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## Nanoalumina Modified Carbon Paste Electrode for Sensitive and Rapid Determination of Hypochlorite Ion by Differential Pulse Voltammetry

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An anodic stripping differential pulse voltammetric method was proposed for rapid and sensitive determination of hypochlorite ( $\text{OCl}^-$ ) ion. A modified electrode was prepared by modification of carbon paste using alumina nanopowder. This rapid, simple and accurate method is based on the electrooxidation of  $\text{OCl}^-$  ion accumulated at the electrode surface. Nanoalumina modification increased the oxidation peak current for  $\text{OCl}^-$  ion. The effects of different parameters on the electrode response were studied and the optimum condition was established. The response of the sensor was linear in the range  $0.1\text{--}800\ \mu\text{g ml}^{-1}$  of  $\text{OCl}^-$  ion, with a correlation coefficient of 0.9992 at the optimum condition. The limit of detection was obtained as  $0.025\ \mu\text{g ml}^{-1}$ . The effects of some cations, anions and organic species, which may coexist with  $\text{OCl}^-$  ion in real samples on the current response of  $\text{OCl}^-$ , were investigated. The investigated chemical species did not interfere with the  $\text{OCl}^-$  electrochemical signal.  $\text{OCl}^-$  ion in water and dairy product samples was successfully determined using the proposed electrode.

**Keywords:** Hypochlorite determination, Chemically modified carbon paste electrode, Differential pulse voltammetry, Nanoalumina, Water samples, Dairy products

### INTRODUCTION

Hypochlorite ion ( $\text{OCl}^-$ ) is widely used as a cleaning, bleaching, disinfection and odor removal agent in household uses. It also is used in large scales in water disinfection and also in fabrics, wood pulp and food industries including milk industries for disinfection and bleaching purposes [1].  $\text{OCl}^-$  oxidation reactions are corrosive. Also contact with  $\text{OCl}^-$  solution causes damage to human organs [2,3]. This may lead to several diseases including cancer, lung injury, rheumatoid, atherosclerosis, hepatic ischemia-reperfusion injury, neuron degeneration, arthritis and cardiovascular diseases [4,5]. Therefore, quantitation of  $\text{OCl}^-$  in the samples is important both in different industries and in daily life.

Various analytical methods such as colorimetry [6],

iodimetry [7], chemiluminescence [8], potentiometry [9], spectrophotometry [10] and fluorimetry [11] have been applied for the determination of  $\text{OCl}^-$  ion. Electrochemical methods using modified electrodes, because of their efficiency and selectivity are used to quantify both organic and inorganic chemical species [12-18]. These methods are simple and suitable for designing and fabrication of reliable and cost effective sensors. Introduction of new electrochemical methods for rapid and accurate determination of  $\text{OCl}^-$  ion is of great importance.

Electrochemical sensors are widely used for the detection and quantitation of different organic and inorganic chemical substances. They provide good selectivity and sensitivity. In this work, an electrochemical sensor is reported for the determination of  $\text{OCl}^-$  ion. Alumina nanopowder was used for the modification of carbon paste. The modified paste was then used to prepare the working electrode (MCPE). The prepared sensor was used for the

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analysis of  $\text{OCl}^-$  samples using anodic stripping differential pulse voltammetric technique (ASDPV).  $\text{OCl}^-$  ion was accumulated at the electrode surface mainly by adsorption at alumina nanoparticles. The electrode is suitable for the detection of trace amount  $\text{OCl}^-$  ion as low as  $0.1 \mu\text{g ml}^{-1}$  in various real samples.

## EXPERIMENTAL

### Materials and Apparatus

Analytical grade reagents (Merck or Aldrich) and double distilled water were used throughout. Among the investigated electrolyte solutions, the  $\text{KNO}_3$  solution at pH 12 was selected as the supporting electrolyte. A Metrohm model 827 pH lab (Herisau, Switzerland) pH-meter with a combined glass electrode was used for the pH measurements. Voltammetric system was conducted using a potentiostat/galvanostat (Autolab PGSTAT302 N) and it was controlled by a computer using Nova version 1.7 software. Voltammograms were obtained using a three electrode cell system. The alumina modified CPE ( $\text{Al}_2\text{O}_3/\text{CPE}$ ) was used as the working electrode. The counter electrode was platinum wire and the reference electrode was a saturated  $\text{Ag}/\text{AgCl}$ .

### Preparation of MCPE

The MCPE was prepared by mixing 67.5, 7.5 and 25% (w/w) graphite powder, alumina nanopowder and paraffin oil in a mortar and pestle and homogenized for 30 min. Then 0.2 g of the mixture was homogenized in the mortar for 30 min. The homogenized paste was then inserted into a plastic needle-type capillary tube with a 2.5 mm inner diameter and a 5 cm length, using a 0.5 mm diameter copper wire connected to the measurement system. After that, smoothing of the electrode tips was performed manually with a clean paper and then at a clean plane glass surface to produce a flat surface.

### General Procedure

A 10 ml beaker was used as the voltammetric cell and  $\text{KNO}_3$  solution at pH 12 as the supporting electrolyte. The voltammograms were recorded at the optimum conditions as: the dc voltage step height of 5 mV, resting time of 10 s and pulse amplitude of 70 mV. The analyte was

preconcentrated at the electrode surface in the stirred solution. The preconcentration time and voltage were 120 s and 0.5 V, respectively. The stirring was stopped and the solution was settled by applying a rest time of 10 s. After that the voltammograms for the electro-oxidation of  $\text{OCl}^-$  ion were recorded in the positive going scan in the potential range 0.60-1.40 V vs.  $\text{Ag}/\text{AgCl}$ . To minimize the memory effect electrode surface was renewed after each measurement as described above. All the voltammetric measurements were performed at  $25.0 \pm 0.1$  °C. The measured anodic peak currents were corrected against the blank. Calibration graph was constructed using the net peak currents.

### Real Sample Analysis

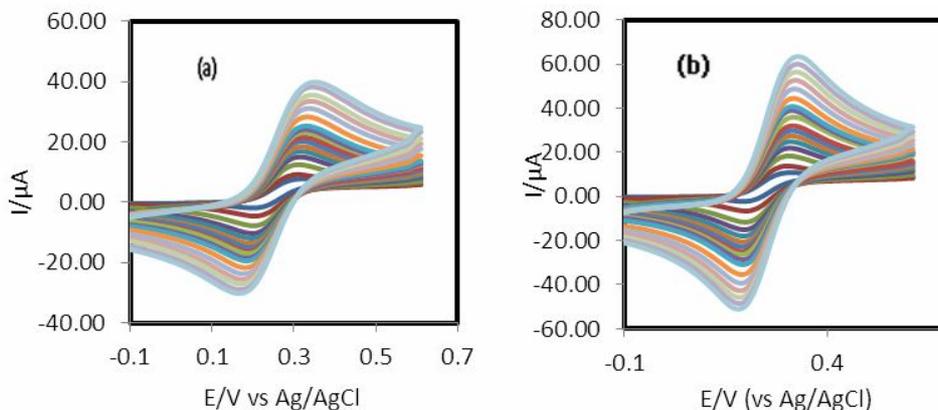
Real samples including tap water, swimming pool water, well water, milk, and yoghurt were tested by the proposed method. Before the determination, treatment of water samples was performed by adding and mixing a 1.0 ml of the solution of 0.2 M in NaOH and EDTA to the sample. The solution was centrifuged to remove any precipitate formed. The centrifugate solution was transferred to a 10 ml volumetric flask for further analysis [19].

Dairy samples were pretreated according to the previous report [20]. As the samples were found to be free from  $\text{OCl}^-$  ion, they were spiked with different amounts of  $\text{OCl}^-$  ion. A 3 ml acetonitrile was added to the mixture and mixed to remove proteins. The procedure was followed by 10 min shaking and then centrifuging at 3500 rpm for 10 min. The pH of the supernatant was adjusted at 12 with NaOH solution before being centrifuged for another 5 min. The final supernatant was used for the analysis.

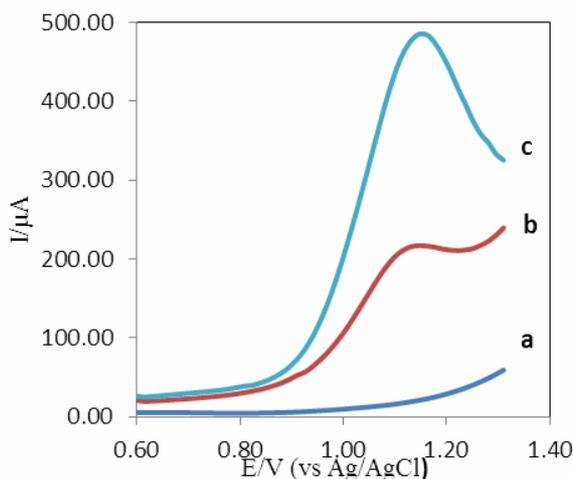
## RESULTS AND DISCUSSION

### Surface Area Study

Microscopic surface area is an important parameter for characterizing the analytical performance of the electrode. For a reversible process microscopic surface area of the electrode can be determined using cyclic voltammetry (CV) at different scan rates using the Randles-Sevcik equation (Eq. (1)). CVs for CPE and  $\text{Al}_2\text{O}_3/\text{CPE}$  electrodes in 1.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ , as a reversible redox system, were



**Fig. 1.** Cyclic voltammograms for (a) CPE and (b) Al<sub>2</sub>O<sub>3</sub>/CPE in  $1.0 \times 10^{-3}$  M K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.1 M KNO<sub>3</sub> at different scan rate, Scan rates: 5 to 250 mV s<sup>-1</sup> (from bottom to top).



**Fig. 2.** Differential pulse voltammograms for (a) blank (b) CPE, and (c) Al<sub>2</sub>O<sub>3</sub>/CPE 500 μg ml<sup>-1</sup> of OCl<sup>-</sup> in KNO<sub>3</sub> solution. Conditions: pH 12.0; deposition potential, 0.500 V vs. Ag/AgCl; deposition time, 120 s; resting time, 10 s; pulse amplitude, 0.07 V.

obtained in 0.1 M KNO<sub>3</sub> solution at different scan rates (Fig. 1). The relation between  $I_p$  and  $v^{1/2}$  is linear as follows:

$$I_p = (2.69 \times 10^5) n^{3/2} A C_0 D^{1/2} v^{1/2} \quad (1)$$

in this equation  $I_p$ ,  $C_0$ ,  $A$  and  $v$  are the anodic peak current, concentration of K<sub>3</sub>Fe(CN)<sub>6</sub>, the surface area of the electrode and the scan rate, respectively. By substitution of the amounts of diffusion coefficient and  $n$ , that are equal to  $7.60 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> [21] and 1, respectively, surface

area can be calculated from the slope of the line. The linear regression equation was  $I_p = 5.3 \times 10^{-5} v^{1/2} + 2.9 \times 10^{-6}$  ( $R^2 = 0.995$ ) and  $I_p = 1.01 \times 10^{-4} v^{1/2} + 8.0 \times 10^{-7}$  ( $R^2 = 0.995$ ) for CPE and Al<sub>2</sub>O<sub>3</sub>/CPE, respectively. The microscopic area for Al<sub>2</sub>O<sub>3</sub>/CPE was calculated as 0.14 cm<sup>2</sup>, which was 2 times greater than the surface area for CPE (0.07 cm<sup>2</sup>).

### Electro-oxidation of OCl<sup>-</sup> Ion

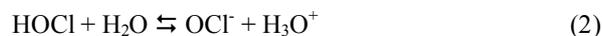
Figure 2 shows the differential pulse voltammograms

(DPVs) for 500  $\mu\text{g ml}^{-1}$  of  $\text{OCl}^-$  ion at  $\text{Al}_2\text{O}_3/\text{CPE}$  and CPE. The voltammograms were recorded in the positive going scan at pH 12. The deposition potential and deposition time were 0.50 V vs. Ag/AgCl and 120 s, respectively. The DPV at the unmodified CPE showed a broad peak (Fig. 2, curve b). A stripping peak was observed at 1.12 V vs. Ag/AgCl for  $\text{Al}_2\text{O}_3/\text{CPE}$  (Fig. 2, curve c). The peak corresponds to the electro-oxidation of  $\text{ClO}^-$  ion at the electrode surface. Fig. 2 shows that  $I_p$  for the electro-oxidation of  $\text{ClO}^-$  at  $\text{Al}_2\text{O}_3/\text{CPE}$  is higher than that for CPE. It can be concluded that modification caused a better sensitivity and detection limit. The enhancement in the anodic peak current is due to the increase in the working electrode surface area by modification of the electrode and also due to the preconcentration of the analyte ion at the electrode surface by adsorption at nanoalumina [22]. These results confirm that the proposed  $\text{Al}_2\text{O}_3/\text{CPE}$  electrode is suitable for the determination of  $\text{ClO}^-$  by DVP method. Both the modified and unmodified electrodes did not show any anodic peak in the blank solution.

### Effect of Variables

The electrode response is affected by the electrode composition. To find the best composition for the construction of  $\text{Al}_2\text{O}_3/\text{CPE}$ , several electrodes with constant amounts of paraffin and various amounts of nanoalumina and graphite powder were constructed. The ASDPV peak current for the electrodes for a 500.0  $\mu\text{g ml}^{-1}$  of  $\text{ClO}^-$  in a  $\text{KNO}_3$  solution of pH 12 was determined. The amount of paraffin oil in all the prepared electrodes was 25.0% (w/w) and the total amount of graphite and alumina was 75.0% (w/w). The deposition time was 120 s. Figure 3 shows the results. As it was expected, an increase in the anodic peak current of the  $\text{OCl}^-$  ion took place by increasing  $\text{Al}_2\text{O}_3$  in carbon paste up to 10.0% (w/w) and slightly decreased beyond it. As mentioned before, the addition of nanoalumina to the paste causes an increase in the electrode surface area. Also  $\text{OCl}^-$  ion becomes adsorbed at alumina surface. Therefore, an increase in the amount of alumina at the electrode surface increases the amount of  $\text{OCl}^-$  ion at the electrode surface, which results in an enhancement in the stripping current. The decrease in the electrode response at nanoalumina amounts beyond 10% can be due to the decrease in electrode conductivity of the electrode.

Both the chemistry of the solution and surface of the electrode may be affected by the pH of the solution. The influence of pH in the range 5.0-12.5 on the peak current for  $\text{OCl}^-$  determination was studied using  $\text{KNO}_3$  solution (Fig. 4). NaOH solution was used for adjustment of the pH of the  $\text{KNO}_3$  solutions at desired value. As Fig. 4 shows, increasing the pH of the solution up to 7.0 caused an increase in the electrode response. The peak current remained nearly constant in the range 7-10, increased again up to pH 11.5 and remained constant beyond pH 11.5. Therefore,  $\text{KNO}_3$  solution with pH 12.0 was used as the optimal. The peak potential for  $\text{OCl}^-$  ion oxidation at the electrode was not dependent on the solution pH. This means that only  $\text{OCl}^-$  ions are oxidized at the electrode and hypochlorous acid oxidation does not take place at the applied potential range. Therefore proton does not contribute in the electrode reaction [23]. The concentration of  $\text{OCl}^-$  ion in water is dependent on the pH as follows:

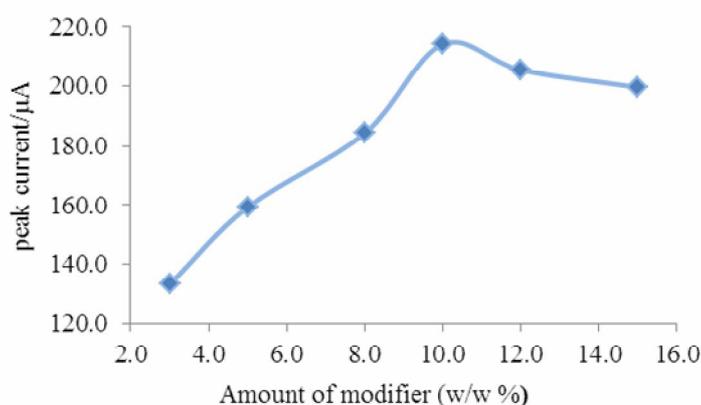


The equilibrium constant of HOCl is reported as  $2.9 \times 10^{-8}$  M at 25 °C [24]. Therefore at pH < 8.5 HClO is the dominant form, while at pH > 8.5  $\text{ClO}^-$  is the dominant form. Therefore, the enhancement in peak current at higher pH values can be due to the dominance of  $\text{OCl}^-$  ion [25,26].

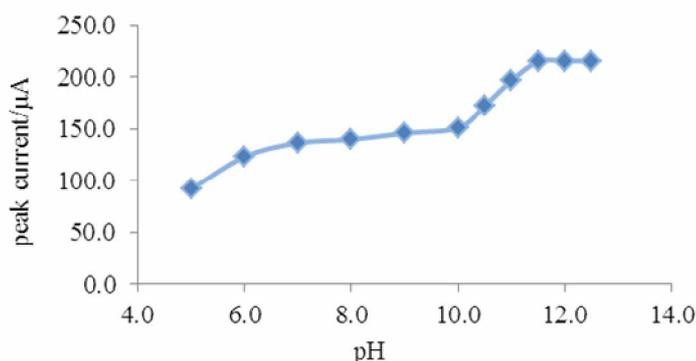
The effect of potential scan rate on the cyclic voltammetric response of  $\text{OCl}^-$  ion was studied. Peak current is dependent on the scan rate. This dependency can be used to deduce the corresponding electrochemical parameters. The effect of scan rate in the range 5-400  $\text{mV s}^{-1}$  was studied. Figure 5 shows the cyclic voltammograms for the oxidation of 500  $\mu\text{g ml}^{-1}$   $\text{OCl}^-$  ion on the modified CPE at different scan rates in 0.1 M  $\text{KNO}_3$  solution at pH 12.0. The relation between  $\text{OCl}^-$  ion oxidation peak current ( $I_p$ ) and the scan rate ( $v$ ) was linear. This confirms that the electrode process is predominantly adsorption controlled. The linear regression equation was obtained as:

$$I_{pa} (\mu\text{A}) = 0.4119 v (\text{mV s}^{-1}) + 19.738 (r^2 = 0.998) \quad (3)$$

This figure also shows that the potential of the electro-



**Fig. 3.** Effect of the electrode composition on the stripping peak current for 500.0 µg ml<sup>-1</sup> of ClO<sup>-</sup> solution. Condition: deposition potential, 0.500 V vs. Ag/AgCl; deposition time, 120 s; resting time, 10 s; pulse amplitude, 0.07 V; dc voltage step height, 5 mV.



**Fig. 4.** Effect of pH on the stripping peak current for 500.0 µg ml<sup>-1</sup> of ClO<sup>-</sup> solution. Condition: deposition potential, 0.500 V vs. Ag/AgCl; deposition time, 120 s; resting time, 10 s; pulse amplitude, 0.07 V; dc voltage step height, 5 mV.

oxidation peak is positively shifted by increasing the scan rate. This confirms the irreversibility of the electro-oxidation reaction of OCl<sup>-</sup> ion [27]. The plot of  $E_p$  vs.  $\log v$  was linear with a correlation coefficient of 0.992. The dependency of peak potential and  $\log v$  was obtained as:

$$E_p(\text{V}) = 0.108 \log v (\text{V s}^{-1}) + 1.326 \quad (4)$$

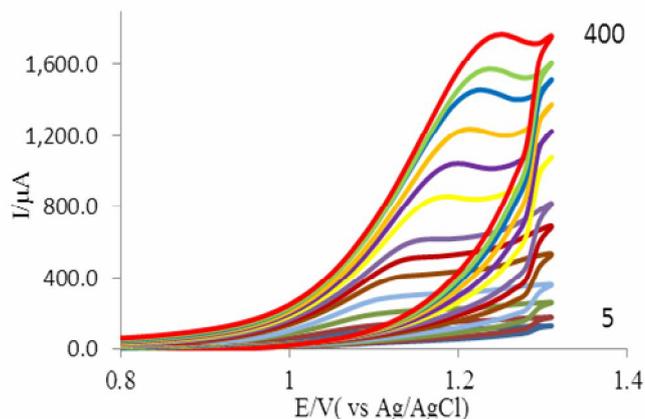
The linear relationship between  $E_{pa}$  and the  $\log v$  indicates a kinetic limitation in the reaction between Al<sub>2</sub>O<sub>3</sub>/CPE and OCl<sup>-</sup> ion. Therefore according to Laviron [28]  $E_p$  can be expressed by the following equation,

$$E_p = E^0 + (2.303 RT/\alpha nF) \log (RTk_0/\alpha nF) + (2.303 RT/\alpha nF) \log v \quad (5)$$

The slope of the plot of  $E_p$  vs.  $\log v$  can be used for the determination of  $\alpha n$ . The slope of the  $E_p - \log v$  line was obtained as 0.108. By considering the obtained slope, at 298 K,  $\alpha n$  was found to be 0.45. The following equation is used to calculate  $\alpha$  [28]:

$$E_{p/2} - E_p = 1.857(RT/\alpha F) \quad (6)$$

$E_{p/2}$  stands for the potential at  $I_p/2$ . From this equation  $\alpha$  was



**Fig. 5.** Dependence of the cyclic voltammetric response at  $\text{Al}_2\text{O}_3/\text{CPE}$  on sweep rate in  $500 \mu\text{g ml}^{-1}$   $\text{OCl}^-$  in  $\text{KNO}_3$  solution at pH 12.0. Scan rates from bottom to top: 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400  $\text{mV s}^{-1}$ .

found to be 0.38 for the modified electrode. Therefore, from the slope of the Eq. (5)  $n$  was calculated as  $0.97 \approx 1$ . The first elementary reaction of  $\text{ClO}^-$  (*ca.* 1.1 V *vs.* Ag/AgCl) is its oxidation to chloroxyl radical ( $\text{ClO}^\cdot$ ) at the electrode surface [26]:



The produced chloroxyl radical is converted to the final products by a disproportionation reaction [29]:



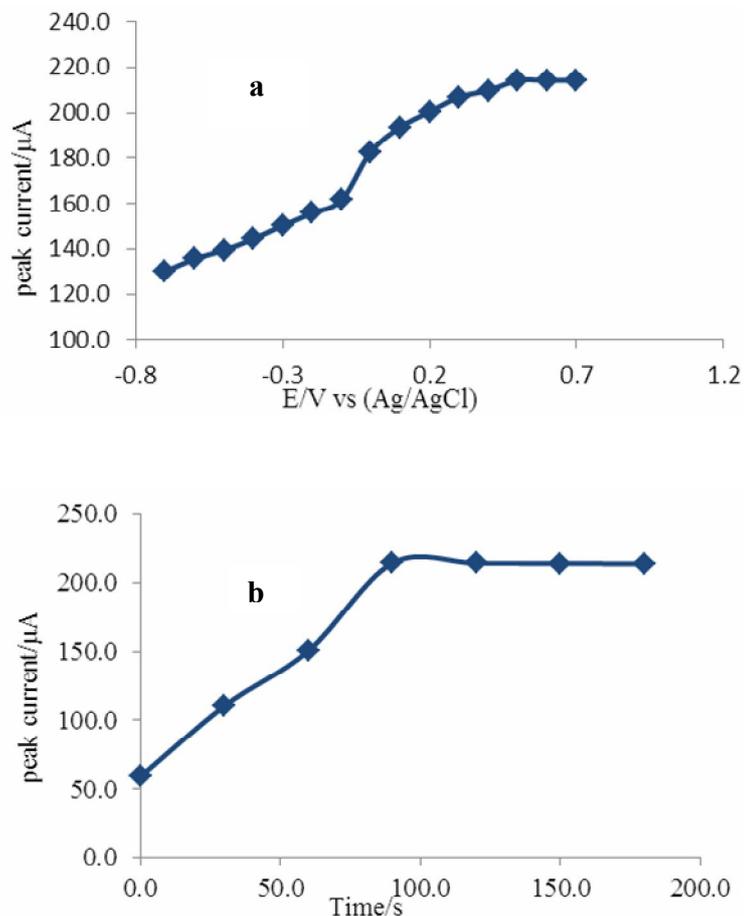
Accumulation time and potential may affect the response of the adsorption controlled electrode processes. As described above, the results of the investigations showed that the electro-oxidation of  $\text{ClO}^-$  at  $\text{Al}_2\text{O}_3/\text{CPE}$  was found to be predominantly adsorption controlled. Therefore, the effects of accumulation potential in the potential range  $-0.700$  to  $0.700$  V *vs.* Ag/AgCl and accumulation time in the range 0-180 s on the electrode response were investigated. Other parameters were selected in their optimum values described above. The results are given in Fig. 6. As Fig. 6a shows the peak current increased by changing accumulation potential from  $-0.700$  V up to  $0.500$  V and then remained nearly constant. This is due to the better adsorption of negatively charged  $\text{OCl}^-$  ion at the positively charged

electrode surface. Therefore, in order to accumulate  $\text{ClO}^-$  at the electrode surface a potential of  $0.500$  V *vs.* Ag/AgCl was applied. Increase in accumulation time between 0-100 s increased  $I_p$  linearly, and remained nearly constant after that (Fig. 6b). Other parameters were adjusted in their optimum values. Therefore a preconcentration time of 120 s was selected as optimal.

Instrumental parameters including pulse amplitude, resting time and dc voltage step height were also optimized to obtain maximum anodic peak currents and also well-defined peak shapes. Based on the results, pulse amplitude of  $0.07$  V, a resting time of 10 s and a dc voltage step height of  $5$  mV were selected as the optimum values.

### Analytical Characteristics

To obtain the calibration equation, anodic stripping peak current for  $\text{Al}_2\text{O}_3/\text{CPE}$  at different concentrations of  $\text{OCl}^-$  ion under the optimum conditions described above were determined. The calibration equation was then obtained by regression of the anodic stripping peak current on  $\text{OCl}^-$  ion concentration. Figure 7a shows the DPVs for different concentration of the analyte. The net differential pulse voltammogram peak currents were plotted against the analyte concentration in Fig. 7b. As shown in Fig. 7b, the relationship between anodic stripping peak current with  $\text{OCl}^-$  ion concentration was linear in the range  $0.1$ - $800 \mu\text{g ml}^{-1}$ . The linear regression equation was



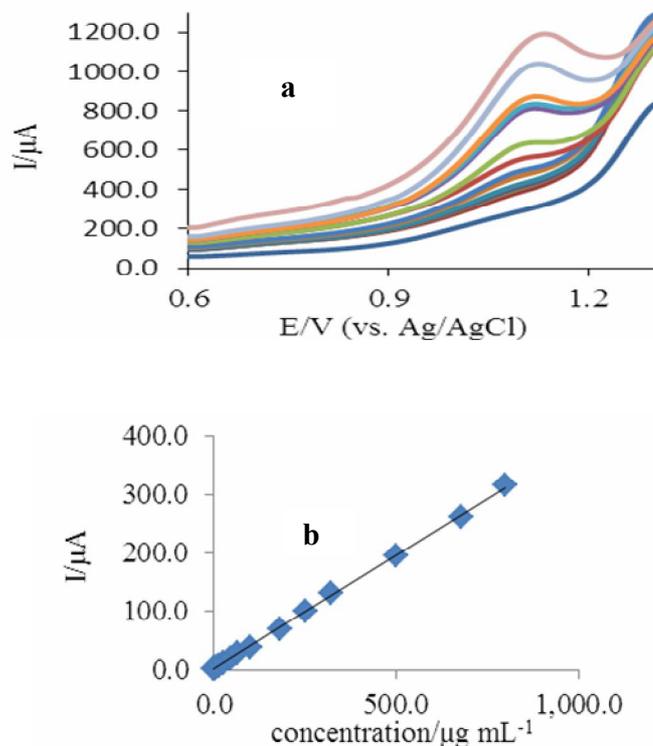
**Fig. 6.** Effect of deposition potential (a) and deposition time (b) on the anodic stripping peak current for 500.0  $\mu\text{g ml}^{-1}$  of  $\text{OCl}^-$  solution. Condition: pH 12.0; deposition potential, 0.500 V vs. Ag/AgCl or deposition time, 120 s; resting time, 10 s; pulse amplitude, 0.07 V.

$I_p (\mu\text{A}) = 0.388 C_{\text{ClO}^-} (\mu\text{g ml}^{-1}) + 1.061$  ( $r^2 = 0.999$ ). The detection limit ( $3S_b/m$ ) and quantification limit ( $10S_b/m$ ) was determined from 10 blanks as 0.02 and 0.08  $\mu\text{g ml}^{-1}$ , respectively.

#### Repeatability, Reproducibility and Stability of the $\text{Al}_2\text{O}_3/\text{CPE}$

To obtain the repeatability of the proposed sensor, the proposed modified electrode was applied to the six determinations of standard  $\text{ClO}^-$  solutions with the same concentration using the same electrode and the relative standard deviation (RSD) was calculated. The results showed an RSD of 2.3% for six determinations

of 500.0  $\mu\text{g ml}^{-1}$  of  $\text{ClO}^-$  solution. To evaluate the reproducibility of the electrode six different electrodes were prepared from the same batch. The electrodes were then applied to the analysis of 500.0  $\mu\text{g ml}^{-1}$  of  $\text{ClO}^-$  solution. The RSD for the responses between electrodes was found to be 2.8%. Therefore the repeatability and reproducibility of the method is acceptable. The stability of the electrode was tested by comparing the obtained electrode response at different weeks. The electrode response towards 500.0  $\mu\text{g ml}^{-1}$  of  $\text{ClO}^-$  solution remained at more than 95% of the response for freshly prepared electrode even after 9 weeks. After 9 weeks the response of the electrode decreased and the noise in the responses increased.



**Fig. 7.** (a) Net differential voltammograms for  $\text{Al}_2\text{O}_3/\text{CPE}$  in the solutions with different concentrations of  $\text{ClO}^-$ . Conditions: pH 12.00; deposition potential, 0.500 V vs. Ag/AgCl; deposition time, 120 s; resting time, 10 s; pulse amplitude, 0.07 V. (b) calibration curve.

Therefore, the proposed electrode is suitable for the routine analysis of  $\text{ClO}^-$  in real samples due to its good repeatability, reproducibility and stability.

### Selectivity

Selectivity of the proposed sensor was determined by investigation of the effect of various chemical species on the determination of  $50.0 \mu\text{g mL}^{-1}$   $\text{ClO}^-$  ion in optimum condition. The investigated chemical species are those which may coexist with the target analyte in real samples. A relative error of less than  $\pm 5\%$  was considered tolerable. The desired species was added to the  $\text{ClO}^-$  solution and the recommended procedure was followed. The results showed that the following ions did not interfere at  $5000.0 \mu\text{g mL}^{-1}$ :  $\text{IO}_4^-$ ,  $\text{IO}_3^-$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ . Ethanol (200), uric acid (100), HOAc (100), ascorbic acid (100), glucose (100),  $\text{H}_2\text{O}_2$  (100) and cysteine (100), did not interfere with

the determination of  $100.0 \mu\text{g mL}^{-1}$   $\text{ClO}^-$ , where the data in the parentheses are the concentration ratios. Results show good selectivity for the proposed sensor.

### Analytical Applications

To study the applicability of the proposed sensor to real samples, it was used to quantitate  $\text{ClO}^-$  in tap water, stank water, liquid milk and yogurt samples.  $\text{ClO}^-$  has been added to milk to increase the product shelf life [30]. The samples were also tested after spiking with different known concentrations of the analyte. Results are given in Table 1. As the results show there is a good agreement between the proposed method and reference method [31] for the determination of  $\text{ClO}^-$  ion in the investigated samples. The recovery values were between 96.0 and 104.5%, which is an acceptable range. This indicates great potential of the proposed sensor for rapid, simple and accurate determination of  $\text{ClO}^-$  ion in water and dairy samples.

**Table 1.** Results for the Determination of  $\text{ClO}^-$  ( $\mu\text{g ml}^{-1}$ ) in Various Water and Dairy Samples Using the Proposed Electrode (N = 5)

Sample	Added ( $\mu\text{g ml}^{-1}$ )	Found ( $\mu\text{g ml}^{-1}$ ) <sup>a</sup>	Reference method [31] ( $\mu\text{g ml}^{-1}$ )	Recovery
Tap water	0.0	$0.5 \pm 0.1$	0.6	-
	5.0	$5.6 \pm 0.2$	-	102
	10.0	$10.2 \pm 0.1$	-	97
Swimming pool water	-	$4.5 \pm 0.2$	4.3	-
	10.0	$14.1 \pm 0.3$	-	96
	20.0	$25.2 \pm 0.1$	-	103.5
Well water	-	$8.5 \pm 0.4$	8.8	-
	5.0	$13.9 \pm 0.3$	-	108
	10.0	$18.9 \pm 0.3$	-	104
Milk 1	0.0	ND <sup>b</sup>	-	-
	5.0	$5.1 \pm 0.3$	-	102
	10.0	$10.4 \pm 0.4$	-	104
Milk 2	0.0	ND	-	-
	5.0	$4.8 \pm 0.3$	-	96
	10.0	$10.2 \pm 0.5$	-	102
	20.0	$20.5 \pm 0.08$	-	102.5
Yogurt	0.0	ND	-	-
	5.0	$4.8 \pm 0.7$	-	96
	10.0	$10.3 \pm 0.4$	-	103
	20.0	$20.9 \pm 0.6$	-	104.5

<sup>a</sup>Mean $\pm$ standard deviation (n = 5). <sup>b</sup>Not detected.

### Comparison of the Proposed Electrode with other Electrodes

A comparison between the analytical characteristics for the proposed modified electrode for the determination of  $\text{ClO}^-$  with the previously reported modified electrodes is given in Table 2. The proposed electrode provides a wider linear range and much better LOD as compared to the

reported ones [32-35].

### CONCLUSIONS

Alumina nanopowder was an efficient modifier for modification of CPE using as an electrochemical sensor for the determination of  $\text{OCl}^-$  ion. The sensor exhibited

**Table 2.** Comparison of some Characteristics of the Different Modified Electrodes Reported for the Determination of ClO<sup>-</sup>

Technique <sup>a</sup>	Type of electrode <sup>a</sup>	LOD ( $\mu\text{g ml}^{-1}$ )	Linear range ( $\mu\text{g ml}^{-1}$ )	Ref.
Amperometry	MnTAPP- nano Au modified GCE	-	797.15-1.78	[32]
Amperometry	AuNPs/PEDOT modified GCE	0.07	0.07-69.43	[33]
LSV	Gold, platinum and GC electrode	1.0	4.0-400.0	[34]
LSV	Graphite electrode	1.0	12.5-300.0	[35]
DPASV	Al <sub>2</sub> O <sub>3</sub> /CPE	0.02	0.1-800	This work

<sup>a</sup>LSV: linear sweep voltammetry, DPASV: differential pulse anodic stripping voltammetry, MnTAPP: manganese tetra (o-amino phenyl) porphyrin, GCE: glassy carbon electrode, AuNPs/PEDOT: poly (ethylenedioxythiophene) and gold nanocomposite, CPE: CPE.

excellent analytical performance and can be used for the determination of the analyte in water and dairy samples. The modified electrode enhanced the OCl<sup>-</sup> ion electrooxidation peak current by both increasing the electrode surface and its preconcentration by adsorption process. The modifier did not exhibit electrocatalytic effect on the oxidation of the analyte. The electrooxidation peak potential was pH independent. This shows the electrode reaction is the electrooxidation of OCl<sup>-</sup> ion to chloroxyl radical.

