Sensors and Actuators B 223 (2016) 1–8

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A visible colorimetric sensor based on nanoporous polypropylene fiber membranes for the determination of trihalomethanes in treated drinking water

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ARTICLE INFO

Article history:
Received 6 May 2015
Received in revised form 31 August 2015
Accepted 1 September 2015
Available online 10 September 2015

Keywords:
Syndiotactic polypropylene
Nanoporous fiber membrane
Electrospinning
Halogentaed organic compounds
Trihalomethane
Visible colorimetric sensor

ABSTRACT

Water is an integral part of our society, and it is of the utmost importance that this water is clean and safe for potable use. Drinking water sources can become contaminated with halogenated organic compounds (HOCs) via improper disposal of refrigeration or air conditioning units, industrial usage, and even through the disinfection of our drinking water (chlorination). One class of these HOCs regulated by the U.S. Environmental Protection Agency (USEPA) is trihalomethanes (THMs). THMs have been found to cause adverse health effects and can even be carcinogenic, they are limited to 80 ppb in treated water by the USEPA. Currently THM concentrations are detected in treated water using expensive analytical equipment, which have high sensitivity, but lack any portability or ease-of-use. Here we show a syndiotactic polypropylene (sPP) nanoporous electrospun fiber membrane capable of visible colorimetric detection of trihalomethanes (THMs) at environmentally relevant levels (ppb-scale), without a separate preconcentration step. The developed detection method includes a two-fold preconcentration technique coupled with a colorimetric detection reaction, integrated into a single sensor device. Here, the utilization of the colorimetric Fujiwara reaction serves as the detection reaction. This long-studied reaction has a response that is normally limited to a beaker scale visible detection range on the order of 80 ppm THMs, when a separate preconcentration step is not present. The two-fold integrated preconcentration technique consists of a thermodynamic method based on the utilization of the THM: water equilibrium in the vapor phase of the system *as well as* a physical method using a sPP nanoporous membrane capable of concentrating THMs in a contaminated aqueous sample. The developed device has successfully lowered the portable single-step visible THM detection concentration by an order of magnitude (80 ppm → 80 ppb). This sensor was also successfully applied for the determination of the total THM (t-THM) concentration in spiked and actual treated water samples, and these results correlated well with the GC/MS results of the corresponding sample, showing its real world applicability.

1. Introduction

Contamination of drinking water is a serious concern throughout the third and developed world, and can lead to a number of long term problems. Drinking water sources can easily become contaminated with halogenated organic compounds (HOCs) via improper disposal of refrigeration or air conditioning units, industrial usage, and even through the disinfection of our drinking water (chlorination), resulting in the formation of disinfection byproducts (DBPs). DBPs are formed when chlorinated disinfectants applied at drinking water treatment plants react with dissolved organic matter resulting in the formation of known and suspected carcinogens [1]. *Gem.*-polyhalogens such as trihalomethanes (THMs), a common class of DBPs, are regulated and monitored by the U.S. Environmental Protection Agency (USEPA), which has set the maximum contaminant limit (MCL) of four THMs (i.e.—chloroform, bromoform, bromodichloromethane, and dibromochloromethane) to a sum total concentration of the four species to be 80 ppb in treated water [1]. HOCs, such as THMs and other contaminants found in water, are known to cause adverse health effects, damaging the liver, kidneys, and central nervous system

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http://dx.doi.org/10.1016/j.snb.2015.09.004
0925-4005/

(CNS), as well as being suspected carcinogens [2] and being environmentally harmful [3]. The environmental flux of chloroform alone can total over 660 ± 220 Gg/year (±1σ) [4]. A novel method capable of rapidly monitoring the potential t-THM concentration of source and finished drinking water could help mitigate potential health concerns as well as improve the quality of water being delivered to the homes of consumers. A number of detection methods to determine the toxicity of water using a portable device have been developed [5–7]; however, none of these portable devices are able to detect THMs.

Here, a newly devised detection method utilizes an electrospun syndiotactic polypropylene (sPP) fiber membrane. Through the use of a functionalized, nanoporous membrane, THMs simultaneously undergo a two-fold preconcentration step simultaneously coupled with visible colorimetric detection, integrated into a single sensor device. Hydrophobic polymer membranes have previously been used for organic–inorganic separations [8,9]. Electrospun sPP, in particular, has shown superior membrane functionality and hydrophobicity [10,11]. This electrospun membrane is hypothesized to enhance the selectivity of the organic analytes allowed through the membrane, while reducing the water molecules which are detrimental to the Fujiwara Reaction—entering the Fujiwara reactants. Electrospinning is a popular fiber fabrication technique that has gained much interest due to great control over the fibers produced [12–17]. This technique can be used to produce continuous fibers of polymers and ceramics from nanometer to micrometer scale widths. In this process, a solution or melt being extruded out of a syringe is charged by a high voltage electric field, causing the formation of a Taylor cone – due to Coulombic repulsion and the liquid surface tension being overcome – from which a continuous stream of charged polymer is ejected [18]. Due to the electrically-driven polymer jet instability, solidification and elongation occur, leading to the formation of micro- or nanofibers on a grounded collector. The morphology of these fibers can further be controlled via adjusting the electrospinning parameters, such as solution concentration, solvent, flowrate, applied voltage, syringe-collector distance and collector type [19,20]. The accumulation of fibers will occur after electrospinning for an extended time, leading to robust, easily fabricated, reproducible, and extremely high-surface area nanoporous fiber membranes.

