Full Length Research Paper

Assessment of dissolved manganese (II) pollution in river water by differential pulse cathodic stripping voltammetry: A case study of River Boubo, Côte d'Ivoire

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Boubo river and lagoon, south Côte d'Ivoire, are contaminated by manganese released in wastewater from manganese exploitation and from the soil of Grand-Lahou region in Côte d'Ivoire. So, there is a need to develop a simple method for the evaluation of manganese present in natural water. This work reports the utility of rapid and inexpensive method for determination of dissolved manganese (II) in natural water by cathodic stripping voltammetry using rotating carbon paste disk electrode. The experimental parameters for the determination of manganese (II) were optimized. Under the optimum conditions, the method was successfully applied to determination of free manganese in river and lagoon samples taken near the manganese exploitation in the area of Grand-Lahou, Côte d'Ivoire.

Key words: Manganese, cathodic stripping voltammetry, carbon paste electrode, rotating disk electrode, river water, lagoon water.

INTRODUCTION

Manganese is an essential element for all organisms (plants, humans, animals) (Rehm, 1986) but is potentially toxic at high concentrations. It plays an important role in the activation of many enzymes, in metabolism of carbohydrate and cholesterol (Nielsen, 1999). The average dietary intake of manganese is approximately 11 mg/day for adults and 2-5 mg/day for children (FNB, 2000; ATSDR, 2000). The maximum allowed content in

domestic water is 0.05 and 2 mg/L for irrigation water (Colombini and Fuoco, 1983).

Manganese is toxic at high concentrations (INERIS, 2007) affecting the central nervous system and can contribute to neurological diseases such as manganism with symptoms resembling those of Parkinson's disease (Calne et al., 1994). It has been established that the concentration of manganese in body fluids such as

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serum, blood and urine can often be used as biological indicators of human health, disease and nutrition condition. Because manganese is important and due to its very low concentrations in environment (air, water, food), any analysis requires the use of an accurate analytical method with sufficient selectivity and sensitivity. Various techniques have been used for the determination of trace manganese such as atomic absorption spectrometry (Sarzanini et al., 2001), X- ray fluorescence (Bilinski et al., 1996) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Boevski et al., 2000). Usually such techniques need enrichment steps. As regards selectivity and sensitivity, it often favors only one of these two aspects. However, these techniques require considerable time between sample collection and analysis. Consequently, these techniques are not suitable for rapid monitoring. For the above reasons, the electrochemical techniques are highly attractive alternative due to their rapid, selective and portable nature (Brett, 1999). Among electrochemical techniques, the combination of an effective preconcentration step with advanced electrochemical measurements of the accumulated analytes makes stripping analysis the most sensitive electroanalytical technique. Traditionally, anodic stripping voltammetry at hanging mercury drop or mercury film electrode (Portela and Capelo, 2004; Locatelli, 1996; Locatelli and Torsi, 2000) has been the most used form of electrochemical stripping analysis for the determination of manganese (II). However, the low solubility of manganese in mercury, the reduction deposition potential for Mn(II) which is close to the hydrogen ion reduction potential, the formation of intermetallic compounds at the mercury electrode and the toxicity of mercury hindered its use. Recently, cathodic stripping voltammetry been used for manganese determination; it can be carried with no interference from dissolved oxygen. Mn(II) is preconcentrated on an electrode surface by electrodeposition, it is anodically oxidized to Mn(IV). Traces of manganese have been determined by cathodic stripping voltammetry using a variety of solid electrode (Roitz and Bruland., 1997; Maali and Hady, 1998; Welch et al., 2006; Filipe and Brett, 2003; Banks et al., 2005) but the electrode surface contamination problems and matrix effects resulting in electrode passivation leads to inherent loss of sensitivity. To resolve these problems, different techniques were used such as ultrasound (Goodwin et al., 2005) or the electrochemical pretreatment of electrode (Di and Zhang 2003). It is well known that Voltammetric methods coupled with hydrodynamic sensors is very advantageous. Detection of heavy metals with the Rotating carbon Disk Electrode (RDE) has the dual purposes. On the one hand, the RDE is a very efficient mixing device for all the components in the electrochemical cell, and the injected product generated will be dispersed uniformly in the electrochemical cell. On the other hand, experiments with rotating disk electrodes have been found to provide higher levels of sensitivity

and very low detection limits (Wijayawardhana et al., 1999).

In this work, the use of carbon paste electrode is proposed as an inexpensive and renewable material avoiding the problems of surface contamination. The major aim of this study was to combine carbon paste electrode and rotating disk electrode to determine dissolved manganese in natural waters by cathodic stripping voltammetry. We performed also a study of parameters affecting the performance of electrode such as supporting electrolyte, speed of rotation, deposition potential and pH. Finally, all the results obtained were validated by ICP-AES.

MATERIALS AND METHODS

Apparatus

Voltammetric experiments were carried out using autolab potentiostat PGSTAT 10 (Ecochemie, Utrecht, Netherlands) controlled by GPES 4.8 software. Measurements were made in glass cell containing platinum foil auxiliary electrode and a saturated calomel electrode (SCE) as reference. A rotating carbon paste disk model 616 series 4030 EGG made in USA served as the working electrode. The pH of solution was measured by using a pH-meter model Accumet Scientifique AB 15 BASIC. Inductively coupled plasma AES measurements were carried out using Ultima 2 Jobin Yvon spectrophotometer.

Reagents

All solutions were made from analytical grade reagents. Aqueous solutions were prepared with distilled water. Mn (II) stock solution (100mg/L) was prepared by dissolving 0.036g of $MnCl_2$ (Riedel-de-Häen) in 100 mL distilled water. More dilute manganese standards were prepared from this solution. Supporting electrolyte Solutions were 0.1 M CH_3COOH/CH_3COONa buffer, 0.2 M NaH_2PO_4/Na_2HPO_4 buffer, 0.1 M CH_3COONH_4 and 0.2 M H_2BO_3 in 0.1 M KCl, adjusting the pH with 1 M NaOH. All experiments were carried out at room temperature (25 ± 1°C) without the removal of oxygen.

Preparation of carbon paste electrode (CPE)

The CPE was prepared by mixing 1 g of graphite powder "Fluka" (particle diameter < 0.1 mm) and 300 µl of paraffin oil using mortar and pestle until homogenous paste was obtained. The paste was then incorporated into the electrode cavity and polished on smooth paper.

Procedure for Manganese determination by DPCSV method

In the present work, the analysis of manganese in natural water was evaluated by using differential pulse cathodic stripping voltammetry (DPCSV). All measurements were carried out in solution containing an appropriate concentration of Mn (II) in boric acid (pH 7.0). The solution containing an appropriate concentration of Mn(II) and H_3BO_3 in KCl (pH 7.0) was placed in the electrochemical cell. The carbon paste electrode was rotated at 300 rpm, and accumulation potential (0.8V) was applied to a fresh electrode for 120 s to deposit manganese onto the electrode surface. At the end of accumulation, the rotation of electrode was
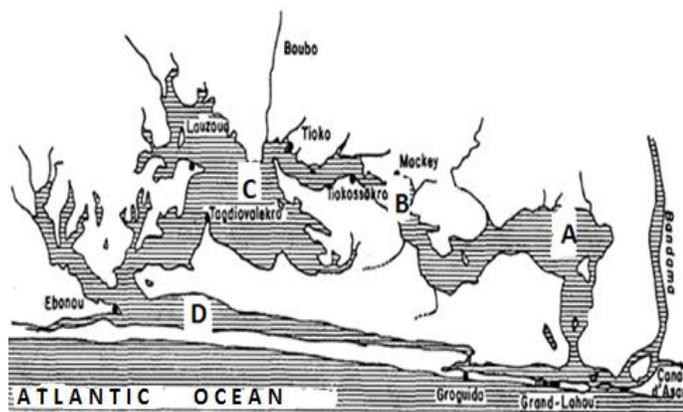
Figure 1. Geographic location of Grand-lahou lagoon and Boubo River, south Côte d'Ivoire. A: Lagoon Tagba; B: Lagoon Mackey; C: Lagoon Tadio ; D: Lagoon Niouzoumou.
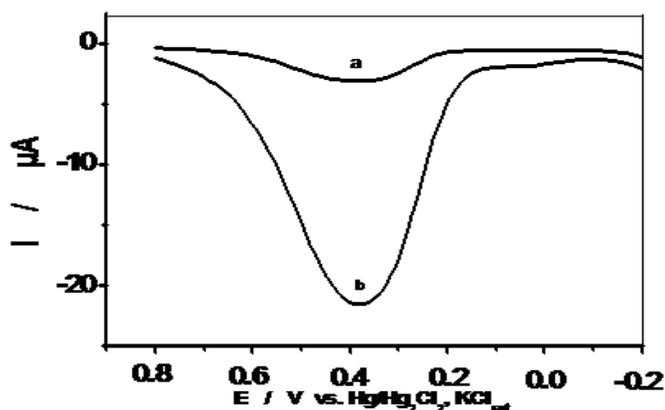

