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A novel high selective and sensitive para-nitrophenol voltammetric sensor, based on a molecularly imprinted polymer–carbon paste electrode

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ABSTRACT

By using a molecularly imprinted polymer (MIP) as a recognition element, the design and construction of a high selective voltammetric sensor for para-nitrophenol was formed. Para-nitrophenol selective MIP and a non-imprinted polymer (NIP) were synthesized, and then used for carbon paste (CP) electrode preparation. The MIP–CP electrode showed greater recognition ability in comparison to the NIP–CP. It was shown that electrode washing after para-nitrophenol extraction led to enhanced selectivity, without noticeably decreasing the sensitivity. Some parameters affecting sensor response were optimized and a calibration curve was plotted. A dynamic linear range of 8×10^{-9} to 5×10^{-6} mol L^{-1} was obtained. The detection limit of the sensor was calculated as 3×10^{-9} mol L^{-1}. Thus, this sensor was used successfully for the para-nitrophenol determination in different water samples.

1. Introduction

Phenol compounds such as nitrophenols are amongst the category of serious environmental contaminants, and their determination in environmental samples has been of high interest due to their toxic effects on humans, animals and plants [1]. Nitroaromatic compounds can be formed by photochemical atmospheric reactions owing to the presence of nitrogen oxides in industrial and automotive emission gases. They are also widely used in the production of pesticides, paints and explosive materials [2,3]. Nitroaromatic compounds are considered by the United States Environmental Protection Agency as main pollutants, because they are toxic to human health [4]. In particular, para-nitrophenol is a toxic hydrolysis product of the insecticides parathion and paraoxon, and also exists in wastewater from industries such as refineries. Detoxification of water contaminated with nitroaromatic compounds is usually a very difficult process since the presence of a nitro-group on the aromatic compound. This confers a strong chemical stability and resistance of microbial degradation [5]. The detection of para-nitrophenol is important for protecting water resources and food supplies in the defense against terrorist activity, and for monitoring detoxification processes [6]. Therefore, there are growing demands for portable devices for reliable on-site monitoring of para-nitrophenol compounds.

Some laboratory-based analytical methods for determining para-nitrophenol compounds such as; gas and liquid chromatography [7–13], UV–vis spectrophotometry [12,13] and spectrofluorimetry [14] have been reported. The use of enzyme-linked immunosorbent assay has also been accounted for [15]. However, for the majority of these methods, some sample pretreatment involving separation, extraction and adsorption is generally necessary. These can be time-consuming and complex.

Electrochemical methods, such as differential pulse polarography, anodic stripping voltammetry and differential pulse voltammetry, have been widely applied for the determination of pharmaceuticals, dyes, insecticides, pesticides and inorganic ions [16–19].

Modified electrodes are being used frequently in the voltammetric determination of organic compounds because of their efficiency and the selectivity that can be obtained by varying the modifier. In recent years, chemically modified electrodes were used for the voltammetric quantification of various organic and inorganic species after their accumulation [20–22]. Multitudes of modifying agents were used either as coatings on solid electrode surfaces, or dispersed within a conductive matrix. Some modified electrodes have been reported such as: a glass carbon electrode impregnated with a lithium tetracyanoethylenide (LiTCNE) [23], and a sodium montmorillonite-anthraquinone chemically modified glass carbon electrode [6], for the determination of para-nitrophenol. These modifiers have advantages—stability for a long duration of time and simplicity in preparation. However, they suffer from a main

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drawback that is: moderate selectivity of the electrode to the target molecule.

MIPs are promising materials continually being used in sensor fields such as, recognition elements or modifying agents (instead of other commonly used modifiers). A MIP is a synthetic polymer possessing selective molecular recognition properties because of its recognition site within the polymer matrix that is complementary to the analyte molecule, regarding the shape and positioning of functional groups. These materials are partially similar to biological specific receptors because of high selectivity to the target molecule and the recognition mechanism [24]. It is well known that the stability of MIPs is superior to that of biological recognition materials, so that a sensor modified with a MIP is easily stored and operated, thus has a long lifetime. The application of MIPs in electrochemistry is rather recent and was directed to combine their intrinsic properties to selected electrochemical reactions, in order to improve the response of the electrode [25,26].

This study has led to the development of a new MIP modified electrode for the determination of para-nitrophenol with improved qualities such as; simplicity of electrode preparation, a wider linear range, lower detection limit (DL), higher selectivity and more stability of the used modifier. The procedure is based on the oxidation of the reduced product of para-nitrophenol. This is a result of the negative pre-potential being applying to the electrode after para-nitrophenol extraction on a carbon paste electrode, modified with the para-nitrophenol selective MIP.

2. Experimental

2.1. Instruments and reagents

Electrochemical data was obtained with a three-electrode system using a potentiostat/galvanostat model PGSTAT302, Metrohm. The differently prepared MIP or NIP involved sensors which were used as the working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes respectively. Methacrylic acid (MAA), obtained from Sigma–Aldrich (Munich, Germany), was purified by passing it through a short column of neutral alumina, followed by distillation under reduced pressure. Ethylene glycol dimethacrylate (EDMA), obtained from Fluka (Buchs, Switzerland), was distilled under reduced pressure in the presence of a hydroquinone inhibitor, and stored at 4 °C until used. Para-nitrophenol, aniline, phenol, nitrobenzene, n-eicosane and 2,2′-azobisisobutyronitrile (AIBN) were supplied by Sigma–Aldrich (Munich, Germany), and used as received. Graphite powder was purchased from Fluka (Buchs, Switzerland). All other chemicals were of analytical grade and were purchased from Merck (Darmstadt, Germany).

2.2. Preparation of the molecularly imprinted polymer (MIP)

The MIP having para-nitrophenol recognition sites was designed and prepared according to the simple precipitation procedure. In order to synthesize the MIP template molecule (1 mmol), methacrylic acid (3 mmol) and 50 ml of dry chloroform were placed into a 100 ml round-bottomed flask, and the mixture was left in contact for 10 min. Subsequently, EDMA (20 mmol) and AIBN (0.2 mmol) were added. The flask was sealed and the mixture was purged with nitrogen for 15 min. Polymerization took place in a water bath at 60 °C for 24 h. After, the final polymer was simply powdered and the template removed by Soxhlet extraction with methanol for 48 h. The complete removal of template from the polymer was traced by the square wave voltammetry method. The non-imprinted polymer (NIP) was prepared similarly to the MIP, except that the template was not present in the polymerization media.

In order to obtain finer and smaller MIP particles, the obtained powder was sequentially immersed three times in acetonitrile and the supernatant portions were collected for final usage.

2.3. Preparation of the sensors

In order to prepare the sensor (MIP–CP or NIP–CP), 0.01–0.08 g of graphite was homogenized in a mortar with different amounts (0.003–0.025 g) of powdered para-nitrophenol MIP or NIP for 10 min. Subsequently, n-eicosane (0.01–0.035 g) was melted in a dish in a water bath heated at 45–50 °C. The graphite/MIP blend was then added to the melted n-eicosane and mixed with a stainless steel spatula. The final paste was used to fill a hole (2.00 mm in diameter, 3 mm in depth) at the end of an electrode body, which had been previously heated at 45 °C. After cooling at room temperature, the excess of solidified material was removed with the aid of sand paper. Optical microscopy (I, II, and III) and scanning electron microscopy (IV) images of the prepared electrode surface are shown in Fig. 1.

2.4. General method for electrochemical measurements

The electrochemical measurement of para-nitrophenol was carried out according to the following procedure:

Extraction step: Each prepared electrode was inserted into solutions containing the para-nitrophenol, in which the pH was fixed by buffer solution. All solutions in the extraction period were stirred at a fixed stirring rate and for a determined period of time.
Washing step: The electrode was removed from the first solution and then inserted into the washing solution which composed of water/acetonitrile (97:3). It remained in this solution for 15 s.
Analyzing step: The electrode was placed in the electrochemical cell containing 0.05 mol L^{-1} buffer solution with determined pH. For any voltammetry experiment, at first a negative pre-potential was applied to the electrode for a fixed time. The potential was then scanned in the appropriate range.

2.5. The measurement of para-nitrophenol in real samples

In order to analyze para-nitrophenol, the imprinted sensor was incubated in the spiked solution, and inserted into a water/acetonitrile (97:3) solution for 15 s. This was followed by transferring it into an electrochemical cell containing 10 ml acetate buffer, pH 4.5. A pre-potential of −1.0 V was applied for 25 s to the electrode, differential pulse voltammograms in the range of 0.0–0.5 V were recorded, and the corresponding maximum current was used for final determination.

3. Results and discussion

3.1. Electrochemical behavior of para-nitrophenol

Cyclic voltammetric studies of para-nitrophenol have been reported [27,28,6,29]. In the current investigation, para-nitrophenol voltammetric behavior was initially investigated with an unmodified carbon paste electrode. For cyclic voltammetry, the potential of the electrode was scanned in the range of −1.5 to +1.5 V, in the solution of an acetate buffer pH 5. The voltammetric behavior of para-nitrophenol is presented in Fig. 2, where the peak R_1 results from an irreversible reduction of the nitro group to give the corresponding hydroxylamine species, which on the return positive scan could be oxidized to give a nitro species. Further oxidation of O_2 is

