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ORIGINAL PAPER

Electrochemical detection and removal of lead in water using poly(propylene imine) modified re-compressed exfoliated graphite electrodes

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Abstract Modification of exfoliated graphite (EG) electrode with generation 2 poly(propylene imine) dendrimer by electrodeposition resulted in an electrochemical sensor which was used to detect lead ions in water to a limit of 1 ppb and a linear response between 2.5 and 40 ppb using square wave anodic stripping voltammetry (SW-ASV). Pb(II) was also removed from spiked water sample using a 40-mm diameter unmodified EG electrode with an applied potential of −1,000 mV for 180 min. A removal efficiency of 99% was calculated from a 150 mL sample. The results obtained in both cases using SW-ASV, correlated with atomic absorption spectroscopy.

Keywords Exfoliated graphite · Lead · Poly(propylene imine) dendrimer · Square wave anodic stripping voltammetry · Water

1 Introduction

The presence of heavy metals in the environment and their potentially toxic effects on the health of living species is a cause for concern. This is because heavy metals tend to bioaccumulate in higher trophic levels within the food chain and can be toxic even in trace quantities [1–3]. Therefore, the challenge to remediate hazardous metal-containing waste streams generated by mining operations, industrial sites and groundwater is immense. Almost all heavy metals are toxic and excess levels are known to cause both acute and chronic health conditions [4]. Heavy metals cannot be degraded and the natural process of metal mineralisation is very slow [5]. Fundamentally, the removal of heavy metals from water and wastewater is best accomplished by immobilisation and concentration on suitable sorbents whereby the sorbed metals can be removed and reused as raw materials [4]. Since heavy metal ions which are generated in wastewater during industrial processing are extremely toxic to the environment and humans, it is very important that treatment be provided in such a way that their pollutant loads are kept at low concentration levels before being discharged into sewers or water systems [1].

Lead (Pb), a heavy metal, is widely used in industries and it is a well-known water pollutant. Lead poisoning is associated with gastrointestinal disorders, constipation, abdominal pain and central nervous system effects [4]. The harmful effect of Pb on child development can occur without clinical symptoms and might not present any abnormalities during routine testing. However, higher levels or prolonged exposure to Pb result in more severe symptoms such as kidney and nervous system damage [4–6]. These adverse health effects necessitated extensive attention in developing sensitive, reliable and rapid analytical methods [7].

Electrochemistry can be used for the treatment or recovery of pollutants in effluents from industries and municipal plants. Electrochemical devices are effective and inexpensive for environmental monitoring of an increasing range of toxic substances [8]. With its unique ability to oxidise or reduce compounds at a well-controlled electrode potential and by just adding (at the anode) or withdrawing

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(at the cathode) electrons, it offers many interesting possibilities in environmental engineering [8, 9]. Anodic processes can be used to oxidise organic pollutants to produce harmless products, while cathodic processes can remove heavy metals from wastewaters down to very low outlet concentrations [8, 9]. Electrochemical methods, compared with conventional methods, are characterised by high sensitivity, good selectivity, rapid response and the instruments are relatively simple to use with the possibility of miniaturisation for in situ measurements which is an advantage for trace metal detection [10–12]. Electrochemical techniques have proved to be powerful tools for removing heavy metals from waste solutions. In many cases, such techniques have demonstrated superiority to other techniques such as chemical precipitation and ion exchange [13, 14]. However, the quest for new electrode materials that are more sensitive and cheaper is ongoing in the area of monitoring and treatment of toxic metals in wastewater [15].

Graphite is a good electrical and thermal conductor within the layers and a poor electrical and thermal conductor perpendicular to the layers (due to weak van der Waals forces between the layers) [16]. This electrical conductivity enables graphite to be used in electrochemical electrodes. Graphite can accommodate intercalates which can be rapidly forced out at high temperatures to form exfoliated graphite (EG) [17]. EG is a puffed low-density material with high temperature resistance and good electrical conductivity [18]. Compression of EG flakes results in mechanical interlocking, thus forming a flexible and resilient sheet called recompressed EG [18, 19]. The flexibility, ease of shaping and unusual microstructure of EG (compared with other forms of carbon) suggest its possible application as an electrode material in batteries, electrolysis and chemical sensors [20].

In this study, square wave anodic stripping voltammetry (SW-ASV) was the electroanalytical technique of choice. This is because stripping voltammetry is particularly useful for trace metal detection where the first step is the preconcentration of the metal ion onto the electrode surface followed by conventional voltammetric detection [21]. There is also an increasing interest in the development of procedures for purification of industrial process wastewaters including those arising from mining and mineral processing. An attractive methodology, with the possibility of in situ applications, is the use of electrochemical or electrosorptive techniques employing large area electrode (like the large surface EG electrode used in this study) or adsorbent materials [22]. Herein, we report the application of a relatively new electrode called EG electrode for the electrochemical studies of Pb in water. First, the EG was modified with a poly(propylene imine) (PPI) dendrimer and used for the sensing or detection of Pb in water. Second, the unmodified EG electrode with a larger surface area was used for the removal of Pb via electrodeposition.

2 Materials and methods

2.1 Materials and reagents

Natural graphite (NG) flakes was purchased from Sigma-Aldrich and Generation 2 (G2) PPI dendrimer was purchased from SyMO-Chem, Eindhoven, Netherlands. All other chemicals such as potassium chloride, lead(II) nitrate, sulphuric acid and nitric acid were obtained from Merck Chemicals. KCl solution (0.1 M) was used as a supporting electrolyte for both the preparation of standards and the spiked water samples. Double-distilled water was used to prepare all solutions.

All electrochemical measurements were done on an Autolab PGSTAT 302N using a three-electrode configuration. Working electrode, counter electrode and reference electrode were an EG (5 and 40 mm diameter), platinum wire and Ag/AgCl (3 M Cl^-), respectively. The counter electrode (platinum wire) was replaced with another EG electrode when a large volume (150 mL) of spiked water was used for lead removal.

2.2 Fabrication procedure for EG electrodes

The EG particles were prepared according to a reported procedure [5, 23]. In brief, NG flakes of particle size 300 µm, were intercalated with bisulphate anion for 24 h using a mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v) under ambient conditions to form graphite intercalated compound (GIC). The intercalated material was washed well, and then subjected to thermal shock at 800 °C for about 30 s forcing the intercalated material out of the graphite lattice, thereby rupturing the layers. This procedure resulted in the puffed material called EG that is characterised by a very low density of 0.0068 g mL^{-1}.

The EG particles were restacked without any binder to form pellets/sheets by compressing approximately 1 g of EG at a pressure of 58 kPa for 6 h. Electrodes were then fabricated from these pellets using a glass rod, copper wire, conduction silver paint and a piece of the recompressed EG. A puncher was used to cut the EG pellet into a circle of 5 mm diameter (for the SW-ASV) or 40 mm diameter (for the lead adsorption). A copper wire was first scratched off the top layer using a blade to remove any oxide on the surface. One end of the Cu wire was coiled to form a flat surface onto which conducting silver paint was pasted and subsequently a piece of EG pellet (5 mm diameter) placed on top. This was left to dry and then placed in the oven for a few minutes. After cooling, the electrode was inserted into a glass tube and coated with an insulator (Araldite epoxy resin) leaving only the basal plane of the pellet. The araldite was left to completely dry overnight. The smaller electrode was also used to monitor the amount of lead at 30 min intervals during the electrochemical removal of Pb(II) ions experiments. The electrode surface was polished using emery sheets P1500-grit followed by 3/0 to obtain a smooth surface. The electrodes were tested for conductivity using a multimeter.

2.3 Electrode modification

The EG electrode (5 mm diameter) was modified according to the procedure reported by Arotiba et al. [24]. In brief, solutions containing 10 mM Generation 2 (G2) PPI at pH 7 phosphate buffer solution were prepared. The PPI solution (10 mL) was used as an electrolyte to perform cyclic voltammetry (CV) between potentials of −400 and 1,100 mV for ten cycles to deposit the PPI dendrimer onto the EG electrode surface. The modified electrode, to be referred to as EG-PPI, was rinsed with distilled water followed by KCl. The EG-PPI was electrochemically characterised using CV and SWV in KCl and equimolar (1:1) mixture of 5 mM $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ ($[Fe(CN)_6]^{3-/4-}$) electrolytes.

2.4 Electrochemical detection of Pb using EG-PPI electrode

At a preconcentration potential of −1,000 mV and time of 180 s, SW-ASV was used to obtain a calibration graph for varying concentrations of Pb. The SWVs were recorded at potentials ranging between −900 and −400 mV to accommodate the oxidation of Pb which occurs at about ca. −600 mV on the EG-PPI electrode. The peak currents obtained from the SW-ASV of the various solutions were used to construct the calibration curve from which the regression equation was obtained. This equation was used to calculate the Pb concentration before and after electrochemical removal using the fabricated EG electrode. The EG-PPI electrode was also used to determine the lead concentration in real water samples using the standard addition method. The electrode was subjected to a potential of −100 mV for 90 s to remove excess Pb which could have been left of the electrode surface. SW-ASV was recorded on the electrode to ensure that there was no Pb left on the electrode surface before introducing a new concentration of Pb.

2.5 Electrochemical removal of Pb

The electrochemical removal of Pb was performed on the working electrode with a diameter of 40 mm. An electrode of the same size as the working electrode was used as the counter electrode while the reference was the Ag/AgCl (3 M Cl^-) electrode. The removal was carried out by holding the potential, while stirring, at −1,000 mV for 180 min in a solution containing 150 mL of 40 ppm Pb(II) ions. The amount of Pb remaining in solution was monitored every 30 min. A small volume of 3 mL was kept aside every 30 min for atomic absorption spectroscopy (AAS) measurements. Energy-dispersive X-ray spectroscopy (EDX) of the working electrode, counter electrode and a fresh EG pellet was recorded.

3 Results and discussion

3.1 Electrode modification and characterisation

The cyclic voltammograms (ten cycles) of the electrodeposition of the dendrimer are shown in Fig. 1. The electrooxidation of the primary amine groups of the dendrimer, which linked PPI dendrimer to the EG electrode through C–N bonding, was accomplished between the potentials 650 and 1,000 mV. The ten voltammetric cycles were used to increase the surface coverage on the EG electrode by the PPI. Similar results have been reported using other forms of carbon electrode namely screen printed carbon and glassy carbon electrodes [24, 25]. The peak current for the electrooxidation of PPI decreased with an increase in scan number owing to electrodeposition. The bulk of the electrodeposition (monolayer coverage) occurred in the first scan where the oxidation radical was generated—the reason for the highest current. Subsequent scans were used to cover any available site on the electrode. These sites are very few compared with the whole surface of the bare

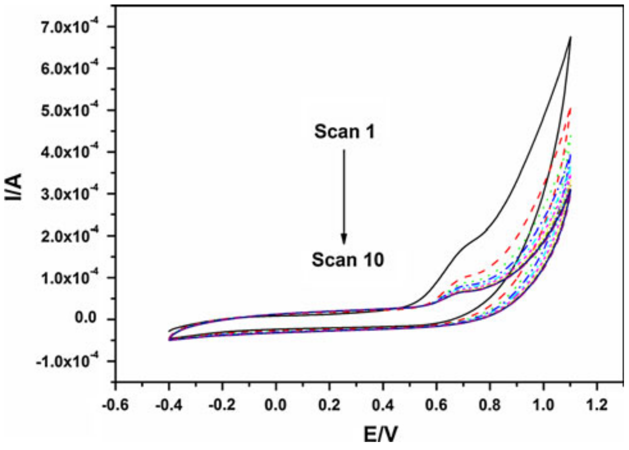

Fig. 1 Cyclic voltammogram of the electrodeposition of G2 PPI dendrimer from a 10 mM G2 PPI solution on the EG electrode surface. Potential scanned from −400 to 1,100 mV for ten cycles at a scan rate of 50 mV s^{-1}

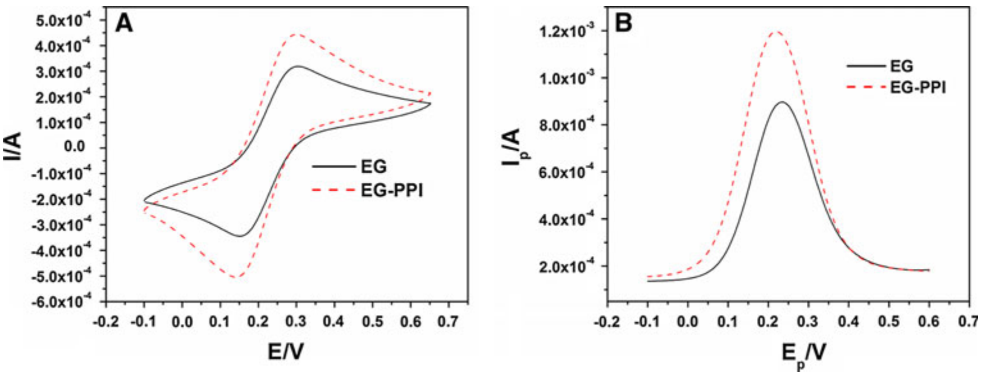

Fig. 2 **a** CV of EG and EG-PPI in 5 mM $[Fe(CN)_6]^{3-/4-}$ electrolyte at a scan rate of 50 mV s^{-1} starting scanning from −100 to −650 mV. **b** SWVs of EG and EG-PPI electrodes in 5 mM $[Fe(CN)_6]^{3-/4-}$ scanning from −100 to −650 mV

electrode available for coverage in the first scan thus lower currents were observed as number of scans increased. This phenomenon has been explained by Arotiba et al. [24–26] where monolayer coverage was proposed.

The effect of the dendrimer modifier on the EG electrode was investigated electrochemically using $[Fe(CN)_6]^{3-/4-}$ redox system (Fig. 2). The peak current of EG-PPI was higher by about 40% than that obtained from unmodified EG in both CV and SWV and this current enhancement is in agreement with earlier report on glassy carbon electrode [25, 26]. This increase is due to the larger electroactive surface area induced on the EG by the dendrimer PPI which is a nanomaterial [27, 28]. The opposing charge of the PPI (cationic) and the redox probe (anionic) may also enhance the concentration of the redox probe on the electrode surface. This increase in current was used as an indicator of successful electrode modification. Impedance measurements (not shown) also suggest a decrease in the charge transfer resistance for EG-PPI (29.0 Ω) as compared with EG (52.9 Ω).

3.2 Electrochemical detection of Pb

In this study, SW-ASV was used to detect the amount of Pb in water. This method was validated by AAS. The SW-ASV was optimised (since it has not been carried out using EG before now) and used to detect lead in real water samples and to monitor the amount remaining is solution at different time intervals for the Pb removal experiments.

The behaviour of both EG and EG-PPI electrodes was investigated in a 40 ppb solution. As depicted in Fig. 3, during the stripping of 40 ppb Pb, the EG electrode could not give a Pb oxidation peak until the electrodeposition time was 600 s (with anodic current of 3.5 μA). While a peak anodic current of ca. 72.5 μA was observed for EG-PPI after 180 s. The shorter preconcentration time and the markedly increased peak current of EG-PPI demonstrate a favourable effect of PPI dendrimer on the EG electrode. The dendrimer, being a nanomaterial, increased surface area of the electrode. In addition to this merit, the modification of EG with PPI also gave more reproducible electrochemical data. SW-ASVs of various Pb concentrations (between 2.5 and 40 ppb) were recorded after optimising the electrodeposition potential and time.

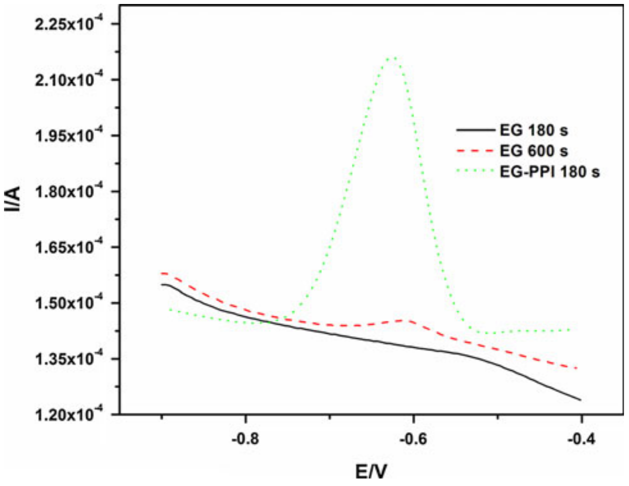

Fig. 3 SW-ASV for 40 ppb Pb in 0.1 M KCl as the supporting electrolyte on EG and EG-PPI electrodes with preconcentration time shown. The preconcentration potential was −1,000 mV

3.2.1 Effect of electrodeposition potential and time

The electrodeposition potential (on EG-PPI) was varied from −700 to −1,200 mV. The results (Fig. 4a) show an increase in the peak current up to −1,000 mV after which there is no significant peak current change. Figure 4b shows the effect of preconcentration time for a 40 ppb solution of Pb. It was observed that after 180 s, there was no significant variation in the peak current intensity. Thus, a potential of −1,000 mV and electrodeposition time of 180 s while stirring were taken as optimum conditions for all electrochemical measurements. The EG-PPI gives higher currents at shorter preconcentration times which suggests that it is efficient and more sensitive to the Pb(II) ions than the unmodified EG electrode.

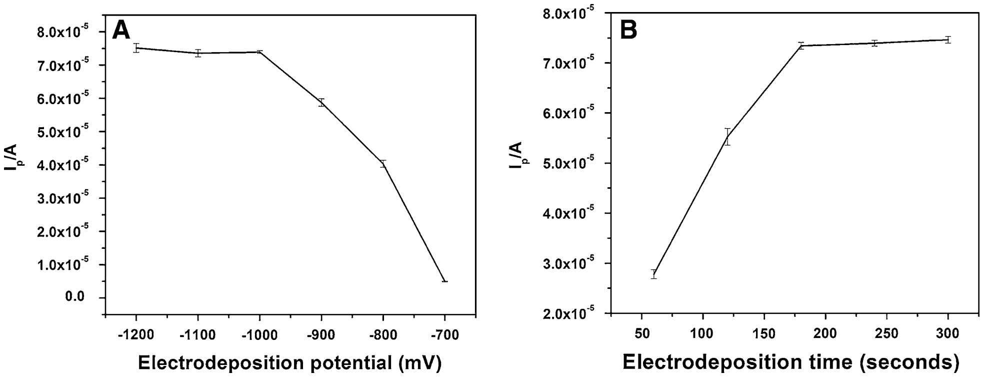

Fig. 4 Effect of **a** electrodeposition potential and **b** electrodeposition time on the peak current. The supporting electrolyte used was 0.1 M KCl

3.2.2 *Calibration curve*

The peak current increased with an increase in Pb concentration. The results obtained were used to plot the calibration graph between 2.5 and 40 ppb. It was observed that there was a linear relationship between concentration and the peak current with a linear regression equation of $y = 1.891 \times 10^{-6}x + 4.315 \times 10^{-8}$ and $R = 0.997$. The limit of detection was calculated to be 1 ppb. The detection limit obtained is comparable with those obtained from other studies [29–34]. The electrode was cleaned by holding the potential at −100 mV for another 90 s to ensure that any Pb that was not stripped off is removed from the electrode surface. This was confirmed by recording SWV in a fresh KCl electrolyte solution.

The experiment (starting from a fresh bare EG electrode) was repeated three times with good reproducibility. For example, a concentration of 30 ppb gave a peak current of $5.76 \times 10^{-5} \pm 6.91 \times 10^{-7}$ A. All the measurements had an average relative standard deviation of 2.6%. The modified electrode was also left overnight and the same range of concentrations was tested on the electrode with good reproducibility. These results show that the electrode is stable and can be used repeatedly without compromising its sensitivity. Another advantage of the EG electrode is that modifications which result in strong covalent bonds can easily be cleaned off the electrode surface by mechanical polishing. This is because when polishing the electrode, the top surface is scrapped off leaving a new fresh surface which can be remodified with the same modifier or even a different one (Fig. 5).

The South African Water Services Act (No. 108 of 1997) states that drinking water quality should comply with prescribed National Drinking Water Standards (South African National Standards (SANS) 241 Drinking Water Specification) [35]. The ideal situation is where drinking water quality satisfies the SANS 241 Class I limits (20 ppb for Pb) which is suitable for lifetime consumptions. However, a class II limit (50 ppb for Pb) is permissible for a short while with the water subjected to further purification. The EG-PPI electrode has a detection limit which was much lower than these limits indicating its analytical importance.

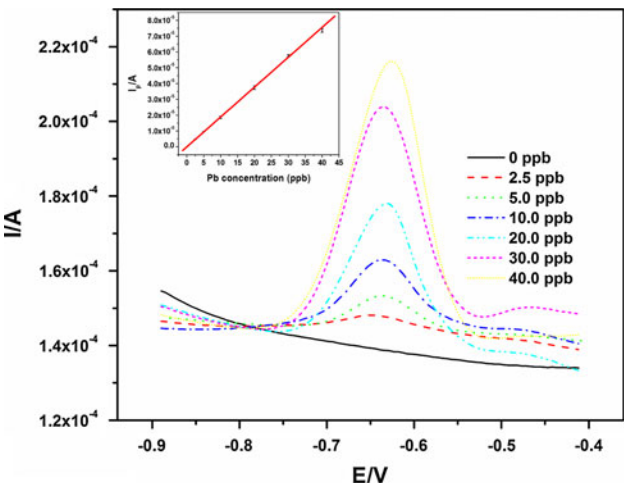

Fig. 5 SW-ASV of different Pb concentrations used to plot the calibration curve. *Inset* calibration curve for the detection of Pb in 0.1 M KCl using EG-PPI electrode. The preconcentration potential was −1,000 mV for 180 s

3.3 Lead detection in real water samples

The EG-PPI electrode was used to detect the amount of Pb in real water sample collected from a water treatment plant (before treatment) in Pretoria. This water was tested for the presence of Pb using standard addition method.

Standard addition was employed to determine the concentration of lead in the real water using the modified electrode and AAS. The results are shown in Table 1 where about 50 ppb of Pb was detected. This level of Pb falls under Class II limits. This suggest that, according to SANS 241, the water can be used for domestic purposes for a short period of time but measures should be taken to try and lower the Pb level. It is believed that the water will have much lower levels of Pb after going through the treatment process. The percentage recovery are also shown in Table 1.

Table 1 Concentrations and % recoveries of Pb obtained using EG-PPI and AAS in real water sample

	EG-PPI electrode	AAS
Pb concentration	49.2 ± 2.3	51.4 ± 1.8
% Recovery	98	102
R^2	0.996	0.998

3.4 Electrochemical removal of Pb

It is very important for industries to monitor the pollution levels of their effluents and also attempt to lower these pollution doses before discharge into water bodies or municipal treatment dams. For industries using Pb in any of their unit operations, Pb concentrations in the ppm levels are not uncommon and thus its removal becomes a worthy task for legislative compliances [36]. Some companies even have in-house treatment plants which they use to lower their pollutant load before they discharge waste to municipal treatment plants. This study brings to light the possibility of using EG electrode for the purpose of Pb removal in a laboratory scale. For this purpose, we used a water sample that has been dosed with high Pb concentration (40 ppm). An unmodified EG electrode was used for Pb removal in contrast to the PPI-modified EG electrode used for the stripping. This is because PPI (in the modified 5-mm diameter electrode) was used to enhance the sensitivity of the stripping technique which forms the quantitative bases for the Pb determination. For removal, however, such sensitivity is not required as the electrode in the unmodified form (40 mm diameter) was able to remove the Pb efficiently. Since the electrode for removal has a larger surface area, modifying it with PPI will increase the cost, a situation we want to avoid so as to maintain the low cost of this system.

A calibration curve for concentrations between 1.0 and 50 ppm, with linear regression equation of $y = 2.645 \times 10^{-5}x + 2.305 \times 10^{-6}$ and $R = 0.996$, was plotted from standard Pb ion solutions. This equation was used to estimate the concentration of Pb remaining in the solution at 30 min intervals in the Pb removal experiment. The amount of Pb decreased quite significantly, by over 60%, within the first 60 min (Fig. 6). The Pb concentration was calculated to be below 0.2 ppm after 180 min. This shows a percentage removal of 99.5% Pb. These results demonstrate good Pb removal efficiency on laboratory samples. Even though there is still need to further test this on real effluent samples, there is hope that this method, if upscaled, can be used for in-house pretreatment process for the removal of lead in wastewater prior to disposal (or feed to treatment plants) by paint, lead-acid batteries, solder and alloy industries which may have very high levels of Pb in their effluent. Removal (or reduction) of heavy metals from effluents prior to discharge will prolong the lifespan of membranes, ion exchange resin (or other materials or process) adversely affected by high Pb loading within treatment processes downstream. The pretreated effluent, depending on the extent of removal, can also be discharged into receiving rivers or sewers for municipal treatment. Some countries have documented the permissible amount of Pb (and other heavy metals) that should be in industrial effluent. For example, the South Australia Trade Waste Guidelines allows not more than 10 ppm of Pb to be discharged by industries [37]. The use of this electrodeposition approach may reduce cost as the industries strive for effluent compliance.

