Supporting Information

Effective adsorption of chromium(VI)/Cr(III) from aqueous solution using ionic liquid functionalized mulitwalled carbon nanotube as a super sorbent

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1. Materials.

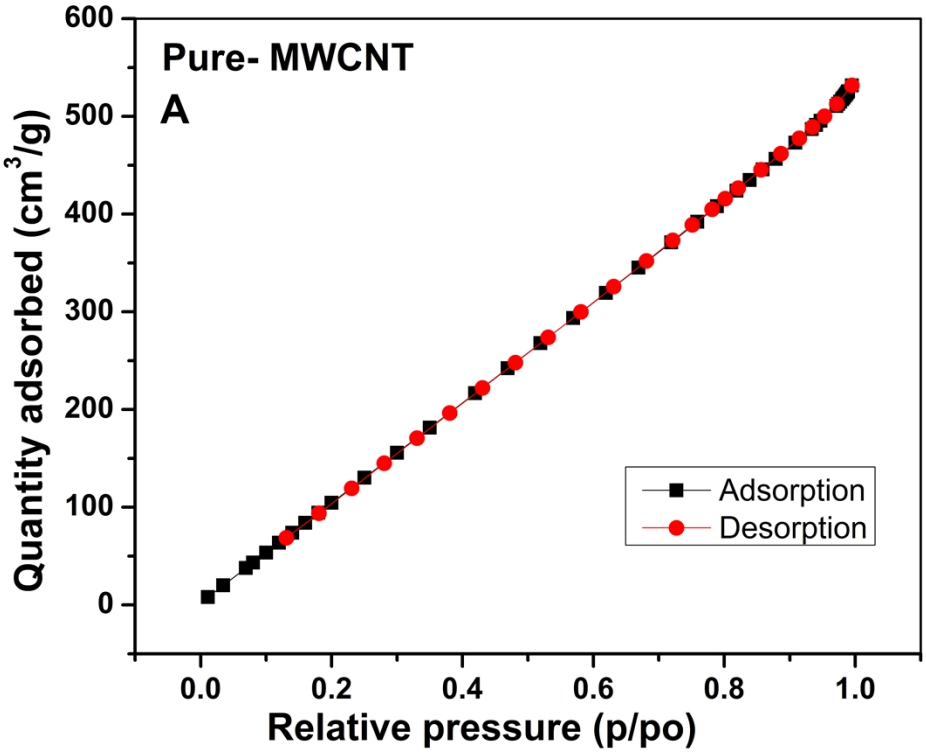
The starting material, mutiwalled carbon nanotube was procured from Sigma Aldrich. A stock solution of 1000 mg L^{-1} Cr(VI) solution was prepared using A. R. grade potassium dichromate a working solution of 20 mg L^{-1} for batch adsorption was prepared by appropriate dilution with Milli Q water. Tetra n heptylammonium bromide was purchased from Alfa Aesar. The other required reagents were procured from Merck Chemicals respectively.

2. Instruments and Characterizations.

Transmission electron microscope (TEM) images were obtained using a PHILIPS CM-200 TWIN instrument an operating voltage of 200 kV. The sample for TEM measurement was prepared by placing a drop of sample solution on a carbon-coated copper grid and dried at 30 °C. Nitrogen adsorption– desorption isotherms were measured with a Micromeritics ASAP 2010 instrument, samples were out gassed for 10 h under vacuum at 200 ^{0}C before measurement. The Brunauer–Emmett–Teller (BET) method was used to calculate the surface areas. The pore size distributions

were derived from the adsorption branches of the Barrett–Joyner–Halenda (BJH) method. Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (^{13}CPMAS-NMR) was analyzed Varian Innova Unity 500 MHz Solid State NMR Spectrometer by superconducting magnet 11.4 Tesla (Proton operating frequency : 500MHz). Raman spectra were recorded on a WITec Confocal Raman Microscope Alpha 300R using a 532 nm He-Ne laser with 5 mW. A Kratos Axis Ultra X-ray Photoelectron Spectroscopy (XPS) instrument was used to record samples, X-ray sources: 500 mm Rowland Circle Monochromator Al Mg/Al achromatic Source 450W max power. The spectra were recorded using a monochromatic Al Kα X-ray source (15 mA, 14 KV). The pressure in the analyzer chamber was 1 x 10^{-8} Torr, surface charging effects were corrected with carbon 1s peak at 284.6 eV as a reference. The conditions applied for the survey scans includes an energy range 0-1200 eV and the survey spectra were collected at pass energy of 160 eV and a step size of 0.7 eV. High resolution spectra were collected using 40 eV pass energy, spot size of 300 x 700 μm slot and 0.05 eV step size. A Perkin Elmer Fourier Transform Infrared Spectroscopy (FT-IR) spectrum100 spectrometer was used to characterize the material functional groups identifications in the range 500−4000 cm^{-1} by mixing 0.01g of the material with 0.1g KBr (spectroscopy grade). The morphology of the samples was studied with a JEOL JSM-6330TF analyzer were used to observe the morphological changes scanning electron microscope(SEM) were recorded and the energy dispersive X-ray analysis spectrum (EDX) was recorded adsorbent and after the adsorption of Cr(VI). Ultraviolet visible spectroscopy (UV–visible) was taken out by the use Jasco V-630 UV–visible spectrometer (Jasco, Japan). Powder X-ray diffraction (Powder-XRD) was carried out on a D8 Discover X-ray diffractometer with Cu Ka radiation (k = 0.1541 nm, Bruker, Germany) was utilized to record the characteristic changes in the diffraction pattern of the adsorbent. The pH adjustments of the aqueous solutions were done using METTLER TOLEDO pH meter S20. The concentration of chromium in the aqueous solution was measured using inductively coupled plasma

mass spectrometry (ICP-MS) Perkin-Elmer, Sciex- Elan DRC Plus, Sotware which we used Elan-6100 DRC PLUS respectively.



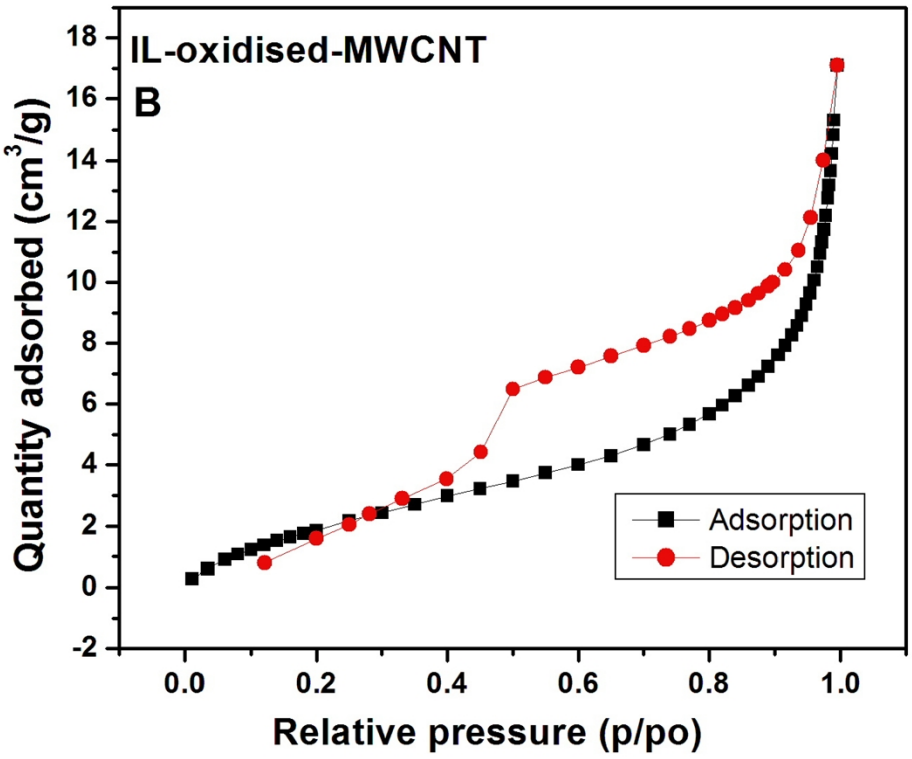


Figure S1. BET Nitrogen adsorption and desorption isotherm (A) Pure MWCNT's (B) IL-oxi-MWCNT's adsorbent

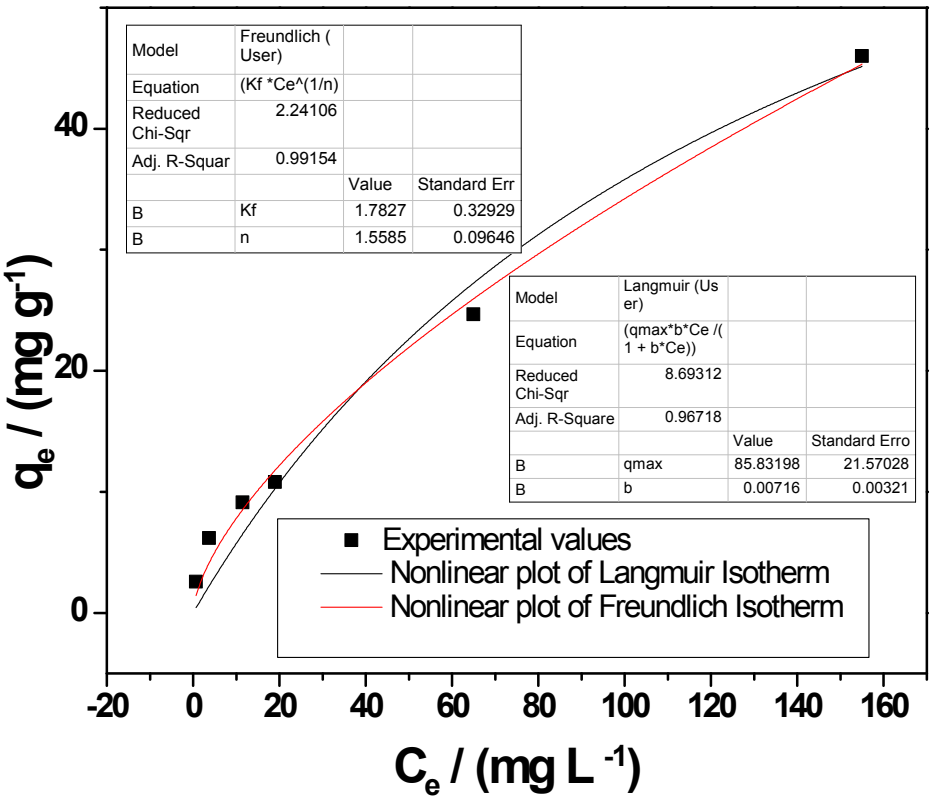


Figure S2 Effect of Langmuir and Freundlich isotherm

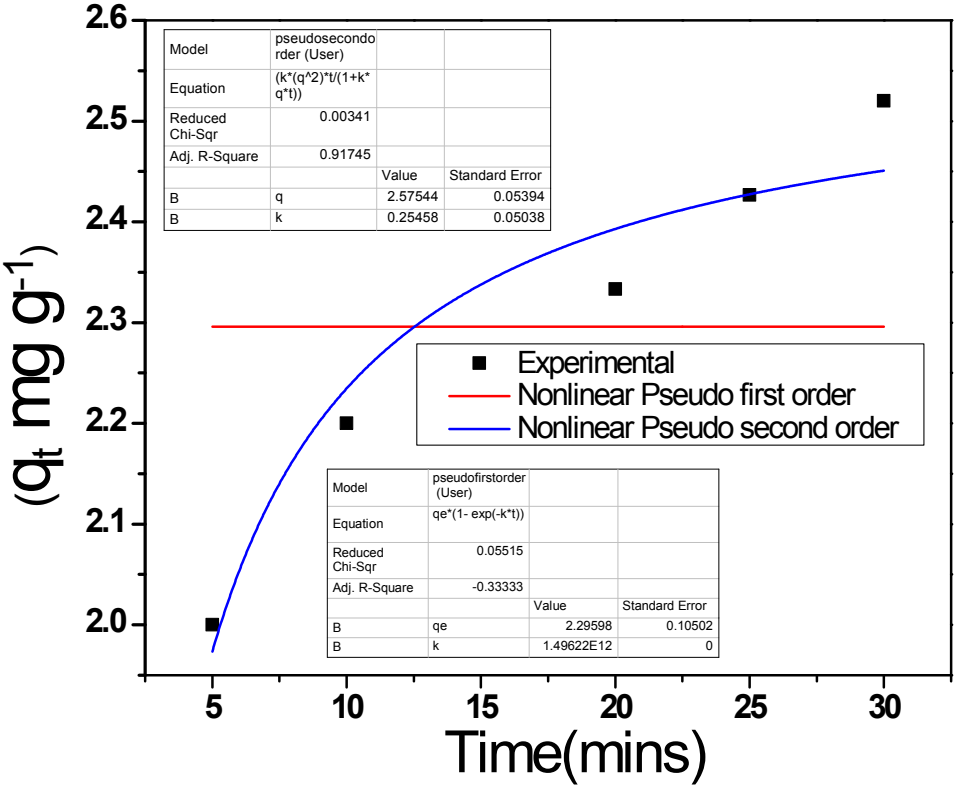


