Effects of Copper, Lead, and Cadmium on the Sorption and Desorption of Atrazine onto and from Carbon Nanotubes

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There are currently few studies on the dual effects of metal ions on the sorption of atrazine and conversely of atrazine on metal adsorption on multiwalled carbon nanotubes (MWCNTs). While a number of sorption models were considered to describe the sorption of atrazine on MWCNTs, the Polanyi-Manes model (PMM) fit the sorption isotherms well with the lowest mean weighted square errors. Atrazine was mainly adsorbed onto the surface and micropores of MWCNTs bundles or aggregates. Hydrogen bonding between azo and amino nitrogen of atrazine and functional groups on MWCNTs also occurred. Oxygenated functionalities, mainly carboxylic groups on MWCNTs surface, decreased the sorption of atrazine. Metal cations Cu^{2+} , Pb^{2+} , and Cd^{2+} diminished the sorption of atrazine depending on the oxygenated functionalities densities. The mechanisms ascribed were due to the formation of surface or inner-sphere complexes of Cu^{2+} , Pb^{2+} , and Cd^{2+} through carboxylic groups and hydration, which may occupy part of the surface of MWCNTs-O. The large hydration shell of metal cations may intrude or shield the hydrophobic and hydrophilic sites and indirectly compete with atrazine for surface sites, leading to the inhibition of atrazine adsorption around the metal-complexed moieties.

Introduction

Carbon nanotubes (CNTs) mainly include single-walled or multiwalled carbon nanotubes (MWCNTs). MWCNTs are becoming of increasingly environmental interest because they have been proposed for widespread applications, including environmental applications as adsorbents, high-flux membranes, pollution prevention strategies (1), and

potentially for in situ environmental remediation (2). It is likely that the increase in the commercial production and the consequential common availability will see the interest in environmental applications of CNTs increase, which will inevitably lead to their more abundant occurrence in the environment. Whereas CNTs are hydrophobic, they can be suspended in an aqueous phase by natural organic matter, which may lead to greater environmental mobility and risk than predicted based on apparent hydrophobicity alone (3). Evidence for toxicological effects of CNTs is currently increasing (4) where the environmental risk due to exposure is not solely ascribed to the inherent nature of CNTs, but also to any adsorbed toxic pollutants (5). For these reasons a better understanding of the fate and transport characteristics of CNTs and the adsorbed pollutants is becoming an environmentally important issue.

CNTs exhibit both high adsorption capacities for metals (6–9) and toxic organic chemicals (10–16). The mechanisms responsible for adsorption include either surface adsorption or micropore diffusion of hydrophobic organic compounds onto the MWCNTs and are ascribed to hydrophobic, dispersion, and weak dipolar forces (11–13). Some other studies have also proposed π – π electron–donor–acceptor (EDA) interactions with polycyclic aromatic hydrocarbons, nitroaromatics, and the CNT surface to explain the observed adsorption (11, 15).

Most current research is focused on the sorption of single metals (6–9) or organic contaminants (10–16) by CNTs in isolation and ignores any potential interactions between mixtures of metals and organic contaminants that may influence sorption. A single-solute system may not adequately represent the majority of mixed contaminant systems commonly encountered in the environment, where complex mixtures of contaminants containing both heavy metals and organic contaminants may coexist at many contaminated sites (17). To the best of our knowledge, the question as to whether metals affect the sorption of organic contaminants and vice versa on CNTs has not been adequately addressed.

In this study atrazine was chosen as a model organic adsorbate because of its frequent worldwide use in agriculture (18), and because it has a relatively high chemical stability in soils and aquifers and a high leaching potential and has frequently been detected in waters (19). Heavy metals such as Cu^{2+} , Pb^{2+} , and Cd^{2+} all commonly exist in the soil environment, especially in soil irrigated by wastewater in the water shortage countries (20). Previous works have reported the sorption of metals and atrazine, separately (7, 10), whereas in this manuscript we extend that work with the focus on the effect of metals on atrazine sorption and desorption in general, and on the relevant mechanisms in particular. Fourier transform infrared (FTIR) and X-ray absorption spectroscopic (XAS) studies were subsequently used to provide insight into the metal–atrazine interactions on the surface of MWCNTs containing oxygen functional groups.

Experimental Section

Chemicals. HPLC-grade atrazine (97.4%) was purchased from Sigma-Aldrich Chemical Co. and was used as-received. Heavy metals were supplied as reagent-grade nitrate salts and all other chemicals used were better than analytical reagent grade.

Materials. MWCNTs produced by CVD method were purchased from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences, and had a purity >95%. The surface functional groups on MWCNTs were determined by

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X-ray photoelectron spectroscopy (XPS) and Boehm titration (21). Preliminary experiments indicated that MWCNTs contained no detectable levels of atrazine, Cu^{2+} or Pb^{2+} or Cd^{2+} impurities.

Batch Sorption and Desorption. Sorption and desorption experiments were conducted using a batch equilibration method at $20 \pm 0.5^\circ\text{C}$. MWCNT (5 mg) and atrazine solution (25 mL of 0.01 M NaNO_3 containing 0.1 g L^{-1} NaN_3) containing initial concentrations of $0.5\text{--}20 \text{ mg L}^{-1}$ were added to a 40 mL glass tube for sorption experiments. The pH of adsorbent suspension was maintained at 6.0 ± 0.1 by dropwise addition of 0.1 M HNO_3 or 0.1 M NaOH three times during the sorption processes at every 12 h intervals. Reactors filled with MWCNTs and atrazine solutions were sealed with Teflon-lined screw caps and shaken at 100 rpm in a shaker (HZQ-F160) for 2 d. Preliminary sorption studies indicated that apparent equilibration was reached in <2 d. After centrifugation at 2000g for 20 min, all glass tubes were placed vertically to stand for 24 h to ensure complete separation of the aqueous phase from the MWCNTs at $20 \pm 0.5^\circ\text{C}$. Supernatants were withdrawn and final atrazine concentrations determined by HPLC. After sorption the suspension was filtered through a Millipore $0.25 \mu\text{m}$ hydrophilic polyethersulfone membrane and final metal concentrations were determined using ICP-AES. Preliminary experiments indicated that recoveries of adsorbates without MWCNTs added were greater than 97% of their initial concentrations, indicating no significant losses or degradation in the time frame of the batch sorption study. Therefore, the amount of atrazine, Cu^{2+} , or Pb^{2+} or Cd^{2+} adsorbed was directly calculated by mass differences between the initial and final concentrations.

Atrazine desorption experiments were conducted using a sequential decant–refill technique immediately following the completion of sorption experiments. A portion of the supernatant (15 mL) was withdrawn using a pipet and immediately replaced by the same volume of fresh desorption solution (0.01 M $\text{NaNO}_3 + 0.1 \text{ g L}^{-1}$ NaN_3) and desorption was initiated immediately for an additional 2 d. As for the sorption experiments at the end of each desorption cycle, the supernatant was sampled and the desorbed atrazine was calculated by mass difference. The desorption process was repeated for three complete cycles and as was done in the sorption experiments the solution pH during desorption processes was readjusted to 6.0 ± 0.1 three times at 12 h intervals. The losses of adsorbates during the removal and replacement were negligible ($<1\%$).

Analysis. The concentrations of atrazine in equilibrium solutions were determined using a HPLC (Agilent Technologies 1200) equipped with a reversed-phase C_{18} column ($5 \mu\text{m}$, $4.6 \times 200 \text{ mm}$) and an UV–visible spectrophotometer (UV–visible HP 8452 A) set at 222 nm. The mobile phase was methanol/water (70/30, volume ratio) and the flow rate was 0.7 mL min^{-1} . All metal concentrations in the equilibrium solutions were determined by ICP-AES (Perkin-Elmer).

FTIR Measurement. FTIR spectra were recorded on a FTIR spectrophotometer (NEXUS 670, Thermo Nicolet). Samples for FTIR analysis were prepared with conditions identical to those used during the sorption experiments. Atrazine-sorbed MWCNTs were washed and freeze-dried overnight and then pressed into potassium bromide pellets. The resolution for FTIR spectroscopy was 6 cm^{-1} , and a total of 100 scans were collected for each spectrum.

X-ray Absorption Measurements and Data Analyses. XAS spectra at Cu K-edge and Pb L_{III} -edge were obtained at the 4W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF) using a Si(111) double crystal monochromator. Electron beam energy was 2.2 GeV with a storage ring beam current of 80 mA. Data analysis was performed using WinXAS2.1 following background correction and normalization, together with cubic spline, Fourier transformed, reverse

TABLE 1. Acidity of Carbon Nanotubes

carbon	carboxylic groups ^a (mmol g ⁻¹)	lactonic groups ^b (mmol g ⁻¹)	hydroxyl groups ^c (mmol g ⁻¹)	total acidic groups ^d (mmol g ⁻¹)
MWCNTs-O (0.85%)	0.143	ND	ND	0.132
MWCNTs-O (2.16%)	0.209	0.181	0.529	0.919
MWCNTs-O (7.07%)	0.392	0.286	0.713	1.391

^a NaHCO_3 uptake. ^b $\text{Na}_2\text{CO}_3\text{--NaHCO}_3$ uptake; ND, not detected. ^c $\text{NaOH--Na}_2\text{CO}_3$ uptake; ND, not detected. ^d NaOH uptake.

