Supporting Materials for

Synergistic Interactions between Multi-Walled Carbon Nanotubes and Toxic Hexavalent Chromium

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Figure S1 UV-vis absorption of the supernatant of 1000.0 µg L⁻¹ Cr (VI) solution (20.0 mL) with different pH values after 30.0-min treatment with 20.0 mg MWNTs at room temperature.

Figure S2 UV-vis absorption of the supernatant of 20.0 mL pH=1.0 Cr(VI) solution with different initial Cr(VI) concentrations after 30-min treatment with 20.0 mg MWNTs at room temperature.
**Figure S3** UV-vis absorption of the supernatant of 20.0 mL pH=1.0 Cr(VI) solution with different initial Cr(VI) concentrations after 30-min treatment with 20.0 mg oxidized MWNTs by nitric acid at room temperature.

**Figure S4** UV-vis absorption of the supernatant of 20.0 mL 1000.0 µg L⁻¹ pH=1.0 Cr(VI) solution after 30-min treatment with different doses of MWNTs at room temperature.
**Figure S5** Cr 2p XPS spectra of the 20.0 mg MWNTs after 20-min treatment with pH=1.0, 2 g L\(^{-1}\) Cr(VI) solution.

**Figure S6** Raman spectrum of the MWNT sample treated with 1000 µg L\(^{-1}\) pH=1.0 Cr(VI) solution for 5 min.
Confirmation of Carboxylate Groups Formation:

**Figure S7** FT-IR spectra of (a) the as-received MWNTs and (b) the MWNTs after 60-min treatment with 20 mL 1000 µg L\(^{-1}\) pH=1.0 Cr(VI) solution.

In Figure S7, the new peaks at around 1635 and 1400 cm\(^{-1}\) appear, which correspond to the vibration of the carboxyl (C=O) and carboxylate (COO\(^-\)) groups,\(^1\) respectively.

**Figure S8** (a) UV-vis spectra of the supernatant of 20.0 mL 1000 µg L\(^{-1}\) Cr (VI) pH=1.0 solution after treated with 20.0 mg MWNTs for different time; and (b) Cr(VI) final concentration of 20.0 mL Cr (VI) pH=1.0 solution with an initial concentration of 1000 µg L\(^{-1}\) after treated with 20.0 mg MWNTs for different time at room temperature.
Adsorption Kinetics

The adsorption kinetics describes the Cr(VI) uptake rate, which controls the residue time of the adsorbent at the solid-solution interface and can define the efficiency of the adsorption.\(^2\) The amount of adsorbed Cr(VI) \((Q_t, \text{mg g}^{-1})\) at time \(t\) was calculated using Equation (S1):

\[
Q_t = \frac{(C_0 - C_t)V}{m_s}
\]

where \(C_0\) is the initial Cr(VI) concentration (\(\mu\text{g L}^{-1}\)) and \(C_t\) represents the Cr(VI) concentrations in \(\mu\text{g L}^{-1}\) at the time \(t\) (min). Recently, pseudo-second-order behavior has been applied to the Cr(VI) adsorption by pomegranate husk carbon, hazelnut shell activated carbon, poly(methylacrylate) functionalized guar gum, and sphagnum moss peat.\(^3-6\) The pseudo-second-order adsorption kinetic rate is described as Equation (S2):\(^5\)

\[
\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2
\]

where \(k_2\) is the pseudo-second-order adsorption rate constant, (g mg\(^{-1}\) min\(^{-1}\)), \(Q_e\) stands for the adsorption capacity at equilibrium time, (mg g\(^{-1}\)). Applying the boundary conditions: \(t=0, Q_t=0\) and \(t=t, Q_t=Q_e\), Equation (S2) is integrated to Equation (S3):

\[
\frac{1}{(Q_e - Q_t)} = \frac{1}{Q_e} + k_2t
\]

(S3)

Equation (S3) can be rearranged:

\[
\left(\frac{t}{Q_t}\right) = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}(t)
\]

(S4)

The \(t/Q_t \sim t\) is observed to be a straight line, and \(Q_e\) and \(k_2\) were calculated from the slope coefficient (\(1/Q_e\)) and intercept (\(1/k_2Q_e^2\)) of the plot. The initial adsorption rate, \(h\) (mg g\(^{-1}\) min\(^{-1}\)) is defined as Equation (S5):\(^7\)

\[
h = k_2Q_e^2
\]

(S5)
Figure S9 (a) UV-vis spectra of the supernatant of 20.0 mL 1000 µg L⁻¹ Cr (VI) pH=7.0 solution after treated with 20.0 mg MWNTs for different time; (b) Cr(VI) final concentration of 20.0 mL Cr (VI) pH=7.0 solution with an initial concentration of 1000 µg L⁻¹ after treated with 20.0 mg MWNTs for different time at room temperature; and (c) Cr(VI) removal rate $Q_t$ vs time $t$.

References: