

Development of highly selective electrochemical impedance sensor for detection of sub-micromolar concentrations of 5-Chloro-2,4-dinitrotoluene

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Abstract. A highly selective and sensitive impedimetric sensor based on molecular imprinted polymer (MIP) has been developed for the detection of 5-chloro-2,4-dinitrotoluene (5CDNT). Computational simulations were carried out for the best combinations of MIP precursors by using Hyperchem software. MIP of 5CDNT is synthesized using the optimized combinations of polymer precursors such as the functional monomer and cross-linker. Synthesized MIP and non-imprinted polymer (NIP) were characterized by Fourier transform infrared spectroscopy (FT-IR) and BET adsorption isotherm analysis. The surface area and pore volume of MIP are quite high compared to that of NIP, while the average pore diameter of MIP is lower than that of NIP. However, the synthesized MIP with high surface area and quite good pore diameter for free flow of analytes is suitable for efficient binding with the analyte 5CDNT. Binding assay studies of MIP by using UV-Visible spectroscopy showed that the molecular imprinting factor is nearly thrice to that of NIP. Carbon paste electrodes incorporated with MIP were employed as a sensor for 5CDNT by applying electrochemical impedance spectroscopy (EIS) as transduction principle. The charge transfer resistance obtained by impedimetric analysis is proportional to the concentration of 5CDNT over a wide concentration range: 10 nM to 100 μ M. A linear determination range of 1.0 to 100 μ M was obtained, and the low-detection-limit was found to be 0.1 μ M. The MIP carbon paste electrode has shown very good selectivity towards specific recognition of 5CDNT despite the coexistence of possible interferents like 2,4-dinitrotoluene and 1,3-dinitrobenzene. The present MIP based sensor system could be used successfully for direct determination of 5CDNT.

Keywords. 5-Chloro-2,4-dinitrotoluene; combinatorial studies; molecular imprinted polymers; ft-ir spectroscopy; binding assay; electrochemical impedance spectroscopy.

1. Introduction

Detection of explosives, including 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and their derivatives is an important analytical problem for the prevention of terrorism activities, detection of military explosives, detection of leftover landmines and environmental hazards from improperly disposed explosives. The direct attempt of TNT detection is difficult for laboratory researchers due to high explosive nature and lack of compound availability. So, the researchers often focus on detecting DNT and its derivatives. The leftover TNT, DNT in landmines, environment and earth have a lot of possibilities to form a variety of derivatives with halides. Among the derivatives, 5-chloro-2,4-dinitrotoluene (5CDNT) is one of the most common and major

derivatives of dinitrotoluene.^{1,2} 5CDNT, which is a common impurity and derivative of DNT-based explosives, exhibits a higher volatility than TNT. Because of these facts, it has been considered that the detection of 5CDNT is very important as much as DNT and TNT.^{1–5}

Many methods were reported in the literature for the detection of DNT and TNT derivatives like fluorescence⁶ and chemiluminescence,³ chromatographic techniques,⁷ electrochemical methods,^{8–10} quartz crystal microbalance,¹¹ electronic noses and sniffers. Among them, electrochemical techniques are very attractive because these techniques exhibit advantages like low cost, rugged instrumentation, high sensitivity, high selectivity, easy portability, feasibility for automation and simplicity.^{12,13} By considering these benefits, the adaptation of an electrochemical impedimetric technique to detect explosive compounds is considered rather simple and uncomplicated.

Molecular imprinting technology^{14–18} is one of the most efficient generic method which introduces

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Dedicated to Professor R. Ramaraj on the occasion of his 60th birth anniversary

molecular recognition properties into synthetic polymers with the use of appropriate templates. Molecular imprinted polymers (MIPs) are used in a wide range of applications like chromatographic separations, solid phase extractions, catalysts and sensors. MIPs used as recognition elements for the detection of biomarkers, pharmaceutical drugs and explosives are reported in the literature. MIPs have good advantages compared to other recognition elements, like low cost, long shelf life, high selectivity, sensitivity and inherent stability under drastic conditions. Preparation methods of MIP comprise the following four stages: functional monomer assembly, polymerization, template extraction and rebinding of template.

The present investigation involves the development of an electrochemical impedimetric sensor based on MIP for the detection of 5CDNT. For the selection of polymer precursors, we performed combinatorial screening procedure by using HyperChem software over a set of twenty monomers and five cross-linkers. MIP of 5CDNT was prepared with methylacrylate as monomer and ethylene glycol dimethacrylate as cross linker in the presence of 5CDNT template. Formation of MIP and non-imprinted polymer (NIP), and template extraction from the MIP were investigated by Fourier transform infrared spectroscopy (FT-IR). Binding assay studies were carried out to analyse the preferential binding of 5CDNT with MIP compared to NIP. Electrochemical impedance of the fabricated MIP carbon paste electrodes was investigated for the detection of 5CDNT, and the sensitivity and selectivity of the electrode in the presence of the homologues of compounds have been investigated.

2. Experimental

2.1 Reagents

5-Chloro-2,4-dinitrotoluene (5CDNT), 2,4-dinitrotoluene (DNT), ethylene glycol dimethacrylate (EGDMA) and n-eicosane were purchased from Sigma-Aldrich (St. Louis, USA), 1,3-dinitrobenzene (DNB) from Reidel Chemicals (India), methylacrylate and graphite fine powder from Loba Chemie (India) and azo-bis-isobutyronitrile (AIBN) from Spectrochem (Mumbai, India). All other chemicals were of analytical grade and were used as received. Phosphate buffered saline solution (PBS) of pH 7.4 was prepared by using 5 M NaCl, 1 M KH_2PO_4 and 1 M K_2HPO_4 according to the Sigma Aldrich procedure. All aqueous solutions were prepared using double distilled water finally passed through 0.22 micron filter cartridge (Whatman).

2.2 Combinatorial Screening

Combinatorial studies were carried out following the procedure reported elsewhere¹⁹ for the selection of polymer precursors for MIP preparation. The parameters were optimized by the simulation studies with MM+ and semi-empirical methods using HyperChem 8.0 Professional molecular modelling system. Initially, the possible minimum energy conformations of the monomers and 5CDNT were optimized using the MM+ and semi-empirical (PM3) quantum methods. Then, the binding energy between the functional monomer and the template (5CDNT) was computed. From these computational results, we selected methyl acrylate (MA) as monomer and ethylene glycol dimethacrylate (EGDMA) as cross linker for the preparation of 5CDNT imprinted polymer.

2.3 Preparation of molecular imprinted polymers

5CDNT MIP was prepared by a procedure similar to Wang *et al.*²⁰ by the polymerization of methylacrylate monomer and ethylene glycol dimethacrylate cross linker in presence of the template 5CDNT. Methylacrylate (MA; 0.5 g), EGDMA (5.7 g) and 5CDNT (0.3 g) were dissolved in 20 mL chloroform, and AIBN (0.3 g) was added to the mixture.²¹ The resultant mixture was heated for 24 h at 60–70°C. A solid polymer was formed which was centrifuged, dried and collected in petri dish. For the extraction of the template molecule, the polymer matrix was treated with methanol : acetic acid mixture (80:20) for 6 h by Soxhlet extraction method. The resultant imprinted polymer of 5CDNT was labelled as 5CDNT-MA-MIP. For control experiments, a non-imprinted polymer (NIP) was prepared similarly, in the absence of 5CDNT, and the resultant polymer matrix was treated with methanol:acetic acid mixture (80:20), similar to MIP. The resultant NIP was labelled as 5CDNT-MA-NIP.

2.4 Carbon paste electrode preparation

Carbon paste electrodes were prepared by mixing different weight proportions (1:1:1, 1:2:1 and 2:1:1) of MIP, graphite powder and n-eicosane, and the optimum weight proportion was chosen based on the redox activity of potassium ferricyanide at the carbon paste electrodes. Carbon paste electrode (CPE) incorporated with MIP was prepared^{22,23} by mixing the optimized combination of 0.5 g MIP, 1.0 g graphite powder and 0.5 g n-eicosane. The resultant carbon paste was filled into a hollow Teflon tube of 10 mm diameter. The other end of the Teflon tube was connected to a copper wire for

electrical contact. The exposed electrode surface was polished on a butter paper to get a smooth and fresh surface. For every set of experiments, a fresh electrode surface was exposed by polishing.

