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Detection of Chloridazon in Aqueous Matrices Using a Nano-Sized Chloridazon-Imprinted Polymer-Based Voltammetric Sensor

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This study attempts to present the validation and of an efficient and development reliable detection technique for determining chloridazon in surface, ground, and drinking water. This method is essentially based on Differential pulse voltammetric (DPV) determination of chloridazon (CLZ) at a nano molecularly imprinted polymer (MIP) modified carbon paste electrode. Due to the weak electroactivity of the organochlorine herbicide, developing the voltammetric methods for electrochemical assay of CLZ gives rise to problems. Herein, utilizing a simple precipitation polymerization technique, CLZ-imprinted nanopolymer was polymerized. The resultant polymer, accompanied by MWCNT, was consequently utilized for producing the modified carbon paste electrode that indicated a straightforward cathodic peak for CLZ at almost -0.6 V (vs. Ag/AgCl); however, at the same circumstances the associated blank electrode showed substantially lower signal. Using MWCNTs, the remarkably efficient MIP, (caused an increase in the charge transfer at the electrode surface) introduced the method as a selective and greatly sensitive tool for CLZ measurement. In favorable investigational circumstances, the provided sensor, showed the detection limit of 6.2×10^{-8} mol L^{-1} and linear response range of 5.0×10^{-7}-4.0×10^{-4} mol L^{-1}. Here, the first MIP voltammetric sensor for CLZ, ever reported, is shown. It seems that this method provides an operative way for fast screening of CLZ in water specimens.

Keywords: Chloridazon, Voltammetric sensor, Carbon paste electrode, Molecularly imprinted polymer

1. INTRODUCTION

Chloridazon (CLZ) is a productive herbicidal element of numerous pesticides utilized post and pre-emergence for controlling road leaved weeds in crop-plants (for example all beet varieties). As a discriminating systemic herbicide, it stops electron transfer in photosynthesis, and is metabolized in various forms in plants and soil [1]. Since enzymatic and microbial degradation can involve redox character as well, the redox features of this herbicide have a key role in its biological activity (along with the temperature, structure and acidity of the soil, and the humic substances and water content in soil) and can be utilized for analytical objectives, for example in determining chloridazon and its remainders in the environment.

Molecularly imprinted polymers are favored for frequent utilization in sensor fields as the recognizing modification agent. An MIP is a polymer with selective molecular recognizing features for positioning and configuring the functional groups as a result of its recognizing sites in the polymer matrix supplementary to the analyte molecule and the great selectivity of these materials to the target molecule and their recognition mechanism [2,3]. MIPs are employed for developing electrochemical sensor as the greatly selective recognizing parameter of the sensor [4–10].

To determine CLZ, a number of methods have been devised including liquid chromatography/electrospray ionization/tandem mass spectrometry (LC–ESI–MS/MS) utilizing a high performance liquid chromatography and an ultra-high performance liquid chromatography (UHPLC) [11], gas chromatography–mass spectrometry (GC–MS) [12] and electrochemical reduction at mercury electrodes [13]. However, standard methods for preparing specimens like liquid–liquid extraction or solid-phase extraction require a huge deal of time and are not effective since the CLZ's high polarity results in low recoveries [14]. These approaches need wide specimen processing like pretreating the samples.

Therefore, there is an increasing demand for proper sensing systems able to determine CLZ sensitively, fast and with low cost. Electroanalytical sensing approaches were recognized as popular analytical instruments because of their numerous benefits like great sensitivity, fast response, and cheap equipment. Limited numbers of studies exist conducted on the voltammetric determining CLZ [15-18]. To date, reports exist on voltammetric CLZ determining on mercury electrode [13].

In the current study, a molecularly imprinted polymer was prepared with recognizing sites for chloridazon and then utilized to produce the CLZ selective potentiometric sensor, to create the first MIP-CNT sensor. It was discovered that the MIP composition which is recognized by the monomers' nature utilized in preparing MIP had a substantial impact on the ultimate sensor behavior.

2. EXPERIMENTAL

2.1. Tools and reagents

A potentiostat/galvanostat Autolab type III armed with a three electrode system was used to record the electrochemical results. Carbon paste electrodes, improved with Molecularly Imprinted Polymer (MIP) or non-imprinted polymer (NIP) were utilized as the working electrodes. An Ag/AgCl, KCl (sat.) electrode and a platinum wire were utilized as reference and counter electrodes, respectively. Chloridazon were obtained from merck (Germany). Vinyl benzene (VB), supplied by Sigma–Aldrich (Munich, Germany). Methacrylic acid (MAA), purchased from Sigma–Aldrich (Munich, Germany). Ethylene glycol dimethacrylate (EGDMA), purchased from Fluka (Buchs, Switzerland). N-eicosane and

2,2-Azobisisobutyronitrile (AIBN) were obtained by Sigma– Aldrich (Munich, Germany) and utilized as received. Graphite powder was bought from Merck (Germany).

2.2. Preparing Chloridazon-imprinted and non-imprinted polymer

CLZ-imprinted polymer particles were made by taking 0.8 mmol MAA and 0.2 mmol of (VB) as a functional monomer and 0.2 mmol of CLZ in a 50-ml flask. Then, for prearrangement, the mixture was put contacted for 5 minutes. Then, 0.1 gr initiator (AIBN) and 3.2 mmol of cross-linker (EGDMA) were dissolved in 2 mL dry acetonitrile and 10 mL dry chloroform. The mixture was purged with nitrogen for 10 min and under this setting the round-bottom flask was sealed. It was then continually agitating in an oil bath hold at 55°C to initiate the polymerizing procedure. After 8 hours, the attained polymer substances were milled and sieved. The unpolymerized monomers and CLZ were eliminated by Soxhlet extraction with 50 ml of methanol by refluxing for 8 hours. The not sedimented particles were discarded and sedimented ones were gathered by centrifuging. Acetone was used to wash the collected particles again, after centrifuging. The whole process was carried out four more times. The resultant MIP particles were dried at 65°C for 10 h. Non-imprinted polymer (NIP) particles were made similarly with no adding CLZ within preparing polymer material.

2.3. Preparation of the modified carbon paste electrode

The modified electrode, improved simultaneously by the multi-walled carbon nanotubes (MWCNTs) and Molecularly imprinted polymer-carbon nanotube-carbon paste electrode (MIP-CNT-CPE) was prepared by combining carbon nanotube, graphite, *n*-eicosane, and MIP with a ratio of 8: 60: 20: 10 (weight %). Then the attained carbon paste was applied to occupy a hole at the end of a Teflon electrode body (diameter of 4.0 mm, depth of 3 mm). The excess of carbon past was eliminated from the electrode's surface by polish over a paper sheet. The NIP electrode was also fabricated based on the above explained stages but instead of the MIP, the NIP material was applied. The polymer free electrode (CNT-CPE) was made as well by combining carbon nanotube, graphite, and *n*-eicosane with a ratio of 8: 72: 20 weight percent.

2.4. Analytical procedure

Electrochemical data were gathered utilizing a potentiostat/galvanostat Autolab type III system. The measurements were completed in a system containing three electrodes of working electrode (MIP/NIP- CP electrodes), a reference electrode (Ag/AgCl), and a counter electrode (platinum wire). Dissolving the standard in methanol-water, stock solutions of chloridazon ($c=5\times10^{-3}$ mol L^{-1}) were made; standards were kept in darkness. Methanol was also utilized for more dilution. The stock solutions' stability was checked every day for 30 days using DPV in Britton–Robinson buffers. Variations in the current's time-dependence were within the ranges of investigational error.

Since chloridazon is weakly soluble in water, at concentrations $>10^{-6}$ mol L^{-1}, a methanol content of 10% v/v was needed to measure cells and maintain the solutions' homogeneity. All specimens in voltammetric cells were purged with nitrogen for 10 minute.

The made MIP sensor was introduced into the solution containing 22.5 mL of Britton–Robinson buffers (pH 3) and 2.5 ml methanol and CLZ (different concentrations), being at agitating mode. After 10 minutes, the electrode was washed with deionization water and then transmitted into the voltammetric cell containing 22.5 mL of Britton–Robinson buffers (pH 3) and 2.5 ml methanol. Ultimately, the differential pulse voltammetry procedure was used for recording the CLZ’s current response. The potential was scanned from -0.1 to -0.9V. Scan rate of the potential applied were 50 mVs^{-1}.

