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Adsorption of antibiotics and iopromide onto single-walled and multi-walled carbon nanotubes

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HIGHLIGHTS

- Lincomycine, sulfamethoxazole, and iopromide adsorbed onto CNT.
- Freundlich isotherm model well fit adsorption of all target compounds.
- Adsorption of target compounds more onto single walled CNT than multi-walled CNT.
- Higher specific surface area of single walled CNT causing it to adsorb more organics.

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ABSTRACT

Engineered carbon nanotubes (CNTs) have shown a great promise for many remediation applications. The adsorption of two antibiotics (lincomycine and sulfamethoxazole) and one contrast medium (iopromide) on single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) was investigated using batch adsorption experiments. These selected pollutants have high detection frequencies in aquatic environments. The adsorption results were compared with those of conventional powdered activated carbon (PAC). Adsorption isotherms for all pollutants on CNTs and PAC were nonlinear and could be described reasonably well with the Freundlich isotherm model. The adsorption generally followed the order SWCNT > PAC > MWCNT. The relatively low adsorption on MWCNT was probably due to its lower specific surface area than other carbon materials. However, correlation of adsorption to the surface area of carbon materials suggests other factors such as properties of adsorbate and type of interaction between pharmaceuticals and CNTs may also contribute to the adsorption processes. Implications of the adsorption results for the removal of pharmaceuticals from aqueous solution using CNTs are briefly discussed.

1. Introduction

There is an increasing concern on the impact of pharmaceuticals on drinking water supplies, which are usually not easily biodegradable and pose a risk of their deleterious effects to human beings and ecosystems [1–4]. Among the various pharmaceuticals, antibiotics have raised issues of antibiotic resistant bacteria and genes in the aquatic environment [5–9]. Besides antibiotics, there is also a concern on X-ray contrast medium, which has been detected in wastewater effluents, surface water, and drinking water at concentrations ranging from 0.5 to 15 $\mu g\,L^{-1}$ [4,10–12]. Wastewater treatment plants (WWTPs), which receive waste from hospitals or radiological clinics, have particularly shown high concentrations. Removal of pharmaceuticals and the contrast medium in water is immense important to meet the urgent need to clean water. Effective and sustainable water treatment technologies are critically required to meet the global demand of purified water.

Since the discovery of carbon nanotubes (CNTs) in 1991, engineered CNTs have shown great potential in many medical and environmental remediation applications [13,14]. CNTs contain cylindrical graphite sheets, which have very high van der Waals index [15]. The benzenoid rings of graphite sheets have sp^2-hybridized carbon atoms with high polarizability. These properties of CNTs make them superhydrophobic materials that may also strongly interact with aromatic pollutants through π–π coupling/

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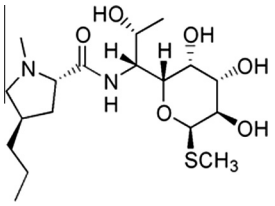
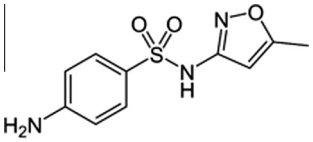
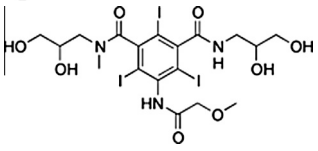
Table 1
Properties of studied antibiotics and contrast medium.

Name	Molecular formula	Structure	M.W.	M.V. (Å^3)[a]	Water Sol. (mg/L)	pK_a	K_{ow}
LCN (antibiotics)	$C_{18}H_{34}N_2O_6S$		406.5	384.9	927	7.8	0.56
SMX (antibiotics)	$C_{10}H_{11}N_3O_3S$		253.3	204.6	610	pK_{a1} = 1.7[b] pK_{a2} = 5.6[c]	0.89
IPR (contrast medium)	$C_{18}H_{24}I_3N_3O_8$		791.1	445.3	23.8	9.9[b]	−2.05

[a] van der Waals molecular volume (from http://www.chemicalize.org).
[b] [25].
[c] [26].

stacking [16,17]. Examples include nitroaromatics and amino- and hydroxyl-substituted aromatic compounds [18,19].

