

## Selective Electrochemical Detection of Toxic Heavy Metals at Ultra Trace Levels using Natural Clay-Modified- Electrode

Ayman Abdulla A. Issa, Yahya Salim Al-Degs<sup>1</sup> and Nancy A. A. Al-Rabady

Chemistry Department, The Hashemite University, P. O. Box 150459, Zarqa, Jordan

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### Abstract

Clay-modified platinum electrodes (CMEs) were prepared using naturally occurring Jordanian silicates, kaolinite and montmorillonite. Modified electrodes, which prepared using spin-coating procedures, were used for the selective and sensitive determination of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at ultra trace levels. Prior to clay deposition onto Pt surface, the extent of uptake of different organic and inorganic compounds were tested for kaolinite; the adsorption parameters for  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  were described using the popular Langmuir isotherm. The results of these analyses, using linear regression procedures, were also disclosed in the study. The shapes of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  adsorption isotherms were of "L2" and "L1" types indicating a favorable uptake of cations and a high electrochemical function of the modified electrode. Cyclic voltammetry and differential pulse voltammetry, combined with anodic stripping voltammetry, were employed for the qualitative and quantitative analysis of the tested cations. The modified electrodes showed a remarkable selectivity and sensitivity for  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions in natural water. Using montmorillonite-modified platinum electrodes, very low detection limits for cations were reached,  $2.0 \times 10^{-7}$  and  $3.0 \times 10^{-9}$  mol L<sup>-1</sup> for  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$ , respectively. The earlier detections limits were much lower than those reported in literature.

### Keywords:

Clay-modified electrode; Cyclic voltammetry; Differential pulse voltammetry; Trace metals determination

### 1. Introduction

Clay minerals are fine particles with particle diameters ranging from 2 to 5  $\mu\text{m}$ . They are physically and chemically active. The internal structure of clays gives a specific characteristic of its chemical activity, where the small size and a specific crystal shape give the physical properties [1]. The crystal lattice of clay is basically a tetrahedral silicate  $\text{SiO}_4$  and / or octahedral aluminates Al-O, Al-OH sharing of oxygen atoms in tetrahedra or octahedrons results in a sheet [1]. Clays can be classified according to their layer type; where the number of combined tetrahedral and octahedral sheets is different. In 1:1 layer type one tetrahedral sheet fused with an octahedral sheet like kaolinite  $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ . While, in 2:1 layer type two tetrahedral sheets fused to an octahedral sheet like montmorillonite  $[(\text{Na},\text{Ca})_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$  [1]. Summaries on clay-modified electrodes have been fully reviewed in the literature. Particularly, the development of the film clay electrodes preparation, studies of the charge transport mechanisms, diffusion processes on the film clay electrodes and analytical applications of using clay-modified electrodes were discussed in

<sup>1</sup> Corresponding Author

Phone: +962(05)3903333  
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Fax: +962(05)3903349  
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E-mail: yahyaaldeqs@yahoo.com

literature [1-2]. Bard and coworkers have demonstrated that montmorillonite and other clays can be used to modify the electrochemical properties of electrode surfaces substantially [3-4]. The earlier studies utilized composite coatings containing clay, polyvinyl alcohol and colloidal platinum, but other reports [5-6] showed that clay coatings not modified with polymer or dispersed metal were also electrochemically active. Fitch and coworkers have investigated the effect of electrolyte concentration as well as shifts on the apparent formal potential in the ion exchange voltammetry [7]. The effect of film preparation conditions and film thickness on the electroactivity at clay modified electrodes had been studied [8]. In addition, the effect of solution pH on the electroactivity of clay modified electrode was also investigated and the results indicated that electroactivity of cations toward modified electrode is highly dependant on solution pH [9]. Electroactivity of the film clay electrodes has been studied by using cationic complexes such as  $\text{Fe}(\text{bpy})_3^{2+}$ ,  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{Ru}(\text{NH}_3)_6^{3+}$ , and  $\text{Os}(\text{bpy})_3^{2+}$  adsorbed on the montmorillonite-modified-electrode [9-10]. The outputs of the earlier studies indicated that the electroactivity of the adsorbed cations is highly dependant on the soaking time of the film in the solution of the electroactive ion, the ion concentration, the film preparation and its thickness, and the identity of the incorporated ion. Anions such as  $(\text{HgCl}_4)^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ , and  $\text{Mo}(\text{CN})_8^{4-}$  were also studied using montmorillonite-modified-electrodes [11-12].  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$  anions highly improved the electrochemical properties of electrode modified with metal hydroxides [13-14]. There are many analytical applications reported for clay modified electrodes and these including: preconcentration/determination of metal cations in natural waters [15], determination of organic molecules in water or drugs formulations [16-18], electrochemical sensors [19] and recently as biosensors [20].

In a previous study, the authors have successfully prepared natural clay-modified-Pt electrode using spin-coating method [21]. The prepared electrodes (prepared using natural kaolinite and montmorillonite) were durable and stable as indicated from the characterization studies [21]. In this work, the modified electrodes were further tested for selective determination of two common toxic metals ( $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$ ) using cyclic and anodic stripping voltammetric techniques. Real wastewater samples were also analyzed using the proposed analytical method. The raw clays showed a high adsorption extent toward tested cations, therefore, no attempts were made to enhance their electrochemical properties.

## 2. Experimental

### 2.1. Chemicals and Solutions

All reagents used were analytical grade chemicals supplied by various companies and were used without any further treatment. The gases used were of ultrapure quality supplied by The Industrial and Medical Liquid Gas (Amman, Jordan). The gas cylinders were coupled with Oxosorb cartridges (Supelco) for removal of traces of oxygen. All solutions were prepared in triply distilled water, where the second distillation was carried out from basic potassium permanganate solution to destroy any organic impurities (less than 1  $\mu\text{S}$ ).

### 2.2. Natural clay samples

The clay samples employed in the research were donated from the Natural Resources Authority (Amman, Jordan). The samples were washed with deionized water several times with constant stirring. After drying at 105 °C for 24 hours, the samples were crushed, and finally sieved into different particle size ranges. Sorption tests were conducted on an average size particle of 45-125  $\mu\text{m}$ . The clays (in Na-form) were used in all experiments and prepared by adding 5 g of clay to 200 ml of a 1.0 mol  $\text{L}^{-1}$  NaCl solution and stirred for 24 h.

### 2.3. Adsorption experiments

The adsorption capacities of different organic and inorganic compounds were tested for both clays. Experimental conditions were: the initial solute concentration range: 0-100 mg L<sup>-1</sup>, mass of clay: 0.100 g, particle diameter: 45-125 μm, pH: for metals 4.5 and 6.0 for organic solutes, volume of solution: 100 ml, and agitation time: 24 h for metals and 5.0 days for organics. The remaining levels of solutes were analyzed with atomic absorption spectrophotometer for metals and spectrophotometrically for organics. The measured concentrations were used to calculate the sorption capacity  $q_e$  (mg g<sup>-1</sup>) of the sorbent using the following mass balance equation [22]:  $q_e$  (mol g<sup>-1</sup>) =  $[C_o - C_e]V/m$ , where  $C_o$ ,  $C_e$ ,  $V$ , and  $m$  are initial metal concentration (mol dm<sup>-3</sup>), metal concentration at equilibrium (mol dm<sup>-3</sup>), total volume (dm<sup>3</sup>) and weight of sorbent, respectively.

### 2.4. Electrochemical Measurements

Cyclic voltammograms were obtained by means of a 746 VA Trace Analyzer (Metrohm, Switzerland), modified by disabling the mercury electrode and connecting the platinum electrode instead. The output was taken from a thermoprinter installed with the potentiostat. The reference electrode was Ag/AgCl/3.0 mol L<sup>-1</sup> Cl<sup>-</sup> and all reported potentials are referenced to this electrode. The working electrodes used in electrodeposition were polycrystalline platinum (0.3 mm-diameter, 99.99% pure, Johnson Matthey), rounded at the end to provide reproducible surface area upon immersion beneath the surface. On the other hand, the electrode used in spin-coating method was polycrystalline platinum (0.5 mm-diameter, 99.99% pure, Johnson Matthey), shrouded with PTFE keeping 0.5 mm in contact with solution. The auxiliary electrode was a platinum wire (2-mm diameter, 99.99% pure, Metrohm). A three-electrode cell was used, where all electrodes were housed in the same compartments, with ultrapure nitrogen purging and blanketing inlets. The IR-spectra were recorded in the range (400-4000 cm<sup>-1</sup>) for the clay materials by means of FTIR-spectrophotometer (Perkin-Elmer, Niclet model). The pH measurements were made with a WTW-Inolab (Germany) pH-meter using a combined glass electrode. A thermostated shaker (GFL 1083, Germany) and a centrifuge operated under variable powers (Hermle Z200A, Germany) were employed in this work.

### 2.5. Spin-coating method

The electrode surface was initially cleaned in a freshly prepared chromic acid solution, rinsed with triply distilled water, and placed in the electrochemical cell that contained a purged solution of 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (or 1.5 mol L<sup>-1</sup> NaOH for the basic medium experiments). The electrode surface was conditioned by cathodization at -0.20 V in a nitrogen-purged 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution to remove any oxides from the surface, then cyclization of the electrode potential between -0.20 and +1.30 V to remove surface impurities. Surface cleanliness was verified by reproduction of the voltammogram of platinum polycrystalline surface electrode at slow scan rate (50 mV/s) [21]. This procedure was repeated prior to each deposition experiment.

