# Analysis of Some Selected Persistent Organic Chlorinated Pesticides in Marine Water and Food Stuffs by Differential Pulse-Cathodic Stripping Voltammetry

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**Abstract**
Based on the redox characteristics of two selected organochlorine pesticides namely alachlor (ALC) and chlorfenvinphos (CHL) in Britton–Robinson (B–R) buffer at a hanging mercury drop, Pt and Au working electrode (HMDE), a fast, simple and selective differential pulse cathodic stripping voltammetric (DP CSV) method was developed for their determination. The cathodic stripping peak currents for ALC versus concentrations was linear in the range from $7.4\times10^{-9}$ to $1.4\times10^{-7}$ mol L$^{-1}$ and in the range from $2.7\times10^{-9}$ to $1.6\times10^{-8}$ mol L$^{-1}$ for CHL. The method was applied for the analysis of trace concentrations of ALC and CHL in fresh- and marine water (Atlantic and Red Sea) and sediment samples and food stuffs.

**Keywords:** Organochlorine pesticides, Stripping voltammetry, Determination, Maine water and sediment, Food stuffs

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## 1 Introduction

After the Second World War, scientists began to recognize that, certain chemical pollutants were capable persistent in the environment for long time, migrating in air, water, soil and sediments and accumulating to levels that could harm wildlife and human health. These chemical pollutants are called Persistent Organic Pollutants (POPs) [1]. POPs are typically "water-hating" and "fat-loving" chemicals, i.e. hydrophobic and lipophilic. In aquatic systems and soils they partition strongly to solids, notably organic matter, avoiding the aqueous phase [1]. POPs are toxic chemicals, characterized by being subject to bioaccumulation potential and long-range transport capacity [2]. These contaminants are present at different concentrations in sewage sludge and are transferred to soil matrix, as soils have a high capacity to act as reservoirs of organic pollutants [2]. For agrochemical POPs the source is clear – the deliberate application to crops and soils. POPs are also entered our environment from a whole host of combustion sources, from metal refining and as impurities other, deliberately manufactured chlorinated compounds e.g. pentachlorophenol and organochlorinated pesticides (OCPs).

Organochlorine pesticides (OCPs) have been of great concern because of their harm effects, their deleterious effect on nontarget organism, large production and usage, ubiquity, bioaccumulation and magnification in the food chain and persistence in our environment [3]. Herbicides or pesticides, define as a class of chemical substances used against organisms damaging humans, animals and plants, like insects, fungi, moulds, nematoda, and rodents. For their wide spread use and physical–chemical properties, these compounds represent an important class of pollutants for ground and surface water resources. The persistence of pesticides in the water environment depends upon doses, nature (that characterizes resistance to degradation process, dispersion and mobility), pedologic recipient soils and the hydrogeologic characteristics of the area involved. Contamination of ground waters may take a long time, even decades [4,5]. The concept of quality in analytical chemistry is mainly associated with the fact of reaching the maximum level of analytical properties for a given method [6].

Last decades have seen an upsurge of interest on developing precise methods for the determination of persistent organic pollutants (POPs) e.g. chlorinated pesticides, polychlorinated biphenyls in the environment [1]. The determination of pesticides and herbicides in many environmental matrices is generally determined by SPE-LC-ESI-MS/MS [7], UPLC-MS/MS [8], HPLC [9], GC/MS [10,11] and LC-MS/MS [12] and polarographic [15,16] and voltammetric [17–19] methods. Recent years have seen an upsurge of interest for rapid and sensitive analyti-

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cal methods for the determination of chlorinated pesticides in environmental samples e.g. water, sediment and air. A recent literature survey on the analysis of POPs has revealed little work [15–17] on the use of stripping voltammetry or any other electrochemical technique for the analysis of OCPs. Thus, the present manuscript reports the redox behavior of the pesticides alachlor and chlorfenvinphos at the hanging mercury drop, Pt and working electrodes in an attempt to develop a fast, simple, low cost and selective DP CSV method for their analysis in vegetables (spinach and carrot), cow cheese, tap and marine water (Red Sea and Atlantic Ocean) and sediment. On the other hand, the most probable reduction mechanism of the electrogenerated species was properly assigned.

## 2 Experimental

### 2.1 Apparatus

A Metrohm 757 VA trace analyzer and 747 VA stand (Basel, Switzerland) were used for recording the cyclic, linear and differential pulse cathodic stripping voltammetry. A three-compartment borosilicate (Metrohm) voltammetric electrochemical cell (10 mL) configuration incorporating hanging mercury drop electrode (HMDE, drop surface area 5 $mm^2$) as a working electrode, double-junction Ag/AgCl,(3 M) KCl, as a reference and platinum wire (BAS model MW-1032) as counter electrodes, respectively. Platinum (Pt, surface area 2 $mm^2$) and gold (Au, surface area 2 $mm^2$) were also used as working electrodes. Pesticide was measured with a Shimadzu GC-17A, GC MS QP-5000 Mass spectrometer, Colum C18. The detector and the injector temperature were maintained at 280 °C. The column was held isothermally at 50 °C $min^{-1}$, then the temperature was programmed at 25 °C $min^{-1}$ to 150 °C and finally programmed at 10 °C $min^{-1}$ from 125 to 280 °C with a holding time of 10.5 min and injection volume of 2 μL [18]. A digital micropipette 10–100 μL (Volac) was used for transferring the sample solutions to the electrochemical cell. A pH-meter (model MP220, Metter Toledo) was used for pH measurements. A soxhlet extractor and a rotary evaporator were used for the extraction of the pesticides from the sediment or vegetables samples with *n*-hexane–acetone [19], respectively. An aqua wave Barnstead/Lab–Line ultrasonic bath (Model 9372) was used for the extraction of ALC and CHL compounds from the vegetable samples. Deionized water was obtained from A Milli-Q Plus water purification system (Milford, MA, USA) throughout the work.

### 2.2 Reagents and Materials

Analytical reagent grade (A.R) chemicals were used except otherwise specified. Standard solutions of the chlorinated pesticide alachlor (ALC) and chlorfenvinphos (CHL) in methanol (10.0 μg $mL^{-1}$) were purchased from Merck (Darmstadt, Germany) and stored in a refrigerator at 4 °C. Diluted solutions of each pesticide were prepared in water. A series of B–R buffer (pH 2.3–11) solutions was prepared [20] and was used as supporting electrolyte. Silica gel, anhydrous sodium sulfate, anhydrous magnesium sulfate, acetone and *n*-hexane were purchased from BDH (Poole, England).

