A new polymeric ionic liquid-based magnetic adsorbent for the extraction of inorganic anions in water samples

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ABSTRACT

In this work, a novel type of polymeric ionic liquid (PIL)-based magnetic adsorbent was successfully synthesized and applied for the extraction and determination of seven inorganic anions in water samples by coupling with ion chromatography. The new adsorbent was synthesized by simple free radical copolymerization of 1-ally-3-vinylimidazolium chloride, ethylene glycol dimethacrylate and silica-coated magnetite. The adsorbent exhibited well-defined core-shell structure and good magnetic response ability. Furthermore, due to the presence of abundant anion-exchange groups in the PIL, the adsorbent displayed expected extraction performance for anions including F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}. Various experimental parameters that could affect the extraction performance, such as the amount of adsorbent, desorption solvent, extraction and desorption time, the pH value of sample solution were investigated in detail. Under the optimized conditions, low limits of detection (S/N = 3) and quantification limits (S/N = 10) of the proposed method for the target anions were achieved within the range of 0.061–0.73 μg/L and 0.19–2.41 μg/L, respectively. The repeatability was investigated by evaluating the intra-day, inter-day precisions and batch-to-batch reproducibility with relative standard deviations (RSDs) lower than 11%. At the same time, the method also showed high extraction speed, simplicity, practicality and low cost for the extraction inorganic anions. Finally, the proposed method was used to detect anions in different water samples successfully. The recoveries were in the range of 71.0–111%, and the RSDs were below 12% in the all cases.

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1. Introduction

Magnetic nanoparticles (MNPs), mainly including Fe_3O_4 nanoparticles, are one of the most exciting composite materials in analytical chemistry because of their unique size and super paramagnetic property. The MNPs can be collected easily and conveniently by external magnetic forces. So far, MNPs have been widely applied in various scientific fields such as biosensors [1,2], protein separation and purification [3,4] and biomedicine [5]. In 1999, Šafaříková and Šafařík first proposed magnetic solid-phase extraction (MSPE) using MNPs as adsorbents. There are several outstanding advantages of MSPE. Firstly, the preparation and surface modification of MNPs is simple and convenient. Secondly, MSPE possesses a high extraction capacity and efficiency because of the high surface area-to-volume ratio of MNPs. Thirdly, MNPs can be easily and conveniently separated from the solution by magnetic field, which eliminates the centrifugal or filtration step. MSPE has been successfully used for the extraction and pre-concentration of peptides [6] and small molecules such as polycyclic aromatic hydrocarbons [7], perfluorinated compounds [8] and ergosterol [5] in various complex matrices.

In MSPE, the core is the extractive media-MNPs, which determines the extraction targets and performance. At the same time, the sensitivity and precision of the analysis are also affected strongly by MNPs. However, MNPs based on nano-Fe_3O_4 should be processed surface modification to prevent aggregation and oxidation of iron-oxide particles. At the same time, surface modification can introduce abundant adsorption sites and functional groups of MNPs. So far, all kind of MNPs such as C18-functionalized magnetic silica nanoparticles [9], layered double hydroxides coated MNPs [10] and polymer coated MNPs [11,12] have been prepared. As surface modifications, polymeric ionic liquids (PILs) immobilized MNPs (PIL/MNPs) are attracting increasing interest because of the unique properties of PILs. PILs refer to a subclass of polyelectrolytes that feature an ionic liquid (IL) species in each monomer repeating unit, connecting through a polymeric backbone to form a macromolecular architecture [13]. PILs combine the properties

of ILs and polymers, it expands the applications of ILs and common polyelectrolytes. He et al. [14] reported a novel magnetic adsorbent based on poly (1-vinyl-3-hexylimidazolium) bromide. The adsorbent provided expected extraction efficiency, high extraction speed and satisfactory enrichment factors for the extraction of organophosphorus pesticides. The study well indicates that PILs are ideal materials for the modification of nano-Fe_3O_4 magnetite. Up to now, the extractive analytes of PIL/MNPs focus on organic compounds, there is no report about the extraction of inorganic ions such as anions. Therefore, developing new PIL/MNPs and using them to extract anions is interesting.

So far, several extraction methods such as solid-phase extraction (SPE) [15,16], membrane extraction (ME) [17], solid-phase microextraction (SPME) [18], stir bar sorptive extraction (SBSE) [19], stir cake sorptive extraction (SCSE) [20] have been used to extract and pre-concentrate anions. However, SPE is inconvenient because multi-step processes are involved in the extraction and pre-concentration. Low extractive capacity limits the application of ME and SPME. SBSE and SCSE possess expected extraction capacity for anions, but long time should be needed to reach extraction equilibrium. For example, in our previous study, a new SCSE based on poly (1-ally-3-methylimidazolium) chloride (PAMC) was prepared. The PAMC-SCSE could extract anions effectively. However, because the thickness of the extraction medium was as thick as 3.0 mm, long time was needed for target analytes to contact with ion-exchange sites and the extraction did not reach equilibrium until 180 min [20]. Hereby, there is still an urgent need to develop a new extraction and pre-concentration format with simple procedure, satisfactory capacity and high extraction speed for the analysis of anions.