Mixtures of PVC (polyvinyl chloride) and clay in different stoichiometric ratios (*w/w*) were prepared in acetone. 2.0-mL aliquots of these mixtures and the cleaned platinum electrode were placed in a test tube and centrifuged at different centrifugation speeds (1000-3000 rpm) for 2-10 minutes. The clay-modified electrode was removed, rinsed with triply distilled water. The cyclic voltammetric characterization of the modified electrode was performed in a nitrogen-purged 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution. Cyclic voltammograms were then recorded, under different experimental conditions, for CMEs to test the magnitude of surface coverage with clay and durability of these modified electrodes.

### 3. Results and Discussion

#### 3.1. Modified electrodes

It is important to mention that the most adopted technique employed for clay immobilization or deposition onto electrode surfaces is the spin-coating, which ensures the unique, uniform, “well-ordered”, face-to-face clay structure [8]. In this work, the presence of polyvinyl chloride (PVC) was essential to bind clay particles with the electrode surface and to ensure a stable and durable modification [21]. The SEM pictures of montmorillonite and kaolinite modified electrodes were indicated the presence of clay layers as inferred from the white shadows that covered the electrode surface [21]. The SEM pictures recorded for the unmodified pt electrode were entirely dark and do not show any white images [21].

#### 3.2. Sorption capacity of clay minerals for cations

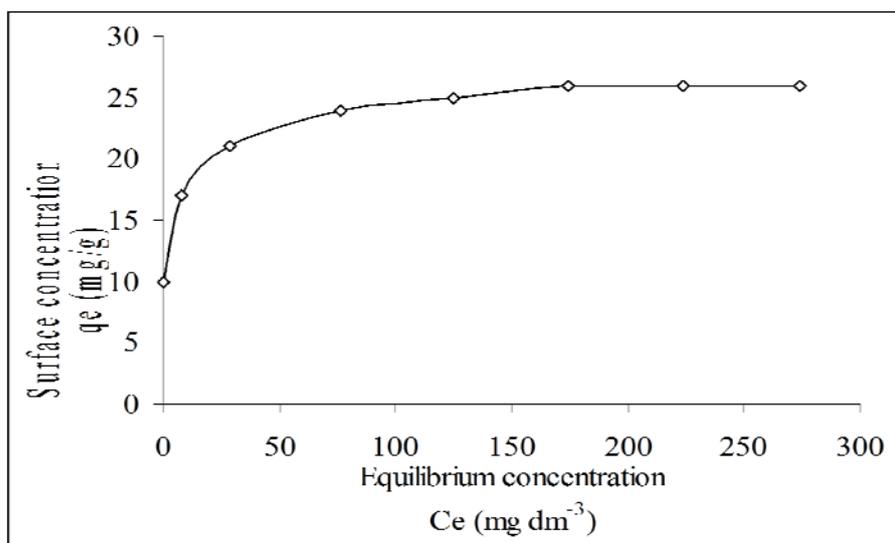
In fact, clay of high affinity for metal cations is usually has high electrochemical activity and there is no need to enhance its electrochemical properties via surface modification. Accordingly, the favorability of  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  adsorption on kaolinite and montmorillonite were investigated. The adsorption capacities (in  $\text{mg g}^{-1}$ ) of a number of solutes including the metals of interest were shown in Table 1 and the adsorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at pH 5 and 25 °C were depicted in Fig. 1 and 2, respectively.

**Table 1.** Adsorption values ( $\text{mg g}^{-1}$ ) of different solutes by clays\*

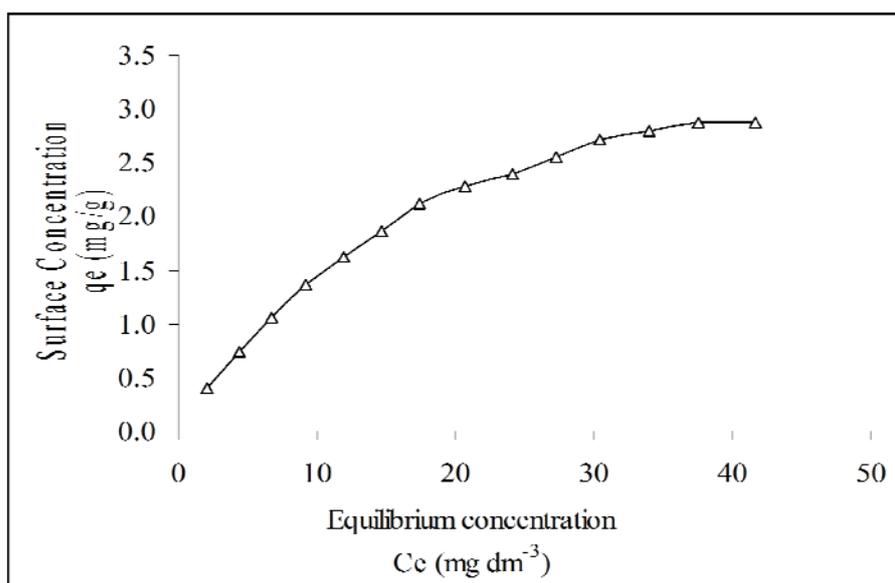
Solute	Kaolinite		Montmorillonite	
	Adsorption value	$r^2$	Adsorption value	$r^2$
$\text{Ag}^+$	35.0	0.9962	46.2	0.9922
$\text{Cu}^{2+}$	26.5	0.9997	38.6	0.9752
$\text{Hg}^{2+}$	3.5	0.9982	6.5	0.9782
$\text{Co}^{2+}$	8.3	0.9766	11.6	0.9834
$\text{Pb}^{2+}$	25.4	0.9788	28.2	0.9752
$\text{Zn}^{2+}$	16.5	0.9922	19.3	0.9632
Phenol	5.0	0.9652	6.4	0.9887
P-Chlorophenol	4.5	0.9980	5.2	0.9902
m-Chlorophenol	3.1	0.9882	4.3	0.9822

\*the initial solute concentration range (for metals and organics): 0-100 ppm, mass of clay: 100 mg, particle diameter: 45-125  $\mu\text{m}$ , pH: for metals 5.0 and 6.0 for organics, volume of solution: 100 ml, and agitation time: 24 hr for metals and 5.0 days for organics. CEC (in  $\text{cmol}(+)/\text{kg}$ ): 17.8 (for Kaolinite) and 40.0 (Montmorillonite) [21].

The adsorption data for all solutes were fairly presented using Langmuir isotherm and the maximum adsorption values were obtained. The shape of  $\text{Cu}^{2+}$  isotherm is of “L2” type, while that of  $\text{Hg}^{2+}$  is “L1” type according to Giles classification for isotherms [22]. The curve of L2 isotherm (Fig. 1) indicated that sorption of  $\text{Cu}^{2+}$  has reached a maximum value which is indicated by the presence of the plateau. On the other hand, this was not the case in L1 curve where only the initial part of the isotherm is present and the plateau is not entirely present (Fig. 2).



**Fig.1.** Adsorption isotherm of  $\text{Cu}^{2+}$  by kaolinite at 25 °C and pH = 5.0



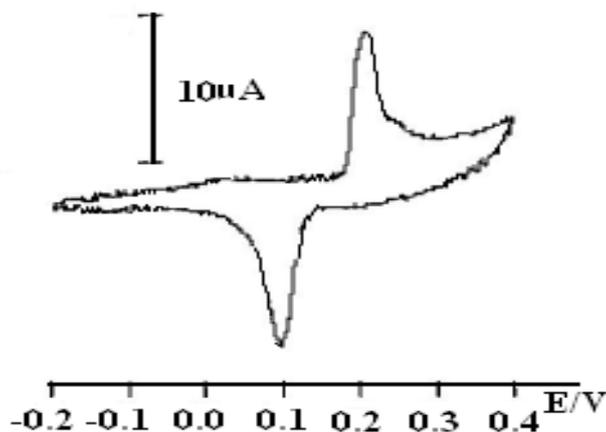
**Fig.2.** Adsorption isotherm of  $\text{Hg}^{2+}$  by kaolinite at 25 °C and pH = 5.0.

Another important difference between both isotherms is that the slope of L2 isotherm is steeper than that of L1 isotherm [22]. L-isotherm type (or Langmuir isotherm type) is usually associated with ionic substrates (*e.g.*, metal cations) sorption with weak competition from the solvent molecules [22]. The results of analysis of adsorption data for all solutes using Langmuir models were summarized in Table 1. The results indicated that Langmuir model was satisfactory for presenting adsorption data for most solutes with a regression coefficients ( $r^2$ ) ranging from 0.9997 and 0.9652 for  $\text{Cu}^{2+}$  and phenol, respectively. Using Langmuir model, the maximum adsorption capacity for solutes was ranged from 3 to 35  $\text{mg g}^{-1}$  for kaolinite and from 4 to 46  $\text{mg g}^{-1}$  for montmorillonite as shown in Table 1. Generally, the adsorption capacity was higher for metals compared to organics and this mainly attributed to the high cation exchange capacity for clays as reported in our previous papers [21-22]. Accordingly, clay-modified-electrode would be much sensitive toward metals compare to organic solutes.

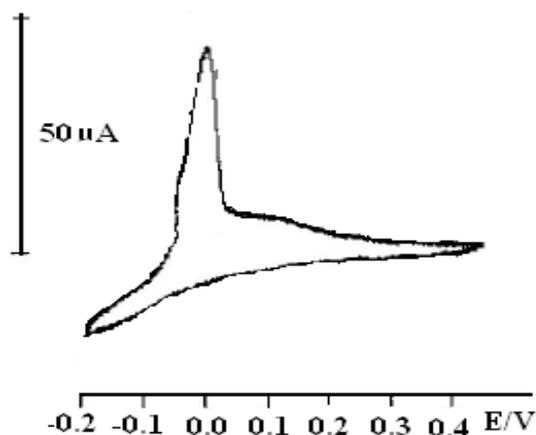
### 3.3. Electrochemical behavior of montmorillonite and kaolinite modified-platinum electrodes

The cyclic voltammograms reported for electrochemical detection of cations were depicted in Figs. 3 – 6. The CVs of  $\text{Hg}^{2+}$  indicated the presence of well resolved anodic and cathodic peaks. For montmorillonite-modified Pt electrode, the peaks appeared at 0.21 and 0.10 mV, while for kaolinite-modified Pt electrode the peaks were appeared at 0.25 and 0.05 mV. Relatively speaking, the magnitude of electrochemical peaks were similar (8-10  $\mu\text{A}$ ) in both cases which reflected the high sensitivity of the modified electrodes toward  $\text{Hg}^{2+}$  ions. For  $\text{Cu}^{2+}$ , the CVs were not complete and only anodic peaks was observed as can be noted in Figs. 4 and 6 and the position of anodic peaks were centered at -0.09 and -0.01 mV for montmorillonite-modified and kaolinite-modified Pt electrodes, respectively. Moreover, the magnitude of anodic peak due to  $\text{Cu}^{2+}$  oxidation was two fold higher in the case of montmorillonite-modified Pt electrode. Due to the high oxidation current response for cations, these currents were considered for electrochemical studies. Clay films concentrate electroactive cations by the effect of ion exchange. However, clay films are not electrically conductive. Electron transfer in clay-modified electrodes depends mainly on the physical diffusion of the adsorbed electroactive species in and out of the clay films. The intensity of electrochemical signals of silver and mercury ions have been significantly improved when detected by cation-modified-clay-electrodes [5, 23].

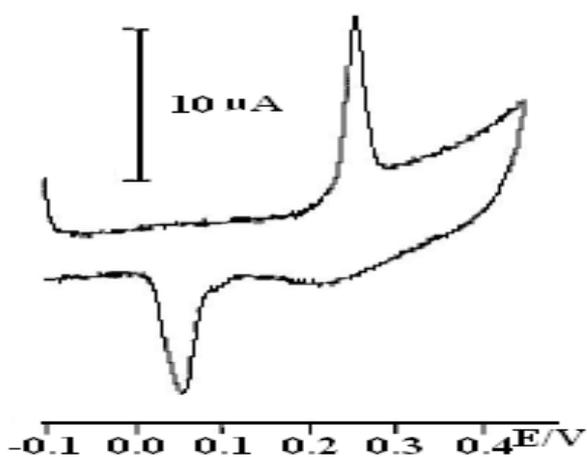
Cyclic voltammetry and differential pulse coupled with anodic stripping techniques were used to study the response of modified electrodes toward several cations. The tested cations include:  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  ions. Their concentrations ranged from  $1.0 \times 10^{-5}$  -  $5.0 \times 10^{-4}$  M. The anodic stripping technique was conducted at an accumulation potential of -0.20 V for 5-15 minutes. Except for  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions, all other tested ions did not show any significant electrochemical signal using both CMEs. It seems that the adsorption affinity of the clays has no effect on the electrochemical behaviors of the CMEs, for example, the adsorption values of  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  ions were high (16-28 mg/g) and similar to  $\text{Cu}^{2+}$ , however, no electrochemical signals were observed for these ions. Moreover, no electrochemical signal was observed for acetone, acetonitrile, benzene, dichloromethane, ethanol, phenol, chlorophenols, methanol, toluene, formaldehyde, and formic acid which indicated a high sensitivity/selectivity of the CMEs toward  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  ions in complex matrices as will be shown later.



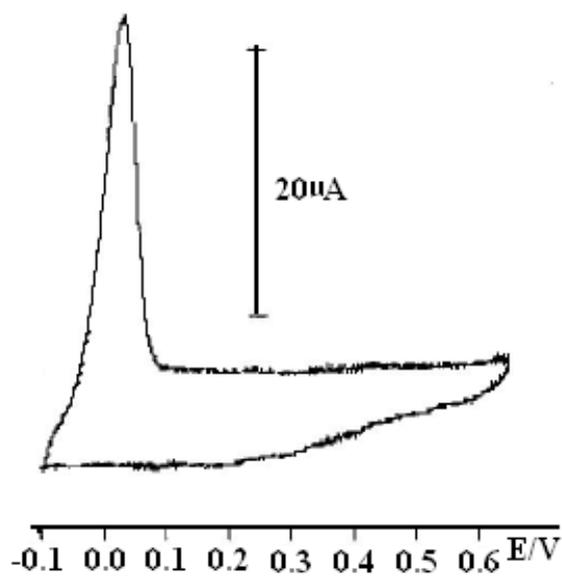
**Fig.3.** Cyclic voltammogram of  $1.5 \times 10^{-6}$  M  $\text{Hg}^{2+}$  using montmorillonite-modified Pt electrode. Conditions: 0.5 M  $\text{H}_2\text{SO}_4$  and scan rate 50 mV/s.



