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Research Article

Use of Nano-Sensors of the Interferences between Pb((II) with Each of Mg(II), Zn(II), Mn(II), Ca(II), Co(II) and PO_4^{-3} in Blood Medium: An Electrochemical Study

Yousif Kadhim Abdul-Amir[1], Muhammed Mizher Radhi[2], Emad Abbas Jaffar Al-Mulla[3]

[1]Department of Chemistry, College of Science, Al-Mustanssiria University, Baghdad, Iraq.
[2]Department of Radiological Techniques, Health and Medical Technology College-Baghdad, Middle Technical University (MTU), Iraq.
[3]College of Health and Medical Techniques, Al-Furat Al-Awsat Technical University, 54003 Al-Kufa, Iraq.

Corresponding author. E-mail: emadalmulla@atu.edu.iq

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Abstract

Lead is considered a key element in causing autism disease in children due to the pollution of this dangerous element to human. The aim of this research is to obtain a chemical compound with the effect of inhibiting the oxidation of lead ions on the brain that causes the autism disease. Cyclic voltammetric technique was used to study the effect of interferences between lead ions with selected elements such as Mn(II), Mg(II), Zn(II), Ca(II), PO_4^{-3} and Co(II) in blood medium. Multi wall carbon nano tube (MWCNT) which was modified with glassy carbon electrode (GCE) was used as a working electrode sensor in cyclic voltammetric method. The results showed that the oxidation and reduction current peaks of Pb(II) ions in the blood medium appeared at −0.2 and −0.8 V respectively. It was found that Co(II) ions had a significant effect on the Pb(II) ions in blood medium as anti-oxidative reagent by reducing the anodic current peak of Pb(II) with five folds and enhancing the cathodic current peak. But other ions such as Mn(II), Mg(II), Zn(II), Ca(II) and PO_4^{-3} reduced both redox current peaks of Pb(II) in blood medium. It means that Co(II) ions acted as a good anti-oxidative reagent in blood medium which reduced the effect of lead ions on brain cells by the blood stream. Hence, cobalt compounds could be used as drugs for treatment of the autism disease in children.

Keywords: Nano-sensor; Pb(II); Co(II); Blood medium; Autism; Cyclic voltammetry

Introduction

Scientists have been interested in the studies of the effect of pollutants on human blood as they cause serious diseases, such as autism disease which is caused by the contamination of lead in children. Electrochemical studies by cyclic voltammetric method with modified working electrodes were realized for the redox current peaks of the pollutants in the blood medium [1-7]. Children polluted with higher levels of metals, such as lead and antimony in their urine suffered from more severe autism, suggesting that metal levels in their bodies may contribute to its seriousness [8-10]. Electrochemical analysis is a powerful analytical technique used in pharmaceutical industry, metal industry and environmental applications [11].

Novel nanostructure materials using carbon nanotubes as a sensor to detect Pb(II) in urine, blood and saliva was coupled with plasma-mass spectrometry. This improvement in the analytical sensor platforms will facilitate our ability to conduct biological monitoring programs to understand the relationship between chemical exposure assessment and disease outcomes [12].

Glassy carbon electrode (GCE) was modified with carbon nanotubes CNT and C_{60} by attachment and solution evaporation techniques, respectively. The sensing characteristics of the modified film electrodes were demonstrated in this study for interference of Mn^{2+} in different heavy metals ion such as Hg^{2+}, Cd^{2+} and Cu^{2+}. The interfering effect was investigated which showed that positive interference was exerted on the redox peaks of Mn^{2+} [13].

Heavy metal pollution is one of the most serious environmental problems. Electrochemical sensors were used for the detection of heavy metals such as lead, cadmium, mercury, arsenic, etc. The stripping voltammetry techniques was used with unmodified electrodes of mercury, bismuth or noble metals in the bulk form, or electrodes modified at their surface by nanoparticles, nanostructures (CNT, graphene) or other innovative materials such as boron-doped diamond [14].

A new electrochemical method using gold nanoparticle-graphene-selenocysteine modified bismuth film GCE was applied, so as to improve the simultaneous determination of cadmium and lead trace in square wave anodic stripping voltammetry. The detection limit was 0.08 and 0.05 ppb for metal ions, and there was a high correlation coefficient of 0.9811 and 0.99 respectively [15].

The electrochemical characterization of graphite electrodes modified with hexadecylpyridinium-bis(chloranilato)-antimonyl(V) and their behavior as electrocatalysts toward the oxidation of sulfide were described in voltammetric technique [16].

The suggested mercury sensor was successfully applied for the determination of the trace of Hg^{2+} in different real samples. Satisfactory results were given by a simple, novel and very sensitive carbon paste sensor composed of nanomaterials [17].

In this study, a novel electrochemical sensor, GCE modified with carbon nanotubes was used to detect the effect of different chemical elements on the present of lead ions in blood medium as oxidative reagent which causes autism disease.

Experimental

Reagents and chemicals

$PbSO_4$ lead sulfate was from Central Drug House (CDH). $MnCl_2$, $MgCl_2$, $CoCl_2$, $ZnCl_2$, $CaCl_2$, and KH_2PO_4 in high purity were from SCRC, China. Healthy human blood samples were received from Iraqi Blood Bank in Baghdad City of Medicine. Carbon nanotubes (CNT) with the diameter of 10 nm and the purity of 99% were supplied from Fluka, Germany. The other chemicals and solvents were of annular grade and used as received from the manufacturer. Deionize water was used for the preparation of aqueous solutions. All solutions were deaerated with oxygen free nitrogen gas for 10-15 min prior to making the measurement.

Apparatus and procedures

Instruments: EZstat series (potentiostat/glvanostat) NuVant Systems Inc. pioneering electrochemical technologies USA. Electrochemical workstations of Bioanalytical system with potetiostate driven by electroanalytical measuring softwares was connected to personal computer to perform Cyclic Voltammetry (CV), an Ag/AgCl (3M NaCl) and Platinum wire (1 mm diameter) was used as a reference and counter electrode respectively. The glassy carbon working electrode (GCE) modified with MWCNT was used in this study after cleaning with alumina grand.

Preparing the MWCNT modified GCE (MWCNT/GCE)

A mechanical attachment technique was employed [18, 19]. This technique included abrasive application of MWCNT nanoparticles at the clean surface of GCE, forming an array of MWCNT nanoparticles as MWCNT/GCE which immerse in 10 mL of electrolyte or blood sample in the cyclic voltammetric cell.

Results and Discussion

The effect of different chemical elements on the pollutant that causes different diseases in humans especially in blood components was studied. One of the diseases that afflict children is autism which is due to the exposure to pollution of lead element in the blood and its effect on the brain [20, 21]. One of the main subjects in this field was the presence of lead ions in blood medium and its impact on the brain which causes autism by electrochemical study with cyclic voltammetric technique [22-25].

Effect of Co(II) on Pb(II) in blood medium using CNT/GCE

In the latest studies of autism among children, the analysis of blood was made by electrochemical method. Lead ions effected on blood mainly as an oxidative stress that caused the disease (autism). Fig. 1 illustrates the redox current peaks of Pb(II) in blood medium and the impact of Co(II) ions on both redox current peaks of Pb(II) by decreasing the oxidative stress of Pb(II) and enhancing the reduction current peak of Pb(II) as a result of anti-oxidative effect. Therefore, Co(II) had an anti-oxidative effect in presence with Pb(II) in blood medium. A new method was found for the inhibition of lead ions in blood medium by using cobalt compounds as a treatment of the autism disease. Fig. 2 & 3 show that different concentrations of cobalt ions with lead ions in blood medium were affected by decreasing the anodic current peak of the lead ions and by enhancing the cathodic current peak of lead ions with a good sensitivity respectively.

Effect of redox current peaks of Zn(II) on Pb (II) in blood medium

In the case of using zinc ions as interference with lead ions in blood medium. as is evident in Fig. 4 which shows that the effect of redox current peaks of zinc ions on the lead ions in blood medium. It was noted that both redox current peaks of lead decreased when using zinc ions. Fig. 5 & 6 show that the relationship between the oxidation and reduction current peaks of Pb(II) decreased in the presence of Zn(II) at different concentrations with high sensitivity.

