Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information (SI)

Surface functional groups and defects on carbon nanotubes affects adsorption-desorption hysteresis of metal cations and oxoanions in water

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SI-1. Metal ion species distribution

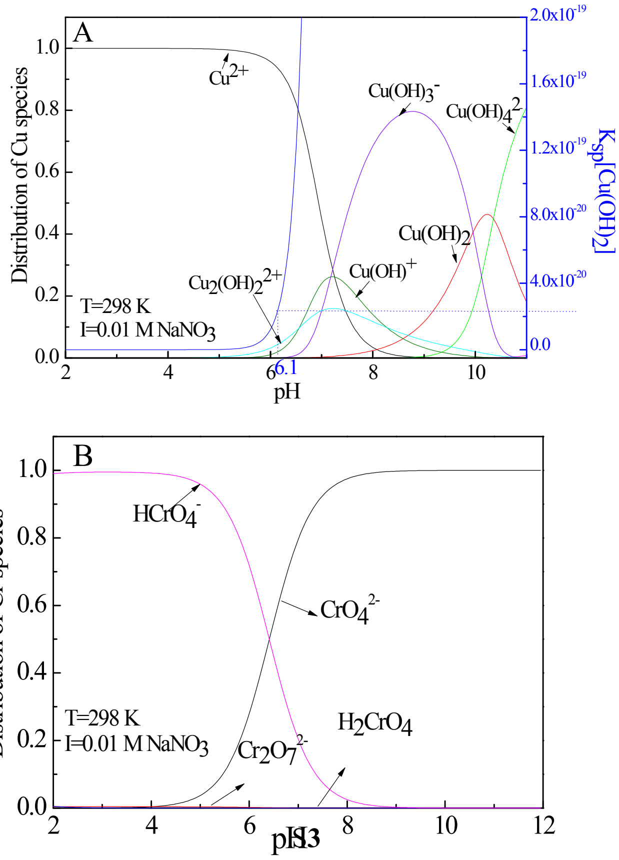
Copper as well as other heavy metal ions, is considered as high relative mammalian toxic which can often be detected in chemical effluents. However, with the rapid industrialization, too many Cu-based chemicals from copper mining activities, smelting, electroplating industries, and brass manufacture make copper-pollution more severe.[1,2] As is known to all, the continued inhalation of copper containing sprays is relevance with an increase in lung cancer among exposed workers, therefore the removal of copper can be paid significant attention.[3] As a matter of fact, such methods to remove Cu(II) from industrial wastewaters, as chemical precipitation, coagulation, ion exchange, electrolytic methods, reverse osmosis and adsorption were reported. Among them, adsorption is considered more effective especially in the trace amounts cases for its far higher capacity and selectivity.

Chromium, one of the most highly toxic heavy metal pollutants in wastewater, is widely used in a variety of industries, such as pharmacy, electroplating, tanning, metallurgy, battery, textile and catalyst synthesis. Cr(VI) is a known carcinogen [4] which is listed in the 25 most toxic hazardous elements posing the greatest risk to human health and environment. Because of its high toxicity, it is necessary to remove Cr(VI) from industrial wastewater before discharging it into inland surface water in order to prevent its deleterious impact on the ecosystem and public health. Elevated concentrations of chromium in drinking water are linked to health problems such as lungs cancer, bronchial asthma, stomach cancer and hepatotoxicity [5] in human health because of its high toxicity, World Health Organization [6] have set the maximum permissible limit as 0.05 mg L^{-1}. Chromium exists in different oxidation states ranging from −2 to +6. In aqueous solution, Cr(VI) exists in different ionic forms such as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or hydrochromate ($HCrO_4^{-}$). The proportion of Cr(VI) ions in solution is pH-dependent as CrO_4^{2-} ions dominate in the neutral and basic pH while $Cr_2O_7^{2-}$ ions are the dominant species at low pH. Such pH-dependency of different ionic species in aqueous solution makes Cr(VI) separation also pH-dependent.[7]

Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, the use of arsenic pesticides, herbicides or crop desiccants and the use of arsenic additives to livestock feed create additional impacts. Two predominant species found in natural waters are inorganic forms of arsenic namely, arsenate As(V) and arsenite As(III). Their presence depends on the pH and redox conditions of the medium. As(V) which is the thermodynamically stable form, is found in oxic surface waters, rivers and lakes.[8] Furthermore, arsenate possesses three pKa values (2.3, 6.99 and 11.80),[9] therefore in most of natural waters, As(V) exists mainly in the $H_2AsO_4^{-}$ or $HAsO_4^{2-}$ forms.[10] Arsenic in natural waters is a serious worldwide problem. Long term drinking water exposure causes skin, lung, bladder and kidney cancer as well as pigmentation changes, skin thickening, neurological disorders, muscular weakness, loss of appetite and nausea. Because of this, World Health Organization (WHO), European Union (EU) and US Environmental Protection Agency (USEPA) set the maximum permissible limits for arsenic in drinking water as 10 µg $L^{-}1$.[11] To achieve this, the only possible way is to remove arsenic from water.

Table S1. **Equilibrium constants logK_a of Cu(II), Cr(VI) and As(V) hydrolysis reactions**

Hydrolysis reactions	logK_a
Cu(II)[12]	
$Cu^{2+} + OH^{-} = Cu(OH)^{+}$	-7.5
$2Cu^{2+} + 2OH^{-} = Cu_2(OH)_2^{2+}$	-10.4
$Cu^{2+} + 2OH^{-} = Cu(OH)_2^{0}$	-17.3
$Cu^{2+} + 3OH^{-} = Cu(OH)_3^{-}$	-27.3
$Cu^{2+} + 4OH^{-} = Cu(OH)_4^{2-}$	-39.6
Cr(VI)[9]	
$CrO_4^{2-} + 2H^+ = H_2CrO_4$	6.31
$CrO_4^{2-} + H^+ = HCrO_4^-$	6.51
$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O$	14.56
As(V)[13]	
$H_2AsO_4^- + H^+ = H_3AsO_4$	2.30
$HAsO_4^{2-} + H^+ = H_2AsO_4^-$	6.99
$AsO_4^{3-} + H^+ = HAsO_4^{2-}$	11.80



S3

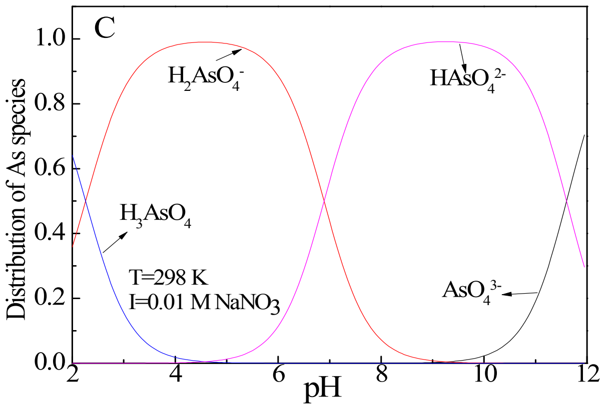


Fig. S1 Cu(II), Cr(VI) and As(V) species distribution as a function of pH based on the equilibrium constants.