Fourier transformed, and EXAFS fitting. In the fitting procedure, the coordination number was fixed for the reference compounds, whereas the Debye–Waller factor was fixed for samples. Phase shifts and backscattering amplitudes were obtained from the theoretical calculation using FEFF 7.0.

Results and Discussion

Characterization of MWCNTs. Selected structure properties are listed in Table S1. XPS shows that carbon and oxygen are present in the outer 10–20 nm diameters of the MWCNTs (Figure S1), and that the oxygen content was 0.85%, 2.16%, and 7.07%. Deconvolution of the C 1s peak resolved a main peak of $\text{sp}^2\text{C=C}$ (284.4–284.5 eV), attributed to the graphitic structure and a peak of $\text{sp}^3\text{C-C}$ (285.1–285.5 eV) attributed to defects in the nanotube structure. Peaks of C–O (286.2–287.5 eV), $>\text{C=O}$ (286.5–287.9 eV), $-\text{COO}$ (288.4–289.5 eV), and O–COO (289.0–291.6 eV) were assigned to carbon atoms attached to different oxygen-containing moieties (22). Oxygen-containing functional groups such as carboxylic, hydroxylic, and lactonic groups in the three MWCNTs were determined with Bohem titration (21) (Table 1).

Sorption of Atrazine. Atrazine is a weak base, with a pK_a of 1.68, density of 1.187 g mL^{-1} , and a water solubility of 28 mg L^{-1} at 20°C (23). Near or below the pK_a atrazine is present as the protonated species, and the increased sorption with decreasing pH could be ascribed to the sorption of this protonated species by exchange forces. However, such low pH is unlikely to be encountered under typical environmental conditions, and at more typical pHs, such as pH 6 used in this study, atrazine would not be protonated and other weak forces such as H bonding and hydrophobic interactions would become more important. The sorption of atrazine on both MWCNTs-O (0.85%) and MWCNTs-O (2.16%) remained unchanged over the pH range 3.5–9 (Figure S2), whereas the sorption of atrazine onto MWCNTs-O (7.07%) gradually decreased between pH 3.5 and pH 5, and there was no further decrease above pH 5.

Five nonlinear sorption isotherm models, Freundlich (FM), Langmuir (LM), Dual Mode (DMM), Dual Langmuir (DLM), and Polanyi-Manes models (PMM) (Table S2) were tested to fit the sorption of atrazine on MWCNTs. Three of the models (FM, LM, and DMM) failed to adequately describe the isotherm, greatly over- or underestimated q at low equilibrium concentration (C_e), and exhibited high mean weighted square errors (MWSE) (Figure S3, Table S3). The DLM model fit the isotherms well in most cases with the exception of MWCNTs8 and MWCNTs-O (2.16%) at lower concentrations (Figure S3, Table S3). The PMM model fit all of the sorption isotherms well with the lowest MWSE (Figure 1, Table S3) and consequently the following discussion was based on the adsorption parameters calculated from PMM fitting.

The Polanyi-Manes equation describes a nonlinear isotherm model where there is a variable adsorption potential

FIGURE 1. PMM fit the sorption isotherms of atrazine on six MWCNTs.

at the surface and consequentially distinguishes between the energy required to remove solute into the saturated solution from the solid surface and the energy required to move solute into the subsaturation solution from the surfaces of one or more other solids. The Polanyi-Manes equation thus describes a two-domain model to separately account for contributions from partition and adsorption, more accurately, pore filling (24). This theory would appear to be applicable in this case because MWCNTs form bundles in aqueous media and the spaces between the tubes within the bundles can be regarded as pores. The molecular volume-based value of Q^0 [$\text{cm}^3 \text{g}^{-1}$], taking the liquid density of atrazine to be 1.187 g cm^{-3} , correlates well with V_{micro} , giving a slope of about 0.71 (Figure S4). Polanyi theory is applicable for either pore filling or flat surface adsorption (25). The molecular surface area-based value of Q^0 [$\text{m}^2 \text{g}^{-1}$], taking the molecular surface area of atrazine to be 2.19 nm^2 per molecule (26), correlates strongly with A_{surf} , giving a slope of about 0.82 (Figure S4). These results suggest that atrazine was mainly adsorbed onto the surface and within the micropores of MWCNTs bundles or aggregates. This result is consistent with previous reports which indicated that PAHs, bisphenol A, and 17 α -ethinyl estradiol were mainly adsorbed onto the external surface of MWCNTs (11, 12).

The influence of oxygen on the sorption of atrazine was evaluated using three samples, MWCNT-O (0.85%), MWCNT-O (2.16%), and MWCNT-O (7.07%), containing variable oxygen content but otherwise having similar physical properties. The physical dimensions including the outer diameter (10–20 nm) were identical, whereas MWCNT-O (2.16%) and MWCNT-O (7.07%) had slightly larger surface area, mesoporosity, and microporosity (Table S1). Maximum capacity (Q^0) was negatively related to the carboxylic group, total acidic or surface oxygen content of the MWCNT's (Figure S5), and the carboxyl group density of MWCNT-O (Figure S6). The mechanism responsible for this was ascribed to a more negatively charged MWCNT surface due to deprotonation of carboxylic groups at the equilibrium sorption pH 6, where the adsorption of water is more energetically favorable relative to the sorption of atrazine.

Functionalized CNTs decreased the sorption of hydrophobic organic pollutants (10, 16) while increasing the sorption of metals (8, 9). The true revolutionary potential of nanosorbents lies in the diverse number of pathways available for tailoring nanotube surface chemistry for specific purposes, which complements the existing suite of relatively unspecific conventional sorbents.

Desorption of Atrazine. Desorption of atrazine showed a pronounced hysteresis for MWCNTs-O (7.07%) (Figure 2), but no desorption hysteresis was observed for either MWCNTs-O (2.16%) or MWCNTs-O (0.85%) (data not shown). The thermodynamic index of irreversibility (TII) was used to quantify the hysteresis (27). The TII values for atrazine desorption are 0.14–0.75 and 0.17–0.63 for MWCNTs-O (7.07%) in the absence and presence of Cu^{2+} , respectively (Figure 2). Generally, there were no significant differences

FIGURE 2. Sorption and desorption of atrazine onto and from MWCNTs-O (7.07%) in the absence (a) and presence (b) of Cu^{2+} . Numbers correspond to the Thermodynamic Index of Irreversibility (TII) $\pm$ standard deviation.

FIGURE 3. FTIR spectra of MWCNTs-O (7.07%) (a), atrazine adsorbed MWCNTs-O (7.07%) (b), and atrazine (c).

between the TII values for atrazine sorption alone and for atrazine- Cu^{2+} cosorption. Because MWCNTs-O (7.07%) had larger mesopore and micropore volumes than both MWCNTs-O (0.85%) and MWCNTs-O (2.16%) (Table S1), the observed hysteretic desorption provides support for pore filling as a possible mechanism for atrazine sorption to and hysteretic desorption from MWCNTs-O (7.07%). Hysteresis probably resulted due to an entrapped fraction of sorbate that was unable to re-equilibrate when decreased solute concentrations were achieved during desorption. These unrecoverable and recoverable fractions could potentially be kinetically tracked to final equilibrium or irreversible conditions and the chemical stoichiometry for kinetics and equilibrium could then be established based on the measured functional groups on MWCNTs to calculate the reaction sites for atrazine.

FTIR Analysis. FTIR spectra of MWCNTs-O (7.07%), atrazine-MWCNTs-O (7.07%), and atrazine are shown in Figure 3. For MWCNTs-O (7.07%) (Figure 3a), the peaks at $\sim 1592 \text{ cm}^{-1}$ corresponded to the carbonylic group ($>\text{C}=\text{O}$), whereas the peaks at $\sim 1384 \text{ cm}^{-1}$ and $\sim 1730 \text{ cm}^{-1}$ corresponded to the carboxylic group ($-\text{COOH}$) (6, 13). The peaks at $\sim 1118 \text{ cm}^{-1}$ and $\sim 1045 \text{ cm}^{-1}$ were assigned to aliphatic C–O and alcohol $-\text{OH}$ or adsorbed water (28). The peak at $\sim 1264 \text{ cm}^{-1}$ was assigned to the aromatic C–O and phenolic $-\text{OH}$ stretching (29). For atrazine (Figure 3c), the peaks at $\sim 1555 \text{ cm}^{-1}$ and $\sim 1622 \text{ cm}^{-1}$ were assigned to the C=N bond in the atrazine skeleton (30) and N–H deformation (31), respectively, and the peak at 806 cm^{-1} was assigned to the C–H wagging vibration of atrazine (32). After atrazine was adsorbed to MWCNTs-O (7.07%) (Figure 3b), a new peak appeared at $\sim 1625 \text{ cm}^{-1}$, which was assigned to the N–H

