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Abstract

Although carbon nanotubes (CNTs) are well known to have a strong affinity to various heavy metals in aqueous solution, little research has been dedicated to exploit their use in fixed-bed water treatment systems (e.g., trickling filters). In this work, batch sorption and fixed-bed experiments were conducted to examine the ability of functionalized multi-walled CNTs as filter media to remove two heavy metal ions (Pb^{2+} and Cu^{2+}) from infiltrating water. Batch sorption experiments confirmed the strong sorption affinity of the CNTs for Pb^{2+} and Cu^{2+} in both single and dual metal solution systems. In addition, sonication-promoted dispersion of the CNT particles enhanced their heavy metal sorption capacity by 23.9-32.2%. For column experiments, laboratory-scale fixed-bed columns were packed with CNTs and natural quartz sand by three different packing: layered, mixed, and deposited. While all the three packing methods enhanced the fixed-bed filtering efficiency of Pb^{2+} and Cu^{2+} from single and dual metal systems, the CNT-deposited packing method was superior. Although the amount of the CNTs added into the fixed-bed columns was only 0.006% (w/w) of the sand, they significantly improved the fixed-bed's filtering efficiency of Pb^{2+} and Cu^{2+} by 55%-75% and 31%-57%, respectively. Findings from this study demonstrate that functionalized multi-walled CNTs, together with natural sand, can be used to effectively and safely remove heavy metals from water.

Keywords: carbon nanotube, natural sand, fixed-bed, heavy metal, sorption, filtration

1. Introduction

The exceptional properties of nanomaterials, particularly carbon nanotubes (CNT), have revolutionized the electronic and optic industries, energy sectors, and material engineering and manufacturing. Much research on carbon-based nanoparticle in the environment has been devoted to elucidate the physical, chemical, and biological mechanisms that affect their stability, mobility, and toxicity [1]. Relatively less attention has been paid to their potential application for addressing a number of environmental problems [2, 3].

The hollow and layered nanostructure of CNTs endow them with a characteristically large surface area and a correspondingly high potential sorption capability for chemical pollutants [4]. Several studies have demonstrated that CNTs, particularly those that are functionalized, have a strong affinity to many common water pollutants, including heavy metals [5] and organic pollutants [6]. It is well accepted that pristine CNTs are insoluble in water [7], therefore oxidative treatments are often used to introduce hydrophilic functionalities to their surfaces in order to facilitate aqueous dispersion. This functionalization procedure is suspected to improve CNTs' ability to remove heavy metals in aqueous phase by increasing their cation exchange capacity as well as promoting attractive electrostatic interactions [8]. As such, functionalized CNTs have been reported to have a superior sorption ability to heavy metal ions than pristine CNTs and have been recommended as a potential adsorbent for the removal of heavy metals in contaminated water [9-11].

A vast proportion of published investigations concerned with the removal of contaminants by CNTs have investigated sorption characteristics and mechanisms

through batch sorption experiments [5, 12, 13]. To the authors' knowledge, no study has previously examined the feasibility and effectiveness of using CNTs as filter media in fixed-bed settings to remove contaminants from aqueous solutions. A potential deterrent for the novel application of CNTs for water treatment is the concern of nanoparticle elution from the fixed-bed reactors, which could result in secondary contamination of the receiving water bodies.

A recent study by the authors suggested that natural sand media can be used as a good natural filter to remove functionalized CNTs from water [5]. The deposition of functionalized CNTs on natural sand surface is mainly controlled by strong surface interactions that are irreversible despite chemical and hydrodynamic disturbances [12]. This makes it possible to envision the development of a new technology to use sand as a safeguard for functionalized CNTs in a fixed-bed filter to remove contaminants from water. Sand is very a common filter material used in water treatment, but it has relatively poor ability to remove heavy metals from water [13, 14]. We hypothesize that the combination of sand media with functionalized CNTs would greatly improve the performance of fixed-beds for removing heavy metals from water.

