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New Carbon Paste Modified Micro Electrode Based on Haematoxylin for Determination of Aluminum in Underground Water

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A novel, simple and highly sensitive micro electrode based on carbon paste modified with haematoxylin (HCPME) was suggested for the determination of aluminum. HCPME was prepared by mixing graphite powder and haematoxylin with hot paraffin oil. The surface of the prepared electrode was characterized using scanning electron microscope (SEM). Various experimental parameters, which influenced the electrochemical behavior of HCPME, were optimized. Applying the cyclic voltammetric technique under the optimized conditions, HCPME gave one anodic oxidation peak at + 0.77 V and one reduction cathodic peak at + 0.0 V (*vs.* Ag/AgCl reference electrode). The proposed method relies on the linear decease of the cathodic peak of haematoxylin offered by square wave voltammogram (SWV) with the addition of Al(III), while the peak potential remains the same. A linear response with Al(III) concentration is observed over the range of 1.0×10^{-9} to 1.0×10^{-2} mol L^{-1} with a detection limit of 1.0×10^{-9} mol L^{-1}. The relative standard deviation (n= 8) at a concentration level of 1.0×10^{-7} mol L^{-1} is 2.65%. The prepared electrode was successfully applied for the determination of Al(III) in different real water samples. These samples were collected from the underground water of Taif City. In order to investigate the reliability of the suggested electrode, the tested samples were also determined by independent standard method using ICP-OES. The merits offered by the new electrode including small size, simple construction, low cast, good accuracy and high precision.

Keywords: Micro electrode, modified carbon paste, aluminum determination, haematoxylin, cyclic voltammetry, underground water

1. INTRODUCTION

Aluminum is a widely dispersed element on earth. It occurs in various forms in most rocks and soils and is also present in gemstones like topaz and garnet. It can be found in vegetation and in all of the earth's water. The toxicity of aluminum towards fish, algae and plants roots in acidic media is well documented. Today, aluminum has also been implicated in the etiology neurological such as Alzheimer`s disease (AD) and other diseases. Hence, a sensitive and selective method is of primary importance for the accurate determination of aluminum at the trace level in biological and environmental matrices. Different methods have been used for the determination of aluminum such spectrophotometric [1-4], flow – injection analysis [5-6], liquid chromatography [7-9], but these methods needs costly apparatus.

The most reliable methods used for the determination of toxic and heavy metal ions are the electrochemical methods, where they have many advantages such as high sensitivity and selectivity with high speed, less cost, relative simplicity and low detection limit. Although the voltammetric techniques have been widely used, the direct electrochemical determination of aluminum using voltammetric techniques is very difficult, due to the highly negative reduction potential of aluminum (about -1.75V versus SCE) which is distorted by the hydrogen evaluation background current [10] and is very close to the reduction peaks for different cations such as sodium and potassium [11]. For this reason two strategies were used for the determination of aluminum, namely the anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV). Cathodic stripping voltammetric method involves the complexation of aluminum in a preliminary reaction in solution, and adsorption of the complex as the concentration step at the electrode surface. The most commonly used ligands for complexation with aluminum in CSV are, N, N' –bis-2-hydroxy-2-amino-ethane sulphonic acid (BES) [12], cupferron [13,14], 1,2-dihydroxyanthraquinone-3-sulfonic acid (DASA) [15,16], solochrome violet [17], pyrocatechol violet [18], tetramethylammonium chloride (TMAC) [19], alizarin S [20,21], pyrogallol red [22], morin [23], arsenazo III [24], camagite [25] and norepinpghrine [26]. There are a few reports on the application of anodic stripping voltammetric determination of aluminum by indirect method such as using L-dopa under alkaline conditions [27] and pyrocatechol violet modified electrode [28]. Alternatively, the chemically modified carbon paste electrodes based on different electroactive materials have been recently developed. These electrodes have different advantages such as improving the selectivity and sensitivity as well as wide potential range, low background current and inexpensive. Based on these advantages, many CMCPEs have been reported for determination of some species and metal ions namely; ascorbic acid [29], copper II [30], Lead II [31], Iron II [32], Mercury [33], Copper II and Mercury II [34] and Vanadium [35]. However, only one electrode has been found in literature for determination of Aluminum [36].

