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SUPPLEMENTARY MATERIAL TO

Removal of heavy metals from water using multistage functionalized multiwall carbon nanotubes

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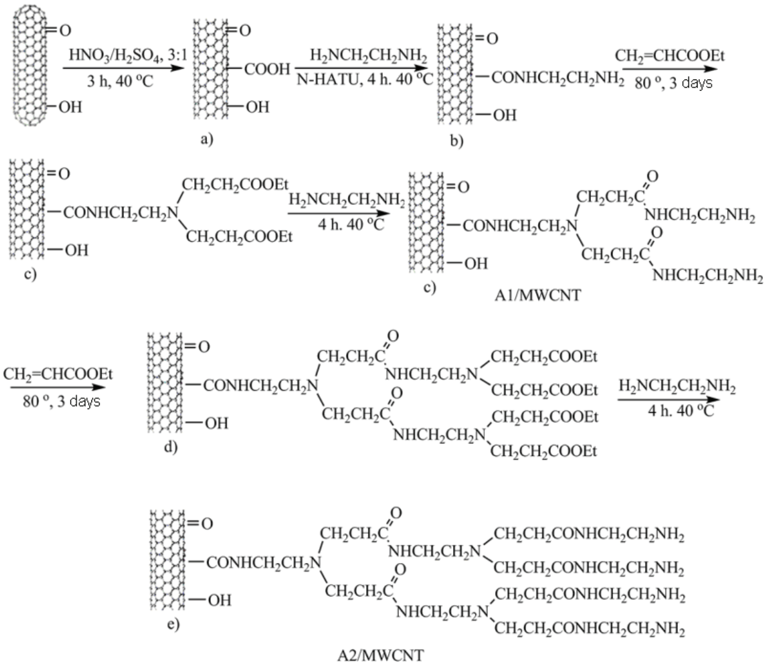

Scheme S-1. Schematic presentation of the modifications of MWCNT: a) oxidation, b) functionalization with EDA, c) nucleophilic addition of on EA and d) and e) synthesis of second generation of adsorbent.

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Adsorption experiments

Solutions of Cd^{2+}, Pb^{2+} and As(V) ions with initial concentrations, C_i, of 0.1, 0.2, 0.5, 1, 2, 5 and 10 mg L^{-1} were used in the batch adsorption experiments. In order to investigate the influence of pH values on the adsorption of Cd^{2+}, Pb^{2+} and As(V) ions, initial pH values of the solutions were varied between 3.0 and 10.0. Thermodynamic and kinetic experiments were performed at 298, 308 and 318 K. The influence of reaction time on the lead and cadmium ions adsorption was monitored in the interval between 5 and 90 min. The amount of the adsorbed ions was calculated from the difference between the initial and equilibrium concentration. Furthermore, the influence of the ultrasound on the adsorption process during the stirring of the adsorbent–adsorbate solution was investigated in the preliminary trials in order to compare it to classic stirring methods.

The results were analyzed using normalized standard deviation, Δq / %, calculated using Eq. (S-1):

$$\Delta q(\%) = 100\sqrt{\sum \frac{\left[(q_{\mathrm{exp}} - q_{\mathrm{cal}}) / q_{\mathrm{exp}}\right]^2}{N-1}} \qquad \text{(S-1)}$$

where q_{exp} and q_{cal} are experimental and calculated amounts of Cd^{2+}, Pb^{2+} and As(V) ions adsorbed on A1/ and A2/MWCNT, and As(V) ions adsorbed on A1/ and A2/MWCNT–α-FeO(OH),and$N$ is the number of data used in the analysis. The adsorption experiments were performed in triplicate and only mean values were reported. Maximum deviation is <3 % (experimental error). The kinetic, isotherm and thermodynamic parameters and their standard errors were calculated, using commercial software (OriginPro 8).

Concentrations of Cd^{2+}, Pb^{2+} and As(V) ions were measured using Agilent Technologies 7500ce ICP-MS system (Agilent Technologies, Inc.).

Adsorbent characterization

Adsorbent was characterized with different methods. Specific surface area, pore volume, and pore size distribution were obtained from the nitrogen adsorption–desorption isotherm measured at 77.4 K using a Micrometrics ASAP 2020 V1.05H surface area analyser.The FTIR measurements were performed at room temperature in the transmission mode between 400 and 4000 cm^{-1}, at resolution of 4 cm^{-1}using a BOMEM (Hartmann & Braun) spectrometer. Scanning electron microscopy was performed with field emission scanning electron microscopy (FE-SEM) and electronic microscope SUPRA 35 VP (Carl Zeiss). The pH values at the point of zero charge (pH_{PZC}) were measured using the pH drift method.[1,2] The amino group content in modified MWCNT was determined with the indirect volumetric titration[3] according to the following procedure: 10 mg of modified MWCNT was dispersed in 20 mL of 1.0 mmol L^{-1}

HCl solution and stirred for 30 min. MWCNTs was separated by centrifugation at 15000 rpm for 10 min, and 10 mL of supernatant was collected to be titrated with the standardized 1.0 mmol L^{-1} NaOH solution in the presence of phenolphthalein indicator. From the difference of HCl concentration after treating with modified MWCNT, the molar concentration of amine sites on the modified MWCNT (10 mg) was calculated.

TABLE S-I. FTIR spectra wavelengths (cm^{-1}) of the adsorbent A2/MWCNT after Cd^{2+} and Pb^{2+} solution treatment and adsorbent A1/MWCNT–α-FeO(OH) after solution treatment (C_i= 5 mg L^{-1}, m/V=100 mg L^{-1}, pH 6.0)

Bond	Complex		
	A2/MWCNT/Cd^{2+}	A2/MWCNT/Pb^{2+}	A1/MWCNT–α-FeO(OH)/As(V)
N–H	3362	3367	–
NH_2	800, 3400	800, 3400	–
C–H	2934	2932	–
C=O	1738	1734	–
C=N	1640	1647	–
C–N	–	1297	–
C–O	1045, 1185	1048, 1187	–
Fe–OH	–	–	1124, 1043, 974
As–O	–	–	824
As–O–Fe	–	–	866

Morphological analysis

The morphology and structure of A2/MWCNT and A1/MWCNT–α-FeO(OH) samples are studied with SEM microscopy and representative images are shown in Fig. S-1. These figures show that the basic and smooth structure of A2/MWCNT and A1/MWCNT-α-FeO(OH) is altered due to the modification process.

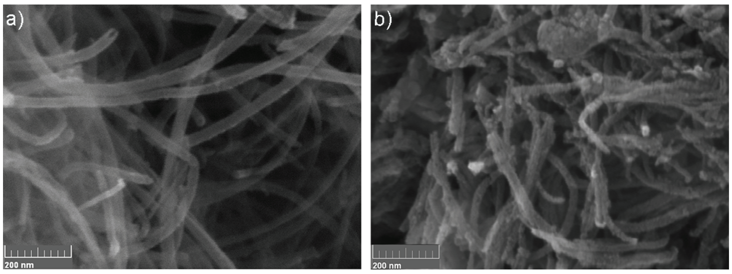

Fig. S-1. SEM images of A2/MWCNT(a) and A1/MWCNT–α-FeO(OH) (b) adsorbent.

The similar morphologies of both adsorbents A2/MWCNT and A1/MWCNT–α-FeO(OH) can be noticed. The coarse surface of A1/MWCNT–α-FeO(OH) is changed due to modification/precipitation of nanoscale deposit α-FeOOH on the surface of A2/MWCNT precursor material.

Adsorption parameters

Table S-II. Adsorption isotherm parameters for As(V) on A1/MWCNT–α-FeO(OH) and Pb^{2+} and Cd^{2+} on A2/MWCNT

	Dubinin–Radushkevich								
q_m / mg g^{-1}	20.440	21.160	21.800	18.718	20.006	20.883	15.93	16.23	16.56
B	8.61	8.58	8.57	9.312	9.245	9.202	8.46	8.44	8.44
E / kJ mol^{-1}	7.619	7.634	7.633	7.327	7.354	7.371	7.689	7.698	7.707
Δq/ %	13.33	14.21	13.7	17.23	17.11	16.56	9.13	9.21	9.23
R^2	0.845	0.860	0.847	0.749	0.766	0.775	0.901	0.901	0.907
	Temkin								
B / mg g^{-1}	4.70	4.86	4.90	5.118	5.400	5.539	2.67	2.72	2.71
B	526.97	527.43	540.22	484.37	474.43	477.54	928.8	943.1	974.6
Δq/ %	16.01	16.88	18.00	21.05	20.32	19.96	10.12	11.89	10.05
R^2	0.845	0.843	0.824	0.731	0.733	0.738	0.902	0.903	0.909

Surface complex formation

The maximum adsorption capacity of the adsorbent increases in the temperature range from 298 to 318 K (Table III), suggesting that a complex adsorption mechanism is operative. Changes in the contributions of an appropriate adsorption mechanisms, such as co-existence of physisorption, that is, the exchange of ions, electrostatic and chemisorption, namely the creation complex on the surface change in the course of establishment of equilibrium. On the surface of the adsorbent A2/MWCNT, a large number of free amino groups exist (Table I), so the interaction among other additional coordinations and electrostatic interactions between the $Cd^{2+}$and/or $Pb^{2+}$and unprotonated amino groups, at pH value higher than pK_a, are possible:

$$\text{A2/MWCNT–NH}_2\text{+Cd}^{2+}\leftrightarrow \text{Cd[A2/MWCNT-NH}_2]^{2+} \tag{S-2}$$
$$\text{A2/MWCNT–NH}_2 + \text{Pb}^{2+}\leftrightarrow\text{Pb[A2/MWCNT-NH}_2]^{2+} \tag{S-3}$$

In addition, the amino groups on the adsorbent can be incorporated into chelating interactions during the adsorption process Cd^{2+}[14] and Pb^{2+}.[4]

Divalent cations can form complexes with amino groups, and favourable interaction can occur at pH higher than pK_a (pK_a 3–6), where amino groups exist in ionized form and can readily interact with divalent cations. The modification reaction and proposed adsorption mechanism are shown in Scheme S-1, and Eqs. (S-2) and (S-3), respectively. The adsorption capabilities of surface functional groups on A2/MWCNTadsorbent and potential interactions with divalent cation binding depend primarily on the solution pH.[5,6]

Deposition of iron(oxy)hydroxide nanoparticles of in the form of goethite on A2/MWCNT contributed to improvement of adsorption efficiency of the adsorbent with respect to As(V) anion. It is known from previous studies that iron in the form of goethite has good sorption characteristics according to arsenic.[7–9] For A1/

/MWCNT–*α*-FeO(OH) at $pH < 7.12$ (pH_{PZC}), the positively charged surface of adsorbent attracts the negatively charged arsenate ions, while at $pH > pH_{PZC}$ electrostatic repulsion between arsenate ions and surface takes place, causing the decrease of the amount of arsenate adsorbed. At lower pH values, the surface charge is neutralized by the attraction of H_3O^+, and the adsorption of arsenic species takes place. In the pH range 3.0–5.0, when the highest adsorption degree was obtained for A1/MWCNT–*α*-FeO(OH), in the water solution are dominant $H_2AsO_4^-$ (Fig. 3c). The adsorption Gibbs energy change of $H_2AsO_4^-$ may be lower than that of $HAsO_4^{2-}$ and AsO_4^{3-}, and this would explain why $H_2AsO_4^-$ adsorption is more favourable.[6,7]

Competitive adsorption of As(V) on A1/MWCNT–α-FeO(OH)

Adsorption study in a non-competitive condition offers limited results for the consideration of affinity/selectivity of adsorbents surface sites with respect to ions commonly present in natural water. It is of particular interest to study effects of competitive anions, like bicarbonate, sulphate, phosphate, silicate, chromate, fluoride and selected natural organic matter (NOM), on the efficiency of arsenate adsorption. These anions generally co-exist in natural water and groundwater. In this study, humic acid (HA) was chosen as a representative of NOM due to the prevalence of humic-like substances in surface waters and wastewater effluent. As it is seen in Fig. S-3, the presence of these competitive anions and HA shows certain interferences on the arsenate adsorption, similar to published research.[4]

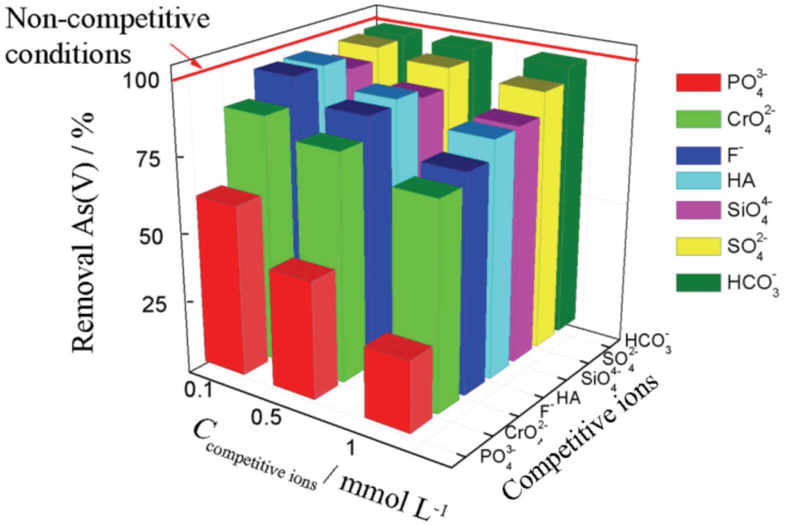

Fig. S-3. Effects of co-existing anions and HA in solution on the As(V) adsorption on A1/MWCNT–*α*-FeO(OH); $C_{i[As(V)]} = 0.2$ mg L^{-1}, $m/V = 100$ mg L^{-1}, $T = 298$ K, pH 6.0).

Single competitive As(V) adsorption study (Fig. S-3) showed the highest influence of phosphate, followed by chromate and fluoride. Similar chemistry of arsenate with respect to phosphate and chromate was reflected in a competitive adsorption for the same adsorption sites which contribute to the significant decrease of the efficiency of arsenate removal.

Competitive adsorption of Cd^{2+} and Pb^{2+} on A2/MWCNT

To examine the effects of competitive metal ions on adsorption onto testing materials, batch adsorption experiments were carried out by using binary metal solutions of Cd^{2+} and Pb^{2+}. The binary metal solutions of Cd^{2+} to Pb^{2+} were placed in the relationship shown in Fig. S-4, with the appropriate initial concentrations of Cd^{2+} 0.2 mg L^{-1} and Pb^{2+} 0.5 mg L^{-1}.

Similar results for the competive adsorptios of Cd^{2+} and Pb^{2+} have been reported.[10–14] The adsorption capacity of the lead uptake is slightly improved, while the adsorption capacity of cadmium is slightly decreased when compared with the adsorption capacities of the single solutions.

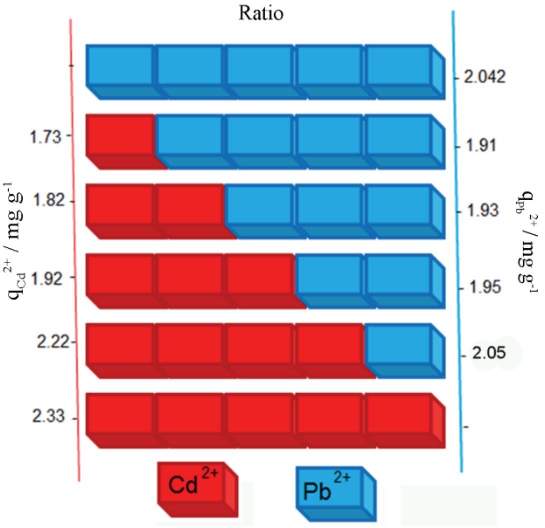

Fig. S-4. Changes adsorption capacity depending on the attitude of Cd^{2+} and Pb^{2+} in binary metal solution; $C_{i[Cd^{2+}]} = 0.2$ mg L^{-1}, $C_{i[Pb^{2+}]} = 0.5$ mg L^{-1}, t = = 60 min, T = 298 K and pH 6.0).

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