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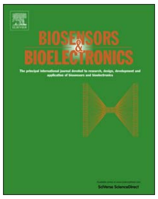

Rapid and reliable determination of *p*-nitroaniline in wastewater by molecularly imprinted fluorescent polymeric ionic liquid microspheres

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ABSTRACT

Rapid and efficient detecting trace amount of environmental *p*-nitroaniline (*p*-NA) is in urgent need for security concerns and pollution supervision. In this work we report the use of molecularly imprinted polymeric ionic liquid (MIPIL) microspheres to construct recognizable surfaces for detection of *p*-NA through fluorescence quenching. The *p*-NA imprinted microspheres are synthesized by precipitation polymerization upon co-polymerization of 3-(anthracen-9-ylmethyl)-1-vinyl-1H-imidazol-3-ium chloride (Fluorescent IL monomer) with ethyleneglycol dimethacrylate (EGDMA). The electron-rich group alkenyl imidazole in IL functional monomer can dramatically improve the emission of anthracene fluorophore and the π-π stacking, electronic, and hydrogen bond between *p*-NA and MIPIL can efficiently enhance the selective recognition force. The as-synthesized MIPIL microspheres present spherical shape, high fluorescence emission intensity and specific recognition, which showed rapid detection rate (1 min), stable reusable property (at least 4 time recycles), wonderful selectivity over several structural analogs, wide linear range (10 nM to 10 M) with a correlation coefficient of 0.992, and excellent sensitivity (LOD, 9 nM). As synthesis and surface functionalization of MIPIL microspheres are well established, the methods reported in this work are facile, rapid and efficient for monitoring *p*-NA in environmental wastewater.

1. Introduction

Detection of organic pollutants is considered as one of the vital factors of security concerns and pollution supervision (Guo et al., 2006; Sun et al., 2014; Wang et al., 2014; Zhao et al., 2007). The environmental contamination resulting from organic pollutants is becoming an overwhelming problem throughout the world with the industrialization and urbanization. Aromatic amines have been pervasively used in various industries such as cosmetics, pharmacy, leather, textile and so on (Han et al., 2009; Lenghartova et al., 2015; Pfeifer et al., 2016; Sun et al., 2014). They are known as disreputable environmental contaminants, are often discharged into the environment from textile, chemical, pharmaceutical and tannery industries along with wastes as well as from the decomposition of azo dyes in tens of thousands daily necessities (Deshmukh et al., 2016; Guo et al., 2006; Lenghartova et al., 2015). Aromatic amines are important chemical intermediate that holds an irreplaceable significance for synthesizing a large amount of chemical products. However, they may react with substances excreted from human bodies to generate blood poisoning, skin eczema, dermatitis disease and even induce cancer causing high risks to human health and the environment (Chen et al., 2009; Guo et al., 2006; Wu et al., 2016b; Zhao et al., 2007). Therefore, the development of a facile and economic analytical method for nondestructive, rapid and efficient monitoring of aromatic amines is not only increasing importance for environmental protection, but also an urgent demand in the field of public security.

Currently, various methods have been developed for the detection of aromatic amines including capillary electrophoresis (Huang et al., 1999; Onal et al., 2013; Schnierle et al., 1998), thin-layer chromatography (Guo and Chen, 2010; SpencerBeach et al., 1996), liquid chromatography coupled with mass spectrometry (LC-MS) (Busquets et al., 2009; Mutsuga et al., 2010) or gas chromatography-mass spectrometry (GC-MS) (Mishra et al., 2001; Skog et al., 1998; Yan et al., 2007), electrochemistry (Lizier and Zanoni, 2012; Pfeifer et al., 2016; Zhao et al., 2007), surface enhanced Raman scattering (Ma et al., 2014; Wu et al., 2016b), fluorescence (Shaligram et al., 2014; Wang et al., 2015a; Xu and Lu, 2015) and so on (Han et al., 2009; Wu et al., 2016a). Although various documented technologies responded well in the detection of aromatic amines, most of them suffer from more or less drawbacks, such as expensive instrumentation, time-consuming pro-

