this study, we prepared improved versions of Cd (II)-selective electrodes using palm shell activated carbon based on task-specific ionic liquids. We report the investigation of trioctylmethylammonium salicylate (TOMAS) in ion-selective electrodes to fully understand its functions as both an ionophore and a plasticiser in a potentiometric sensor. The proposed electrode has mainly been used in the determination of the amount of cadmium (II) ions in water samples. Additionally, this electrode has been used for kinetic adsorption studies of cadmium (II) on to palm shell activated carbon impregnated with TOMAS. The purpose of this in vitro kinetic investigation was to develop a potentiometric kinetic method to study the kinetic parameters of cadmium adsorption.

Materials and methods

Chemicals and reagents

Analytical reagent grade chemicals and distilled, de-ionised water were used for preparing all aqueous solutions. Commercially available granular palm shell activated carbon (PSAC) was provided by Pacific Activated Carbon, a local manufacturer in Johor Bahru, Malaysia. Activated carbon granules with particle sizes <40 μm were used throughout the potentiometric experiments. For kinetic studies, activated carbon was sieved to particle sizes ranging from 0.50 to 0.60 mm, washed with distilled water to remove fines and dirt, and dried in an oven at 110 °C for 24 h. The pH of the solutions was adjusted by adding appropriate amounts of concentrated hydrochloric acid (1 M HCl) and/or sodium hydroxide (2 M NaOH).

Metal salts were purchased from Merck. Sodium salicylate was purchased from R&M chemicals. Trioctylmethylammonium chloride (Aliquat® 336) was purchased from Sigma-Aldrich.

Apparatus

All potentiometric measurements were made with a pH/ion meter (Metrohm-781, Germany) and pH Module (Metrohm-867) using the proposed electrode in conjunction with a double junction Ag/AgCl reference electrode, and the temperature of the cell holder was maintained at 25 °C. The electrochemical cell used in this study was constructed as follows:

Ag(s), AgCl(s) | KCl(3 M sat.) || Sample solution| modified palm shell activated carbon paste electrode.

Images of the electrode surfaces were obtained using scanning electron microscopy (SEM; AMETEK, advanced microanalysis solutions) at an accelerating voltage of 25 kV. The BET surface area, pore size and total pore volume of palm shell activated carbon samples were determined using N_2 adsorption at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyser. Cd(II) samples were analysed by inductively coupled plasma emission spectroscopy ICP (PerkinElmer, model ICP optima 7000DV).

Preparation of trioctylmethylammonium salicylate (TOMAS)

Trioctylmethylammonium salicylate was synthesised according to (Egorov et al. 2008) as a slightly yellowish viscous liquid (yield: 85 %), analysed by nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy FTIR, then used without further purification. The method is illustrated in Fig. 1. Aliquat® 336 (0.1 mol) was mixed with an equal molar amount of sodium salicylate in 200 mL of acetone. The mixture was shaken for 5 h and left overnight. The precipitate was then filtered off and acetone was evaporated from the filtrate using a rotary evaporator. The obtained RTIL was rinsed 10 times with a large amount of distilled water and the remaining liquid was heated to 100 °C under reduced pressure for 5 h. A clear, slightly yellowish, viscous liquid (TOMAS) was obtained. TOMAS is a clear liquid with a density of slightly less than 1 g cm^{-3} (0.945). TOMAS is immiscible with water. FTIR, ^{1}H and ^{13}C NMR spectra confirmed the identity of the obtained TOMAS.

Modified palm shell activated carbon paste electrode preparations and potential measurements

Modified palm shell activated carbon paste was prepared by hand mixing measured quantities of palm shell activated carbon (PSAC) powder and TOMAS. The optimal paste quality was obtained by mixing 0.18 g of PSAC and 0.12 g of TOMAS in the ratio of 60:40 (%). The constituents were thoroughly hand-mixed in a 50-mm Petri dish to produce the optimal paste quality and then the paste was poured and packed into empty glassy carbon electrodes (5 mm diameter) connected to the pH/ion meter by a thin copper wire to produce an electrical contact. The composite surface was smoothed on weighing paper until the surface displayed a shiny appearance. The surface was rinsed carefully with double-distilled water prior to each experiment.

The potentiometric measurements were taken as follows. The modified carbon paste electrode was placed in 50 mL of a stirred, 0.1 M Cd (II) solution until the potential reading was constant. The addition method was used to investigate the electrode response characteristics. Cadmium salt standard solutions were added so that the cadmium concentration ranged between 10^{-10} and 10^{-1} M. The potential readings were recorded after each addition when stable values had been obtained.

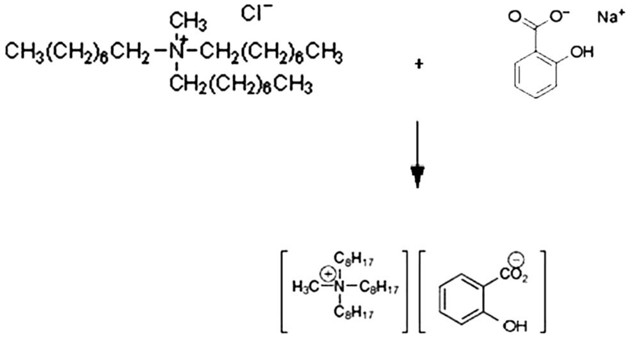


Fig. 1 Synthetic pathway for trioctylmethylammonium salicylate (TOMAS)

The electrode potential of the electrochemical cell (E_{cell}) is described by the following Nernst equation:

$$E_{\text{cell}} = E_{\text{cons}} + 2.303\frac{RT}{zF} \times \log a \tag{1}$$

where E_{cons} is a constant term (the sum of the standard potential and liquid junction potential), R is the ideal gas constant, T is the absolute temperature, F is the Faraday constant, z is the charge of the ion, and a is the activity of the ion. At low concentrations, the activity value a can be replaced with the concentration value C. The pre-logarithmic factor $2.303\frac{RT}{zF}$ is obtained from the slope (S) of the plot of E_{cell} versus $log\ C$ and the equation becomes:

$$E_{\text{cell}} = E_{\text{cons}} + S \log C \tag{2}$$

Potentiometric selectivity of this electrode towards different cations was calculated with the matched potential method (MPM) (Gadzekpo and Christian 1984). In this method, the activity of Cd(II) was increased from $aA = 1.0 \times 10^{-5}$ M (primary ion) to $\acute{a}A = 5.0 \times 10^{-5}$ M and the corresponding potential change (ΔE) was measured. Then, a solution of an interfering ion (aB) in the concentration range of 1.0×10^{-1}–1.0×10^{-2} M was added to a new primary ion ($\acute{a}A$) until the same potential change (ΔE) was recorded. The selectivity factor, $K^{\text{pot}}A, B$, was calculated for each interferent using the following equation:

$$K^{\text{pot}}A, B = (\acute{a}A - aA)/aB \tag{3}$$

Preparation of impregnated palm shell activated carbon with TOMAS

For the preparation of impregnated palm shell activated carbon with task-specific ionic liquids, 1 g of the activated carbon series and 0.00–0.3 g TOMAS were placed in 250-mL Erlenmeyer flasks with 50 ml methanol. The solutions were then agitated in an orbital shaker at 180 rpm and 25 °C for 2 days. Subsequently, the solutions were evaporated and the remaining impregnated palm shell activated carbon was weighed. The overall loading of TOMAS on palm shell activated carbon was calculated using the weight loss data for virgin and impregnated palm shell activated carbon.

Kinetic studies

The kinetic parameters of the adsorption process were determined using ion-selective electrode (ISE) potentiometry with a proposed electrode, and they were compared with those obtained by the conventional adsorption kinetic method.

In the potentiometric kinetic method, the adsorption rate constant and the adsorption characteristics of cadmium to modified palm shell activated carbon were investigated in vitro. Ion-selective electrode (ISE) potentiometry, based on the selective, direct and continuous monitoring of cadmium ions with the proposed electrode, was used. The pair of reference and working electrodes was immersed in a stirred aqueous solution, which contained 50 ml of a 60 mg L^{-1} cadmium solution, and the electrode potential was measured. After stabilisation, 0.1 g modified palm shell activated carbon was rapidly added to 50 mL of 60 mg L^{-1} cadmium solution with stirring and the electrode potential was continuously recorded until equilibrium was established. The process was repeated for 40, 20 and 10 mg L^{-1} cadmium solutions. The potential difference ΔE between the readings at the beginning of the experiment and at any time t can be used to calculate the decrease in the cadmium-free concentration based on the following equation:

$$C_{\mathrm{ad},i} = C_{\mathrm{o}}(1 - 10^{-\Delta Ei/S}) \tag{4}$$

where $C_{\mathrm{ad},i}$ is the concentration of adsorbed metal at time t, C_{o} is the total metal concentration in the solution and S is the slope of the calibration curve.

Estimates for the apparent adsorption rate constants were estimated from the adsorption data using the pseudo-second-order adsorption kinetics as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{1}{q_{\mathrm{e}}} t \tag{5}$$

where q_{e} (mg g^{-1}) and q_{t} (mg g^{-1}) are the amounts adsorbed at equilibrium and at any time t (min), and k_2 is the rate constant of the pseudo-second-order reaction.

In the conventional kinetic study using the batch adsorption technique, the adsorption experiments were carried out in 250-mL Erlenmeyer flasks at different temperatures between 10 and 35 °C. In each experiment, 50 mL of a Cd(II) solution of a concentration that varied between 10 and 60 mg L^{-1} was treated with a known amount of modified activated carbon (0.1 g). Then, the solutions were shaken in an orbital shaker at 180 rpm for a specified period of time. Subsequently, the adsorbent was separated from the solution using Whatman filter paper No. 42. The equilibrium concentrations of Cd(II) remaining in solution were measured with ICP. The cadmium uptake by the modified activated carbon was calculated as follows:

$$q_e = \frac{V(C_{\mathrm{o}} - C_{\mathrm{e}})}{m} \tag{6}$$

where q_{e} is the amount of cadmium ion adsorbed per gram of modified activated carbon (mg g^{-1}), V is the sample volume (L), C_{o} is the initial Cd(II) concentration (mg L^{-1}), C_{e} is the equilibrium Cd(II) concentration (mg L^{-1}) and m is the weight of the adsorbent.

Results and discussion

Cadmium electrode response

The behaviour of potentiometric sensors with carbon paste electrodes depends on the composition of the electrode material used and the condition of the contact solution. The potentiometric response of the proposed electrode towards Cd(II) ions was greatly improved in the presence of TOMAS as both an ionophore and a plasticiser. Therefore, the use of the considerably viscous simplex TOMAS ionic liquid, which is chemically inert and electrochemically conductive, as a pasting binder may be an ideal alternative for an improved paste electrode. One of the key characteristics of the proposed electrode is its ability to lower the overpotential of electroactive compounds and to increase the rate of electron-transfer processes, which is believed to be due to the modification of the microstructure of the electrode surface with TOMAS as the binder.