In this work, a nanoporous, electrospun membrane is functionalized for the preconcentration *and* detection of THMs at or below the MCL set by the USEPA. Using differences in thermodynamic properties between the HOCs and water, one may show that the concentration of THMs in the vapor phase (head-space) of a vapor–water system is much higher than in the aqueous phase, assuming the temperature of the system is kept below the boiling point of water. In addition, manipulating the temperature of the system will reduce the number of water molecules and increase the ratio of THMs to water molecules in the headspace.

Once in the vapor phase, the THMs are further preconcentrated using a functionalized sPP membrane capable of simultaneously concentrating and detecting halogenated species in a contaminated aqueous sample. The membrane reduces the amount of water vapor diffusing through the membrane, as a function of temperature, allowing the THMs to flow through and react with the colorimetric detection chemistry—functionalized on top of the membrane.

The detection chemistry utilizes the Fujiwara reaction [21], first discovered in 1916, has been employed in a number of schemes to detect halogenated compounds in such media as blood [22], bodily tissues [23], air [24], and water [25]. Through the use of this colorimetric method, HOCs can be detected at concentrations of approximately 100 ppm. However, the beaker-scale Fujiwara reaction cannot detect at the parts per billion (ppb) range – as needed to meet USEPA regulations – without first being preconcentrated [6,21,26]. HOCs can be detected colorimetrically using the Fujiwara reaction through conjugation with pyridine in the presence of a base. The detection can be seen when the heated reactants form an intermediate that changes the solution from clear to a purple, red, pink, or yellow color, upon addition of HOCs. This is the only reaction known to detect THMs spectrophotometrically in the visible spectrum [26]. This is accomplished by the formation of an intermediate chromophore, at a high pH, that emits a red/pink color when visible light is absorbed [25,27]. The original pyridine/aqueous sodium hydroxide/THM reaction has been modified throughout the years in a number of ways to tailor it to specific chemistries and increase the sensitivity, including experimenting with one [26,28] and two [28] phase systems, a variety of basic compounds [26], pyridine derivatives [26], solvents [24], and various compound ratios [29]. This has led to the Fujiwara reaction being a highly customizable reaction, suiting the needs of many various applications. One drawback of the Fujiwara reaction is its accelerated intermediate decomposition in the presence of water [24,30], causing no color change to be seen [26], and has proven problematic in testing actual potable water samples. One solution to this problem would be a simultaneous two-fold preconcentration system to isolate/concentrate THMs from the water, thereby increasing the sensitivity of the detection method—as described.

The overall schematic of the sensor can be seen in Fig. 1a. Initially, the water sample contains THMs in the solution (represented as black dots). After heating the system to a desired temperature (between 60 °C and 90 °C), the THMs evaporate and become highly concentrated in the headspace above the test solution (represented as more concentrated black dots in headspace). The THM molecules then diffuse through the functionalized membrane and react to form a red/pink complex via the Fujiwara reaction (Fig. 1b). In this work, the electrospun membrane and colorimetric sensor are investigated and optimized. The colorimetric sensor is found to exhibit high analytical performance with excellent selectivity. This would be the first colorimetric sensor of its

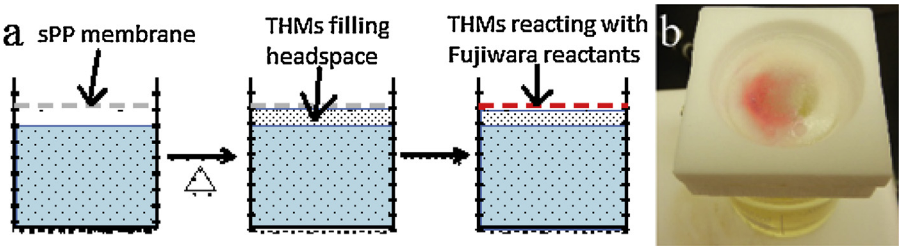

Fig. 1. (a) Conceptual illustration of a colorimetric membrane in a proof-of-concept device used for sensing THMs in a contaminated water sample. Initially, the water sample contains THMs in the solution (represented as black dots). After heating the system to a desired temperature, the THMs evaporate and become highly concentrated in the headspace above the test solution. The THM molecules then diffuse through the sPP membrane and react with the Fujiwara reactants to form a red/pink complex. (b) Photograph of the laboratory testing setup, where the colorimetric response can be seen with the naked eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)