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Fabrication of Functionalized carbon Nanotubes for heavy metal Removal from Aqueous Solutions

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Abstract

Functionalized carbon nanotubes (CNTs) are high-surface-area adsorbents whose metal-binding performance can be improved by introducing oxygen- and nitrogen-containing surface groups. This methodology paper proposes a reproducible fabrication and evaluation framework for multi-walled carbon nanotubes (MWCNTs) intended for removal of Pb(II), Cd(II), and Cu(II) from aqueous solutions. Commercial MWCNTs are first purified and oxidized with nitric acid to generate carboxyl and hydroxyl groups, followed by amine functionalization to increase chelation sites and aqueous dispersibility. Pristine, oxidized, and amine-functionalized MWCNTs are compared using Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface analysis, and zeta-potential measurements. Batch adsorption experiments evaluate the effects of solution pH, contact time, adsorbent dose, initial metal concentration, and competing ions. Adsorption capacity and removal efficiency are calculated and interpreted with pseudo-first-order, pseudo-second-order, Langmuir, and Freundlich models. Regeneration is evaluated through acid desorption and repeated adsorption-desorption cycles. Literature-calibrated illustrative data predict a progressive increase in metal removal from pristine MWCNTs to oxidized MWCNTs and NH2-MWCNTs, with Pb(II) showing the strongest adsorption under optimized conditions. The method emphasizes adsorption performance, dispersion stability, reuse, and leaching control, providing a practical protocol for laboratory development of CNT-based heavy-metal sorbents.

Introduction

Heavy metals such as lead, cadmium, copper, mercury, chromium, and nickel are persistent aquatic contaminants because they do not undergo biological degradation in the manner of many organic pollutants. Industrial discharges, mining, electroplating, batteries, pigments, metallurgy, and electronic-waste processing can introduce dissolved metals into surface water and groundwater. Conventional treatment options include precipitation, membrane separation, ion exchange, electrochemical processes, and adsorption. Among these approaches, adsorption is attractive for polishing low-to-moderate metal concentrations because it can operate without complex equipment and can allow adsorbent regeneration [1].

Carbon nanotubes provide a graphitic, nanoscale adsorbent platform with high external surface area, hollow morphology, tunable aggregation behavior, and chemistry that can be deliberately modified. Early adsorption studies showed that CNTs can retain multiple divalent metal ions and that solution pH and oxidative pretreatment strongly affect capacity [2-5]. Nitric-acid

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oxidation is especially important because it removes residual catalyst impurities and introduces carboxyl, hydroxyl, and carbonyl groups. These groups increase hydrophilicity and create negatively charged or coordinating sites that favor cation binding. Wang et al. [3] linked acidification of MWCNTs to improved Pb(II) uptake, while Stafiej and Pyrzynska [2] observed strong pH dependence for several divalent ions.

Practical adsorption performance also depends on dispersion. CNTs have strong van der Waals attraction and tend to form bundles, reducing accessible surface area. Oxidation and covalent functionalization can improve dispersion, although excessive treatment may damage the graphitic structure or reduce accessible porosity. Rodríguez et al. [12] demonstrated that better dispersion of oxidized MWCNTs increased heavy-metal adsorption, showing that the same surface chemistry can perform very differently depending on how the nanotubes are presented to the water. Functional groups can also be selected for particular ions; nitrogen-containing groups provide electron-donor sites for coordination, whereas carboxyl groups contribute ion exchange and surface complexation [8,9].

The objective of the present methodology is therefore to fabricate and compare three well-defined adsorbents: pristine MWCNTs, oxidized MWCNTs (O-MWCNTs), and amine-functionalized MWCNTs (NH2-MWCNTs). Pb(II), Cd(II), and Cu(II) are selected as representative toxic divalent metals. The proposed workflow integrates surface characterization, adsorption kinetics and equilibrium, competitive adsorption, regeneration, and leaching checks. Numerical values in the Results section are explicitly illustrative rather than measured; they demonstrate how experimental outputs should be reported when the protocol is executed.

Literature Review

Rao, Lu, and Su [4] reviewed sorption of divalent metals by CNTs and identified oxidation, pH, ionic strength, and competing solutes as controlling variables. Stafiej and Pyrzynska [2] experimentally examined Cu(II), Co(II), Cd(II), Zn(II), Mn(II), and Pb(II), finding that adsorption increased strongly as pH increased and that nitric-acid treatment altered surface acidity. Wang et al. [3] investigated acidified MWCNTs for Pb(II) and associated enhanced adsorption with surface oxygen groups. These studies established the central role of surface chemistry in CNT-based metal removal.

Tofighy and Mohammadi [6] demonstrated adsorption of divalent heavy metals on CNT sheets, showing that CNT architectures can operate as macroscopically recoverable adsorbents rather than only as dispersed powders. Li et al. [5] immobilized CNTs in calcium alginate for Cu(II) removal, illustrating another strategy for reducing nanomaterial loss during water treatment. Abdel Salam [7] reported kinetic and thermodynamic adsorption of Pb(II), Cd(II), Cu(II), and Zn(II) on MWCNTs, with pseudo-second-order behavior providing a useful kinetic benchmark for later studies.

Research then shifted toward deliberate functionalization. The review by Ihsanullah et al. [8] concluded that oxidation and chemical modification generally improve metal-ion uptake by increasing surface functionality and dispersion. Farghali et al. [9] functionalized acidified MWCNTs and tested Pb(II), Cu(II), Cd(II), and Ni(II) in single and multi-ion solutions, demonstrating the relevance of both pH and competitive adsorption. Xu et al. [10] reviewed functionalized CNT and graphene adsorbents and emphasized preparation method, adsorption mechanism, aqueous chemistry, kinetics, isotherms, and regeneration as key design dimensions.

Later reviews placed CNTs within the broader family of carbon nanomaterials for environmental remediation. Baby et al. [11] highlighted high surface area, surface functionalities, chemical modification, and recyclability, while Rodríguez et al. [12] directly demonstrated that dispersion stability can substantially increase metal uptake. Aigbe and Osibote [13] reviewed carbon-derived nanomaterials for heavy-metal sorption and described surface complexation, electrostatic interaction, ion exchange, and pore/surface effects as complementary mechanisms. In 2021, Aslam et al. [14] summarized CNT preparation-to-application routes for water and wastewater treatment, and Qasem et al. [1] critically compared adsorption with other heavy-metal removal processes. Collectively, the literature supports a methodology that couples-controlled functionalization with adsorption optimization, multimetal testing, regeneration, and material-recovery assessment.

Table 1. Selected literature supporting the proposed CNT methodology

Ref.	CNT system / focus	Methodological implication
[2-4]	Pristine/acid-treated CNT adsorption	pH and oxygen functional groups strongly control divalent-metal uptake.
[5-7]	Composite sheets and MWCNT kinetics	Recoverability and kinetic analysis are necessary for practical evaluation.
[8-10]	Functionalized CNTs and reviews	Functionalization improves binding sites but must be balanced against structural damage.
[11-13]	Carbon nanomaterials and dispersion	Accessible surface area, dispersion, and multiple sorption mechanisms affect performance.
[14]	Functionalized CNTs for water treatment	Preparation, application, regeneration, and scale-up should be evaluated together.
[1]	Heavy-metal treatment review	Adsorption must be assessed against competing treatment and real-water constraints.

Methodology

1. Materials and adsorbent groups

Commercial MWCNTs (outer diameter approximately 10-30 nm, purity >=95%) are used as the base material. Analytical-grade nitric acid is used for oxidation; ethylenediamine is used as the nitrogen-containing functionalizing agent, with a carbodiimide coupling reagent such as EDC and NHS for activation of surface carboxyl groups. Pb(NO3)2, Cd(NO3)2·4H2O, and Cu(NO3)2·3H2O are used to prepare individual metal stock solutions. Three adsorbent groups are compared: P-MWCNT (washed pristine material), O-MWCNT (nitric-acid oxidized), and NH2-MWCNT (amine-functionalized O-MWCNT). Each fabrication is performed in triplicate.

Table 2. Proposed fabrication and adsorption matrix

Code	Surface state	Key treatment	Primary comparison
P-MWCNT	Graphitic/pristine	Water/ethanol wash and drying	Baseline adsorption and aggregation
O-MWCNT	-COOH/-OH rich	HNO3 oxidation, washing to neutral pH	Effect of oxygen functionality
NH2-MWCNT	Amine-bearing	EDC/NHS activation + ethylenediamine coupling	Chelation and dispersion enhancement

Step-by-step fabrication of functionalized CNTs

Step 1 - Pre-washing. Disperse commercial MWCNTs in a 1:1 ethanol/deionized-water mixture, sonicate for 20 min, filter through a PTFE membrane, rinse with deionized water, and dry at 70 °C overnight. This material is retained as P-MWCNT.