The overarching goal of this work is to assess the best procedures and their respective effectiveness of the CNT-sand filter media for heavy metal removal from water. First, functionalized multi-walled CNTs were incorporated to natural quartz sand media in laboratory fixed-bed columns via three packing methods: 1) layered, where CNTs and sand were packed as separate layers in the columns; 2) mixed, where CNTs and sand were mixed together and subsequently packed in the columns; and 3) deposited, where a well-dispersed CNT suspension was applied to the columns and allowed to

become deposited onto sand surface via filtration. Second, filtration experiments were conducted with the CNT-sand columns in which the removal efficiency of two heavy metals in aqueous phase (Pb^{2+} and Cu^{2+}) was evaluated. The specific objectives of the work included: 1) determine the effect of sonication-promoted dispersion on sorption capacity of the functionalized multi-walled CNTs to Pb^{2+} and Cu^{2+} in single and dual (competing) metal systems; 2) compare removal efficiency of single metal solution (Pb^{2+} or Cu^{2+}) across the three packing types of CNT-sand media; and 3) compare removal efficiency of dual metal solution (Pb^{2+} and Cu^{2+}) across the three packing types of CNT-sand media.

2. Materials and methods

2.1. CNTs

Multi-walled CNTs were produced using a chemical vapor deposition method with nickel and magnesium catalysts. Subsequently, these were functionalized by an acid mixture of concentrated sulfuric and nitric acids (3:1, v:v) to introduce carboxyl and hydroxyl functional groups to the nanotube surface [14, 15]. CNTs produced from this method have high purity with negligible metal content [15]. Average diameter and length of the CNTs were around 40 and 400 nm, respectively, as determined with scanning electron microscope (JEOL 6335F, Tokyo, Japan) [16]. Fourier transform infra-red (FTIR) analysis was used to characterize those functional groups. To obtain the observable adsorption spectra, the CNTs were mixed with KBr to 0.1 wt % and then pressed into pellets. The spectra were measured using a Bruker Vector 22 FTIR spectrometer (OPUS 2.0 software).

Part of the functionalized CNTs was used directly in some of the sorption and column experiments without any dispersion promoting treatments and was referred here as undispersed CNTs. A separated dispersed CNT suspension was produced by suspending the functionalized CNTs in deionized (DI) water at a desired concentration and then sonicated with Misonix S3000 ultrasonicator (QSonica, Newtown, CT) for 30 min, and was referred here as dispersed CNTs.

The physiochemical characteristics of the CNTs were measured for: i) Surface area via the Brunauer–Emmett–Teller (BET) nitrogen adsorption method at 77 K (NOVA 1200 surface area analyzer, Quantachrome Instruments, Boynton Beach, FL), ii) point of zero charge (PZC) via the mass titration method [17], iii) hydrodynamic diameter of dispersed CNTs by dynamic light scattering (ZetaPlus, Brookhaven Instruments Corporation, Holtsville, NY), and iv) electrophoretic mobility (EPM) of dispersed CNTs (ZetaPlus), which was used estimating their zeta potential via Smoluchowski's model. Concentrations of the dispersed CNT suspensions were determined through measuring their spectroscopic light absorption at a wavelength of 255 nm using an Evolution 60 UV-Vis Spectrophotometer (Thermo Scientific, Waltham, MA). The absorbance spectra and calibration curve of the CNT suspensions at this wavelength can be found in the supplementary data (Figure S1). FTIR analysis was conducted with the post-sorption CNTs (i.e., metal laden CNTs) to examine the functional groups using the method described above.

2.2. Sand

Quartz sand of grain size 0.5-0.6 mm (Standard Sand & Silica Co., Davenport, FL) was washed sequentially with tap water and DI water to remove loose impurities. Quartz fragmentation by ultrasonication procedure proposed by Johnson et al. [18] was used to create quartz colloids, which were subsequently filtered through a 0.45 μm filter. The quartz suspension was then used to measure the sand's EMP and PZC. Trace metal identification and concentration on the sand surface were determined by inductively coupled plasma with optical emission spectrometry (ICP-OES, Optima 2100 DV, PerkinElmer Inc., Waltham, MA), as per EPA protocol 200.7.

2.3. Heavy metals

Lead nitrate and copper nitrate were used to prepare stock solutions. Single metal solutions were prepared at concentrations of 10 mg L^{-1} of Pb^{2+} or Cu^{2+}. In addition, a dual metal solution containing 10 mg L^{-1} of Pb^{2+} and 10 mg L^{-1} of Cu^{2+} was prepared. ICP-OES was used to monitor the metal concentration in the solutions. HCl was used to adjust the pH of the metal solutions to 5.6.

2.4. Batch sorption experiment

Batches of each sorbent (dry CNTs, dispersed CNTs, or 1g of sand) were added to 20 mL of each metal solution (Pb^{2+}, Cu^{2+}, and Pb^{2+} and Cu^{2+}) at seven different concentrations to build adsorption isotherms. The resultant CNT dosages were 10 mg in the 20 mL of the mixture. The mixtures were shaken in a shaker for 12 h at room temperature, which was determined sufficient time to ensure equilibration [19, 20]. After

equilibrium was reached, the suspensions were filtered through 0.1 μm membranes, and the initial and equilibrium metal concentrations then measured using the ICP-OES. The mass of sorbed metal was calculated as the difference between initial and equilibrium metal concentration.

2.5. Fixed-bed column experiment

Fixed-bed column experiments were used to investigate the removal and transport of heavy metals in CNT-sand media via three different CNT packing methods. Layered, mixed and deposited CNTs were the three ways in which about 10 mg of CNTs were incorporated into 16.8 g of sand for each CNT-sand packed column. Columns packed with only natural sand were used as the control in the study.

For the layered CNT packing method, natural sand was first wet-packed into an acrylic column (1.5 cm inside diameter ´ 5 cm height), and undispersed CNTs were evenly placed on the top of the sand packed in the column as a separated layer. Membranes with 50 μm pores (Spectra/Mesh, Spectrum Laboratories, Inc.) were used at the column inlet and outlet to distribute the flow. For the mixed CNT packing method, natural sand was thoroughly mixed with the undispersed CNTs and subsequently wet packed into the column. For the deposited CNT packing method, the column was first wet-packed with the sand, and the dispersed CNT suspension was then applied as a pulse (in downward flow direction) using a peristaltic pump set at a steady flow rate of 1 mL/min. After continuous CNT pulse injection, the influent was switched to DI water for an additional 2 hrs to flush out unretained CNTs. Effluent concentration of CNTs was monitored in discrete samples via UV-Vis Spectrophotometry at a wavelength of 255 nm

to determine when 10 mg of CNTs had been deposited in the sand column. Because small amount of CNTs (~0.06% w/w of CNT/sand) were used in the fixed-bed columns, the bed porosity of all three types of column packing was maintained at 0.40.

Once packed with sand and CNTs, the columns were subjected to pulses of single and dual metal solutions and the removal efficiency evaluated according to the metal breakthrough from the columns. Prior to metal pulse injection, the columns were flushed with DI water (pH 5.6) for more than 1 hr and no CNT was detected in the eluents of any the columns. Metal removal experiments consisted of two stages. At stage one, the single (Pb^{2+} or Cu^{2+}) or dual (Pb^{2+} and Cu^{2+}) metal solutions (as described above) were injected into the top of the column for 2 hrs at a steady flow rate of 1 mL/min. At stage two, the influent was switched to metal-free DI water for an additional 2 hrs to elute unfiltered metals from the column. Effluent samples were collected discretely with a fraction collector and the metal concentration monitored with the ICP-OES.

3. Results and discussion

3.1. CNT and sand properties

In dispersion, CNTs were very stable and their concentration maintained unchanged after 24 hrs (Figure S2, supplementary data). All the experiments with dispersed CNTs were finished within 24 hrs to avoid any potential aggregations. The pH of the dispersed CNT suspension was 5.6. Hydrodynamic diameter of the dispersed CNTs was around 180 nm, and their EPM was recorded at -2.99×10^{-8} m^2 V^{-1} s^{-1}. Mass titration curves (Figure S3, supplementary data) indicated that PZC of the CNTs was 2.4, corroborating their negative charge under the tested experimental conditions. Those surface charges

may arise from the abundances of acidic functional groups. FTIR spectrum of the CNTs were characterized by four significant bands at wave number 3445 (O-H stretch), 1635 (C=O bond), 1045 (alkene, C-O bond), and 1385 (vibrational band of $-NO_2$) cm^{-1} (Figure 1). The first three bands confirmed the presences of carboxyl and hydroxyl functional groups on the CNT surface.

BET nitrogen adsorption measurement revealed a surface area of undispersed CNT powder of 112.7 m^2 g^{-1}, a significantly lower value than previously reported for well-dispersed CNTs (>1000 m^2 g^{-1}) [21]. This result suggests that undispersed CNT powders cannot exhibit their 'true' surface area, unless they are well-dispersed in a medium. Thus, it is anticipated that the dispersed CNTs could display higher sorption capacity for metals than the undispersed CNTs based solely on the available surface area for sorption.

The PZC of the sand was 3.0 (Figure S1, supplementary data), indicating that its charge was negative under the tested conditions. Surface element analysis revealed the presence of metal impurities (mainly iron oxyhydroxides) on the sand surface [13], which could potentially serve as adsorption sites for heavy metal ions [17].

3.2. Sorption ability of the CNTs

Both dispersed and undispersed CNTs were much more efficient adsorbents of heavy metals than the sand (Figure 2), which is consistent with the literature that functionalized CNTs have strong affiliations to heavy metal ions in aqueous solutions [14, 22-25]. The dispersed CNTs had greater adsorption ability to both aqueous metals in single and dual metal systems than the undispersed CNTs, which probably could be attributed to the lager surface area of the dispersed CNTs. The isotherms also suggest that

the sonication-promoted dispersion processes could potentially improve the performance of the CNTs in water treatment to remove heavy metal contaminants.

The Langmuir model used to describe the experimental isotherms was: $\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Kq_mC_e}$, where q_e is the mass of metals sorbed per mass of sorbent at equilibrium (mg g^{-1}), q_m the maximum mass of metals sorbed per mass of sorbent as the concentration of metal increases (mg g^{-1}), K is the Langmuir equilibrium constant for mass of metal (L mg^{-1}), and C_e the dissolved metal concentration at equilibrium. The model fit the experimental data very well, as indicated by R^2 values exceeding 0.92 (Table 1).

The q_m values of Pb^{2+} and Cu^{2+} sorption on the sand were low in both single and dual metal systems (Table 1), indicating that natural sand alone is not an effective sorbent for heavy metals in solution. The single-metal maximum sorption capacity of the CNTs was 74.5 and 92.3 mg g^{-1} (0.36 and 0.45 mmol g^{-1}) for Pb^{2+} and 51.3 and 67.8 mg g^{-1} (0.81 and 1.07 mmol g^{-1}) for Cu^{2+} for undispersed and dispersed CNTs, respectively. The maximum sorption capacity measured for the CNTs in this study is several fold higher than that of the natural sand and is even better than metal sorption maxima reported for some activated carbons [26-28]. The dual-metal maximum sorption capacity for undispersed CNTs for Pb^{2+} and Cu^{2+} was 49.3 and 33.0 mg g^{-1} (0.24 and 0.52 mmol g^{-1}), while that for dispersed CNTs was 65.0 and 43.6 mg g^{-1} (0.31 and 0.69 mmol g^{-1}), respectively. A likely explanation for higher molar sorption capacity of Cu^{2+} than for Pb^{2+} is the atomic radii of these ions, which is 70 and 112 pm, respectively. Because of a steric over-crowding, larger ionic radius of Pb^{2+} compared to that of Cu^{2+} may induce a quick saturation of adsorption sites, resulting in lower molar capacity [29].

Compared to the undispersed CNTs, the sorption capacity of the dispersed CNTs increased for 23.9-32.2% for Pb^{2+} and Cu^{2+} in both single and dual metal systems. These data further confirm the importance of CNT dispersal in order to maximize its sorption capacity for water treatment purposes.

It is suggested that the adsorption of heavy metals onto the CNTs are mainly controlled by the strong interactions between the metal ions and hydrophilic surface functional groups, especially carboxyl and hydroxyl groups [30-32]. Comparison of the FTIR spectra of CNTs before and after metal sorption confirmed this mechanism (Figure 1). Compared to the original FTIR spectrum, the adsorption of heavy metals on the CNTs resulted in variations of FTIR peaks at wavenumbers of 1635 (C=O) and 1045 (C-O) cm^{-1}, which could be attributed to the interactions between metal ions and carboxyl and hydroxyl groups. Previous studies have suggested that positively charged metal ions can form strong complexes with these two functional groups through electrostatic and/or hydrogen-bonding interactions [1, 33-35]. A recent study has suggested that metal impurities in the CNTs could play an important role in their sorption of Pb^{2+} in aqueous solutions [36]. This mechanism might not be a dominant factor to the sorption of the two heavy metals here because high-purity CNTs were used in this study.