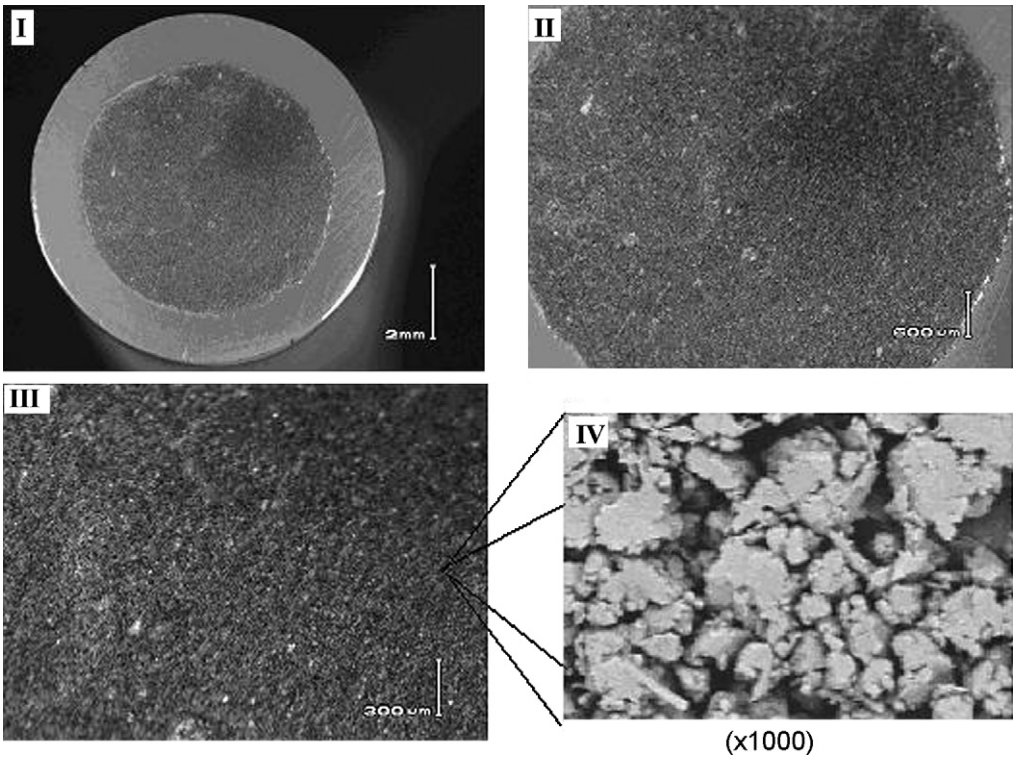

Fig. 1. Optical microscopy (I, II, and III) and scanning electron microscopy images of prepared electrode surface.

observed for PNP and is possibly due to oxidation of the phenol group, giving a radical species which can undergo dimerization. It was found that pre-reduction of para-nitrophenol at the negative potential is necessary for O_1 peak creation. The voltammogram was predominated on the forward negative scan by a single reduction peak R_1. On the return positive scan, two oxidation signals O_1 and O_2 were seen, however, no redox couples for these latter two peaks were observed on the second negative scan. If the scan direction was switched before the oxidation process O_2 (not shown in figure), a further reduction signal R_2, would appear on the second negative scan. R_1 is the result of an initial reduction of the nitrogroup of PNP (I) to give the hydroxylamine species (II). This undergoes loss of water to give the quinoneimine species (III). As the reduction potential of the quinoneimine species (III) is more positive than that required to initially reduce PNP, the latter species readily undergoes a further two electron reduction to give PAP (IV). Therefore, the result is an overall six electron reduction. On the return positive scan, PAP (IV) is oxidized through a reversible two electron process to go back to the quinoneimine species (III), producing the redox couple O_1/R_2. It should be mentioned that species (V) is formed as a result of oxidation at the phenolic group of PNP, which occurs at high positive potentials [30,31].

3.2. MIP–CP and NIP–CP electrodes responses to para-nitrophenol and washing effects

In order to study the para-nitrophenol recognition ability of MIP, the MIP–CP, NIP–CP and CP electrodes were prepared and inserted into the para-nitrophenol containing solutions. After 7 min the electrodes were removed from the para-nitrophenol solution and cyclic voltammetry was carried out. The obtained results are shown as recorded voltammograms related to O_1/R_2 electrochemical reactions. They were obtained after applying the pre-potential of −0.8 V to the electrodes, for 15 s (Fig. 3(I)). As can be seen, the

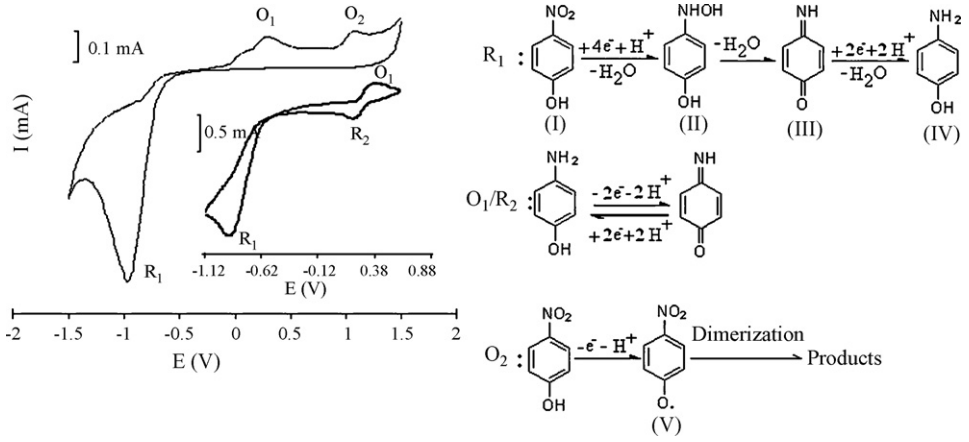

Fig. 2. Electrochemical behavior of para-nitrophenol in the carbon paste electrode and the proposed electrochemical reaction mechanism.

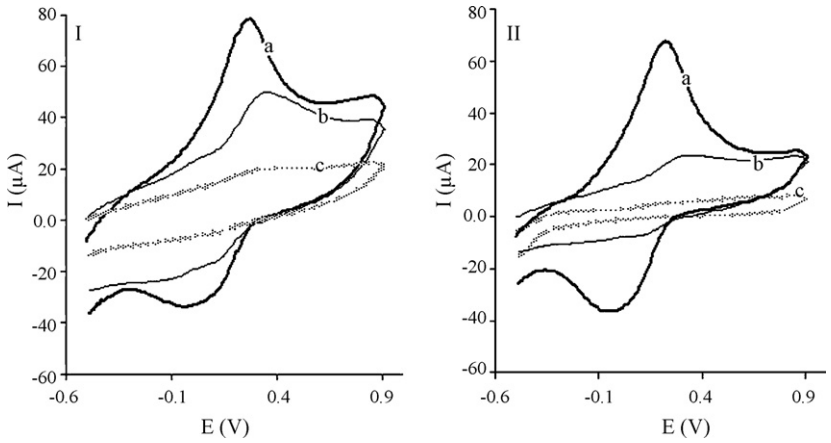

Fig. 3. Recorded para-nitrophenol responses from different electrodes immersed in the para-nitrophenol solution (3×10^{-6} mol L^{-1}) (I) and the effect of electrode washing on the related cyclic voltammetry response after removing the electrodes from para-nitrophenol solution (3×10^{-6} mol L^{-1}) (II). The voltammograms of (a), (b) and (c) are those respectively obtained from the electrodes of MIP–CP, NIP–CP, CP. para-nitrophenol extraction conditions; pH 5, extraction time = 7 min, washing time = 15 s. The potential was scanned with rate of 0.03 V s^{-1} in the solution with pH of 5, after applying pre-potential of −0.8 V for 20 s.

CV signal of the MIP–CP electrode (voltammogram a) is higher than those for the NIP–CP and CP electrodes. This indicates that the MIP in the CP electrode intensively uptakes para-nitrophenol from the aqueous solution, in comparison to NIP–CP and CP electrodes. In order to evaluate the para-nitrophenol keeping power by MIP, after its extraction, we performed other experiments in which the previous experiments were repeated again. In this case, after the electrodes were removed from the para-nitrophenol solution, they were inserted into the washing solution for a short time (15 s). The obtained results are displayed in the Fig. 3(II). Washing the electrodes after para-nitrophenol extraction does not considerably affect the para-nitrophenol signal in the MIP–CP. In comparison to this, the response of the NIP–CP and CP electrodes decrease to a large extent. Hence, it is clear to see there is greater affinity of the MIP–CP electrode for para-nitrophenol. This observed distinction of MIP–CP can be used for selectivity enhancement of MIP–CP by a simple washing step. The washing process can remove weakly adsorbed and non-specifically absorbed para-nitrophenol molecules from the electrode surface, the state which is dominant in the case of NIP–CP and CP electrodes. But, para-nitrophenol molecules which are incorporated in the MIP containing selective sites are not removed so easily by the washing process.

The constructed MIP particles during the non-covalent approach usually contain selective sites with various affinities for the template. Some of them are cavities with the sizes matching exactly with that of the template molecule. These are template recognition sites, formed with regular and perfect shape in the polymerization period and thus have more affinity for para-nitrophenol. Para-nitrophenol molecules in existence in such cavities are tightly absorbed to the MIP, and therefore the washing of the electrode, modified with the MIP does not noticeably disrupt the corresponding interactions [32].

A main drawback of non-covalent systems is the unavoidable heterogeneity of the binding sites arising from the multitude of complexes formed between the template and the functional monomers. These are preserved to some extent during the polymerization. Usually an excess of functional monomer relative to the template is required to favor template-functional monomer complex formation, and to maintain its integrity during the polymerization. As a result, a fraction of the functional monomers are randomly incorporated in the polymer matrix resulting in the formation of non-selective binding sites [33–36].

The cavities with incomplete or irregular shape, and also the non-selective binding sites cannot absorb para-nitrophenol molecules so tightly. The portion of para-nitrophenol molecules absorbed by such mentioned binding sites can be removed from MIP–CP electrodes by the washing process.

In the case of NIP–CP electrodes, the washing step removes the para-nitrophenol from the electrode easily, because the binding site in the NIP is non-selective and acts almost similar to non-selective sites of MIPs.

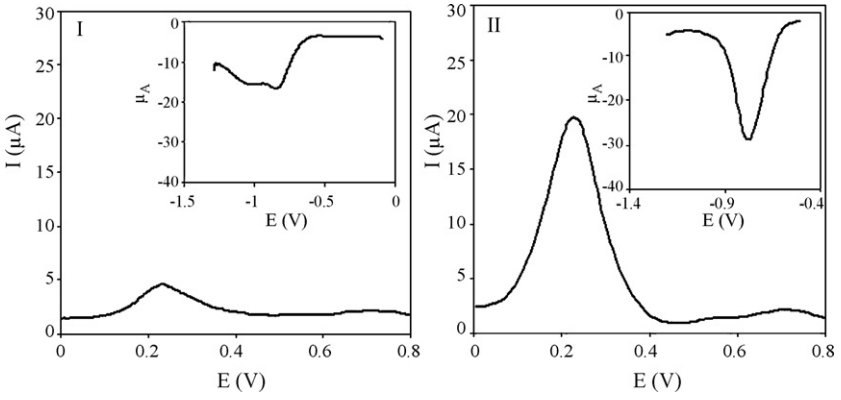

Fig. 4. Comparison of square wave voltammetry (I) and differential pulse voltammetry (II) for para-nitrophenol determination by proposed sensor after applying pre-potential of −1.0 V for 15 s to the electrode. Insets are corresponding voltammograms of para-nitrophenol recorded in the negative potentials. The extraction and measurement conditions were the same for two methods.

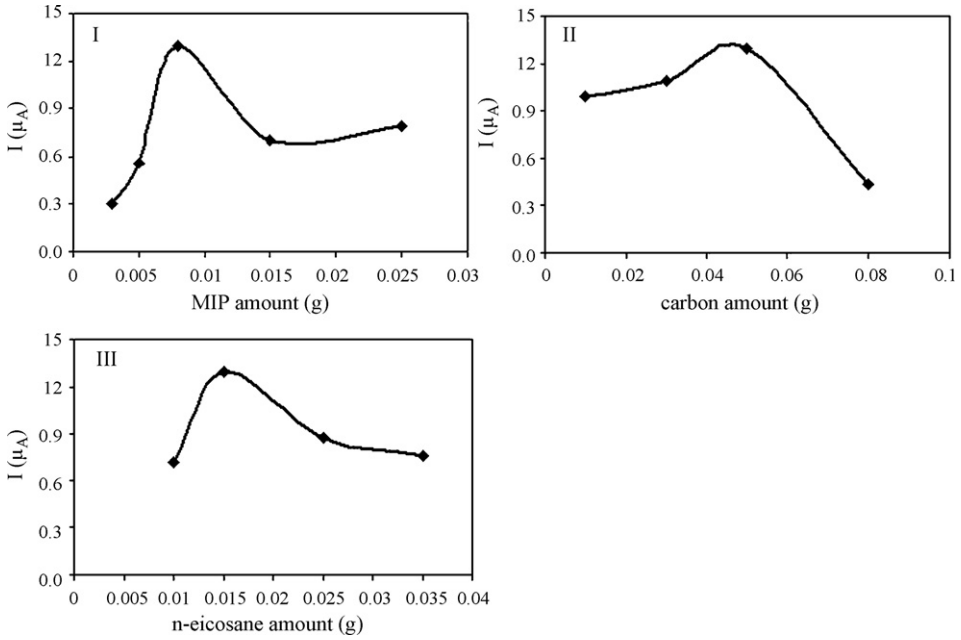

Fig. 5. Optimization of carbon paste electrode compositions; variation of electrode response for para-nitrophenol with changing of (I) MIP, (II) carbon and (III) n-eicosane amounts of MIP–CP electrode. The curves are based on the differential pulse voltammetry responses (recorded after applying pre-potential of −0.8 V for 20 s) against different variable changing.

MIPs can act more selectively than other artificial recognition elements. However, according to what was explained above (because of the presence of non-selective and poorly selective sites in the MIP, and the non-selective absorption property of carbon particles in the MIP–CP), importance of the washing step in our proposed method is explicit.

3.3. Electrochemical method selection

In order to achieve a high sensitive sensor, the selection of a proper electrochemical technique is of great importance. So, we tested different voltammetric methods such as differential pulse voltammetry and square wave voltammetry, known as high sensitive electrochemical methods. The obtained results of this experiment are shown in Fig. 4. As it is evident, the response obtained by differential pulse voltammetry is better than that obtained by square wave voltammetry for para-nitrophenol in the same conditions of extraction and determination.

3.4. Optimization of parameters for para-nitrophenol detection

The optimization process for the designed sensor was divided into three sections including: optimization of carbon paste composition, extraction parameters and electrochemical determination conditions.

3.4.1. MIP–CP composition optimization

In order to find the best composition for MIP–CP electrodes, the amount of different ingredients of the electrode including MIP, carbon and n-eicosane were changed in the fixed conditions of extraction and voltammetric determination. The obtained responses were used for conclusion. For initial optimization purposes, the MIP–CP electrodes were prepared with fixed amounts of carbon and n-eicosane and different amounts of MIP. The resulted electrodes at each case were used for para-nitrophenol extraction and determination. The obtained results are presented in Fig. 5(I). It is clear that the maximum response for the prepared sensor appeared in the MIP amount of 0.01 g. Higher amounts of MIP in the MIP–CP electrode can increase the sensor response due to providing more recognition sites on the electrode surface. This is illustrated in the corresponding curve. However, enhancement the MIP amount more than a threshold level, leads to a decrease in the prepared sensor response, probably because of electrode surface conductivity decreasing. Similar experiments were also carried out in order to investigate the effect of carbon and n-eicosane amounts on the prepared electrode response. By changing the parameter amounts of the MIP–CP electrode, the recorded results were obtained, as shown in Fig. 5(II) and (III). From the corresponding curves, the optimum amount of carbon and n-eicosane was defined as 0.05 and 0.015 g for carbon and n-eicosane amounts, respectively. Increasing the carbon content of MIP–CP electrode leads to an increase in the corresponding electrode response because of electron transferring capability enhancement of the electrode. The amount of carbon increases, as does the electrode sensitivity. This continues to a limited point and afterwards the electrode response decreases with carbon content enhancement. The amount of carbon on the electrode surface, leads to a decrease of the MIP content on the electrode. The optimum amount of n-eicosane is necessary for the MIP–CP electrode preparation. Presence of higher amounts of binder (n-eicosane) in the MIP–CP electrode leads to a decrease in electrode response. This is because the electrode surface conductivity is decreasing, due to the insulating effect of the binder.