On the other hand, inductively coupled plasma optical emission spectroscopy (ICP-OES) represents one of the most widely technique used in the trace analysis of heavy metal cations in water, food and soil environmental samples. The advantages offered by this technique include high stability, a multi-element measurement capability, superior dynamic range of concentration, and optimum selectivity as well as data reporting and data reprocessing.

In this paper, we report preparation, characterization and analytical application of new haematoxylin carbon paste modified microelectrode. Applying the cyclic voltammetric technique, the micro electrode has been successfully used in the determination of Al(III) in real underground water samples collected from Taif city. The results obtained are in good agreement with those obtained by ICP-OES independent standard method.

2. EXPERIMENTAL

2.1. Apparatus

Cyclic voltammetry (CV) and square wave voltammetry were performed using an Autolab potentiostat PGSTAT 302 (Eco Chemie, Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (GPES, software version 4.9, Eco Chemie). The pH values were measured using a Hanna pH-meter (Model pH 211) with a combined glass pH electrode (Model Hi 1131).

The standard determination of aluminum metal ions was achieved using Perkin-Elmer Optima 2100 Dual View inductively coupled plasma optical emission spectrometry (ICP-OES) instrument connected with AS 93 Plus autosampler. The carrier gas flow rate was optimized to obtain maximum signal-to-noise ratios. The 40-MHz free-running generator was operated at a forward power of 1.3 kW; the outer, intermediate and Ar carrier gas flow rates were 15.0, 0.2 and 0.8 L/ min, respectively.

2. 2. Reagents and solutions

All the chemicals were of analytical grade and used without further purification. Haematoxylin, graphite powder, and paraffin wax were obtained from Sigma-Aldrich Chemical Company. CH_3COOH, CH_3COONa and NaOH were of obtained from Merck. De-ionized water was used throughout. High purity standards (2 % HNO_3, Al 1000 mg Kg^{-1}) were used for ICP-OES validation measurements after appropriate dilution with de-ionized water. The pH adjustment was achieved by the addition of small aliquots of 0.2 mol L^{-1} NaOH or HNO_3**.**

2.3. Preparation of haematoxylin carbon paste modified micro electrode

Haematoxylin carbon paste modified micro electrode (HCPME) was prepared by mixing 60% graphite powder, 35% paraffin wax, and 5% haematoxylin. Graphite powder was mixed very well with haematoxylin and to this mixture, hot paraffin wax was added to produce a homogeneous paste. The resulted paste was then packed into the end of an insulin syringe (i.d.: <1 mm). External electrical contact was established by forcing a copper wire down the syringe. The surface of the electrode was polished with a piece of weighting paper and then rinsed with distilled water thoroughly.

2.4. Aluminum measurements

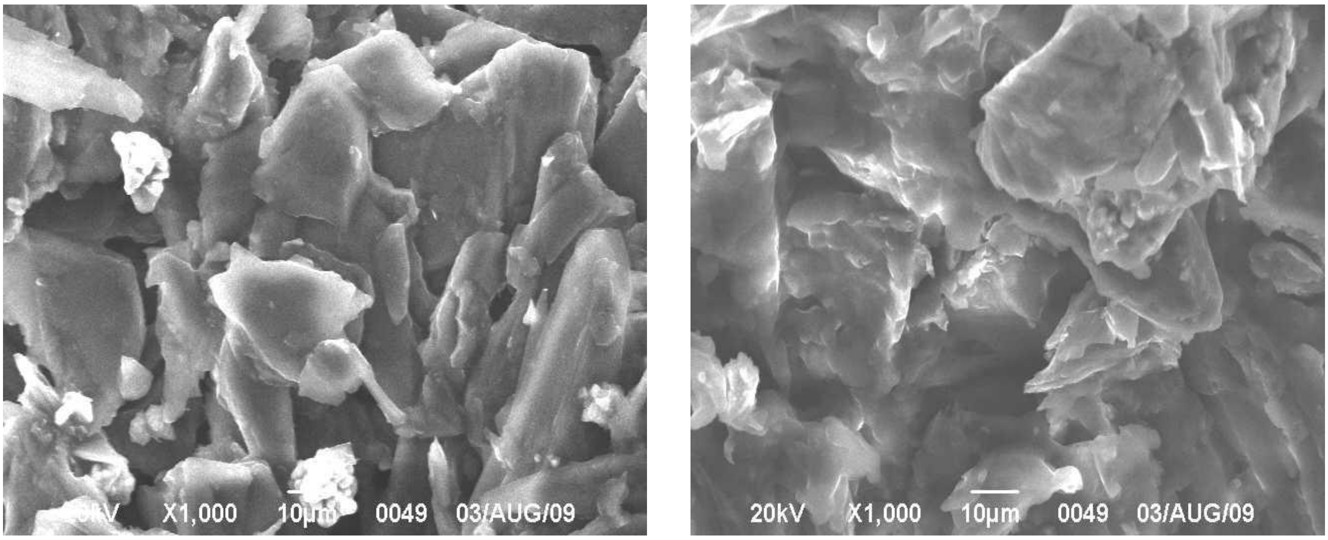
The electrochemical measurements of aluminum were achieved using electrochemical cell with three electrodes; carbon paste electrode was used as a working electrode, SCE was used as a reference electrode and platinum wire was used as a counter electrode.