## REFERENCES

- [1] W. Shu, L. Yan, Z. Wang, J. Liu, S. Zhang, C. Liu, B. Zhu *Sens. Actuators B* 221 (2015) 1130.
- [2] J. Fauvarque, *Pure Appl. Chem.* 68 (1996) 1713.
- [3] M. Zehnder, D. Kosicki, H. Luder, B. Sener, T. Waltimo, *Oral Surg. Oral Med. Oral Pathol. Oral Radiol. Endod.* 94 (2002) 756.
- [4] S. Khatib, R. Musa, J. Vaya, *Bioorg. Med. Chem.* 15 (2007) 3661.
- [5] K. Xiong, F. Huo, C. Yin, J. Chao, Y. Zhang, M. Xu, *Sens. Actuators B* 221 (2015) 1508.
- [6] D.J. Leggett, N.H. Chen, D.S. Mahadevappa, *Analyst* 107 (1982) 433.
- [7] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, *Vogel's Text Book of Quantitative Chemical Analysis*, 6th Ed., Pearson, 2009
- [8] J. Ballesta Claver, M.C. Valencia Mirón, L.F. Capitón-Vallvey, *Anal. Chim. Acta* 522 (2004) 267.
- [9] A.P. Soldatkin, D.V. Gorchkov, C. Martelet, N. Jaffrezic-Renault, *Sens. Actuators B* 43 (1997) 99.
- [10] A.Y. Olenin, E. G. Olenina, *J. Anal. Chem.* 73 (2018) 465.
- [11] M. Vedamalai, D. Kedaria, R. Vasita, I. Gupta, *Sens. Actuators B* 263 (2018) 137.
- [12] A. Afkhami, M. Moradi, A. Bahiraei, T. Madrakian, *Anal. Bioanal. Chem. Res.* 5 (2018) 41.

- [13] M. Kotoucek, M. Opravilova, *Anal. Chim. Acta* 329 (1996) 73.
- [14] A. Guiberteau, T.G. Diaz, F.Salinas, J.M. Ortiz, *Anal. Chim. Acta* 305 (1995) 219.
- [15] M. Javanbakht, H. Khoshsafar, M.R. Ganjali, *Electroanalysis* 20 (2008) 203.
- [16] V. Izadkhah, M. Rezaei, J. Mahmoodi, *Anal. Bioanal. Chem. Res.* 6 (2019) 405.
- [17] M. Mazloun Ardakani, H. Beitollah, M.K. Amini, F. Mirkhalaf, M.A. Alibeik, *Sens. Actuators B* 151 (2010) 243.
- [18] M.A. Sheikh-Mohseni, *Anal. Bioanal. Chem. Res.* 6 (2019) 341.
- [19] B. Narayana, M. Mathew, K. Vipin, N.V. Sreekumar, T. Cherian, *J. Anal. Chem.* 8 (2005) 706.
- [20] U.T. Yilmaz, Z. Yazar, *Food. Anal. Methods* 5 (2012) 119.
- [21] D.K. Gosser, *Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms*, VCH, New York, 1993, pp. 43.
- [22] E.M. Morefie, G.E. Peck, S.L. Hem, J.R. Feldka, J.L. White, *J. Pharm. Sci.* 47 (1985) 1019.
- [23] A. Tasaka, T. Tojo, *J. Electrochem. Soc.* 132 (1985) 1855.
- [24] J.C. Morris, *J. Phys. Chem.* 70 (1966) 3798.
- [25] N. Ibl, D. Landolt, *J. Electrochem. Soc.* 115 (1968) 713.
- [26] A.B. Djordjevic, B.Z. Nikolic, I.V. Kadija, A.R. Despic, M.M. Jaksic, *Electrochim. Acta* 18 (1973) 465.
- [27] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
- [28] E. Laviron, *J. Electroanal. Chem.* 101 (1979) 19.
- [29] L. Czarnetzki, L.J.J. Janssen, *Electrochim. Acta* 33 (1988) 561.
- [30] C.F. Nascimento, P.M. Santos, E.R. Pereira-Filho, F.R.P. Rocha *Food Chem.* 221 (2017) 1232.
- [31] L.H. Keith, *Compilation of EPA's Sampling and Analysis Method*, CRC Press Inc., Boca Raton, FL, 2000.
- [32] S. Thiagarajan, Z.Y. Wu, S.M. Chen, *J. Electroanal. Chem.* 661 (2011) 322.
- [33] T.H. Tsai, K.C. Lin, S.M. Chen, *Int. J. Electrochem. Sci.* 6 (2011) 2672.
- [34] F. Kodera, M. Umeda, A. Yamada, *Anal. Chim. Acta* 537 (2005) 293.
- [35] K.A.S. Pathiratne, S.S. Skandaraja, E.M.C.M. Jayasena, *J. Natu. Sci. Foundation Sri Lanka* 36 (2008) 25.