Several electrode compositions were investigated by varying the ratio of palm shell activated carbon and TOMAS. The best quality paste was obtained by mixing PSAC and TOMAS in the ratio of 60:40 (%).

The calibration for the developed electrode over a wide range of Cd^{2+} solution activities is shown in Fig. 2. The slope of the calibration curve (30.9 mV dec^{-1}) is close to the curve that is predicted (29.5 mV dec^{-1} for bivalent cation) by the Nernst equation, indicating that the electrode was sensitive to Cd (II) over a wide range of activities (1×10^{-9}–1×10^{-2} M).

In addition, the electrode showed a linear response over this range of activities, showing a departure from linearity (i.e. a loss of sensitivity) at activities lower than 10^{-9} M Cd (II). The unique sensitivity and selectivity towards Cd(II) obtained for a given electrode depends on the coordinate interaction between TOMAS and the Cd(II) ion, which may be explained by the chelating effect of the ortho-positioned carboxylate group on the TOMAS molecule grafted on the palm shell activated carbon, in addition to the known formation of metal hydroxylates. When TOMAS was also used as a solvent mediator and played an important role as a plasticiser, it combined certain properties and characteristics, such as having high lipophilicity, high molecular weight and low vapour pressure to good effect. Additionally, its viscosity and dielectric constant were adequate for use as plasticiser. The critical response characteristics of the proposed electrode were evaluated

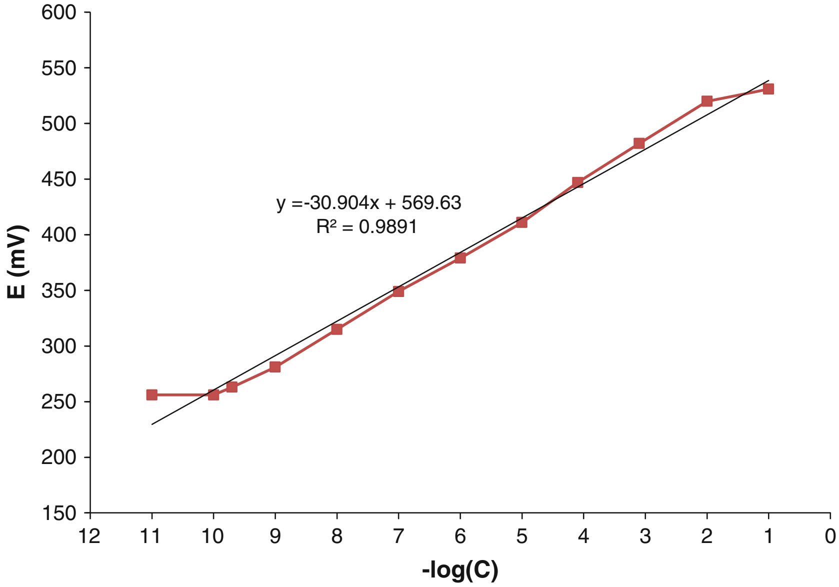


Fig. 2 The calibration curve for a modified palm shell activated carbon paste electrode over a wide range of Cd^{2+} solution activities

according to IUPAC recommendations (Buck and Lindner 1994).

Effect of pH on electrode response

The pH of each solution was verified, and its effect on the electrode potential at various cadmium concentrations was studied. For this purpose, several Cd (II) concentrations (1.0×10^{-6}, 1.0×10^{-4} and 1.0×10^{-3} M Cd (II)) were prepared and the potential variations of the electrode over a pH range of 1–12 were followed. The pH was adjusted by adding small volumes of hydrochloric acid (1 M) and/or sodium hydroxide (2 M) to the sample solution.

The obtained results are shown in Fig. 3. It can be seen that the electrode potentials remain almost constant in the pH range of 4–9. The change in potential at higher pH values may be due to the formation of hydroxy complexes of Cd(II) (Rezaei et al. 2008a, b). At lower pH values, a sharp decrease in the electrode response is observed; this result is due to the protonation of carboxylic groups situated in the selective cavities of TOMAS.

Potentiometric selectivity coefficients

It is well known that the selectivity behaviour of an electrode is one of the most important factors in its evaluation,

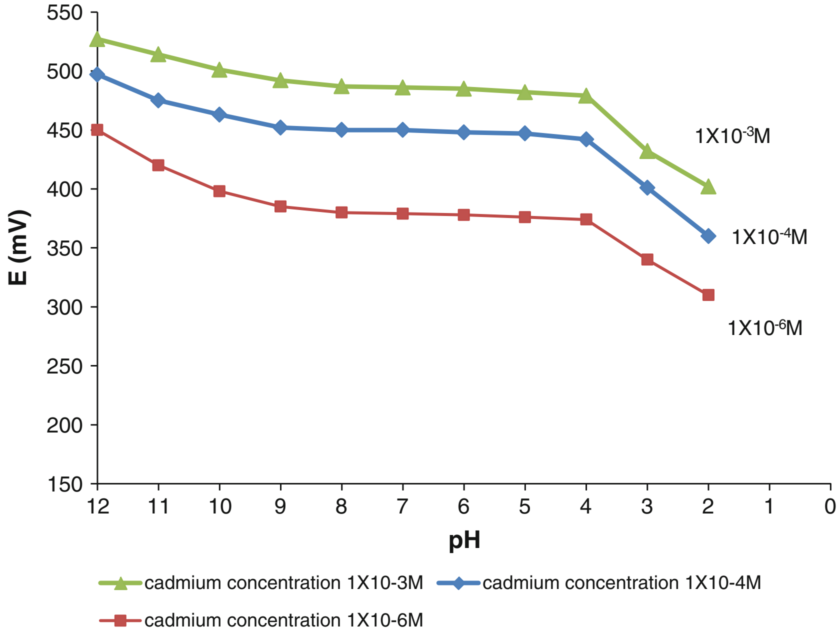


Fig. 3 Effect of pH on the potential response of Cd^{2+} palm shell activated carbon paste electrode

