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ORIGINAL PAPER

Biomimetic electrochemical sensor based on molecularly imprinted polymer for dicloran pesticide determination in biological and environmental samples

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Abstract Dicloran pesticide is used to inhibit the fungal spore germination for different crops. Because of the increasing application of pesticides, reliable and accurate analytical methods are necessary. The aim of this work is designing the highly selective sensor to determine the dicloran in biological and environmental samples. Multi-walls carbon nanotubes and a molecularly imprinted polymer (MIP) were used as modifiers in the sensor composition. A dicloran MIP and a nonimprinted polymer (NIP) were synthesized and applied in the carbon paste electrode. After the optimization of electrode composition, it was used to determine the concentration of analyte. Parameters affecting the sensor response were optimized, such as sample pH, electrolyte concentration and its pH, and the instrumental parameters of square wave voltammetry. The MIP-CP electrode showed very high recognition ability in comparison with NIP-CP. The obtained linear range was 1×10^{-6} to 1×10^{-9} mol L^{-1}. The detection limit was 4.8×10^{-10} mol L^{-1}. This sensor was used to determine the dicloran in real samples (human urine, tap and river water samples) without special sample preparation before analysis. All important parameters were optimized, improving the sensor response considerably.

Keywords Dicloran · Molecularly imprinted polymer · Voltammetric sensor · Carbon paste electrode · Biological monitoring

Introduction

Since the middle of last century, organic pesticides are being used to prevent, repel, and control pests. Despite increasing the food production by application of pesticides, the wide use of them during production, processing, and transport of agricultural crops can lead to environmental pollution and their residues in food. The exposure of humans, particularly workers, to pesticides can cause different adverse effects. Dicloran (2,6-dichloro-4-nitroaniline), as an chlorinated nitroaniline fungicide, is used to inhibit the fungal spore germination for different crops [1–3]. Exposure to dicloran may occur from skin contact, breathing polluted air, and eating contaminated food. According to some studies, fungicides indicated increased incidences of developmental toxicology and oncogenesis. Also the excessive heat production, hyperpyrexia, liver damage, and corneal opacities may be occurred [4]. Thus, the target organs for this pesticide include the liver, kidney, and hematopoietic system, particularly red blood cells [3].

Because of the increasing application of pesticides, reliable and accurate analytical methods are necessary to analyze different occupational and environmental samples such as air, water, soil, and also food containing these compounds [2, 5, 6]. Human biomonitoring is being used in occupational health as a useful tool to assess the exposure to low levels of chemicals. In this regard, developing the

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new sensitive procedures allows the reliable, easy to use, and cost-effective assessment.

There are some traditional techniques to determine the pesticides such as liquid chromatography and gas chromatography with electron capture detection with very low detection limits. Other determination methods reported by the literature are spectrophotometry [7, 8], immunoassay [7], infrared spectroscopy [9], solid-phase extraction [10] or enzymatic techniques [11] sometimes in combination with mass spectrometry [12], or the flow injection technique [7, 13]. There are some reasons to develop novel, simple, and inexpensive methods for determining the pesticides. The mentioned techniques are very expensive, and a well-equipped laboratory and well-trained analysis operators are required; in the developing countries, the MS instrumentation is so expensive for wide usage, although need for pesticide analysis is greater in these countries because of the agrarian basis of them; the classical gas chromatographic methods are not satisfactory due to the thermal instability of some pesticides molecules; a sample preparation or preconcentration step is needed to determine the analytes at ppb levels. Therefore, in the last few years many sensitive, selective, and accurate methods have been developed to determine the trace toxic species like pesticides [6, 14, 15].

On the other hand, miniaturizing the analytical instruments has been considered for field studies. Electrochemical sensors are the appropriate and interested devices in this regard to monitor the trace and even ultra-trace pesticides. Modified electrodes are being used in the electrochemical determination of many compounds. Molecularly imprinted polymers (MIPs) can be used as recognition elements or modifying agents in sensors structure to increase their selectivity [16–19]. A MIP is a synthetic polymer containing selective adsorption sites that their size, shape, and functional groups are complementary to the analyte molecule [20, 21]. The properties of the final polymer are dependent on the various parameters such as functional monomers, initiator, porogenic solvent, and the ratio of monomer to cross-linker. Therefore, the effective variables must be carefully selected to synthesize an optimal polymer with high selectivity for analyte of interest [22–24].