3.4.2. Optimization of para-nitrophenol extraction conditions

The pH of the para-nitrophenol solution as a commonly considered parameter was noticed, and its effect on the para-nitrophenol extraction in the electrode studied. For this purpose, the pH of para-nitrophenol solution was fixed at different pH ranges and at each case the prepared electrode was inserted into the para-nitrophenol solution for 10 min with stirring. After the allocated time, the electrode was removed from the solution and then taken into the solution of the electrochemical cell. The results of this experiment are represented in Fig. 6(I). In the pH range of 3–6, the para-nitrophenol related electrochemical signal is seen, hence, the para-nitrophenol extraction is higher and has no considerable variation in this pH range. For pHs less than 3 and higher than 6, the

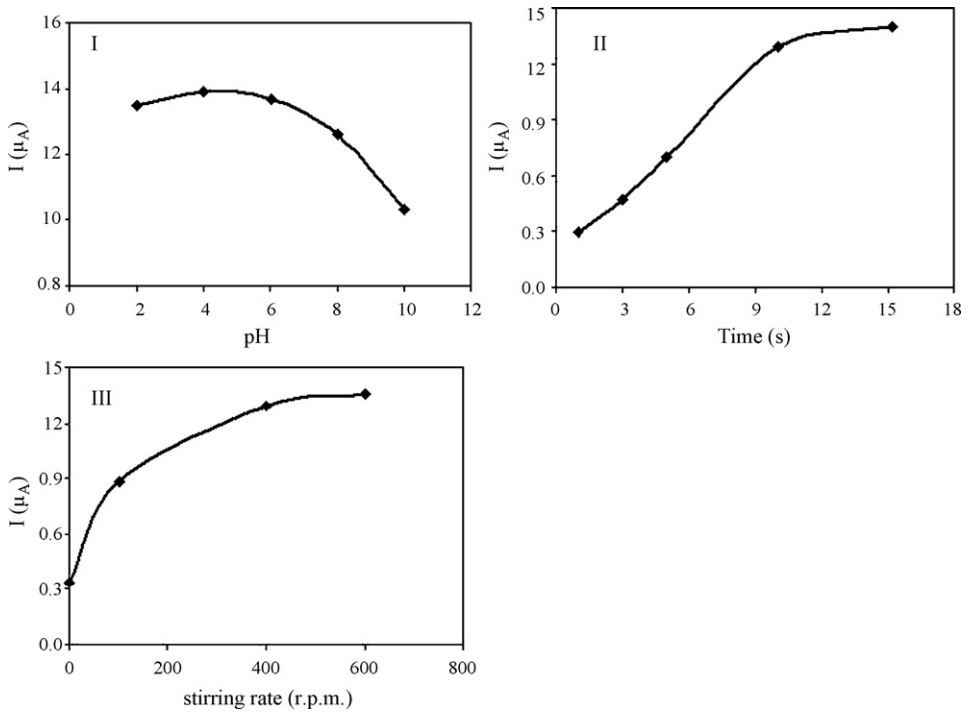

Fig. 6. Optimization of different conditions affecting the para-nitrophenol extraction in the MIP–CP electrode; variation of electrode response for para-nitrophenol with changing of (I) para-nitrophenol solution pH, (II) electrode incubation time and (III) stirring rate. The curves are based on the differential pulse voltammetry responses (recorded after applying pre-potential of −0.8 V for 20 s) against different variable changing.

extraction amount tends to decrease. According to these results the pH of 5 was chosen as an optimum for parathion extraction in the electrode.

Since the electrode contact area with the parathion containing solution was partially small, the analyte extraction in the electrode was carried out with stirring. In order to optimize the stirring rate in the extraction period, para-nitrophenol was extracted in the prepared MIP–CP electrodes at the assorted stirring rates, whereas the other extraction parameters such as time, pH and concentration remained constant. The obtained results showing the parathion DPV signal variation against the stirring rates are presented in Fig. 6(II). The higher the stirring rate, the greater the electrode response is for para-nitrophenol. This indicates the high effect of stirring on the para-nitrophenol extraction in the case of the MIP–CP electrode. The growth in the para-nitrophenol voltammetric response with an increase in stirring rates continues noticeably until 400 rpm. However after, it seems that the para-nitrophenol extraction enhancement is not so much and the variation of extraction with the stirring rate changing is small. Therefore, we selected the value of 500 rpm as an optimum for this optimization purpose.

Extraction time was another main parameter which was examined. The prepared electrodes were inserted into the para-nitrophenol solutions of fixed concentrations and stirring rates for the allocated times, and afterwards, the electrodes were removed from the solutions followed by differential pulse voltammetry analysis. The obtained results are shown in Fig. 6(III). According to this figure, the increasing extraction time leads to an intensive increase in the parathion extraction amount in the electrode until about 10 min; afterwards the increasing rate with time enhancement is not so considerable. In order to decrease the analyzing time, 10 min was selected for the extraction time.