3.3. Single metal removal in the CNT columns

The evaluation of three packing methods of CNT-sand media was conducted through analyses of effluent breakthrough of dissolved metals in water. Breakthrough curves (BTCs) for single-metal pulse injections were analyzed for filtration and transport as they moved through the fixed-bed sandy columns with and without CNTs as illustrated

in Figure 3. The BTCs were constructed as plots of the cumulative pore volume of liquid eluted versus the relative concentration (C/C_0) of the injected metal in the effluent. For injections of single-metal (Pb^{2+} and Cu^{2+}) pulses, the BTCs corresponding to fixed-beds with deposited CNTs (inverted triangle in Figure 3) had the lowest mass of metal eluted and the most delayed breakthrough elution, indicating that deposited CNT packing method was the most effective way in improving the fixed-bed's heavy metal removal performance. This superior metal sorption efficiency of deposited CNT fixed-beds agrees with the sorption experiment results that indicated that dispersed CNTs were better sorbents than undispersed CNTs, which were used for layered and mixed CNT fixed-beds. Based on the BTC shapes and arrival times, the metal removal efficiency of the fixed-bed columns was ranked in decreasing order as: deposited CNT > mixed CNT > layered CNT > CNT-free sand.

The following three filtration performance parameters were calculated to evaluate the column packing methods against the different combination of metals in solution: removal rate (r_m), breakpoint (b_p, defined as the BV at which the metal concentration in the effluent reaches 5% of the initial metal concentration [37]), and recommended bed capacity (q_r) (Table 2). The recommended bed capacity represents the capacity in practice at which the sorbent in the fixed-bed column should be replaced or regenerated, and can be determined as [38, 39]: $q_r = \frac{C_0 \times Q}{m} \int_{t=0}^{t=t_h} (1 - \frac{C}{C_0}) dt$, where Q is the flow rate (L min^{-1}), m is mass of the sorbent in the fixed (g), t is time (min), and t_h is time when the metal concentration in the effluent reaches half of that in the influent (i.e., $C/C_0 = 0.5$). As a conservative measure, the calculated q_r of a sorbent should not exceed its Langmuir capacity, as determined from batch sorption experiment.

The CNT-free sand columns were able to remove 32.0% and 12.5% of the inputted single-metal Pb^{2+} and Cu^{2+}, respectively. In contrast, the CNT-sand columns improved the metal removal performance of the columns at r_m values of up to 75.0% for Pb^{2+} and 56.9% for Cu^{2+} for the best performing CNT packing method (deposited), and for 55.3% for Pb^{2+} and 31.4% for Cu^{2+} for the worst performing CNT packing method (layered). Whereas the range of removal efficiency varied for the three types of CNT packing, the r_m of all CNT-sand columns in all cases exceeded that for the CNT-free sand columns. The breakpoints (b_p) of the single-metal pulses in the CNT-sand columns were also much longer than those in the CNT-free sand columns. The most delayed b_p was observed for deposited CNT columns, which was recorded at 9.5 min for Pb^{2+} and 5.2 min for Cu^{2+}, indicating that metal elution in these CNT-enabled columns was delayed by more than twice the time metals were eluted from CNT-free sand columns (Table 2).

The recommended bed capacities (q_r) were the lowest for CNT-free sand columns (q_r of 0.016 mg g^{-1} for Pb^{2+} and 0.011 mg g^{-1} for Cu^{2+}, in Table 2), indicating that sand alone is not an effective heavy metal removal system. The q_r values for CNTs in all the CNT-sand columns were three to four orders of magnitude higher than that for sand, with deposited CNTs at the highest capacity and layered CNTs at the lowest (Table 2). These trends are consistent with the findings of individual material batch sorption experiments. The q_r values for deposited CNTs in CNT-sand columns (Table 2) corresponded to 87% and 63% of their measured Langmuir maximum sorption capacity q_m (Table 1) for Pb^{2+} and Cu^{2+}, respectively. The apparent reduced capacity of the metal sorption for the same quantity of CNTs when added to a fixed-bed system is likely due to the shorter residence time between metal ions and the CNTs when flow of the metal solution was passed

through the column, compared to the longer contact time between the metals and the sorbents in batch tests.

3.4. Dual metal removal in the CNT columns

The three types of CNT-sand columns were also superior at removing Pb^{2+} and Cu^{2+} simultaneously from the solution than the CNT-free sand columns (Figure 4). Similar to the single-metal experiments, the metal breakthrough in the CNT-sand columns were lower in mass and more delayed than that in the CNT-free sand columns, where deposited-CNT method was ranked with the best filtration performance. These results are in agreement with the sorption and single-metal removal experiments for dispersed CNT sorption efficiency of metals.