### 2.3 Recommended DP CSV Procedures

The electrochemical cell was precleaned by soaking in nitric acid (10 % v/v) and washed with de ionized water. The general procedures were preceded as follows: An accurate volume (10 mL) of an aqueous solution containing B–R buffer as supporting electrolyte of pH 2–3 was placed in the cell. The solution was stirred and purged with nitrogen gas for 10 min before recording the voltammogram. The stirrer was then stopped and after 10 s quiescence time, the background voltammogram of the supporting electrolyte was recorded by applying a negative going potential scan from 0 to −1.5 V vs. Ag/AgCl at a deposition potential of −0.35 V, accumulation time of 660 s and 750 s; scan rate of 50 mV $s^{-1}$ and pulse amplitude of 50 mV. After recording the voltammogram of the blank solution, an accurate concentration ($8.35\times10^{-8}$–$11.1\times10^{-8}$ mol $L^{-1}$) of the chlorinated pesticide was placed into the electrochemical cell. The solution was stirred and purged with nitrogen gas for 5 min and the stirrer was then stopped. After 10 s quiescence time, the voltammogram of the pesticide was finally recorded by applying a negative going potential scan from 0.0 to −1.5 V vs. Ag/AgCl under the same experimental conditions as for the blank set up.

### 2.4 Applications

#### *2.4.1 Analysis of the Chlorinated Pesticides in Fresh and Marine Water Samples*

Tap- or Red Sea water samples collected from the coastal area of Jeddah City, Saudi Arabia and Atlantic Ocean (Elizabeth Port, South Africa) water were filtered through 0.45 μm cellulose membrane filter and stored in LDPE sample bottles. The recommended electrochemical procedures used for the standard curve of pesticides determination at pH 2–3 were finally followed. Alternatively, the standard addition method was used as follows: transfer known volumes (1.0–2.0 mL) of sample extract adjusted to pH 2–3 into the electrochemical cell. Measure the peak current displayed by the test solution before and after addition of various volumes of the standard ALC or CHL pesticide. The change in the peak current was then recorded and used for determining both pesticides.

#### *2.4.2 Analysis of the Chlorinated Pesticides in Marine Sediment (Elizabeth Port, South Africa)*

An accurate weight (5.0 ± 0.001 g) of the marine sediment was extracted with *n*-hexane –acetone (1:1 v/v, 90.0 mL)

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for 8 h in a soxhlet extractor. The organic extract was then filtered through the filter paper as reported [19]. The *n*-hexane–acetone extract and the washings were transferred to measuring flask (250 mL) and completed to the mark with the same solvent. An accurate volume (2.0 mL) of the *n*-hexane–acetone extract was transferred to the voltammetric cell and analyzed by the recommended DP CSV procedure in the presence of various volumes (10–60 μL) of the standard (1.0 μg mL$^{-1}$) pesticide. The pesticide concentration was then determined via the standard curve.

#### 2.4.3 *Analysis of the Chlorinated Pesticides in Vegetable Samples*

Spinach and Carrot are the most common plants to be affected by the chlorinated pesticides [7]. Therefore, the edible part of spinach and carrot samples was first removed, freeze-dried and stored and analyzed according the method of Gonzalez-Rodriguez et al. [7] as follows: An accurate weight (20–25 g) of the shopped vegetable samples were placed in a 125 mL glass container and extracted with *n*-hexane–acetone (1:1 v/v, 60 mL).The glass container was vigorously homogenized in an ultrasonic bath for 10 min followed by NaCl (3 g) and anhydrous magnesium sulfate (12 g). The sample solution was then shaken vigorously with *n*-hexane–acetone for 5 min and left for equilibration for 10 min. The organic extract was separated out by filtration through filter paper and concentrated in a rotary evaporator [21,22].

#### 2.4.4 *Analysis of the Chlorinated Pesticides in Cheese of Cow Milk Sample*

The extraction of the tested compounds from cheese of cow milk samples ((taken from animals grazing on polluted field) was carried out by matrix solid phase dispersion (MSPD) as reported earlier by Bordajandi et al. [22]. In this experiment, an accurate weight (5–10 g) of the cheese sample was mixed with 20 g of a solid mixture containing silica gel and anhydrous sodium sulfate (1:1 w/w). The solid mixture was homogenized, grounded to a fine powder and homogenously packed onto the column accurately. The required compounds were then recovered from the column with *n*-hexane–acetone (150 mL) at a reasonable flow rate (7–10 mL min$^{-1}$) and finally subjected to clean up process as described [21].

## 3 Results and Discussion

### 3.1 Electrochemical Behavior of the Tested Chlorinated Pesticides

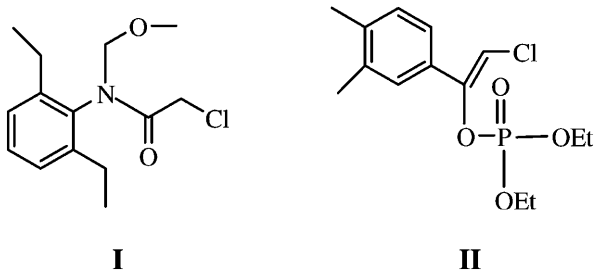
The influence of the aqueous solution pH employing B–R buffer (pH 2.3–11) on the DP CSV behavior of the pesticides ALC and CHL species at the HMDE surface was critically investigated. Over the studied pH 2.3–6.0, the DP CSV of the two pesticides displayed two well defined cathodic peaks in the range from −1.05 to −1.08 V (peak I) and −1.3 to −1.4 V (peak II) versus Ag/AgCl electrode. Representative results are given in Figure 2. In the DP CSVs of ALC and CHL pesticides at $2 < pH < 6$, the first cathodic peak is most likely assigned to the reduction of the carbonyl group (–C=O) and phosphate ester (–P=O) (Figure 1) in one step via 2 $H^+$/2e electrochemical process forming –CH–OH– and –PH–OH reduced species, respectively. A representative assignment is given in Scheme 1. The second cathodic peak is safely assigned to the reduction of the adsorbed hydrogen ($H^+ + e \leftrightarrow H$ ads.) catalyzed by the pesticide. The second cathodic peak is safely assigned to the reduction of the adsorbed hydrogen. The assignment of this peak of ALC or CHL pesticide was confirmed by recording the residual current of the DP CSVs at the same pH 2–3 in the absence and in the presence of various concentrations of ALC or CH (Figure 3). The observed increase in the second peak on raising the pesticide concentrations confirms that, the reduction of hydrogen was catalyzed by ALC and CHL.

In the DP CSV, on raising the solution pH to pH 6, the potential of the cathodic peaks of both pesticides are shifted cathodically confirming the dependence of both peaks on the hydrogen ion concentration [22]. In solutions of $pH > 6$, no cathodic peaks for both pesticides were observed due to the difficulty of the reduction of –C=O of ALC and the –P=O phosphate ester of CHL and/or it may be reduced at more negative potentials outside the allowed potential window of the HMDE. The linear electrochemical processes for ALC and CHL can be expressed by the following regression equations:

$$E_{p,c1} = -0.029\ pH - 1.0074 \qquad (R^2 = 0.918) \qquad (1)$$

$$E_{p,c1} = -0.027\ pH - 1.0416 \qquad (R^2 = 0.841) \qquad (2)$$

with slopes of 0.029 and 0.027 mV/pH for ALC and CHL, respectively. These data confirmed the involvement of 2 $H^+$/ 2e in the first cathodic peak of both pesticides. On raising the solution pH, the first cathodic peak potential was shifted to more negative values suggesting that the electrode reactions involved hydrogen ions [22,23]. These data added further confirmation of the direct exchange of $2H^+/2e^-$ in one reduction processes converting the carbonyl and the phosphate ester groups in ALC and




**I** **II**

Fig. 1. Chemical structures of alachlor (I) and chlorfenvinphos (II).

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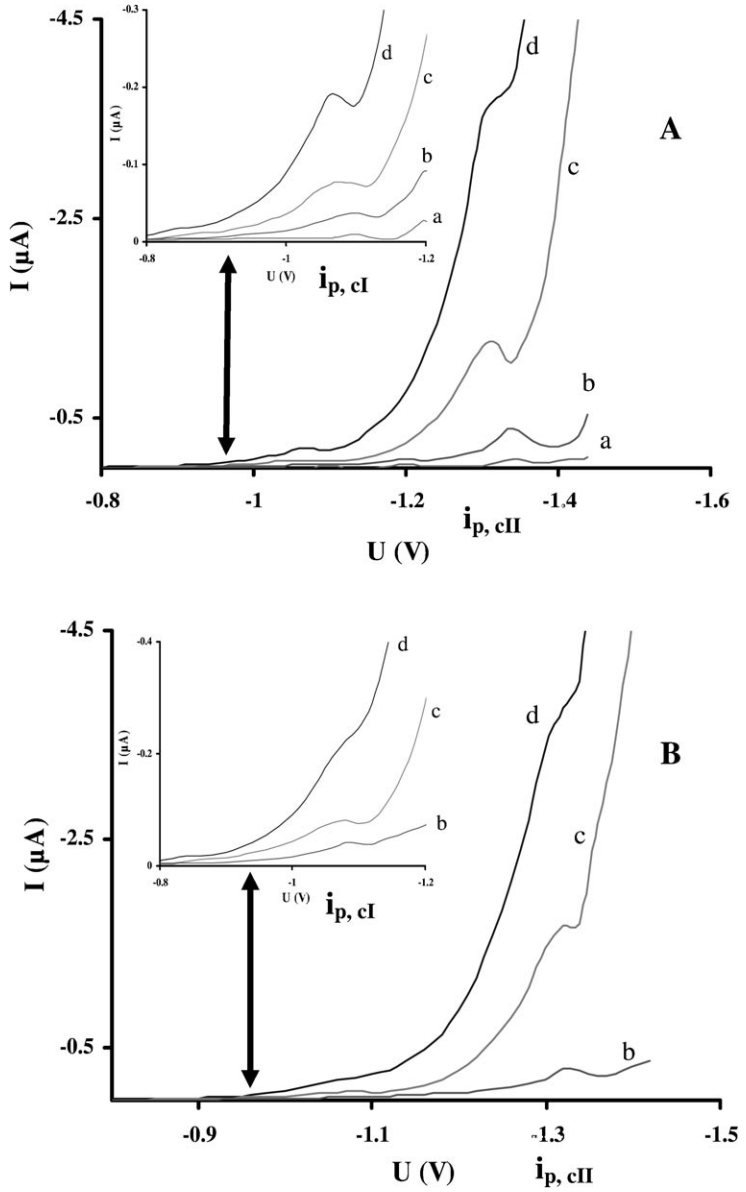
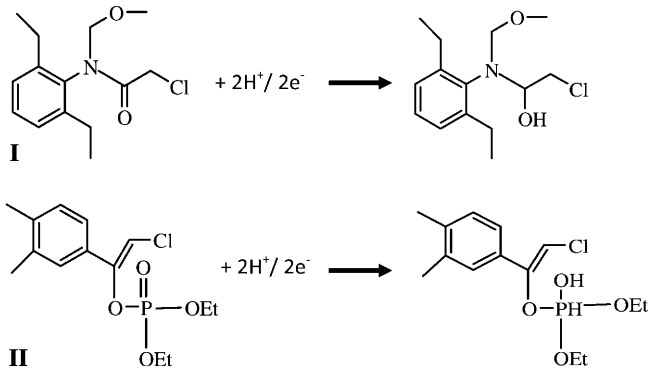



Fig. 2. DP CSV of alachlor (A) and chlorfenvinphos (B) in aqueous B–R buffer solution of pH 2.18 (a), 2.71 (b), 3.93 (c), and 5.08 (d) at the HMDE. Deposition time of 650 s; accumulation potential of −0.35 V; scan rate = 50 mV $s^{-1}$ and pulse amplitude of 50 mV vs. Ag/AgCl electrode.




Scheme 1. The proposed reduction mechanism of ALC (I) and CHL (II) at the HMDE.

CHL pesticides to –CH–OH and –PH–OH groups at pH < 6, respectively. Similar results were observed in previous studies [23]. At pH > 6, the reduction waves are ill defined and poorly resolved. The instability of the electrogenerated species, the fast electrode kinetics and the poor adsorption of the reduced species and hydrogen at the the surface of the HMDE may account of the observed trend [24]. Also, in slightly and/or alkaline solutions, such compounds may be reduced at more negative potential than the allowed potential window of the HMDE. Thus, the cleavage of the C=O and P=O groups of ALC and CHL in acidic solution involves $2H^+/2e^-$ electrochemical process in one single step, respectively. Therefore, it seems reasonable to assume from DP CSV voltammograms in the acidic media that, the reduction of

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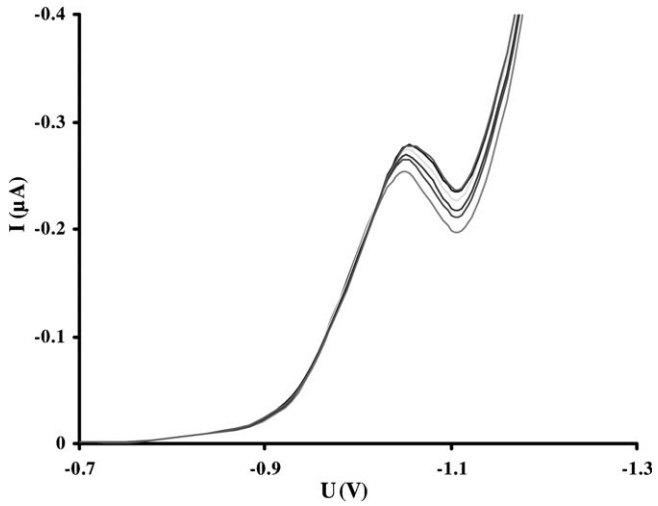


Fig. 3. DP-CSVs of chlorfenvinphos at pH 2–3 at HMDE vs. Ag/AgCl electrode at various concentrations. Deposition time of 650 s; accumulation potential of −0.35 V; scan rate = 50 mV $s^{-1}$ and pulse amplitude of 50 mV vs. Ag/AgCl electrode.

the –C=O and P=O groups for ALC and CHL is most likely involved two protons/two electrons (2 $H^+$/2e) reduction process. Figure 2.The DP-CSV of the complex showed a well-defined reduction peak in the range −0.1 to −0.55 V vs. Ag/AgCl reference electrode. At pH 2–3, well defined and symmetric cathodic peak was observed and the cathodic peak current ($I_{p,c}$) reached maximum. Thus, in subsequent work, the solution pH was adjusted at pH 2–3.At this pH, the cathodic peak was reproducible, sharp and symmetric with low background current.

The CVs of the ALC ($1.11\times10^{-6}$ mol $L^{-1}$) and CHL ($8.35\times10^{-6}$ mol $L^{-1}$) pesticides at pH 2–3 at different scan rates ($v$ = 20–5000 mV $s^{-1}$) in the potential range 0.2 to −1.5 V were carried out at the HMDE, Pt and Au working electrodes vs. Ag/AgCl electrode. Representative CVs at HMDE are given in Figure 4. At the HMDE, the CVs of both pesticides at −0.4 V deposition potential displayed one well defined cathodic peak in the range −1.1 to −1.18 V assigned to the reduction of the –C=O and P=O groups of ALC and CHL to CH-OH-and –PH-OH via 2 $H^+$/2e reduction process, respectively. On reversing the scan, no anodic peaks were observed suggesting the irreversible nature of the electrochemical process of both pesticides. At low scan rate (< 50 mV $s^{-1}$), the CVs of both pesticides showed no cathodic and/or anodic peaks indicating the poor adsorption and/or the instability of the reduced species at the HMDE.

In the CV, on raising the scan rate, the cathodic peak potential of both pesticides progressively shifted to more negative values and the plots of $E_{p,c}$ versus the scan rate (log $v$) were linear confirming the irreversible nature of the observed reduction processes and the surface reaction of the adsorbed pesticides [25]. Representative data are shown in Figure 5. The product of the number ($N_\alpha$) of the electron transfer involved in the reduction step and the corresponding charge transfer coefficient ($\alpha$) i.e. $\alpha$ $N_\alpha$ of the surface reaction of the adsorbed pesticides were calculated from the slope of the linear plot (Figure 5) employing the equation:

Assuming $n=2$, the values of α were found in the range 0.16–0.2 confirming the irreversible nature of the observed cathodic processes at the surface of the HMDE [24]. The number of the electrons transfered in the rate-determining step ($N_\alpha$) and the corresponding charge transfer coefficient ($\alpha$) i.e. $\alpha$ $N_\alpha$ at the HMDE were also determined from the influence of the scan rate Sawyer et al., 1984 [26]. Assuming $N_\alpha=2$, the values of $\alpha$ calculated from equations [26] was found < 0.5 confirming the irreversible nature of the electrode process.

The variations of the cathodic peak current function ($i_{p,c}/v^{1/2}$) with the scan rate were investigated. The $i_{p,c}/v^{1/2}$ was decreased progressively on raising the scan rate. Thus, the reduction process of the pesticides favor the well known chemical reaction coupled between two charge-transfer processes) of the type EC mechanism [27]. In the EC mechanism with an irreversible chemical reaction, the $i_{p,c}/v^{1/2}$ should decrease continuously with increasing scan rate. Thus, the product of this reduction step undergoes a very rapid follow-up chemical reaction [27]. The observed behavior may possibly be explained by considering that, the protonation reaction is very fast or virtually complete in an acid medium [27,28].

The effect of the type of the working electrode (HMDE, Pt, Au) was studied on the absence and presence of various concentrations of ALC and CHL pesticides at pH 2–3 at a wide range of scan rate (20–500 mV $s^{-1}$) vs. Ag/AgCl electrode. In the absence of the pesticide, the residual current was negligible. Representative CVs of CHL at Pt working electrode are shown in Figure 6A. At scan rate 20–200 mV $s^{-1}$, the CV of CHL showed one ill defined cathodic peaks in the range from −0.7 to −0.86 V (Peak I). On reversing the scan rate, one well defined anodic peak in the range from −0.28 to 0.02 V was observed. Similar trends were also observed for ALC confirming the irreversible nature of the reduction process of both pesticides at Pt electrode. On increasing the scan rate, the cathodic was shifted to more negative values, while the anodic peak was shifted anodically confirming the irreversible nature of the observed electrode couple [27].

The CVs of CHL at Au electrode (Figure 6B) at various scan rate (20–500 mV) were also recorded. At scan rate < 500 mV $s^{-1}$, two ill defined cathodic peaks (like shoulder) in the potential range −0.58 to −0.66 (peak I) and −0.7 to −0.8 (peak II) coupled with one well defined anodic peak in the potential range −0.2 to 0.14 V versus Ag/AgCl electrode (Figure 6B). A similar trend was noticed for the CV of ALC pesticide, too, where one cathodic peak in the range from −0.58 to −0.64 to −0.86 coupled with one anodic peak in the range from −0.22 to −0.14 V.

The dependence of the CV response on the analyte concentration was investigated at constant scan rate (200 mV $s^{-1}$).The results revealed no significant changes

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on the cathodic peak current vs. Ag/AgCl electrode indicating that, the electrochemical process is typical of an electrode coupled chemical reaction mechanism (EC) in which an irreversible first-order chemical reaction is interposed between the charges [27,28]. A comparison of the redox potentials of the ALC or CHL at HMDE, Pt and Au working electrodes indicated that, the two pesticides are easily reduced on the following order of potential:

$$Pt > Au > HMDE$$

The electron donating nature of mercury compared to Au and Pt electrodes may account for the observed trend. The surface coverage ($\Gamma$) of the tested pesticides (ALC or CHL) onto the working electrodes HMDE, Pt and Au was determined from their CVs at various scan rate by adopting the method used by Sharp et al. [29]. According to this method, the cathodic peak current is related to the surface concentration of the electro active species by the following equation [30,31]:

$$I_{p,c=}n^2F^2A\ \Gamma\ v/4RT \quad (4)$$

where $n$ represents the number of electrons involved in the reduction process, $A$ is the geometric surface area of the working electrode (HMDE, Pt, Au), $\Gamma$ (mol cm$^{-2}$) is the surface coverage, $v$ is the scan rate and other symbols have their usual meaning. Assuming $n=2$, the surface concentration ($\Gamma$) was calculated using the slopes of the linear regions of the $I_{p,c}$ versus scan rate plots. For ALC it resulted in $7.14\times10^{-5}$, $3.89\times10^{-1}$ and $5.08\times10^{-1}$ mol cm$^{-2}$ while, for CHL it resulted in $9.24\times10^{-5}$, $4.31\times10^{-1}$and $4.69\times10^{-1}$ mol cm$^{-2}$ at HMDE, Pt and Au electrodes, respectively, suggesting the possible use of the DP CSV at HMDE for the analysis of ALC or CHL in various environmental samples. Also, at the HMDE, the cathodic peak was well defined, sharp and symmetric. On the other hand, HMDE is the only electrode type sensitive enough for in situ measurements in natural waters [32–34]. This electrode is safe as long as storage and disposal of Hg is undertaken in a safe manner. Thus, in the subsequent work, HMDE was selected.

### 3.2 Analytical Parameters

The results of the surface coverage of the analytes and the sensitivity of the developed cathodic peak of ALC or CHL using DP CSV at HMDE, suggest the application of this technique for developing an accurate procedure for the determination of ALC and CHL pesticides in fresh and marine water, sediment and food stuffs e.g. vegetable, cheese of cow milk samples. Therefore, a detailed investigation was carried out to study the influence of different parameters that control the peak current, sensitivity and selectivity of the observed cathodic peaks. The influence of the pH employing (B–R) buffer on the peak current at peak potential of −1.07 V (peak I) for ALC and −1.05 V (peak I) for CHL versus Ag/AgCl electrode was studied

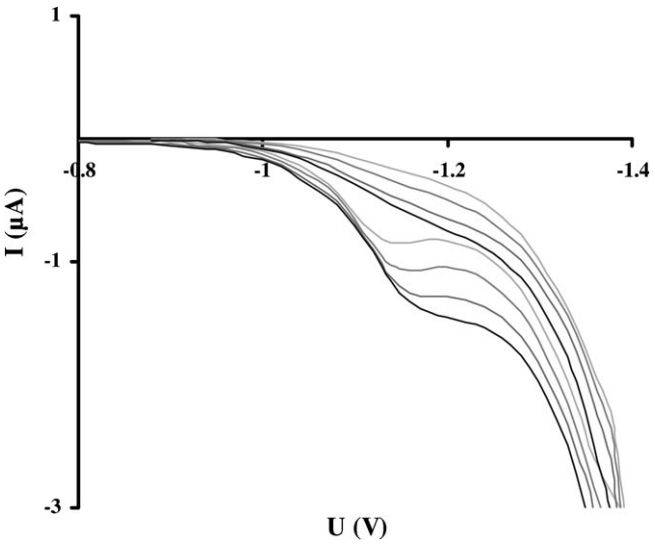


Fig. 4. Cyclic voltammograms of alachlor ($1.1\times10^{-6}$ mol L$^{-1}$) in B–R buffer (pH 2–3) at various scan rates: 500, 1000, 2000 and 3000 mV s$^{-1}$ at the HMDE vs. Ag /AgCl electrode.

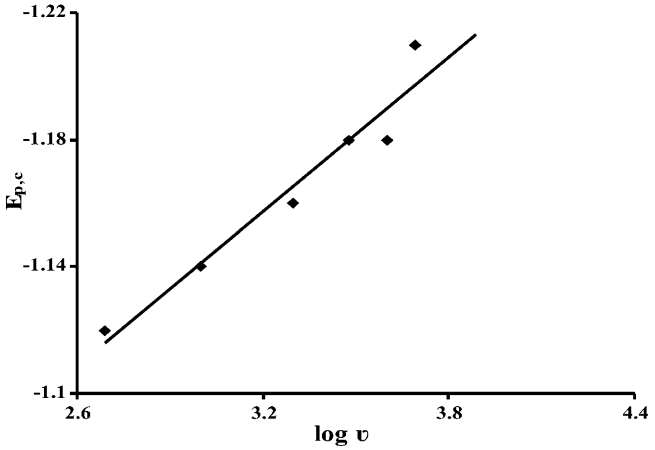


Fig. 5. Plots of $E_{p,c}$ vs. log $v$ of alachlor in B–R buffer (pH 2–3) at HMDE vs. Ag/AgCl electrode.

over a wide range of pH 2.3–11.0 at the HMDE. At pH 2–3, maximum peak current and well defined; symmetric, excellent background of the blank reading and reproducible peak was achieved for both ALC and CHL (Figure 2). Thus, in the subsequent work, the pH of the aqueous solution was kept at pH 2–3.

Accumulation time ($t_{acc}$) is one of the most important parameters in stripping procedures that has a pronounced effect on sensitivity, linear range and lower limit of detection [35]. Maximum peak current, well defined and sharp peak were obtained for both ALC and CHL was achieved at a deposition time of 660 and 750 s for both ALC and CHL pesticides (Figure 7). At longer adsorption time, peak current began to decrease suggesting saturation of the electrode surface with the pesticides species.

The effect of deposition potential (0.0 to −0.6 V) on the cathodic peak current was evaluated at the HMDE.

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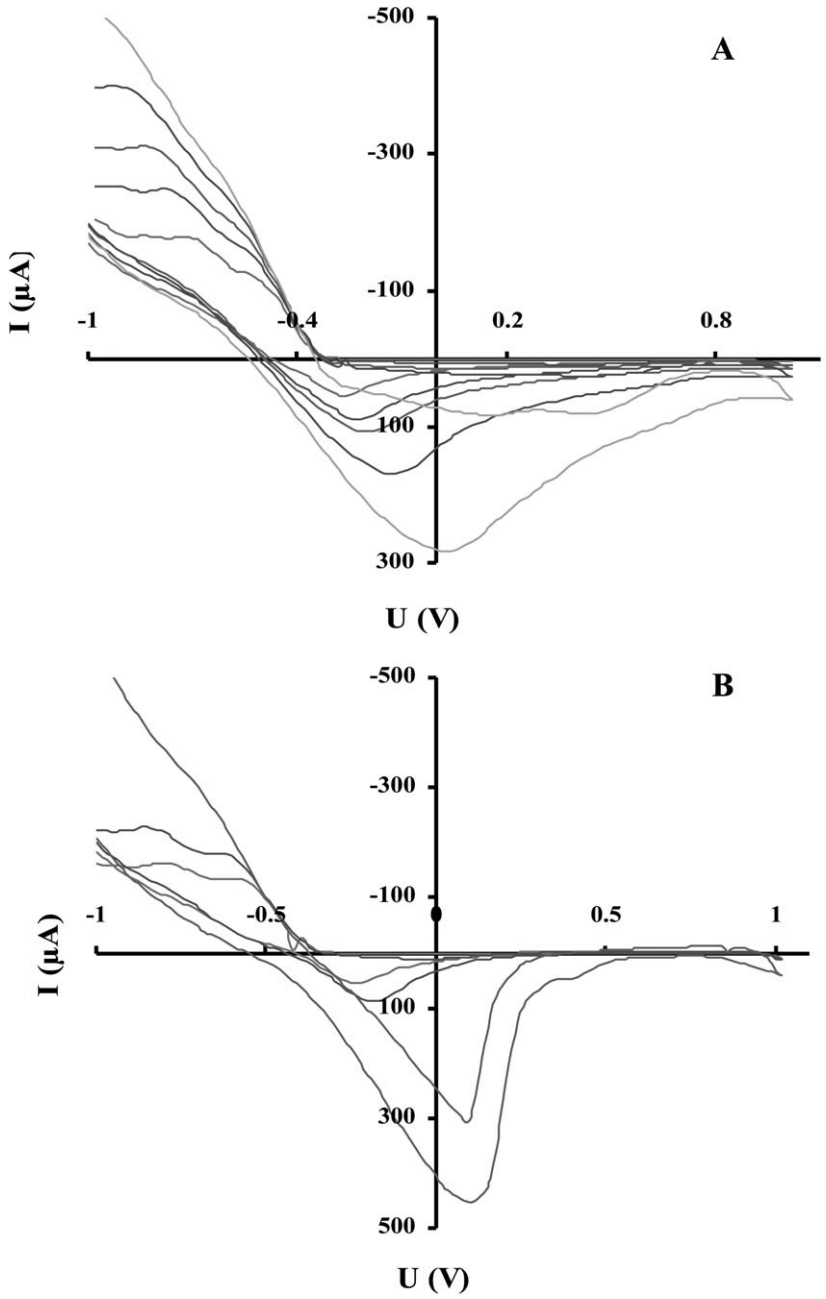


Fig. 6. Cyclic voltammograms of chlorfenvinphos in B-R buffer (pH 2–3) at Pt (A) and Au (B) electrodes vs. Ag/AgCl electrode at different scan rates: 20, 50, 100, 200 and 500 mV $s^{-1}$.

The plot of the deposition potential versus peak current for ALC and CHL pesticides is shown in Figure 8. Peak current reached maximum at an accumulation potential of −0.35 V. At a deposition potential $< -0.35$ V, the peak current decreased gradually. Moreover, at a deposition potential of −0. 35 V, the peak was symmetric and well defined. Thus, a deposition potential of −0.35 V was selected in the subsequent work.

The effect of scan rate on the $i_{p,c}$ of ALC and CHL was studied at pH 2–3 at the HMDE under the optimal accumulation time and potential. The $i_{p,c}$ was directly proportional to the scan rate over the range of 20 to 80 mV $s^{-1}$ which suggested a surface-controlled process on the surface of the HMDE [27,28]. Good sensitivity, sharp and symmetric cathodic peak and excellent background was achieved at 50 mV $s^{-1}$ scan rates. Thus, in the next work a scan rate of 50 mV $s^{-1}$ was adopted. The influence of the pulse amplitude (10–100 mV) on the DP CSV peaks of ALC and CHL at pH 2–3 was tested at the optimal conditions. The peak current increased steadily on increasing the pulse amplitude. However, 60 mV pulse amplitude was selected in the next work, where good background and best sensitivity were achieved.

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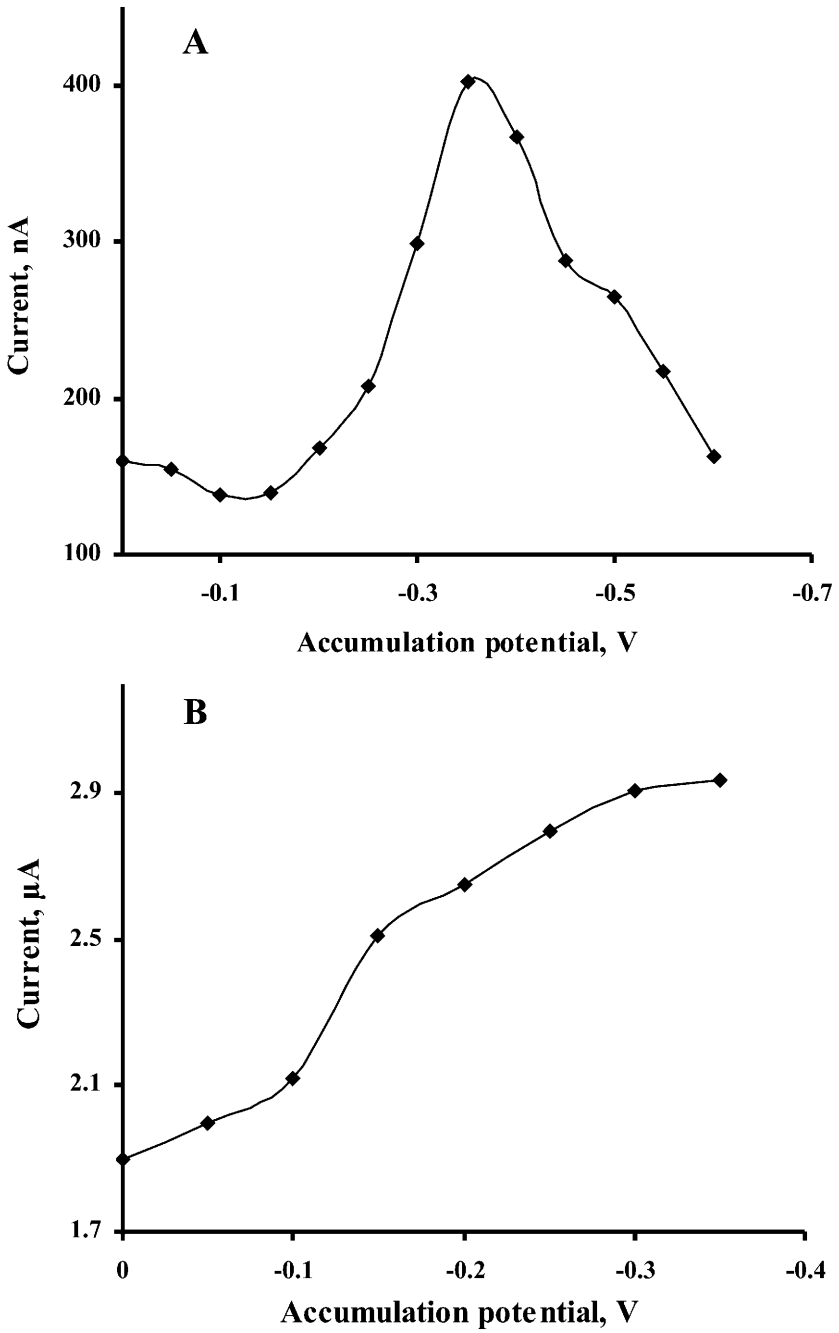


Fig. 7. Plots of the $i_{p,c}$ of alachlor (A) and chlorfenvinphos (B) vs. accumulation time at HMDE versus Ag/AgCl electrode. Deposition potential of −0.35 V; scan rate = 50 mV $s^{-1}$ and pulse amplitude of 60 mV vs. Ag/AgCl electrode.

### 3.3 Figure of Merits of the Developed DP CSV Method

Under the optimum experimental conditions of pH, deposition time, accumulation and scan rate, the figure of merits (dynamic linear range, lower limit of detection and quantification, repeatability, recovery and specificity) of the developed DP CSV for the determination of ALC and CHL was determined. The DP CSVs of both chlorinated pesticides ALC and CHL pesticides at various concentrations ($2.7\times10^{-9}$–$5.41\times10^{-7}$ mol $L^{-1}$) of each pesticide were recorded individually at the HMDE. The plot of $i_{p,c}$ of peak II for ALC versus concentrations was linear in the range $7.4\times10^{-9}$ (1.99 ppb)–$1.4\times10^{-7}$ mol $L^{-1}$ (37.73 ppb) (Figure 9), while for CHL pesticide at peak I, the plot was linear in the range $2.7\times10^{-9}$ (0.97 ppb)–$1.6\times10^{-8}$ mol $L^{-1}$ (5.75 ppb), respectively. At ALC concentration $>1.4\times10^{-7}$ mol $L^{-1}$ and CHL $>1.6\times10^{-8}$ mol $L^{-1}$, the calibration plots leveled off because of the adsorption saturation [27,28]. According to IUPAC [36], the values of *LOD* and *LOQ* for ALC were found equal $6.18\times10^{-12}$ (1.67 ppt) and $2.06\times10^{-11}$ (5.56 ppt) mol $L^{-1}$, respectively, while, for CHL, the values of *LOD* and *LOQ* at peak I was found equal $4.34\times10^{-12}$ (1.56 ppt) and $1.44\times10^{-11}$

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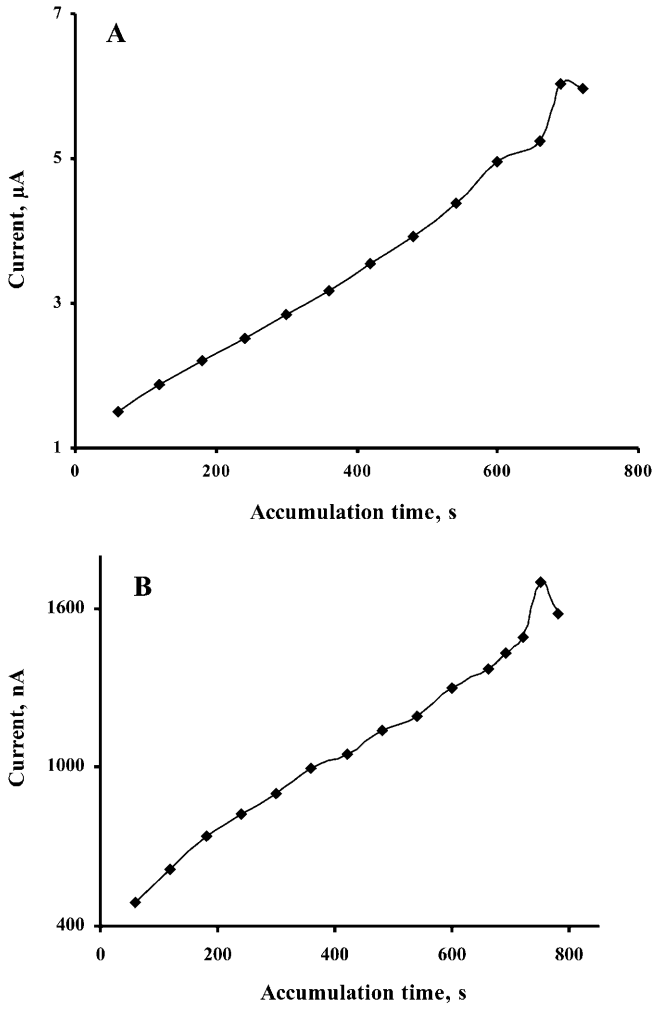


Fig. 8. Plots of $i_{p,c}$ of peak I (A) and peak II (B) of alachlor vs. deposition potential at HMDE vs. Ag/AgCl electrode. Alachlor concentration = $1.16 \times 10^{-7}$ mol $L^{-1}$; sweep rate = 50 mV $s^{-1}$.

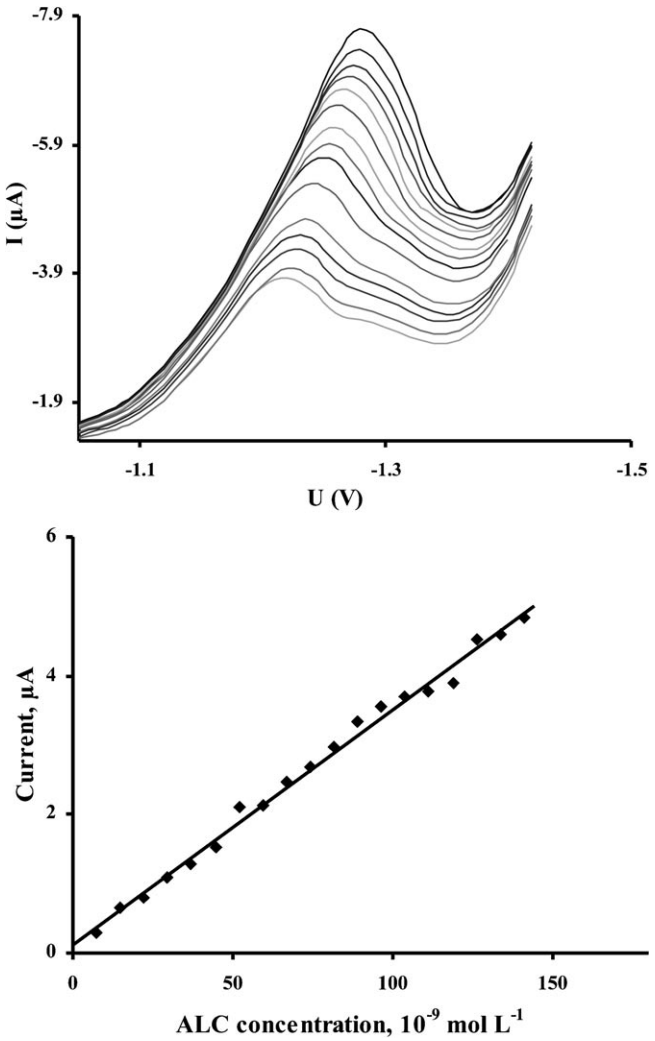


Fig. 9. DP-CSVs and calibration curve of alachlor at pH 2–3 at −1.3 V at HMDE vs. Ag/AgCl electrode. Deposition time of 660 s; accumulation potential of −0.35 V; scan rate = 50 mV $s^{-1}$ and pulse amplitude of 60 mV vs. Ag/AgCl electrode.

(5.19 ppt) mol $L^{-1}$, respectively. Both *LOD* and *LOQ* values confirmed the sensitivity of the proposed DP CSV procedure compared to most of the reported chromatographic methods e.g. SPE-LC-ESI-MS/MS [26], UPLC-MS/MS [8], HPLC [9], GC/MS [10] LC-MS/MS [12] and polarographic [13,14] and voltammetric [15–17] methods. The main analytical features of the proposed method were compared successfully with many of the previously published chromatographic methods (Table 1). The relative standard deviation (*RSD*) of ALC and CHL based on five replicate measurements at concentrations $3.0 \times 10^{-8}$ and $8.0 \times 10^{-8}$ mol $L^{-1}$ were found equal 2.9, 2.1, 2.76 and 2.39%, respectively confirming the precision and the performance of the developed DP CSV method for determination of the tested pesticides. Such limits could be improved to lower values by increasing the equilibrium and accumulation time at the optimized experimental conditions. Such level of precision is suitable for quality control analysis of pesticides in environmental samples.

### 3.4 Applications

#### *3.4.1 Analysis of the Tested Chlorinated Pesticides in Water Samples*

The proposed DP CSV method was used for the assay of ALC and CHL in various water samples (tap-, Red Sea- and Atlantic Ocean close to Elizabeth Port, South Africa water). The water samples were processed as described. The results are summarized in Table 2. An acceptable recovery ($97 \pm 0.02$–$104 \pm 0.06$) with a relative standard deviation (*RSD*) in the range 4.2–14.6% of the tested pesticides were successfully achieved (Table 2). The results are close to the values obtained by GC MS confirming the sensitivity and selectivity of the method for the analysis of the tested pesticides in complicated matrices compared to the highly cost chromatographic methods [7], GC/MS [10,11] and other methods [12].

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Table 1. Figure of merits of the developed DP CSV and some of the reported methods [a].

| Method | Pesticide | *LOD* ($ng\,L^{-1}$) | *LOQ* ($ng\,L^{-1}$) | Dynamic range ($ng\,mL^{-1}$) | Reference |
|---|---|---|---|---|---|
| SPE-LC-ESI-MS/MS | ALC | 18 | 47 | 0.05–1 | [37] |
| UPLC-MS/MS | ALC | 6 | 17 | 0.02–0.5 | [38] |
| HPLC | CHL | 100000 | 333000 | 500–15000 | [39] |
| GC/MS | ALC | 75.1 | 250 | 25–200 | [40] |
| | | | | 200–10000 | |
| LC-MS/MS | ALC | 6000 | 19980 | 0.1–2 | [12] |
| | CHL | 4000 | 13320 | 0.03–2 | |
| GC/SQ-MS | | 400 | 1200 | | [41] |
| DP CSV | ALC | 1.67 | 5.56 | 1.99–37.73 | |
| | CHL | 1.56 | 5.19 | 0.97–5.75 | Present work |

[a] SPE-LC-ESI-MS/MS: solid phase extraction – liquid chromatography – electrospray tandem mass spectrometry; UPLC-MS/MS: ultraperformance liquid chromatography combined with tandem mass spectrometry; HPLC: high performance liquid chromatography; GC-MS: gas chromatography – mass spectrometry; LC-MS/MS: liquid chromatography – tandem mass spectrometry; GC/SQ-MS: gas chromatography coupled to single quadropole.

Table 2. Levels ($ng\,mL^{-1}$) of the tested pesticides ALC and CHL in fresh-, Red Sea (coastal area of Jeddah City, Saudi Arabia) and Atlantic Ocean (Elizabeth port, South Africa) water determined by the developed DP CSV method [a].

| Water sample | Pesticide added ($ng\,mL^{-1}$) | | Found ($ng\,mL^{-1}$) | | Recovery (%) | | *RSD* (%) | |
|---|---|---|---|---|---|---|---|---|
| | ALC | CHL | ALC | CHL | ALC | CHL | ALC | CHL |
| Tap | 0 | 0 | $0.56\pm0.04$ | $0.06\pm0.002$ | – | – | – | – |
| | 8 | 4.99 | $8.69\pm0.05$ | $5.05\pm0.003$ | $101\pm0.05$ | $99\pm0.003$ | 4.2 | 4.2 |
| Red Sea | 0 | 0 | $0.67\pm0.06$ | $0.35\pm0.04$ | – | – | – | – |
| | 8 | 5.99 | $8.79\pm0.06$ | $6.42\pm0.04$ | $101\pm0.06$ | $101\pm0.04$ | 7.4 | 4.2 |
| Atlantic Ocean | 0 | 0 | $0.39\pm0.06$ | $0.49\pm0.18$ | – | – | – | – |
| | 8 | 4 | $8.69\pm0.06$ | $4.37\pm0.18$ | $104\pm0.06$ | $97\pm0.18$ | 14.6 | 10.5 |

[a] Average ± standard deviation ($n=7$).

Table 3. Analysis of ALC and CHL in Atlantic Ocean (Elizabeth port, South Africa) marine sediment by the developed DP CSV method [a].

| Sample | Added ($\mu g\,g^{-1}$) | | Found $\pm$ *SD* ($\mu g\,g^{-1}$) | | Recovery (%) | | *RSD* (%) | |
|---|---|---|---|---|---|---|---|---|
| | ALC | CHL | ALC | CHL | ALC | CHL | ALC | CHL |
| Sediment | 0 | 0 | $0.62\pm0.06$ | $0.39\pm0.01$ | – | – | – | – |
| | 8 | 1.99 | $8.55\pm0.06$ | $2.38\pm0.01$ | $99\pm0.06$ | $99\pm0.01$ | 9.17 | 2.78 |

[a] Average ± standard deviation ($n=5$).

### *3.4.2 Analysis of Marine Sediment of Atlantic Ocean*

The proposed DP CSV was used for the analysis of ALC and CHL in the marine sediment of Atlantic Ocean. In this experiment, an accurate weight ($5.0\pm0.001$ g) of the dry marine sediment was extracted and analyzed as described before [19,20]. The results are summarized in Table 3. The content of ALC pesticide in the marine sediment sample was found $2.29\pm0.21$ nM ($0.62\pm0.06\ \mu g\,L^{-1}$) with correlation coefficient of 0.98. The content of the CHL pesticide in the marine sediment was found $1.08\pm0.03$ nM ($0.39\pm0.01\ \mu g\,L^{-1}$) with a correlation coefficient of 0.98. An acceptable recovery percentage and relative standard deviation in the range from $99\pm0.01$ to $99\pm0.06$% and 2.78 to 9.17%, were achieved, respectively. Thus, the developed DP CSV method compared favorably with the reported HPLC [9]. The method provides an alternative approach for the analysis of ALC and CHL pesticides in different matrices.

### *3.4.3 Analysis of the Chlorinated Pesticides in Food Samples*

The high sensitivity of the developed DP CSV method for the analysis of the tested compounds in various water samples and solid sediment suggested the application of the method for the determination of trace concentrations of ALC and CHL residues in spinach, carrot and cheese samples. Various volumes of pesticides (10–50 μL) were added to the food samples and analyzed as described. The results (Table 4) of the analysis of ALC and CHL confirmed the sensitivity and precision of the method.

## 4 Conclusions

The developed DP CSV method for ALC and CHL determination is characterized by instrumental simplicity, economy, convenient, rapid, and accurate. The method

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Table 4. Analysis of ALC and CHL in different food samples by the developed DP-CSV method [a].

| Sample | OCPs added ($\mu g\,g^{-1}$) | | Found $\pm$ *SD* ($\mu g\,g^{-1}$) | | Recovery (%) | | *RSD* (%) | |
|---|---|---|---|---|---|---|---|---|
| | ALC | CHL | ALC | CHL | ALC | CHL | ALC | CHL |
| Spinach | 0 | 0 | $0.89 \pm 0.09$ | $0.62 \pm 0.03$ | – | – | – | – |
| | 8 | 3.99 | $8.96 \pm 0.09$ | $4.63 \pm 0.03$ | $103 \pm 0.09$ | $100 \pm 0.03$ | 10.57 | 4.65 |
| Carrot | 0 | 0 | $0.55 \pm 0.31$ | $0.18 \pm 0.01$ | – | – | – | – |
| | 8 | 2.01 | $9.33 \pm 0.31$ | $2.19 \pm 0.01$ | $109 \pm 0.31$ | $100 \pm 0.01$ | 11.32 | 8.16 |
| Cheese | 0 | 0 | $0.89 \pm 0.07$ | $0.40 \pm 0.03$ | – | – | – | – |
| | 8 | 3.99 | $8.94 \pm 0.07$ | $4.41 \pm 0.03$ | $100 \pm 0.07$ | $100 \pm 0.03$ | 8.21 | 7.14 |

[a] Average $\pm$ standard deviation ($n = 5$).

compared favorably with the reported HPLC [7], GC/MS [10,11] and other methods [12] and provides an excellent alternative approach for the analysis of ALC and CHL pesticides in different matrices because of its sufficient precision. Work is still continuing for the possible application of on-line DP CSV determination in various environmental samples.

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