An electrode modified with a MIP as the sensing material is easily stored and operated. The response of this electrode, as a working electrode, can be improved using the MIPs. In the other word, in comparison with natural antibodies, longer lifetimes and even higher sensitivities can be obtained by using these synthetic antibodies and their extraction capabilities are considerable [25]. Recently, modified electrode by different modifying agents like MIPs and various nanostructures are being used for quantification of analytes because of their interesting advantages [21, 26, 27]. Modified electrodes may be used in combination with different electrochemical techniques like potentiometry, differential pulse voltammetry (DPV), differential pulse polarography (DPP), and adsorptive stripping voltammetry (AdSV) to analyze the environmental and occupational samples [28]. The aim of this study was to synthesize a molecularly imprinted polymer for dicloran for first time and then to apply it as a recognition element in the nanocomposite carbon paste electrode for selective and sensitive electrochemical determining the mentioned pesticide in environmental and biological samples.

Experiment

Instruments and reagents

A three-electrode system using an AUTOLAB PGSTAT302 electrochemical analysis system was applied to obtain electrochemical data. The modified sensors with MIP or NIP were used as working electrodes. An Ag/AgCl electrode and a graphite rode were selected as the reference and counter electrodes, respectively. Methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Fluka (Buchs, Switzerland). Dicloran (Dr Ehrenstorfer, Germany), Paraffin oil (Merck), and 2,2-azobisisobutyronitrile (AIBN) from Sigma-Aldrich (Munich, Germany) were used. Multi-wall carbon nanotubes (MWCNTs) were provided from Research Institute of the Petroleum Industry (Iran). Graphite powder (1–2 μm particle size) and all other chemicals in analytical grade were purchased from Merck (Germany).

Preparation of the molecularly imprinted polymer (MIP)

The molecularly imprinted polymer synthesis includes the complexation of the template molecule dicloran (1 mmol) with functional monomers MAA (4 mmol) through noncovalent bonds and then the polymerization of MAA around the template with the help of the cross-linker EGDMA (20 mmol) in the presence of initiator AIBN (60 mg). All polymer compounds were dissolved in chloroform (10 mL) in a 75-mL glass tube. The mixture was purged with nitrogen for 10 min. The glass tube was sealed under nitrogen, and polymerization was conducted at 60 °C for 18 h, using a water bath. After that, synthesized polymer was dried, powdered and the template molecule removed by extensive washing via Soxhlet extraction with ethanol/acetic acid (9:1 v/v) for 48 h. Finally, more washing was performed by ethanol to remove dicloran completely, so that no template was detected in the effluent by UV–Vis spectrometry and square wave voltammetry methods. The nonimprinted polymer (NIP) was prepared in the same way, except for addition of the template molecule to the mixture.

Preparation of the electrode

To prepare the bare carbon paste electrode (CP), graphite, MWCNT, and paraffin oil were mixed in a 72:3:25 (w/w/w %) ratio. The MIP-CP and NIP-CP were prepared by mixing different percentages of graphite, MWCNT, paraffin oil, and MIP or NIP. This mixture was homogenized in a mortar for at least 10 min. The final paste was packed into the end of an electrode body (id: 3 mm, paste deep: 1 cm) in which electrical contact was made with a copper rod. After that, the electrode surface was polished using a paper to remove the excess of material. For affirmation the role of each component to improve the electrode response, several electrodes with different compositions were prepared.

Electrochemical measurements

In order to achieve optimum analytical voltammetric conditions for dicloran determination, the square wave voltammetry technique was selected as one of the most sensitive. The electrochemical measurement of dicloran was done according to the following steps:

Extraction step Each prepared electrode was inserted into the dicloran solution with determined concentration, and its pH was adjusted on 6. All solutions for a determined time were stirred at fixed stirring rate.