SI-2. Boehm titration method

Surface acidic groups (i.e., carboxyl, hydroxyl and lactonic groups) of carbon nanotubes (CNTs) were determined using Boehm titration method.[14] Prior to measurement, the CNTs were equilibrated with dilute HNO_3 at pH=1 for 3 days, followed by a thorough washing with deionized water, and then dried in 105 ^{o}C for 48 h. The weighted CNTs (0.25 g) were mixed with 20 mL of 0.02 mol/L NaOH, 0.01mol/L Na_2CO_3 and 0.01 mol/L $NaHCO_3$, respectively. Blank experiments without CNTs were prepared for each experimental condition and all samples, including the blanks, were run in duplicate. The mixtures were shaken for 48 h (200 rpm) and then centrifugated at 18000 g for 10 min, followed by filtration using 0.22 micron filters to separate the CNTs. 15 mL of the filtrate was mixed with 15 mL 0.02 mol/L HNO_3 and the excess acid was titrated with 0.01 mol/L NaOH, using phenolphthalein indicator. Surface acidity was calculated based on the assumption that $NaHCO_3$ neutralizes carboxyl groups only, Na_2CO_3 neutralizes carboxyl and lactonic groups, and NaOH neutralizes all acidic groups including carboxyl, lactonic and hydroxyl groups.

SI-3. XPS analysis

The CNTs' chemical composition was determined using X-ray photoelectron spectroscopy (XPS). For XPS, CNTs were adhered to double-sided copper tape and mounted onto a sample stub. Care was taken to ensure that the CNTs completely covered the copper tape. In all XPS experiments, AlKα (1376.0 eV) X-ray radiation was generated from a Φ 04–500 X-ray source.

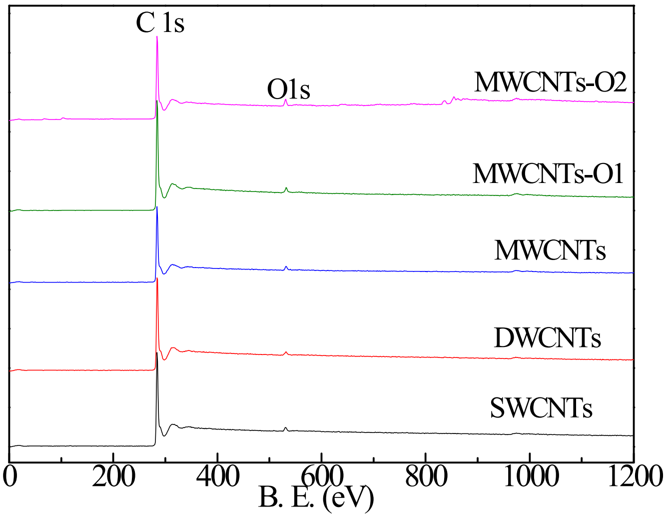
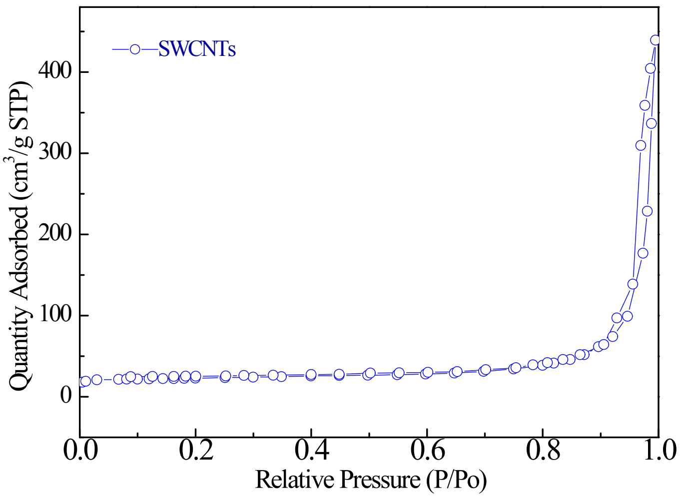
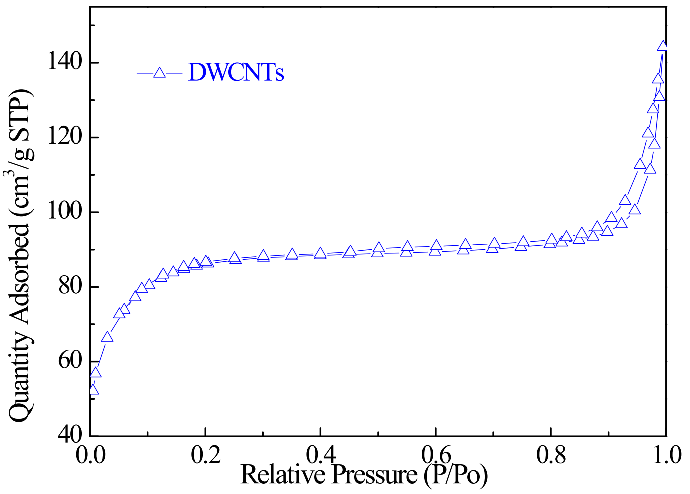


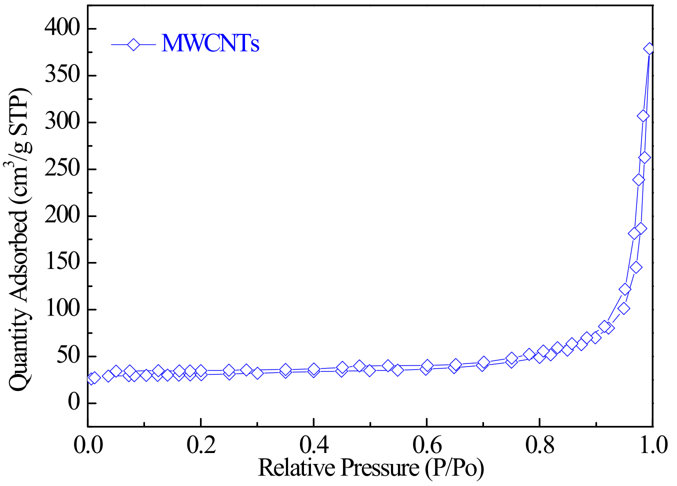
Fig. S2 XPS survey spectra of five CNTs.

SI-4. BET measurement

For BET measurement of CNT SSA, N_2 adsorption data at 77 K were obtained using a high-resolution gas adsorption analyzer with high vacuum capacity (10-3 mmHg) (TriStar II 3020 V1.03 Micromeritics). All samples were outgassed at 300 ^{o}C for 5 h prior to analysis.


SWCNTs
Quantity Adsorbed (cm^3/g STP)
400
300
200
100
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)


DWCNTs
Quantity Adsorbed (cm^3/g STP)
140
120
100
80
60
40
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)


MWCNTs
Quantity Adsorbed (cm^3/g STP)
400
350
300
250
200
150
100
50
0
0.0
0.2
0.4
0.6
0.8
1.0
Relative Pressure (P/Po)

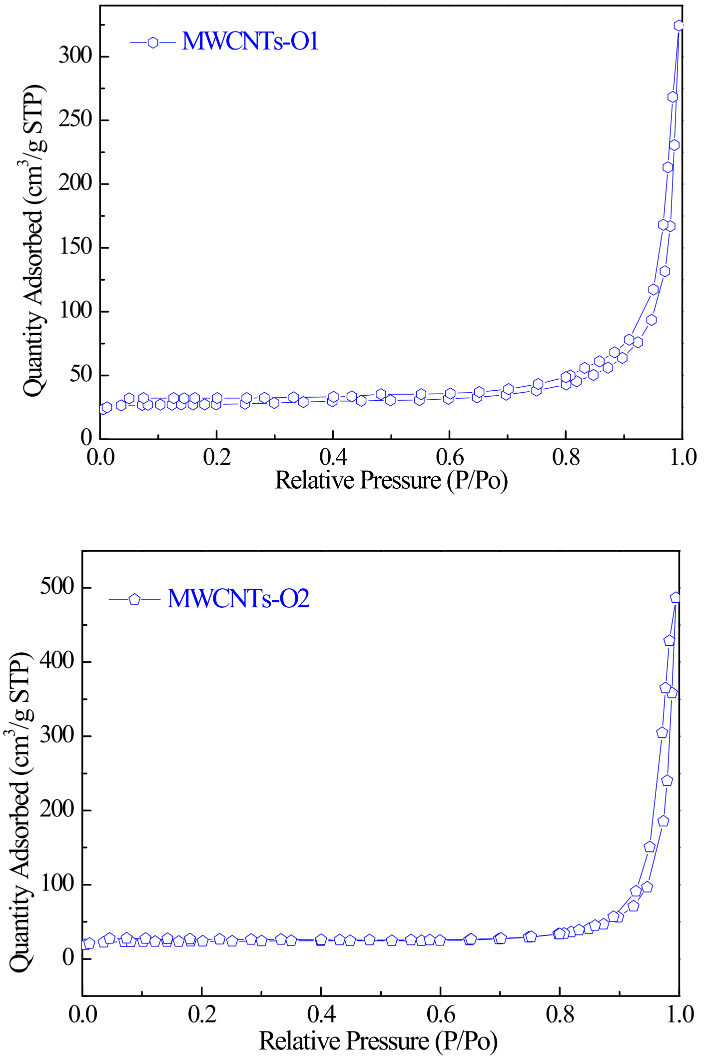


Fig. S3 Adsorption-desorption isotherms of N_2 on five CNTs.

Table S2 The Langmuir model fitted results to adsorption-desorption on CNTs.

CNTs	pH	Adsorption				Desorption 1			Desorption 2		
		Q_{max} (mmol/g)	Q_{max}/ASS (μmol/m^2)	b (L/mmol)	R^2	Q_{max} (mmol/g)	b (L/mmol)	R^2	Q_{max} (mmol/g)	b (L/mmol)	R^2
Cu(II)											
SWCNTs	5.0	0.689±0.046	1.813±0.042	16.77±3.59	0.958	1.125±0.114	11.91±3.15	0.970	1.134±0.414	5.123±6.83	0.963
DWCNTs	5.0	0.659±0.091	2.221±0.050	22.62±5.98	0.912	1.108±0.160	11.23±2.80	0.964	1.118±0.132	13.40±5.81	0.935
MWCNs	5.0	0.584±0.079	4.431±0.452	39.9±2.54	0.997	1.011±0.287	21.91±9.97	0.932	1.031±0.273	11.02±4.66	0.942
MWCNs-O1	5.0	0.755±0.030	8.324±0.331	70.2±10.5	0.959	1.134±0.099	19.94±3.43	0.975	1.161±0.025	18.60±5.54	0.960
MWCNs-O2	5.0	0.783±0.007	9.962±0.089	43.5±7.31	0.965	1.145±0.218	26.74±6.02	0.951	1.278±0.295	33.25±6.71	0.971
Cr(VI)											
SWCNTs	4.0	0.040±0.002	0.105±0.068	51.79±8.25	0.974	0.043±0.002	102.5±17.48	0.945	0.045±0.002	163.5±25.4	0.956
DWCNTs	4.0	0.042±0.003	0.140±0.055	55.17±10.65	0.951	0.050±0.002	73.90±7.28	0.985	0.056±0.004	113.9±18.9	0.963
MWCNs	4.0	0.045±0.003	0.341±0.038	44.97±6.99	0.971	0.056±0.001	229.9±17.32	0.986	0.059±0.007	239.8±96.4	0.968
MWCNs-O1	4.0	0.038±0.002	0.419±0.026	41.41±10.41	0.914	0.041±0.002	132.9±25.33	0.928	0.044±0.003	206.3±21.1	0.976
MWCNs-O2	4.0	0.036±0.001	0.447±0.007	84.15±19.67	0.925	0.037±0.002	48.06±8.58	0.954	0.041±0.001	63.76±9.93	0.978
As(V)											
SWCNTs	4.0	0.038±0.009	0.100±0.050	21.54±5.54	0.959	0.077±0.006	12.42±5.31	0.964	0.082±0.044	15.25±6.88	0.969
DWCNTs	4.0	0.041±0.010	0.137±0.022	26.97±7.31	0.949	0.081±0.045	53.71±7.13	0.981	0.085±0.036	52.39±9.89	0.974
MWCNs	4.0	0.045±0.013	0.341±0.038	29.33±8.98	0.938	0.089±0.039	51.34±8.20	0.974	0.103±0.001	28.69±10.5	0.957
MWCNs-O1	4.0	0.033±0.029	0.364±0.008	9.734±7.07	0.911	0.075±0.004	16.90±5.28	0.953	0.080±0.009	18.12±6.28	0.974
MWCNs-O2	4.0	0.031±0.006	0.394±0.020	3.189±1.21	0.905	0.065±0.011	5.25±2.73	0.978	0.067±0.017	19.5±20.1	0.955

All estimated parameter values and their standard errors determined by Origin 7.0 software programs. Desorption 1 is hysteresis indexes of the first desorption cycle. Desorption 2 is hysteresis indexes of the second desorption cycle.

SI-5. Adsorption and desorption kinetics

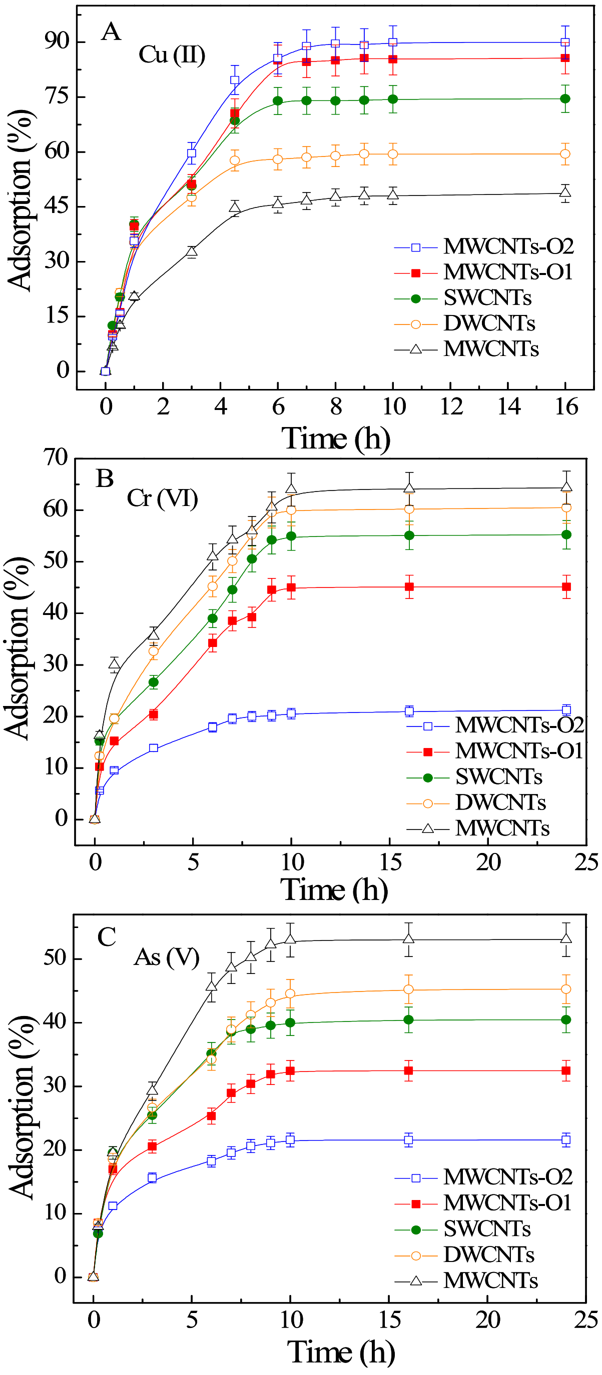


Fig. S4 Adsorption kinetics on the five types of CNTs, Cu(II) (A), Cr(VI) (B) and As(V) (C), at $C_{\mathrm{Cu(initial)}}$ = 0.15 mmol/L, $C_{\mathrm{Cr(initial)}}$ = $C_{\mathrm{As(initial)}}$ = 0.05 mmol/L, pH =5.0 for Cu(II) and pH = 4.0 for Cr(VI) and As(V) , m/V = 1.0 g/L, I = 0.01M $NaNO_3$, and T = 298 K.

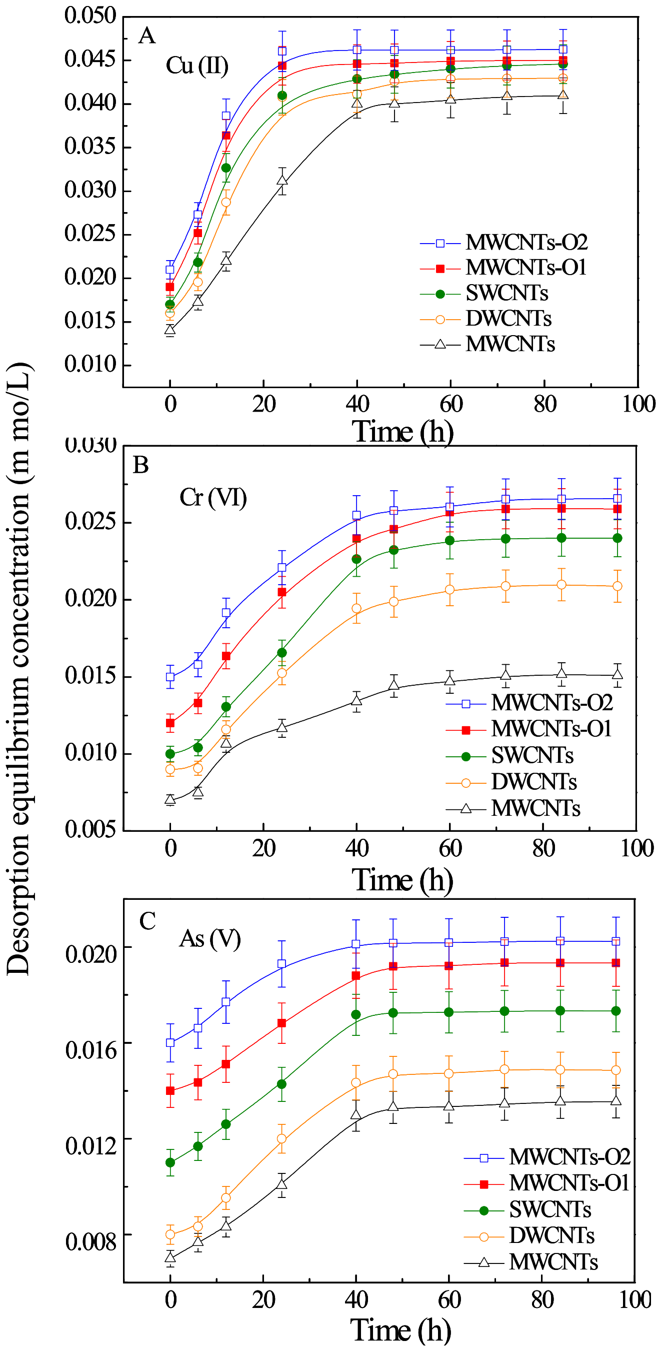


Fig. S5 Desorption kinetics on the five types of CNTs, Cu(II) (A), Cr(VI) (B) and As(V) (C), at pH =5.0 for Cu(II) and pH =4.0 for Cr(VI) and As(V) , m/V = 1.0 g/L, I = 0.01 M $NaNO_3$, and T = 298 K.

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