Figure S3 Effect of pseudo first order and pseudo second order kinetics

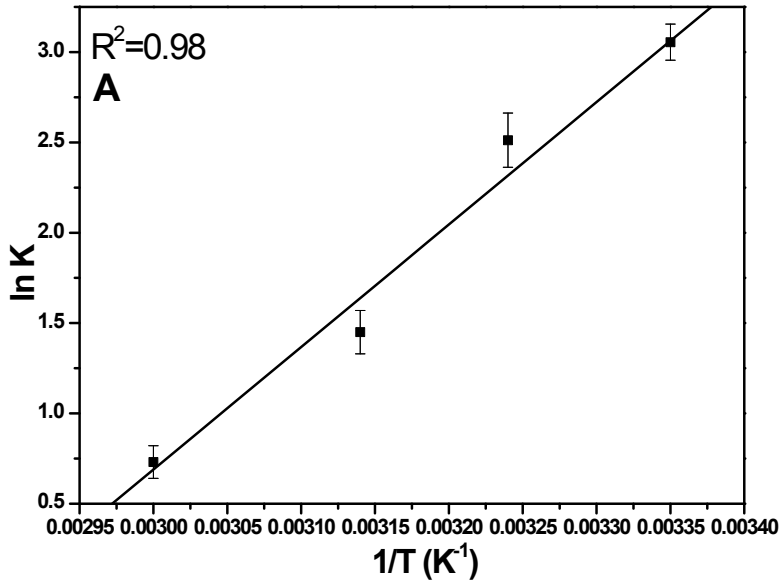


Figure S4A. Van't Hoff Plot.

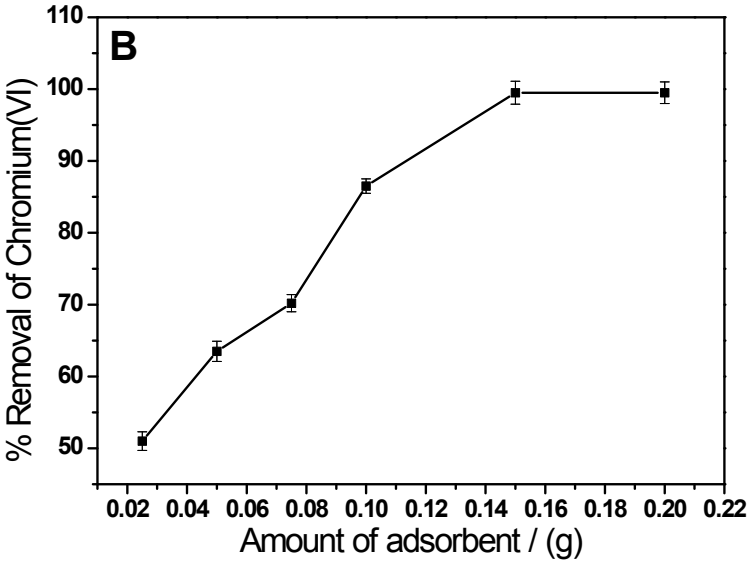


Figure S4B. Amount of adsorbent

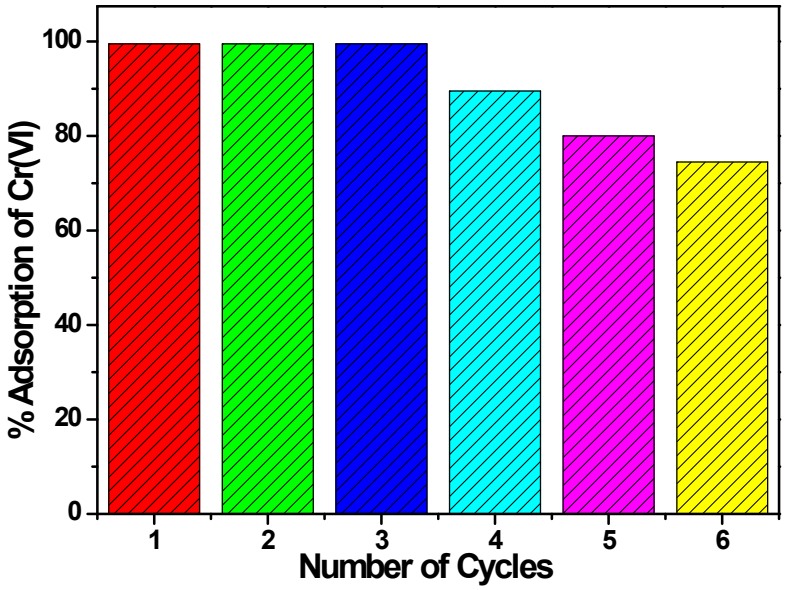


Fig. S4C Adsorbent regeneration cycles

Table T1. Operating conditions of ICP-MS analysis

SI.No	ICP-MS plasma	Parameters
1	RF power	1300 W
2	Plasma gas (Ar) flow rate	15 L min^{-1}
3	Auxiliary gas (Ar) flow rate	1.325 L min^{-1}
4	Carrier gas (Ar) flow rate	0.97 L min^{-1}
5	Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
6	Data acquisition scanning mode	Peak-hopping
7	Dwell time	50 ms
8	Points per spectral peak	1
9	Isotopes	^{53}Cr
10	Integration mode	Peak area

Table T2. Isotherm parameters

Sl. No	Isotherm	Non-Linear Equation	Characteristic values	
1	Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	q_{max} (mg g^{-1})	85.83
			b (L mg^{-1})	0.0071
			R_L	0.875
			Adj. R^2	0.96
			SSE	34.77
			χ2 red	8.69
			AIC	18.54
2	Freundlich	$q_e = K_F C_e^{1/n}$	K_F (mg $^{1-1/n}$ g^{-1} $L^{1/n}$	1.78
			n	1.55
			Adj R^2	0.99
			SSE	8.96
			χ2 red	2.24
			AIC	10.40

Table T3. Adsorption kinetics

Sl. No	Kinetic parameters	Non-Linear Equation	Characteristic values	
1	Pseudo first order	$q_t = q_e\left(1 - e^{-K_1 t}\right)$	q_e (mg g^{-1})	2.29
			k_1	1.49
			Adj. R^2	-0.33
			$\chi 2$ red	0.05
2	Pseudo second order	$q_t = \frac{k_2 q_e^2}{1 + k_2 q_e t}$	q_e (mg g^{-1})	2.57
			k_2	0.25
			Adj R^2	0.91
			$\chi 2$ red	0.003

Table T4. Adsorption thermodynamics

Temperature/ (Kelvin)	ΔG^0/ (kJ mol^{-1})	ΔS^0/ (J mol^{-1} K^{-1})	ΔH^0/ (kJ mol^{-1})
298	-7.56	-56.38	-163.37
308	-6.43		
318	-3.83		
333	-2.02		