Influence of pH, ionic strength and natural organic matter concentration on a MIP-Fluorescent sensor for the quantification of DNT in water

Jingjing Dai, Maria Fidalgo de Cortalezzi *

Department of Civil and Environmental Engineering, University of Missouri, E2509 Lafferre Hall, Columbia, MO, 65211, USA

**ARTICLE INFO**

Keywords:
Environmental Science
Nanotechnology
Civil Engineering
Chemical engineering
Molecular imprinted polymers
Sensor
Dinitrotoluene
Natural water
Quenching

**ABSTRACT**

The effect of sample water chemistry on a carbon dot labeled molecularly imprinted polymer (AC-MIP) sensor for the detection of 2,4-dinitrotoluene (DNT) was investigated. Hydrogel MIP films were fabricated and tested in DNT solutions in various matrices, representative of natural water conditions, to assess applicability of the sensors to real water samples. The effect of pH, natural organic matter (NOM), ionic strength and cation type on the swelling of the hydrogel and fluorescence quenching was investigated. An increase in ionic strength from 1 mM to 100 mM produced a quenching amount of MIPs decreased of about 19% and 30% with NaCl and CaCl₂ respectively. In the range of pH tested, from 4 to 9, quenching was higher at basic environment for both MIPs and non-imprinted polymers (NIPs) due to increased hydrogel swelling. NOM contributed to the background quenching, but the effect could be addressed by an adjusted calibration equation. In both lake and tap water, DNT concentrations read by the sensors were close to the values measured by HPLC, within 72%–105% of true values. The AC-MIP films fabricated in this work are promising materials for the detection of water contamination in the field and the quantitative analysis of DNT concentration.

1. Introduction

Molecular Imprinted Polymer (MIP) based sensors had been successfully applied to the quantitative detection of specific contaminants. In order to obtain a useful sensor device, different transducer mechanisms have been combined with MIPs, based on optical, chemical or electrochemical properties. Among them, optical MIP-based molecular recognition sensors have been developed due to the covalent linkage of MIPs to optical transducers. The MIP binding efficiency, recognition processes and selectivity have been intensively studied by optical means due to the general high sensitivity and simplicity of the utilization of optical techniques [1]. The sensing properties can also be characterized by parameters such as linearity, limit of detection, sensitivity, selectivity, reproducibility, accuracy, robustness, response time and lifetime [2]. However, the effects of sample characteristics commonly encountered in natural waters (i.e. variations of pH, ionic strength, natural organic matter content) on the sensing performance of optical MIPs are not fully understood, which is a limitation for environmental applications. MIPs have been reported which respond to stimuli such as change in temperature [3], pH [4], and ionic strength [5]. Interferences, either with the imprinted molecule or transducer mechanism, are another concern because they can affect the recognition ability and sensing response of MIPs. Potential interferences in natural waters are dissolved organic matter, dissolved salts, inorganic colloidal particles, and microorganisms. Given the fact that most efforts have been devoted to the synthesis of MIPs as solid phase extraction (SPE) media, research in this area has been directed mostly towards the conditioning, washing and eluting stages of the process rather than the capture and sensing, or the actual mechanisms by which this interference may occur. The potential for MIP-based sensors to be used in-situ is promising if the influences of these parameters are explored and interpreted accurately.

Some researchers have reported the use of MIPs as the SPE sorbent for natural water samples [6, 7], but the direct use of MIPs and MIP-enabled devices as sensors in natural waters has not been fully explored [8, 9], especially regarding the effects of the different parameters of the water chemistry matrix. A conductometric transducer based atrazine sensor was reported for the monitoring of atrazine and structural analogs, both in contaminated and uncontaminated natural waters with a detection limit of 1 ppb [10, 11]. In another study, diphenolic Acid (DPA) and bisphenol A (BPA) were used as dummy template molecules for the capture of tetrabromobisphenol A (TBBPA). With recoveries of TBBPA in tap, river and lake water ranged from 85% to 97% and detection limit as low as 2 ppb [12].

Dinitrotoluene (DNT) is an aromatic explosive that exists as six isomers; the forms 2,4-DNT and 2,6 DNT account for more than 95% of the total concentrations found in contaminated soils and sediments. The limits of detection and quantification for DNT in water samples are 1 ppb and 10 ppb respectively [13].

* Corresponding author.
E-mail address: fidalgom@missouri.edu (M. Fidalgo de Cortalezzi).

https://doi.org/10.1016/j.heliyon.2019.e01922
Received 31 July 2018; Received in revised form 14 May 2019; Accepted 4 June 2019
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explosive trinitrotoluene (TNT) [13, 14]. DNT is also employed in the manufacturing of polyurethanes, dyes, plastics and herbicides [15]. Due to its water solubility (300 ppm at 22 °C) and low vapor pressure (1.47 × 10⁻⁴ mmHg at 25 °C), 2,4-DNT may remain in water for a long time. US EPA has classified DNT as a probable human carcinogen and established a 1-day and 10-day health advisory of 1.0 ppm for 2,4-DNT in drinking water for a 10-kilogram (kg) child, which corresponds to a drinking water equivalent level of 0.04 ppm [15]. DNT is commonly detected in surface water, groundwater and soil at hazardous waste sites related to ammunition facilities or other industries that use it in as part of their process [14].

Fluorescence-based sensors are particularly suited for field use, as they are generally sturdy and easy to measure. In this area, fluorescent nanoparticles are preferable to fluorescent polymers, as they have shown to be brighter and more stable; however, leakage of the nanomaterial into the sample may be a concern if the particles are not strongly bonded to the MIP matrix. We recently reported a novel C-dot fluorescent labeled MIP based sensor for the detection of 2,4-dinitrotoluene (DNT) in water samples in a range from 1 to 15 ppm, with a detection limit of 0.28 ppm; the fluorescent C-dots were covalently bonded to a hydrogel thin film polymer, which provided stability to the sensor even under several consecutive cycles of use and regeneration [16].

Sample components may interfere with the measurement of the analyte in two ways: by interacting or preventing interaction between the target compound and the MIP cavities, or by non-specifically adsorbing on the fluorescent nanoparticles, potentially leading to quenching and over or underestimations of the true concentration of the target. Detection of contaminants in natural waters at environmentally relevant concentrations is particularly challenging, due to the complexity and potential variability of its chemical composition. Although several MIP-based sensors have been reported in laboratory studies of controlled samples, the technology has not yet been successfully translated to realistic samples and environmental conditions. One of the hurdles to overcome is the correct interpretation of the sensor output, as interferences may potentially induce substantial deviations from initial calibration. Errors due to non-specific binding can be minimized if the sample is pretreated, for example by a phase change (aqueous to non-polar) of the analyte before measurement, or corrected if non-imprinted polymers are used alongside MIPs [17]. The objective of this study is the identification of sources and mechanisms of said interferences for a fluorescence-MIP sensor and the assessment of their effects on the sensor response, under environmentally relevant conditions.

We investigated the application of the amino functionalized carbon dot (AC-dot) labeled MIP sensor for the detection and quantification of DNT in natural water conditions. The effects of salinity, pH and dissolved organic matter on the sensor performance were analyzed. Two factors may play important roles: (1) interference with the nonspecific and specific adsorption of DNT onto the MIP, and (2) quenching by solutes other than DNT. Sample ionic strength and pH influence the surface charge and electrostatic interactions between polymer chains, which in turn change the morphological conformation of the film or swelling of the hydrogel. Additionally, acid based groups on the surface of the C-dots are responsible for variations in fluorescence intensity with pH, and dissolved organic matter may adsorb non-specifically to both polymer and nanoparticles. A methodology was established to minimize those effects and/or create an adjusted calibration for determination of DNT concentrations under different background water matrices.

2. Results and discussion

2.1. MIP film characterization

The fabricated MIP films were characterized with respect to key properties that would be altered in complex chemical environments: AC-Dots and polymer surface functional groups, and swelling behavior of the hydrogel. The FTIR spectrum of AC-Dots revealed abundance of amino groups on the surface [16]. The surface basic groups resulted in a positively charged surface due to protonation of amino groups. The amino groups can be further protonated with decreasing pHs [18]. The quenching ability may be hindered when amino groups are well protonated and thus unable to form complexes with quenchers [19].

The degree of swelling of hydrogels at equilibrium depends on the cross-linking and charge densities of the polymer network. Polyacrylic acid can shrink or swell in response to changes in temperature, pH, ionic strength, solvent quality, electronic field, etc. [20]. The swelling ratio (SR) was calculated from the expression (1):
of such dependency showed that AC-dots (0.2 ppm in aqueous suspension) exhibited the highest FL intensity at pH 4, and decreased with increasing pH (Fig. 3). Their FL activities were strong at weakly acidic media (pH 4–6), but weaker at higher pH, especially above 10. This observation is in agreement with previous reports [19], and constitutes a limitation to the application of carbon dots as labeling materials for sensing.