FIGURE 4. Effect of Cu^{2+} , Pb^{2+} , and Cd^{2+} (0.225 mM) on sorption of atrazine by MWCNTs-O (7.07%), MWCNTs-O (2.16%), and MWCNTs-O (0.85%).

deformation of atrazine at $\sim 1622\text{ cm}^{-1}$ (31). The $\text{C}=\text{O}$ stretching mode band of MWCNTs-O (7.07%) at $\sim 1592\text{ cm}^{-1}$ (Figure 3a) was also shifted to 1584 cm^{-1} (Figure 3b), which was assigned to the ring stretching of atrazine and the interaction between the carbonylic group of MWCNTs-O and the heterocyclic nitrogen in the triazinic ring plane (33). The appearance of peaks at $\sim 1625\text{ cm}^{-1}$ and 1584 cm^{-1} provided strong evidence for the existence of atrazine on the surface of MWCNTs-O (7.07%), implying that atrazine was surface-adsorbed by hydrogen bonding through the $\text{C}=\text{O}$ groups (34).

Sorption and hysteretic desorption, in conjunction with FTIR, revealed that atrazine was mainly adsorbed onto the surface and micropores of MWCNTs bundles or aggregates by a combination of hydrogen bonding and hydrophobic effects.

Sorption of Atrazine in the Presence of Cu^{2+} , Pb^{2+} , and Cd^{2+} . To evaluate the effects of heavy metals on the sorption of atrazine, 0.225 mM Cu^{2+} , Pb^{2+} , and Cd^{2+} (14.3, 46.6, and 25.3 mg L^{-1} of Cu^{2+} , Pb^{2+} , and Cd^{2+} , respectively) was simultaneously sorbed with atrazine at an initial concentration range of 0.5–20 mg L^{-1} . The concentration of heavy metals was set at 0.225 mM for Cu^{2+} and Pb^{2+} because this concentration corresponds to the second level of Environmental Quality Standard for copper (150 mg kg^{-1}) and lead (250 mg kg^{-1}) in Chinese soils if all Cu^{2+} and Pb^{2+} were adsorbed. From pH 2–7, the adsorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} generally increases with pH (8) and at pH 6 hydrolysis and precipitation of these metals is unlikely.

The coadsorption of atrazine and Cu^{2+} , Pb^{2+} , and Cd^{2+} indicated that metal cations significantly suppressed the sorption of atrazine on MWCNTs-O (7.06%) and had a lesser effect on MWCNTs-O (2.16%) and almost no effect on MWCNTs-O (0.85%) (Figure 4). The suppression effect was in the order $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$, consistent with the electronegativity order Cu^{2+} (1.9) $>$ Pb^{2+} (1.8) $>$ Cd^{2+} (1.7), suggesting that the more electronegative metals tended to more easily dissociate H from the functional groups of MWCNTs (35). The impact of heavy metals on atrazine sorption was expressed as $(K_d^2 - K_d^1)/K_d^1$, where K_d^2 and K_d^1 correspond to the distribution coefficients of atrazine with and without heavy metals, respectively (Table S4). Cu^{2+} , Pb^{2+} , and Cd^{2+} decreased atrazine sorption onto MWCNTs-O (7.07%) by ~ 30 –40, ~ 20 –30, and ~ 10 –19%, respectively. In contrast, coadsorption of atrazine at its concentration of 4 mg L^{-1} had little effect on the adsorption of Cd^{2+} , Cu^{2+} , and Pb^{2+} for all types of MWCNTs (data not shown).

XAS Analysis. XAS was used to identify the formation of surface complexes on any hydrophilic sites through the modification of oxygen-containing groups and to obtain the coordination environment of Cu^{2+} and Pb^{2+} adsorbed onto MWCNTs. Identification of such complex formation could provide insight into the suppression mechanism of atrazine

FIGURE 5. Normalized XANES spectra (pre- and near-edge region) of Cu^{2+} -MWCNTs-O (7.07%) and Cu^{2+} -MWCNTs-O (2.16%) (a), and corresponding first derivatives (b), EXAFS spectra ($\chi(k)$ -function) (c), and Fourier transformation of EXAFS spectra (d). Solid lines represent the experimental data and dotted lines correspond to lines of best fit.

sorption by heavy metal cations. As previously observed by Frenkel et al. (36), XANES spectra of adsorbed Cu^{2+} show a very weak peak just before the edge jump corresponding to $1s \rightarrow 3d$ (Figure 5a,b). The pre-edge peak is sensitive to the presence of a center of symmetry, and its intensity increases with distortions that remove this center of symmetry. The first derivative of the XANES spectrum shows two obvious peaks at 8.979 (α peak) and 8.984 (β peak) keV, which were qualitatively related to the difference between the equatorial and axial Cu–O distances in the CuO_6 octahedron (36). The decreased α peak intensity of Cu^{2+} adsorbed compared to that of aqueous $\text{Cu}(\text{NO}_3)_2$ (the insert of Figure 5b) suggested that for MWCNTs-O (7.07%) and MWCNTs-O (2.16%) the stronger field water molecules in the tetragonal plane had exchanged with different field organic moieties such as carboxylic and hydroxylic groups. The decreased α peak intensity in Cu-MWCNTs also suggested that MWCNTs-O (7.07%) and MWCNTs-O (2.16%) were sterically hindered due to their three-dimensional structure and that when Cu^{2+} approached the surface, Cu^{2+} could not be bound in the equatorial plane with the same degree of angular overlap as that of water.

The normalized k^3 -weighted EXAFS spectrum showed oscillations of about equal amplitude across the entire k range, but also amplified spectral noise at high k (Figure 5c). The strongest radial structural function derived from Fourier transformation occurring at 1.53 Å corresponded to first Cu–O shell (Figure 5d). The best fit of the first shell leads to 4.14 equatorial oxygen atoms at 1.94 and 1.98 Å, 2.64 axial oxygen atoms at 2.20 and 2.16 Å, for Cu^{2+} adsorbed on MWCNTs-O (7.07%) and MWCNTs-O (2.16%), respectively. The data are consistent with those obtained from XANES (i.e., a slightly distorted octahedral coordination around adsorbed Cu^{2+}) (37). The results of four short equatorial bonds and two elongated axial bonds were due to the Jahn–Teller effect of the Cu–O clusters. This suggested that Cu^{2+} was adsorbed on MWCNTs through formation of an inner-sphere complex in which the water molecules were partly displaced by the carboxylic and hydroxylic groups of MWCNTs-O (7.07%) and MWCNTs-O (2.16%). There were no high- Z backscatters beyond the first shell, suggesting that no metal–metal bond or coprecipitation occurred, which was consistent with Flogeac et al. (37).

As with Cu^{2+} , XAS also suggested that Pb^{2+} formed inner-sphere complexes in which the water molecules were partly displaced by carboxylic and hydroxylic groups of MWCNTs (data not shown). XAS spectra of Cd^{2+} adsorbed on were not obtained because of the practical limitations to the energy available in BSRF.

The batch adsorption together with the XAS study can be used to explain the mechanisms of metal-induced atrazine adsorption suppression. It was initially expected that chemisorption or chemicomplexation of Cu^{2+} , Pb^{2+} , and Cd^{2+} would neutralize the MWCNTs-O surface charge, enhancing the hydrophobic effect, thus increasing atrazine sorption. However, the presence of Cu^{2+} , Pb^{2+} , and Cd^{2+} all actually decreased the sorption of atrazine. This was probably because chemisorption or chemicomplexation does not decrease the much more competitive sorption of water molecules. A two-step mechanism may therefore be responsible for the diminishing sorption of atrazine in the presence of heavy metals. First, inner-sphere complexes of Cu^{2+} , Pb^{2+} , and Cd^{2+} are formed through carboxylic groups and hydration, which occupy part of the surface of MWCNTs-O. Second, because metal cation hydration reactions are still strong, the complexed metal ions are likely to host one or more hydration shells of dense water (38). These large metal cation hydration shells may intrude or shield the MWCNTs hydrophobic and hydrophilic sites and therefore indirectly compete with

atrazine for surface sites, leading to the inhibition of atrazine adsorption around the metal-complexed moieties.

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Supporting Information Available

Four tables and six figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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