2.5 FT-IR, UV-Visible, BET and electrochemical impedance experiments

The prepared MIP, NIP and template-extracted MIP polymers were characterized by using FT-IR spectrophotometer (Perkin Elmer, model100) employing KBr pellet method in the frequency range of 400 – 4000 cm^{-1} with a resolution of 2 cm^{-1} . The results were analyzed by using Spectrum software. Binding assay studies of MIP and NIP were carried out by using UV-Visible spectrophotometer (Perkin Elmer Lambda 25). From the difference in absorbance values, the amount of 5CDNT absorbed onto MIP or NIP was calculated and the imprinting factors of MIP and NIP were calculated. The specific surface area, pore volume and pore diameter of the imprinted and non-imprinted polymers were determined by using a Micromeritics ASAP 2020 V3.00H analyzer, and the obtained results were analyzed by the Brunauer-Emmett-Teller (BET) method. A sample of MIP (300 mg) was degassed at 150°C for 24 h under nitrogen flow prior to the measurements. The dried degassed polymer was used for the experiment. The nitrogen adsorption/desorption isotherms were recorded, and Barrett-Joyner-Halenda (BJH) method was applied to analyze the pore size, pore volume and pore diameter.

Electrochemical impedance measurements were performed on electrochemical workstation (Model IM6e), Zahner-Eletrik GmbH, Germany. The frequency range of 10 mHz to 100 KHz was used, and the results were

analyzed by using Thales 3.08 USB software. Three electrode system was used for impedance analysis, where the carbon paste electrode acts as working electrode, Pt spiral wire as counter electrode and Ag|AgCl (3 N KCl) as reference electrode. The experiments were carried out at the open circuit potential with small excitation amplitude of 10 mV peak-to-peak. All the experiments were carried out in aqueous phosphate buffer solution (PBS) of pH 7.4. Before the experiments, the experimental solution was purged with nitrogen gas for 15 min to eliminate the dissolved oxygen.

3. Results and Discussion

3.1 Computational studies

Molecular dynamics simulation studies^{24,25} were exploited to select the best monomer and cross-linker combination for MIP. The molecular dynamic (MD) simulations were performed at 298 K for the calculation of interaction energy of constructed molecular systems. In the first step, 2-D chemical structures of the functional monomers (a virtual library of 20 monomers), template, and cross linking agents were prepared using HyperChem software. Using the molecular builder option, the 2-D structures were converted to 3-D structures. Then, geometric optimization was carried out by using Molecular Mechanics (MM+) and semi-empirical (SE) methods to obtain minimum energy structures. In this analysis, we have chosen Polak-Ribiere algorithm, which is a conjugate gradient method used specifically for aromatic and conjugated organic compounds.

Using conformation optimization, the interaction energy or binding score (ΔE) of 5CDNT–monomer–

Table 1. Geometrical optimization of template-monomer cross linker interactions in vacuum by molecular mechanics and semi-empirical method.

Template-Monomer	Cross linker	Bond Energy	Binding Score (ΔE)
		(kcal/mol)	
5-Chloro-2,4-DNT + Methyl acrylate	DVB	-5307.68	-0.56
	EGDMA	-5943.86	-3.69
	MBAA	-5234.92	-1.21
	DAPZ	-5956.44	-1.62
5-Chloro-2,4 DNT + Diethylaminoethylmethacrylate	DVB	-7144.88	0.54
	EGDMA	-7788.76	-2.91
	MBAA	-7882.84	-2.05
	DAPZ	-7794.72	-1.60
5-Chloro-2,4 DNT + Itaconic acid	DVB	-5697.94	0.16
	EGDMA	-6342.29	-3.67
	MBAA	-5627.32	-2.63
	DAPZ	-6348.02	-2.22

DVB – divinylbenzene; MBAA – N,N'-methylenebisacrylamide.

cross linker complexes was calculated. The ΔE values were calculated using the following equation:

$$\Delta E = E_{(\text{template}-\text{monomer})} - E_{(\text{template})} - \Sigma E_{(\text{monomer})} \quad (1)$$

$$\Delta E = E_{(\text{template}-\text{monomer}-\text{cross linker})} - E_{(\text{template})} - \Sigma E_{(\text{monomer})} - \Sigma E_{(\text{cross linker})} \quad (2)$$

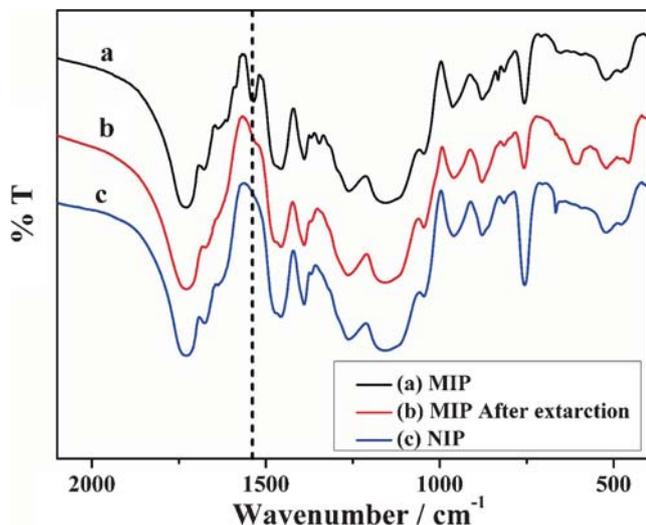


Figure 1. FT-IR spectra of 5CDNT-MA-MIP before (a) and after template extraction (b) and of 5CDNT-MA-NIP (c).

The most stable template-monomer-cross linker complex was selected based on the interaction energy (table 1), and the 5CDNT template-methyl acrylate-EGDMA combination has been selected. Consequently, the MIP for 5CDNT has been synthesized accordingly.

3.2 FT-IR study

The infrared spectral properties of the synthesized MIP and NIP of 5CDNT were studied by FTIR spectrophotometry. FTIR spectra of 5CDNT MIP, NIP and template-extracted MIP are shown in figure 1. The vibrational peak of nitro group assigned to 5CDNT at $\sim 1520 \text{ cm}^{-1}$ is present in the FTIR spectrum of MIP (figure 1 (a)) along with various vibrational peaks of the MIP matrix, while that of nitro group is not present in the FTIR spectra of both NIP and template-extracted MIP (figure 1 (b, c)). The presence or absence of the vibrational peak of nitro group, respectively, confirmed the capture and removal of the template molecule in MIP and template-extracted MIP (figure 1 (a, b)). The vibrational frequency of nitro group of the 5CDNT template in MIP matrix ($\sim 1520 \text{ cm}^{-1}$) is slightly higher than that of free 5CDNT molecule, indicating the existence of substantial weak interactions between