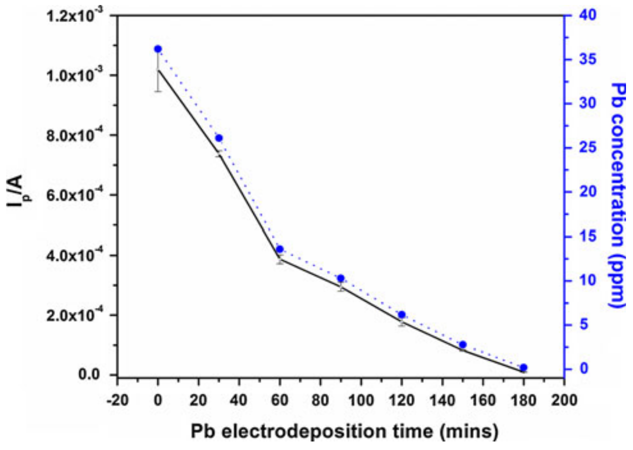

Fig. 6 A plot showing the decrease of Pb concentration with time. The *left y axis* (*solid line*) shows the peak currents obtained, while the *right y axis* (*dotted line*) shows the calculated concentration remaining in solution at 30 min intervals in a total time of 180 min. The preconcentration potential and electrolyte were −1,000 mV and 0.1 M KCl, respectively

Table 2 Estimated concentrations of lead with increasing electrodeposition time

Electrodeposition (min)	Electrochemical concentration (ppm)	AAS concentration (ppm)
0	36.2	34.1
30	28.1	27.6
60	13.1	11.4
90	10.3	8.1
120	6.2	5.1
150	2.8	1.9
180	0.17	N/D

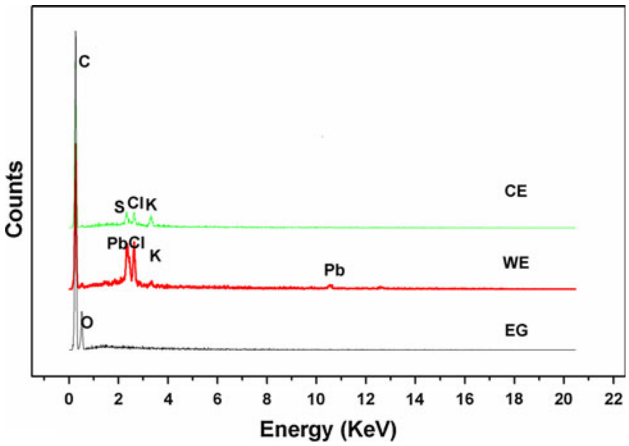

Fig. 7 An overlay of EDX spectra of a fresh EG pellet, counter electrode (CE) after Pb removal and the working electrode (WE) after lead removal

3.4.1 AAS measurements

During the 30 min intervals, 3 mL samples were kept aside for measurements using the AAS. Standard solutions were prepared for concentrations between 1 and 50 ppm and an AAS calibration plot ($R = 0.996$) was obtained with a line equation of $y = 1.110 \times 10^{-2}x + 1.902 \times 10^{-2}$. The AAS results were consistent with the electrochemical results as there was a decrease in the Pb ion concentration over time. The Pearson's correlation coefficient, r, for the AAS and electrochemical measurements was calculated to be 0.998 showing positive correlation between the two methods. The concentrations of Pb determined using AAS as compared with that of SW-ASV are shown in Table 2. These also show a steady decrease of the metal ion concentration which suggest that there was no leaching of the metal ions back into the water samples. By using EG electrode, recovery of these metals for other purposes is also possible.

The deposition was visually evident as the EG working electrode appeared metallic grey compared with a fresh EG pellet. EDX measurements (Fig. 7) were taken on a fresh EG pellet, working and the counter electrodes to confirm the presence of Pb via electrodeposition. The only detected elements from a fresh EG pellet were carbon and oxygen. The oxygen may have remained after the exfoliation of the intercalates from GIC. The counter electrode had K and Cl (from the supporting electrolyte) in addition to C and O; while Pb was only detected on the EG working electrode.

4 Conclusion

A relatively new, low cost and easy to use EG electrode has been fabricated for use in the detection and removal of lead in water. The graphitic nature of the electrode lends it to ease of modification using PPI dendrimer. The method used for both the detection and removal is simple, time efficient, reproducible and correlates well with the classical AAS method. The detection limit of 1 ppb obtained is below the accepted drinking water standards showing its analytical significance. The EG electrode shows remarkable lead removal efficiency with no leaching. This technique could be applied effectively by industries that produce effluents with high heavy metal pollutant loads for in-house pollution reduction before discharge while simultaneously recovering these metals for reuse or for commercial purposes.

