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Removal of triazine-based pollutants from water by carbon nanotubes: Impact of dissolved organic matter (DOM) and solution chemistry

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ABSTRACT

Adsorption of organic pollutants by carbon nanotubes (CNTs) in the environment or removal of pollutants during water purification require deep understanding of the impacts of the presence of dissolved organic matter (DOM). DOM is an integral part of environmental systems and plays a key role affecting the behavior of organic pollutants. In this study, the effects of solution chemistry (pH and ionic strength) and the presence of DOM on the removal of atrazine and lamotrigine by single-walled CNTs (SWCNTs) was investigated. The solubility of atrazine slightly decreased (~5%) in the presence of DOM, whereas that of lamotrigine was significantly enhanced (by up to ~70%). Simultaneous introduction of DOM and pollutant resulted in suppression of removal of both atrazine and lamotrigine, which was attributed to DOM-pollutant competition or blockage of adsorption sites by DOM. However the decrease in removal of lamotrigine was also a result of its complexation with DOM. Pre-introduction of DOM significantly reduced pollutant adsorption by the SWCNTs, whereas introduction of DOM after the pollutant resulted in the release of adsorbed atrazine and lamotrigine from the SWCNTs. These data imply that DOM exhibits higher affinity for the adsorption sites than the triazine-based pollutants. In the absence of DOM atrazine was a more effective competitor than lamotrigine for adsorption sites in SWCNTs. However, competition between pollutants in the presence of DOM revealed lamotrigine as the better competitor. Our findings help unravel the complex DOM–organic pollutant–CNT system and will aid in CNT-implementation in water-purification technologies.

1. Introduction

In recent years, pesticides, pharmaceuticals and personal care products have been frequently detected in aquatic environmental systems (Del Rosario et al., 2014; Ferrer and Thurman, 2010; Liu and Wong, 2013; Loos et al., 2010). Among these pollutants, the herbicide atrazine and the anticonvulsant drug lamotrigine have both been identified at relatively high concentrations in water bodies (Ferrer and Thurman, 2010; Jablonowski et al., 2009; Loos et al., 2010). Though the use of atrazine has been banned in Europe for over a decade, it is still used in many countries, including the USA and Brazil, and is thus detected frequently in soils, lakes, groundwater and even drinking water (Benotti et al., 2009; Cerejeira et al., 2003; Jablonowski et al., 2009; Ochoa-Acuña et al., 2009; Villanueva et al., 2005). Lamotrigine is considered a fairly new anticonvulsant drug; nevertheless, it has already been detected in several surface water samples and in 94% of all wastewater effluents collected across the USA (Ferrer and Thurman, 2010; Writer et al., 2013). For the future safety of global water systems, effort must be invested in expanding our knowledge of the behavior of such pollutants in the aquatic environment, and in examining methods for their removal, particularly by adsorption.

Carbon nanotubes (CNTs) are efficient adsorbents that are being extensively investigated for their potential use in water-treatment technologies (Qu et al., 2013; Wu et al., 2016; Yu et al., 2014). Adsorption of atrazine by CNTs has been previously investigated (Chen et al., 2009; Yan et al., 2008), however that of lamotrigine has not been studied. Multiple factors can influence the adsorption of chemical compounds by CNTs, such as solution chemistry and the presence of dissolved organic matter (DOM) (Liu et al., 2014; Zhang

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et al., 2010). To the best of our knowledge, the former has not been studied for triazine-based pollutants. DOM has been shown to significantly reduce the adsorption of phenanthrene, pyrene and trichloroethylene by CNTs, likely due to reduction in adsorption sites by competition and/or blockage of these sites by DOM (Ersan et al., 2016; Zhang et al., 2011, 2012). On the other hand, humic acid-coated CNTs exhibited only a slight reduction in adsorption of phenanthrene, naphthalene and 1-naphthol, which was attributed to newly exposed adsorption sites (Wang et al., 2008). The adsorption coefficients of sulfamethoxazole on humic acid-suspended CNTs were up to two orders of magnitude higher than those on aggregated CNTs. The authors suggested that pre-adsorbed humic acid exposed new sites for sulfamethoxazole adsorption by CNTs (Pan et al., 2013). Moreover, DOM and its hydrophobic fractions have been reported to reduce carbamazepine adsorption by CNTs, whereas the hydrophilic neutral fraction did not impact adsorption (Lerman et al., 2013). It is apparent that the influence of DOM on adsorption of organic pollutants by CNTs is highly variable, warranting further investigation.

Even though adsorption of organic compounds by CNTs has been widely researched, the effects of DOM on removal of pollutants under different solution conditions have rarely been addressed. Therefore, the main objective of this study was to systematically research the influence of DOM on the adsorption of atrazine and lamotrigine by single-walled CNTs (SWCNTs) under different solution conditions (i.e., with various pHs and ionic strengths). Both atrazine and lamotrigine are triazine based-compounds with many similarities in their physicochemical parameters. However each exhibits different practice; atrazine is a model herbicide (Cerejeira et al., 2003) whereas lamotrigine is a model pharmaceutical (Kumar et al., 2014). The findings in this study contribute to our understanding of interactions between organic pollutants and CNTs in environmental systems and will assist in the implementation of CNTs in organic pollutant removal technologies.

2. Materials and methods

2.1. Materials and characterization

Pristine SWCNTs (outer diameter 1–2 nm, length 5–30 μm) were purchased from Chengdu Organic Chemistry Co. Ltd. (Chengdu, China). Atrazine (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, 90% purity) was obtained from Agan Chemicals (Ashdod, Israel). Lamotrigine (6-(2,3-dichlorophenyl)-1,2,4-triazine-3,5-diamine, 98% purity) was purchased from EnzoBiochem Inc. (New York, NY, USA). Selected physicochemical properties of the organic compounds are presented in Table S1. Deionized water and analytical-grade solvents (Sigma-Aldrich, Rehovot, Israel) were used in all experiments. DOM was isolated from composted biosolids, as previously described (Engel and Chefetz, 2015, 2016). Carbon concentration of DOM (i.e., dissolved organic carbon—DOC) was determined using a V_{CSH} total organic carbon analyzer (Shimadzu, Japan; quantification limit was 0.5 mg C L^{-1}).

2.2. Adsorption of pollutants by SWCNTs: single- and bi-solute systems

Stock solutions of atrazine and lamotrigine were dissolved in acetone and methanol, respectively. The stock solutions were diluted to a series of concentrations (50–5000 μg L^{-1} for atrazine and 150–6000 μg L^{-1} for lamotrigine) in Pyrex bottles with Teflon screw caps. The background solution (pH 7) was prepared using chloride salts to obtain a constant ionic composition (Ca^{2+} 4.4 mg L^{-1}, Mg^{2+} 3.8 mg L^{-1}, Na^{+} 12.5 mg L^{-1} and K^{+} 28.8 mg L^{-1}) which simulated the composition of the DOM extract (Engel and Chefetz, 2015). The SWCNT-to-water ratio was 1:100,000 for atrazine, and 1:50,000 for lamotrigine. The amount of organic solvent (i.e., methanol or acetone) was less than 0.5% in the final solutions to minimize co-solvent effects.

Adsorption experiments were conducted using the batch-equilibration technique. Samples were rotated vertically (200 rpm, 25 °C) until equilibrium, 2 days for atrazine and 1 day for lamotrigine according to adsorption kinetics experiments (Fig. S1). Triplicate samples and controls without SWCNTs and without the pollutant were set up for each concentration. After equilibrium was achieved, an aliquot of the sample was removed and filtered (0.45 μm, PALL Corp., Ann Arbor, MI, USA) before quantitative analysis. Adsorbed amounts of organic pollutants were calculated by mass difference between initial and equilibrated concentrations; mass losses for control samples were less than 1%. The validity of the mass-balance calculation was confirmed by solvent-extraction recovery experiments (with methanol). The calculated recovery for atrazine and lamotrigine was 101 ± 1% and 95 ± 2%, respectively.

Bi-solute experiments were performed in order to examine competitive adsorption. In these experiments both organic pollutants were added to solution; the competitor was introduced at a constant concentration to varying concentrations of the main adsorbate. The experimental conditions for the bi-solute experiments were identical to those of the single-solute experiments.

2.3. Adsorption experiments in the presence of DOM

Experiments were conducted with and without DOM at pH 4, 7 and 10 at constant ionic strength of 2 mM and 25 °C, and at increased ionic strength of 154 mM (pH 7 and 25 °C). DOM was introduced at different concentrations (~6 or 30 mg C L^{-1}). pH was adjusted by addition of either NaOH or HCl (variations in ionic strength between pH values were negligible) and measured at the beginning and end of the experiment. The ionic strength was increased with a background solution of simulated seawater (EPA, 2002) diluted to 25% (154 mM). To examine competition between the organic pollutant and DOM, organic pollutant adsorption was examined in samples that were either pre- or post-exposed to DOM. For pre-DOM exposure, SWCNTs were first agitated in a DOM solution for 2 days (Engel and Chefetz, 2016), and then the solutions were spiked with the organic pollutant and further agitated for the required equilibration time. Similarly, post-DOM exposure experiments were performed by agitating the SWCNTs in the presence of the organic pollutant, then DOM was introduced by spiking. Organic pollutant adsorption by DOM-coated SWCNTs was evaluated in a DOM-free solution. DOM-coated SWCNTs were prepared by agitating SWCNTs in a DOM solution (6–7 mg C L^{-1}) for 2 days at the same solid-to-water ratio used for each organic pollutant. The DOM-coated SWCNTs were filtered from the solution and dried prior to use. In addition, competition between atrazine and lamotrigine was examined in the presence of DOM.

2.4. Solubility assays

The impact of DOM and solution chemistry (i.e., pH and ionic strength) on pollutant solubility (C_s) was examined for all tested conditions and DOM concentrations described above. An excess of solid atrazine or lamotrigine was added to the different solutions (Table 1), then the vials were agitated for 24 h, filtered and analyzed.