Studies on adsorption of pharmaceuticals onto CNTs are forthcoming [20–24]. The focus of the present study is on the removal of selected pharmaceuticals and a contrast medium through their adsorption onto CNTs, which have different structural and surface properties. The antibiotics under study were lincomycine (LCN) and sulfamethoxazole (SMX), which have amide and sulfonamide moieties, respectively (Table 1). The contrast medium was iopromide (IPR) that has also amide moieties (Table 1). These pollutants have been detected in water and wastewaters [4]. The tested CNTs for sorption experiments were single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). The experiments with powdered activated carbon (PAC) were also performed for the comparative purpose. Sorption studies on SMX using CNTs have been carried out [20], but no similar studies with LCN and IPR are known in literature. The objectives were (i) to investigate the sorption behavior of the selected pharmaceuticals onto CNTs, (ii) to understand the influence of particle size and surface area of engineered carbon materials on the interaction between the studied molecules and CNTs, and (iii) to evaluate the potential of CNTs for enhanced removal of micropollutants.

2. Materials and methods

2.1. Standards and reagents

SWCNTs (purity > 95%, length 1–5 μm, and outer diameter 1.5 nm) and MWCNTs (purity > 95%, length 1–5 μm, and outer diameter 15 ± 5 nm) were purchased from Nano Lab (Newton, MA, USA) and were used without further purification. Based upon the information provided by the manufacturer, both CNTs have a hollow structure and were produced by a conventional chemical vapor deposition (CVD) method. Coconut-based PAC was obtained from Dongyang Carbon Co., Korea (Cheonan, Korea). Prior to use, the PAC was ground to reduce their particle sizes down to 60–140 mesh (100–250 μm).

Three pharmaceuticals, i.e., LCN (Sigma–Aldrich, St. Louis, MO, USA), SMX (Sigma–Aldrich, St. Louis, MO, USA), and IPR (USP, Rockville, MD, USA) all of reagent-grade were purchased for use. Stock solutions of three pharmaceuticals (concentration: 12,000 mg L^{-1}) were prepared by dissolving into HPLC-grade methanol (J.T. Baker, Philipsburg, NJ, USA).

2.2. Sorption experiments

All sorption experiments were carried out using a batch reactor. Sorption experiments onto three adsorbents (i.e., SWCNT, MWCNT, and PAC) were performed as a function of pharmaceutical concentration. The stock solutions of target pharmaceuticals were obtained by dissolving their solids into methanol, whereby the content of methanol in the final aqueous phase did not exceed 0.1% of total volume. Before adsorption experiments, the equilibrium between dried adsorbent and NaCl background solution was initially obtained by mixing appropriate amounts of the adsorbent and 0.01 M NaCl background solution into 40 mL amber EPA vials, equipped with Teflon-lined screw caps (Samsung Tech, Kyunggi, Korea). The resulting mixture was shaken for 24 h.

In the adsorption experiments, a certain volume of the concentrated stock solutions of LCN, SMX, and IPR (concentration: 12,000 mg L^{-1}) were added into tubes containing equilibrated adsorbent in NaCl background solution. The tubes were sealed with Teflon-lined screw caps and shaken at 150 rpm at 20 ± 1 °C. For kinetic study, the supernatants were withdrawn from the tubes after shacking them for 0, 6, 24, 72, 120, and 264 h, and filtered using a 0.2 μm pore size filter. For equilibrium study, the tubes containing the adsorbents were shaken for 72 h. The filtered solutions were stored in a dark place at 4 °C before subjected to analyses. At the end of each adsorption experiments, the equilibrium pH was measured; it was 6.0 ± 0.2.

2.3. Analysis

The concentrations of pharmaceuticals in the supernatant were measured using a liquid chromatography–mass spectrometry/mass spectrometry (LC–MS/MS) technique. The LC–MS/MS system consisted of LC (LC-20A, Shimadze, Kyoto, Japan) and a triple quadruple MS (API-3200, AB-Sciex, MA, USA) with an electrospray ionization (ESI) probe. The column used for analyzing LCN and SMX was a Shim-pack XR-ODS II (length: 75 × 3.0 mm; particle size: