Nickel Iso-nicotine MOFs as Adsorbent of Solid Phase Extraction for Determination of Polycyclic Aromatic Hydrocarbon in Water

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ABSTRACT

The method of solid phase extraction (SPE) combined with high performance liquid chromatography (HPLC) was established while nickel iso-nicotine MOFs was employed as adsorbent of SPE to concentrate eight kinds of PAHs in water. The chromatographic conditions, such as flow rate of mobile phase and composition of mobile phase, were investigated. Several important factors of extraction efficiency of SPE, including mass of absorbent, volume of water sample, content of methanol and pH were discussed. The detection limit, precision and recovery rate were calculated.

INTRODUCTION

The metal-organic frameworks (MOFs) are recognized as a series of novel porous material in two decades. With different metals as central structure and organic compound as ligand, MOFs can be applied in adsorption, separation and catalysis etc [1-3]. Recently, the more and more severe environmental problems, especially the water pollution problems, are widely concerned about by environmental researchers. Unfortunately, the concentration levels of pollutants in water are too low to detect. Usually, it is necessary to enhance the sampling concentration of pollutants by different pre-treatment modes. Solid phase extraction (SPE) is one of the most practically feasible and suitable techniques and does not require sophisticated equipment and provides high pre-concentration efficiency [4]. The copper(II) isonicotinate coordination polymer, which was the first MOFs emloyed as adsorption of SPE, showed excellent adsorption efficiency for POPs [5].

Polycyclic aromatic hydrocarbons (PAHs), which contain at least two benzene rings, are neutral or non polar hydrocarbons [6,7]. The amounts of PAHs increase with the continuous development of human society. As one kind of the persistent
organic pollutants, PAHs have carcinogenicity, teratogenicity, and mutagenicity and have great harm to humans and environment [8-9].

Herein, the main purposes of this research were to prepare an interesting MOFs constructed by nickel (II) isonicotinate to explore as sorbent for the SPE of trace PAHs from water samples.

EXPERIMENTAL

Chemicals And Materials

All reagents were of the highest available purity and at least of analytical grade. Doubly deionized water (DDW, 18MΩ/cm) obtained from a Millipore-Q water system (Merk Millipore, MA, USA) was used throughout. The stock standard solutions of the PAHs were: (1) naphthalene (250 mg/l), (2) acenaphthylene (300 mg/L), (3) acenaphthene (250 mg/L), (4) phenanthrene (5 mg/L), (5) anthracene (5 mg/L), (6) fluoranthene (10 mg/L), (7) pyrene (10 mg/L), (8) benzanthracene (10.6 mg/L). Testing solutions were prepared from the standard stock solutions by stepwise dilution in DDW just before use.

Apparatus And Analytical Conditions

The chromatographic system consisted of a Waters 600 HPLC pump and a Waters UV detector (Milford, MA, USA). All separations were achieved on an analytical reversed-phase column (ZORBAX SB-C18 5 μm, 4.6mm I.D.×15 cm long, Agilent, USA) at a mobile flow rate of 1.0 ml/min under isocratic conditions at a column temperature of room temperature The N2010 Software was used to acquire and process spectral and chromatographic data. The UV detector was operated between 214 nm.

The pre-column used for the SPE pre-concentration of PAHs was a 1 ml plastic syringe dry-packed with a small amount of the nickel(II) iso-nicotinate polymer. The two ends of the pre-column were plugged with glass wool. Before measurements, the pre-column was conditioned by flushing with mobile phase until the detector response reached stability.

Best chromatographic resolution for the separation of PAHs was obtained with a mixture of acetonitrile (Concord Technology Co. Ltd., Tianjin, China) and water (77:25) at a column temperature of 25 °C.