In the ICP-OES measurements, the autosampler has been used to nebulize the measured samples downstream to the plasma and the concentrations were automatically determined using the standard calibration plot. The system adjusted to measure the samples in triplicates and the relative standard deviation was calculated. The RSD was < 2 % and the correlation coefficient was > 0.99998.

3. RESULTS AND DISCUSSION

3.1. Characterization of the prepared haematoxylin modified carbon paste micro electrode (HMCPE)

The surface morphology, microstructure and local composition of the prepared CPE and HCPME were investigated using SEM and the results were presented in Figs 1a and 1b. As can be seen, SEM images of the CPE (Fig. 1a) revealed the uniform shape while HCPME (Fig. 1b) showed lamellar shape of the crystals with clear spaces. The two images are relatively, different and the haematoxylin is uniform distributed on the HCPE surface.



(a) (b)

Figure 1. Scanning electron microscopic images of (a) Carbon paste electrode, CPE and (b) Haematoxylin modified carbon paste electrode, HMCPE.

3.2. Voltammetric behavior of haematoxylin modified carbon paste micro electrode

The electrochemical behavior of carbon paste electrode and haematoxylin carbon paste modified electrode was studied using cyclic voltammertic techniques in acetate buffer pH 3.1. Fig. 2a shows the electrochemical response for unmodified electrode, where no oxidation or reduction process appeared. Fig 2b shows the electrochemical response for haematoxylin carbon paste modified electrode; the modified electrode showing a quasi-reversible pair of redox peaks, a well anodic peak at + 0.77 V (*vs*. Ag/AgCl reference electrode) at the forward scan of the potential related to the oxidation of haematoxylin to haematein and a cathodic peak appears at + 0.0 V (*vs*. Ag/AgCl reference electrode) in the reverse scan of potential, related to the reduction of haematein to haematoxylin (Scheme 1).

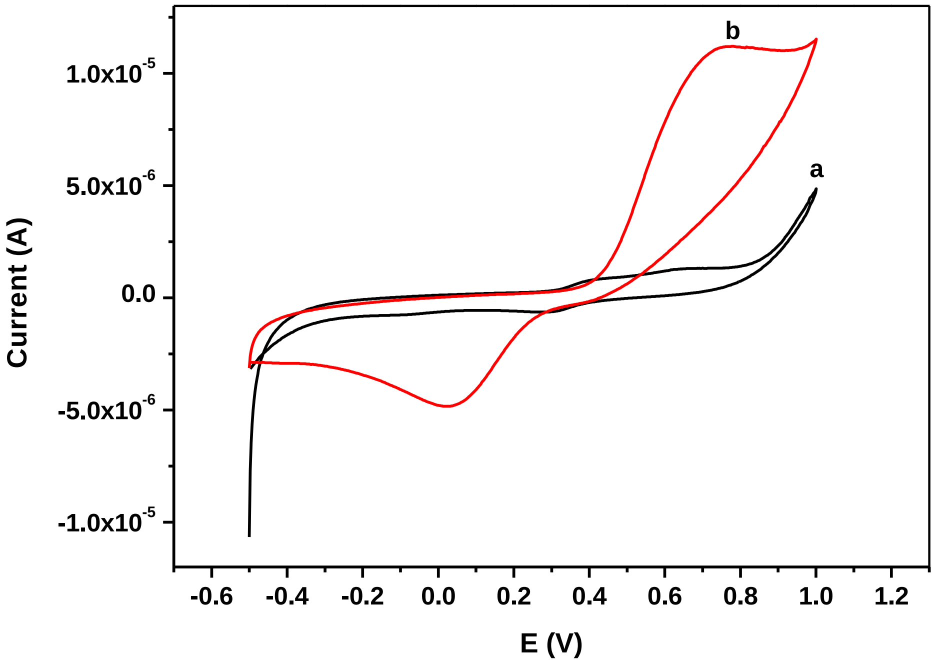
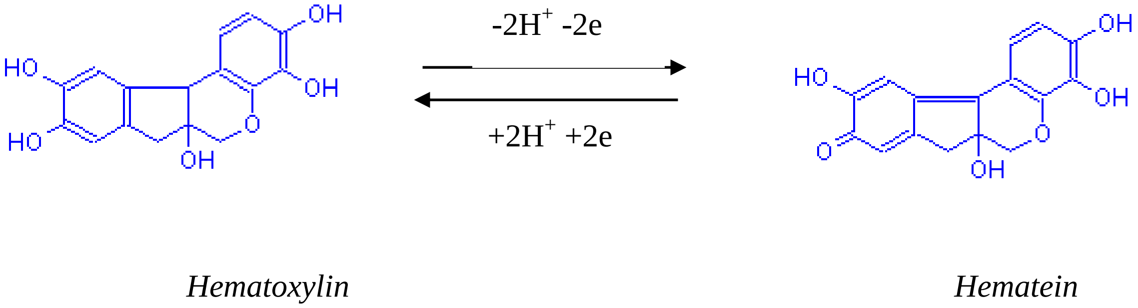


Figure 2. Cyclic voltammograms for CPE (a) and HCPE (b) in 0.1 mol L^{-1} acetate buffer (pH = 3.1), scan rate of 100 mV/s.



Scheme (1). Oxidation reduction of hematoxlin-hematein.

The effects of scan rate on the cyclic voltammograms of haematoxylin carbon paste modified electrode were studied at different scan rates from 25 to 300 mV/s and the results obtained were presented in Fig. 3a. Fig. 3b illustrates the dependence of anodic and cathodic peak currents with the square root of scan rate in 0.1 mol L^{-1} acetate buffer. In this figure, the currents increased linearly by increasing the scan rates from 25 to 300 mV/s. The linear relation between the peak current and square root of the scan rate, indicating that, the redox process is controlled by diffusion.

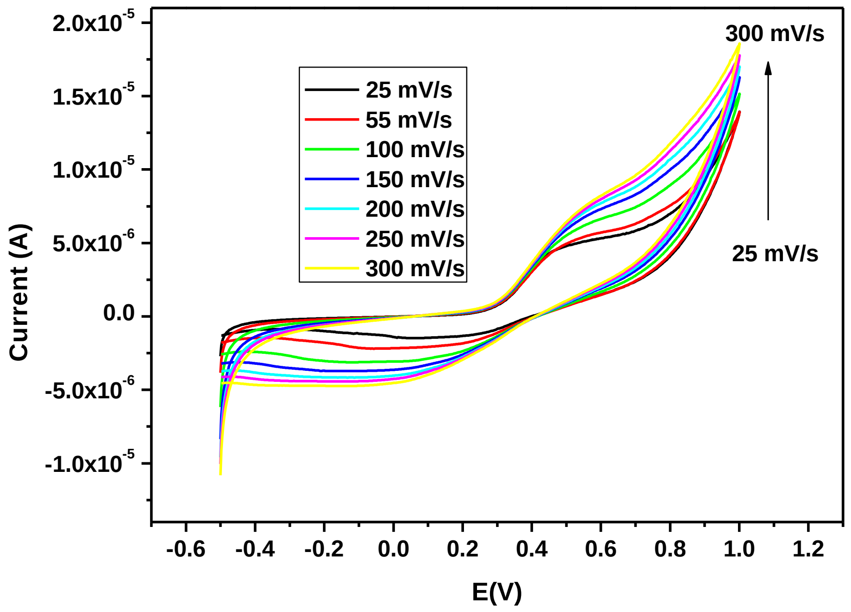


Figure 3a. Cyclic voltammograms of haematoxylin carbon paste modified electrode at different scan rates.

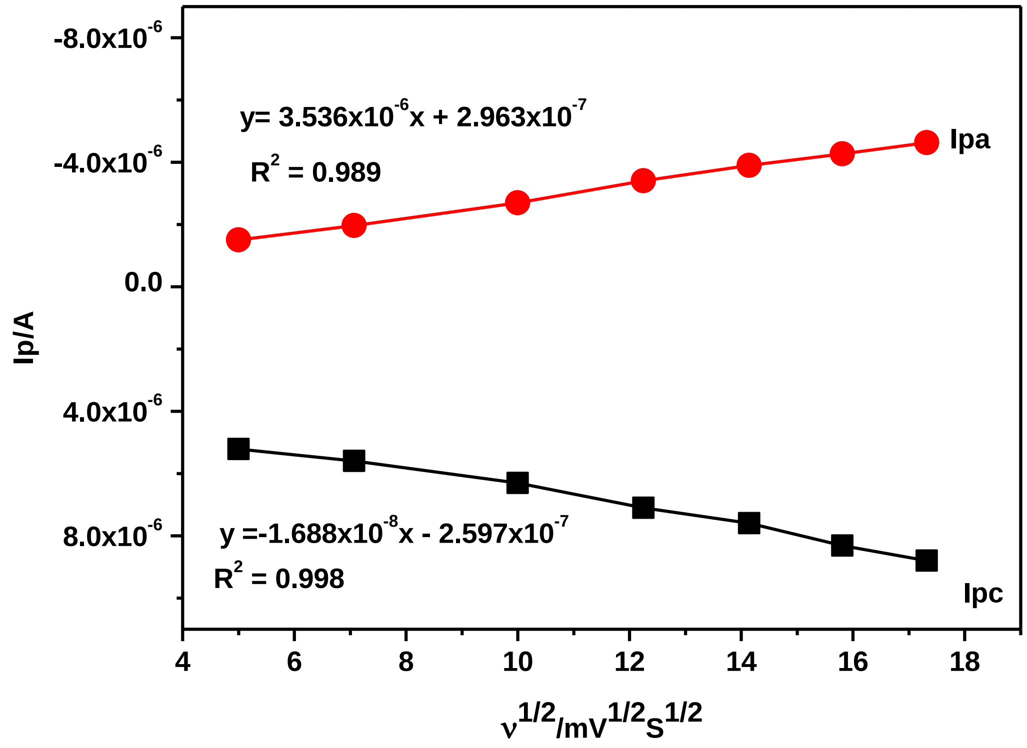


Figure 3b. Dependence of anodic and cathodic peak currents with the square root of scan rate.

3.3. Effect of pH

The influences of pH on the oxidation peak current and peak potential of the haematoxylim carbon paste micro electrode were investigated in the pH range of 3.1 to 5.0 using 0.1 mol L^{-1} sodium acetate buffers applying square wave voltammerty. The results obtained are presented in Fig. 4. It can be seen that the oxidation peak current is significantly affected by changing in pH of the supporting electrolyte in the lower pH range. As the pH value increase, the oxidation peak of haematoxylim carbon paste electrode sharply decreased from 3.1 to 3.8 and at higher pH values the peak current slightly decreased. The highest peak current was observed at pH 3.1, which was chosen for the present analytical applications. The influence of pH on the peak potentials of haematoxylim carbon paste micro electrode was also examined. The oxidation peak potential shifted to more positive values by increasing the pH of the supporting electrolyte.

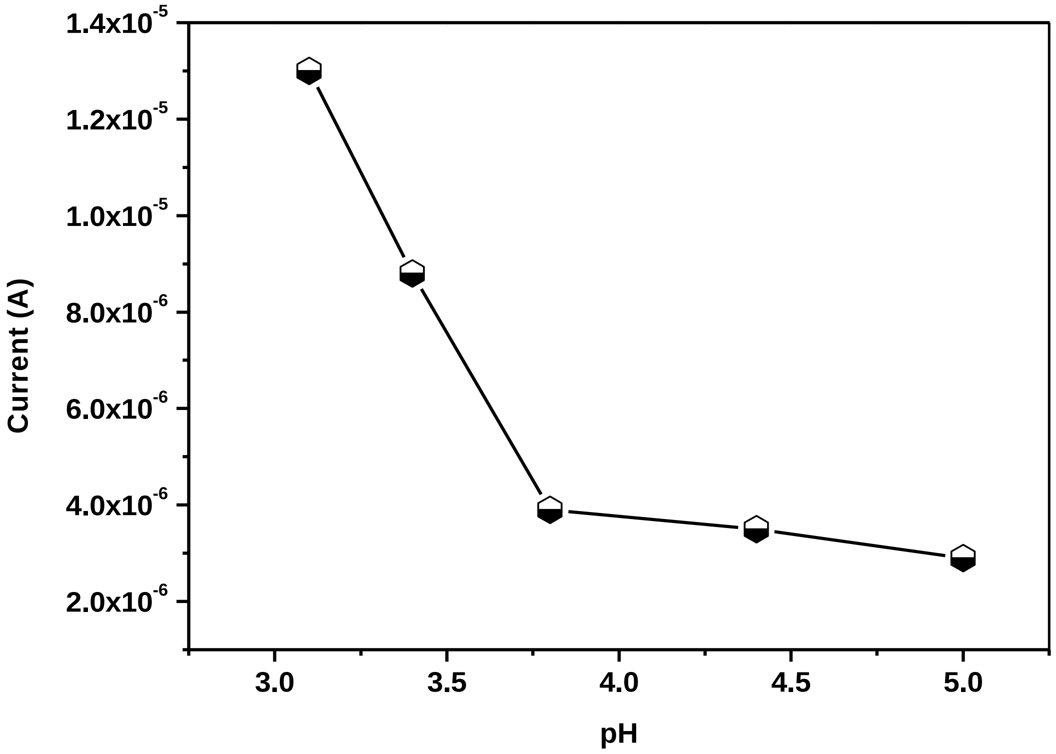


Figure 4. The effect of pH on the peak current of the haematoxylim carbon paste micro electrode.

3.4. Effect of Aluminum (III) addition

In our preliminary studies for haematoxylin at carbon paste micro electrode using cyclic voltammetry, the addition of Al(III) to the cell containing 1 mmole of haematoxylin results in decreasing of the oxidation and reduction current. This may be due to the decreasing of the haematoxylin concentration resulting from the complex formation between haematoxylin and Al(III). The peak current decreased linearly by the successive addition of Al(III). Therefore, Al(III) can be determined by indirect method through measuring the decrease in the peak current for haematoxylin. Square wave voltammetry was used for the indirect determination of Al(III) at haematoxylin carbon paste electrode. The effect of the addition of different Al(III) concentration in the range from $1x10^{-9}$ to $1x10^{-2}$ mole L^{-1} on the square wave voltammetry of HMCPE has been investigated and the results obtained was presented in Fig. 5a. Consequently, a linear correlation between the Al(III) concentration and the resulted graph current was obtained (Fig. 5b). The linear regression equation was Ip = 1.168×10^{-7}C + 8.48×10^{-8} (r = 0.989). The detection limit was 1 x 10^{-9} mole L^{-1}.

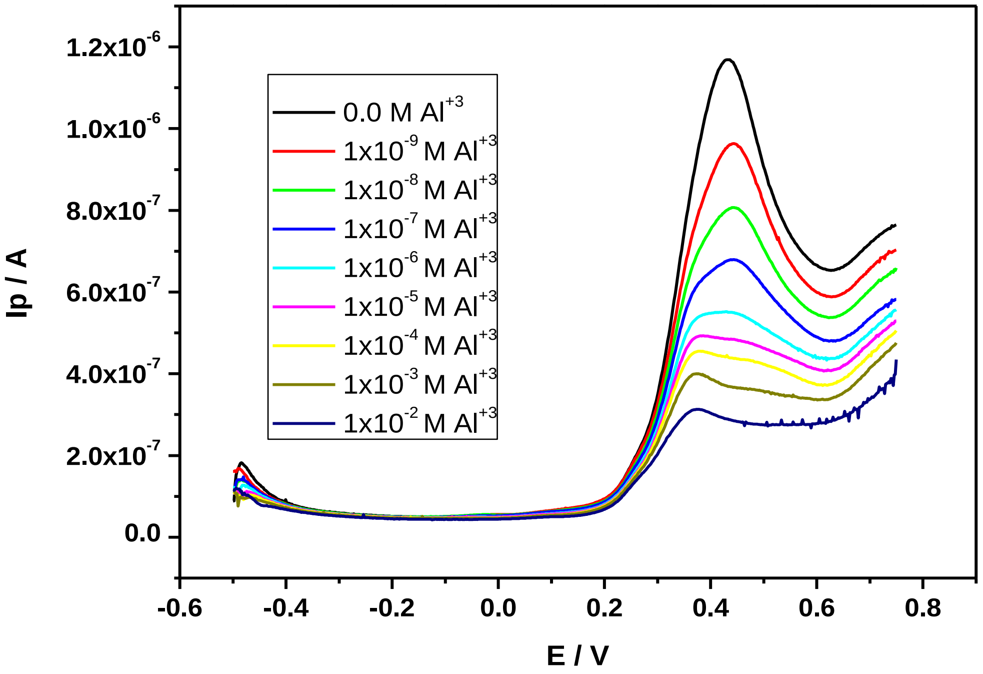


Figure 5a. Square wave voltammograms for HMCPE at different Al(II) concentration.

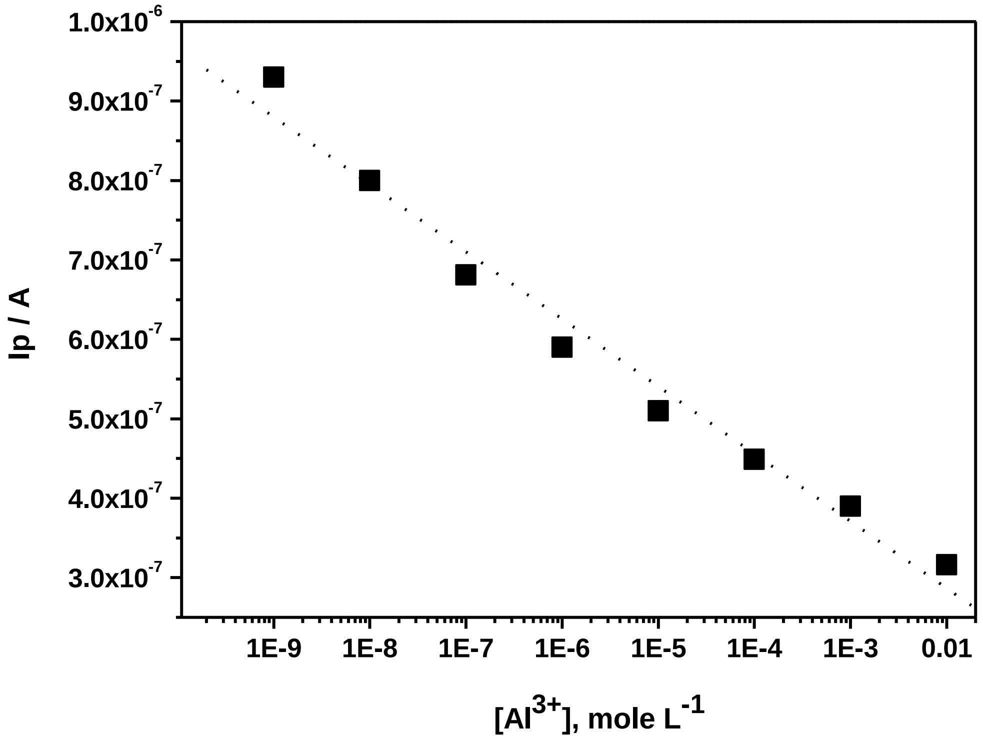


Figure 5b. Typical calibration graph of the HMCPE electrode towards Al(III).

3.5. Effect of Interferences

In this research, the effect of some interferences at different concentrations of common metal ions on the peak current of Al(III) has been studied. The data collected for the addition of 1x10^{-6} and 1x10^{-5} mole L^{-1} from Zn^{2+}, Fe^{3+}, Pb^{2+} and Cu^{2+} to 1x10^{-6} mole L^{-1} Al(III) were presented in Table 1. The results obtained showed that the suggested method is reasonably selective to Al(III).

Table 1. Effect of some metal ions as interferences on the peak current of 1x10^{-6} mol L^{-1} Al(III).

Additive	Zn^{2+}, mol L^{-1}		Fe^{3+}, mol L^{-1}		Cu^{2+}, mol L^{-1}		Pb^{2+}, mol L^{-1}	
	1×10^{-6}	1×10^{-5}	1×10^{-6}	1×10^{-5}	1×10^{-6}	1×10^{-5}	1×10^{-6}	1×10^{-5}
Percent of error (%)	2.24	5.57	7.53	8.89	6.32	7.43	7.35	7.85

3.6. Analytical Applications

The concentration of aluminum in natural waters can vary significantly depending on various physicochemical and mineralogical factors. Dissolved aluminum concentrations in waters with near-neutral pH values usually range from 0.001 to 0.05 mg L^{-1} but rise to 0.5–1 mg L^{-1} in more acidic waters. In slightly alkaline solution aluminum precipitates as fine particles.

Fig. 5b shows the calibration graph of the HMCPE electrode towards Al(III). The decrease of the redox current of the suggested electrode was proportional to the concentration of Al(III). This was due to the complexation between Al(III) and haematoxylin and this represents the basis of the quantitative determination of Aluminum in the proposed method. Under adjusted optimized conditions, the proposed method was applied for the determination of Al(III) in some different real water samples using the mentioned calibration curve.

For this purpose, about 20 real water samples were collected from different wells in Taif city as sources of drinking water. The adjusted experimental parameters were: hematoxylin carbon paste micro electrode as a working electrode using acetate buffer pH 3.1 and square wave voltammetric techniques. In order to assess the reliability of the new electrode the investigated real water samples were also determined using, inductively coupled plasma-atomic emission spectroscopy ICP-AES, independent standard methods. The results obtained were presented in Table 2.

Although the suggested electrode is simply fabricated and inexpensive, the measurements data showed a good agreement with those obtained by standard ICP-AES for the investigated real samples. Moreover, the levels of aluminum in the underground water samples collected from different wells in Taif city as sources of drinking water are lower than those reported by WHO, EPA and FPT regulations for drinking waters. In some samples the aluminum levels is lower than those generally reported for the natural underground water. This is due to the investigated water samples are slightly alkaline solutions (pH ~ 8.4) and aluminum precipitates as fine particles in such media.

4. CONCLUSIONS

A new modified carbon paste micro electrode has been suggested and characterized for indirect determination of aluminum (III). Many experimental parameters, which influenced the electrochemical behavior of the proposed method, were optimized using haematoxylin as a modifier. Under optimum condtion, the prepared electrode offer linear response covering wide concentration rang of $1x10^{-2}$ – $1x10^{-9}$ mole L^{-1}. The response characteristics of the electrode are similar and relatively better -in some cases- than those reported for similar electrodes. The suggested electrode has been successfully applied in the determination of aluminum (III) in real drinking water samples. The results obtained show a good agreement with those obtained by standard ICP-OES for the same samples as well as with those reported by WHO, EPA and FPT.

Table 2. The accuracy study for the proposed electrode in different real drinking water samples.

Sample No.	Proposed Methods* [Al], ppb	ICP-OES* [Al], ppb	Relative error (%)
1	13.0	13.3	- 2.5
2	37.0	35.0	5.7
3	34.8	36.9	-5.6
4	12.0	13.0	-7.6
5	20.0	22.0	-9.0
6	43.0	42.0	2.3
7	22.0	21.5	2.3
8	32.6	31.1	4.8
9	13.4	14.0	-4.2
10	16.1	15.6	3.2
11	13.3	12.8	3.9
12	27.4	28.0	- 2.1
13	29.6	28.3	4.5
14	24.3	26.1	-6.8
15	27.0	29.1	-7.2
16	21.5	20.0	7.5
17	18.4	16.9	8.8
18	22.4	21.2	5.6
19	37.7	40.1	-5.9
20	3.6	4.0	-10.0

**The value is a mean of three measurements.*

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