Voltammetric Monitoring of Pb (II) by TiO2 Modified Carbon Paste Electrode

3 authors, including:

Najet Belkhamssa
École de Technologie Supérieure
15 PUBLICATIONS **127** CITATIONS

SEE PROFILE

Mohamed Ksibi
University of Sfax/High Institute of Biotechnology
154 PUBLICATIONS **7,683** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project   SfP 983311 : Remediation Processes in Uranium and other Mining Exploration areas View project

Project   Tracking microplastics in the environment View project

Voltammetric Monitoring of Pb (II) by TiO$_2$ Modified Carbon Paste Electrode

Najet Belkhamsa,[a] Lassine Ouattara,[b] and Mohamed Ksibi[a,z]

[a]*Laboratoire Eau, Energie et Environnement ENIS, University of Sfax, Sfax 3038, Tunisia*
[b]*Laboratory of Physical Chemistry, University UFR SSMT, Felix Houphouet-Boigny-Cocody, Abidjan 22, Cote d'Ivoire*

The objective of the current work was to investigate the performance of a carbon paste electrode (CPE) modified by TiO$_2$ for the analytical detection of trace lead (II) in drinking water by square wave voltammetry. The results showed that TiO$_2$ plays an important role in the accumulation process of Pb (II) on the modified electrode surface. The electroanalytical procedure employed for the determination of Pb (II) comprised two steps: chemical accumulation of the analyte under open-circuit conditions, followed by the electrochemical detection of the pre-concentrated species using square wave voltammetry. The analytical performance of this system has been explored by studying the effects of preconcentration time, potential scan rates and various concentrations of lead ions, as well as interferences due to other ions. The determined detection and quantification limits were 4.5×10^{-8} M and 9.5×10^{-5} M. The reproducibility for three replicate measurements at 25 μM lead level was 4.4%. The results indicated that this electrode is sensitive and effective for the determination of Pb^{2+}.
© 2015 The Electrochemical Society. [DOI: 10.1149/2.0491508jes] All rights reserved.

Lead is one of the most toxic elements and has accumulative effect. As described elsewhere,[1] continuous exposure to this element may cause adverse and poisoning effects to the brain, blood, kidneys and nervous system along with other diseases. Nowadays, the importance of controlling the level of environmental pollutants in natural waterways and potable water has generated increasing interest in the development of novel sensors for the detection and determination of heavy metals such as lead ions. Moreover, lead is easily found in high concentrations in industrial wastewaters which can gradually seep into surface water bodies. Lead in environment is generally present as inorganic Pb^{2+} and it has toxic effect to human health, such as renal disease, cardiovascular effects and reproductive toxicity.[2] Thus, the increasing industrial use of lead and its serious effect on human health make it necessary and challengeable to develop methods for the determination of lead (II) in various environmental samples. Some analytical techniques such as atomic absorption spectrometer (AAS), inductively coupled plasma mass spectrometer (ICP-MS), or polarographic analysis and atomic spectroscopy with high capability of determination of trace elements have already been used. However, due to their high cost, need for experts, special solvents, analysis of turbid solutions and need of maintenance, necessitate the development of methods that eliminate these complications.[3] In comparison with membrane electrodes, carbon paste electrodes as ion selective electrodes have gained considerable attention mainly due to their advantages such as renewability, stable response, low ohmic resistance and no need for internal solution.[4–11] The introduction of a chemical modifier, which is able to preconcentrate metallic ions into the electrode surface by either complexation or electrostatic attraction, can lead to more sensitive electroanalytical procedures with lower detection limit values.[12] A wide variety of applications have been developed for TiO$_2$ nanomaterials since the discovery of TiO$_2$ in early 19th century.[13] In the daily life of human being, titanium dioxide is commonly used as a pigment for providing whiteness and opacity to some products such as paints, coatings, plastics, paper, food and cosmetics. In science and engineering world, TiO$_2$ nanomaterials have found a broad range of applications. For instance TiO$_2$ nanomaterials can be used to construct electrochemical sensors using its intrinsic properties, such as large surface area, high adsorptive property. Nanostructured TiO$_2$, such as TiO$_2$ nanoparticles and TiO$_2$ nanoparticulate thin film, has abundant adsorption sites for organic compounds. This property can be used for enrichment and measurement of organic compounds.[14] TiO$_2$ nanoparticles can be incorporated into carbon paste matrix to prepare TiO$_2$ modified carbon paste electrode (CPE) for the sensing of an antidepressant, buzepidemethiodide (BZP).[15] TiO$_2$ nanoparticles contribute to increase the electron transfer kinetics between drug and the electrode. In the current work, regarding the properties of TiO$_2$, it will be associated to a carbon paste electrode for the detection and quantification of leads by voltammetric techniques.

Experimental

The minerals and chemicals used in this investigation were commercial TiO$_2$ and sodium acetate from Sigma. The commercial graphite powder was supplied from France (Carbone, Lorraine, ref 9900). Solutions were prepared using distilled water.

Cyclic and square wave voltammetry were carried out with a voltalab potentiostat (model PGSTAT 100, Ecochemie B.V., Utrecht, The Netherlands) driven by the general purpose of the electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes by using TiO$_2$/CPE as the working electrode, platinum plate for counter and saturated calomel electrode (SCE) as reference electrodes.

The carbon paste electrodes were prepared by mixing high purity graphite powder and TiO$_2$ with paraffin oil. That mixture (TiO$_2$/CPE) was then compacted carefully in the electrode cavity. The electrical connection was provided by a bar of carbon.

The initial procedure consisted in measuring the electrochemical response at the TiO$_2$/CPE electrode at a fixed concentration of lead. Standard solution of lead was added into the electrochemical cell containing 0.1 M of the supporting electrolyte (buffer of sodium acetate). The lead containing supporting electrolyte was kept during 20 s at open circuit before performing the voltammetric measurements. The square wave voltammetry was recorded in the range from –1.5 V to 1.5 V with a potential scan rate of 100 mV.s^{-1}, a step potential of 50 mV, the amplitude of 2 mV and 0.1s duration. Optimum conditions were established by measuring the peak currents versus various investigated parameters such as preconcentration time, potential scan rate and concentration of lead ions. All the experiments were performed at room temperature (25°C).

The TiO$_2$/CPE modified electrode was tested in drinking water samples under the optimized conditions. For each sample, four solutions have been prepared by adding the Pb^{2+} ions in the domestic water, and analyzed without any previous pre-treatment.

Results and Discussion

Surface electrochemical characterization.— Cyclic voltammetry technique was used to investigate the effect of modifiers on the electrochemical response of the developed bare CPE and modified CPE at 100 mV/s electrodes in 0.1 M of acetate buffer solution as supporting electrolyte in the absence and in presence of 25 μM of Pb (II) ion. The recorded voltammograms were presented in Figure 1. In
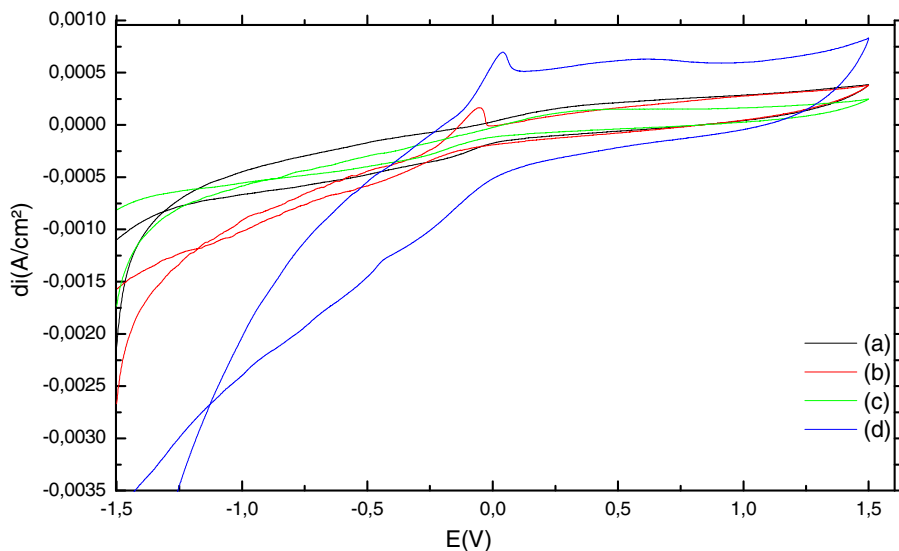
Figure 1. Cyclic voltammograms of Bare-CPE in absence (a) and in presence of lead ions (b) and on TiO$_2$-CPE in absence(c) and in presence of lead ions (d). 0.1 M of acetate buffer solution was used as supporting electrolyte and a potential scan rate of 100 mV.s^{-1} have been used. T = 25°C, CE: platinum plate, RE: SCE.

lead ions containing electrolytes, optimal accumulation time that is 15 min has been applied for lead accumulation over the electrode's surface. Figure 1a and Figure 1b show the voltammograms that have been recorded on a bare CPE in absence and in presence of lead ions respectively. In absence of lead ions, the voltammogram presents a background current with a high voltammetric charge. No peaks other than waves related to surface redox process of the Csp^2 around 0 V was observed.[16] In Figure 1b, in presence of leads ions in the acetate buffer electrolyte, an oxidation peak appeared at −0.1 V. An increase in the background current over the whole potential domain explored is observed. Indeed, the increase in the background current can be related to physical adsorption of the preconcentrated lead ions into the electrode's surface. In Figure 1c, the voltammograms recorded on TiO$_2$/CPE present a relatively low background current compared to that of bare CPE indicating that adding TiO$_2$ to CPE leads probably to a decrease in the electrode surface pores size reducing the penetration of the electrolyte into pore holes. In presence of lead ions, high capacitive charge was recorded and an oxidation peak appears at 0 V. Indeed, the oxidation peak is the consequence of the oxidation of accumulated lead ions on the electrode's surface. The increase of the capacitive charge and the increase of the peak current intensity from 1.63 to 6.91 × 10^{-4} A/cm^2 on unmodified and modified CPE respectively indicate that in presence of TiO$_2$, more leads ions

accumulate on the electrode's surface. The positive shift in the lead oxidation potential can be due to the increase in the irreversibility of such process due probably to the use of a semiconductor as modifier for the electrode preparation. Moreover, the presence of the TiO$_2$ in the carbon paste composition improves markedly the sensitivity of the carbon paste electrode toward leads ions accumulation compared to unmodified CPE. This phenomenon certainly arises due to the high affinity between TiO$_2$ and lead ions favoring more accumulation of Pb (II) ion on the CPE surface in the preconcentration stage. Considering the obtained results, TiO$_2$/CPE will be used for all the subsequent experiments in this study.

Under the following condition, square wave voltammograms have been recorded on the composite TiO$_2$/CPE. The obtained results are depicted in Figure 2. In Figure 2, we observe a well-defined anodic peak potential shifting from 0.04 to 0.187 V as the accumulation time increases. That peak corresponds to the accumulated lead oxidation peak. SQW voltammetry appears to be a good technique for lead detection and analysis.

In order to optimize the detection of lead ions and the analysis parameters, many investigations have been performed such as the effect of lead ions accumulation time, the effect of potential scan rates. In such a way, the effect of the preconcentration and the deposition time of the lead ions have been performed. Figure 3 shows that the surface
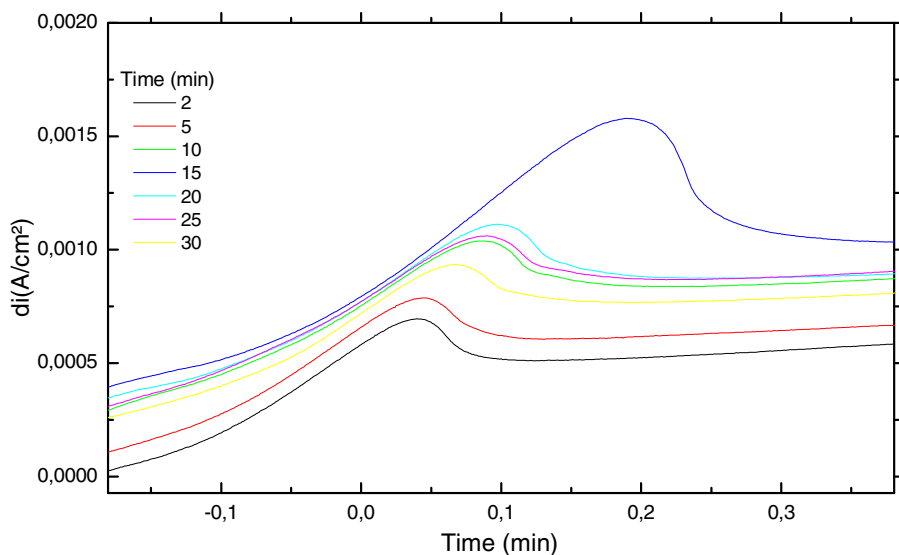

Figure 2. Square wave voltammogram of 2.5 × 10^{-5} M lead ions in presence of acetate buffer 0.1 M; scan rate 100 mV.s^{-1}.
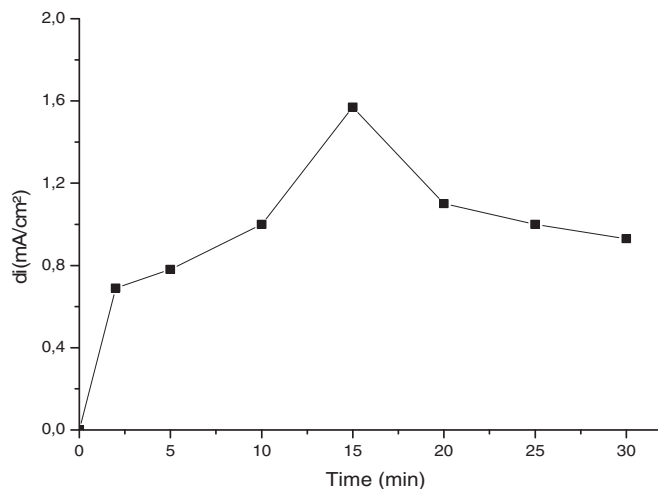
Figure 3. Effect of accumulation time on the SQW voltammetric peak current of 2.5×10^{-5} M lead ions in presence of acetate buffer 0.1 M; scan rate 100 mV.s^{-1}.

concentration of the lead (II) species increases with the preconcentration time until the saturation surface concentration is reached. Since the electrode process was adsorption-controlled, the accumulation time of lead ions was investigated. It can be seen that the peak current reached its maximum for 15 min of lead species accumulation. This

result indicates that 15 min can be considered as the optimum time for lead (II) accumulation.

The effect of the potential scan rates have been performed on the lead oxidation peak current intensity. For that purpose, various scan rates from 30 to 150 mV.s^{-1} have been chosen. The investigation has been carried out in 25 μM of Pb (II) acetate buffer solution. The resulting data are shown in Figure 4. In that figure, the observed anodic peak (Figure 4a) was plotted either against the potential scan rates or against the square root of the potential scan rates (Figure 4b and 4c). As it can be seen in Figure 4b, a linear evolution of the anodic peak current intensity versus potential scan rates (v) in the range of 30 - 150 mV.s^{-1} was observed. The obtained straight line has a slope of 0.03 with a correlation coefficient of 0.991. That linearity between the oxidation current peak and the potential scan rate is an indication of an adsorption-like behavior occurring at electrode surface. In Figure 4c, we observe also that lead oxidation current peak presents a linear evolution with the square root of the potential scan rates. The straight line has a correlation coefficient of 0.991.This result indicates also that electrode surface processes have a diffusion-controlled behavior. From those observations, it can eventually be concluded that a combined process consisting in a diffusion and adsorption controlled processes occurred at the electrode surface.[17–20] Furthermore, by enhancing the scan rate, the peak potential (Ep) shifted to more positive values, approving the kinetic limitation i.e. the irreversibility in the interfacial dynamic process that occurs at the CPE/solution interface (Figure 4d).

In order to determine the performance of the prepared TiO$_2$ modified carbon paste electrode, linear range (LR) and limit of detection (LOD) have been explored. In fact, these two analytical characteristics
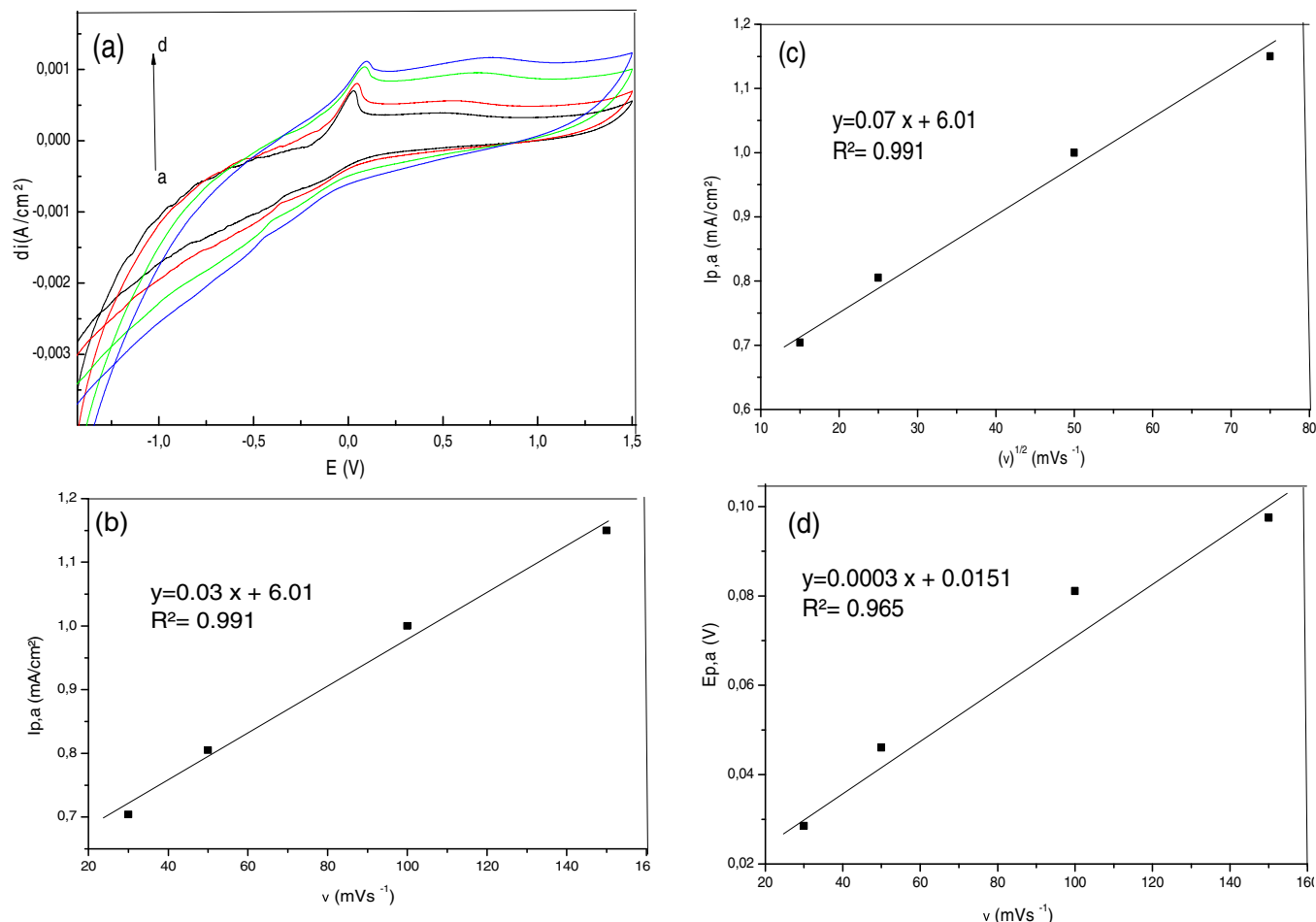

Figure 4. (a) Cyclic voltammograms of the TiO$_2$-CPE in sodium acetate buffer 0.1 M solution containing 25 μM of Pb (II) at various a to d scan rates of 30, 50, 100, 150 mV s^{-1} respectively, and variation of the (b) Ip,avs. v, (c) Ip,avs. $(v)^{1/2}$ and (d) Ep, avs. v. (all experimental conditions are exactly same as Figure. 3).
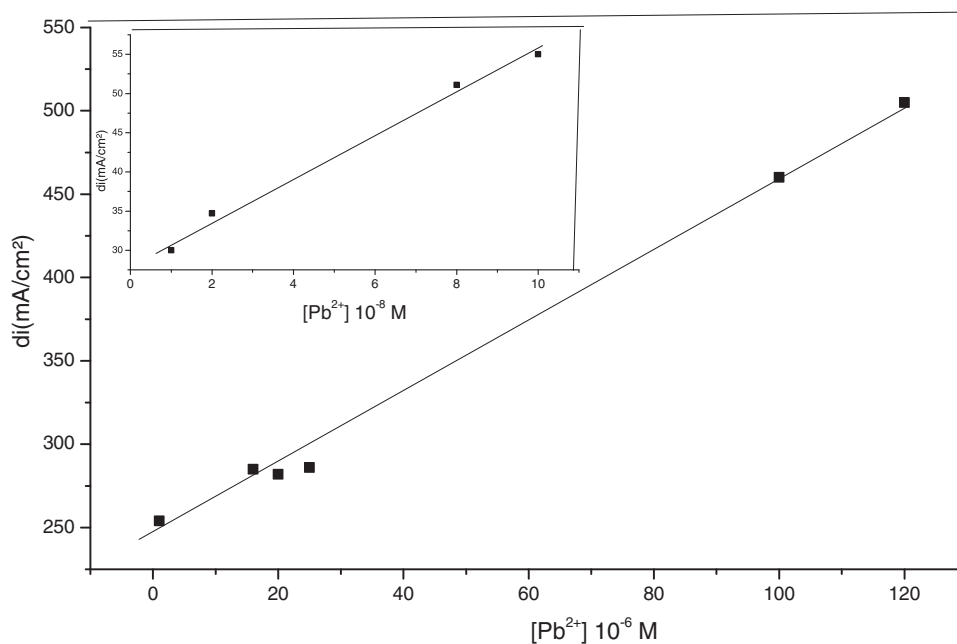
Figure 5. Linear calibration graphs of TiO$_2$/CPE at higher and lower (inset) Pb^{2+} ion concentrations under optimized experimental conditions.

are important to be checked. Under optimum experimental conditions, the calibration graph of the modified TiO$_2$/CPE was investigated and the results for both low and high concentration levels are illustrated in Figure 5. The calibration graph (Figure 5) of the sensor showed two linear dynamic ranges (LDR) over lead concentrations of 10^{-8} M - 10^{-7} M and 1–120 µM with a limit of detection (LOD) of 4.5 10^{-8} M (S/N = 3). Depending on the lead concentration investigated, linear ranges described by different regression equations have been obtained. For the lower range of 10^{-8} M to 10^{-7} M, the linear regression equation was Ipa (mA / cm^2) = 28.26 + 2.742 [Pb(II)], with a correlation coefficient of 0.992. The anodic peak current at the carbon paste modified electrode TiO$_2$ was proportional to the concentration of Pb(II) in the range of 1 to 120 µM, with a correlation coefficient of 0.995. The linear regression equation was: Ipa (mA / cm^2) = 243.9 + 2.158 [Pb(II)]. The detection and quantification limits obtained were 4.5 × 10^{-8}, 1.5 × 10^{-7} M and 9.5 × 10^{-5}, 3.2 × 10^{-5} M for the range of 10^{-8} M to 10^{-7} M and 1 to 120 µM, respectively.

