



Potentiometric detection of AFFFs based on MIP

Cheng Fang*, Zuliang Chen, Mallavarapu Megharaj, Ravendra Naidu*

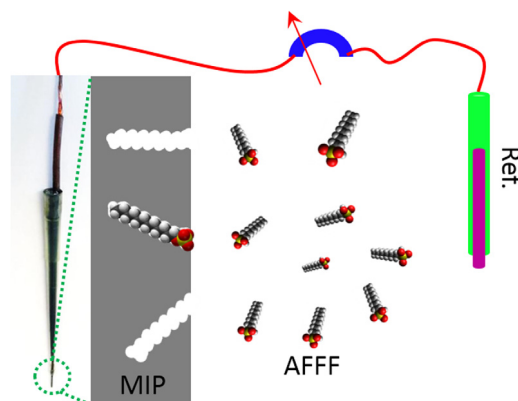
Global Centre for Environmental Remediation (GCER), University of Newcastle, Callaghan NSW 2308, Australia¹

Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRCCARE), University of Newcastle, Callaghan NSW 2308, Australia

HIGHLIGHTS

- Potentiometric detection of AFFFs using molecular imprinted polymer on pencil lead.
- Introduction of methylene blue (MB) into polymer matrix due to ion-pairs of AFFF-MB.
- Specific detection of PFOA, PFOS and 6:2FTS in a range of 10 μM –10 mM.
- Discussion on the interferences and negative response.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 September 2015

Received in revised form 16 December 2015

Accepted 16 December 2015

Available online 19 December 2015

Keywords:

AFFF
MIP
Polypyrrole
PFOA
PFOS
6:2FTS

ABSTRACT

Potentiometric detection of fluoro-surfactants formulated in aqueous film-forming foams (AFFFs) is demonstrated using molecular imprinted polymer (MIP) formed on pencil lead. We introduce an ingredient of methylene blue (MB) into the polymer matrix of polypyrrole (PPY) to increase the selectivity due to the formation of ion-pairs of AFFF-MB. Fluoro-surfactants including perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (6:2FTS) are specifically detected in the range of 10 μM –10 mM with the limit-of-detection (LOD) down to ~ 100 nM (or ~ 41 ppb for PFOA). The interference caused by anionic surfactants of sodium dodecyl sulphate (SDS) and dodecylbenzenesulfonic acid sodium (SDBS) is tested and the negative response is discussed.

© 2016 Published by Elsevier B.V.

* Corresponding authors. Tel.: +61 2 4913 8705; fax: +61 2 4913 8705.

E-mail addresses: Cheng.fang@newcastle.edu.au (C. Fang), Ravi.naidu@unisa.edu.au (R. Naidu).

¹ Formerly Centre for Environmental Risk Assessment and Remediation (CERAR), Mawson Lakes, University of South Australia, SA, 5095, Australia.

1. Introduction

It is estimated that over 10 million tons of toxic chemicals are released into environment every year as a consequence of anthropogenic activities including industry, agriculture, mining, construction, building etc. (Naidu, 2013). In these activities, aqueous film-forming foams (AFFFs), usually formulated with fluoro-surfactants and used in low expansion foam (20:1), have been employed to extinguish fuel or hydrocarbon fires (Kärman et al., 2011). Unfortunately, perfluorinated compounds (PFCs) including AFFFs have been detected worldwide because they contain fluoride-carbon skeletons that are difficult to degrade in the natural environment. Their continued accumulation has resulted in toxicity to people and the environment (Boulanger et al., 2004; Buck et al., 2011). Clearly, a suitable detection method is needed to monitor them in the environment.

Much effort has been devoted to detect AFFFs in the environment. The most common method is based on extraction from water samples using an organic phase, such as chloroform in MBAS (methylene blue active substrates) (George and White, 1999). The disadvantage of this method is the lack of specific detection and concerns regarding the toxicity of chloroform. Other methods include HPLC (Fang et al., 2015), capillary electrophoresis (Masár et al., 2005) etc. Overall these technologies offer a good range of detection, but suffer from severe limitations. They are expensive and generally not portable for test in field.

