

Supporting Information

Environmental Conditions Influencing Sorption of Inorganic Anions to Multiwalled Carbon Nanotubes Studied by Column Chromatography

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SI.1 Sketch of the HPLC device

Figure S1 shows a sketch of the chromatographic system used for sorption studies. The most important fact is the serial connection of the two detectors (diode-array-detector and refractive index (RI)-detector), which allows the detection of the analytes and deuterium oxide (D_2O) at the same time. Consequently, the stability of the column could be regularly tested during sorption experiments using D_2O as non-retarded tracer between analyte measurements without interruption or the necessity to switch capillary tubing to another detector. Injection of sorbates as well as the tracer was done using the autosampler for automated and reproducible injection.

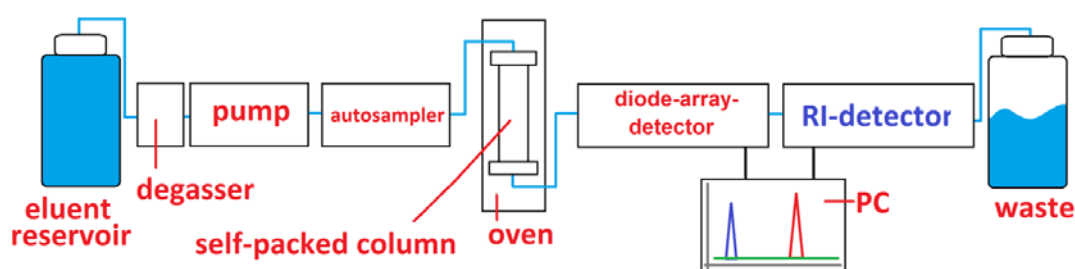


Figure S1: Schematic representation of the HPLC-system used in sorption studies.

SI.2 Column packing procedure

The following section describes in detail the procedure used for column packing. It was adapted from a previous study ¹ and adjusted to the actual materials. First, MWCNTs were ground manually by pestle and mortar to a particle size less than 63 μm , which was checked by sieving analysis. Material properties of MWCNTs were not altered significantly by grinding as shown in table S1. In the beginning an empty HPLC-column was connected to an also empty precolumn using a connecting nut. The column outlet was closed as follows: one stainless steel sieve, three glass fiber filters, one stainless steel sieve and a PTFE seal. The packing materials were premixed in the respective ratio and carefully filled in the combination of column and pre-column using a stainless steel spatula. During transfer of packing material the column was slightly tapped with its outlet on the laboratory bench to increase the density of the packing inside the column. When column and precolumn were filled completely and tapping did not result in further compression of the packing bed, the column was encased and connected to the HPLC-pump for the liquid compression process. The precolumn was used to ensure that after liquid compression the column used for sorption experiments was completely

filled with the packing material without unnecessary void volume at the column head caused by compression while packing. Ultrapure water was used as packing solvent. It was started with a low flow rate ($10 \mu\text{L min}^{-1}$) to get rid of any air entrapped between the particles inside the column and evenly saturate the column with water. The flow rate was increased gradually to a high backpressure (max. 25 MPa) in steps of 15 min for each flow rate. The maximum flowrate (max. 3.5 mL min^{-1}) was held for 4 h with a stable backpressure to ensure complete compression of the material and avoid changes in the packing bed in sorption experiments. In sorption experiments the flow rate was several times lower so that changes in the packing bed could be excluded. Afterwards, the precolumn was removed and the column head cleaned immediately using a spatula to avoid relaxation of the packing material. After cleaning the column head, the column was closed using filters, sieves, PTFE seal as described above.

Table S1: Determined properties of the pristine and ground MWCNTs.

	native material	ground material
specific surface area [$\text{m}^2 \text{ g}^{-1}$]¹	211	228.07
C–C content [%]²	75.23	74.91
C–O- content [%]²	10.40	10.66
C=O content [%]²	0.97	0.97
COOH content [%]²	5.23	5.43
π-π^* content [%]²	8.17	8.03

¹⁾ determined using BET-measurements; ²⁾ relative content of functional groups under the C1s-peak were determined by XPS-measurements.

Table S2: Summary of columns used in this study with their dimensions, packing material composition, bulk density and porosity.

column	dimension (L × ID) [mm]	packing material [w.-%]	bulk density ρ_b [kg L⁻¹]	porosity θ [-]
Q1	53 × 3	100% quartz	1.55	0.45
CNT1	14 × 3	95% quartz / 5% MWCNTs	1.34	0.63
CNT2	14 × 3	95% quartz / 5% MWCNTs	1.44	0.61
CNT3	14 × 3	95% quartz / 5% MWCNTs	1.44	0.60
CNT4	14 × 3	95% quartz / 5% MWCNTs	1.33	0.59
CNT5	14 × 3	95% quartz / 5% MWCNTs	1.29	0.59

SI.3 Comparison of evaluation methods (Apex, Half-mass, First-moment)

Determined distribution coefficients (K_d) for three different evaluation methods to determine the retention time (Apex, Half-mass, First-moment) are presented in table S3 at an injected concentration of 63 mg L^{-1} with 1 mM NaCl as eluent. Determined K_d -values agreed rather well for all three evaluation methods but increase in the order $K_d \text{ Apex} < K_d \text{ Half-mass} < K_d \text{ First moment}$. Nevertheless, the overall trend observed in previous studies for tailing peaks is confirmed ¹. This increase in K_d is connected to the slight tailing of peaks recorded for the different analytes. For symmetrical peaks without tailing or fronting all three methods would yield the same result. Determined maximum errors are smallest for the half-mass method so that this method is applied for evaluation of chromatograms.