Considering the properties of MNPs and PILs, in this work, a novel magnetic adsorbent modified with PIL was prepared and used to extract anions under the format of MSPE. The PIL/MNPs were prepared using 1-ally-3-vinylimidazolium chloride as monomer, ethylene glycol dimethacrylate as cross-linking agent, and nano-Fe_3O_4 magnetite coated with SiO_2 ($Fe_3O_4@SiO_2$) as magnetic component. The chloride ions in the new PIL/MNPs could be replaced with hydroxyl ions and showed expected anion-exchange character. The characterization of the PIL/MNPs and its extraction performance for anions including F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were investigated in detail. After that, a new methodology combining PIL/MNPs-MSPE and ion chromatography with conductivity detector (PIL/MNPs-MSPE-IC/CD) for the analysis of trace anions in tap water, river water and commercial purified water was developed.

2. Experimental

2.1. Chemicals

1-Ally-3-vinylimidazolium chloride (AVIC) (99%) was purchased from Cheng Jie Chemical Co. LTD (Shanghai, China); Ethylene dimethacrylate (ED) (98%) were supplied by Alfa Aesar Ltd. (Tianjin, China); 3-(Trimethoxysilyl)-propyl methacrylate (γ-MAPS) (95%) were supplied by Tokyo kasei kogyo Co. (TCI, Japan); Azobisisobutyronitrile (AIBN) (97%, re-crystallized before use), $FeCl_3 \cdot 6H_2O$ (99%), $FeCl_2 \cdot 4H_2O$ (98%), tetraethylorthosilicate (TEOS) (98%), PEG600 and trifluoroacetic acid (TFA) (98%) were purchased from Xilong Chemical Co.(Guangzhou, China); HPLC-grade acetonitrile (ACN), methanol and ethanol were purchased from Tedia (Fairfield, USA); Water used throughout the study was purified using a Milli-Q Reference water-purification system (Merck Millipore, Germany). The resistivity value of ultrapure water used in present study was 18.2 MΩ cm, and no anion was detected. Sodium fluoride, sodium chloride, sodium nitrite,

potassium bromide, potassium nitrate, sodium sulfate and potassium phosphate are all analytical reagents and were supplied by Xilong Chemical factory in Guangdong (China). The other compounds used in the present study are analytical reagents.

The standard mixtures of seven anions were prepared by dissolving 1.00 mg of each compound in ultrapure water in 100 mL volumetric flask. The stock solution was stored at 4 °C and diluted with ultrapure water to give the required concentration. The purified water was purchased from local supermarket and tap water was collected in our lab. River water was collected from Jiulong river in Fujian province, and the water filtered by 0.22 μm membrane before use. All the water samples were stored at 4 °C.

2.2. Equipments and materials

Ion chromatography (IC) analyses were carried out with a DIONEX ICS-2500 IC instrument equipped with GP50 Gradient Pump, ED40 electrochemical detector operated in the conductivity mode and P/N9750E-029 manual injector. All experiments were performed at room temperature.

Oscillator (SHZ-82) was purchased from Guohua Electrical Equipment Co. (Jiangshu, China). The morphologies of PIL/MNPs were investigated using transmission electron microscopy (TEM) (JEOL 2011 microscope, Japan) and scanning electron microscopy (SEM) (Philips, Eindhoven, The Netherlands). Magnetic properties were analyzed by using a vibrating sample magnetometer (VSM, Lake Shore 7404, USA). Elemental analysis (EA) was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400. FT-IR was performed on an Avatar-360 FT-IR instrument (Thermo Nicolet, Madison, WI, USA).

2.3. Chromatographic conditions

The separation was performed on an IonPac AS14A (250 mm × 4.0 mm i.d.). The mobile phase consisted of 35 mmol/L Na_2CO_3-10 mmol/L $NaHCO_3$-H_2O (23/10/67, v/v/v). Eluent suppression was provided by a DZS-4A operated in the recycle mode under the 43 mA current. The flow rate was 1.0 mL/min and injection volume was 20 μL.

2.4. Synthesis of PIL/MNPs

2.4.1. Synthesis of magnetic nanoparticles

Magnetic Fe_3O_4 nanoparticles were prepared by chemical co-precipitation method [11,21]. Briefly, $FeCl_3 \cdot 6H_2O$ (5.8 g) and $FeCl_2 \cdot 4H_2O$ (2.2 g) were dissolved in 200 mL ultrapure water with a mechanical stirring at 80 °C, then 10 mL ethanediamine was added dropwise into above solution under nitrogen gas protection and vigorously mechanical stirring for 2 h. After the reaction, the obtained Fe_3O_4 particles were separated from the reaction medium by a magnetic field. The Fe_3O_4 particles were washed with water/methanol repeatedly with the aid of a magnet, and then dried under vacuum at 60 °C to get Fe_3O_4 nanoparticles.

Magnetic $Fe_3O_4@SiO_2$ nanoparticles were prepared by sol-gel polymerization method [22]. The prepared Fe_3O_4 particles (1.0 g) were dispersed in 100 mL 2-propanol by sonication for more than 15 min, following by the addition of 60 mL ammonia (25%, w/v) and 10 mL TEOS sequentially. The mixture was reacted for 12 h at room temperature under continuous stirring. The resultant product was collected by an external magnetic field, thoroughly rinsing with water/methanol repeatedly. After that, the product was dried to powder in vacuum to get $Fe_3O_4@SiO_2$.

2.4.2. Synthesis of PIL/MNPs

γ-MAPS-modified $Fe_3O_4@SiO_2$ nanoparticles ($Fe_3O_4@SiO_2@γ$-MAPS) were synthesized by reacting 1.0 g of $Fe_3O_4@SiO_2$ with