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Multiwalled carbon nanotube based molecular imprinted polymer for trace determination of 2,4-dichlorophenoxyaceticacid in natural water samples using a potentiometric method

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ABSTRACT

A novel potentiometric sensor based on ion imprinted polymer inclusion membrane (IPIM) was prepared from the modification of multiwalled carbon nanotube (MWCNT) based molecularly imprinted polymer for the trace determination of the pesticide 2,4-D (2,4-dichlorophenoxyacetic acid) in natural water samples. MWCNTs are initially functionalized with vinyl groups through nitric acid oxidation along with reacting by allylamine. MWCNT based imprinted polymer (MWCNT-MIP) was synthesized by means of methacrylic acid (MAA) as the monomer, trimethylol propane trimethacrylate (TRIM) as the cross linker, α,α′-azobisisobutyronitrile (AIBN) as the initiator and 2,4-D an organochlorine pesticide molecule as the template. Organized material was characterized by means of FTIR, XRD and SEM analyses. The sensing membrane was developed by the inclusion of 2,4-D imprinted polymer materials in the polyvinyl chloride (PVC) matrix. The optimization of operational parameters normally used such as amount and nature of plasticizers sensing material, pH and response time was conducted. From the non-imprinted (NIPIM) and imprinted polymer inclusion membrane (IPIM) sensors the response behavior of 2,4-D was compared under optimum conditions. The IPIM sensor responds in the range of 1×10^{-9}–1×10^{-5} M and the detection limit was found to be 1.2×10^{-9} M. The stability of MWCNT-IPIM sensor was checked by various methods and it is found to be 3 months and it can be reused many times without losing its sensitivity. For the application of sensor experiments with ground and tap water samples were performed.

1. Introduction

Our water resources are infected by enlarged utilizes of pesticides in cultivation, forestry, and household activities intended for controlling pests and this type of water pollution is caused by the leaching run-off from farming as well as woods lands; deposition from aerial applications and discharge of industrial wastewaters [1]. Apart from this it is important to point out that, these pesticides are nonbiodegradable and also carcinogenic to human beings. For that reason, toxicity of pesticides and their degradation products are building these chemical substances a potential risk by means of contaminating our surroundings [2] and many water resources [3]. 2,4-Dichlorophenoxyacetic acid (2,4-D) is generally used pesticide found in surface and ground waters. Considering its health and other toxicological effects, World Health Organization (WHO) recommended a maximum contaminant level of 20 μg L^{-1} for 2,4-D in drinking water [4]. Therefore the detection of 2,4-D at low concentrations in natural water is a major challenge for chemists in recent times.

Molecular imprinting is a technique for the preparation of synthetic polymers by means of specific binding sites for a target molecule and it is usually used for preparing resources with unusual identification capability toward target molecule through mimicking the lock and key principle in the biosphere [5–7]. Molecular imprinted polymers are at presently being explored in areas such as catalytic applications [8], solid phase extraction [9], membrane separations [10] and developing sensors [11]. The future of the imprinted polymers is very promising because the high level of selectivity and recognition ability and also only limited imprinted polymer work has been done for direct recognition and sensing of pesticides [12,13]. The potentiometric transduction approach is an easy type and on combining it with the imprinted polymer as the recognition moiety serves an ultimate approach for the selective sensing of analytes. For atrazine, triazine herbicides D'Agostino

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et al. [14] and Pogorelova et al. [15] developed potentiometric and ion sensitive field effect transistor membrane or films intended for the selective detection. For the selective monitoring of uranium, atrazine and phorate molecules, Metilda et al. [16] recently been developed an imprinted polymer inclusion membrane (IPIM) based sensor. Zhou et al. [17] and Prathish et al. [18] demonstrated in their work that a potentiometric sensor can be used for the selective detection of methylphosphonic acid (MPA), a degradation product of chemical warfare agents.

Multiwalled carbon nanotubes have been attracted great attention recently because they are ideal support materials, strong interactions, stable under acidic conditions, no swelling and large surface area [19]. Liu et al. [20] reported that, by oxidized CNTs (CNTs–COOH) covered on the external surface of the fused-silica tube as solid-phase micro extraction sorbent was used to identify the substituted aniline compounds [20]. It is also used as the reinforcing element in a polymer or metal matrix in fabricating novel sophisticated resources (CNT-incorporated films) [21–23].

There have been reports on the development of electrochemical sensor from modified MWCNT for the determination of trace amount of thiocyanate [24] and for the immobilization of $Ru(bpy)_3^{2+}$ [25]. To date, there are no literature reports on the utilization of imprinted polymer inclusion membrane (IPIM) based sensor prepared from the modification of MWCNT for the trace determination of pesticides. The present work reports on the fabrication of one such IPIM based biomimetic potentiometric sensor for routine monitoring of 2,4-D down to 1×10^{-9} M levels in natural waters by inclusion of 2,4-D imprinted material in polyvinyl chloride (PVC) matrix.