Tests of the effects of pH on the MIP sensor were conducted with initial FL intensities (F₀) measured in DI water. Then, the MIP-sensors were dipped in acidic, neutral, or basic 10 ppm DNT solutions, and rinsed with DI water before measuring the FL intensities (F), again in clean water. Although the sensor initially showed different responses for the three pH levels, those were minimized after the rinsing step was introduced. In the absence of DNT, exposing the MIP films to acid or base solutions, the fluorescence intensity changed accordingly (Fig. 4). However, after the clean water rinse (pH = 6), the effects were less evident and F₀/F much closer to 1 as expected since no DNT molecules were present. This represents a significant advantage over sensing approaches involving the direct addition of C-dots to the water sample or non-covalent bonded fluorescent labels, where the inherent limitation of the pH dependence of the FL of the nanomaterials cannot be overcome.

However, a diminished selectivity of the sensor at acidic pH could not be completely avoided. The recognition capacity (RC) of the MIP is defined as the ratio of specific to non-specific adsorption, i.e. binding to the imprinted molecular cavities versus adsorption to a random area of the polymer surface, and it can be considered a measurement of the selectivity of the sensor. Fig. 5 showed the F₀/F ratios for both MIPs and NIPs, after placed in contact with a 10 ppm DNT solution. RC decreased with increasing pH, as it is assumed that binding to MIPs occurs predominantly at the imprinted sites, while binding to NIPs is purely non-specific. Quenching amounts between 1.3 and 1.6 for the NIPs show the incidence of non-specific adsorption; the observed upward trend can be related to the changes induced by the sample pH to the surface of AC-Dots and the corresponding change in their FL intensity as presented in Fig. 4 after rinse with DI water, which results in an apparent lower quenching (due to increased FL) at acidic pH. F₀/F increased at a faster rate in the case of MIPs, with swollen, charged hydrogels displaying better performance. Results suggest that non-specific adsorption is fairly constant for the pH range considered, but access and binding to the imprinted cavities was favored at higher swelling conditions that resulted in more space for the diffusion of the DNT molecules between the polymer chains.

A deviation of the sample pH from the value of the measuring solution (DI water, pH = 6) would introduce a measurement error, overestimating the imprinted molecular cavities versus adsorption to a random area of the polymer surface, and it can be considered a measurement of the selectivity of the sensor. Fig. 5 showed the F₀/F ratios for both MIPs and NIPs, after placed in contact with a 10 ppm DNT solution. RC decreased with increasing pH, as it is assumed that binding to MIPs occurs predominantly at the imprinted sites, while binding to NIPs is purely non-specific. Quenching amounts between 1.3 and 1.6 for the NIPs show the incidence of non-specific adsorption; the observed upward trend can be related to the changes induced by the sample pH to the surface of AC-Dots and the corresponding change in their FL intensity as presented in Fig. 4 after rinse with DI water, which results in an apparent lower quenching (due to increased FL) at acidic pH. F₀/F increased at a faster rate in the case of MIPs, with swollen, charged hydrogels displaying better performance. Results suggest that non-specific adsorption is fairly constant for the pH range considered, but access and binding to the imprinted cavities was favored at higher swelling conditions that resulted in more space for the diffusion of the DNT molecules between the polymer chains.

A deviation of the sample pH from the value of the measuring solution (DI water, pH = 6) would introduce a measurement error, overestimating
2.3. Effect of ionic strength and salt type

The sensor was applied to the quantification of DNT in solution with variable dissolved salts concentration, resulting in a smaller FL intensity change for both MIP and NIP films (Fig. 6). In this case, the effect of ionic strength (IS) on the FL of AC-Dots suspensions was investigated, as any possible surface effects due to charge screening in a high electrolyte concentration medium cannot be isolated from the effects on the aggregation of the nanoparticles under increased IS. The latter would dominate the FL behavior for AC-Dots in suspension but would be absent in the AC-Dot labeled sensors, making the experiment irrelevant. However, comparison FL intensities of labeled films after equilibration in different ionic strength solutions and subsequent rinsing with DI water did not showed significant differences in emission intensity and thus we focus our analysis on the effects of IS on the rebinding of DNT to the hydrogel.