For portable sensor development, electrochemical detection (mainly including potentiometry and amperometry) exhibits advantages including easy reading and operation of electrical signals, capacity for integration and multiplex detection, and versatile modification of electrode surface for selectivity and sensitivity, etc. (Gerlache et al., 1996). In the latter case, molecular imprinted polymer (MIP) offers an artificial and effective approach to achieve selectivity and molecular recognition when a polymer is doped by the target moiety as template during the polymerisation process (Cai et al., 2010; Merkoçi and Alegret, 2002). Upon removal of the moiety template, the polymer matrix retains its template-shaped complementary nano-cavities. Those cavities in the polymer matrix feature the selectivity to capture and rebind the target moieties, akin to a “lock–key interaction” (Shen et al., 2012; Malitesta et al., 2012; Michalska et al., 2004). Due to the stable chemical structure of fluoro-surfactants it cannot be easily oxidised or reduced under natural conditions to get amperometric response (Zhuo et al., 2012; Carter and Farrell, 2008). Therefore, the MIP technique provides a convenient approach to specifically detect AFFFs' fluoro-surfactants.

In this study we demonstrate the potentiometric detection of fluoro-surfactants via a MIP technique. Polypyrrole (PPY) was electrodeposited onto an electrode surface as polymer matrix and electron–ion transducer (Cai et al., 2010; Merkoçi and Alegret, 2002; Tran. T et al., 2014). This polymer was *in situ* doped or coined by anions of fluoro-surfactants as imprints. Fluoro-surfactants included perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS) and 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (6:2FTS). Other anionic surfactants including sodium dodecyl sulphate (SDS) and dodecylbenzenesulfonic acid sodium (SDBS) (a linear alkylbenzene sulfonate (LAS)) were chosen for interference test. We optimised the MIP formation conditions, supporting electrolytes, and electrode conditioning concentration etc. In an effort to reduce cost, we selected pencil leads as the electrode material (Bendikov and Harmon, 2005), which differed from other materials such as porous carbon (Chen et al., 2013), or TiO₂ nanotube (Tran. T et al., 2014).

2. Material and methods

2.1. Chemicals and materials

All chemicals including pyrrole (PY), methylene blue (MB), PFOA, PFOS, 6:2FTS, SDS and SDBS were purchased from Sigma–Aldrich (Australia) and were used as supplied. Because PPY film is sensitive to pH, all the solutions have been adjusted to pH 5.1–5.6.

2.2. Pencil lead electrode

Commercial pencil lead (0.7 B, diameter of ~0.5 mm, Faber-Castell) was purchased and sealed with a plastic tip using epoxy cement. Electrical connection between the pencil lead and copper wire was achieved utilising active carbon powder. The pencil lead had an exposed length of ~5 mm as the working area (~8 mm²). The electrode was washed with acetone, ethanol and then dipped into Piranha solution (2:1 H₂SO₄ : H₂O₂, v/v) (note that this solution reacts vigorously with organic compounds) to remove any possible organic contaminants. The electrode was finally washed with Milli-Q water.

2.3. Fabrication of PFOA-MIP

An electrochemical analyser (BAS100B) was employed for *in situ* electropolymerisation of the MIP film, which was conducted in an aqueous solution containing 0.2 M PY and 0.01 M PFOA via cyclic voltammetry (CV) in the potential range of 0–3.0 V at a scanning rate of 100 mV/s (Lakard et al., 2007). MB was introduced into this solution to increase the sensitivity of MIP sensor, as discussed in the following. Fresh solution was used within 5 min after preparation.

Download English Version:

<https://daneshyari.com/en/article/4428194>

Download Persian Version:

<https://daneshyari.com/article/4428194>

[Daneshyari.com](https://daneshyari.com)