Figure 2. Differential pulse voltammograms, after deposition of 10-5 mol. L-1 Mn^{2+} for 120 s. at pH 8 on carbon paste electrode (a) without rotation of electrode; (b) speed of rotation 300 rpm.
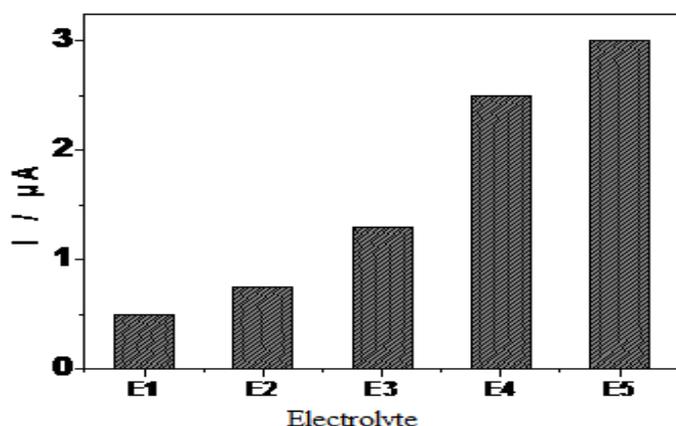

Figure 3. The effects of different supporting electrolytes on peak current after the preconcentration of the carbon paste electrode in solution containing 10-8 mol. L-1 Mn^{2+} for 120 s; deposition potential 0.8V.

stopped. The electrode potential was scanned from 0.8V to -0.2 V, and a stripping voltammograme was recorded in the DPCSV mode, using pulse amplitude 100 mV and a step potential 10 mV.

Sample collection

River water samples were taken in river Boubo from Adahidougou village which is situated in region of Divo (Côte d'Ivoire) (Figure 1). The samples were collected at the vertical profile on four selected stations at a depth of three meters. These sites are close to the manganese exploitation site. Lagoon water samples were taken at a depth of three meters from various lagoons in department of Grand-Lahou in Côte d'Ivoire. Samples were acidified with nitric acid (70%, Aldrich) placed into polyethylene bottle at 4°C.

RESULTS AND DISCUSSION

Preliminary studies of manganese accumulation were performed on carbon paste electrode (CPE) and on a rotating carbon paste electrode (RCPE). Figure 2 shows a cathodic stripping voltammetry recorded at a CPE electrode between 0.8 and -0.2 V after the accumulation in boric acid solution containing 10^{-5} mol. L^{-1} of Mn (II) without rotation of electrode. As can be seen from Figure 2 (a), a cathodic stripping peak at 0,4 V was observed at carbon paste electrode. Figure 2 (b) shows a CSV recorded at a carbon paste electrode in the same solution, under the same conditions and under rotation of electrode at 300 rpm. A well defined peak was observed at the same potential. More than the fold increase in the current peak on the rotating disk electrode was obtained compared to those of CPE as observed by others authors (Jorge et al., 2007; Manivannan et al., 2005). It is reported by some authors (Christine et al., 2006; Yoleydis et al., 2011) that, the intra and inter reproducibility of carbon paste electrode (CPE) are poor, with the sensitivity varying considerably from electrode to electrode. However, in electrochemical stripping analysis, CPE represent one of the most frequent types of working electrode. Recently, traces of different metal ions have been determined by CSV or ASV using CPE with a good reproducibility (Senthilkumar and Saraswathi, 2009; Svobodova et al., 2011; Enass, 2010; Bang et al., 2012, Brett and Brett, 1992). Also, the one of hydrodynamic electrode advantage is to increase the reproducibility (Brett and Neto, 1989). It is important to mention that the carbon paste electrodes were found to be less efficient and less reproducible compared to the rotating electrodes.