Table S3: Determined distribution coefficients (K_d) of the different analytes at an injected concentration of 63 mg L^{-1} and 1 mM NaCl as eluent with column CNT1 (pH 6; 25°C). Determined errors represent the maximum error estimated via error propagation from the standard deviation of three replicates.

analyte	$K_d \text{ Apex}$ [L kg ⁻¹]	$K_d \text{ Half-mass}$ [L kg ⁻¹]	$K_d \text{ First moment}$ [L kg ⁻¹]
bromide	15.0 ± 2.1	15.3 ± 1.1	16.0 ± 2.7
nitrite	17.2 ± 3.7	18.1 ± 2.5	19.4 ± 3.7
nitrate	27.8 ± 3.6	29.8 ± 1.8	32.1 ± 2.2
iodide	44.9 ± 4.5	48.0 ± 4.0	51.7 ± 3.8

SI.4 Comparison of different sorption models

Two different sorption isotherm models are compared in this study: the linear sorption model (equation 1) and the non-linear Freundlich model (equation 2). Sorption isotherms were determined with column CNT1. Determined regression factors are shown in table S4. Determination coefficients (R^2) are highest for the Freundlich model, while values of the linear model are lower. Consequently, the Freundlich model is used in this study to describe sorption isotherms.

$$c_{s,eq} = K_d \times c_{w,eq} + b \quad (1)$$

$$c_{s,eq} = K_F \times c_{w,eq}^n \quad (2)$$

Table S4: Comparison of regressions of the linear sorption model and the Freundlich model for bromide, nitrite, nitrate and iodide with 1 mM NaCl as eluent (pH 6; 25 °C). Injected concentrations range from 0.6 – 63 mg L⁻¹. K_d is the distribution coefficient [L kg⁻¹], b the y-intercept of the regression, R^2 the determination coefficient, K_F the Freundlich coefficient [(mg kg⁻¹) (mg L⁻¹)⁻ⁿ] and n the Freundlich exponent [-]. Errors shown in the table are the standard errors of the regression parameters.

Analyte	Linear model			Freundlich model		
	K_d	b	R^2	K_F	n	R^2
bromide	15.3 ± 0.1	0.3 ± 0.1	0.9998	15.7 ± 1.0	0.988 ± 0.005	0.9999
nitrite	18.0 ± 0.3	0.8 ± 0.6	0.9989	19.4 ± 1.0	0.974 ± 0.008	0.9997
nitrate	29.6 ± 0.7	1.5 ± 1.0	0.9977	32.6 ± 1.0	0.960 ± 0.012	0.9994
iodide	47.7 ± 0.9	1.3 ± 0.9	0.9985	50.9 ± 1.0	0.961 ± 0.008	0.9997

SI.5 Comparison of ultrapure water with 1mM NaCl as eluent

Chromatograms determined for the analytes with ultrapure water and 1mM NaCl as eluent are shown in figure S2. Retention inside the column is stronger with ultrapure water as eluent compared to 1 mM NaCl as indicated by the higher retention time in the chromatogram. The general sequence of elution is similar in ultrapure water and 1mM NaCl, but retention times are strongly reduced by the addition of NaCl indicating the competing effect between the analytes and chloride anions present in the eluent.

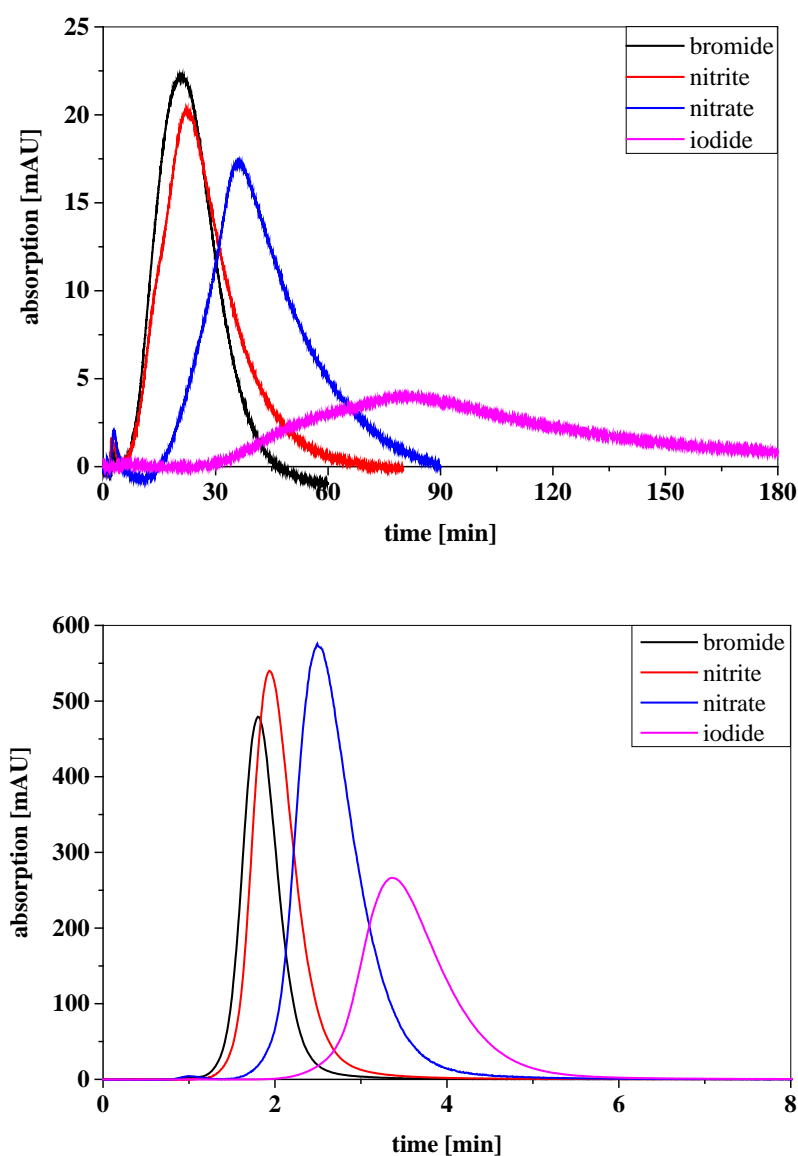


Figure S2: Comparison of chromatograms of the analytes measured with ultrapure water as eluent (top) to chromatograms measured with 1 mM NaCl as eluent (bottom) (pH 6; 25 °C). Injected concentration was in all cases 63 mg L⁻¹. Column CNT4 was used for measurements.

As the reproducibility of chromatograms is worse in ultrapure water as indicated in figure S3 for repeated injections of bromide, these data were not used to calculate distribution coefficients. Standard deviations would be very high. With 1 mM NaCl retention time of bromide and all other analytes was stable. This is shown for bromide in figure S4.

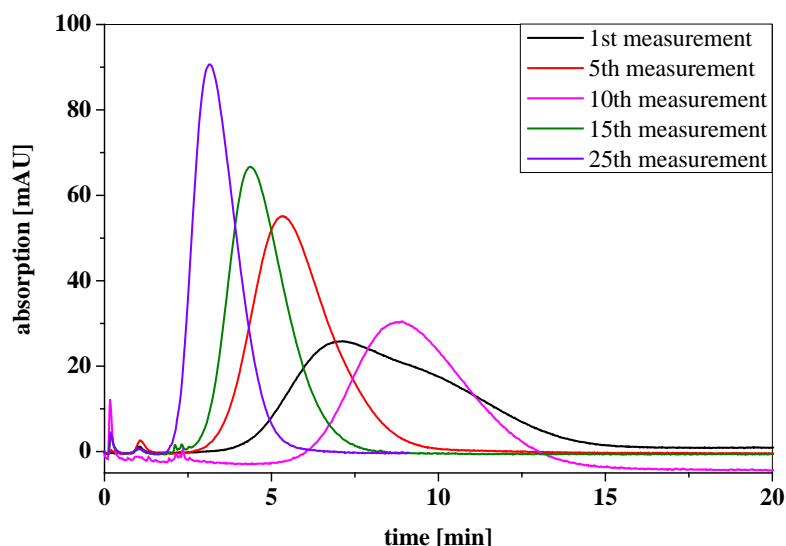


Figure S3: Chromatograms of repeated bromide injections with 63 mg L⁻¹ injected concentration using column CNT1 and ultrapure water as eluent (pH 6; 25 °C).

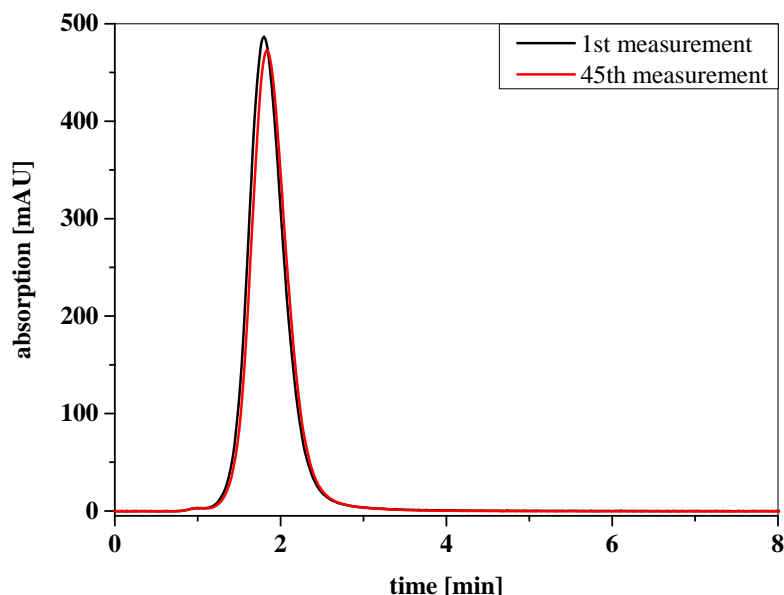


Figure S4: Chromatograms of repeated bromide injections with 63 mg L⁻¹ injected concentration using column CNT1 and 1 mM NaCl as eluent (pH 6; 25 °C).

SI.6 Sorption isotherms of analytes depending on the ionic strength

Figure S5 summarizes the sorption isotherms of the different sorbates determined with eluents of different ionic strength reached by the addition of 1 – 100 mM NaCl. Column CNT1 was used here. Bromide and nitrite at the highest concentration of 100 mM NaCl are not shown as no retention inside the column is observed. Determined Freundlich coefficients (K_F) and Freundlich exponents (n) are given in table S5.