2. Experimental

2.1. Reagents

2,4-D was purchased from SUPELCO, USA. MWCNTs were obtained from Shenzhen Carbon Nanotechnologies Co. Ltd. Trimethylolpropane trimethacrylate (TRIM), methacrylic acid (MAA), 2,2′-azobis isobutyronitrile (AIBN), dioctyl phthalate (DOP), 2-nitrophenyloctyl ether (NPOE), bis-(2-ethylhexyl) sebacate (BEHS), tris-(2-ethylhexyl) phosphate (TEHP), high molecular mass poly(vinyl chloride) (PVC) were obtained from Aldrich (Milwauke, WI, USA). The analytical grade reagents were used throughout the experiments.

2.2. Apparatus

Potentiometric response characteristics were studied with a 4½ Digit True RMS Multimeter (MODEL 1085). The concentrations of 2,4-D were determined by spectrophotometrically on a JASCO UV-Visible (model V-530, Japan) spectrophotometer. The morphological study of MWCNT-MIPs was obtained by scanning electron microscopy (SEM, S4800). The Fourier transform infrared (FTIR) spectra were recorded with a Shimadzu FTIR spectrometer in the wavelength range 800–4000 cm^{-1} using a KBr window at a resolution of 4 cm^{-1}. The X-ray diffraction (XRD) patterns of the adsorbent were recorded using an X'Pert Pro X-ray diffractometer using Cu Kα radiations at a scanning speed of 2°/min and at a wavelength of 1.5406 Å. All pH measurements were carried out on a Systronic (model μ pH system 362)-pH meter (Systronic India Ltd.).

2.3. Synthesis of vinyl group functionalized MWCNTs

About 2.0 g of crude MWCNTs were added to 80 mL of HNO_3 under sonication for 10 min. The obtained mixture was stirred under 75 °C for 18 h. After that the mixture was filtered through a 0.22-μm polycarbonate membrane and washed thoroughly with distilled water. Washing was repeated until the pH value of the filtrate was neutral. The obtained solid residue, carboxylic acid-functionalized MWCNTs (MWNT-COOH) was dried under vacuum. It was then converted to acid chloride-functionalized MWCNT (MWCNT–COCl) via reacting by means of thionyl chloride at 80 °C for 18 h and remaining thionyl chloride was detached by filtration followed by washing with anhydrous THF for a number of times. About 1.0 g of MWCNT–COCl was assorted with 60 mL of DMF in a three-neck flask through ultra-sonication. After that a mixture of 70 mL of allylamine and 50 mL of DMF was added drop wise under vigorous magnetic stirring and finally reflexed at 70 °C for 76 h, to get vinylic group functionalized-MWCNT (MWCNT–CH=CH_2).

2.4. Synthesis of 2,4-D imprinted and nonimprinted polymer materials

About 2.0 g of MWCNT–CH=CH_2 was added to the solvent mixture of 50 mL of acetonitrile and 5 mL of toluene in a 500 mL round-bottom flask. Then the mixture was purged with N_2 gas under a constant magnetic stirring. A mixture of 2,4-D and MAA dissolved in 35 mL of N,N dimethylformamide was added to the reactor. It is mixed for 30 min to get a compound of template molecule and functional monomer. The cross linker TRIM and initiator AIBN were also added to this mixture and temperature of that system was kept at 70 °C, the reaction was allowed to proceed for 16 h. The resultant product was centrifuged and washed thoroughly with ethanol to discard the unreacted reagents. Acetic acid solution was used to remove template molecules. A blank non-imprinted polymer (MWCNT-NIP) was prepared via the same procedure, only without using the template molecule.

2.5. Fabrication of membrane based sensor

About 90 mg of PVC and 25 mg of OA were dissolved in 2.5 mL of tetrahydrofuran (THF). Polymeric substances (90 mg, 40–100 μm size) were dispersed in 0.2 mL of NPOE (or BEHS or TEHP) and were added to the above solution. The resulted mixture was homogenized in a sonicator and then immersed into a Teflon mold of 18 mm inner diameter. It is kept at room temperature to evaporate THF and the obtained membrane has the thickness of ~0.70 mm. In a similar manner a blank membrane was also arranged maintaining the identical composition not including imprinted or non-imprinted polymer particles. The membranes were glued to one end of a pyrex glass tube with Araldite and the tube was then filled with an internal filling solution of 10^{-3} M 2,4-D solution. A schematic diagram of MWCNT based MIP formation, membrane structure as well as manufacture of biomimetic potentiometric sensor is given in Scheme 1. The sensor was stored in air when not in use.

2.6. Analysis of ground and tap water samples

For the study of ground and tap water samples the pH of the solution (45 mL) was adapted to pH 5 subsequent to the addition of 5 mL of 1 M Tris buffer via HCl or NaOH. Samples were analyzed via standard addition way through measuring the electromotive force (EMF) of the following electrochemical cell; Ag, AgCl 1.0×10^{-3} M 2,4-D/PVC membrane/sample solution//KCl (saturated)/$HgCl_2$, Hg.

3. Results and discussion

3.1. Characterization

FTIR spectra of MWCNT, MWCNT–COOH, 2,4-D loaded MWCNT-MIP, MWCNT-MIP, and MWCNT-NIP is shown in Fig. 1. In the IR spectrum of original MWCNT, almost featureless band are appeared in the range of 1200–1700 cm^{-1}. But in the spectrum

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