Effect of the supporting electrolyte

Figure 3 shows the influence of supporting electrolyte buffers on the redox process of manganese. The oxidation process of manganese is very dependent on pH and supporting electrolyte. Usually, CH_3COOH/CH_3COONa buffer, NaH_2PO_4/Na_2HPO_4
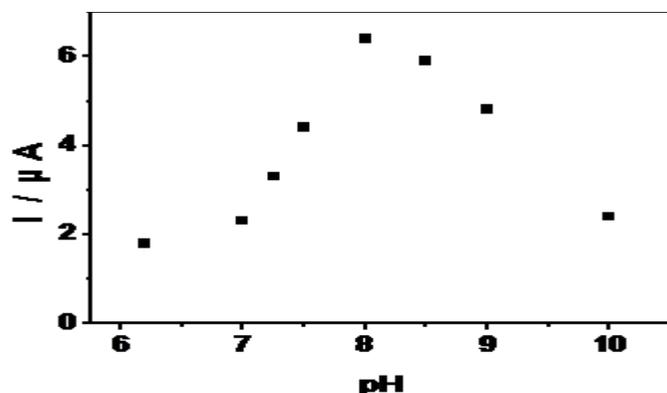
Figure 4. Influence of pH on the differential pulse stripping current of accumulation 10-7 mol.L-1 Mn2+ in 0, 2 mol.L-1 H3BO3/0,1 mol .L-1 KCl; accumulation time120 s; speed of rotation 300 rpm; deposition potential 0.8V.
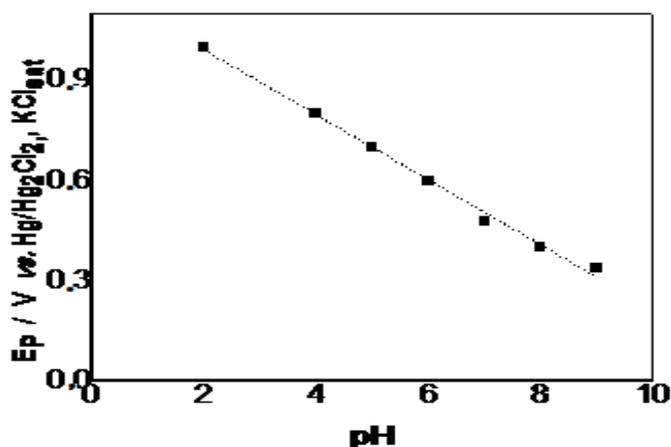

Figure 5. Relationship between the reductions peak potential of MnO_2 on pH of electrolyte
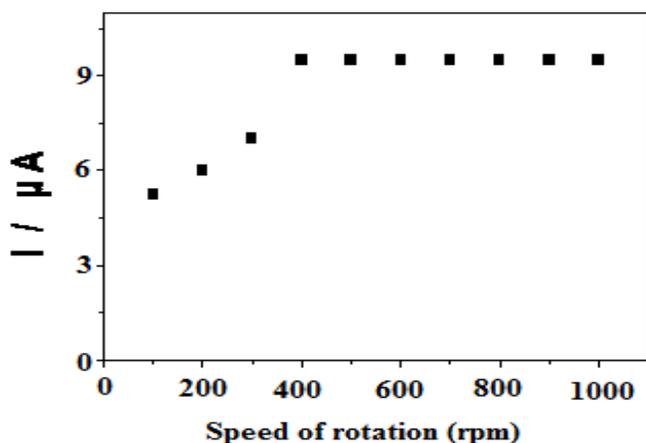

Figure 6. Influence of speed rotation on the differential pulse cathodic stripping current of accumulation 10-7 mol.L-1 Mn^{2+} in 0, 2 mol.L-1 H3BO3/0,1 mol .L-1 KCl; accumulation time120 s; deposition potential 0.8V.

buffer, CH_3COONH_4 and H_3BO_3 in KCl buffer solutions were used. The effect of supporting electrolyte on the peak current of the preconcentrated manganese species from electrode surface was also studied. The best result was found with 0.2 M H_3BO_3 in 0.1 M KCl as shown in Figure 3. This result is in good agreement with a previous work (Brett, 1999). Then, boric acid was chosen for further studies.