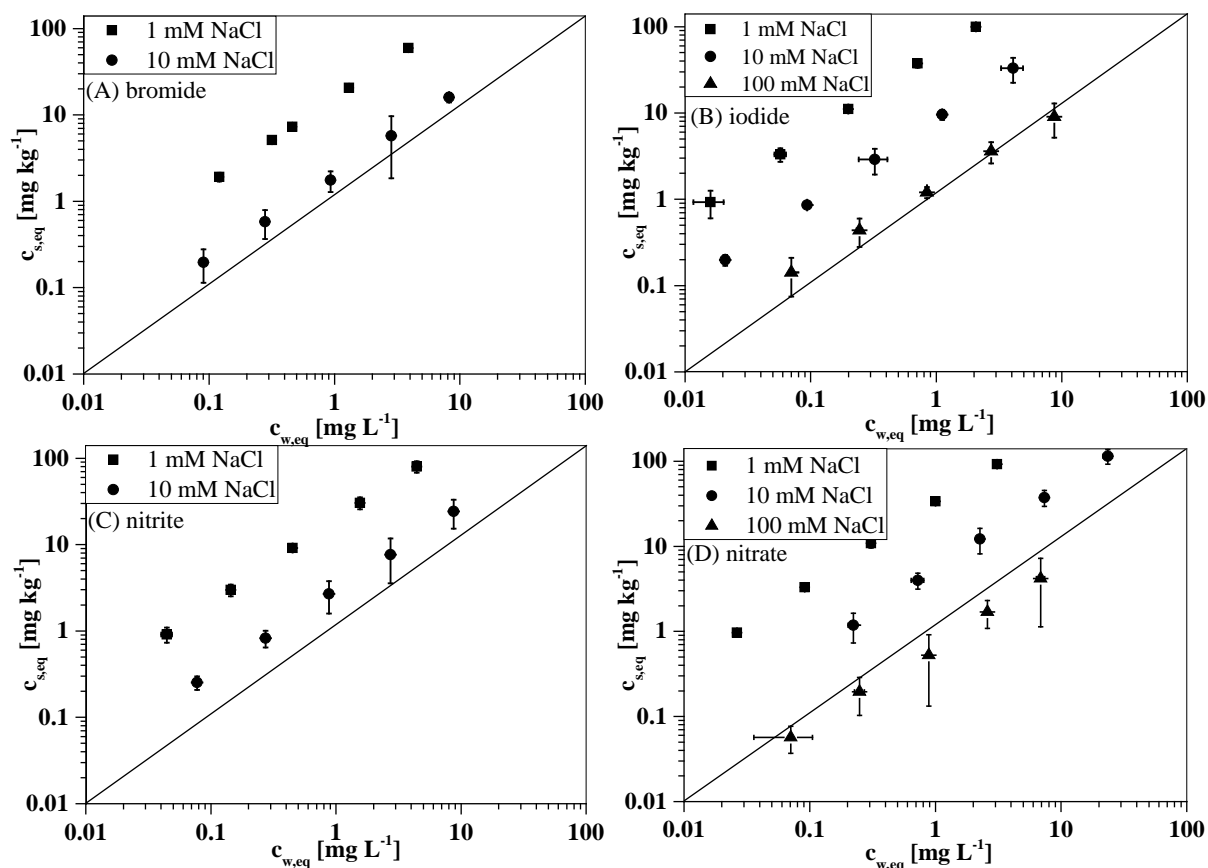


Figure S5: Sorption isotherms determined for bromide (A), iodide (B), nitrite (C) and Nitrate (D) at different ionic strengths / concentration of NaCl in the eluent ranging from 1 mM to 100 mM NaCl (pH 6; 25 °C). The straight line indicates a slope of 1.

Table S5: Logarithmic Freundlich coefficients (K_F) [$(\text{mg kg}^{-1}) (\text{mg L}^{-1})^{-n}$] and Freundlich exponents (n) [-] determined for the different isotherms of bromide, nitrite, nitrate and iodide with different concentrations of NaCl ranging from 1 mM to 100 mM NaCl in the eluent (pH 6; 25 °C) in combination with the corresponding determination coefficient (R^2). Errors represent the standard error of the regression parameters.

	1 mM NaCl			10 mM NaCl			100 mM NaCl		
analyte	log K_F	n	R^2	log K_F	n	R^2	log K_F	n	R^2
bromide	1.20 ± 0.01	0.988 ± 0.01	0.9999	0.30 ± 0.01	0.978 ± 0.013	0.9993	-	-	-
nitrite	1.28 ± 0.01	0.974 ± 0.01	0.9998	0.47 ± 0.01	0.966 ± 0.007	0.9998	-	-	-
nitrate	1.51 ± 0.01	0.960 ± 0.01	0.9994	0.73 ± 0.01	0.979 ± 0.009	0.9997	-0.17 ± 0.02	0.934 ± 0.025	0.9971
iodide	1.71 ± 0.01	0.961 ± 0.01	0.9997	0.93 ± 0.01	0.969 ± 0.01	0.9999	0.16 ± 0.01	0.863 ± 0.01	0.9993

SI.7 Sorption isotherms of analytes depending on cation type

Figure S6 summarizes the sorption isotherms determined with 1 mM NaCl or 0.5 mM CaCl₂ as eluent. Column CNT2 was used for these measurements. Determined Freundlich coefficients (K_F) and Freundlich exponents (n) are given in table S6.

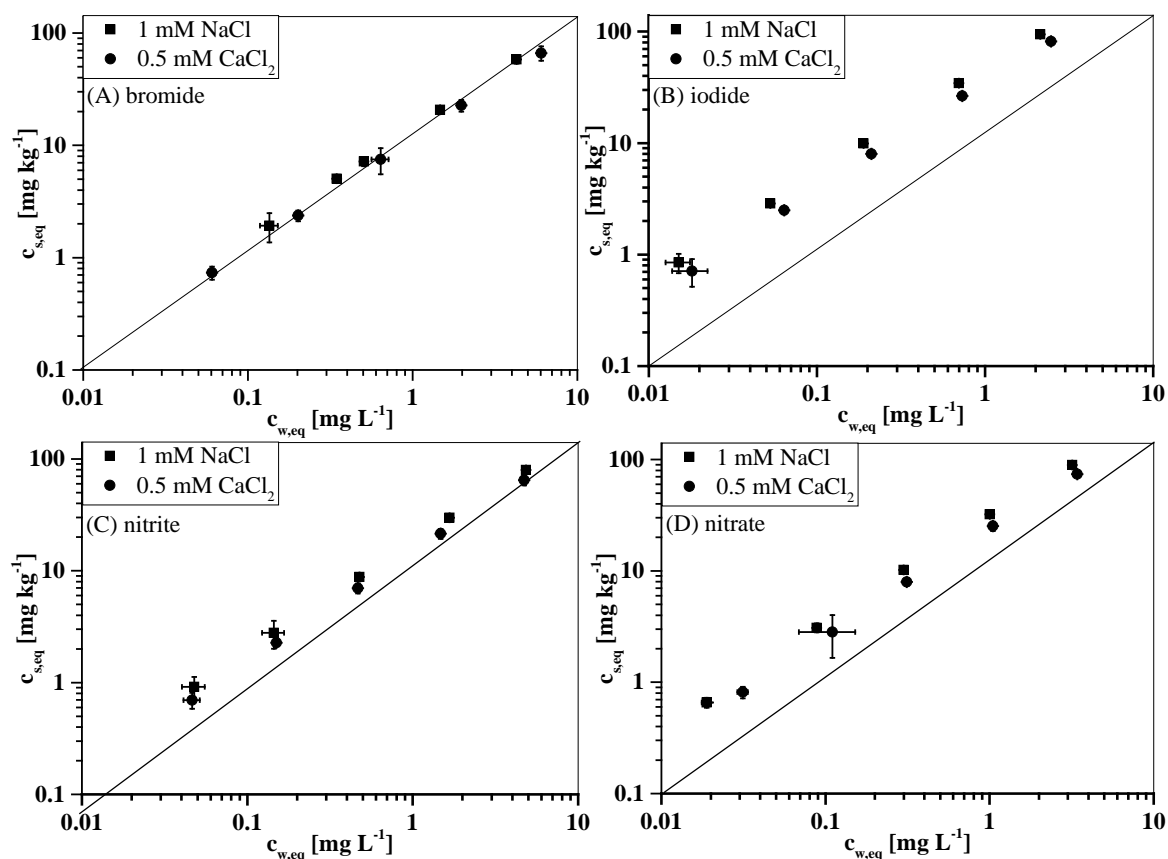


Figure S6: Sorption isotherms determined for bromide (A), iodide (B), nitrite (C) and Nitrate (D) with 1 mM NaCl or 0.5 mM CaCl₂ as eluent (pH 6; 25 °C). The straight line indicates a slope of 1.

Table S6: Logarithmic Freundlich coefficients (K_F) [$[(\text{mg kg}^{-1}) (\text{mg L}^{-1})^{-n}]$] and Freundlich exponents (n) [-] determined for the different isotherms of bromide, nitrite, nitrate and iodide with 1 mM NaCl or 0.5 mM CaCl_2 as eluent (pH 6; 25 °C) in combination with the corresponding determination coefficient (R^2). Errors represent the standard error of the regression parameters.

	1 mM NaCl			0.5 mM CaCl_2		
analyte	log K_F	n	R^2	log K_F	n	R^2
bromide	1.14 ± 0.01	0.984 ± 0.01	0.9998	1.06 ± 0.01	0.981 ± 0.004	0.9999
nitrite	1.25 ± 0.01	0.968 ± 0.01	0.9998	1.16 ± 0.01	0.981 ± 0.01	0.9998
nitrate	1.49 ± 0.01	0.960 ± 0.01	0.9992	1.37 ± 0.01	0.963 ± 0.01	0.9995
iodide	1.68 ± 0.01	0.954 ± 0.01	0.9998	1.55 ± 0.01	0.965 ± 0.01	0.9997

Figure S7 shows the correlation between the ionic strength of the eluent and the determined distribution coefficient.

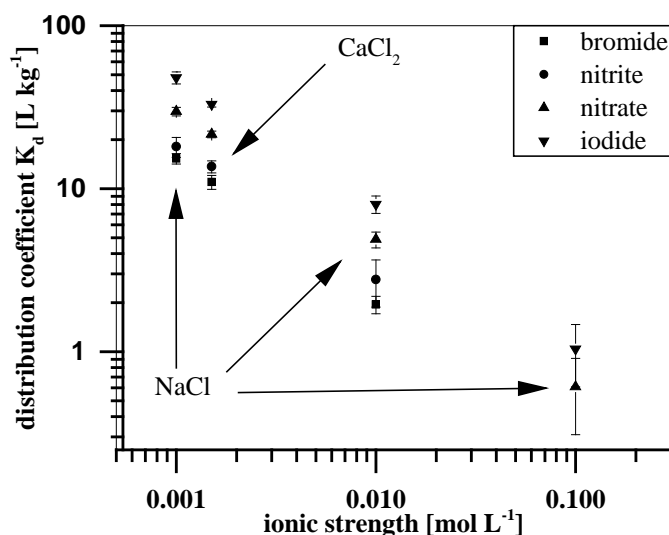


Figure S7: Correlation of K_d -values of the different analytes determined using NaCl plotted against the corresponding ionic strength of the eluent in comparison to the K_d -values of the analytes determined using 0.5 mM CaCl_2 at an ionic strength of 0.0015 (pH 6; 25 °C). The injected concentration was for all analytes 63 mg L⁻¹. Values of Br^- and NO_2^- at an ionic strength of 0.1 mol L⁻¹ are left out as no sorption could be detected.

SI.8 Sorption isotherms of iodide depending on anion type

Figure S8 summarizes the sorption isotherms determined with 1 mM NaCl or 1 mM NaBr as eluent (column CNT2), while figure S9 summarizes sorption isotherms determined with 1 mM HCl or 1mM HClO₄ as eluent (column CNT5). Determined Freundlich coefficients (K_F) and Freundlich exponents (n) are given in table S7.

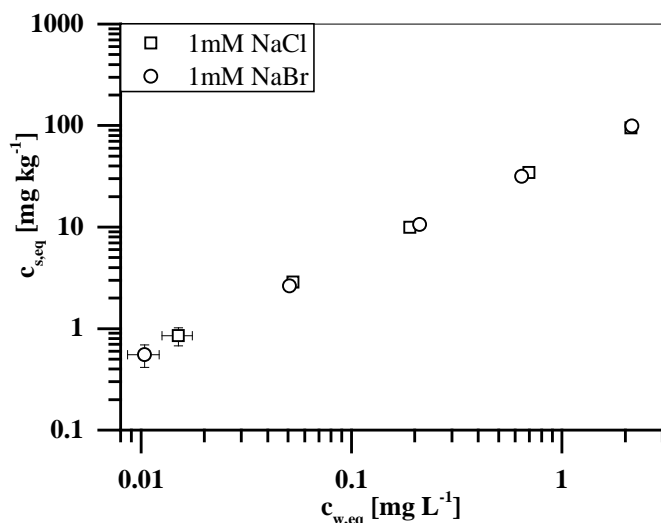


Figure S8: Sorption isotherms of iodide using 1 mM NaCl or 1 mM NaBr in the eluent (pH 6; 25 °C). Error bars represent the calculated maximum error.

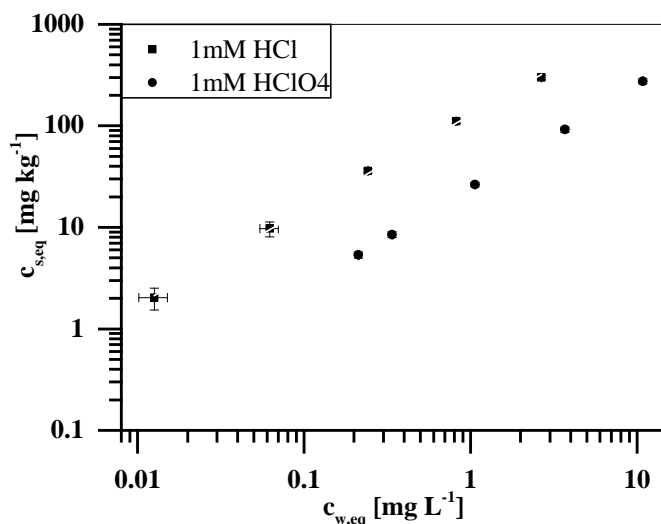


Figure S9: Sorption isotherms of iodide using 1 mM HCl or 1 mM HClO₄ in the eluent (pH 3; 25 °C). Error bars represent the calculated maximum error.

Table S7: Determined Freundlich coefficient (K_F), Freundlich exponent (n) and determination coefficient (R^2) of iodide isotherms determined using 1 mM NaCl or 1mM NaBr (pH 6; 25 °C) and 1 mM HCl or 1 mM HClO₄ in the eluent (pH 3; 25 °C). K_F is given in (mg kg⁻¹) (mg L⁻¹)⁻ⁿ and n is dimensionless. Error of K_F and n represent the standard errors of the regression coefficients.

	1 mM NaCl			1 mM NaBr		
analyte	log K_F	n	R^2	log K_F	n	R^2
iodide	1.67 ± 0.01	0.95 ± 0.01	0.999	1.68 ± 0.01	0.97 ± 0.01	0.999
	1 mM HCl			1 mM HClO₄		
analyte	log K_F	n	R^2	log K_F	n	R^2
iodide	2.11 ± 0.01	0.95 ± 0.02	0.999	1.40 ± 0.01	1.00 ± 0.01	0.999

SI.9 Sorption isotherms of analytes depending on pH

Figure S10 summarizes the sorption isotherms of the different sorbates determined with eluents at pH 3, 6, and 9 at a constant ionic strength of 0.001 mol L^{-1} . Column CNT3 was used for these measurements. Determined Freundlich coefficients (K_F) and Freundlich exponents (n) are given in table S8. Nitrite at pH 3 was not measured as pH below pKs of nitrous acid of 3.3 may lead to the formation of nitrous gases.

