Hierarchical porous nanostructured polypyrrole-coated hydrogel beads containing reduced graphene oxide and magnetite nanoparticles for extraction of phthalates in bottled drinks

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ARTICLE INFO

ABSTRACT

A hierarchically porous polypyrrole-coated nanostructured composite of reduced graphene oxide and magnetite nanoparticles (PPy-$rGOx$-Fe_3O_4) incorporated into alginate hydrogel microspheres was synthesized and applied as a magnetic solid phase extraction adsorbent. The double network porous nanostructure of the composite hydrogel was created by CO_2 produced from the reaction of hydrochloric acid with the $CaCO_3$ in the hydrogel. The developed hydrogel microsphere was characterized and evaluated for the extraction and enrichment of phthalates. Several parameters that could potentially affect the extraction efficiency of the developed hydrogel microspheres were investigated. The developed method provided a wide linear range from 0.005 to 500 $\mu g\,L^{-1}$ for dibutyl phthalate, 0.01 to 500 $\mu g\,L^{-1}$ for diethyl phthalate, benzylbutyl phthalate and bis(2-ethylhexyl) phthalate, and 0.02 to 500 $\mu g\,L^{-1}$ for dimethyl phthalate and di-n-octyl phthalate. Low limits of detection were obtained in the range of 0.005–0.01 $\mu g\,L^{-1}$. The developed adsorbent was successfully used to extract phthalates in bottled water and beverages and the recoveries achieved were between 87.5 and 99.1%. The developed adsorbent can be used as an alternative rapid, convenient and cost effective adsorbent for the enrichment and analysis of trace phthalates.

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1. Introduction

Phthalates are extensively used as plasticizers in the production of various kinds of PVC-based rubber and plastic food packaging products [1] because they improve their durability and flexibility. However, when incorporated in plastics, phthalates do not chemically bond to the polymer matrix, and therefore they can migrate from the packaging or bottling material into the food or drink [2]. Phthalates biodegrade slowly and can accumulate in human tissue. Phthalates have been classified as endocrine disrupting compound and are potentially harmful to humans, causing conditions such as asthma, cancer, and low birth weight. For food safety and to protect human health, the monitoring of phthalates in food and drinks is clearly very important. Generally, the analytical methods used for the determination of phthalates are liquid chromatography [3–5] and gas chromatography [6–8]. However, the matrices of food and drink samples are complex and the phthalates present are at trace levels, which makes detection difficult without sample preparation. Thus, sample pretreatment procedures are usually required prior to chromatographic analysis.

Several pre-concentration and clean-up methods have been reported for the enrichment of phthalates. These have included solid phase extraction (SPE) [9–13], solid phase microextraction (SPME) [6,14,15], dispersive liquid liquid-microextraction (DLLME) [16], ultrasound assisted emulsification microextraction (USAEME) [17], dispersive solid phase microextraction (DSPME) [18], and magnetic solid phase extraction (MSPE) [5,19–23]. Among these techniques, MSPE, which is based on magnetic adsorbents, has attracted much attention due to its ease of use. Fast separation of the adsorbent from the sample solution is achieved without the centrifugation and filtration required by some other extraction methods. In addition, the MSPE adsorbent can be reused by washing away contaminating compounds with a suitable solvent [24].

However, the chemical agents in the sorptive layer that functionalizes the surface of the magnetite nanoparticles can form agglomerations and large particles which reduce the specific surface area and adsorption sites available to the target analytes. To

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CHROMA-359586; No. of Pages 9

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overcome this shortcoming of MSPE sorbents, nanomaterials and magnetite nanoparticles have been incorporated into porous polymeric hydrogels [25]. One of these porous supporting materials is Ca-alginate hydrogel microspheres. The inert environment and water insolubility of alginate hydrogel allows the entrapment of nanomaterials [26]. The porosity of Ca-alginate facilitates the diffusion of target analytes into the microspheres, where they come into contact with the entrapped nanomaterial [27]. Alginate hydrogel is also biodegradable, nontoxic and low cost [28]. Moreover, alginate is a hydrophilic polymer, which can increase adsorption ability by improving the dispersion of the adsorbent in aqueous samples.

Efficient extraction of target analytes by the MSPE method, requires suitable adsorptive coatings or composites containing magnetite nanoparticles. Several adsorptive materials have been used to prepare the MSPE adsorbent for the extraction or adsorption of organic compounds. These materials have included nanographite carbon [29], multiwall carbon nanotubes [24], molecularly imprinted polymers [30], octadecyl silica [31] and ionic liquids [32]. For the extraction and enrichment of phthalates, reduced graphene oxide (rGOx) has attracted much attention as a potential adsorbent due to its large surface area and abundant aromatic rings that can adsorb phthalates through π-π and hydrophobic interaction [33,34]. In order to improve adsorption ability of target analytes, conducting polymers have been used as coating materials. They are inexpensive and easily synthesized. Supporting materials have been coated with polypyrrole [35–38], polyaniline [39], polythiophene [40] and polydopamine [41,42] to adsorb analytes.

In this work, a hierarchically porous composite nanostructure of polypyrrole, reduced graphene oxide, magnetite nanoparticles and alginate hydrogel microspheres (PPy-rGOx-Fe$_3$O$_4$) was prepared and characterized. The hierarchically porous nanostructure was created by the reaction of hydrochloric acid with the CaCO$_3$ in the hydrogel. This reaction produced bubbles of CO$_2$, which created the pores in the alginate hydrogel. The reduced graphene oxide entrapped in the porous hydrogel microspheres and the coating of polypyrrole improved the adsorption of phthalates. The PPy-rGOx-Fe$_3$O$_4$/MSPE/GC–MS-MS technique combined the high extraction efficiency of PPy and rGOx, and a simple and rapid of MSPE method.

2. Experimental

2.1. Chemicals and materials

Dimethyl phthalate (DMP), dibutyl phthalate (DBP), diethyl phthalate (DEP), benzylbutyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DNOP) were from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Alginate, graphene oxide (4–10 % edge-oxidized), pyrrole, iron (III) chloride hexahydrate, methanol and calcium carbonate were from Sigma–Aldrich (Steinheim, Germany). Calcium chloride, 2-propanol was from Merck (Darmstadt, Germany).

2.2. Instrumentation

Gas chromatography analysis was performed using a triple quadrupole GC–MS/MS system Agilent 7890B operated in MRM mode (CA, USA) with automated injection by a PAL RTC 120 autosampler (CTC Analytics AG, Zwingen, Switzerland). The separation was carried out on an HP-5MS UI (30 m x 0.25 mm ID $\times$ 0.25 μm; J & W Scientific, Folsom, CA, USA). The GC was operated in splitless injection mode and the injection volume was 1.0 μL. The oven temperature was programmed as follows: start at 100 °C (hold for 1 min), increase to 190 °C at the rate of 20 °C min^{-1} (hold for 1 min), then increase to 290 °C at 30 °C min^{-1} (hold

for 4 min). The carrier gas was helium (99.999%) at a flow rate of 2.0 mL min^{-1}. Temperatures of the front inlet, interface, MS source, and MS quad were set at 250, 290, 230 and 150 °C, respectively. The quantification and identification ions and collision energy of phthalates are summarized in Table S1. Scanning electron microscopy (SEM) images were observed on a JSM–5200 scanning electron microscope (JEOL, Tokyo, Japan). The specific surface areas were determined using ASAP 2060 analyzer (Micromeritics, USA).

2.3. Preparation of composite porous nanostructured polypyrrole, reduced graphene oxide, magnetite nanoparticle alginate hydrogel microspheres

Magnetite nanoparticles (Fe$_3$O$_4$) were synthesized using a method previously reported [22]. Briefly, 5.0 g of FeCl$_3$.6H$_2$O and 2.0 g of FeCl$_2$.4H$_2$O were dissolved in deionized water (100 mL) and transferred to a three-necked flask. The mixture solution was heated to 85 °C, then 15 mL of ammonium hydroxide (30% v/v) was added and the solution was then continuously refluxed for 40 min. The obtained Fe$_3$O$_4$ nanoparticles were separated using external magnets, washed twice with 200 mL deionized water and dried in an oven at 50 °C for 6 h.

To prepare the composite hydrogel microspheres, 1.0 g of Fe$_3$O$_4$ nanoparticles, 5.0 mg of graphene oxide, and 0.5 g of calcium carbonate were added to 2.0% w/v sodium alginate solution (100 mL) and stirred at 30 °C for 2 h to achieve a homogeneous solution. Then, the mixture solution was added dropwise into 4.0% w/v calcium chloride solution. The composite hydrogel microspheres rapidly formed when the drops came into contact with the calcium chloride solution. The hydrogel microspheres were further incubated in the calcium chloride solution for a further 2 h to complete the composition. Subsequently, the incorporated graphene oxide in hydrogel microspheres were reduced to graphene by adding the composite hydrogel microspheres to 100 mL of ascorbic acid (0.2% w/v) and heating at 85 °C for 6 h. When the graphene oxide was completely reduced to graphene, the color of the hydrogel beads changed from brown to black. The obtained composite reduced graphene (rGOx-Fe$_3$O$_4$-CaCO$_3$) alginate hydrogel microspheres were separated from the ascorbic acid solution and washed with 50 mL of deionized water.

To produce the hierarchical porous nanostructure, the composite rGOx-Fe$_3$O$_4$-CaCO$_3$ hydrogel microspheres were added to 100 mL of hydrochloric acid (20% w/v). The CaCO$_3$ in the hydrogel microspheres reacted with the hydrochloric acid to produce bubbles of CO$_2$ which created the pores to make the double network in the hydrogel microspheres. The composite porous nanostructured hydrogel microspheres were then coated with polypyrrole. The microspheres (20 g) were incubated with 20 mL of 2-propanol for 1.0 h, followed by incubation in 20 mL of pyrrole monomer for 1.0 h. Subsequently, the pyrrole-saturated composite porous nanostructured hydrogel microspheres were separated from the pyrrole solution and polymerized in 20 mL of 0.2 M ferric chloride solution for 1 h at room temperature (26 $\pm$ 1 °C) under rotation. Finally, the obtained composite porous nanostructure PPy-rGOx-Fe$_3$O$_4$ hydrogel microspheres were washed successively with 2-propanol (20 mL), methanol (20 mL) and deionized water (100 mL). The preparation procedure of the composite hierarchical porous nanostructured PPy-rGOx-Fe$_3$O$_4$ hydrogel microspheres is illustrated in Fig. 1.

2.4. Magnetic solid phase extraction procedure and optimization condition

First, 0.75 g of PPy-rGOx-Fe$_3$O$_4$ alginate hydrogels were introduced into a glass bottle containing 20 mL of sample and continuously stirred at room temperature (27 $\pm$ 2 °C) for 15 min