Electrode sensitivity and selectivity.— The reproducibility and stability of TiO$_2$/CPE were further investigated. A relative standard deviation was found to be 4.4% for three determinations of 25 µM of Pb (II) in the experimental conditions previously optimized. The results indicate that the TiO$_2$ modified carbon paste electrode showed good reproducibility. In order to investigate the performance of the prepared electrode for the detection of lead among other ions, interference study has been carried out. For that purpose, selectivity of the electrode will be investigated since is it known that selectivity is one of the most critical and important characteristics of the electrode which can often be an excellent parameter for the selection of an electrode from many others for the same analytical aim. Thus, the performance of the proposed electrode in the determination of the lead in presence of some

Table I. Results of determination of Pb^{2+} in drinking water samples.

Water samples	Added (M)	Found (M)	RSD %	Recovery (%)
Drinking water	6.97 × 10^{-5}	4.82 × 10^{-5}	1.75	69.15
	9.65 × 10^{-5}	8.01 × 10^{-5}	1.60	83.00
	1.44 × 10^{-4}	1.32 × 10^{-4}	3.52	91.66
	1.93 × 10^{-4}	1.95 × 10^{-4}	3.03	101.03
	2.41 × 10^{-4}	2.47 × 10^{-4}	2.23	102.48

interfering ions Cu^{2+} and Zn^{2+} has been carefully evaluated. For this purpose, the modified electrode was immersed in a solution of Pb^{2+} (5 × 10^{-5} M) and interfering ion (4 × 10^{-5} M) for 15 min. It has been obtained from these investigations an improvement in selectivity with the TiO$_2$/CPE modified electrode, compared to the unmodified CPE for Pb^{2+} in the presence of Cu^{2+} and Zn $^{2+}$ ions.

Analytical characterization.— The feasibility of the proposed electrode for Pb^{2+} detection was evaluated by determining the recoveries of 6.97 × 10^{-5}, 9.65 × 10^{-5}, 1.44 × 10^{-4}, 1.93 × 10^{-4} and 2.41 × 10^{-4} M of Lead in drinking water by standard addition methods. The experimental results were listed in Table I. As is seen from it, the recovery was in the range of 69.15–102.48%, suggesting that the developed electrode has high accuracy and is feasible for determining Pb^{2+} in real sample. The variance was mainly due to the manual steps in the detection procedure; nevertheless, the range was good enough for quantification. The lowest tested concentration was 6.97 × 10^{-5} with 69.15% accuracy. The detection capability of this method was sufficiently sensitive to detect the lead in drinking water. In Table II, the proposed electrode was compared with number of

Table II. Comparison of the response characteristics of different Pb^{2+} ion-selective electrodes.

Electrode materials	Linear range(M)	Detection limit (M)	Ref. no
MWCNTs and nanosilica a carbon paste electrode	1.0 × 10^{-7} –1.0 × 10^{-2}	7.3 × 10^{-8}	21
Poly-microparticles phenylenediamine	3.16 × 10^{-6} –3.2 × 10^{-2}	6.31× 10^{-7}	22
Phenylhydrazone derivative Carbon composite	7.7 × 10^{-7} –1.0 × 10^{-1}	3.2 × 10^{-7}	23
TiO$_2$/CPE	10^{-8} – 10^{-7}	4.5 × 10^{-8}	This work

previously reported Pb (II) voltammetric sensors. As can be seen, the electrode here described is simple and has lower detection limit.

Conclusions

The determination of lead using a carbon-paste electrode modified with TiO_2 was improved when compared to unmodified CPE. TiO_2 modified electrode has a great potential to be used in the development of portable analyzers for monitoring lead ions, its analytical utility has been demonstrated by measuring Pb^{2+} in drinking water. The selectivity of the TiO_2 modified electrode, compared with the unmodified CPE toward Pb^{2+} analysis, is quite good in the presence of Cu^{2+} and Zn^{2+} ions, and the response characteristics of the proposed electrode are in a good comparison with those previously reported electrodes.

Acknowledgments

References

1. M. K. h. Aroua, S. P. P. Leong, L. Y. Teo, C. Y. Yin, and W. M. A. W. Daud, *Bioresour. Technol*, **99**(13), 5786 (2008).
2. V. K. Gupta, A. K. Jain, and P. Kumar, *Sens. Actuat. B*. **120**(1), 259 (2006).
3. S. Shiri, A. Delpisheh, A. haeri, A. Poornajaf, B. golzadeh, and S. Shiri, *Anal. Chem. Insights*, **6**(45), 15 (2011).
4. E. Bakker and Y. Qin, *Anal. Chem*, **78**(12), 3965 (2006).
5. I. Svancara, K. Vytras, K. Kalcher, A. Walcarius, and J. Wang, *Electroanalysis*, **21**(1), 7 (2009).
6. T. Mikysek, I. Svancara, K. Kalcher, M. Bartos, K. Vytras, and J. Ludvik, *Anal. Chem*, **81**(15), 6327 (2009).
7. E. Tesarova, L. Baldrianova, S. B. Hocevar, I. Svancara, K. Vytras, and B. Ogorevc, *Electrochim. Acta.* **54**(5), 1506 (2009).
8. I. Svancara, P. Foret, and K. Vytras., *Sensor. Talanta*, **64**(4), 844 (2004).
9. M. Javanbakht, M. R. Ganjali, P. Norouzi, A. Hashemi-Nasa, and A. R. Badei, *Electroanalysis*, **19**(12), 1307 (2007).
10. M. Javanbakht, A. Badiei, M. R. Ganjali, P. Norouzi, A. Hasheminasab, and M. Abdouss, *Anal. Chim. Acta*, **601**(2), 172 (2007).
11. R. N. Goyal, M. Oyama, V. K. Gupta, S. P. Singh, and R. A. Sharma, *Sens. Actuators B*, **134**(2), 816 (2008).
12. J. Lu, R. Chen, and X. He, *J. Electroanal. Chem*, **528**(2), 33 (2002).
13. L. Wang and G. Q. Lu, *Recent. Patents Mater. Sci*, **1**(2), 165 (2008).
14. S. Zhang, W. Wen, H. Zhang, and H. Zhao, *J. Photochem. Photobiol, A. Chemistry.* **208**(2–3), 97 (2009).
15. S. S. Kalanur, J. Seetharamappa, and S. N. Prashanth, *Colloids. Surf. B*, **78**(2), 217 (2010).
16. I. Duo, A. Fujishima, and C. H. Comninellis, *Electrochem. Comms*, **5**(8), 695 (2003).
17. A. Salimi, C. E. Banks, and R. G. Compton, *Analyst*, **129**(3), 225 (2004).
18. J. S. Ye, Y. Wen, W. D. Zhang, H. F. Cui, H. F. Xu, and F. S. Sheu, *Electroanalysis*, **17**(1), 89 (2005).
19. M. P. Siswana, K. I. Ozoemena, and T. Nyokong, *Electrochim. Acta*, **52**(1), 114 (2006).
20. A. Salimi, L. Miranzadeh, and R. Hallaj, *Talanta*, **75**(1), 147 (2008).
21. M. R. Ganjali, N. Motakef-Kazami, F. Faridbod, S. Khoee, and P. Norouzi, *J. Hazard. Mater.* **173**(1–3), 415 (2010).
22. M. R. Huang, X. W. Rao, X. G. Li, and Y.B. Ding, *Talanta*, **85**(3), 1575 (2011).
23. A. Abbaspour, E. Mirahmadi, A. Khalafi-nejad, and S. Babamohammadi, *J Hazard. Mater*, **174**(1–3), 656 (2010).