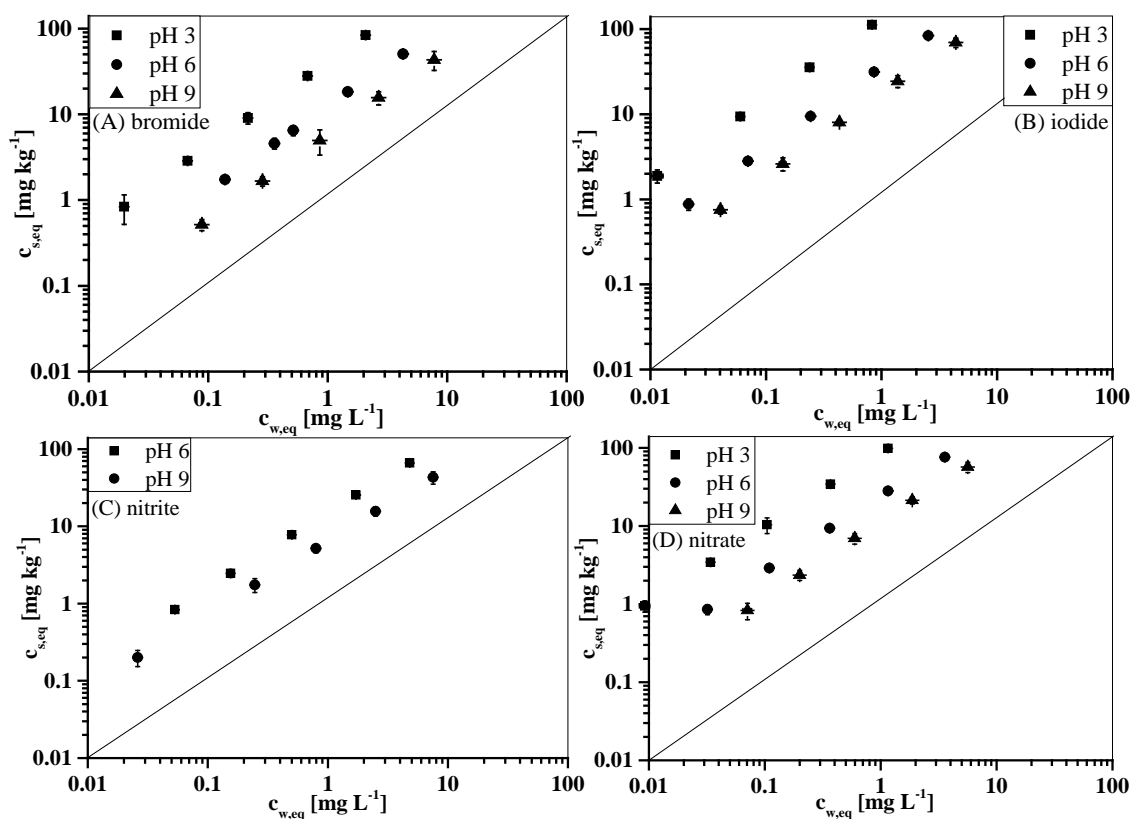


Figure S10: Sorption isotherms determined for bromide (A), iodide (B), nitrite (C) and Nitrate (D) with eluents at pH 3, 6, and 9 (constant ionic strength of 0.001 mol L^{-1}) (25°C). The straight line indicates a slope of 1.

Table S8: Logarithmic Freundlich coefficients (K_F) [$[(\text{mg kg}^{-1}) (\text{mg L}^{-1})^{-n}]$] and Freundlich exponents (n) [-] determined with eluents at pH 3, 6, and 9 at a constant ionic strength of 0.001 mol L^{-1} (25°C) in combination the corresponding determination coefficient (R^2). Errors represent the standard error of the regression parameters.

	pH 3			pH 6			pH 9		
analyte	log K_F	n	R^2	log K_F	n	R^2	log K_F	N	R^2
bromide	1.61 ± 0.01	0.990 ± 0.01	0.9999	1.09 ± 0.01	0.981 ± 0.01	0.9998	0.76 ± 0.01	0.991 ± 0.01	0.9999
nitrite	-	-	-	1.17 ± 0.01	0.971 ± 0.01	0.9997	0.81 ± 0.01	0.948 ± 0.01	0.9999
nitrate	1.94 ± 0.01	0.962 ± 0.01	0.9997	1.37 ± 0.01	0.955 ± 0.01	0.9993	1.05 ± 0.01	0.970 ± 0.01	0.9993
iodide	2.14 ± 0.01	0.956 ± 0.01	0.9999	1.55 ± 0.01	0.956 ± 0.008	0.9997	1.24 ± 0.01	0.968 ± 0.012	0.9994

Figure S11 shows the isotherms of iodide determined at pH 3 using 1 mM HCl as eluent at different ionic strengths (conditions: 1 mM HCl; 1 mM HCl + 9 mM NaCl; 1 mM HCl + 99 mM NaCl). Column CNT5 was used for the measurements. Determined Freundlich coefficients (K_F) and Freundlich exponents (n) are given in table S9.