3. RESULTS AND DISCUSSION

3.1. CLZ- Imprinted polymer synthesizing

The fabrication of Chloridazon Imprinted polymer was done following established procedure, initiating from prepolymerization mixtures with CLZ as a template, ethylene glycol dimethacrylate (EGDMA) as a crosslinking monomer, vinyl benzene (VB) and methacrylic acid (MAA) as functional monomers. It is expected that the MAA functional monomer approaches the template through interacting MAA’s carbonyl group by CLZ’s ammonium group. In contrast, vinyl benzene functional monomer implicates in a π-π interactions with the CLZ’s benzene rings. Fig. 1 represents the scanning electron microscopy image of the MIP, indicating the creation of polymer nanoparticles, obtained by the precipitation polymerization method.

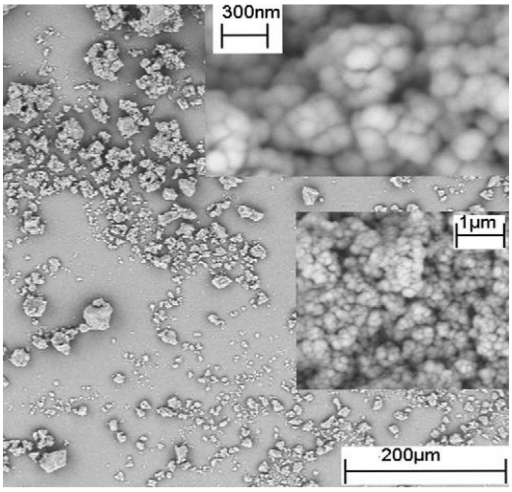


Figure 1. Scanning electron microscopy images of the MWCNTs-MIP composite.

3.2. Preparation of the nano-MIP-CP sensor

In this stage, to consider the effect of CNT presence as well as the capability of the imprinted polymer on the sensor response, 4 kinds of electrodes (MIP-CNT-CPE, NIP-CNT-CPE, CPE and CNT-CPE) were made. The obtained results, illustrated in Fig. 2, show that the current response for the CNT-CP electrode is greater than CPE response. This study indicates the impact of CNT increasing charge transfer and improving the electrode's active surface [19-23]. Moreover, a remarkable difference exists between the responses obtained from the NIP-CNT and MIP-CNT modified electrodes illustrating the selective binding sites in the MIP. Despite NIP able to only gather the analyte via the surface adsorption process, the selective sites in MIP structure can preconcentrate target species semi-specifically from specimen solution. Thus, this performance can be the source of observing greater current response in the MIP-CNT modified electrode in comparison with the NIP-CNT modified electrode.

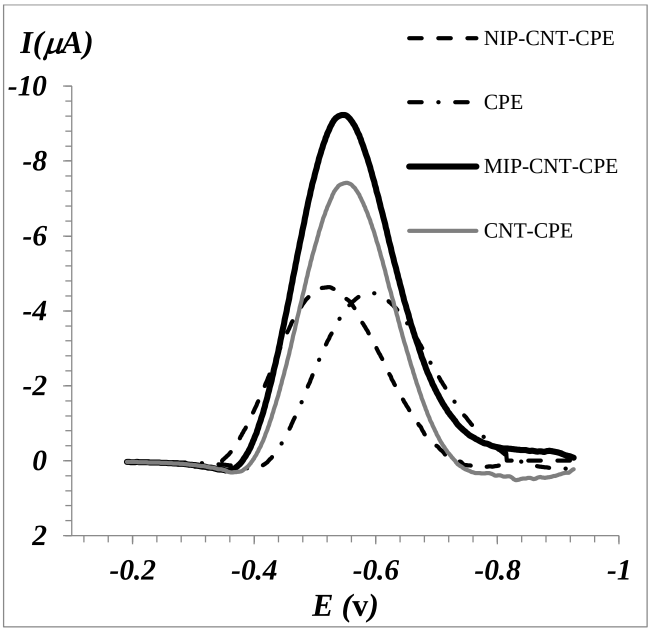


Figure 2. DPV responses in 4 kinds of electrodes (MIP-CNT-CPE, NIP-CNT-CPE, CPE and CNT-CPE)

3.3. Optimizing the effective elements on sensor behavior

Figure 3 represents optimizing electrolyte pH through application of Britton–Robinson buffers and various concentrations of NaOH. As it is obvious, the maximum current response is attained at pH<3 and decrease signal in higher concentrations of sodium hydroxide. This result proves that the chloridazon current response in acidic solution equals to transferring 4 electrons [13].