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References

1. Elsherief AE (2003) Electrochim Acta 48:2667
2. El-Sherif IY, Ashmawy A, Badr S (2008) J Appl Sci 4:391
3. Wong ELS, Chow E, Gooding JJ (2007) Electrochem Commun 9:845
4. Ruparelia JP, Duttagupta SP, Chatterjee AK, Mukherji S (2008) Desalination 232:145
5. Bonnissel M, Luo L, Tondeur D (2001) Carbon 39:2151
6. Fletcher AM, Gelberg KH, Marshall EG (1999) J Community Health 24:215
7. Sun D, Sun Z (2008) J Appl Electrochem 38:1223
8. Simonsson D (1997) Chem Soc Rev 26:181
9. Gasparotto LHS, Bocchi N, Rocha-Filho RC, Biaggio SR (2006) J Appl Electrochem 36:677
10. Chen MH, Chou TC (2003) J Electrochem Soc 150:H214
11. Kaisheva A, Iliev I, Christov S, Kazareva R (1997) Sens Actuators B Chem 44:571
12. Liu Z, Du J, Qiu C, Huang L, Ma H, Shen D, Ding Y (2009) Electrochem Commun 11:1365
13. Juttner K, Galla U, Schmieder H (2000) Electrochim Acta 45:2575
14. Zaki MM, Nirdosh I, Sedahmed GH (2007) Chem Eng J 126:67
15. Ramesham R (1999) J Mater Sci 34:1439
16. Chung DDL (2002) J Mater Sci 37:1475
17. Cai D, Song M (2007) J Mater Chem 17:3678
18. Chung DDL (1987) J Mater Sci 22:4190
19. Hristea G, Budrugeac P (2008) J Therm Anal Calorim 91:817
20. Chung DDL (2000) J Mater Eng Perform 9:161
21. Economou A, Voulgaropoulos A (2007) Talanta 71:758
22. Ayranci E, Conway BE (2001) J Appl Electrochem 31:257
23. Cao X, Yang G, Wei S, Li C (2008) J Appl Electrochem 38:1571
24. Arotiba OA, Owino JH, Baker PG, Iwuoha EI (2010) J Electroanal Chem 638:287
25. Arotiba OA, Songa EA, Baker PG, Iwuoha EI (2009) Chem Today 27:55
26. Arotiba OA, Baker PG, Mamba BB, Iwuoha EI (2011) Int J Electrochem Sci 6:673
27. Krasteva N, Guse B, Besnard I, Yasuda A, Vossmeyer T (2003) Sens Actuators B Chem 92:137
28. Arotiba OA (2008) Electrochemical impedance modelling of the reactivities of dendrimeric poly(propylene imine) DNA

nanobiosensors. PhD Thesis, Department of Chemistry, University of the Western Cape
29. Truzzi C, Annibaldi A, Illuminati S, Bassotti E, Scarponi G (2008) Anal Bioanal Chem 392:247
30. Laschi S, Palchetti I, Mascini M (2006) Sens Actuators B Chem 114:460
31. Zou Z, Jang A, Macknight E, Wu P, Do J, Bishop P, Ahn C (2008) Sens Actuators B Chem 134:18
32. Švancara I, Baldrianová L, Tesařová E, Hočevar SB, Elsuccary SAA, Economou A, Sotiropoulos S, Ogorevc B, Vytřas K (2006) Electroanalysis 18:177
33. Hwang G, Han W, Park J, Kang S (2008) Sens Actuators B Chem 135:309
34. Jung W, Jang A, Bishop PL, Ahn CH (2011) Sens Actuators B Chem 155:145
35. SANS 241 (2005) Drinking water quality management guide for water services authorities, 6th edn. http://www.dwaf.gov.za/Documents/Other/DWQM/DWQMWSAGuideSept05.pdf. Accessed 25 Mar 2011
36. World Health Organisation (WHO) guidelines for drinking-water quality, 3rd edn incorporating the 1st and 2nd addenda, vol 1. Geneva (2008). http://www.ncbi.nlm.nih.gov/pubmed/15806952. Accessed 25 Mar 2011
37. South Australia (SA) Water Trade Waste Branch Standards of Acceptance of Liquid Waste to Sewer: as required by the sewage Act 1929 2009. http://www.sawater.com.au/NR/rdonlyres/9009B116-51C4-4A2B-84DF-D21B97141DE8/0/stdsofA.pdf. Accessed 11 Jun 2011