Potentiometric detection of AFFFs based on MIP

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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 μ M–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 salt (SDBS) is tested and the negative response is discussed.

▪ 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 (Kärrman 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, Megharaj, and Naidu 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 oxidized or reduced under natural conditions and its specific detection remains a challenge (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) ammonium salt, perfluorooctanesulfonic acid (PFOS) potassium salt and 1H, 1H, 2H, 2H-perfluorooctanesulfonic acid (6:2FTS). Other anionic surfactants including sodium dodecyl sulphate (SDS) and dodecylbenzenesulfonic acid sodium salt (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.

The electrochemical cell included the pencil lead working electrode, an Ag/AgCl reference electrode (3 M KCl) and a platinum wire counter electrode. Following modification by electropolymerisation, all the electrodes were conditioned in 0.01 M or 0.1 mM PFOA overnight in the dark.

A similar approach was pursued to prepare other MIP matrix using other target moieties, such as PFOS-MIP, SDS-MIP, etc.

2.4 Surface characterization.

Scanning electron microscopy (SEM) (Quanta 450, FEI Co., USA) served to characterise the surface topography of the MIP film. Raman spectra were collected in air using a Witec confocal Raman microscope (Alpha 300RS, Germany) equipped with a 532 nm laser diode (< 60 mW). A CCD detector (cooled to –60°C) was used to collect Stokes Raman signals under a 40× objective (Nikon) at room temperature over the 0–3000 cm^{–1} wavenumber range with an integration time of 5 s for measurements of single spectra.

2.5 Potentiometric testing.

All the potential differences between the modified pencil lead electrode and a mini-leakless reference electrode (Harvard) were recorded with a pH-voltmeter (Eutech Instruments, PC 510). The reading usually reached a stable value within 2 min in a stirred solution and was then recorded within another 1 min whilst the solution was kept static, just like the pH measurement. The potentiometric measurement was carried out at room temperature ($\sim 24^{\circ}\text{C}$).

All the testing sample solutions including PFOA, PFOS, SDS, etc. were dispersed at different concentrations into aqueous solutions of 1×PBS or 0.1 M NH_4Cl , K_2SO_4 , etc. as supporting electrolytes. The potential selectivity coefficient (K^{pot}) was measured at the same concentration of interfering ions using the same supporting electrolyte. All raw data are presented without offset in this article. The variation on the initial potential reading can be calibrated using a standard solution, as conducted for pH measurement.

▪ 3. Results and discussion

3.1 Polymerisation and characterisation

The CVs in Figure 1 present the *in situ* electropolymerisation (Lakard et al. 2007) in the solution of 0.01 M PFOA + 0.2 M Py in the absence (a) and in the presence (b) of an additive of 0.01 mM MB. In the first scanning segment in Figure 1 (a), the oxidising current appeared at ~ 0.6 V and thereafter (ramping-up curve), suggesting the electropolymerisation on the electrode surface. Subsequently, a quasi-resistance (almost a linear response, marked with a red line, between the working electrode and the reference electrode) was assigned to the solution resistance (Fang, Ellis, and Voelcker 2011) and the over-oxidised PPY film (Allen J. Bard and Faulkner 2001; Fang, Ellis, and Voelcker 2011; Komaba et al. 1997; Lakard et al. 2007). Taking this red line as a baseline, the current shifted from the line and peaked at ~ 1.9 V, originating from the diffusion-controlling process of PY from the bulk solution to the electrode surface (Allen J. Bard and Faulkner 2001). Similar CVs appeared in the subsequent potential scanning segments with increased slopes, suggesting decreased electrical resistance between the working electrode and the reference electrode. The possible reason is either the initialised polymerisation was self-accelerated or a modification occurred on the electrode surface due to the formation of the PPY film.

Figure 1(b) depicts the CVs in the presence of MB that was introduced to increase the affinity and selectivity of the MIP matrix for AFFFs (George and White 1999). Compared to Figure 1 (a), the current density decreased and the oxidation peak had shifted positively (~ 2.1 V vs. ~ 1.9 V) (Allen J. Bard and Faulkner 2001). The reverse scanning segment was not a linear response (between current and potential) and peaked at ~ 2.1 V too, suggesting the contribution from MB. The detailed explanation is not clear but it may be due to the interaction between MB and PFOA-PPY matrix (George and White 1999), such as the stabilised radicals by MB for the electropolymerisation (Han et al. 2005). Another possible reason is the simultaneous electropolymerisation of MB on the electrode surface (Damos, Luz, and Kubota 2005).

The SEM image in Figure 2 (a) represents an overarching view of the polymer-covered pencil lead tip. Figure 2 (b) shows the zoomed-in image and a uniform polymer film is observed. Note part of the polymer has lifted off to expose the pencil lead at the bottom. The polymer thickness was estimated to be ~ 600 nm, which agrees well with the literature considering the different concentrations of PY (0.2 M vs. 0.1 M) (Lakard et al. 2007). Due to the limited molecular size of PFOA (~ 0.5 nm $\times$ ~ 0.8 nm (Macdonald, Cole, and Koutsos 2004; Fang et al. 2008; Sperati and Starkweather 1961)), there is no obvious difference before and after the removal of imprinted moieties under the SEM image.

EDX and Raman spectra were collected to analyse the components in the polymer. In Figure 2 (c), the EDX spectrum reveals evidence for the existence of elements C/N/O/F, etc. C/N/O are assigned to the PPY film and PFOA. F is contributed by PFOA alone, suggesting its doping into the PPY matrix.

Figure 2 (d) highlights the Raman spectrum of the as-made film matrix (polymer). The typical peaks of PPY appeared at 935 cm^{-1} , 987 cm^{-1} , 1052 cm^{-1} , 1330 cm^{-1} and 1581 cm^{-1} (arrowed), confirming the formation of the PPY film (Chen et al. 2003; Han et al. 2005). In the meantime, the peaks at 454 cm^{-1} , 510 cm^{-1} , 602 cm^{-1} , 679 cm^{-1} , 782 cm^{-1} , 1401 cm^{-1} and 1636 cm^{-1} are assigned to the MB dopant when compared with its standard spectrum (MB), suggesting the PPY film has also been doped with MB (dashed lines). Due to the low Raman activity or molecular cross-section (Haynes, McFarland, and Duyne 2005; Stiles et al. 2008), PFOA's Raman scattering is not significant from the polymer matrix.

We therefore produced a PFOA/MB/PPY MIP (PFOA-MIP), in which PFOA was employed as the template whilst MB served to increase the AFFF's affinity and MIP's selectivity.

3.2 Optimisation of PFOA-MIP

The thickness of MIP plays a critical role in the electrode's potentiometric response (Cai et al. 2010; Merkoçi and Alegret 2002; Lakard et al. 2007; Tran.T et al. 2014). Figure 3 (a) shows that 3 cycles of CVs provided higher slope (compared to 5 cycles) and without saturation response (compared to 1 cycle). We thus selected 3 CVs to prepare the MIP film.

MB has been widely used to detect anionic surfactants because the cationic MB can form ion-pairs with anionic surfactants, which are not soluble in aqueous solution (George and White 1999). MB was thus introduced into the PPY MIP film in order to increase the affinity to AFFFs. Figure 3 (b) indicates the influence of the MB. Basically 10 μ M MB in the electropolymerisation solution gave the best response (i.e. the highest slope). We thus fixed this concentration for the MIP film preparation.

After the film preparation and before the potentiometric test, the PFOA-MIP should be activated by dipping it into a PFOA solution for conditioning. During the conditioning process, a diffusion equilibrium will be established between the MIP and the solution by removing a part of imprinted PFOA molecules from the membrane. The conditioning period of the PFOA-MIP was checked and presented in Figure 3 (c) (Lai et al. 2007; Lai et al. 2009). Usually 1 day's conditioning in 10 mM PFOA results in the best response. The responding slope decreased when conditioning time was prolonged which is likely due to the limited stability of PPY in the conditioning solution (Lakard et al. 2007). In the subsequent experiments, 1 day's conditioning was carried out before the potentiometric tests. Thus, the reproducibility of the sensor is also justified from the time dependence.

During the potentiometric test, the supporting electrolyte controls the pH value and the conductivity of the sample solution. Furthermore, the anion from the supporting electrolyte may interfere with the MIP's measurement for anionic PFOA (Allen J. Bard and Faulkner 2001). In Figure 4 (a), the solution with K₂SO₄ as supporting electrolyte featured the best performance (a wider linear response with a higher slope). Figure 4 (b) shows that a lower limit of detection (LOD, ~0.1 µM vs. ~1 µM) was achieved in a lower concentration of supporting electrolyte (0.1 mM vs. 10 mM K₂SO₄). However, the low concentration of supporting electrolyte (<10 mM) might lead to a conductivity problem in the sample solution. We therefore selected 10 mM K₂SO₄ as the supporting electrolyte for subsequent tests.

3.3 Selectivity

Following the preparation of the PFOA-MIP film, when a template moiety (e.g. PFOA) is removed from the polymer matrix by conditioning, a cavity is left behind. The selectivity of the MIP film mainly originates from the matching of the space size, the charge density/environment and the physical/chemical interaction between the cavity and the target moiety (Merkoçi and Alegret 2002; Tran.T et al. 2014), which can be characterised with potential selectivity coefficient ($K^{pot}_{i,j}$) according to equation (1).

$$E = E^0 + (RT/z_i F) \ln(a_i + \sum K^{pot}_{i,j} a_j^{(z_i/z_j)}) \quad (1)$$

where E is the measured potential, E^0 a constant linked to electrode materials, polymer components, solution components and R , T and F are the gas constant, absolute temperature and Faraday constant, respectively. a_i is the target ion's activity whilst z_i is its charge number. a_j and

z_j is the interfering ion's activity and charge number. We fixed the concentration of the interference ion at 1.0 mM to estimate the value of $K^{pot}_{i,j}$ and the results are listed in Table 1. Note that the values depended on the measurement approach (Shen et al. 2012; Malitesta et al. 2012; Michalska et al. 2004).

In Table 1, of the inorganic anions, $K^{pot}_{i,j}$ for SO_4^{2-} is the smallest, suggesting this ion made the least interference and is in well agreement that the results shown in Figure 4 (a). Consequently we selected K_2SO_4 as the supporting electrolyte.

PFOS, 6:2FTS, SDBS, SDS and citrate behaved with a similar molecular structure with PFOA so that their corresponding $K^{pot}_{i,j}$ differ from that of inorganic anions (Malitesta et al. 2012). As mentioned above, the moiety molecular size plays a critical role in selectivity (Shen et al. 2012; Malitesta et al. 2012; Michalska et al. 2004) and Figure 5 (a) shows their molecular structures. With respect to the carbon chain (the hydrophobic tail), their molecular length is in the following order: $\text{PFOA} < 6:2\text{FTS} \sim \text{PFOS} < \text{SDS} < \text{SDBS}$ (Macdonald, Cole, and Koutsos 2004; Fang et al. 2008; Sperati and Starkweather 1961). Here 6:2FTS is similar to PFOS except four F atoms on the carbon chain have been replaced by H, while SDBS is similar to SDS except for an additional benzyl group. For this reason their molecular structures are not shown here.

Figure 5 (b) further assesses the selectivity of the PFOA-MIP film. Note that 6:2FTS exhibits a limited solubility in aqueous solution whilst SDS easily forms micelles ($> 3 \text{ mM}$ (Tang et al. 2009)) so that their highest concentrations for testing were 1 mM. The similar potential reading at the low concentration implies the good reproducibility of the sensor.

In Figure 5 (b), PFOS and 6:2FTS exhibit similar potentiometric responses with PFOA except for the smaller slope (5 mV vs. 12 mV). As said, they share similar molecular structure. However,

because PFOS/6:2FTS behave a larger size of hydrophilic tail of the sulfonic group rather than the carboxyl group in PFOA, they cannot freely enter the cavity coined by PFOA in the PPY polymer matrix. As a consequence, PFOS/6:2FTS exhibited a lower slope.

Surprisingly, SDS exhibits a negative response (concentration increased from 10 μM onwards, potential decreased). Perhaps the SDS, a commonly used detergent, washed off the dopant of PFOA in the outer layer of MIP. A similar phenomenon was observed for SDBS (another detergent) at a high concentration (1 mM). These negative response offers promise to justify their interference. However, unlike SDS, SDBS exhibits a response similar to PFOA in the 0.1 μM – 1 mM concentration range. The detailed reason for the difference between SDS and SDBS is unknown but most likely originates from the additional benzyl group in SDBS, and their interaction with the MIP matrix.

In an effort to push down the LOD of the PFOA-MIP, the concentration of PFOA in the conditioning solution was optimised. In Figure 5 (c), a smaller conditioning concentration leads to a lower LOD (Lai et al. 2007; Lai et al. 2009). When conditioned in a higher concentration solution, PFOA's amount (dopant concentration) in the MIP film was larger. As a consequence, the leakage of PFOA from the MIP film into the testing solution will be serious (Malitesta et al. 2012). However, too low a concentration for conditioning will bring about poor selectivity. Under optimised conditions, the response slope is in the range of 9-12 mV (Figures 5 (b, c)) with a LOD of 0.1 μM (~ 41 ppb) PFOA.

Admittedly, there was no Nernst response (with a slope of ~ 59 mV for $E/\log[PFOA]$) (Lai et al. 2007; Bendikov and Harmon 2005), which is similar to other organic moieties such as urea (Malitesta et al. 2012). The explanation may be linked to the electromotive efficiency of PFOA,

and its failure to form an ideal Donnan diffusion layer in the PPY matrix (Allen J. Bard and Faulkner 2001; Bendikov and Harmon 2005).

3.4 PFOS-MIP and SDS-MIP

We prepared PFOS-MIP and SDS-MIP via a similar approach by replacing PFOA with PFOS or SDS. Their potentiometric responses are presented in Figure 6. For PFOS-MIP in Figure 6 (a), SDS again shows a negative response. PFOA and PFOS have similar molecular structures (Figure 5 (a)), so that they exhibit a similar response on a PFOS-MIP electrode (as well as 6:2FTS, not shown here). The difference is the negative or saturation response of PFOA at a high concentration (10 mM) (Wang, Liu, and Shih 2012).

Interestingly, in Figure 6 (b), SDS-MIP indicated no discernible response for SDS, PFOS or PFOA (and 6:2FTS, SDBS as well, not shown here) with increased slope (29 mV vs. 12 mV). The dopant of SDS moiety has a longer carbon chain than others (~1.3 nm vs. 0.8-0.9 nm)(Macdonald, Cole, and Koutsos 2004; Fang et al. 2008; Sperati and Starkweather 1961). In the polymer matrix, it produces a cavity that is able to embed not only SDS but also PFOA and PFOS due to them being smaller than SDS. As a consequence, almost no discernible response was observed.

4. Conclusions

We successfully detected anionic surfactants of PFOA, PFOS, 6:2FTS, SDS and SDBS based on the MIP technique. Sensitivity was improved from 6 mV per decade of concentration to 29 mV

by introducing additive into the MIP, changing the coining moieties in the MIP matrix, etc. Due to the small cavity coined by PFOA, PFOA-MIP show a high selectivity for PFOA over others. SDS-MIP revealed no discernible response for all the five targets due to the large cavity coined by SDS in the PPY matrix. The specific detection of anionic surfactants including AFFFs was therefore achieved by combining PFOA-MIP, PFOS-MIP and SDS-MIP modified electrodes. Thus, the potentiometric detection of AFFFs has great potential for its application as a pre-screening tool at contaminated sites.

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Notes

The authors declare no competing financial interest.

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Table 1. K^{pot}_{ij} of the PFOA-MIP electrode

Ion	PO_4^{3-}	SO_4^{2-}	Cl^-	HCO_3^-	PFOS	6:2FTS	SDBS	SDS	citrate
K^{pot}_{ij}	1×10^{-2}	1×10^{-4}	1×10^{-3}	1×10^{-3}	0.5	0.5	1	1×10^{-3}	0.5

Figure 1. CVs of the electropolymerisation of MIP in a solution of 0.01 M PFOA + 0.2 M PY without (a) or with (b) 0.01 mM MB. The scanning rate was 100 mV/s. The arrows indicate the scanning direction and the CV's shifting direction. For clarification the straight lines are presented.

Figure 2. SEM images (a, b), EDX (c) and Raman spectra (d) of the polymer formed in Figure 1 (b). Inset in (a) shows the photographed image of the MIP electrode whilst the standard Raman spectrum of MB (red) is presented in (d) for comparison.

Figure 3. Potentiometric response of the PFOA-MIP depending on the thickness of the MIP film (the cycle number of CV) (a), the concentration of MB during the electropolymerisation (b) and conditioning time in 10 mM PFOA after electropolymerisation (c). The slopes of the response curves ($E/\log[\text{PFOA}]$) are presented in (b) and (c) for clarification. Another concentration unit of ppb was provided for comparison. All the PFOA testing solutions were prepared in $1 \times \text{PBS}$.

Figure 4. Potentiometric response of the PFOA-MIP depending on the supporting electrolyte, the type (a) and the concentration (b).

Figure 5. Schematic drawing of anions (a) and the potentiometric response of the PFOA-MIP depending on the concentrations of different anions (b) and the concentration of PFOA conditioning solution before the test. All the supporting electrolytes were 10 mM K_2SO_4 for the potentiometric test.

Figure 6. Potentiometric response of PFOS-MIP (a) and SDS-MIP (b) depending on the concentration of different anions (indicated). Other conditions were kept the same as those in Figure 5 (b).