Effect of redox current peaks of Mn(II) on Pb(II) in blood medium

In the other stud on the effect of Mn(II) on Pb(II) ions in blood medium, a different property was shown (Fig. 7): both the oxidation-reduction current peaks of Pb(II) were enhanced with the interference of Mn(II). Also, the calibration curves for both anodic and cathodic current peaks against the different concentrations of Mn(II) showed a good sensitivity (Fig. 8 & 9). It was found that Mn(II) in blood medium effected on the blood

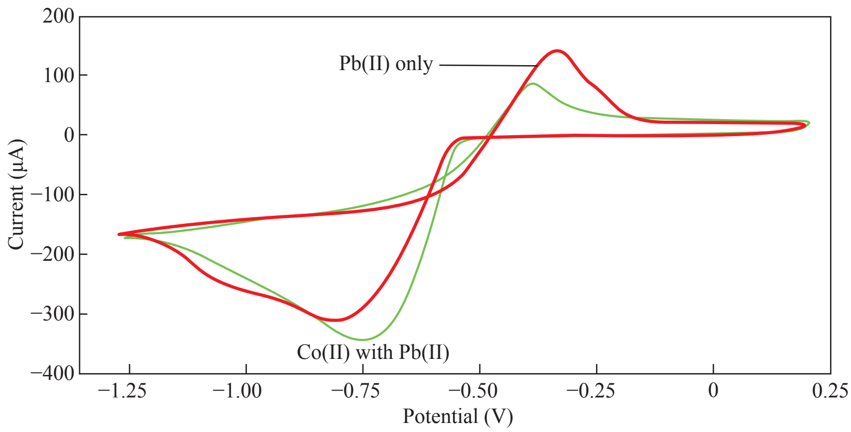

Fig. 1 Cyclic voltammogram of 0.1 mmol Co(II) with 1 mmol Pb(II) in blood medium using MWCNT/GCE vs Ag/AgCl as reference electrode at SR 100 mV/s.

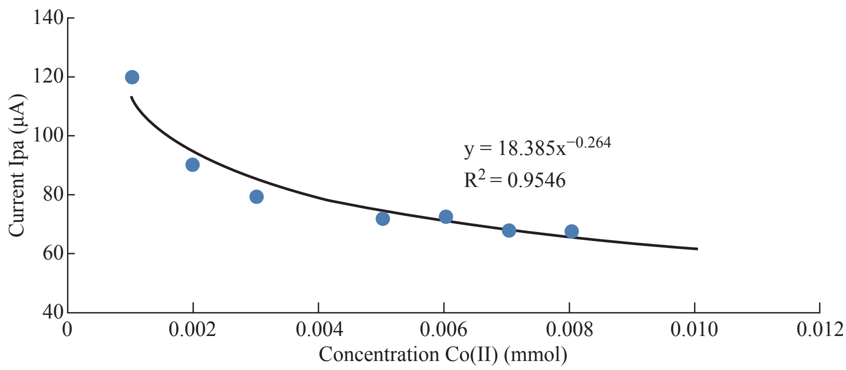

Fig. 2 Plot Ipa (anodic current) versus different concentration of Co(II) (0.01-0.07 mmol) in 1 mmol Pb(II) at scan rate 100 mV/s using MWCNT/GCE versus Ag/AgCl.

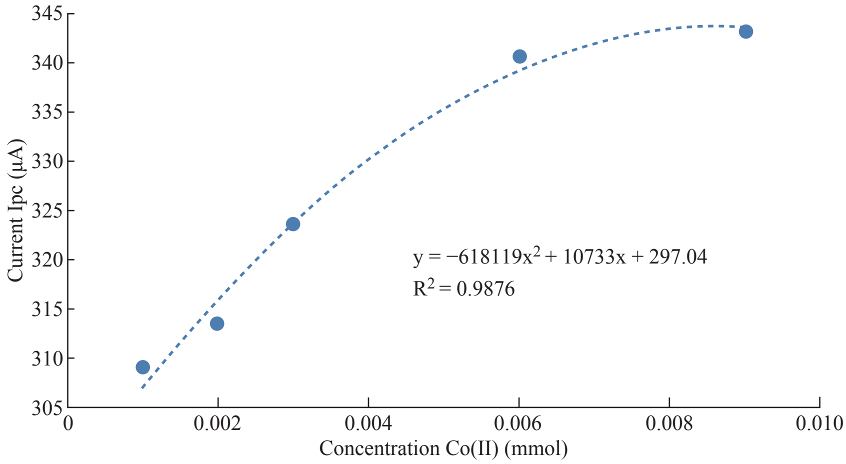

Fig. 3 Plot Ipc (cathodic current) versus different concentration of Co(II) (0.001-0.009 mmol) in 1 mmol Pb(II) at scan rate 100 mV/s using MWCNT/GCE versus Ag/AgCl.