The presence of competing metal ions in the solution for the sorption sites reduced the removal rate, the breakpoint, and the recommended bed capacity in all the columns for the removal of the individual metals (Table 2). It is known that both Pb^{2+} and Cu^{2+} cations react strongly with the carboxyl and the hydroxyl groups of the CNT surfaces [39, 40] and competition for these sites on the CNTs is expected. As a result, the removal rates of the two heavy metal ions in the dual metal system in the three CNT-sand columns ranged from 50.2% to 63.7% for Pb^{2+} and 23.6%-39.9% for Cu^{2+}. Although the molar concentration of Cu^{2+} in the dual metal solution was much higher than that of Pb, the competition only reduced about 9-14% of Pb^{2+} removal in the three CNT-sand columns. On the other hand, the presence of Pb^{2+} reduced about 25-30% of the Cu removal. These results suggest that the functionalized CNTs have a higher affinity to Pb^{2+} than to Cu^{2+} ions in aqueous solutions. Similar trend was observed in previous studies of heavy metal

sorption onto CNTs and it has demonstrated that Pb^{2+} has a much stronger affinity to the surface function groups on CNTs than Cu^{2+} in aqueous solutions [31, 35, 39].

4. Conclusions

Laboratory experimental results indicated that functionalized multi-walled CNTs had strong sorption ability to aqueous Pb^{2+} and Cu^{2+}. Dispersion of the CNT particles enhanced their sorption ability to the heavy metals. As a result, the CNT-sand columns packed with CNT deposited method showed the best effect to remove the heavy metal from aqueous solutions. All the three CNT-sand packing methods, however, were effective and safe ways use the CNTs as filter media to remove heavy metal contaminants from water. These results suggest that, the high metal sorption affinity of CNTs along with the high porosity of natural sand could be exploited jointly in a single filter to effectively remove multiple types of heavy metals from water.

Although CNTs have been referred as potentially promising sorbents for heavy metal removal in the literature; however, little research effort has been made to apply them in fix-bed setting to purify water. As the first of this kind of study, findings from this work may inform the development of innovative and high efficiency CNT-based filters for various environmental applications, especially for the treatment of heavy metal contaminated water. With recent capacity scale-ups driving prices down ($25-38 per kg) [41], CNTs can make an important contribution to wastewater treatment.

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Tables

Table 1. Summary of the best-fit Langmuir model parameters.

Adsorbent	Pb^{2+}			Cu^{2+}		
	q_m (mg g^{-1}) / (mmol g^{-1})	K (L mg^{-1})	R^2	q_m (mg g^{-1}) / (mmol g^{-1})	K (L mg^{-1})	R^2
Single-metal						
Sand	0.027 / 1.31E-04	0.28	0.98	0.015 / 2.32E-04	0.04	0.92
Undispersed CNT	74.5 / 0.36	0.33	1.00	51.3 / 0.81	0.19	0.99
Dispersed CNT	92.3 / 0.45	0.37	0.99	67.8 / 1.07	0.31	1.00
Dual-metal						
Sand	0.018 / 8.83E-05	0.40	0.99	0.006 / 9.75E-05	0.09	0.98
Undispersed CNT	49.3 / 0.24	0.20	1.00	33.0 / 0.52	0.07	1.00
Dispersed CNT	65.0 / 0.31	0.21	0.98	43.6 / 0.69	0.13	0.99

Table 2. Summary of fixed-bed column experimental results.

Sand column	Pb^{2+}			Cu^{2+}		
	r_m	b_p	q_r	r_m	b_p	q_r
	(%)	(min)	(mg g^{-1}) / (mmol g^{-1})	(%)	(min)	(mg g^{-1}) / (mmol g^{-1})
Single-metal						
CNT-free	32.0	4.4	0.016 / 7.72E-05	12.5	1.2	0.006 / 9.44E-05
Layered CNT	55.3	6.0	25.9 / 0.13	31.4	3.1	12.6 / 0.20
Mixed CNT	65.9	7.3	44.3 / 0.21	41.6	3.3	21.1 / 0.33
Deposited CNT	75.0	9.5	80.1 / 0.39	56.9	5.2	42.6 / 0.67
Dual-metal						
CNT-free	23.1	2.4	0.011 / 5.31E-05	5.4	1.2	0.006 / 9.44E-05
Layered CNT	50.2	5.4	25.3 / 0.12	23.6	2.2	15.3 / 0.24
Mixed CNT	56.7	6.7	29.9 / 0.14	30.1	3.1	18.0 / 0.28
Deposited CNT	63.7	9.5	40.9 / 0.20	39.9	4.5	21.2 / 0.33

Figure Captions

Figure 1. FTIR spectra (average of 32 scans) of CNTs before and after heavy metal adsorption.