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cedures, complicated operation, low accuracy and poor stability, which have made them unsuitable for on-site, rapid and handy detection. Fluorescent sensing has been proven to be an outstanding analytical technology for detecting aromatic amines based on the fluorescence quenching or enhancement with simple and reliable mechanism. However, many of the current fluorescence sensors, such as the metal-organic framework, don't have good enough specificity for detecting aromatic amines. For example, Wang et al. (2015a) developed a method to detect aromatic amines by applying two functional metal organic frameworks, which can only distinguish electron rich and electron deficient aromatic amines that resulting in fluorescence enhancing and decreasing respectively.

The construct of the specific recognition site in a fluorescent probe is essential in selective detecting aromatic amines. Among multi-sensors, the recognition and capture elements mainly acquired from various biological systems, e.g., aptamers and antibodies that are extraordinary suitable for the detection of bio-macromolecules (Altintas et al., 2015; Awino and Zhao, 2013; Liu and Wulff, 2008; Yang et al., 2017). However, these biological systems are not particularly useful in identifying low molecular weight analytes and they have only limited stability and easy to lose recognition activity. Molecularly imprinted polymers (MIPs) for small molecule detection have shown the great potential. MIPs having a pre-designed molecular identification ability can be applied to construct robust and label-free chemical detection sensors (Chen et al., 2015; Takeda et al., 2009; Wu et al., 2015). Spatial cavity which is accordingly in shape for the matched analyte is formed in addition to a combination of hydrophobic, hydrogen bonding, and electronic interactions after extraction of template molecule. Benefiting from above advantages, MIPs are frequently applied in electrochemical, surface-enhanced Raman scattering, surface plasmon resonance and fluorescent sensors (Cennamo et al., 2013; Gao et al., 2014; Li et al., 2007; Singh and Singh, 2015; Tu et al., 2016; Wang et al., 2015b, 2014).

It is still challenging in selective and sensitive detecting aromatic amines with rapid sensing response. Moreover, most MIP related sensors are labor intensive because their operation requires multiple steps. Here, we proposed a novel and simple synthesized fluorescent molecularly imprinted polymeric ionic liquid microspheres for specific detection of *p*-nitroaniline. MIPIL microspheres were obtained using *p*-nitroaniline as template, fluorescent functional monomer 3-(anthracen-9-ylmethyl)−1-vinyl-1H-imidazol-3-ium chloride was co-polymerized with EGDMA. It should point out that the electron-rich group alkenyl imidazole in functional ionic liquid monomer can significantly enhance the fluorescent emission intensity of anthracene fluorophore. Besides, spatial cavity in MIPIL for selective recognization target is formed with the help of the π-πstacking, electronic, and hydrogen bonding interactions between temperate molecules and MIPIL spheres after extraction of *p*-NA (Baggiani et al., 2012; Bui et al., 2010; Wang et al., 2016; Zhang et al., 2016). The resultant MIPIL microspheres applied for *p*-NA detection showed excellent performance of facile, rapid, reusable, specificity and sensitivity. To check the efficiency of this handy sensor for detection of *p*-NA, we chose the environment water samples in Jiaxing city and mimic dye wastewater as real sample. Therefore, in addition to the immediate advantage in selective detection of aromatic amine pollutant from wastewaters, the efficient ability for *p*-NA detection demonstrated in this strategy is promising in the environmental safety analysis.

2. Experiment section

2.1. Materials

9-chloromethylanthracene, 1-vinylimidazole, and 4,4-diaminodiphenyl methane were obtained from TCI (Japan). Ethylene glycol dimethacrylate (EGDMA), *p*-nitroaniline, 3-aminobiphenyl, 1-naphthylamine and 2-naphthylamine were purchased from Sigma-Aldrich Chemical Company (USA). 2,2'-Azo-bisisobutyronitrile (AIBN) and *p*-chloroaniline were acquired from Aladdin Internet Reagent Database Inc. (Shanghai, China). Methanol, ethanol, sodium dihydrogen phosphate, disodium phosphate, acetonitrile and anhydrous ether were all attained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Aniline was supplied by J & K Scientific Ltd. (Beijing, China). *p*-Toluidine was purchased from Tingxin Chemical Reagent Factory. Acetonitrile and aromatic amines were prepared from chromatographically grade and other chemicals were analytical grade. Milli-Q water (18 MΩ•cm resistivity) was used for preparing all aqueous solutions and cleaning processes.

2.2. Instruments

The relative molecular mass was calculated on a LCT priemier XE ultra performance liquid chromatography-mass spectrometer (Waters, USA). ^{1}HNMR and ^{13}CNMR spectroscopy were recorded on a Varian 400 M Nuclear magnetic resonance instrument (Varian, USA). Fourier transform infrared (FT-IR) were obtained by a Nicolet NEXUS-470 FTIR apparatus (USA) using KBr pellets. Agilent Technologies Cary 60 UV–vis was used to determine the concentration of *p*-NA. N_2 sorption isotherms were measured using Micro TriStar 2020 at 100 °C. All the samples were degassed under vacuum for 20 h before measurements. The specific surface area and pore size distribution were calculated by using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method, respectively. The micropore surface area was calculated by the DFT method. The morphologies of prepared samples were observed by a Hitachis-4800 scaning electron microscope (SEM) (Hitachi, Japan). Fluorescence intensity were performed on Cary Eclipse fluorescence spectrophotometer (Varian, USA). Fluorescence confocal microscopy images of MIPILs samples were obtained via a TCS SP5 II confocal microscope (Leica, Wetzlar, Germany) with a 405 nm solid state laser light source. Particle size were measured by a Nano-Zs90 laser particle size analyze (ZETA SIEER). High performance liquid chromatography analyzing various samples were carried out by using Agilent 1200 (Agilent, USA).

2.3. Synthesis of IL functional monomer and MIPIL microspheres

A mixture of 1-vinylimidazole (0.94 g), 9-chloromethylanthracene (1.133 g) and acetonitrile (30 mL) was heated and stirred in a thermostatically controlled oil bath at 70 ℃ for 12 h. Then cooled to room temperature and washed with anhydrous ether, dried in vacuum overnight to get bright yellow fluorescent ionic liquid crystal named 3-(anthracen-9-ylmethyl)-1-vinyl-1H-imidazol-3-ium chloride.

MIPIL microspheres were prepared from 3-(anthracen-9-ylmethyl)-1-vinyl-1H-imidazol-3-ium chloride as fluorescent functional monomer (64 mg), EGDMA (198 mg) as cross-linker, and *p*-nitroaniline (7 mg) as the template in methanol. 3-(anthracen-9-ylmethyl)-1-vinyl-1H-imidazol-3-ium chloride and *p*-nitroaniline were added to a 100 mL round-bottomed flask and dispersed in 40 mL methanol by stirring for 15 min. Then, AIBN and EGDMA were added in the round-bottomed flask. After purged with N_2 for 30 min, the flask was sealed and submerged in a thermostatically controlled oil bath and then the mixture was stirred. The temperature raised from room temperature up to 60 ℃, and the flask was maintained at 60 ℃ for 12 h. At the end of the reaction, the particles were collected from the reaction medium by filtration, which were then cleaned successively by ultrasound with ethanol to remove the templates. Finally, the products were dried in vacuum overnight at 60 ℃. Non-imprinted polymeric ionic liquid (NIPIL) spheres were prepared under nominally duplicate conditions as MIPILs in the absence of the template *p*-nitroaniline.

2.4. *p*-NA adsorption experiment

The *p*-NA adsorption of MIPIL (or NIPIL) microspheres in methanol/water (4:1 v/v) or water solution was investigated in batch