As expected, NIPs showed consistently less quenching amount than MIPs (Fig. 6). With the increase in ionic strength from 1 mM to 100 mM, the quenching amount of MIPs decreased 19% and 30% in the presence of NaCl and CaCl2, respectively. For NIPs, ionic strength from 1 mM to 100 mM, the quenching amount decreased 25% and 38% with NaCl and CaCl2, respectively. Both cations decreased the binding of DNT; cations were reported to have a significant influence on the binding capacity following the Hofmeister series [23]. Thus, we expected to see a more profound effect for Na+, but larger influence for Ca2+ was observed. In a prior published work, we showed that calcium specifically interacts with AC-dots surface, resulting in significant alteration of its zeta potential [18], and thus can prevent further interaction with DNT molecules needed for quenching.

The diminishing gap between MIP and NIP quenching with increasing IS suggested that binding to the cavities was also affected, in agreement with the decreased swelling ratio observed with ionic strength given by the polymer are deprotonated; the higher concentration of charged species will compress the electric double layer thickness, shortening the range of influence of the repulsive forces and producing less swelling than under DI water solutions [24]. Lower water adsorption and a deformation of the shape and size of cavities in the shrunken hydrogel contribute to the underestimated of true DNT concentrations in the samples with moderate to high ionic strength by 12%/18% and 20%/30% (NaCl/CaCl2), respectively.

2.4. Effect of NOM concentration

Although their exact composition is variable, natural organic matter compounds are expected to be quenchers of AC-dots fluorescence and therefore may produce higher than true value concentrations when the sensor is used in natural waters [25]. In order to investigate this phenomenon, the quenching effect of Suwanee River Natural Organic Matter (SRNOM) was first determined in the absence of DNT, in a range of concentrations plausible to be encountered in environmental samples. Fig. 7 illustrated the decreased fluorescence intensity in the presence of variable concentration of SRNOM from a suspension of 0.2 ppm AC-dots and from the MIP films. The fitting of the experimental data points in the Stern-Volmer plot showed a linear relationship between F0/F and SRNOM concentrations for both AC-Dots and MIP systems, (r2 = 0.9991 and 0.9995).

Consequently, the quenching amount increased when NOM existed in the DNT solutions (Fig. 8) with respect to the pure water DNT solution. The rate of quenching amount increase with DNT concentration (slope of F0/F vs. DNT concentration curve) for MIPs (0.0054) was very similar to that corresponding to the NIPs (0.0052), which implies that the rise was mainly related to nonspecific adsorption and not to interactions between the SRNOM and the imprinting cavities, such as occupying or blocking DNT access to the sites. SRNOM in samples produced a decrease in the initial intensity of the sensor, potentially impacting the limit of detection. Even in the presence of SRNOM background quenching level, the concentration of DNT could still be accurately obtained by subtracting the NOM quenching amount from the raw sensor reading.

A linear relationship was obtained for the sensor quenching due to DNT in the absence of NOM, and described by the following equation [16]:

$$\frac{F_0}{F} = 0.117 \times C_{DNT} + 0.98551.$$  

(2)

The NOM content of the sample can be estimated from the NIP reading (Fig. 9) linear fit as shown by the following equation:

$$\frac{F_0}{F} = 0.0054 \times C_{NOM} + 1.$$  

(3)

The NOM adjusted calibration curve for the sensor can be obtained combining Eqs. (2) and (3), resulting in Eq. (4).

$$\frac{F_0}{F} = 0.117 \times C_{DNT} + 0.0054 \times C_{NOM} + 1.$$  

(4)

Applying the modified equation to the 10 ppm DNT test solutions in the presence of NOM, values of 10.2, 10.6 and 10.3 ppm, were obtained by the sensors at SRNOM concentrations 1, 10, 50 ppm respectively.
proving the feasibility of abating NOM interference based on this method.

Sorption/complexation of organic and metal ions to humic substances is common in natural waters [26]. Therefore, it is important to note that MIPs equilibrate with free species in solution and therefore the measurement may result in underestimation of the total concentration of species if they bind to significant level to dissolved organic matter in the samples.

2.5. Application to real water samples

Real natural water samples are complex solutions, where pH, dissolved solids and natural organic compounds are probable challenging components for the sensor.

To further test its applicability in the environmental field, the AC-MIP films were used for the determination of DNT concentrations in two real water samples: Stephens Lake water and tap water from our laboratory at the University of Missouri. The collected samples were spiked with DNT and its concentration measured by the newly fabricated sensor and compared to the results from the HPLC analysis.

The experiments were conducted at different DNT concentrations, and the corresponding analysis results are listed in Table 1. DNT concentrations were calculated using Eq. (4).