Effect of pH of the supporting electrolyte

As was shown above, the presence of boric acid is necessary to observe the enhancement of manganese peak. Figure 4 shows the effect of pH on the manganese peak current, measurements were carried out in 0.2 M boric acid containing 10^{-7} mol. L^{-1} of manganese. The effect of pH was investigated in the pH range between 6 and 10. The others conditions were reported in paragraph 3. The response increases rapidly with the pH between 6 and 8, and decreases rapidly at higher pH values. These results are consistent with those reported previously. At higher pH (pH > 8), the decrease in the peak height was due to the increasing competitive production of $Mn(OH)_2$ which can subsequently be oxidized and precipitate as $Mn (OH)_4$ by dissolved oxygen in the solution (Brett and Neto, 1989). Therefore, pH 8 was chosen for the analysis. Since the redox process of manganese is dependent on pH, Figure 5 shows the influence of pH on the reduction potential of the cathodic stripping of Mn(II) in the range of pH between 2 and 9. A plot of pH versus reduction potential (E) shows a linear relationship, with a slope of 113 mV. The predicted slope corresponding of Nernst equation is 118 mV, indicating a four proton and two electron processes. The experimental value of 113 is close (precision 4.3%) to the value predicted by Nernst equation. That confirms that the equation of the reaction during the electrochemical stripping is:

$$MnO_2 + 4\ H^+ + 2\ e \longrightarrow Mn^{2+} + 2\ H_2O$$

Effect of electrode rotation speed

Many authors using rotating disk electrode in metal ion analysis reported that RDE improved sensitivity and reproducibility of analysis (Jorge et al., 2007; Manivannan et al., 2005; Ghanjaoui et al., 2009; Tanaka et al., 1993). The RDE improved the hydrodynamic flow of electrolyte at the electrode surface and increasing mass transport to the electrode. The influence of electrode rotation speed on the reduction peak of manganese in a solution containing 10^{-7} mol.L^{-1} of Mn(II) in the range 100 to 1000 rpm is illustrated in Figure 6. The flux of rotation to the electrode surface generated by forced convection causes an improvement in sensitivity between 100 to 400 rpm. The rotation speed does not have any more influence on

the peak current for the rotation speed under 400 rpm. These results indicate that at rotation speed over 400 rpm, we have reached saturation of the surface of the electrode. We choose 300 rpm as rotation speed for the rest of work. Our results are in a good agreement with the results reported by (Tanaka et al., 1993). Under the optimized conditions (speed of rotation 300 rpm; deposition potential 0.8 V; and pH 8), a linear response of peak height versus concentration over the range 2 10-8 mol.L^{-1} to 2×10^{-6} mol.L^{-1}(1-100 µg.L^{-1}) has been obtained. The equation for calibration graph and the correlation coefficient were I$_p$(µA) = 7.21 + 0.18 C$_{Mn}$ (µg L^{-1}); and 0.997 respectively. The detection limit was obtained as 4×10^{-9} mol. L^{-1} (0.2 µg L^{-1}). The Relative standard deviation (RSD %) for five measurements was 3%. An increase in the deposition time may, in principle, be applied to improve the limit of detection. This linear range of concentration and limit of detection are useful in the field monitoring of manganese in real sample, because the literature reports suggested that the concentration of manganese in river water is a round 10 µg.L^{-1} (Schiele, 1991). In order to evaluate the performance of the rotating carbon paste disk electrode, river water and lagoon water were analyzed.

Interferences

To assess the selectivity of this method, the same experiment was carried out in the presence of different metal ions under the optimized conditions given above. According to the literature data, interference from some metal ions: Pb(II), Cd(II), Zn(II), Ni(II), Fe(II), Cu(II) were investigated. The results show that the presence of Cu(II), Pb(II), Cd(II), Zn(II), Ni(II) in solution in concentration 100 fold excess to that manganese does not interfere. Many studies using different electrodes showed that copper, lead, iron(III), nickel or cadmium have not notable influence manganese signal even when present in 100 fold excess (Di and Zhang., 2003; Banks et al., 2005; Ján et al., 1989; Sarterlay et al., 1999). The interference of Fe(II) in the current stripping peak was investigated by adding increasing amount of this metal to a solution containing 10^{-8} mol L^{-1} manganese. The results indicated that the peak current intensity of Mn(II) was affected by 10% in concentrations equal of Fe(II). At high concentration, 100 fold excess over Mn(II) in the analyte solution, the presence of Fe(II) affects by 100% the peak current intensity of Mn(II). This result is in agreement with Saterlay et al., (1999). The interference of Fe(II) can be eliminated using flour or tartaric acid (Pakkermans et al., 1998).