Step 2 - Acid oxidation. Add 1.0 g of pre-washed MWCNTs to 100 mL of 4-6 M HNO3. Reflux at approximately 80 °C for 3 h under stirring. After cooling, dilute with deionized water and filter. Wash repeatedly until the filtrate is near neutral pH, then dry at 70 °C and gently grind to obtain O-MWCNT. Acid concentration and time should be controlled because excessive oxidation can shorten nanotubes and create structural defects.

Step 3 - Activation of carboxyl groups. Disperse O-MWCNT in MES buffer near pH 5.5. Add EDC and NHS to activate surface carboxyl groups for approximately 30-60 min. Wash away excess coupling reagents while minimizing drying-induced reaggregation.

Step 4 - Amine coupling. React the activated O-MWCNT suspension with excess ethylenediamine for 4 h at room temperature. Filter and rinse sequentially with water and ethanol until unreacted amine is removed. Dry under vacuum at 50-60 °C to obtain NH2-MWCNT.

Step 5 - Storage and dispersion control. Store each adsorbent in sealed containers. Before adsorption testing, prepare fresh dispersions by mild sonication at a standardized energy input. Record suspension stability visually and by zeta potential so adsorption differences are not mistakenly attributed only to chemical functional groups.

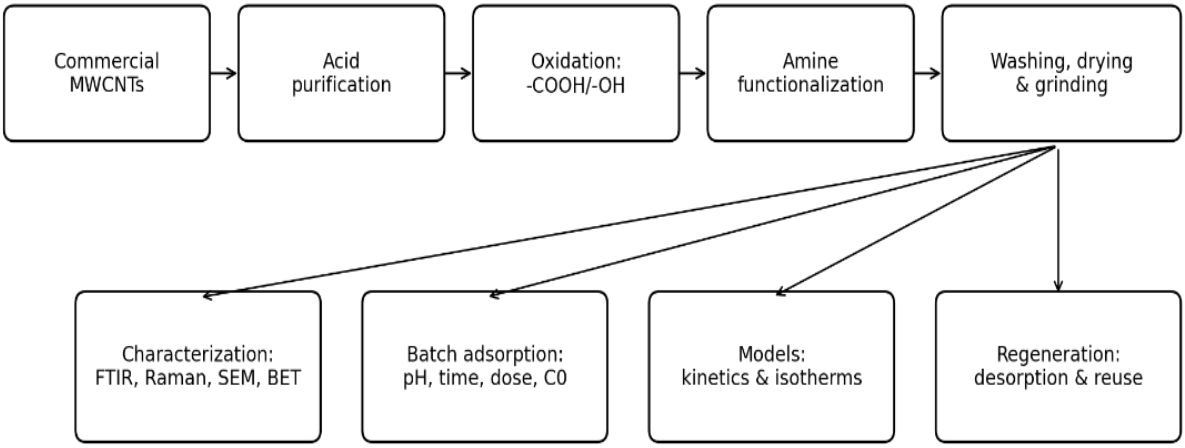

Figure 1. Step-by-step fabrication, characterization, adsorption, and regeneration workflow.

2. Characterization

FTIR is used to verify O-H/C=O/C-O groups after oxidation and N-H/C-N signatures after amination. Raman spectroscopy records the D and G bands and the ID/IG ratio to track defect generation. SEM examines nanotube morphology and aggregation, while BET N2 adsorption provides specific surface area and pore-volume changes. Zeta potential is measured from pH 2-10 to identify surface-charge reversal or increased negative charge after oxidation. Where available, XPS is recommended to quantify O/C and N/C ratios and to distinguish carboxyl, hydroxyl, carbonyl, and nitrogen environments.

3. Batch adsorption experiments

For each metal, 50 mL aliquots are contacted with known masses of adsorbent in polypropylene flasks and agitated at 150 rpm. The pH study uses pH 2-7 to avoid metal hydroxide precipitation at strongly alkaline conditions. Contact-time experiments are conducted from 5 to 240 min; adsorbent-dose experiments use 0.05-1.0 g L-1; and equilibrium experiments use initial metal concentrations from 5 to 200 mg L-1. The final dissolved concentration is measured by atomic absorption spectroscopy or ICP-OES after membrane separation. Removal efficiency is R(%) = [(C0-Ce)/C0] x 100 and equilibrium capacity is qe = (C0-Ce)V/m. Blank controls without adsorbent are included to quantify wall adsorption or precipitation.