For optimizing the polymer quantity in the sensor composition, the improved sensors were made with various contents of MIP (4-16%) and examined in the similar circumstances.

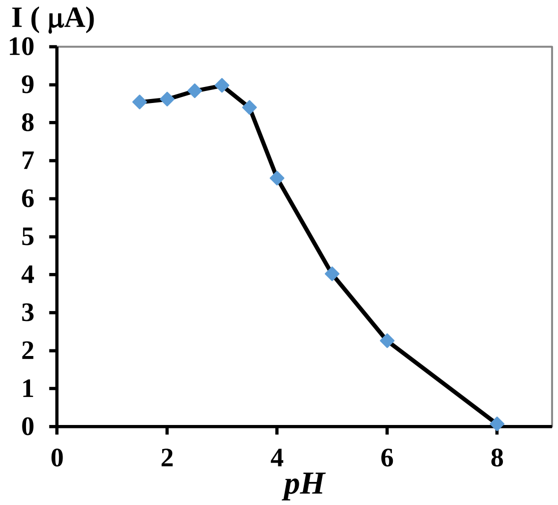


Figure 3. Effect of pH on peak current in Britton-Robinson buffer using differential puls voltammetry at MIP-CNT-CP electrode. Chloridazon concentration, 2×10^{-4} mol L^{-1}, scan rate, 15mVs^{-1}, puls amplitude, 105mV.

According to Figure 4, the electrode response increases, up to 10% of the MIP and the current response reduces considerably at more contents of polymer. This finding indicates that the existence of MIP in a given percentage increments the CLZ's pre-concentration at the surface of electrode with no remarkable destructive impact on the conductivity of electrode. Nevertheless, by enhancing the MIP amount further than 10%, the current signal and the electrode surface conductivity are decreased as a result of the polymer's insulating nature. Hence, 10% of the MIP was chosen as the optimum quantity.

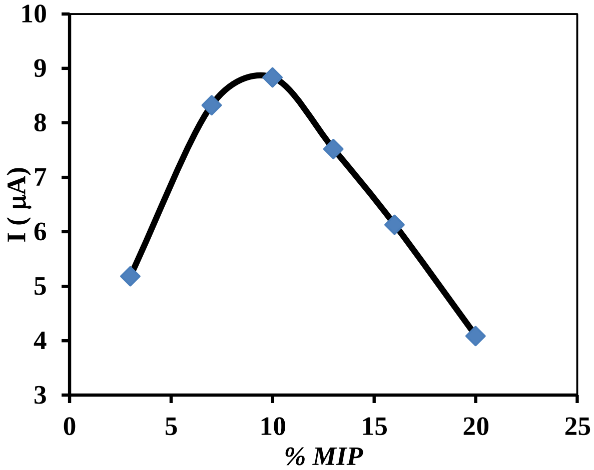


Figure 4. Optimizing sensor response by changing the MIP percentage (extraction volume = 25 mL, in Britton–Robinson buffers at pH=3 and [CLZ]= 2×10^{-4} mol L^{-1}).

Fig. 5 shows changing the electrode response to chloridazon as a function of extraction time. For recording such a curve, the electrode was incubated in the CLZ's constant concentration for various times. The electrode was then immersed into the electrochemical cell solution. Based on the explained curve, by increasing the extraction time, a distinct increment is obtained in the electrode signal to chloridazon. Nevertheless, followed by elapsing for 10 min, the electrode's signal considerably declines.

The signal decline at extended extraction time may be allocated to penetrating the chloridazon to the MIP nanoparticles' parts, which appears to be scarcely released in the electroanalysis phase. Considering that the best electrode signal is attained at almost 10 min, the extraction time of electrode is 10 min.

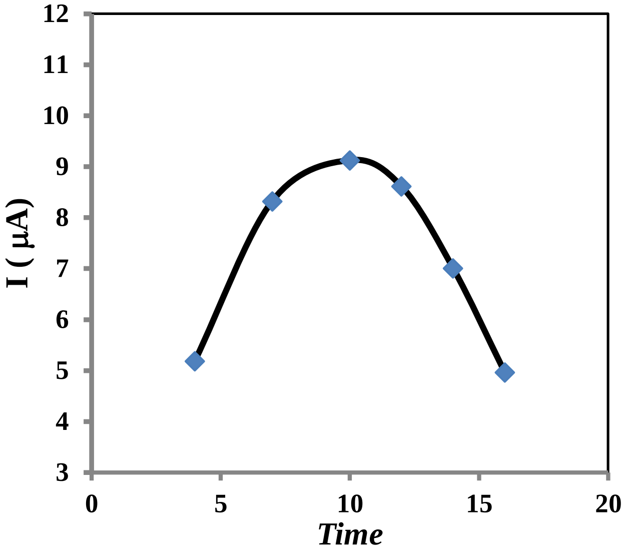
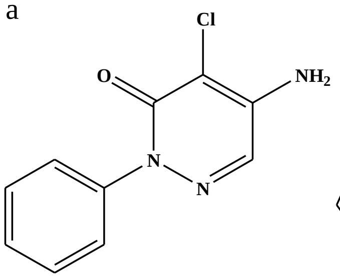


Figure 5. The effect of CLZ (C=2×10^{-4} mol L^{-1}) extraction time on the nano-MIP-CNT modified electrode response

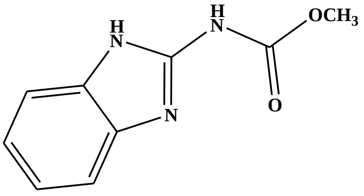
3.4. Interferences study and sensor selectivity

The CLZ sensor's selectivity, was compared with equivalent compounds (Fig. 6). The finding illustrated in Fig. 6, indicates that the equivalent pesticides impose no considerable current response utilizing the CLZ electrode. As it is observed, the sensor response against carbendazim is almost 0, and the response to metamitron is ignorable (regardless of its great structural similarity to CLZ). In the other hand, the impact of interferences on CLZ determination was studied under optimum circumstances. The toleration limit was made as the highest concentration of other compounds resulting in a relative error of 5% in the analytical response of 5× 10^{-4} mol L^{-1} of CLZ. The findings indicated that this value was less than 1200 for carbendazim and less than 200 for metamitron.

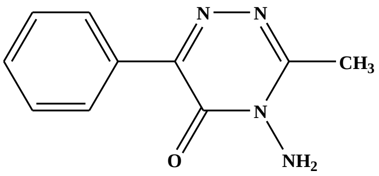
a



Chloridazon



Carbendazim



Metamitron

b

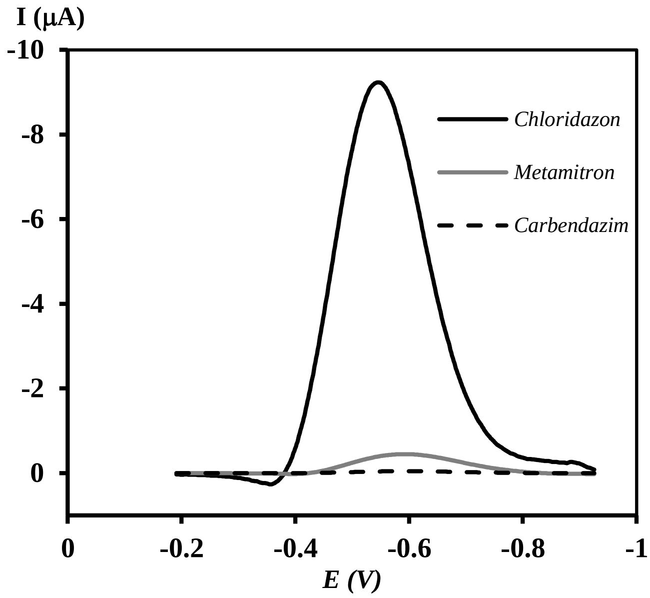


Figure 6. Chloridazon, metamitron and carbendazim (a), attained voltammogram for various compounds utilizing the suggested CLZ electrode at enhanced circumstances (b).

3.5. Calibrating the MIP-CNT modified electrode

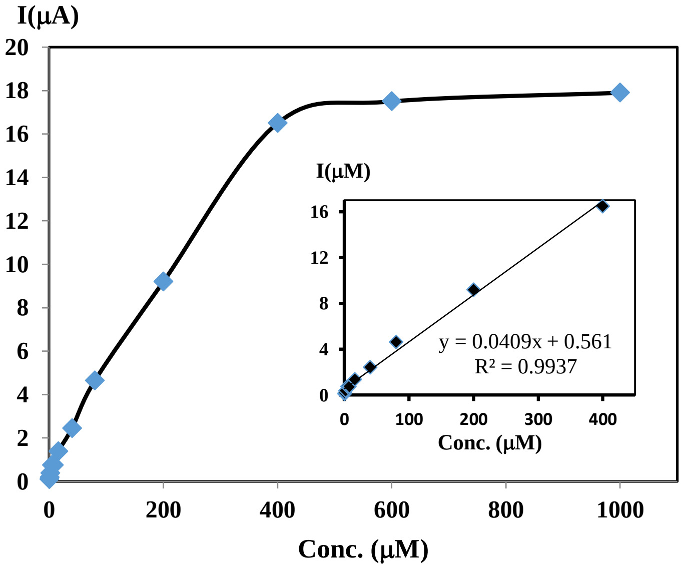


Figure 7. The calibration curve of the established sensor, obtained at the enhanced condition; (nsets represent two linear ranges of chloridazon, 5.0×10^{-7}-4.0×10^{-4} mol L^{-1}.

The established electrode was utilized for plotting the calibration curve. The current response values utilized for the calibration curve are in fact the absolute values of the reduction peak current obtained for blank solution followed by spiking various CLZ solutions' concentrations. According to the calibration curve of the sensor (Fig. 7), it is indicated that the current signal of the sensor to CLZ amount was linear within the concentration range of 5.0×10^{-7}-4.0×10^{-4} mol L^{-1}. This electrode's LOD was computed 6.2×10^{-8} mol L^{-1}.

3.6. Real sample analysis

The developed sensor was applied for determination of chloridazon in water samples such as ground water, surface water, sea water and drinking water samples (Table 1). All water samples to be analyzed were transferred into 50-mL flasks and then, 2 ml and 200 μL of the stock solution of chloridazon ($c=5\times10^{-3}$ mol L^{-1}) was added to the samples to acquire a concentration of 2×10^{-4} mol L^{-1} and 2×10^{-5} mol L^{-1} in the sample. Favorable recovery percentages is good indicatives for the reliability of the suggest method. In addition, the comparison of CLZ determination results of the sensor with those obtained using the GC-MS, as a reference method, showed no significant difference between the reference analytical method and the proposed sensor for CLZ evaluation.

Table 1. Determination of chloridazon in different water samples by the developed sensor

Sample	Spiked (mol/L)	Found (mol/L)	Recovery% (5, n=3)	GC-MS (mol/L)
Ground water	2×10^{-5}	1.90×10^{-5}	95.0	1.91×10^{-5}
Ground water	2×10^{-4}	1.92×10^{-4}	96.0	1.93×10^{-4}
Surface water	2×10^{-5}	1.85×10^{-5}	92.5	1.83×10^{-5}
Surface water	2×10^{-4}	1.88×10^{-4}	94.0	1.86×10^{-4}
Drinking water	2×10^{-5}	1.92×10^{-5}	96.0	1.90×10^{-5}
Drinking water	2×10^{-4}	1.93×10^{-4}	96.5	1.93×10^{-4}
Sea water	2×10^{-5}	1.81×10^{-5}	90.5	1.82×10^{-5}
Sea water	2×10^{-4}	1.84×10^{-4}	92.0	1.85×10^{-4}

4. CONCLUSION

This paper tried to introduce a novel electrochemical sensor for determining chloridazon at trace levels. Using MIP as a new modification agent in the carbon paste electrode made it very discriminating for determining CLZ in the existence of usual potential interfering agents. The MIP, utilized in the carbon paste composition, had the performance as the pre-concentrating agent and the sensor's selective chemical interface.

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