Analyzing step The electrochemical cell containing 0.04 mol L^{-1} KCl solution with determined pH was used for voltammetry experiments. At first, a negative deposition potential was applied to the electrode (placed in the cell), and then, the potential was scanned in defined range.

Preparation of samples

The stock solution of dicloran (1×10^{-2} mol L^{-1}) was prepared in ethanol. The working solutions for optimization experiments were made by diluting a certain amount of the stock with deionized water. In order to assess the possibility of dicloran determination in real samples, unexposed urine, tap and river samples were considered as biological and environmental ones. There was no need for special preparation procedures for these samples. Only urine samples were diluted 1:2 with deionized water. The specified amount of dicloran was spiked in all solutions to do the optimization process. The working electrode (MIP-CP) was placed in the solutions for 20 min to extract the dicloran. Then, the measurement was completed in the analyzing step via inserting the electrode into an electrochemical cell with optimized characteristics. After applying deposition potential of −0.5 V, square wave voltammograms were recorded in the scan range of −0.5 to 0.5 V.

Results and discussion

Electrochemical behavior of dicloran

Based on the review literature in the beginning of this study, there was no report on electrochemical behavior of dicloran. Therefore, its voltammetric behavior was investigated by a bare carbon paste electrode inserted in a dicloran solution with defined concentration. The potential was swept in a wide interval (−1.5 to +1.5 V) by cyclic voltammetry to find the redox peaks and proper scan range. Two peaks were appeared resulting from reduction and oxidation reactions. The oxidation peak (0.1 V) was chosen for all later voltammetric experiments because of higher sensitivity in square wave analysis.

Optimization of carbon paste electrode composition

The base of carbon pastes is usually a mixture of powdered graphite and binder. The carbon paste can be modified with other components as modifying agents. The choice of suitable components and their ratio is important to have the optimum construction. In this study, the multi-wall carbon nanotubes (MWCNTs) and MIP were used as modifiers. Different amounts of modifiers were added to mixture, and soft paste was packed into the electrode body. For exact comparison, bare carbon paste electrode and the electrode modified with NIP were also considered. Eventually, electrochemical experiments were carried out by various prepared CPEs inserted to defined dicloran solutions to select the most efficient electrode. Table 1 shows different electrode compositions and their responses in the same electrochemical conditions. Findings illustrate that both the modifier kind and its amount play the significant role in the electrode response. Nanoparticles such as MWCNTs can improve the properties of the obtained CPE because of vast surface area, high electrical conductivity, and proper chemical stability. Therefore, the application of carbon nanotubes in electrochemical studies can be led to desired new sensors with appropriate characteristics. Furthermore, carbon paste electrodes modified with MIPs offer very good performance due to the special properties of these material as synthetic antibody mimics. It has been proved that the MIPs can be very promising recognition elements because of their intrinsic properties such as high selectivity to the molecule of interest, reusability, physiochemical stability and applicability in rough chemical solutions. As it can be seen in Table 1, the highest electrochemical response is related to carbon paste modified with two modifiers. Therefore, the CPE modified with both MIP

Table 1 Optimization of carbon paste composition for determination of dicloran (5×10^{-7} mol L^{-1})

Electrode no.	Composition of carbon paste (wt%)					Voltammetric response (μA)
	Graphite powder	Binder (paraffin oil)	MWCNTs	MIP	NIP	
1	75	25	0	0	0	1.90 ± 2.9
2	72	25	3	0	0	5.16 ± 3.5
3	53	25	0	22	0	12.50 ± 2.8
4	57	25	3	15	0	16.84 ± 2.6
5	**50**	**25**	**3**	**22**	**0**	**29.10 ± 2.2**
6	45	25	3	27	0	20.20 ± 3.2
7	50	25	3	0	22	9.60 ± 1.7

Bolded values indicate the selected MIP-CP for later experiments

Table 2 Response of prepared sensor for some interferences and for dicloran in the presence of these compounds

Tested compounds	MIP-CP response	
	I (μA) for (5×10^{-7} mol L^{-1})	I (μA) for (1×10^{-7} mol L^{-1})
Carbofuran	N.D	N.D
Diazinon	8.5	4.6
Dimethoate	3.4	0.59
Dichlrofention	11	5.3
Dicloran (in the presence of other compounds)	67.1	24.7

and MWCNT can be considered as a special kind of sensor for selective determination of the target molecule. It is worth mentioning that, the percentage of MIP used in carbon paste is effective parameter. According to results, the CP containing 22 % MIP has the highest efficiency to adsorb the analyte and it was selected for later experiments (electrode No. 5). Higher percentage of MIP leads to reduce the responses because of enhancing the electrode resistance. As it can be seen in next sections, the optimization of instrumental and analysis conditions is led to more enhancements in the voltammetric response of selected electrode.

Effect of interferences

In order to assess the selectivity of prepared MIP-CP sensor, the electrode was inserted into the solutions of dicloran as well as some commonly used pesticides *using the optimal analytical conditions*. At first, the experiments were separately done for each compound to find the probable interference with the dicloran peak position. There was no interference in this respect. Then, the response of sensor was obtained for dicloran in the presence of different concentrations of these interferences. Table 2 shows the response of MIP-CP electrode for each compound and for dicloran. The presence of carbofuran, diazinon, dichlrofention and dimethoate could not interfere with respect to the dicloran peak current using MIP-CP electrode. Also, for further confirmation, the interferences were gradually added to the defined concentration of dicloran. Findings showed that the mentioned compounds had no interfering effect on analyte signal till 1000-fold concentration. Obviously, the modified electrode with MIP was very selective for dicloran, so that other pesticides indicate the negligible responses compared to that. These findings demonstrate the ability of MIP-CP electrode to interact strongly with the target compound due to specific cavities for molecules of interest in the MIP structure.

Optimization of parameters for dicloran detection

The effect of different parameters on dicloran detection was investigated using the designed sensor to optimize the extraction and electrochemical determination conditions.

Optimization of extraction conditions

The extraction of dicloran in the electrode can be dependent on some parameters including the pH of dicloran solution, extraction time, and stirring rate of solution. The effect of pH, as an important parameter, on the response of the sensor was studied. Dicloran solutions with different pH were tested in similar conditions. After extraction, electrochemical experiment was done

Table 3 Effect of extraction parameters on the voltammetric response of dicloran (C: 5×10^{-7} mol L^{-1})

Extraction pH	*I* (μA)	Extraction time (min)	*I* (μA)	Stirring rate (rpm)	*I* (μA)
3	3.1	5	7.30	100	11.91
4	5.61	10	11.01	300	17.18
5	10.15	15	15.61	500	21.50
6	**18.22**	**20**	**22.43**	**700**	**25.14**
7	16.81	25	23.10	800	23.92
8	9.12	30	23.98	–	–
9	6.65	–	–	–	–

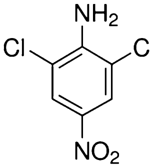

Fig. 1 Chemical structure of dicloran [3]

to determine the sensor response. The peak height increased with increasing the pH in the range of 5–7. In the pH lower and upper than this range, the sensor response decreased. Thus, the pH of 6 was selected for further experiments.

The extraction time is another parameter affecting the sensor response. To optimize this parameter, various extraction times were tested in the same conditions. Square wave voltammetric (SWV) results showed that the increasing time up to 20 min leads to the increase in dicloran extraction in the electrode. After 20 min, there was no significant difference between results with time enhancement; therefore, to decrease the total analyzing time, the time of 20 min was selected for the extraction step.

Since the stirring of solution in the extraction step can be effective on the electrode response, different stirring rates were studied in the constant conditions. The SWV results showed the current height increases with the increasing in stirring rate till 700 rpm, and after that there was no significant variation in the dicloran voltammetric response. Therefore, the rate of 700 rpm was selected for later experiments. As it can be seen in Table 3, after the optimization of each parameter, the current intensity showed further enhancement. Bolded numbers in this table are the selected optimum levels for parameters (Fig. 1).

Optimization of electrochemical conditions

In order to select the best conditions for electrochemical analysis, some important parameters including pH, the concentration of supporting electrolyte, deposition potential amount, time of exerted deposition potential, potential frequency, and amplitude were studied.

Effect of pH The SWV currents of dicloran have been recorded in pH range of 2–9. The pH had an egregious effect on the voltammetric signals. The peak current increased as the pH approached to the basic values. The maximum response was achieved in the range of 8–9. Thus, pH of 8 was selected as the optimum level for further experiments (Fig. 2a).

Effect of deposition potential amount and its exertion time The dependence of the peak currents on the deposition potential value and its exertion time was studied over the ranges from −0.2 to −0.5 V and 5–25 s, respectively. There was no increase in peak current for the potentials under −0.2 V, but exertion of the higher deposition potential led to increase the voltammetric current. The maximum current was observed in −0.5 V, leading to select this value as the optimum one. The exertion of deposition potential to the working electrode causes the molecule of interest to be deposited onto the surface of the electrode. In the case of deposition potential exertion time, the maximum peak current was obtained at range of 15–20 s. To decrease the total time of analysis, the time of 15 s was chosen for further analytical experiments (Fig. 2b, c).

Effect of the concentration of KCl The effect of KCl concentration as the supporting electrolyte was studied in the range 0.01–0.06 mol L^{-1} at constant pH. Maximum peak current was obtained at 0.04 mol L^{-1} KCl solutions. At concentrations lower and higher than 0.04 mol L^{-1}, the peak current decreased. According to studies [29], at low concentration of electrolyte, higher resistance leads to reduction in analyte signal. Also, at high concentration, the competition between electrolyte cations and molecules of interest for the permanent sites on modified electrode decreases the accumulation of these molecules at the electrode surface (Fig. 2d).

Effect of square wave frequency and amplitude Since the peak current in square wave voltammetry can be dependent on frequency and amplitude, the influence of these parameters was also studied. The amplitude range of 50–200 mV and the frequency range of 50–200 Hz were examined, respectively. The increasing in dicloran peak current was seen up to amplitude of 150 mV (0.15 V). In the case of frequency, the maximum current was obtained in 150 Hz and after that there was no increase in the current. Therefore,

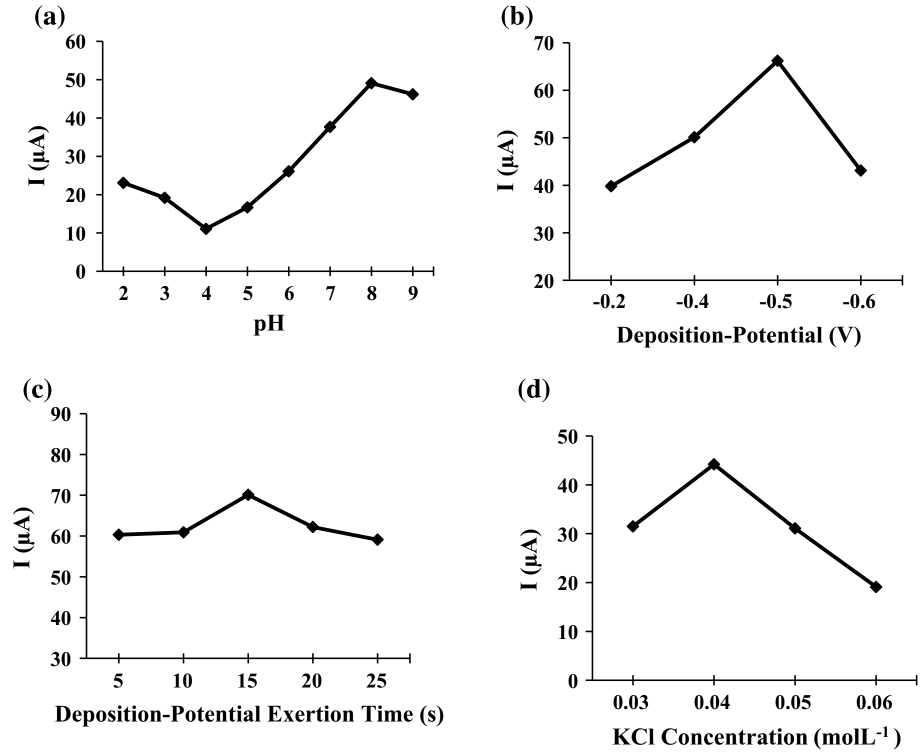

Fig. 2 Optimization of pH (**a**), deposition potential value (**b**), its exertion time (**c**) and electrolyte concentration (**d**) for voltammetric determination of dicloran using MIP-CP as working electrode. Extraction conditions: pH 6, extraction time 20 min and stirring rate 700 rpm; dicloran concentration: 5×10^{-7} mol L^{-1}

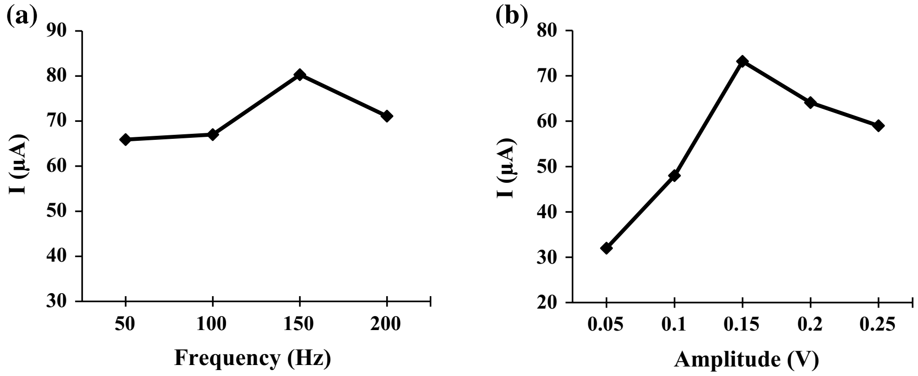

Fig. 3 Optimization of square wave frequency (**a**) and amplitude (**b**) for voltammetric determination of dicloran using MIP-CP as working electrode. Extraction conditions: pH 6, extraction time 20 min and stirring rate 700 rpm; dicloran concentration: 5×10^{-7} mol L^{-1}

150 mV and 150 Hz were selected as the optimum values (Fig. 3a, b).

Comparison of the prepared MIP and NIP

After optimization of all effective parameters on electrochemical determination of dicloran, the difference between responses of prepared MIP and NIP was studied. According to the findings, there was significant difference ($P < 0.05$) between these polymers to adsorb dicloran molecules, proving the formation of selective adsorption sites in the MIP structure. Figure 4 indicates the square wave voltammograms related to determination of defined concentration of dicloran by MIP-CP, NIP-CP, and bare CP.

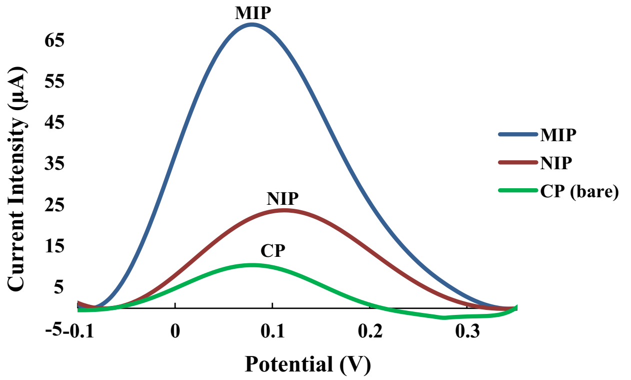

Fig. 4 Voltammograms of MIP-CP, NIP-CP, and CP for defined concentration of dicloran (5×10^{-7} mol L^{-1})

