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Synthesis of nano-sized cyanide ion-imprinted polymer via non-covalent approach and its use for the fabrication of a CN⁻-selective carbon nanotube impregnated carbon paste electrode

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ABSTRACT

Nano-sized CN⁻-imprinted polymer was synthesized by the copolymerization of methyl methacrylic acid (MAA), vinyl pyridine (VP) and ethylene glycol dimethacrylate in the presence of cyanide ion. The obtained polymeric nanoparticles were incorporated with carbon paste electrode (CPE) to produce a CN⁻-selective electrode. Functional monomer kind had crucial influence on the efficiency of the sensor. The presence of both VP and MAA in the structure of the imprinted polymer improved the sensing characteristics of the electrode. Also, the mole ratio of MAA/VP, cross-linker kind, cross-linker amount, solvent kind and amount were found to be effective factors in the electrode behavior. Presence of little amount of multi-walled carbon nanotubes (MWCNTs) in the CPE improved the detection range and response time of the electrode at the expense of small decrease in Nernstian slope. The electrode, containing CN⁻-imprinted polymer and MWCNTs showed a dynamic linear range of 1×10^{-6} – 1×10^{-1} mol L⁻¹, Nernstian slope of $46.3 \pm (0.6)$ mV and detection limit of 7.5×10^{-7} mol L⁻¹; whereas, the same electrode in the absence of MWCNTs led to linear range, Nernstian slope and detection limit of 1×10^{-5} – 1×10^{-1} mol L⁻¹, $55.3 \pm (0.7)$ mV and 8×10^{-6} mol L⁻¹, respectively. The utility of the electrodes was checked by determination of cyanide ion in some real samples.

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1. Introduction

Molecularly imprinted polymers (MIPs) and ionic imprinted polymers (IIPs) are solid-phase artificial receptors that are prepared using templates during the polymer network forming step. As a result of subsequent removal of entrapped template the selective receptor sites are generated within the polymeric network [1]. One of the most attractive characteristic of molecular/ionic imprinting is its applicability to wide diversity of analytes. The templates, ranging from small molecules to macromolecules as well as different kinds of ions have been used for imprinted polymers (IPs) synthesis [2–14]. Nevertheless, anionic templates have seldom been considered as a template agent for imprinting. It is generally known that the design of anion receptors is a challenging task, especially in contrast to cation host design [1]. Anions have a lower charge to radius ratio compared to cations. This means that electrostatic binding interactions are markedly diminished in the anions. It is therefore more difficult to develop

specific binding sites via imprinting technology for their recognition. Another significant hindrance to the development of anion-recognition IPs has been the fact that anionic species are generally incompatible with apolar media, used usually as porogen in the preparation of imprinted polymers [1].

Cyanide is one of the most toxic inorganic substances. Cyanide occurs naturally in some foods. It is emitted into the environment mainly with industrial waste water. Cyanide is used in the fabrication of plastics; in the extraction of gold and silver from ores; and in the electroplating of silver, gold, platinum and copper [15]. It disrupts the electron transport chain in the mitochondria membrane and prevents respiration. This effect can result in death. Chronic exposure to cyanide results in goiters, neuromuscular diseases, weakness, nausea, muscle cramps, paralysis of legs and arms, and loss of appetite and psychoses [16].

Among various methods, developed for the determination of cyanide, CN⁻-selective electrodes are useful, since, they provide high sensitivity and wide dynamic range [17–19]. Metalloporphyrins [20,21] as well as some Co²⁺ and Ni²⁺ ions based metal complexes [22,23] have recently been proposed as effective ionophores for the construction of potentiometric electrodes for

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cyanide ion determination. Although, these membrane electrodes have overcome the interference problems, arisen from halide ions of solid state membrane ion selective electrodes, however, interference from S^{2-} and thiosulfate can be counted as the main drawback of these sensors. In addition, the complexity of the synthesis of the as mentioned ionophores is the other disadvantage of these sensors.

Cyanide imprinted polymer has recently been reported as a new generation of CN^- ion recognition element for the construction of polymeric membrane type ion selective electrode [24]. This approach is interesting because of being pioneering work in the field of IP-based potentiometric sensor for CN^- determination. However, the cited work is based on the copolymerization of ternary complex of methacryloyl histidine–Ni(II)– CN^- in the presence of cross-linker agent, meaning that the covalent approach of the imprinting technology has been employed in the cited work. Furthermore, this ionophore is similar to the previously reported hydrophobic metal ion complex-based ionophores [20–23]; because, the metal ion complex (used as template in the polymerization) plays a prominent role in the cyanide recognition. According to the reported data in the described case, no considerable improvement in the detection limit and linear range of the sensor has been achieved. Furthermore, the interference effect, arisen from some anions capable of interaction with central ion of Ni (II), like S^{2-} , might be a main problem with the reported sensor.