**Fig.4.** Cyclic voltammogram of  $1.0 \times 10^{-4}$  M  $\text{Cu}^{2+}$  using montmorillonite-modified Pt electrode. Conditions: 0.5 M  $\text{H}_2\text{SO}_4$  and scan rate 50 mV/s.



**Fig.5.** Cyclic voltammogram of  $5.0 \times 10^{-6}$  M  $\text{Hg}^{2+}$  using kaolinite-modified Pt electrode. Conditions: 0.5 M  $\text{H}_2\text{SO}_4$  and scan rate 50 mV/s.



**Fig.6.** Cyclic voltammogram of  $1.0 \times 10^{-4}$  M  $\text{Cu}^{2+}$  using kaolinite-modified Pt electrode. Conditions: 0.5 M  $\text{H}_2\text{SO}_4$  and scan rate 50 mV/s.

Effect of solution pH on electrochemical signal of  $\text{Hg}^{2+}$  was carefully studied at earlier stages. Table 2 showed the magnitude of oxidation peaks of  $\text{Hg}^{2+}$  over different pH values reported for both CMEs.

**Table 2.** Effect of pH on electrochemical signal of  $\text{Hg}^{2+}$

pH*	Oxidation peak current (in $\mu\text{A}$ ) of $\text{Hg}^{2+}$	
	Kaolinite-modified-electrode	Montmorillonite-modified-electrode
0.5 M $\text{H}_2\text{SO}_4$	16.0	11.3
3	5.4	1.1
4	1.1	3.3
5	4.7	6.6
6	2.7	3.0
7	1.5	3.0

\* Initial pH was adjusted using 1.0 M  $\text{H}_2\text{SO}_4$  solution. Measurement conditions: metal content  $2.0 \times 10^{-6}$  M, scan rate 50 mV/s.

As indicated in Table 2, high oxidation peaks was observed at 0.5 M  $\text{H}_2\text{SO}_4$  solution for both electrode and electrochemical analysis of  $\text{Hg}^{2+}$  was carried out at this level of acidity in all electrochemical experiments. A similar trend was noted for  $\text{Cu}^{2+}$  ions using both electrodes. Table 3 summarized the results of correlations and analytical studies that related to toxic metal analysis and electrochemical behavior. As indicated in Table 3, the peak current ( $i_p$ ) linearly varied with square root of scan rate ( $v^{1/2}$ ) for  $\text{Hg}^{2+}$ . The plot of  $i_p$  against  $v^{1/2}$  gave straight lines for both electrodes with  $r^2$  within the range: 0.9564–0.9671.  $\log i_p - \log v$  plots reported for  $\text{Hg}^{2+}$  analysis were also showed straight lines with slopes of 0.68 and 1.23 for kaolinite and montmorillonite modified electrodes, respectively. These facts suggest diffusion-controlled mass transfer reactions as discussed in the literature [17-21].

**Table 3.** The correlation results for electrochemical detection of metals

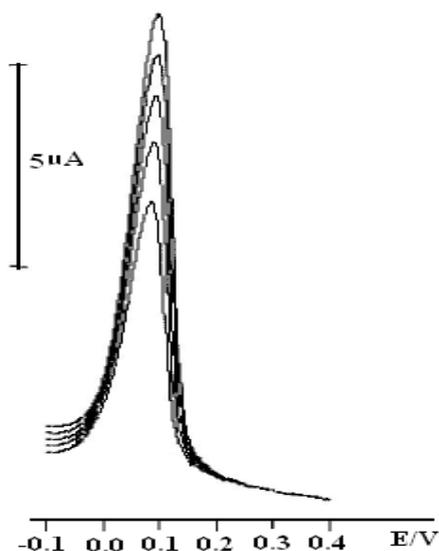
Metal	Kaolinite-modified-electrode		Montmorillonite-modified-electrode	
	$i_p = 0.13 v^{1/2} + 2.71$	$r^2 = 0.9564$	$i_p = 0.27 v^{1/2} + 1.34$	$r^2 = 0.9671$
$\text{Hg}^{2+}$	$\log i_p = 0.68 \log v + 0.54$	$r^2 = 0.9906$	$\log i_p = 1.23 \log v - 0.01$	$r^2 = 0.9778$
	$i_p = 1.06 C_{\text{Hg}} - 0.06$	$r^2 = 0.9991$	$i_p = 0.63 C_{\text{Hg}} - 2.02$	$r^2 = 0.9973$
$\text{Cu}^{2+}$	$i_p = 1.04 C_{\text{Cu}} + 0.98$	$r^2 = 0.9917$	$i_p = 1.71 C_{\text{Cu}} - 2.82$	$r^2 = 0.9953$

### 3.4. Figures of merit for electrochemical detection of metals

Differential plus voltammograms at different concentrations of metals were recorded at the maximum signal conditions which were optimized beforehand. The peak current ( $i_p$ ) linearly increased with an increase in ion concentration for both metals using both electrodes. Fig.7 depicted the differential plus voltammograms of  $\text{Cu}^{2+}$  at different trace levels using kaolinite-modified Pt electrode.

Calibration curves (oxidation peak height against metals concentration) were obtained from triplicate determination using five standard samples in appropriate concentration range for each metal. As shown in Tables 3 and 4, good linearities were found between the electrochemical repose and the studied concentration range, the obtained regression coefficients ( $r^2$ ) were in the range 0.9917 to 0.9919. The limits of detection (LODs estimated

as signal-to-noise ratio of 3), precision, and working ranges were all given in Table 4. In fact, there is no need for any metal-preconcentration step prior to electrochemical analysis because the usual level of target metals is above the reported detection limits.



**Fig.7.** Differential pulse voltammogram of kaolinite-modified Pt electrode in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. Cu<sup>2+</sup> range was 5.0×10<sup>-5</sup>–9.0×10<sup>-5</sup> M at Scan rate of 6.67 mV.

**Table 4.** Analytical parameters for electrochemical determination of Hg and Cu using CMEs

Metal	Electrode Type	Peak position	$r^2$	RSD	LOD mol L <sup>-1</sup>	Working Range mol L <sup>-1</sup>
Hg <sup>2+</sup>	A	0.25	0.9991	2.8	3×10 <sup>-6</sup>	(0.5-3)×10 <sup>-5</sup>
	B	0.21	0.9973	3.6	2×10 <sup>-7</sup>	(6-11)×10 <sup>-7</sup>
Cu <sup>2+</sup>	A	0.01	0.9917	4.3	3×10 <sup>-5</sup>	(5-9)×10 <sup>-5</sup>
	B	-0.01	0.9953	5.2	3×10 <sup>-7</sup>	(5-9)×10 <sup>-7</sup>

A: kaolinite-modified-electrode

B: montmorillonite-modified-electrode

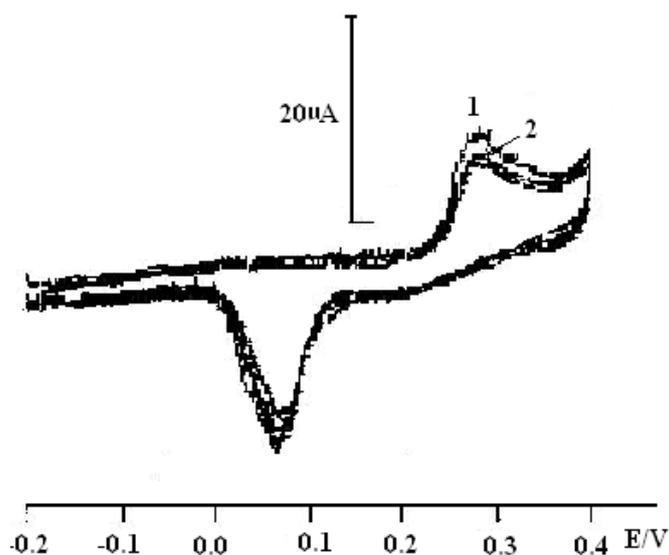
The montmorillonite-modified-electrode has a high sensitivity toward Hg<sup>2+</sup> and Cu<sup>2+</sup> ions with a detection limits of 2×10<sup>-7</sup> and 3×10<sup>-7</sup> mol L<sup>-1</sup>, respectively. The high sensitivity of montmorillonite-modified-electrode could be attributed to its large CEC value compare to kaolinite, 40.0 cmol(+) kg<sup>-1</sup> [21] and high adsorption extent for cations as indicated in Table 1. As previously reported, the detection limit of Ag<sup>+</sup> was 1.0×10<sup>-10</sup> mol L<sup>-1</sup> using CMES-ASV/DPV. The lower detection limit observed for Ag<sup>+</sup> on CMEs compare to Hg<sup>2+</sup> and Cu<sup>2+</sup> ions were attributed to: a) the small size and large mobility of Ag<sup>+</sup> cations, which will improve its movement cross clay films, and b) two Na<sup>+</sup> ions should be exchanged with divalent cations, while one Na<sup>+</sup> with Ag<sup>+</sup> ion and this will accumulate more Ag<sup>+</sup> within clay films. Generally speaking, the reported LODs values for cations were lower than literature values [20].

