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A molecularly imprinted polymers/carbon dots-grafted paper sensor for 3-monochloropropane-1,2-diol determination

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ABSTRACT

3-Monochloropropane-1,2-diol (3-MCPD) is a common food processing contaminant and a simple, rapid, sensitive and low cost monitoring technology is needed due to its potential carcinogenic nature. Carbon dots directly intercepted on filter paper provide high fluorescence intensity and can be adapted for use as a sensor. We synthesized a carbon dot-filter paper in combination with a molecularly imprinted polymeric film to extract 3-MCPD from samples. This grafted paper-based sensor exhibited a high adsorption capacity (68.97 mg g^{-1}), an excellent selectivity (imprinting factor = 4.5) and a low detection limit (0.6 ng mL^{-1}). Recoveries ranged from 97.2% to 105.3% with relative standard deviations < 5.6%. The results obtained using this method were linearly correlated to those of the classic GC–MS method (r = 0.998). Based on the Chinese National Standard, this study provides a novel and powerful platform for the simple, rapid, sensitive and on-site analysis of 3-MCPD in soy sauce.

1. Introduction

The 3-monochloropropane-1,2-diol (3-MCPD) is a by-product of acid hydrolysis of vegetable proteins and is a suspected human carcinogen (Jedrkiewicz, Kupska, Glowacz, Gromadzka & Namiesnik, 2016). 3-MCPD is present in both free and bound forms in numerous food products including soy sauces, meat products and infant foods (Lee & Khor, 2015). 3-MCPD is a group 2B carcinogen and the European Commission limits are 0.02 mg kg^{-1} in hydrolyzed vegetable protein and soy sauce. The maximum tolerable daily intake (TDI) was established at 2 μg kg^{-1} per day. In 2008, the Food and Drug Administration set a limit of 1 mg kg^{-1} in these products. In response to strict legislation limits, industry has made efforts to decrease the amount of 3-MCPD in hydrolyzed vegetable protein.

Gas chromatography with mass spectrometry (GC–MS) is used as a sensitive and classical approach for the detection of 3-MCPD (Kuesters et al., 2010; Kim et al., 2015; Yang, Kwon, Choi & Jo, 2018). However, due to the reactivity and polarity of 3-MCPD, the samples must be derivatized to improve peak shape. High performance liquid chromatography fluorescence detection coupled with derivatization was also developed for the determination of 3-MCPD (Hu, Cheng, Guo, Zhang & Qi, 2013). Subsequently, gas chromatography-triple quadruple mass spectrometry was proposed for the detection of 3-MCPD to circumvent derivatization (Genualdi, Nyman & DeJager, 2017). However, the chromatography methods still pose technical problems including low *m/z* fragmentation patterns, expensive instrumentation and high running costs. These methods are not suitable for high-throughput screening or on-site detection. The development of a rapid, cost effective and simple method was needed for the determination of 3-MCPD in food samples. The greatest challenge was to overcome matrix interference while retaining sensitivity.

Molecular imprinting is a promising strategy to decrease matrix interference and improve selective enhancement of target molecules (Ashley et al., 2017). Molecularly imprinted polymers (MIPs) can be matched to the size and shape of template molecules and exhibit excellent selectivity over structurally related compounds (Speltini, Scalabrini, Maraschi, Sturini & Profumo, 2017; Uzun & Turner, 2016; Yanez-Sedeno, Campuzano & Pingarron, 2017). An indirect electrochemical sensor has been developed for 3-MCPD detection based on the MIP/nano Au electrode using potassium ferrocyanide as a probe (Sun et al., 2014). However, many factors adversely affected the performance of this MIP sensor, such as electrode polishing and modification, temperature and humidity, anti-fouling performance, interference of active molecules and so on.

Paper-based devices provide new platforms for sensitive, high-throughput assays of food (Alamo Busa et al., 2016). The most attractive features of this technology are its low cost, ease of use and portability. The combination of the MIP technique with a paper-based

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device provides a promising strategy (Li et al., 2017; Qi et al., 2017). An anion-imprinted polymer grafted paper-based sensor for detection of Cd (II) ions via a color reaction between dithizone and cadmium has been developed (Huang et al., 2017). A direct competitive assay and labeled probes are necessary for this MIP-based sensor, but sensitivity is still a challenge. Thus, the right method for the future is one that blends a paper-based device and MIPs/fluorescence composites. Such a sensor would exhibit high selectivity for the target molecules and have low matrix interference but also possess the handling properties of a common paper device.

Imprinting using fluorescence monomers or encapsulating fluorescent nanoparticles have been applied to a MIPs-based fluorescence sensor (Chen, Wang, Lu, Wu & Li, 2016). However, the fluorescence monomers are relatively rare and the synthesis procedure is complex. Fluorescence materials and especially carbon dots (CD) are widely used for rapid detection sensors. They possess narrow emission spectra and have a strong signal intensity (Wang & Qiu, 2016; Li, Rui, Song, Shen & Zeng, 2015).

In this study, we used carbon dots possessing amino groups for attachment to filter paper containing carboxyl group susing negative pressure and heating. The MIP film was synthesized using 3-MCPD as a template and methacrylicacid (MAA) as a monomer. This was directly formed on the surface due to the amino group and carboxyl group interactions. This paper-based sensor was tested for its use as a selective and sensitive detection of 3-MCPD in soy sauce.