Optimization Of Mobile Phase Proportion And Flow Rate Of Mobile Phase

The retention time of eight kinds of PAHs was affected by the mobile phase proportion and flow rate of mobile phase. 1.0 ml standard sample and 4.0 ml methanol were put into the centrifuge tube and were prepared testing solution. Then, the flow rate of mobile phase and the proportions of acetonitrile in mobile phase were investigated. The results were shown in figure 1 and figure 2. Finally, the flow rate was chosen as 1.0 ml/min, and mobile phase ratio was chosen as 75% acetonitrile solution (75% acetonitrile, 25% ultra pure water).
RESULTS AND DISCUSSION

Effect Of Different Samples Volume On Pahs

Testing solution was obtained by diluting PAHs standard solution with water containing 5% methanol, and the diluted proportion was fixed at 8000:1. A certain volume testing solution (100 ml, 400 ml, 700 ml, 1000 ml, 1500 ml and 2000 ml) flowed through the home-made SPE extraction column to pre-concentrate PAHs, then the concentrated PAHs was eluted with 1.0 ml methanol. Finally, the collected eluent was separated and detected by HPLC. The results were shown in figure 3. It can be seen that the increasing volume of testing solution led to the increase of peak area of all eight kinds of PAHs. However, much more testing solution meant more time consuming. Therefore, 1000 ml water sample was selected as the optimal condition for subsequent experiment.

Effect Of Mass Of Absorbent On Pahs Pre-Concentration

The effect of mass of absorbent on PAHs pre-concentration was discussed while different mass nickel iso-nicotine (2 mg, 4 mg, 6 mg, 8 mg and 10 mg) were employed as SPE absorbent. It could be seen from fig. 4 that when the mass of absorbent varied from 2 mg to 6 mg, the peak area of all eight kinds of PAHs ascended. While the mass of absorbent continued to increased, the pre-concentration efficiency decreased. Therefore, the mass of absorbent of 6 mg was selected as the optimal condition of the following experiment.
Effect Of Volume Of Eluent On Pahs Enrichment

The effect of eluent volume was investigated while different volume methanol (0.6 ml, 0.8 ml, 1.0 ml, 1.2 ml) as eluent and the results were shown in figure 5. It could be seen that the less methanol volume meant the larger peak area. However, too less methanol volume could lead to incomplete eluting of PAHs and worsen precision. Therefore, 1.0 ml methanol was chosen.

Effect Of Testing Solution Ph On Pahs Enrichment

The effect of pH of testing solution, including 2.0, 4.0, 6.0, 8.0, 10.0, was experimented while the pH of testing solution was adjusted with 0.1 mol/L hydrochloric acid or sodium hydroxide. The results were shown in figure 6. It could be seen that when pH varied from 2 to 10, the peak area of eight kinds of PAHs kept invariable. In view of this situation, the pH of testing solution was not adjusted.

Analytical Merits

The standard solution was diluted by water containing 5% methanol with the ratio of 17000:1. And 1.0 ml methanol was chosen as the eluting solution. Finally, the liquid was analyzed by HPLC. Chromatogram was observed, peak area and peak height were recorded, and RSD and detection limit were calculated.

The use of the nickel(II) iso-nicotinate polymer as sorbent for pre-concentration at a 1000 ml sample loading enhanced the detection sensitivity of PAHs with detection limits (S/N = 3) of 7.0-45 ng/l (see table 1). The precision (RSD) for eight replicate determinations of a mixture of eight PAHs studied was in the range of 1.4-4.0 for peak area. To demonstrate the accuracy of the developed method, a synthetic sample was analyzed for PAHs. The recoveries of eight PAHs were 75.4-140.1%

| PAHs            | Detection limit(ng/l) | Precision(%) | Recovery rate(%) |
|-----------------|-----------------------|--------------|------------------|
| Naphthalene     | 5.80                  | 1.39         | 103.3            |
| Acephaphylene   | 45.83                 | 1.42         | 80.0             |
| Acephenylene    | 17.47                 | 1.68         | 75.4             |
| Phenantrene     | 18.19                 | 2.97         | 50.0             |
| Anthracene      | 18.66                 | 2.69         | 123.9            |
| Fluoranthene    | 11.31                 | 1.99         | 140.1            |
| Pyrene          | 22.82                 | 4.02         | 138.3            |
| Benzanthracene  | 7.37                  | 2.35         | 118.4            |
CONCLUSION

In this paper, a method of SPE-HPLC was established to demonstrated the adsorption performance of nickel iso-nicotine and several important factors were explored. Although the results reported here relate only to 8 PAHs, the principles of the proposed methodology are expected to be applicable to HPLC analysis of other POPs as well.

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