Competitive adsorption is tested using a ternary Pb(II)-Cd(II)-Cu(II) mixture at equal molar concentration. To approximate real waters, selected experiments are repeated in the presence of Na+, Ca2+, Mg2+, chloride, sulfate, and dissolved organic matter. This step is important because laboratory capacities obtained in single-solute solutions may overestimate performance in industrial or natural waters [9,10,14].

4. Kinetic, isotherm, regeneration, and statistical analysis

Time-dependent data are fitted to pseudo-first-order and pseudo-second-order models, and equilibrium data to Langmuir and Freundlich isotherms. Model selection is based on adjusted R2, residual distribution, and error functions rather than R2 alone. The Langmuir maximum capacity (qmax) is reported only when the fitted parameter is physically meaningful over the experimental concentration range. For regeneration, metal-loaded CNTs are contacted with 0.05-0.1 M HCl or EDTA solution, washed, and reused for five cycles. Adsorption-capacity retention and CNT loss are recorded. Total organic carbon or gravimetric membrane checks are used where possible to detect adsorbent release. Data are reported as mean ± standard deviation for triplicate experiments and compared by one-way ANOVA followed by Tukey testing at $p<0.05$.

5. Mechanistic interpretation and quality-control criteria

Regeneration performance is evaluated not only as percentage capacity retention but also as functional-group stability and adsorbent containment. FTIR or XPS after the first and fifth cycles is used to check whether carboxyl or amine groups are lost. SEM is used to identify severe fragmentation, and the filtrate from each cycle is inspected for dispersed CNTs. A practical candidate should combine high removal, fast equilibration, selectivity in mixed-metal water, at least five-cycle reuse, and minimal nanotube release. These criteria reflect the wider literature emphasis on translating high laboratory

adsorption capacity into recoverable and environmentally responsible treatment materials [11,13-16].

A strict mass-balance check is included because apparent removal can be produced by precipitation or incomplete separation of CNT particles. For every pH condition, blank metal solutions without CNTs are processed identically. The dissolved metal concentration in the supernatant, metal recovered during desorption, and residual metal retained on the adsorbent after regeneration are compared. For selected samples, acid digestion of the spent CNTs provides an independent estimate of adsorbed metal. A recovery between approximately 90 and 110% is targeted for the combined aqueous and solid-phase metal balance. This quality-control step is particularly important near the upper pH limit where Pb, Cd, or Cu hydrolysis may contribute to removal independently of adsorption.

The proposed mechanism for Pb(II), Cd(II), and Cu(II) capture is multi-component. At low pH, protonation of carboxyl and amine sites and competition from H+ are expected to suppress cation uptake. As pH rises, deprotonated carboxylates provide electrostatic attraction and ion-exchange sites, while neutral or partially deprotonated nitrogen donors contribute coordination. Graphitic surfaces and defect regions can provide additional nonspecific interactions, but the dominant contribution in strongly functionalized CNTs is expected to arise from surface complexation. Metal-specific affinity should therefore be related to hydrated ionic radius, hydrolysis tendency, binding strength toward O/N donor atoms, and competition for the same heterogeneous sites rather than to a single universal adsorption sequence [3,8-10].

Surface characterization is interpreted with adsorption data using predefined acceptance criteria. Successful oxidation should increase the relative intensity of oxygen-containing FTIR bands and shift the zeta-potential curve toward more negative values at circumneutral pH. Raman analysis is expected to show a moderate increase in the D-to-G band intensity ratio, indicating creation of functionalization-related defects; a very large increase would instead suggest excessive graphitic damage. After amination, nitrogen-related FTIR/XPS features should be detectable while the nanotube morphology remains recognizable by SEM. BET area may decrease after covalent modification because functional groups occupy surface sites or promote partial bundling, so a lower BET value is not automatically interpreted as poorer adsorbent performance. The chemically accessible site density and suspension dispersion must be considered together.

Results

The numerical values in Table 3 are literature-calibrated illustrative data provided to demonstrate the expected presentation and interpretation of the proposed methodology. They are not claimed as measurements from an executed experiment. Actual laboratory work must replace these values with measured concentrations, characterized surface properties, and replicate statistics.