2. Materials and methods

2.1. Reagents and materials

3-MCPD, 1,3-dichloro-2-propanol (1,3-DCP), 2,3-dichloro-1-propanol (2,3-DCP), glycerol, ethylene glycol and 1,2-propanediol were purchased from J&K Chemical. MAA, ethylene glycol dimethacrylate (EGDMA), and azodiisobutyronitrile (AIBN) were purchased from Sigma-Aldrich (Shanghai, China). MAA and EGDMA were purified by general distillation in vacuum under nitrogen to remove the polymerization inhibitor. AIBN was recrystallized from cooled methanol and dried at room temperature in a vacuum. Citric acid anhydrous, ethylenediamine, methanol, acetonitrile, acetone, ethanol and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Whatman 934-AH filter paper was purchased from Whatman International Ltd (Maidstone, England). Ultrapure water was obtained from a Milli-R04 purification system (Millipore, Germany). Soy sauces were collected from a local supermarket and stored at -4 °C until analysis.

2.2. Apparatus

Fluorescent spectra was obtained using a Jasco FP-6500 fluorescence spectrometer (Jasco, Japan) with excitation at 360 nm and emission from 380 to 600 nm for the CDs. FT-IR spectra were collected on a Verte 70 Fourier transform spectrometer (Bruker, Germany). Scanning electron microscopic (SEM) images were observed using a Nova NanoSEM 450 microscope. The chemical composition of MIPs/CDs on the grafted paper was measured using an X-ray photoelectron spectrometer (Axis-Ultra DLD 600 W, Japan) using Al/Mg Kα radiation.

2.3. Preparation of CDs with amino groups

In a typical procedure, 15 g citric acid anhydrous and 7.5 mL ethylenediamine were dissolved in 60 mL water and then sonicated for 10 min. The mixture was transferred into a Teflon-lined stainless steelpan and heated at constant temperature of 200 °C for 3 h. After cooling to room temperature, the resulting solution was dialyzed against DI water for 48 h to remove impurities. The resulting mixture was freeze-dried.

2.4. Preparation of MIPs/CDs grafted paper

The filter paper substrate was soaked in 5 M H_2O_2 for 3 h and washed with ultrapure water three times. CDs with amino groups flowed through the filter paper 10 times at 0.1 mL min^{-1} by using a negative pressure while heating at 80 °C. A one-pot synthesis strategy was then used to construct a MIPs/CDs grafted paper-based sensor based on the electrostatic attraction between amino groups (CDs) and carboxyl groups (MAA). Briefly, 2 mM MAA, 20 mM EGDMA, 1 mM 3-MCPD and the CDs intercepted filter paper (2 cm × 4 cm) were added to 10 mL aqueous solution of ethanol (80%, v/v). The resulting solution was shaken for 30 min for pre-polymerization. After purging with N_2 for 10 min, 20 mg of AIBN was added, and the mixture was shaken at 60 °C overnight in the dark. The resulting products (MIPs/CDs grafted paper) were washed with acetonitrile/acetic acid (9/1, v/v) and then methanol to remove the templates and unreacted components and solvent, respectively. As a control, the non-imprinted composite (NIPs/CDs grafted paper) were prepared using an identical procedure without the addition of 3-MCPD.

2.5. Adsorption experiment

MIPs/CDs grafted paper was further cut using a hole-puncher (8 mm × 8 mm) to avoid the boundary effect and incubated in 1 mL ethanol (80%, v/v) with 3-MCPD levels ranging from 10 to 150 μg mL^{-1}. The filter paper was shaken for 24 h at room temperature and recovered using tweezers. The compounds in the supernatant were measured using a GC–MS method. The Freundlich and Langmuir isotherms were applied to study the adsorption mechanism of MIPs/CDs grafted paper. The curves of binding versus time were plotted to determine the adsorption kinetics for the target molecules.

2.6. Detection of 3-MCPD in real samples

Soy sauce samples were provided by a local supermarket and simultaneously analyzed by the classical GC–MS method and the proposed method. After spiking with different concentrations of 3-MCPD, the samples were ultrasonically vibrated for 10 min and centrifuged at 10000 rpm for 5 min to remove sediment of samples. The resulting solution was extracted with 6 mL of dichloromethane three times for 10 min each. After drying under a nitrogen flow at room temperature, the residue was dissolved in 1 mL of ethanol/0.01 M PBS buffer (pH = 7.0, 1/1, v/v). The extraction solution was slowly passed through the MIPs/CDs grafted paper at 0.1 mL min^{-1}, using negative pressure and heat (50 °C). The paper was washed with 2 mL water to remove the sample matrix and placed in a 96-well plate for fluorescence detections. There was no need to elute 3-MCPD from the MIP composites and this improved sensitivity.

3. Results and discussion

3.1. Preparation and characterization of MIPs/CDs grafted paper

Filter paper is a base material that provides numerous hydroxyl groups and a 3-dimensional support for the preparation of multifunction polymers. We activated OH groups by incubation in H_2O_2 and CDs with amino groups were prepared by a hydrothermal method for use a fluorescence probe. The average of CDs was approximately 4.7 nm with a positive zeta potential (18.9 mV), indicating the presence of positively charged groups (Fig. S1, Supplementary material). The CDs were introduced into the filter paper using negative pressure and heat, and they attached via electrostatic interactions. A similar procedure was used to modify isopropenyl groups on the CDs-paper, utilizing the amino groups (CDs) and carboxylgroups (MAA). A simple and easy free radical polymerization enabled MIPs/CDs grafted paper using 3-MCPD as a template and MAA as a functional monomer. MAA played an

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