Lake water was slightly basic while tap water had a neutral pH. The IS of both lake and tap water was close to 10 mM, which based on the above reported results, was expected to have minor effects on the sensor performance. For the lake, the basic pH may result in overestimation of DNT concentrations, while medium IS could do the opposite. As expected, the TOC level of the lake water was higher than tap water due to the existence of dissolved NOM. Taking NOM in account and assuming NOM = TOC – TOC_dnt, adjusted readings were obtained. The readings by sensors in tap water were closer to the HPLC analysis than in lake water. The sensor consistently underestimated the DNT concentration in the lake sample; in addition to the measured higher TOC content, lake water may have contributions of other unknown pollutants and particulate matter that can further interfere with the sensor detection. Stephen’s lake is located in an urban environment and susceptible to anthropogenic impact as well as natural organic matter inflows, especially after rainfall events. The matrix complexity results in a higher chance to block the cavities or the surfaces of sensor films. Structurally similar compounds may bind to the imprinted cavities, resulting in errors. For example, water samples with equal molar concentration of DNT and phenol, resulted in a 12% underestimation of the DNT concentration [16]. Due to its similar size and functionality, phenol was adsorbed on some of the imprinted cavities but its inability to quench the fluorescent signal resulted in a diminished reading. Alternatively, a sample of DNT and dinitrophenol at equal molar concentrations resulted in a 22% increase in quenching amount, as both compounds have two nitro groups with quenching ability. Although the errors induced by the presence of the analogs are significant, those were produced by very high concentrations of extremely similar compounds; however, organic compounds in general are mostly expected to induce interference by non-specific adsorption, weaker and more reversible than the binding to the imprinted cavities, and only if they have the ability to quench the C-dot fluorescence. In another experiment, 4-nitrophenol was tested instead of dinitrophenol in a solution at equal molar concentration as DNT; the overestimation of the target concentration dropped to less than half its original level due to the loss of the second nitro group of the analog [16].

Still, the values in both tap and lakes were reasonably close to the HPLC measured DNT concentrations. The analytical method EPA-RCA 8330B, HPLC using an ultraviolet detector, reports a multi-laboratory variance of 7% RSD for 2,4-DNT water samples in the order of 0.1 ppm [27]. Given the low cost and simplicity of use of the MIP sensor, the measurements obtained can be considered satisfactory. The results are promissory, showing good recognition ability in challenging, unknown natural water samples.

3. Conclusions

The influence of sample pH, ionic strength and NOM content on the rebinding and fluorescence quenching process are concerns regarding the applicability of the AC-Dot labeled MIP sensor to environmental sensing. Surface chemistry of carbon dots can be affected by pH, resulting in fluorescence emission change, and higher swelling of the polymer favors the rebinding of DNT. These effects resulted in higher quenching at basic environments, which translates in slightly higher readings than real DNT concentrations. The pH effects can be partially averted if the sensors are thoroughly rinsed with clean water before the fluorescence measurement, as this process does not result in loss of bound DNT or C-dot particles. The rinsing is intended to neutralize pH and record sensor fluorescence at the calibration curve conditions of circumneutral pH. While C-dot surface group degree of deprotonation will equilibrate with rinsing water pH, the binding of DNT molecules will not be reversed. On the other hand, with increasing ionic strength, the sensor provided lower than true DNT concentrations due to lower swelling and obstruction of AC-Dot – DNT interactions in the presence of Ca$^{2+}$. NOM acted as a nonspecific quencher, increasing the background “noise” level and negatively impacting detection limit. However, NOM quenching showed to be predominantly non-specific in nature and therefore independent of DNT concentration. Since NOM quenching also obeys the Stern-Volmer
Amino functionalized carbon dots (AC-dots) were synthesized following a published method [31]. Covalent bonding was formed between the porous MIP films and AC-dots in a 0.033 mM EDC/0.033 mM NHS aqueous solution.

4.3. Characterization

Fourier Transformed Infrared Spectroscopy (FTIR) spectrum of AC-dots was collected with a Nicolet 4700 FT-IR in order to identify the functional groups present on the surface of AC-dots.

Swelling experiments of NIP-PMMAA were performed in: (1) phosphate buffer at three different pH values (4, 7 and 10) at room temperature; and (2) NaCl or CaCl₂ solution at different ionic strengths (1, 10 and 100 mM) at room temperature. The polymers were swollen in solutions for 48 h at ambient temperature and the degree of swelling was determined gravimetrically. At least three samples of NIP-PMMAA material was tested under each condition.

