



Synthesis of hydrogen phosphate anion-imprinted polymer via emulsion polymerization and its use as the recognition element of graphene/graphite paste potentiometric electrode



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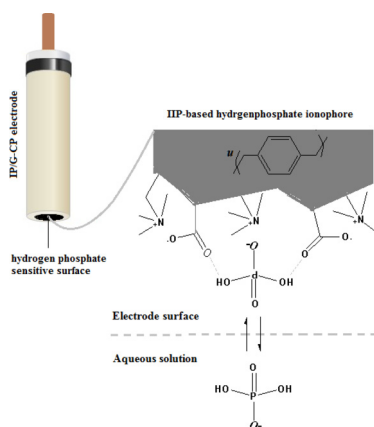
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HIGHLIGHTS

- Monohydrogen phosphate imprinted polymer was prepared via emulsion polymerization.
- Imprinted polymers was used as HPO_4^{2-} ionophore in a potentiometric CP electrode.
- CP electrode was a mixture of graphite, graphene, imprinted polymer and a binder.
- Presence of graphene in the electrode composition improved the electrode efficiency.
- The electrode exhibited response time of 10 s and detection limit of 5.0×10^{-6} M.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen phosphate imprinted polymer was prepared via emulsion polymerization. An oil in water emulsion, stabilized with cetyltrimethylammonium bromide molecules, was used as the polymerization media. Acrylic acid and divinyl benzene, dissolved in chloroform, were used as the functional monomer and cross-linker agent, respectively. hydrogen phosphate anion species, fixed via adjusting the pH of the synthesis environment, was used as the template in the imprinting process. The imprinted polymer obtained was used as the recognition element of a potentiometric sensor, prepared by mixing of graphite, imprinted polymer, graphene and n-eicosane. The electrode incorporated with the imprinted polymer showed a Nernstian response to hydrogen phosphate concentration; whereas, the non-imprinted based electrode had no sensitivity to hydrogen phosphate anions. It was also demonstrated that the presence of graphene material in the electrode composition improved the electrode efficiency in responding to target ion. The imprinted polymer/graphene modified electrode, showed a dynamic linear range of 1×10^{-5} – 1×10^{-1} mol L⁻¹, Nernstian slope of $29.8 \pm (0.4)$ mV decade⁻¹, response time of 10 s and detection limit of 5.0×10^{-6} mol L⁻¹. The utility of the electrodes was checked by determination of phosphate ion in some real samples.

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1. Introduction

Phosphate ions monitoring in various samples is an important analysis task because of its existence in clinical, environmental, agricultural and medical systems. Ion chromatography is the main method for the determination of phosphate ions in real samples [1,2]. However, other kinds of the analytical methods such as Spectrophotometry [3], Fluorescence [4], Chemiluminescence [5], voltammetry [6] and biosensors [7] have been reported for phosphate species determination in various samples. Most of these techniques require sample pre-treatment that can be time consuming, expensive and produce toxic wastes. Therefore, development of the sensing devices for fast, sensitive, selective and accurate determination of phosphate species is of great interest.

Ion selective electrodes provide a convenient and quick analytical approach for the estimation of particular ionic species in the solutions. When the samples are turbid or colored, as the case is in many environmental samples, these methods are particularly useful. In an ion-selective electrode, selectivity is guaranteed by the interaction, established between the target analyte and an ionophore which is usually immobilized in a polymeric membrane. A number of hydrogen phosphate membrane electrodes have already been reported based on different ion carriers [8–14].

However, determination of phosphate and its protonated forms by the ion selective electrodes are actually a challenge, among anions, because of their strongly hydrophilic characteristics which place them at the end of the Hofmeister series, ruling the selectivity of anion selective membrane electrodes, prepared with the conventional ion exchangers [15]. Due to high hydration energy of phosphate ions, ion selective membranes, designed for these ions, should contain carriers capable of establishment of the selective interactions with the analyte [16].

Molecularly imprinted polymer (MIP) and its analogue, namely, ionic imprinted polymer (IIP) are artificial receptors that are synthesized using molecular or ionic templates during the polymer network forming. Removal of the entrapped template leads to the selective receptor sites within the polymeric network [17]. Imprinting based methodology for the creation of the artificial receptors is interesting; since, wide variety of chemical compounds including small molecules [18,19], macromolecules [20], cations [21–23] and anions [24] can be used as template for producing of imprinted materials.

However, the design of anion receptors based on the imprinting technology is a challenging task due to the difficulty in establishing of self-assembly complex between the anionic template and the functional monomers as well as incompatibility of the anions with apolar media, used usually as porogen in the preparation of imprinted polymers. However, some efforts have been made to design and synthesize anion-imprinted polymers and their utilization in ion selective electrodes fabrication [24,25].

Imprinted polymers have been shown to be fascinating materials to utilize as the recognition element of chemical sensors. Useful information about the application of imprinted polymers as the biomimetic recognition element of the chemical sensors has been collected in some recently published review articles [26,27]. Furthermore, the imprinted polymers have also utilized as efficient ionophore agent for the design and fabrication of various kinds of ion-selective potentiometric electrodes [28–32].

Design and synthesis of phosphate ion-imprinted polymers is a challenge in the imprinting field because of serious difficulty for dissolving of phosphate species in non-aqueous solvents, used commonly in the imprinting processes. Several phosphate ion-imprinted polymers have been reported previously [33–36]. However, precise evaluation of these reports reveals that the organic derivatives of phosphate ion have been used as alternative

template in order to overcome the problem of difficulty of dissolving of phosphate ions in non-polar solvents. Moreover, the new synthetic functional monomers have been employed, in place of the commercially available functional monomers, in all above mentioned works. This makes the imprinting process complex and time consuming.

In this approach, an ion imprinted polymer including mono-hydrogen phosphate anion selective sites was synthesized via emulsion polymerization. Hydrogen phosphate was used directly as the template in the imprinting process which can be regarded as an innovative approach, compared to the previously reported phosphate ion imprinted polymers. The oil in water emulsion media helped us to overcome the insolubility problem of hydrogen phosphate anions in apolar media. The hydrogen phosphate-imprinted polymer was used as the ionophore for all-solid-state carbon paste electrode to measure dibasic hydrogen phosphate ion. Moreover, we demonstrated the effect of graphene material to improve the efficiency of the potentiometric electrode, when it was added in the electrode composite.

2. Experimental

2.1. Reagents and instruments

Divinylbenzene (DVB), Methacrylic acid (MAA) 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). Ammonium persulfate and cetyltrimethylammonium bromide were obtained from (Merck, Germany). 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 the imprinted polymer and graphene, 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 imprinted polymer

In order to synthesize the imprinted polymer, hydrogen phosphate (1 mmol) and emulsifier (3 mmol of cetyltrimethylammonium bromide) were dissolved in 20 ml distilled water in a 100-ml three-necked polymerization flask. Then, 2 mmol of methacrylic acid and 8 mmol of divinyl benzene were dissolved in chloroform (4 mL) and added to the emulsifier containing solution. The mixture was sonicated for five minutes to provide oil-in-water emulsions. Then, the stream of nitrogen gas was passed through the solution in order to remove the dissolved oxygen. For starting the polymerization reaction, 0.05 g of ammonium persulfate was added to the mixture and then heated to 50 °C. The polymerization reaction was continued for 24 h. The synthesized polymeric particles were then separated from the solution via centrifuging. The separated polymer was washed several times with hot water and then with ethanol to remove emulsifier and non-reacted functional monomers from the polymer network. After multiple washing steps, the polymer was dried at 50 °C overnight and saved. The non-imprinted polymer was also synthesized according to the MIP synthesis procedure, except that template molecule (hydrogen phosphate) was not present in the polymerization reaction.

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