3.4.3. Optimization of electrochemical measurement conditions

In the case of electrochemical measurement, the main important parameters which could be optimized were; pH, applied pre-potential amount, and time of exerted pre-potential. The pH range is critical for the voltammetric characteristics of para-nitrophenol as well as for the MIP, so the effect of pH on the electrode reaction was studied in detail by DPV. It was found that the anodic peak current was dependent on the pH. The anodic peak current decreased with decreasing pH in the range of 2.0–3.0. Between pH 3.0 and 4.0, the current gave a maximum. A current decline was observed when the pH of the solution was more than 6.0. Thus, the optimum pH for further studies was selected to be 4.5.

The effect of pre-potential magnitude and its exertion time was investigated. The peak current remained almost zero in the potential range of 0.0 to −0.5 V. The reason is obvious since para-nitrophenol cannot be reduced in this potential range. There was a sudden increase in the peak current at −0.6 V and it remained almost constant on further increase of the pre-potential after −1.0 V. Consequently, it was decided that the pre-potential amount was to be −1.0 V.

The peak current was amplified with an increase in the pre-potential applying time until about 25 s where it attained a plateau. Thus, the optimum amount of 25 s was considered for this parameter.

3.5. Analytical characterization

After the optimization and establishment of the determined method for the preparation of the MIP–CP sensor, various ions and molecules were examined with respect to their interference with the determination of para-nitrophenol. For 8×10^{-8} mol L^{-1} of para-nitrophenol, the results showed that over 1000 fold excess

Table 1
Determination of para-nitrophenol in different water samples.

Sample	Spiked (nmol L^{-1})	Found[a] (nmol L^{-1})	Recovery (%)	RSD (%)
Tape water	100.0	99.4	99.4	3.1
River water	80.0	80.3	100.4	2.9

[a] Number of sample assayed = 6.

Table 2
Comparison of introduced sensor with two other previously reported sensors.

Carbon paste modified with	Nature	D.L. (mol L^{-1})	L.D.R (mol L^{-1})	Sel.	Lifetime (week)	Reproducibility% ($n = 5$)	Reference
Moraxella sp.	Biologic	2×10^{-8}	–	Specific	3[a]	4.49	[37]
Apatite	Chemical	8×10^{-9}	2×10^{-7} to 1×10^{-4}	–	–	–	[38]
MIP	Biomimetic	3×10^{-9}	8×10^{-9} to 5×10^{-6}	High	>16[b]	2.25	This work

[a] Stored at 4 °C.
[b] Stored at room temperature.

concentration of; K^+, Ca^{2+}, Cl^-, $SO_4{}^{2-}$, $NO_3{}^-$, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, did not interfere with the para-nitrophenol response. Phenol, aniline, 2,4,6-trinitrotoluene and benzoic acid showed no interference until a 30 fold excess was over para-nitrophenol. The interference for 2,4,6-trinitrotoluene and nitrobenzene appeared in the concentration that was 60 fold higher than that for p-nitrophenol. Phenol and aniline in the concentrations of 100 fold excess than that of p-nitrophenol showed interference.

The developed sensor, at optimized conditions, was used for calibration curve plotting. It is worth noting that the values of the current response used for the calibration curve are actually the absolute values of the oxidative peak current observed after electrode incubation in different concentrations of para-nitrophenol solution. The calibration graph obtained for para-nitrophenol determination of the prepared sensor showed a linear relationship over para-nitrophenol concentration in the range of 8×10^{-9} to 5.0×10^{-6} mol L^{-1} with a detection limit of 3.0×10^{-9} mol L^{-1}.

The analytical utility of the method was assessed by applying it to the determination of para-nitrophenol in different water samples. Samples analyzed did not contain para-nitrophenol, so they had to be spiked with the analyte at a certain concentration. Spiking of the samples was achieved by injection of a para-nitrophenol stock solution and then homogenization. The results for the determination of para-nitrophenol in different water samples are summarized in Table 1. Every reported result is the average of six separate determinations in the corresponding water samples. The observed recoveries of the spiked para-nitrophenol demonstrate that the proposed sensor is a promising approach in sensor preparation, and analysis of para-nitrophenol.

3.6. Comparison of developed sensor with other similar works

In Table 2 the carbon paste electrodes modified with the biologic [37] and chemical [38] modifier are compared with our proposed sensor, regarding some analytical characteristics. In comparison with biosensor the MIP based electrode has lower detection limit, somewhat better reproducibility and very long lifetime. Selectivity of biosensor is more than MIP-based electrode. Because it has been reported that 3-nitrophenol, 2-nitrophenol and phenol had no interference effect on the para-nitrophenol determination, whereas in the case of MIP-based sensor the interference effect of 3-nitrophenol, 2-nitrophenol was appeared in the concentrations of 4 fold excess over para-nitrophenol. However, as mentioned in 3.5, other similar compound had no considerable response in comparison with that for para-nitrophenol in the case of MIP–CP sensor.

In comparison with chemical modifier (apatite), MIP-containing carbon paste electrode has lower detection limit and wider linear dynamic range. No explicit discussion about the selectivity of the sensor has been found in the apatite based sensor, but the matrix effect of real water samples has been reported in the case of related sensor whereas there was no interference effect of common anions and cations on the introduced sensor response for para-nitrophenol.

Totally, except the selectivity characteristic, which is very high in the case of presented biosensor, other considered analytical parameters of MIP containing electrode is better than those of both discussed electrode in the Table 2.

4. Conclusion

A very high selective differential pulse voltammetric sensor for para-nitrophenol determination at low concentrations was proposed. The MIP functioned as both: a pre-concentrator and a high selective recognition element in the carbon paste structure. Washing of the MIP–CP electrode after para-nitrophenol extraction led to enhanced selectivity, without considerable loss in sensitivity and detection limit of the sensor. The proposed sensor was used successfully for para-nitrophenol determination in real samples.

References

[1] R. Herterich, J. Chromatogr. 549 (1991) 313.
[2] M.J. Christophersen, T.J. Cardwell, Anal. Chim. Acta 323 (1996) 39.
[3] H.E. Wise, P.D. Fahrenthold, Environ. Sci. Technol. 15 (1981) 1292.
[4] E.L. Kochany, Chemosphere 22 (1991) 529.
[5] K.H. Lanouette, Chem. Eng. 84 (1977) 99.
[6] S. Hu, C. Xu, G. Wang, D. Cui, Talanta 54 (2001) 115.
[7] J.J. Scanlon, P.A. Flaquer, G.W. Robinson, G.E. Brien, P.E. Sturrock, Anal. Chim. Acta 158 (1984) 169.
[8] A. Brega, P. Prandini, C. Amaglio, E. Pafumi, J. Chromatogr. 535 (1990) 311.
[9] J. Ruana, I. Urbe, F. Borrull, J. Chromatogr. 655 (1993) 217.
[10] S.N. Lanin, Yu.S. Nikitin, Talanta 36 (1989) 573.
[11] B. Makuch, K. Guzda, M. Kaminski, Anal. Chim. Acta 284 (1993) 53.
[12] S. Kusakabe, M. Ohara, Anal. Chim. Acta 282 (1991) 57.
[13] G. Norwitz, N. Nataro, P.N. Keliher, Anal. Chem. 58 (1986) 639.
[14] Z. Wang, J. Zhang, J. Liu, G. Zhao, Chin. J. Anal. Chem. 21 (1993) 581.
[15] A. Oubina, B. Ballesteros, R. Galve, D. Barcelo, Anal. Chim. Acta 387 (1999) 255.
[16] A.J. Reviejo, F.J. Buyo, Electroanalysis 5 (1993) 303.
[17] M. Kotoucek, M. Opravilova, Anal. Chim. Acta 329 (1996) 73.
[18] A. Guiberteau, T.G. Diaz, F. Salinas, J.M. Ortiz, Anal. Chim. Acta 305 (1995) 219.
[19] M. Javanbakht, H. Khoshsafar, M.R. Ganjali, Electroanalysis 20 (2008) 203.
[20] K. Kalcher, J.M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Z. Yang, Electroanalysis 7 (1995) 5.
[21] J. Li, S. Liu, X. Mao, P. Gao, Z. Yan, J. Electroanal. Chem. 561 (2004) 137.
[22] H. Zhang, Z.H. Wang, S.P. Zhou, Sci. China Ser. B 48 (2005) 177.
[23] R.C.S. Luz, F.S. Damos, A.B. Oliveira, J. Beck, L.T. Kubota, Talanta 64 (2004) 935.
[24] T. Alizadeh, Anal. Chim. Acta 623 (2008) 101.
[25] W.M. Yeh, K.C. Ho, Anal. Chim. Acta 542 (2005) 76.
[26] C. Li, C. Wang, S. Hu, Anal. Chim. Acta 545 (2005) 122.
[27] M.D. Rando, M.B. Zamora, J.M. Salvador, I.N. Rodriguez, J.A. Munoz-Leyva, Mikrochim. Acta 132 (1999) 7.
[28] T.G. Diaz, A.G. Cabanillas, N.M. Diez, P.P. Vazquez, F.S. Lopez, J. Agric. Food Chem. 48 (2000) 4508.
[29] V.A. Pedrosa, L. Codognoto, S.A.S. Machado, L.A. Avaca, J. Electroanal. Chem. 573 (2004) 11.
[30] P. Zuman, Substituent Effects in Organic Polarography, Plenum Press, New York, 1967, p. 207.
[31] K.C. Honeychurch, J.P. Hart, Electroanalysis 19 (2007) 2176.
[32] E. Caroa, N. Masque, R.M. Marce, F. Borrulla, J. Chromatogr. A 963 (2002) 169.
[33] V.P. Joshi, S.K. Karode, M.G. Kulkarni, R.A. Mashelkar, Chem. Eng. Sci. 15 (1998) 53.
[34] M.J. Whitcombe, E. Vulfson, J. Am. Chem. Soc. 117 (1995) 7105.
[35] M.J. Whitcombe, C. Alexander, E.N. Vulfson, Trends Food Sci. Technol. 8 (1997) 140.
[36] T. Takeuchi, J. Matsui, Acta Polym. 47 (1996) 471.
[37] P. Mulchandani, C.M. Hangarter, Y. Lei, W. Chen, A. Mulchandani, Biosens. Bioelectron. 21 (2005) 523.
[38] M.A. El Mhammedi, M. Achak, M. Bakasse, A. Chtaini, J. Hazard. Mater. 163 (2009) 323.