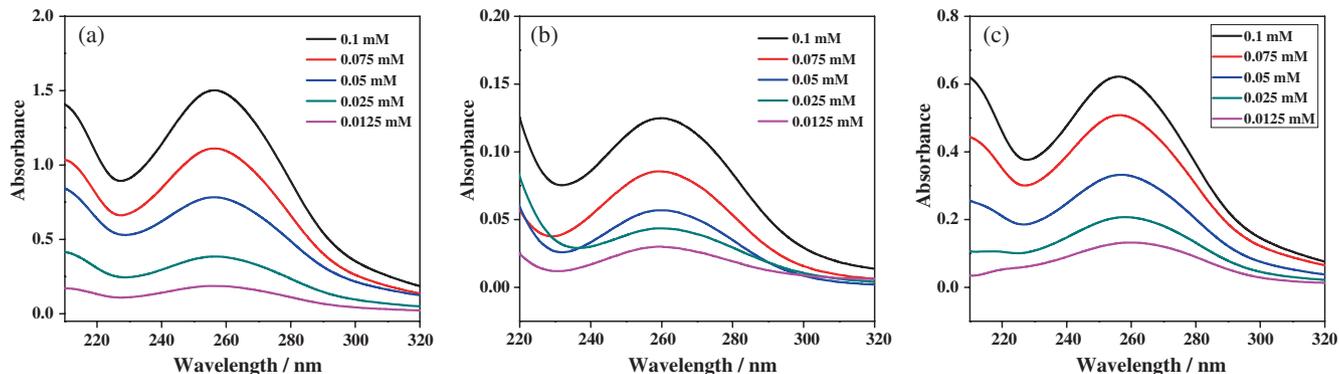


Figure 2. UV-Visible spectra of aqueous 5CDNT solution of different concentrations before (a) and after adsorption with MIP (b) or NIP (c).

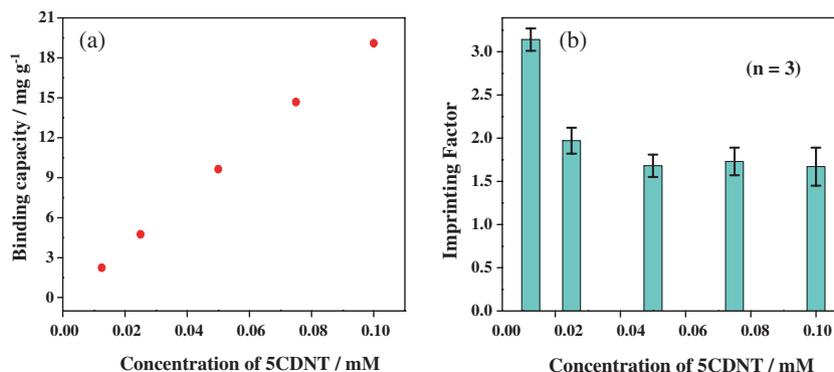


Figure 3. Plots of the binding capacity (a) and imprinting factor (b) of 5CDNT-MA-MIP against the concentration of 5CDNT.

encapsulated 5CDNT and the surrounding MIP matrix. The results clearly indicate that the complex between the MIP matrix and the template had been formed *via* reversible non-covalent interactions.

3.3 Binding assay studies by UV-visible spectroscopy

Binding assay studies^{26–28} of MIP and NIP were carried out by using UV-Visible spectroscopic analysis. 0.25 g of MIP or NIP was added into aq. 5CDNT solutions of five different concentrations (0.1, 0.075, 0.05, 0.025, 0.0125 mM). These mixtures were incubated for six hours with continuous shaking at 300 rpm. UV-Visible spectra of 5CDNT solutions were taken before the treatment with MIP. After the treatment with MIP and NIP for 6 h, the solutions were centrifuged and UV-Vis spectra of the supernatant solutions were recorded. From the difference in absorbance values, the amount of 5CDNT absorbed onto MIP or NIP was calculated. The binding capacity and imprinting factor of MIP and NIP were calculated, similar to Chang *et al.*²⁹

$$\text{Binding Capacity (mg/g)} = \frac{\text{analyte (mg) absorbed}}{\text{polymer (g)}} \quad (3)$$

Table 2. Specific surface area, pore volume and pore diameter of MIP and NIP by BET experiments.

Polymer	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (Å)
5CDNT-MA-MIP	326	0.2416	40
5CDNT-MA-NIP	150	0.1748	51

#Percentage of error: <1%.

$$\text{Imprinting factor} = \frac{\text{Binding capacity of MIP}}{\text{Binding capacity of NIP}} \quad (4)$$

When analyzing the UV-Visible spectra (figure 2) of 5CDNT before and after absorption onto MIP and NIP, the spectra of 5CDNT solutions treated with MIP show less absorbance values compared to those treated with NIP. This observation indicates that 5CDNT molecule interacted with the binding sites of MIP much more effectively than that of NIP. The binding capacity of MIP is higher than that of NIP in a wide range of 5CDNT concentrations (figure 3). The experiments were repeated three times and the resultant imprinting factor values were plotted against the concentrations of 5CDNT. By decreasing the concentration of 5CDNT, the imprinting factor values of MIP becomes more prominent; this result indicates that the prepared MIP shows more specificity towards 5CDNT at low concentrations.

3.4 BET analysis of MIP and NIP

In general, an increase in the surface area and average pore volume of a polymer matrix indicates that the polymer possesses higher accessibility and a better capacity for rebinding in its pores.²⁹ Specific surface area, pore volume and pore diameter of MIP and NIP were measured by BET nitrogen adsorption method (table 2). The specific surface area of MIP is relatively large and is nearly twice to that of NIP, and similarly the total pore volume of MIP also is significantly higher than that of NIP. The average pore diameter of NIP is relatively higher (51.46 Å), though that of MIP (40.47 Å) is high enough for the free flow of the template 5CDNT molecules in the MIP matrix. Overall, the observed results from BET analysis clearly indicated that the MIP

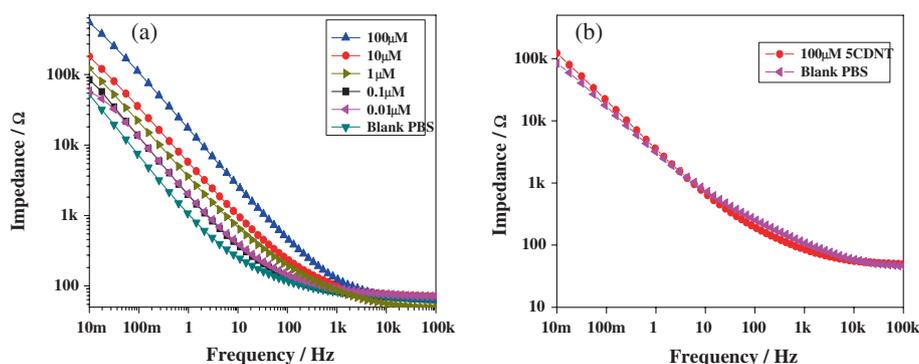


Figure 4. (a) Bode plots of EIS analysis of 5CDNT-MA-MIP carbon paste electrode and (b) 5CDNT-MA-NIP carbon paste electrode in phosphate buffer (pH 7.4) at different concentrations of 5CDNT ((a) 0, 0.01, 0.1, 1, 10, 100 μM, (B) 0, 100 μM).

matrix could interact and bind the template 5CDNT more efficiently than the NIP.

3.5 Electrochemical impedance analysis at MIP and NIP carbon paste electrodes

Electrochemical impedance spectroscopy (EIS) is an effective tool for the analysis of the changes taking place between the electrode surface and solution interface. In EIS experiments, the electrochemical impedance of an electrode is determined by applying a sinusoidal potential and measuring the resultant current. The EIS data are represented in two forms of plots, Bode and Nyquist plots. Bode plot is a plot between the absolute impedance and the phase shift of the impedance each as a function of frequency, which is a useful alternative to Nyquist plot.

EIS analysis of the MIP based carbon paste electrode, 5CDNT-MA-MIP, was carried out in PBS (pH 7.4) in the absence and presence of different concentrations of 5CDNT in the frequency range of 10 mHz to 100 kHz. The Bode plots (figure 4a) of the electrochemical impedance analysis were recorded in the absence and presence of 5CDNT at different concentrations (0.01, 0.1, 1, 10, 100 μM). The MIP carbon paste electrode shows charge transfer resistance behaviour from 2 kHz to 10 mHz. The electrochemical impedance of the MIP carbon paste electrode is dependent on the concentration of 5CDNT in the frequency region of 10 mHz to 10 Hz. We have taken the electrochemical impedance values at the frequency of ~ 0.1 Hz for analysis, similar to previous analysis reports.^{30–32} Interestingly, the magnitude of impedance was found to increase with

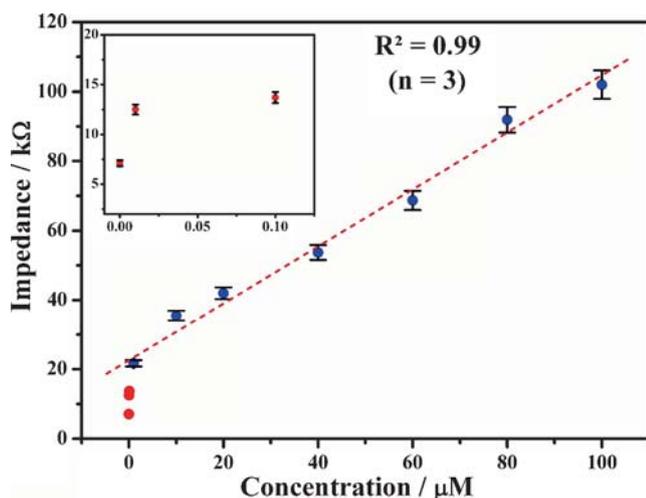


Figure 5. Plot of the electrochemical impedance against the concentration of 5CDNT. Red dots are the low concentration data which are outside the linear range. Inset shows an expanded view in the low concentration region.

Table 3. Comparison of the low-detection-limits of TNT and its analogues by electrochemical and other analytical methods.

Analyte	Technique	Electrode/Surface Modification	Low-detection-limit	Reference
TNT	Gas chromatography	n.a.	26 nM (6 ppb)	Brust et al. 2014 ³⁹
TNT	Quartz crystal microbalance	Phthalocyanine layer	44 nM (10 ppb)	Erbahar et al. 2011 ⁴⁰
TNT	Chemiluminescent ELISA	Monoclonal antibody layer	4.4 μM (1 ppm)	Girotti et al. 2010 ⁴¹
TNT	Surface plasmon resonance	MIP coated optical fibre	50 μM	Cennamo et al. 2013 ⁴²
TNT	Adsorptive stripping voltammetry	Polypeptide doped PANI fibers	100 nM	Wang et al. 2009 ⁴³
TNT	Square wave voltammetry	Ionic liquid film	190 nM	Xiao et al. 2009 ³³
TNT	Amperometry	Dendrimer functionalized nanoAu	26 nM (6 ppb)	Giannetto et al. 2013 ⁴⁴
DNT	Cyclic voltammetry	Ag film on carbon fiber sheet	5 μM	Mbah et al. 2013 ³⁷
DNT	Square wave voltammetry	Ordered macroporous carbon	10 μM	Fierke et al. 2012 ³⁴
DNT	Square wave voltammetry	Ionic liquid film	230 nM	Xiao et al. 2012 ³³
DNT	Cyclic surface polarization impedance	Molecular imprint with cyclodextrin matrix	1 nM	Ju et al. 2007 ³⁶
DNT	EIS	Molecular imprinted monolayer on Au	29.5 μM	Apodaca et al. 2011 ³⁸
5CDNT	EIS	Molecular imprinted polymer in carbon paste	0.1 μM	Present work

ELISA – Enzyme linked immunosorbent assay; PANI – Polyaniline.

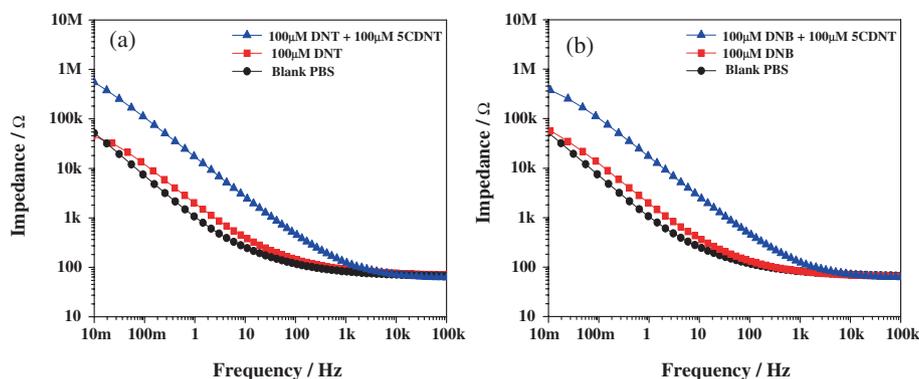


Figure 6. Bode plots of EIS analysis of 5CDNT-MA-MIP carbon paste electrode to the presence of (a) 100 μM DNT or (b) 100 μM DNB, in the presence and absence of 100 μM 5CDNT.

increasing concentrations of 5CDNT, and this observation suggests the accumulation of 5CDNT inside the 5CDNT-MA-MIP polymer matrix.

Similarly, the NIP based carbon paste electrode, 5CDNT-MA-NIP, was examined in PBS (pH 7.4) in the absence and presence of different concentrations of 5CDNT in the frequency range of 10 mHz to 100 KHz. The Bode plot of the electrochemical impedance analysis was recorded in the absence and presence of 5CDNT at different concentrations (0.01, 0.1, 1, 10, 100 μM). The NIP carbon paste electrode shows charge transfer resistance behaviour from 2 kHz to 10 mHz, however the magnitude of the electrochemical impedance was found not to change even by increasing the concentration of 5CDNT to as high as 100 μM (figure 4b). This observation clearly indicates that there is no accumulation of 5CDNT in the 5CDNT-MA-NIP polymer matrix.

A calibration plot (figure 5) has been drawn between the concentration of 5CDNT and the electrochemical impedance values obtained at 5CDNT-MA-MIP based carbon paste electrode. The electrochemical impedance measurements were carried out three times with independent electrodes. The results were reproducible and the difference in the impedance values were only marginal with a relative standard deviation of <4%. From the calibration plot, a linear range of 1 - 100 μM has been established for determination of 5CDNT with a linear regression coefficient of 0.99. The low detection limit (based on three times the standard derivation from the blank) of the sensor system can be determined from the plot to be 0.01 μM . However, since the impedance values observed at both 0.01 μM and 0.1 μM concentrations are quite same, the low detection limit of the sensor system is revised as 0.1 μM .

Performance of the present electrochemical impedimetric sensor is compared with various electrochemical and other analytical methods reported in

the literature³³⁻⁴⁴ for the detection of DNT and TNT (table 3). The low-detection-limit of 5CDNT obtained by the present electrochemical impedimetric sensor is comparable to the detection limits reported previously by other analytical methods.

3.6 Interference studies

Electrochemical impedance responses of the 5CDNT-MA-MIP based carbon paste electrode to the presence of 2,4-dinitrotoluene (DNT) and 1,3-dinitrobenzene (DNB) were examined to investigate interferences due to closely related reactive compounds coexisting with the 5CDNT sample. The Bode plots (figure 6) of the EIS analysis to the presence of DNT (100 μM) or DNB (100 μM) in the absence and presence of 100 μM 5CDNT indicate that the fabricated MIP sensor surface shows a little impedance response to the interference compound DNT or DNB, and the magnitude of the sensor response is minimal (~ 3.7 k Ω) for the interference compounds compared to that for the analyte 5CDNT (96.7 k Ω). Further, the Bode plot observed for 100 μM 5CDNT (figure 4) is nearly identical to those observed for 100 μM 5CDNT along with the presence of DNT or DNB of 100 μM each (figure 6). Overall, all these observations clearly confirm that the recognition sites of MIP are specific towards the analyte 5CDNT, although this sensor is not completely free from the interference response. From these observations, we conclude that the 5CDNT MIP electrode could specifically recognize the template 5CDNT molecule even in the presence of possible interferents.

4. Conclusions

A novel molecular imprinted polymer (MIP) based electrochemical impedimetric sensor was developed for

detection of 5CDNT. The molecular imprinted polymer was incorporated into carbon paste electrodes to facilitate easy renewal of newer sensor surfaces for multiple analyses. The 5CDNT-MIP based electrode responded significantly to the presence of 5CDNT as low as 0.1 μM , while the NIP based electrode did not respond to the presence of 5CDNT even at 10 μM concentration. Furthermore, the MIP based electrode responded specifically to the presence of 5CDNT alone when the analogous compounds, DNT and DNB, coexisted in the sample. Thus, the present methodology based on electrochemical impedance analysis combining MIP and carbon paste electrode could be extended further to the fabrication of sensors for a wide range of explosive compounds.

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