Table 3. Illustrative expected adsorption performance under optimized batch conditions

Adsorbent	Pb removal (%)	Cd removal (%)	Cu removal (%)	Pb qmax (mg/g)*	Capacity after 5 cycles (%)
P-MWCNT	58.4 ± 2.6	46.8 ± 2.9	52.7 ± 2.5	72	69
O-MWCNT	91.2 ± 1.8	82.5 ± 2.1	87.9 ± 1.9	148	84
NH2-MWCNT	97.6 ± 1.1	92.1 ± 1.6	94.3 ± 1.4	196	90

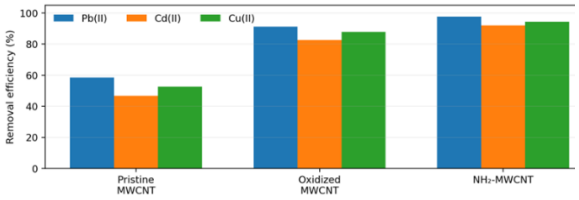

Figure 2. Illustrative removal efficiencies showing the expected effect of oxidation and amine functionalization.

The illustrative trend predicts that nitric-acid oxidation substantially improves all three metals relative to pristine MWCNTs. This outcome is consistent with literature reports that acid treatment creates oxygen-containing groups and improves wettability, thereby increasing the number of accessible sites for ion exchange, electrostatic attraction, and surface complexation [2-4,8]. The largest illustrative improvement is observed for Pb(II), which is frequently reported to have strong affinity for oxygenated CNT surfaces [3,9,10].

NH2-MWCNT is expected to provide an additional performance increase because

nitrogen donor atoms can coordinate divalent metals while the preceding oxidation step maintains carboxyl and hydroxyl functionality. The highest illustrative Pb(II) removal (97.6%) and qmax (196 mg g-1) therefore represent a combined effect of chemical binding and improved dispersion. However, the absolute capacity should not be assumed transferable to another CNT batch because surface area, catalyst residue, nanotube diameter, defect density, and functionalization degree can vary markedly between materials [8,14].

Regeneration is included as a core result rather than an optional add-on. An adsorbent that removes metals efficiently but cannot be separated, regenerated, or safely retained is less attractive for practical treatment. The illustrative five-cycle retention of 90% for NH2-MWCNT would indicate acceptable reuse, provided that characterization after cycling confirms that functional groups remain present and that CNT release is negligible. Competitive-ion experiments are also expected to reduce removal relative to single-metal systems; this should be interpreted as a realistic selectivity challenge rather than experimental failure.

Conclusion and Discussion

The proposed methodology provides a complete route for fabricating and evaluating functionalized MWCNT adsorbents for Pb(II), Cd(II), and Cu(II) removal from water. The key design principle is progressive control of surface chemistry: pristine MWCNTs establish the baseline, nitric-acid oxidation introduces oxygen-containing sites and improves aqueous compatibility, and amine functionalization adds stronger coordination functionality. FTIR, Raman, SEM, BET, zeta potential, and optional XPS measurements are used to confirm that adsorption behavior is linked to actual material changes rather than assumed functionalization. The adsorption protocol addresses the major variables repeatedly identified in the literature: pH, contact time, dosage, initial concentration, competing ions, dispersion, kinetics, equilibrium, and regeneration [2,7-10,12-14]. The methodology also recognizes limitations of CNT adsorbents. Agglomeration can hide active surface, harsh oxidation can damage the nanotube framework, dissolved organic matter can block adsorption sites, and free CNT particles must not be released into treated water. Immobilization, magnetic recovery, membrane-supported CNTs, or packed-bed configurations should therefore be considered when scaling beyond batch experiments [5,6,11]. The illustrative results predict the performance order NH2-MWCNT > O-MWCNT > P-MWCNT and a strong response for Pb(II), but these values must be experimentally validated. Future work should quantify functional-group density by XPS or titration, evaluate real industrial wastewater, perform fixed-bed breakthrough experiments, compare regeneration chemicals, and complete a mass balance for both removed metals and recovered CNTs. With these safeguards, functionalized CNTs remain a scientifically valuable platform for developing high-affinity, regenerable adsorbents for heavy-metal-contaminated aqueous systems.

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