### 3.5. Interferences on electrochemical signals of Hg<sup>2+</sup> and Cu<sup>2+</sup> ions

The effect of other metal cations on electrochemical behavior of Hg<sup>2+</sup> and Cu<sup>2+</sup> was addressed in this work. For these experiments, different amounts of the studied interfering

ions were used. Their concentrations were as large as ten-fold of the target analyte ion. The results indicated that the presence of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  ions have no effect on the position and the magnitude of  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  oxidation-reduction peaks for both kaolinite and montmorillonite-modified Pt electrodes.

However, the results indicated that  $\text{Co}^{2+}$  was strongly affected the position and magnitude of oxidation peak of  $\text{Hg}^{2+}$  when using montmorillonite-modified-electrode, the peak position was shifted by 0.05 V with 10% increase in peak magnitude. Fig.8 showed the positive effect of cobalt and silver ions on  $\text{Hg}^{2+}$  peak current, however, without affecting the peak position. As indicated in Fig.8,  $\text{Co}^{2+}$  ions showed a higher influence on the  $\text{Cu}^{2+}$  peak compare to  $\text{Ag}^+$  ions.



**Fig.8.** Cyclic voltammogram of  $1.0 \times 10^{-4}$  M  $\text{Hg}^{2+}$  on kaolinite-modified-Pt electrode in the presence of  $10^{-4}$  M  $\text{Co}^{2+}$  (1) and  $10^{-4}$  M  $\text{Ag}^+$  (2). Conditions: 0.1 M  $\text{NaClO}_4$  at scanning rate 50mV.

### 3.6. Determination of $\text{Hg}^{2+}$ and $\text{Cu}^{2+}$ ions in natural water

Obviously, the next step is to assess the developed electroanalytical method for analysis of  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  in natural water samples where many chemical interferences are present. Blanks of natural waters were subjected to the proposed analytical method and the results revealed the absence of the metals in the samples. 100 mL of natural water samples were spiked with different concentrations of both metals. The samples were acidified and the differential pulse voltammograms were obtained using montmorillonite-modified Pt electrode as described earlier. The peak currents were converted into concentrations using the earlier calibration equations and the metal recoveries were estimated. The results were compiled in Table 5

The recoveries obtained were satisfactory in all analyzed samples, the RSD values were less than 5%. The sensitive and accurate metals determination by montmorillonite-modified-electrode/DPV is acceptable taking into account the complexity of the natural sample being analyzed at trace metals level. The good agreement between the obtained results using CMES-DPV and the trace spiked values is an indication of the effectiveness of the proposed method for simultaneous determination of  $\text{Hg}^{2+}$  and  $\text{Cu}^{2+}$  in real samples. In fact, other substances that present in natural water sample, e.g.,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , organic matter, etc., did not interfere with metals detection.

**Table 5.** Application of the method for determination of toxic metals in natural water using montmorillonite-modified-electrode/DPV.

Metal	Added (mol L <sup>-1</sup> )	Found (mol L <sup>-1</sup> )	Recovery%	R.S.D. (n=6)
Hg <sup>2+</sup>	2.0×10 <sup>-7</sup>	1.8×10 <sup>-7</sup>	92.6	3.2
	4.0×10 <sup>-7</sup>	3.7×10 <sup>-7</sup>	93.6	3.3
	6.0×10 <sup>-7</sup>	5.8×10 <sup>-7</sup>	97.3	2.6
Cu <sup>2+</sup>	3.0×10 <sup>-7</sup>	2.6×10 <sup>-7</sup>	88.3	1.9
	6.0×10 <sup>-7</sup>	5.6×10 <sup>-7</sup>	92.7	4.4
	9.0×10 <sup>-7</sup>	8.7×10 <sup>-7</sup>	96.3	3.8

The spiked natural water contains (in mg L<sup>-1</sup>): [Cl<sup>-</sup>] = 120, [SO<sub>4</sub><sup>2-</sup>] = 68, [NO<sub>3</sub><sup>-</sup>] = 21, [F<sup>-</sup>] = 0.1, total hardness (as CaCO<sub>3</sub>) = 410, and total organic matter = 2.5 mg L<sup>-1</sup>.

#### 4. Conclusions

Two natural clays modified Pt electrodes showed a unique selectivity toward Hg<sup>2+</sup> and Cu<sup>2+</sup> ions in natural waters. The montmorillonite-modified- Pt electrode showed a unique detection limits for both cations (2-3 ×10<sup>-7</sup> mol L<sup>-1</sup>). The low detection limit of montmorillonite-modified- Pt electrode was attributed to the high CEC of the montmorillonite clay. The earlier results revealed that the modified electrodes can be generated and reused with good efficiency.

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