Application to natural waters

This research aims to apply a rotating carbon paste disk electrode for the determination of free manganese(II) via differential pulse cathodic stripping voltammetry in water

from River Boubo. Unfortunately, trace metals dissolved in natural waters may exist as free ions and in organic and inorganic complexes. Also, we used the filtration to eliminate particulate matter and ultra violet oxidation (UVO) to destroy the complexes (Donat and Bruland., 1988), after labile manganese can be detected by RCPE.

River Boubo

The procedure proposed was used for manganese determination in river Boubo water taken near the site of manganese exploitation. After the filtration and UV irradiation, the river water samples were diluted by factor of 10 with buffer, the pH was adjusted to 8, the samples were injected in the cell and DPCSV was employed to obtain a response for Mn(II) in solution. Additions of an aqueous manganese standard were then performed. Extrapolation of the stripping currents resulting from the standard manganese additions facilitated the quantification of manganese in the water samples, hence the manganese content could be calculated. The results obtained in four stations are summarized in Table 1. The results showed that manganese concentration depends on collected stations. Analysis of sample No. 1 taken from the downstream manganese exploitation, gives results significantly higher than those found in river water. The difference in concentration of four samples could be explained by the transport and partition of manganese in the water, speciation is determined primarily by pH, redox potential and mobility. For high concentration of carbonate, manganese carbonate (MnCO$_3$) is likely to precipitate because of its low solubility (ATSDR, 2000). Other forms of insoluble manganese may also exist by adsorption of manganese hydroxides on iron, clay, manganese dioxide (MnO$_2$), or particulate organic matter (Tessier and Turner., 1995). The manganese content in water depends on the characteristics of the environment and the charge relating in suspension (MES) which would explain the difference in concentration. Since the water of Boubo river is used in different ways by the coastal population, a modification in the nature of water depend on the activity of costal population, while manganese is a bio metal present in very low concentrations in natural waters. The waters of rivers have a manganese content of approximately 10 µg.L^{-1} (Schiele, 1991; Ward, 1995).

Compared with this, we can say that water of Boubo River at the village of Adahidougou have levels of manganese higher than those commonly found in the river waters. The samples were also analyzed by using ICP-AES. The results obtained from "laboratoire d'analyse élémentaire ICP AES" of CNRST at Rabat, Morocco demonstrated good agreement compared to those obtained by the proposed method.

Lagoon of Grand-Lahou

Samples from Grand-Lahou lagoon were analyzed for

Table 1. Results of sampling at Boubo River and Grand-Lahou Lagoon.

		Concentration of manganese µg. L^{-1}		
Sample	Depth (m)	DPCVS	RSD %	ICP - AES
River Boubo				
1	3	1200	1.2	970
2	0	91	1.7	72
3	3	73	1.5	69
4	3	65	2.2	57
Lagoon Mackey				
1	3	36	1.8	34
2	3	49	2.4	45
Lagoon Tagba				
1	3	5.9	1.2	4.8
Lagoon Tadio				
1	3	47	2.6	33

their manganese content both by the differential pulse cathodic stripping voltammetry method and by ICP-AES method. The results using the standard addition method are shown in Table 1. The analysis shows that the manganese in lagoon waters is generally lower than the Boubo river water. Among natural waters, the waters of rivers have levels of manganese higher than those found in ocean waters (Saager et al., 1997; IRSN, 2005). Grand-Lahou lagoons especially Tagba communicate with the ocean resulting in an increase in water salinity. The sediments are an important reservoir of manganese, containing more than 95% of total manganese (IRSN, 2005). The affinity of manganese to the sediment is high depending on chemical and especially salinity; this might explain the lower concentrations of manganese found in lagoons compared to those of the Boubo River. Nevertheless, concentrations of manganese in these lagoons remain very high compared to those reported for the sea water (about 1 µg L^{-1}) (O'Halloran, 1982).

Conclusion

The determination of trace levels of manganese via differential pulse cathodic stripping voltammetry at a rotating carbon paste disk electrode has been evaluated for use in environmental analysis. The results obtained in this article suggest that this method can be used for the routine sensing of manganese in environmental samples. The results obtained with the present method were found to be in good agreement with those obtained by ICP-AES method; this confirms that the suggested method is specific, accurate and sensitive for quantifying and monitoring manganese.

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