4.4. Fluorescence quenching experiments

Hitachi F-4500 Fluorescence Spectrophotometer was used for photoluminescent properties. Emission scans were performed from 300 nm to 700 nm at a speed of 1200 nm min⁻¹ with the slit width of 5 nm at an excitation wavelength of 350 nm.

The initial FL intensity of MIP and NIP films was measured in DI. Secondly, sensor strips were dipped in the corresponding test solutions and incubated for 30 minutes, as determined in previous research [16]. Then, sensors were rinsed with DI water and their FL intensities were measured submerged in pure water at neutral pH. The level of quenching is calculated as the ratio of the initial intensity to the intensity measured after exposure to the sample, F₀/F. The linear relationship between F₀/F and DNT concentration in solution followed Stern–Volmer equation [28].

\[
F_0/F = 1 + K_{sv} C_0
\]

where F₀ and F are the fluorescence intensity in the absence and presence of quencher, respectively, C₀ is the concentration of the quencher, and Ksv, is the quenching constant for the quencher. At least three MIP or NIP films were tested under each conditions; FL intensity measurement was conducted at least three times for each sample.

For all test solutions, DNT concentrations were determined by high-performance liquid chromatography (HPLC) coupled with a 15-cm by 4.6-mm Epic C18 column. Methane/water (50:50, v/v) was used as the mobile phase at flow rate of 0.75 mL min⁻¹ with UV Detection at 254 nm and injection volume of 10 μL.

4.5. Investigations on the effects of interferences

The effect of pH on the detection and quantification of DNT by the MIP sensor was investigated in 10 ppm DNT solutions adjusted at three levels of pH (4, 6, 9), adding HCl (10 mM) or NaOH (10 mM) solutions as needed. The DNT concentration was chosen because it falls into the linear range of the sensor detection range and causes a significant FL decrease. For comparison, the responses of MIPs and AC-Dots (0.2 μμμppm) to pH, both having the similar FL intensities at neutral pH, were tested in

### Table 1 Detection of DNT in natural water samples.

| Sample | Sensor measured DNT concentration (ppm) | Stdev | Error (%) | HPLC measured DNT concentration (ppm) | pH | IS (mM) | TOC (ppm) |
|--------|----------------------------------------|-------|-----------|--------------------------------------|----|--------|-----------|
| Lake   | 5.53                                   | 0.54  | 12.0      | 6.28                                 | 8.5| 7.5    | 4.9       |
|        | 5.77                                   | 0.46  | 9.7       | 7.99                                 |    |        |           |
|        | 12.32                                  | 1.86  | 18.4      | 14.67                                |    |        |           |
| Tap    | 4.02                                   | 0.77  | 20.1      | 3.83                                 | 7.2| 13.8   |           |
|        | 5.53                                   | 0.54  | 12.0      | 6.28                                 |    |        |           |
|        | 5.77                                   | 0.46  | 9.7       | 7.99                                 |    |        |           |
absence of DNT as well. The IS effect was investigated in 10 ppm DNT test solutions with a background concentration of at 1, 10, and 100 mM NaCl or CaCl2.

Organic materials are ubiquitous in natural waters, originating from the decay of plans, animals or anthropogenic pollution. Natural organic matter (NOM) includes substances that can emit or quench fluorescence, as well as adsorb onto the sensor surfaces, and therefore induce error in sensor output. In order to assess this effect, experiments were performed with NIP and MIP sensors in mixture solutions of 10 ppm DNT with different levels of Suwannee River NOM (SRNOM), as a model of natural organic matter, at concentration of 1, 10 and 50 ppm. Control tests performed with NIP and MIP sensors at the same SRNOM concentration levels in the absence of DNT.

Finally, the sensor was tested in real water samples collected from Stephens Lake, Columbia, Missouri, and tap water at the University of Missouri (coming from Water Treatment Plant with Columbia Utilities) that were spiked with DNT. Immediately after collection, the sampled water was characterized by pH, conductivity and total organic carbon (TOC) measurements using a Shimadzu TOC-VC analyzer.

The MIP-sensor was dipped in the spiked solutions, left to equilibrate for 30 minutes and rinsed with DI before reading fluorescence intensity. DNT concentrations were determined by the quenching amount as established by the Stern-Volmer equation. Sensor measurements were validated by analytical determinations of the DNT concentrations in the samples, by high-performance liquid chromatography (HPLC).

Data availability statement

Supporting data is available via the University of Missouri's digital institutional repository (MOspace) web site at https://mospace.umsys tem.edu.

Declarations

Author contribution statement

Jingjing Dai: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Maria F. de Cortalezzi: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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