Figure 2. Sorption isotherms of Pb^{2+} and Cu^{2+} onto sand, and dispersed and undispersed CNTs in single and dual metal solutions.

Figure 3. Transport of Pb^{2+} and Cu^{2+} in single metal solutions through different types of fixed-bed columns.

Figure 4. Transport of Pb^{2+} and Cu^{2+} in dual metal solutions through different types of fixed-bed columns.
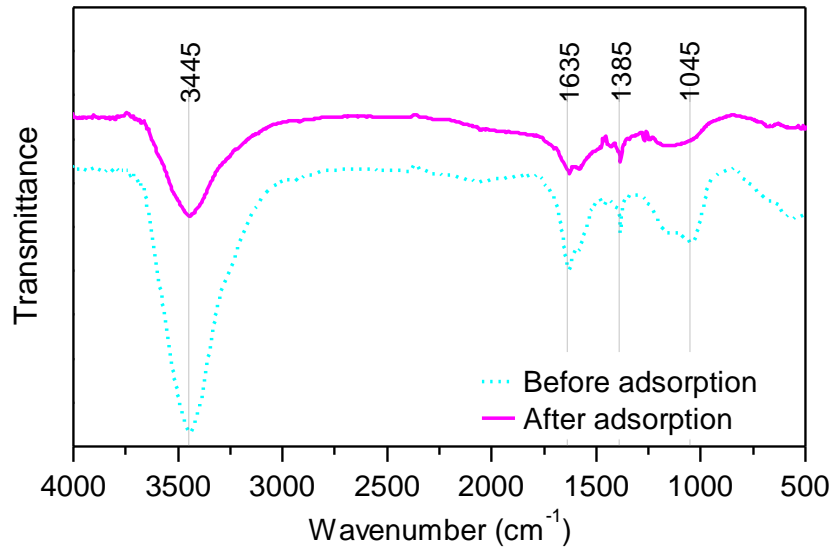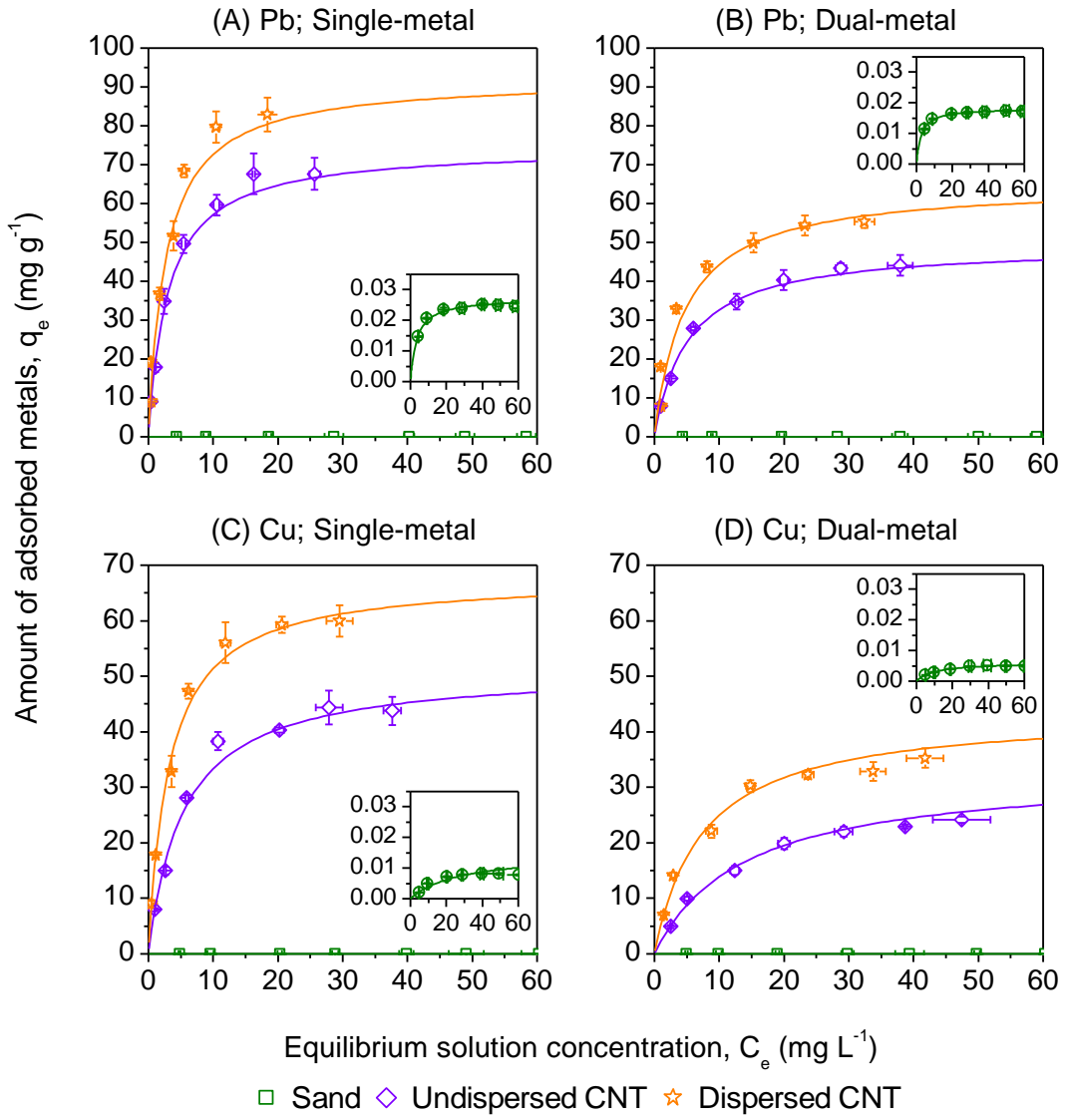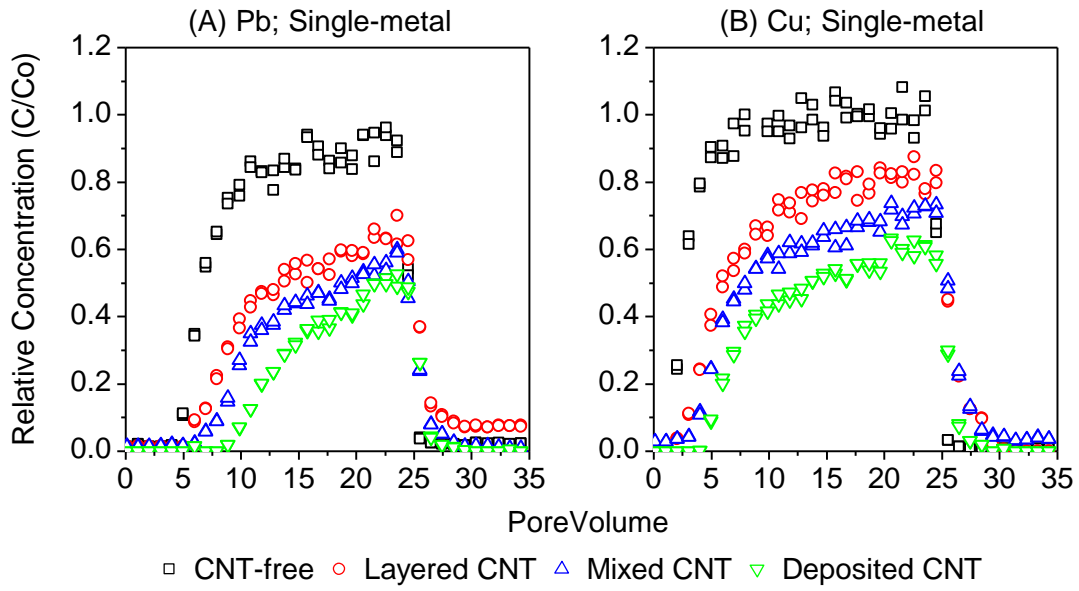
Figure 1

Figure 2

Figure 3

Figure 4

(A) Pb; Dual-metal   (B) Cu; Dual-metal

□ CNT-free   ○ Layered CNT   △ Mixed CNT   ▽ Deposited CNT