Carbon paste electrodes (CPEs) have attracted great deal of attention as the electrochemical transducers. Carbon paste electrodes are generally characterized by broader potential window, higher signal-to-noise ratio, mechanical stability, nontoxicity and resistance toward passivation. In CPEs, the problems related to the electrode surface passivation are easily eliminated by renewal of their surface via removing thin outer layer of the paste [25]. More importantly, the modification of carbon paste electrode with various kinds of organic or inorganic modifiers is an easy task and requires only mixing of the modifier with carbon and binder in the paste preparation step. This characteristic has enabled the electrochemists to fabricate various kinds of highly selective and sensitive electrodes, known as chemically modified carbon paste electrodes, to improve the selectivity and sensitivity of the electrochemical methods [26,27]. Potentiometric ion-selective carbon paste electrodes are further interesting; because, they exhibit low ohmic resistance and need no internal solution, making them as all-solid state ion selective electrodes [28–30].

In this work, we designed a new imprinted polymer containing selective cavities for CN^- ions. The designed synthesis was based upon the non-covalent approach, meaning that no metal ion was involved in the synthesis of the CN^- -selective IP. To the best of our knowledge, this is the first cyanide ion imprinted polymer, prepared via the non-covalent approach. Furthermore this is the first carbon paste based cyanide ion selective potentiometric sensor which utilizes cyanide ion imprinted polymer nanoparticles as the recognition element of the sensor. Our reported sensor led to better cyanide selective sensor, regarding the dynamic linear range, detection limit and resistance against the interfering agents, compared to the previously reported IIP- based sensor, in spite of very simple synthesis method, used in this approach.

2. Experimental

2.1. Reagents and instruments

Divinylbenzene (DVB), 4-vinylpyridine (VB), Methacrylic acid (MAA), ethyleneglycoldimethacrylate (EGDMA), 2, 2'-azobisisobutyronitrile (AIBN) and n-eicosane were purchased from (Sigma-Aldrich, USA). Graphite Powder (Size < 40 μm , 99.99% trace

metals basis) was obtained from Fluka (Buchs, Switzerland). All other chemicals were of analytical reagent grade and purchased from (Merck, Germany). Distilled water was used throughout. Ag/AgCl (sat.) electrode (Azar electrode, Iran) was used as a reference electrode. Carbon paste electrode impregnated with imprinted polymer was used as indicator electrode. A corning ion analyzer 250 pH/mV meter was utilized for potential measurement. Surface morphology of the imprinted polymer particles were studied via LEO 1430VP scanning electron microscope (SEM) (Germany–England), using an accelerating voltage of 15 kV.

2.2. Synthesis of nano-sized cyanid-imprinted polymer

In order to prepare CN^- -imprinted polymer, 0.5 mmol of sodium cyanide was transferred to a vessel, containing 40 mL of ethanol. Then, 1 mmol of methacrylic acid and 0.5 mmol of vinyl pyridine were added to the mixture. After, 4 mmol of EGDMA as well as 0.006 g of AIBN (dissolved previously in 10 mL of ethanol) was transferred to the mixture. This was followed by purging of the resulting mixture with nitrogen gas for 15 min. The vessel was then sealed precisely and transferred to a water bath, fixed at temperature of 60 °C, to start the polymerization reaction. The polymerization reaction lasted 24 h. After completion of the reaction, the obtained polymer powder was filtered and washed several times with water, hot ethanol and HCl solution (1 mol L^{-1}) for the removal of the non-reacted monomers as well as cyanide ion species from the polymer. The non-imprinted polymer was also synthesized similar to the imprinted polymer, except that cyanide was absent in the polymer synthesis process.

2.3. Preparation of the carbon paste electrode

In order to prepare CN^- -selective carbon paste electrode, different amounts (mg) of the synthesized CN^- -imprinted polymer powder was homogenized in a mortar with various amounts of graphite (or graphite+MWCNTs) for 15 min. Subsequently, n-eicosane was melted in a dish at 50 °C. The graphite/imprinted polymer 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 (2.0 mm in diameter, 3.0 mm in depth) at the end of an electrode body, previously heated at 45 °C. After cooling at room temperature, the excess of solidified material was taken off with the aid of a paper sheet. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} mol L^{-1} of NaCN solution. The response of the sensor was examined by measuring the electromotive force (EMF) of the following electrochemical cell:

the developed CP electrode | sample solution | Ag–AgCl (reference electrode). The described reference electrode and the cyanide sensor were connected to a corning ion analyzer 250/pH mV meter for potential measurement at 25 ± 0.1 °C. The EMF was plotted as a function of $\log [CN^-]$.

3. Results and discussions

3.1. Synthesis of different CN^- imprinted polymers and their evaluation

CN^- -imprinted polymers with various formulations were synthesized and tested as ionophore agents for the fabrication of CN^- ion selective electrode. The formulations of the synthesized polymers, namely, the kinds and ratios of the utilized functional monomers as well as the nature of the cross-linkers are listed in table 1. In this table, some important characteristics of the potentiometric carbon paste electrodes, prepared using the described IPs, are also summarized. Furthermore, the potentiometric

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