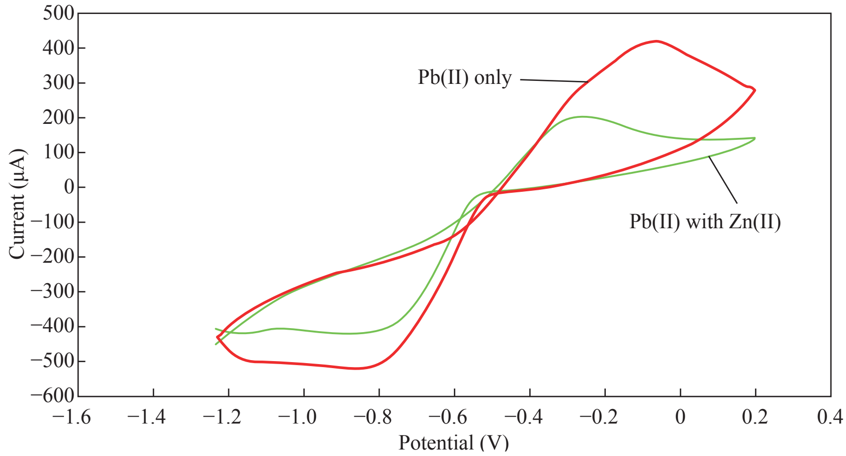

Fig. 4 Cyclic voltammogram of 0.1 mmol Zn(II) with 1 mmol Pb(II) in blood medium using MWCNT/GCE vs Ag/AgCl at SR 100 mV/s.

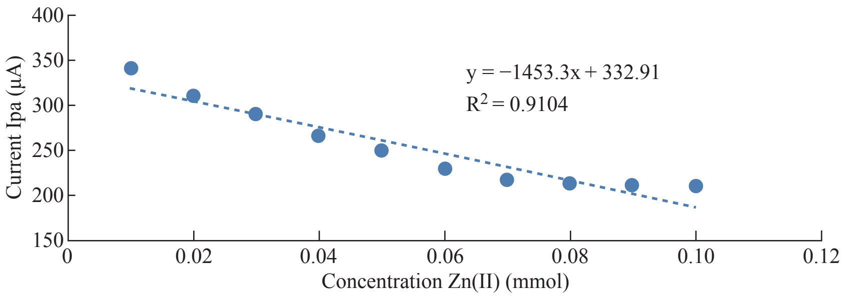

Fig. 5 Plot Ipa (anodic current) versus different concentration of Zn(II) (0.01-0.1 mmol) in 1 mmol Pb(II) at scan rate 100 mV/s using MWCNT/GCE versus Ag/AgCl.

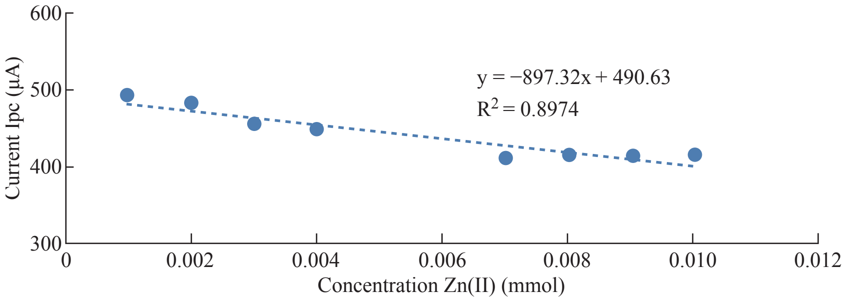

Fig. 6 Plot Ipc (cathodic current) versus different concentration of Zn(II) (0.01-0.1 mmol) in 1 mmol Pb(II) at scan rate 100 mV/s using MWCNT/GCE versus Ag/AgCl.

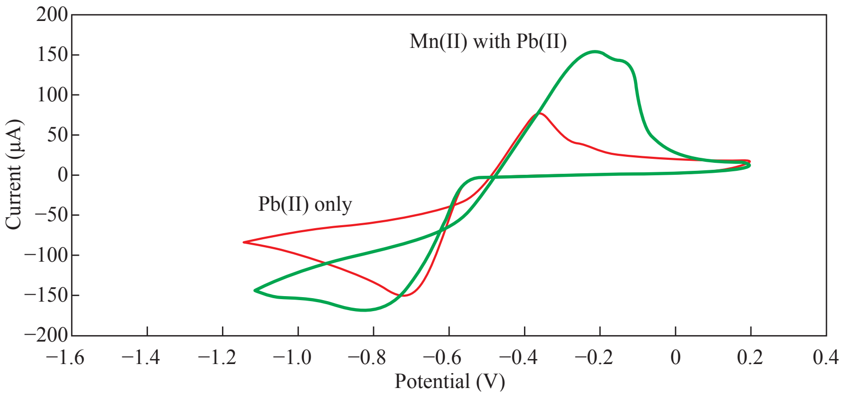

Fig. 7 Cyclic voltammogram of 0.1 mmol Mn(II) with 1 mmol Pb(II) in blood medium using MWCNT/GCE at SR 100 mV/s.

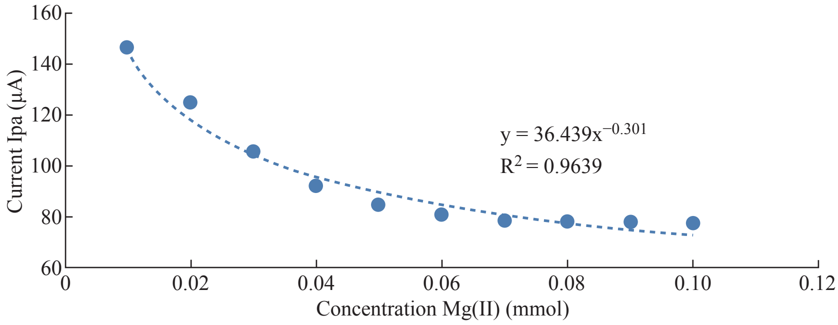

Fig. 8 Plot Ipa (anodic current) versus different concentrations of Mn(II) (0.01-0.1 mmol) in 1 mmol Pb(II) at scan rate of 100 mV/s using MWCNT/GCE versus Ag/AgCl.

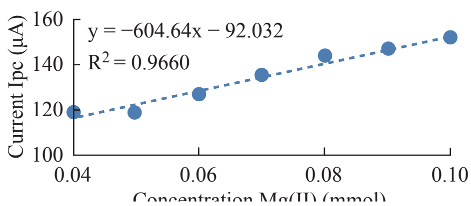

Fig. 9 Plot Ipc (cathodic current) versus different concentrations of Mn(II) (0.04-0.1 mmol) in 1 mmol Pb(II) at scan rate of 100 mV/s using MWCNT/GCE versus Ag/AgCl.

component as an oxidative agent [3].

Effect of redox current peaks of Mg(II) on Pb(II) in blood medium

It was found when using Mg(II) to effecti on Pb((II) in blood medium, both the oxidation and the reduction current peaks of Pb(II) decreased as shown in Fig. 10. A good sensitivity of the calibration curves was shown for both anodic and cathodic current peaks of Pb(II)

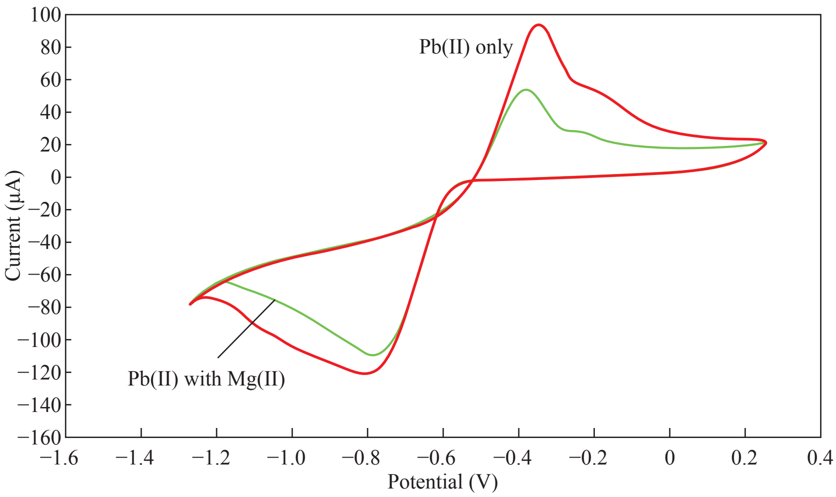

Fig. 10 Cyclic voltammogram of 0.1 mmol Mg(II) with 1 mmol Pb(II) in blood medium using MWCNT/GCE vs Ag/AgCl at SR 100 mV/s.

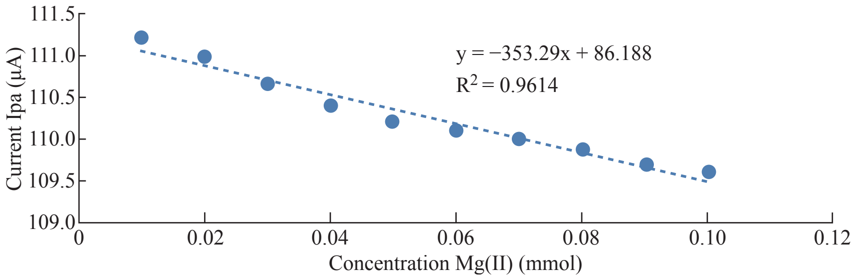

Fig. 11 Plot Ipa (anodic current) versus different concentrations of Mg(II) (0.01-0.1 mmol) in 1 mmol Pb(II) at the scan rate of 100 mV/s using MWCNT/GCE versus Ag/AgCl.

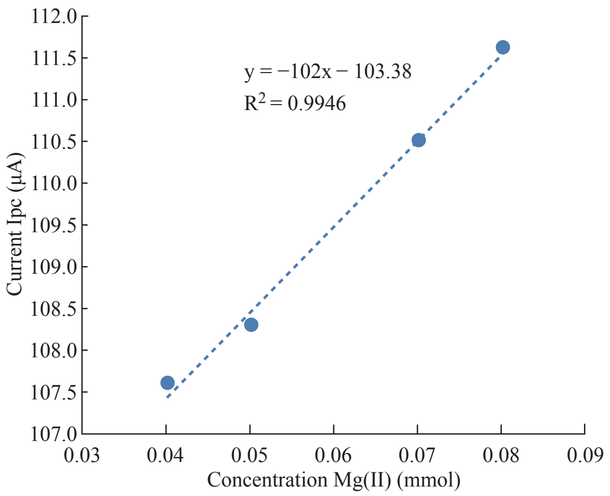

Fig. 12 Plot Ipc (cathodic current) versus different concentrations of Mg(II) (0.04-0.1 mmol) in 1 mmol Pb(II) at the scan rate of 100 mV/s using MWCNT/GCE versus Ag/AgCl.

(Fig. 11 & 12).

Effect of redox current peaks of Ca(II) on Pb(II) in blood medium

Fig. 13 shows the good effect of calcium ions on the lead ions in blood medium which decreased the oxidative effect of Pb(II) in blood components and enhanced the cathodic current peak of Pb(II); hence, Ca(II) ions acted as an inhibitor of the oxidative stress of Pb(II) in blood medium. Fig. 14 & 15 show the good sensitivity of the relationships between both redox current peaks and different concentrations of Ca(II) in blood medium in presence with Pb(II) ions.

Effect of redox current peaks of PO_4(III) on Pb(II) in blood medium

Fig. 16 shows that phosphate ions acted as a good inhibitorof oxidative stress of Pb(II) in blood medium,

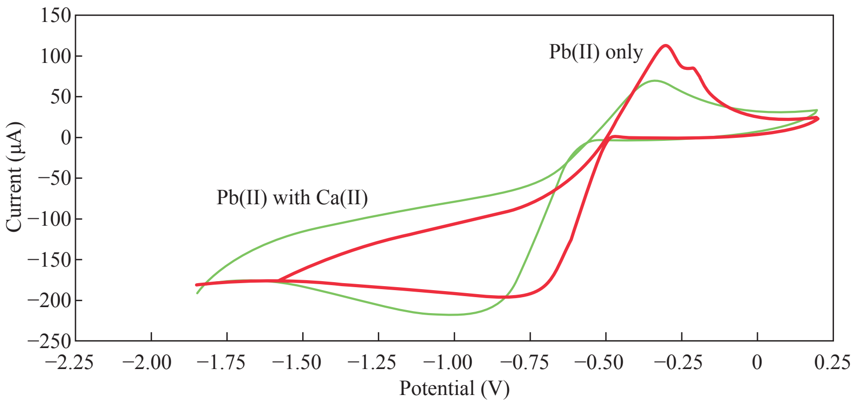

Fig. 13 Cyclic voltammogram of 0.1 mmol Ca(II) with 1 mmol Pb(II) in blood medium using MWCNT/GCE vs Ag/AgCl at SR 100 mV/s.

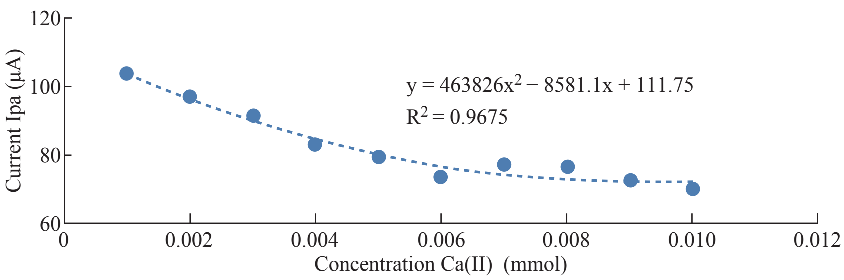

Fig. 14 Plot Ipa (anodic current) versus different concentrations of Ca(II) (0.001-0.01 mmol) in 1 mmol Pb(II) at the scan rate of 100 mV/s using MWCNT/GCE versus Ag/AgCl.

but there was no significant effect of cathodic current peak of Pb(II) in blood medium. It was shown the effect of PO_4(II) on Pb(II) by the relationship between the redox current peaks and different concentrations of phosphate ions in blood medium as shown in Fig. 17 & 18 by good sensitivity in calibration equations.

Conclusions

Cyclic voltammetric technique was used for the first time in determining the impact of pollutants on blood disease that causes autism and how to discourage the use of other elements. Using nanoscale sensors enabled us to study the lead element in blood medium and its interference with other elements such as calcium, zinc, cobalt, manganese and magnesium phosphate as supporting materials for the retardant work of lead in blood.

By using electrochemistry analysis, we found that the cobalt components could effect as an inhibitor

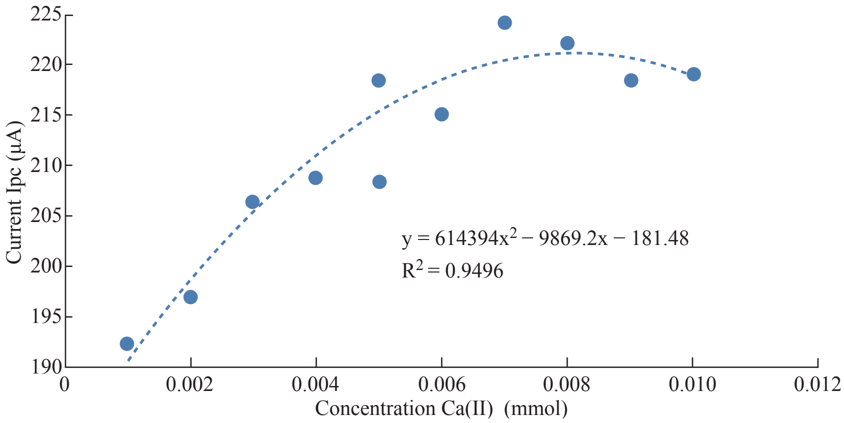

Fig. 15 Plot Ipc (cathodic current) versus different concentration of Mg(II) (0.001-0.01 mmol) in 1 mmol Pb(II) at scan rate 100 mV/s using MWCNT/GCE versus Ag/AgCl.

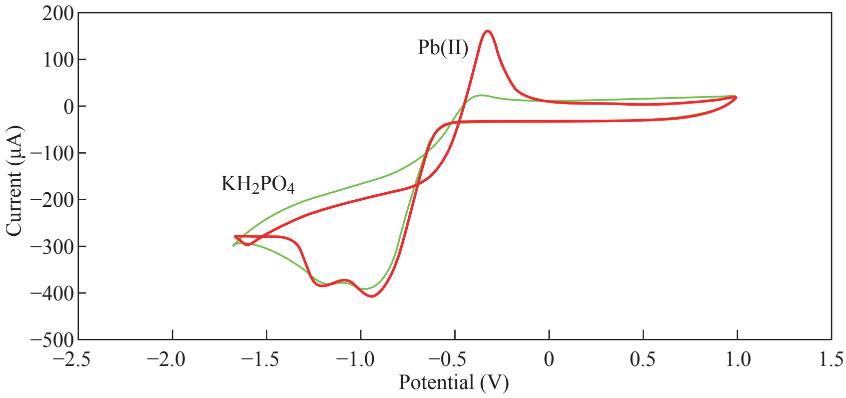

Fig. 16 Cyclic voltammogram of 0.1 mmol KH_2PO_4(II) with 1 mmol Pb(II) in blood medium using MWCNT/GCE vs Ag/AgCl at scan rateof 100 mV/s.

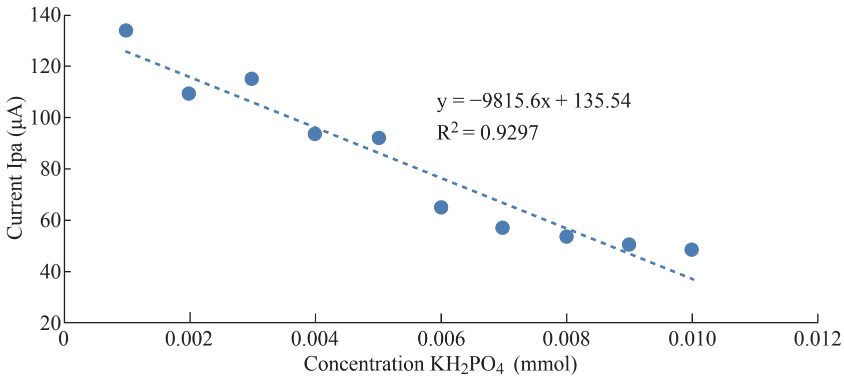

Fig. 17 Plot Ipa (anodic current) versus different concentration of KH_2PO_4 (0.001-0.01 mmol) in 1 mmol Pb(II) at scan rate of 100 mV/s using MWCNT/GCE versus Ag/AgCl.

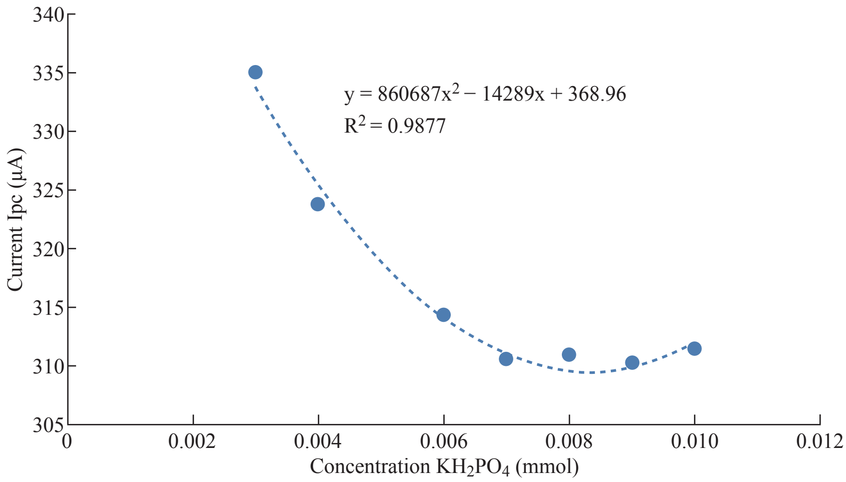

Fig. 18 Plot Ipc (cathodic current) versus different concentration of KH_2PO_4 (0.003-0.01 mmol) in 1 mmol Pb(II) at scan rate of 100 mV/s using MWCNT/GCE versus Ag/AgCl.

of lead components in blood medium and could in a way increase the oxidative stress of lead ions and enhance the reduction current peak as an anti-oxidative reagent; therefore, cobalt and its compounds could be considered as a treatment for autism disease.

In the second order for inhibition of impact of lead ions in blood medium was found in this study each of calcium and phosphate ions with present of the lead ions in blood medium. So, it can be said that the mixing of cobalt, calcium and phosphate compounds could reduce the effect of pollution of lead ions in blood especially in the people suffering from autism disease.

Conflict of Interests

The authors declare that no competing interest exists.

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