which is measured in terms of the selectivity coefficient. The selectivity coefficient not only depends on ion charge and concentration, but it can also be affected by the type of interaction between the ion and the ionophore. The values of the selectivity coefficients, $K_{\mathrm{pot}}A, B$, of the proposed electrodes towards different species (B) were determined by the matched potential method (Gadzekpo and Christian 1984). This method does not depend on the Nicolsky–Eisenman equation. In this method, the potentiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions.

Table 1 shows that the electrode exhibited better selectivity for the cadmium (II) ion over a wide variety of other metal ions. This phenomenon is due to the stability of the complex between cadmium and TOMAS.

The selectivity sequence of the employed modified CPE for different inorganic cations approximately obeys the order: $Hg^{2+} > Fe^{3+} > Ag^{+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Al^{3+} > Zn^{2+} > Ca^{2+} > Pb^{2+} > Mg^{2+} > Cr^{3+} > K^{+} > Na^{+}$.

It is worth mentioning that TOMAS has excellent selectivity for the Cd^{2+} ions over other metal ions; this selectivity may be due to the design of TOMAS to contain negatively charged O-donor groups that enhance its complexing ability for the Cd (II) ion over other metals. Here, it is critical to note the existence of a rule of ligand design that permits fairly predictable control of selectivity on the basis of metal ion size. Ionic radius is an important parameter in the formation and stability of metal complexes. Moreover, Cd (II) (ionic radius of 0.97 Å) ions show a strong tendency towards ligands with donating atoms of hard character, such as N and O. However, it is clear that more work needs to be performed in this area to establish the relative coordinating abilities of TOMAS to a variety of metal ions of different types and sizes.

To investigate the effect of counter ions on the potential response of the electrode, cell potentials were measured using constant concentrations of $Cd(NO_3)_2$, $CdCl_2$ and $CdSO_4$ under the same experimental conditions. It was found that in 1.0×10^{-4} M solutions of different counter ions, the values of the electrode potential were the same (449 mV), indicating a negligible influence of counter anions on the response behaviour of the electrode.

Table 1 Selectivity coefficient values of various interfering ions with Cd^{2+}-selective electrodes using the matched potential method (MPM)

Interferent ion, B	−log KpotCd^{2+}, B	Interferent ion, B	−log KpotCd^{2+}, B
Cu^{2+}	3.26	Na^{+}	4.71
Hg^{2+}	2.47	K^{+}	4.54
Ca^{2+}	3.95	Ni^{2+}	3.29
Mg^{2+}	4.15	Cr^{3+}	4.21
Zn^{2+}	3.83	Co^{2+}	3.37
Al^{3+}	3.74	Ag^{+}	3.10
Fe^{3+}	2.98	Pb^{2+}	4.02

Scanning electron microscopy studies

Surface morphology plays a significant role in determining the surface availability of activated carbon. Scanning electron microscopy was used to observe the surface morphology at high resolution and to study the variation in surface texture. Figure 4 shows the typical morphological features of palm shell activated carbon (PSAC) of a palm shell activated carbon paste electrode based on TOMAS using scanning electron microscopy (SEM). The pure palm shell activated carbon (PSAC) surface (Fig. 4a) has good porosity and smooth surfaces with long linear ridges and rough surfaces with oval ridges and micropores. Figure 4b shows the SEM image of the paste film. As shown, the paste film is not very smooth and has non-uniform surface topography and unique structure. Significant differences in the initial surface structure of the paste and the paste surface after it was dipped in a 1×10^{-4} M Cd (II) solution for 30 min are seen. SEM micrographs obtained at the same magnification indicate significant improvement in the microstructure of the proposed electrode. It can be seen that after binding the TOMAS with Cd(II), the morphology changes. Aggregates of white needles were observed on the surface (Fig. 4c), which were presumably complexes formed between the TOMAS and the Cd (II) ions.

Surface area and pore size analysis

Nitrogen adsorption–desorption isotherms were recorded for the virgin and grafted palm shell activated carbon. The specific surface area obtained according to the Brunauer–Emmett–Teller (BET) model of virgin palm shell activated carbon was 636.1633 $m^2\ g^{-1}$ at 77 K, using N_2 as adsorbate. The specific surface area decreased to 2.0949 $m^2\ g^{-1}$ upon impregnation with the task-specific ionic liquid (TOMAS). As shown in Fig. 5, increasing the impregnation ratio decreases the specific surface area due to filling the pores of the palm shell activated carbon surfaces with active TOMAS functional groups.

Table 2 summarises the pore properties of the virgin and modified palm shell activated carbon samples. The specific surface area of the activated carbon decreased with increasing weight of TOMAS, as stated above, and this result may account for a smaller specific surface area. Accordingly, the average pore diameter increased from 1.845 nm for the virgin samples to 5.27105 nm for the samples impregnated with TOMAS, and the total pore

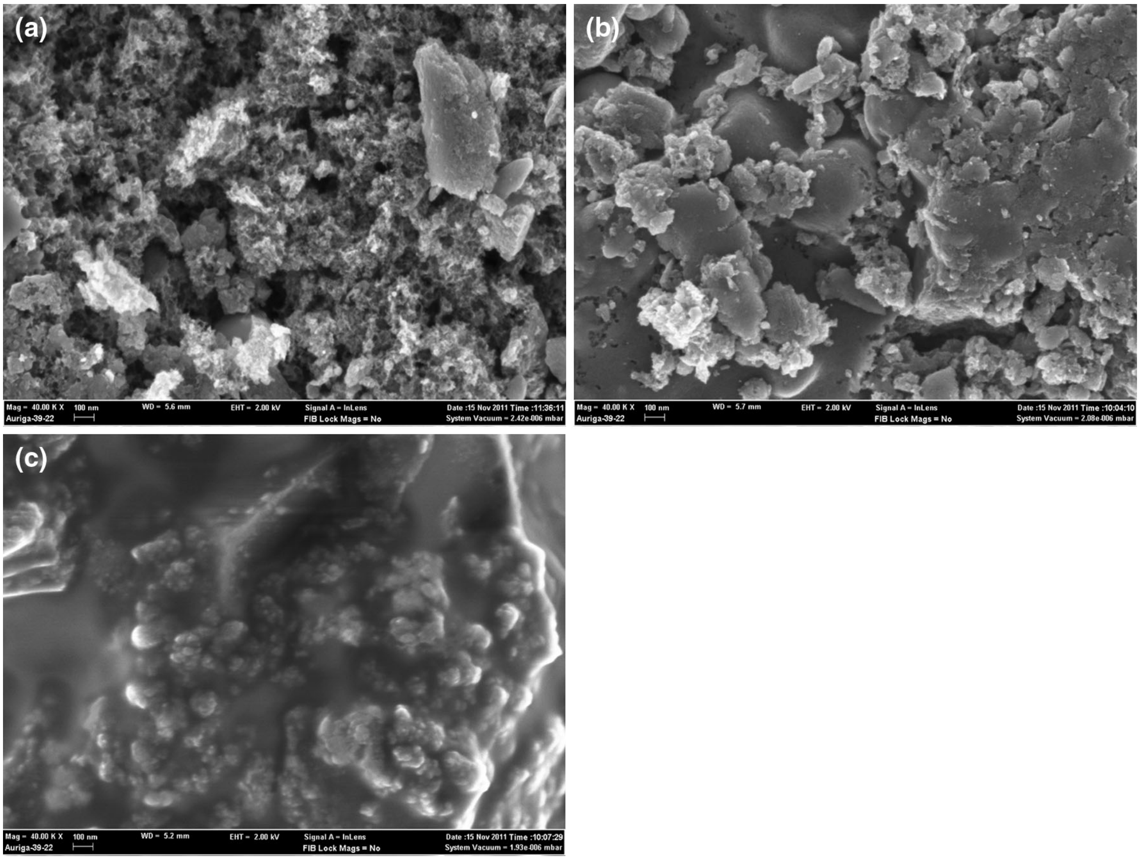
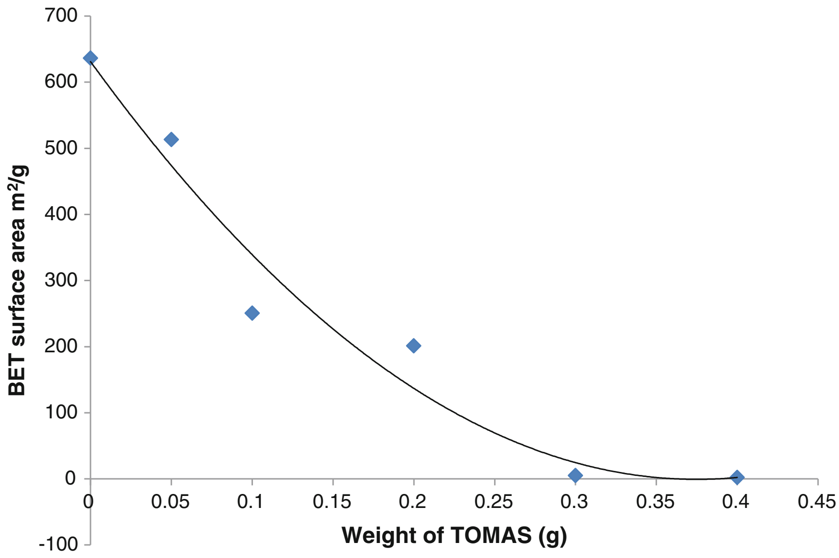


Fig. 4 SEM images of **a** Pure PSAC, **b** PSAC paste electrode based on TOMAS and **c** PSAC paste electrode surface after it was dipped in 1×10^{-4} M Cd^{2+}

Fig. 5 BET specific surface area (m^2 g^{-1}) as a function of TOMAS weight grafted on 1 g of palm shell activated carbon



volume decreased from 0.293430 cm^3 g^{-1} for the virgin activated carbon to 0.001431 cm^3 g^{-1} for the samples impregnated with TOMAS. This result was attributed to the development of microporous and mesoporous structure.