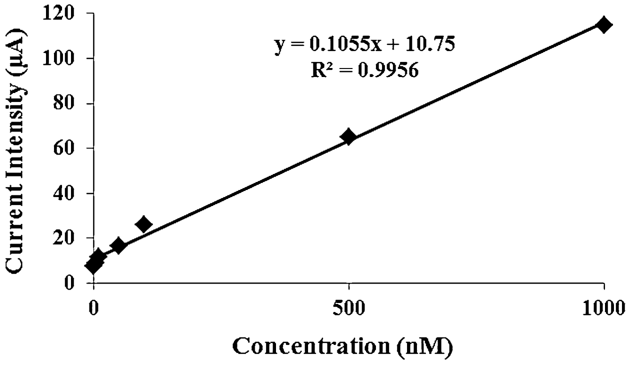

Fig. 5 Calibration curve plotted for voltammetric determination of dicloran with MIP-CP

Method validation

Since the application of MIP-CP sensor in the simultaneous presence of other molecules is important, their interferences with the determination of dicloran were examined. According to obtained results, for defined concentration of dicloran (5×10^{-7} mol L^{-1}), over 1000-fold concentration of some pesticides compounds had no interference effects on the dicloran response.

After the optimization of determination method using described conditions, the prepared MIP-CP sensor was used to plot the calibration curve. The tested concentration interval was from 1×10^{-4} to 1×10^{-9} mol L^{-1}. To plot the calibration curve, MIP-CP sensor was inserted into the dicloran solutions with different concentrations, and then, the analysis was carried out according to optimized conditions. The linear relationship between the peak current and dicloran concentration was obtained over the range of 1×10^{-6} to 1×10^{-9} mol L^{-1} with R^2 of 0.9956 (Fig. 5). The limit of detection (LOD) and limit of quantification (LOQ) were 4.8×10^{-10} and 9.4×10^{-10} mol L^{-1}, respectively. To assess the reproducibility of the voltammetric method, six consecutive experiments were conducted for a single dicloran concentration during 1 day. The Relative Standard Deviation (RSD) of the peak currents was 3.1 %, statistically indicating the satisfactory performance of the optimized method for dicloran determination.

Determination of dicloran in spiked urine and water samples

The optimized electrochemical procedure was successfully applied for dicloran determination in urine and water samples. There was no need for digestion or other special pretreatment steps prior to the voltammetric analysis. Appropriate amounts of dicloran were added to the urine and water samples. The optimized procedure was applied to analyze the samples, and then, dicloran recoveries were calculated. Table 4 indicates the recovery results of dicloran in spiked samples. According to obtained results, the method is sufficiently acceptable for environmental and biological monitoring of dicloran, as a pesticide. It is worth mentioning the preparation of samples, especially biological ones, is one of the most time-consuming, tedious, and error-prone aspects prior to instrumental analysis. The proposed procedure helps solving this problem, because there is no need for preparation the real samples to determine the analyte.

Table 4 Recovery of the prepared MIP-CP in spiked real samples

Sample	Added (ng/ml)	Found (ng/ml)	RSD (%) ($n = 3$)	Recovery (%)
Tap water	0	<0.2	–	–
	20	19.30	3.20	96.50
	200	190.00	2.11	95.00
	2000	1884.00	3.21	94.20
River water	0	<0.2	–	–
	20	18.90	2.22	94.50
	200	185.00	3.01	92.50
	2000	2006.00	2.98	100.30
Urine	0	<0.2	–	–
	20	18.60	3.47	93.00
	200	180.00	3.62	90.00
	2000	1795.0	4.31	89.70

Conclusion

In this work, a high selective square wave voltammetric sensor for the rapid detection of trace amounts of dicloran in environmental and biological samples has been designed and applied. The applying of MIP and MWCNTs in the structure of carbon paste can considerably enhance the selective response of electrode to determine the analyte of interest. Such nanocomposite sensors lead to higher responses because of increasing the surface area of electrode, as well as improving the electron transfer between the electrode and the supporting electrolyte. The presence of MIPs can greatly increase the selectivity of the electrode. The designed sensor was successfully used for determination of dicloran in different real samples with no special sample preparation procedure.

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