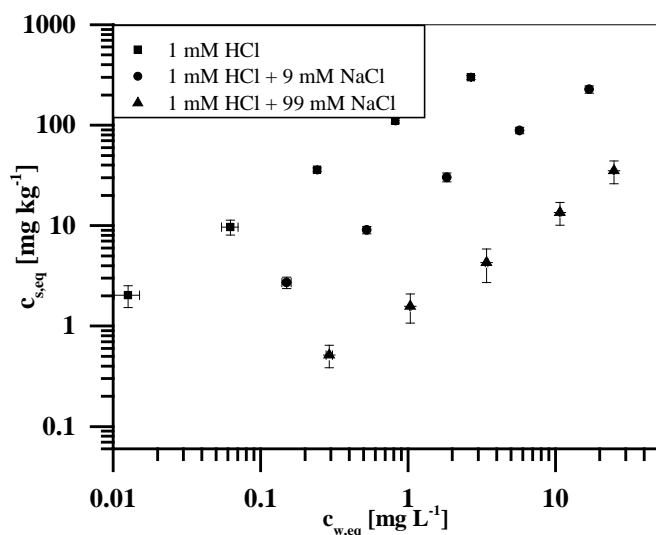


Figure S11: Sorption isotherms determined for iodide with eluents containing 1 mM HCl, 1 mM HCl + 9 mM NaCl or 1 mM HCl + 99 mM NaCl (pH 3, 25°C).

Table S9: Determined Freundlich coefficient (K_F), Freundlich exponent (n) and determination coefficient (R^2) of iodide isotherms determined for iodide with eluents containing 1 mM HCl, 1 mM HCl + 9 mM NaCl or 1 mM HCl + 99 mM NaCl (pH 3, 25 °C). K_F is given in (mg kg⁻¹) (mg L⁻¹)⁻ⁿ and n is dimensionless. Error of K_F and n represent the standard errors of the regression coefficients.

	1 mM HCl			1 mM HCl + 9 mM NaCl			1 mM HCl + 99 mM NaCl		
analyte	log K_F	n	R^2	log K_F	n	R^2	log K_F	n	R^2
iodide	2.11 ± 0.02	0.94 ± 0.02	0.999	1.22 ± 0.01	0.94 ± 0.01	0.999	0.19 ± 0.02	0.94 ± 0.03	0.996

Figures S12 and S13 summarize the results of the zeta-potential and XPS-measurements used to characterize the MWCNTs.

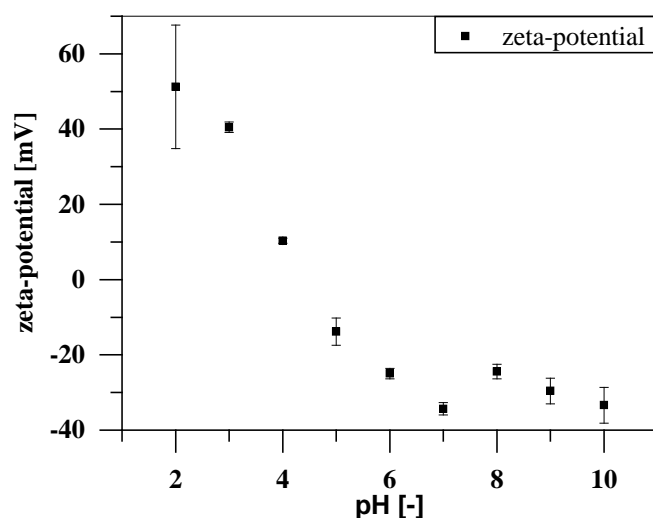


Figure S12: Determined zeta-potential of MWCNTs depending on the pH of the surrounding solution. Error bars represent the standard deviation of 5 replicates.

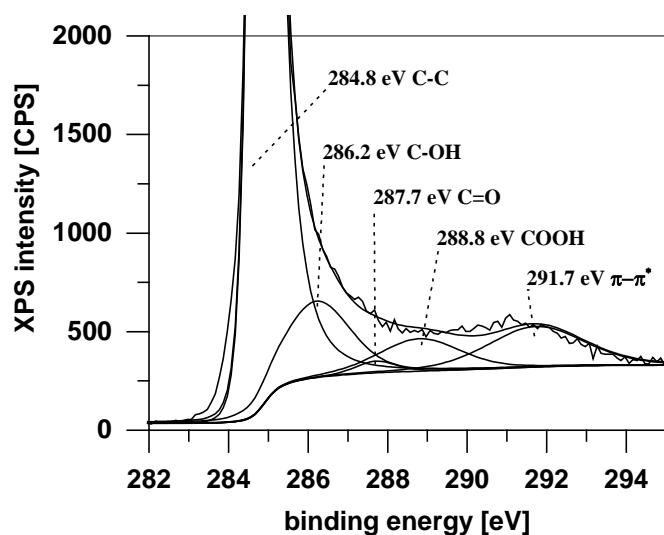


Figure S13: Deconvolution of the C1s peak of the XPS-measurement of MWCNTs ground to a particle size $\leq 63 \mu\text{m}$.

References:

1. Bi, E; Schmidt, T. C.; Haderlein, S. B. Practical issues relating to soil column chromatography for sorption parameter determination. *Chemosphere* **2010**, 80, (7), 787-793.