Potentiometric adsorption kinetics applications

Kinetic models were used to study the mechanism of adsorption process steps, such as mass transport and

Table 2 Surface parameters estimated by the BET method using N_2 as an adsorbent at 77 K for the activated carbon samples

Weight of impregnated TOMAS (g/1 g PSAC)	Specific surface area (m^2/g)	Pore diameter (nm)	Total pore volume (cm^3/g)
0.00[a]	636.1633	1.845	0.293430
0.05	512.9587	2.15389	0.276214
0.1	250.4524	2.23413	0.139886
0.2	200.9343	2.3661	0.118857
0.3	4.8885	5.27105	0.006442
0.4	2.0949	6.4019	0.001431

[a] Virgin palm shell activated carbon

chemical reaction processes. The experiment was based on the ISE technique because a proposed Cd (II) ion-selective electrode is able to directly monitor the free Cd (II) concentration without a need for separation processes and without any disturbance of the binding equilibrium. The results were compared with those obtained by the conventional adsorption kinetic method. The kinetics of Cd(II) adsorption on the modified palm shell activated carbon were analysed using pseudo-second-order models (Ho and McKay 1999).

The values of the rate constant of pseudo-second-order k_2 (g mg^{-1} min), adsorption capacity at equilibrium q_e (mg g^{-1}) and initial adsorption rate h (mg g^{-1} min) are determined from the slope and intercept of the plot of t/q_t against t (Fig. 6). The values are given in Table 3.

The degree of linearity of the plot of these kinetic models was determined by the correlation coefficient of the plot, which can also be regarded as a criterion in the determination of the efficiency of the kinetic model.

Table 3 summarises the values of the pseudo-second-order parameters using ion-selective electrode (ISE) potentiometry with the proposed electrode and compared with those obtained by the conventional adsorption kinetic method. The results showed good agreement with those obtained using ICP. The high values of the correlation coefficients for the pseudo-second-order kinetic model indicate that the adsorption system is probably best described by this model. Moreover, the agreement between the calculated adsorption capacities determined using pseudo-second-order plots and the experimental values are convincing. This result indicates that cadmium adsorption followed pseudo-second-order kinetics, and Cd(II) ions were adsorbed onto modified palm shell activated carbon surfaces via chemical interaction. This result confirmed the chemisorptions aspect of the adsorption process. The decrease in k_2 values with an increase in initial metal ion concentration is a common phenomenon observed with a variety of adsorbents used for the adsorption of metal ions

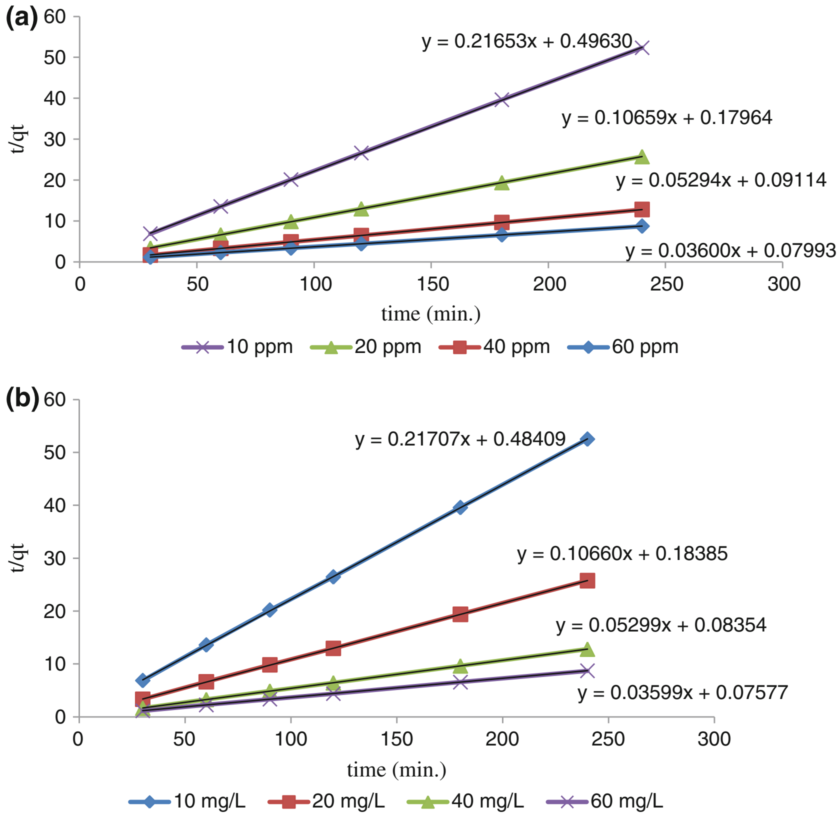


Fig. 6 Pseudo-second-order kinetic plots of Cd (II) ion adsorption onto modified palm shell activated carbon (experimental conditions: adsorbent 0.1 g/50 mL, Cd(II) initial concentration range from 10–60 mg/L, pH 8, orbital shaking for 3 h at 180 rpm and incubation at 30 ± 2 °C. **a** results using ISE method and **b** using the conventional kinetic method

Table 3 Kinetic parameters for the adsorption of cadmium ions on modified palm shell activated carbon (experimental conditions: adsorbent 0.1 g/50 ml, Cd(II) initial concentration range: 10–60 mg/L, pH 8, orbital shaking at 180 rpm and incubation at 30 ± 2 °C)

C_o (mg/L)	Kinetic parameters using ISE					Kinetic parameters using ICP					RSD[a] (%)	Recovery (%)
	q_e (exp)	q_e (cal)	k_2	h	R^2	q_e (exp.)	q_e (calc.)	k_2	h	R^2		
10	4.587	4.618	0.095	2.015	1	4.581	4.607	0.097	2.066	1	0.09	100.13
20	9.339	9.382	0.063	5.567	1	9.34	9.381	0.062	5.439	1	0.01	99.99
40	18.798	18.889	0.053	10.972	1	18.79	18.87	0.034	11.97	1	0.03	100.04
60	27.574	27.778	0.036	12.511	1	27.64	27.79	0.017	13.2	1	0.17	99.76

[a] Relative standard deviation for q_e from experimental results using ISE and ICP

(Igwe et al. 2008; Dizadji and Abootalebi Anaraki 2011). There are many factors that can contribute to this initial concentration effect on the rate of adsorption. Increasing the metal concentration in solution seems to reduce the diffusion of metal ions in the boundary layer and enhance the diffusion in the solid. Another possible cause is the progressive decrease in covalent interactions relative to the electrostatic interactions of the sites with a lower affinity for Cd (II) with an increase in the initial Cd(II) concentration.

The effect of contact time on the adsorption of Cd(II) was studied by keeping particle size, initial concentration, adsorbent dose and pH constant. The results showed that adsorption increased rapidly during the first 3 h. At that time, the adsorption reached an equilibrium state. It can be seen from Fig. 7 that a 3-h contact time was required to attain adsorption equilibrium for the cadmium solution. During this time, more than 90 % of the cadmium was adsorbed due to the initial availability of free TOMAS on the modified activated carbon surface. Over time, coordinate interaction between TOMAS and Cd(II) ions occurred, and adsorption became nearly constant until the end of the experiment. It can be concluded that the binding of cadmium with TOMAS was high in the initial stages, and after a certain period of time, the reactive functional groups of TOMAS were exhausted. Subsequently, it became difficult for the cadmium ions to occupy the modified activated carbon surface.

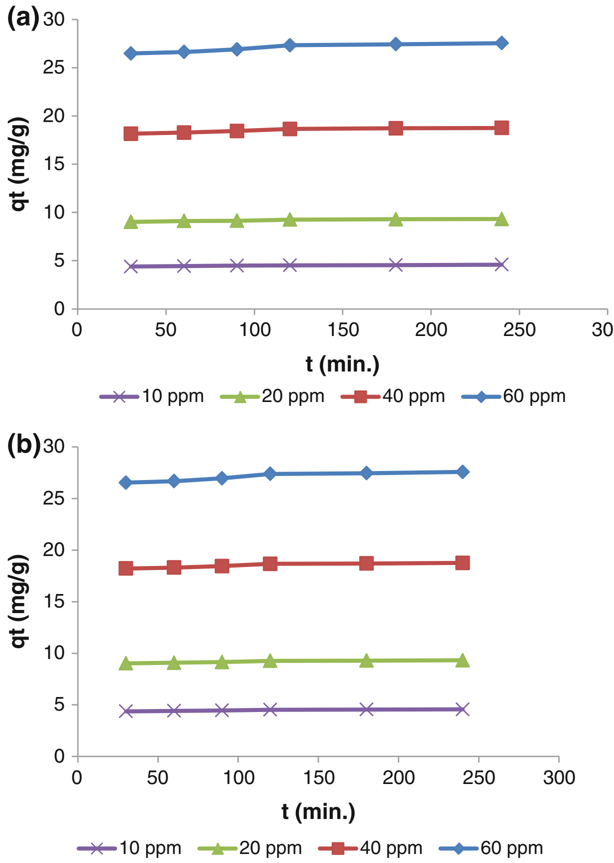


Fig. 7 Plot of adsorption capacity versus time for the adsorption of cadmium ions on modified palm shell activated carbon (**a**) using the ISE method and (**b**) using conventional kinetic methods

Both ISE results and conventional kinetic studies of the rate constant value k_2 usually depend on the initial cadmium concentration. As shown in Fig. 8, the values of the rate constant were found to increase from 0.017 to 0.097 g mg^{-1} min upon a decrease in the initial cadmium concentration. Thus, for higher initial concentrations of adsorbate, longer times are required to reach equilibrium; in turn, the k_2 values decrease.

The second-order rate constants were used to calculate the initial adsorption rate h given by: $h = k_2 q_e^2$.

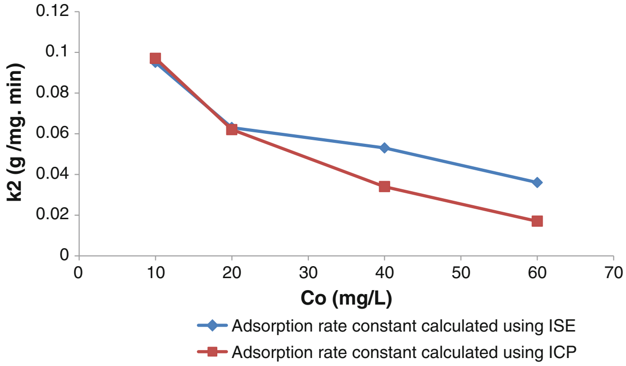


Fig. 8 Adsorption rate constant versus initial concentration for the adsorption of cadmium ions on modified palm shell activated carbon

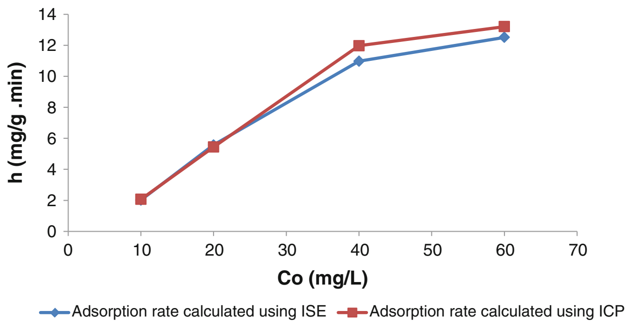


Fig. 9 Initial adsorption rate versus initial concentration for the adsorption of cadmium ions on modified palm shell activated carbon

The calculated *h* values are plotted against the initial concentration, as shown in Fig. 9. Both ISE results and conventional kinetic studies indicate that the value of the initial adsorption rate *h* usually depends on the initial adsorbate concentration. The initial adsorption rate *h* was found to increase with increasing initial cadmium concentration; however, the adsorption rate value started to decrease at higher initial concentrations. This decrease may be due to high solute concentrations slowing down the adsorption process. For all initial concentrations, the same amount of adsorbent was used, which might not have been sufficient for the cadmium ions to adsorb quickly when the initial concentration was overly high.

Table 4 Potentiometric determination of cadmium(II) in water samples using the proposed electrode and ICP

Sample[a]	Cd (II) (mg L^{-1})[b]			
	Proposed electrode	ICP	RSD (%)	Recovery (%)
(1)	0.575	0.55	3.19	104.6
(2)	0.464	0.446	2.90	104.2
(3)	0.480	0.491	1.55	97.8
(4)	0.423	0.412	1.92	102.8

[a] From groundwater wells in the Gaza Strip

[b] Mean data for three replicate measurements

Analytical applications

The proposed electrode was used to determine of the amount of Cd (II) in drinking water samples. Water samples were collected from four domestic wells nearest to the waste water collection area in the Gaza Strip (Palestine). The results of the Cd^{2+} contents measured by the proposed electrode were compared with those obtained by ICP (Table 4). These results show that Cd (II) concentration values obtained with the proposed electrode were similar to those obtained by ICP with deviations below 4 % for all samples.

Comparison of the response for the proposed and the previously reported Cd (II) electrodes

The comparative study of the proposed electrode with some recently reported cadmium electrodes is summarised in Table 5. The results show the superiority of the proposed electrode in terms of its wider linear range, Nernstian slope and lower detection limit when compared with the other electrodes.

Conclusion

The electrode developed in this study shows better sensitivity towards Cd(II) ion determination by potentiometry

Table 5 Comparison of the proposed Cd-PSACPE electrode with previously reported electrodes

Ionophore	Slope (mV/decade)	Linear range (mol L^{-1})	Detection limit (mol L^{-1})	Response time (s)	References
TOMAS	30.90	1.0×10^{-9}–1.0×10^{-2}	1.0×10^{-10}	10	*This work*
4-hydroxy salophen	30.1 ± 1	1.0×10^{-6}–1.0×10^{-1}	8.4×10^{-7}	20	(*Ensafi* et al. 2009)
N,N_-[bis(pyridin-2-yl) formylidene]butane-1,4-diamine	30	7.9×10^{-8}–1.0×10^{-1}	5.0×10^{-8}	10	(*Gupta* et al. 2007)
Dicyclohexano-24-crown-8	30.0 ± 1.0	3.0×10^{-5}–1.0×10^{-1}	–	23	(Gupta et al. 2006)
Tripodal amine	29.4 ± 0.6	1.6×10^{-6}–1.0×10^{-2}	1.6×10^{-6}	10	(Khamjumphol et al. 2011)
3,5-dinitro-N-(tri-2-pyridyl methyl) benzamide	30 ± 1	2.16×10^{-7}–1.00×10^{-1}	1.82×10^{-7}	50	(Abbastabar-Ahangar et al. 2009)
N1, N2-dicyanoethyl-N1, N2-bis(pyridin-2-ylmethyl) benzene-1, 2-diamine	29.5	2.5×10^{-7}–1.0×10^{-1}	7.8×10^{-8}	12	(*Singh* et al. 2011)
Tetrathia-12-crown-4	29 ± 1	4.0×10^{-7}–1.0×10^{-1}	1.0×10^{-7}	10	(Shamsipur and Mashhadizadeh 2001)
N,N- (4methyl-1,2-phenylene) diquinoline-2-carboxamide	29.9 ± 0.5	1.0×10^{-6}–1.0×10^{-1}	8×10^{-7}	3–8	(Rezaei et al. 2008a, b)

compared with previously used techniques such as inductively coupled plasma mass spectrometry, atomic adsorption spectrometry and voltammetry. The modified palm shell activated carbon paste electrode is very simple and cheap to use. The proposed electrode shows good sensitivity and satisfactory reproducibility. Moreover, investigations of real samples show that the proposed Cd(II) ion detection methodology offers a wide linear range and a low detection limit, and it is not significantly interfered with by other heavy metal ions that are usually present in real samples. The experimental results for both analytical and kinetic applications using the proposed electrode agree very well with those obtained using ICP. The experiment based on the proposed electrode was able to directly monitor the cadmium ion concentration without a need for separation processes and without any disturbance of the binding equilibrium. The sensitivity and relatively high stability of the electrode have opened a new avenue for the detection of heavy metal ions via complexation with ionic liquids at the activated carbon surface.

Acknowledgments The authors appreciate the financial support of the Islamic Development Bank, the IDB Merit scholarship programme, and University of Malaya, Postgraduate Research Grant (PPP) Grant No. PS098/2010B.

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