

# Supplementary Material

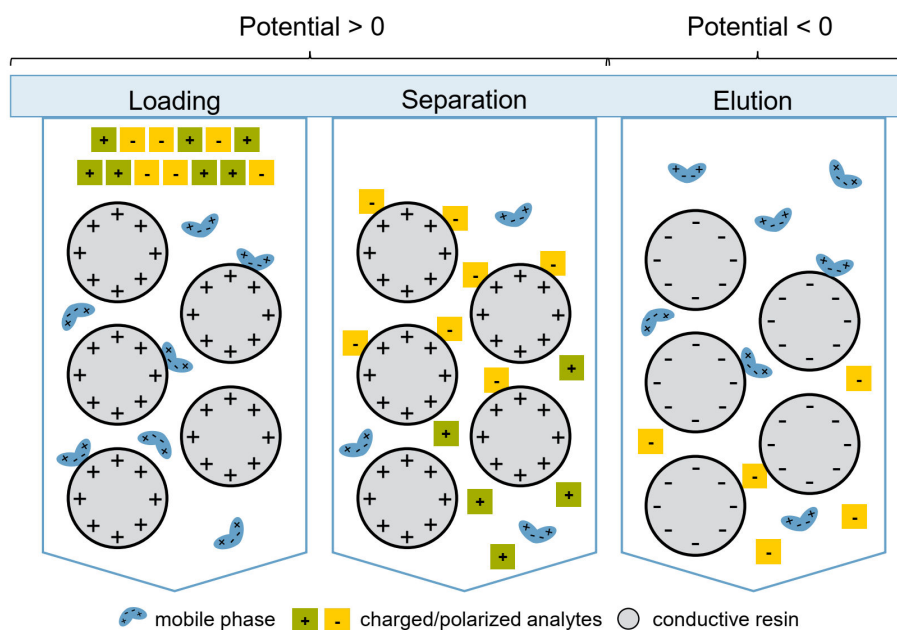
## A Carbon Nanotube Packed Bed Electrode for Small Molecule Electrosorption: An Electrochemical and Chromatographic Approach for Process Description

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### The functional principle of potential-controlled chromatography



**Figure S1:** Working principle of potential-controlled chromatography. Upon the application of an electrical potential at the conductive stationary phase material, the surface charge of the resin is modified leading to the electrosorption of counter charged molecules. Applying a positive potential, the surface charge of the particles is positively charged, and counter charged molecules can be adsorbed in the separation step due to electrosorption. Afterwards, the elution is induced by inverting the potential (direct switch or gradual change) and the adsorbed molecules desorb without the need of any additives.

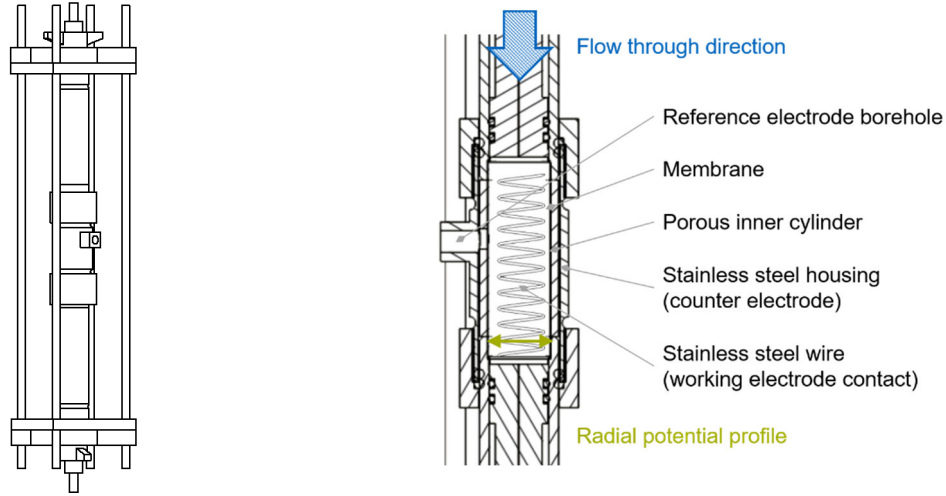
## The column setup

The PCC setup is different to conventional chromatography. It includes:

- A packed bed of nanotubes which acts as working electrode (WE) and is surrounded by a membrane and a highly porous stainless steel cylinder.
- A curled cation exchange membrane which separates the counter electrode (CE) and the particle packed bed.
- A conductive stainless steel wire (height = 50 mm, inner diameter ~ 10 mm, twists = 12) which is installed in the lower stamp and works as contact between the MWCNT particles and the WE pin. Its design has been developed based on fluid dynamical simulations. The wire enhances the conductivity through the packed bed without disturbing the homogeneous, laminar profile of the fluid through the column.
- The CE is comprised of a porous stainless steel cylinder and an outer stainless steel housing. The porous material enhances the area of the CE and significantly reduces the limiting effect of the compact outer housing. Both CE parts provide access to the reference electrode (RE).
- The reference electrode is a screwable Ag/AgCl electrode.
- Membrane caps which have been designed to guarantee a stable and homogenous particle packed bed. They are mounted on the membrane ends to provide lateral flow and optimize the homogeneous fluid distribution.
- A set of column clamps facilitates the stamp screwing by steadily transmitting a homogeneous force.

The improved column design (in comparison to Brammen et al. (2017, J.Sep.Sci) is more stable and robust than the earlier version. Furthermore, it allows a more homogeneous radial potential profile while the through flow direction is axial. It also induces a simpler packing procedure.

The column setup and a cross sectional view are illustrated in **Figure S2**.



**Figure S2:** Scheme of the adapted potential-controlled chromatographic (PCC) column using column clamps and membrane caps for improved packed bed quality, higher pressure stability and a longer column lifetime (left). Cross section of the PCC column, which illustrates all basic column components, the through flow direction of the fluid and the specific potential profile (right).

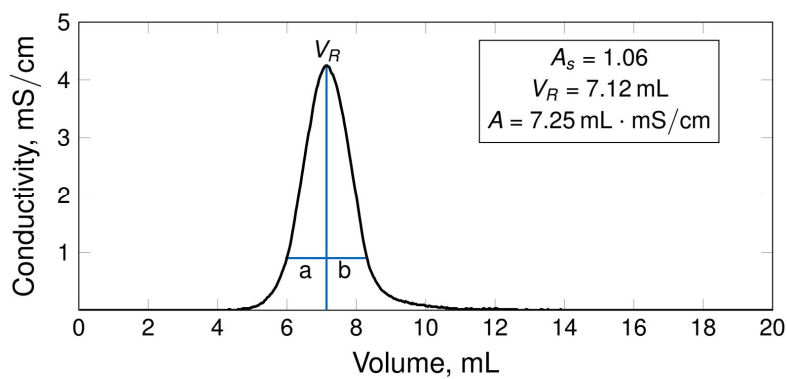
### Characterization of a chromatographic packed bed

Characteristic numbers of a chromatographic column are

- The retention volume,  $V_R$ , which corresponds to the peak maximum.
- The asymmetric factor,  $A_s = \frac{b}{a}$ , which is defined as 10% of the peak height  $w_{10\%}$  and identifies the homogeneity of the packed bed
- The column porosity, which defines the interparticle column porosity without the pores
- The total column porosity, which defines the sum of the inter- and the intraparticle porosity
- The HETP value, which describes the height of the theoretical plates in the column and defines hence the separation efficiency of the column. The HETP value  $HETP = \frac{L}{N}$ , which includes  $L$  as column length and  $N$  as the number of the theoretical plates.

The HETP value is calculated with the Unicorn 7.0 software on basis of Eq. 1

$$N = 41.7 \left( \frac{\left( \frac{V_R}{w_{10\%}} \right)^2}{1.25 + A_s} \right). \quad \text{Eq S1}$$

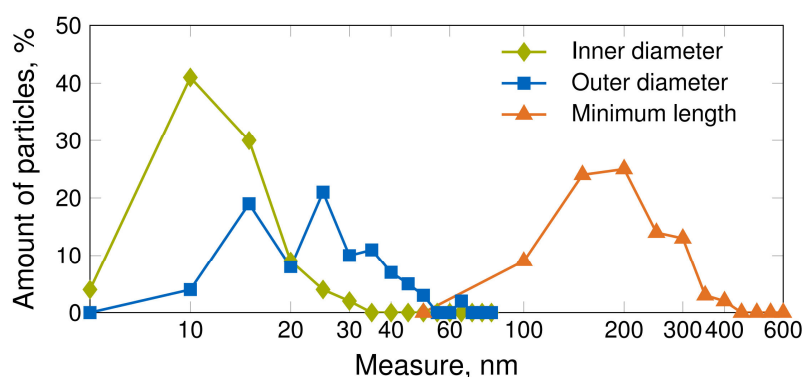


**Figure S3:** 1 M NaCl tracer to determine the quality of a CNT packed bed (1 mL/min, 50  $\mu\text{L}$ , DI-water). The HETP and the asymmetric factor are calculated using the information in the equation above.

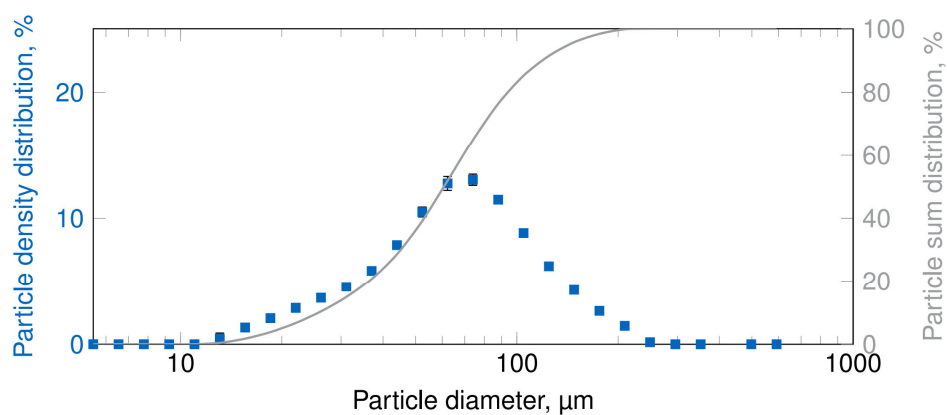
**Table S1:** Long-term stability and quality of different particle packed beds, taken from 10 tracer experiments (1 M NaCl, 50  $\mu\text{L}$ , 1 mL/min, DI-water, 1 mM or 10 mM phosphate buffer, pH = 7.2) over several working days.

Run	Mobile phase	$V_R$ , mL	$A_s$ , -	HETP, cm	$N$ , -
1	DI-water	7.12	1.07	0.0482	103.64
2	DI-water	6.99	0.93	0.0451	110.96
3	DI-water	6.96	1.02	0.0474	105.56
4	1 mM buffer	6.96	1.10	0.0478	104.61
5	1 mM buffer	6.92	1.13	0.0455	109.80
6	10 mM buffer	6.82	1.31	0.0481	103.86
7	DI-water	6.86	1.13	0.0464	107.70
8	10 mM buffer	6.79	1.38	0.0499	100.19
9	DI-water	7.79	1.20	0.0417	120.04
10	DI-water	6.99	1.10	0.0452	110.59

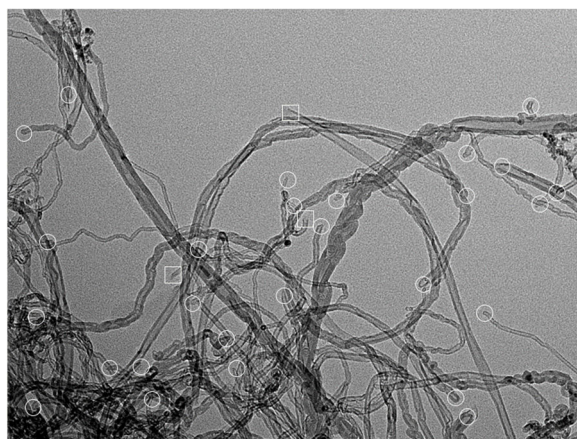
### Characterization of the CNT-K



**Figure S4:** Minimum length, outer diameter and inner diameter of CNT-K, measured at the nano scale with a TEM. At least 30 measurements were carried out from three independent TEM pictures.

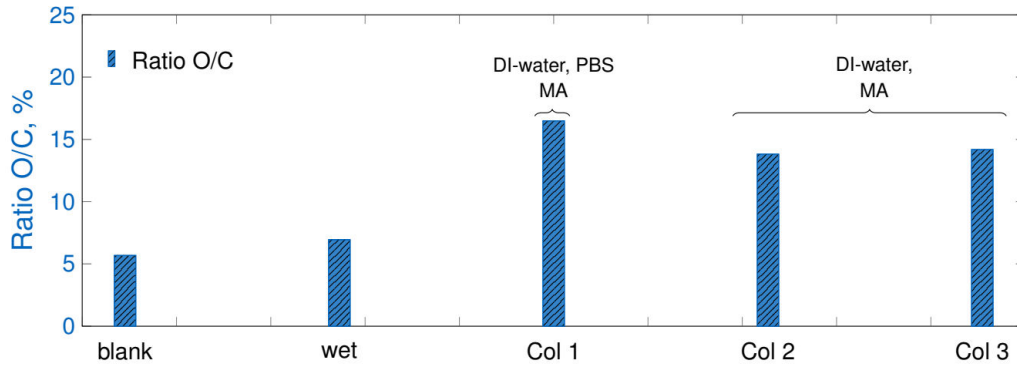


**Figure S5:** Particle size distribution of more than 2000 CNT-K agglomerates was measured with a Microtrac Flex 12.0. The agglomerates were taken from a highly concentrated and a highly diluted DI-water suspension.

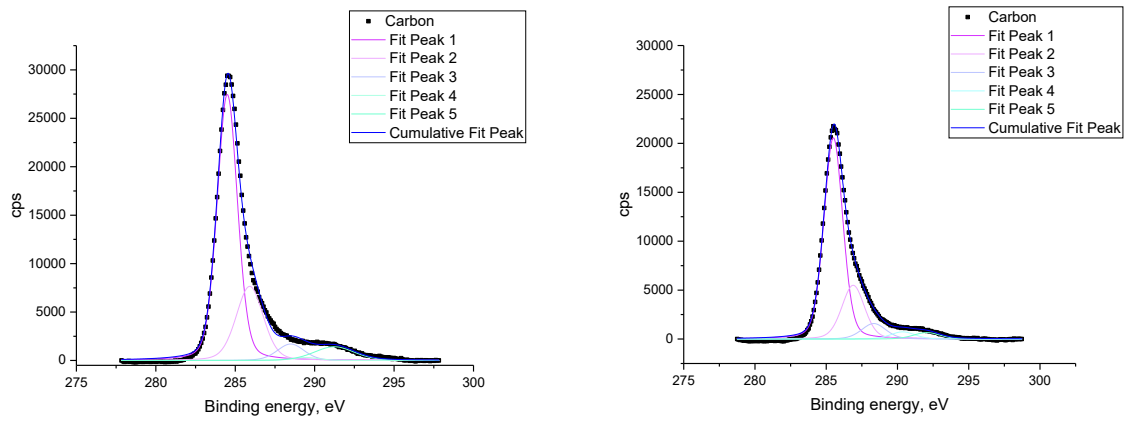


**Figure S6:** Analysis of CNT-K ends. To confirm the specific surface of the CNT-K material, open (□) and closed (○) CNT-K tubes were regarded (> 100 tubes). One TEM image (50000x) is representative. Over 85% of the highlighted tube ends are closed.

## Characterization of the CNT-K surface groups



**Figure S7:** XPS analysis of the CNT functionalization based on the ratios between the surface oxygen/carbon. The CNT particles are analysed after different particle treatments: (1) untreated CNT-K powder (blank), (2) dried CNT-K suspension, which was purified based on the manufacturers' recommendation with 1 M HCl and neutralized with sufficient DI-water, and (3) three CNT-K samples, which were established in the PCC column and treated with different potential-controlled experiments using DI-water or 10 mM phosphate buffer as mobile phase and maleic acid as adsorbate. Exemplary raw data of the XPS measurements is illustrated in **Figure S8**.



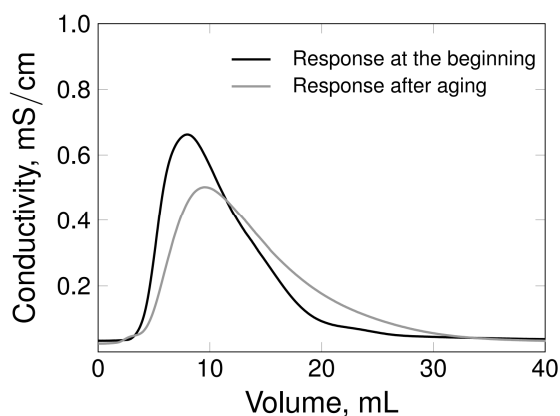
**Figure S8:** Exemplary raw data of the XPS measurements. XPS graph for column 2 (left) and column 3 (right) with C-C bindings at 284.5 eV, C-O bindings around 286 eV and C=O bindings around 288 eV. Perhaps a slight O-C=O signal may be identified from the peak at 292 eV, whereas  $\pi$ - $\pi$  are expected at higher binding energies.

## Electrochemical methods to determine column quality

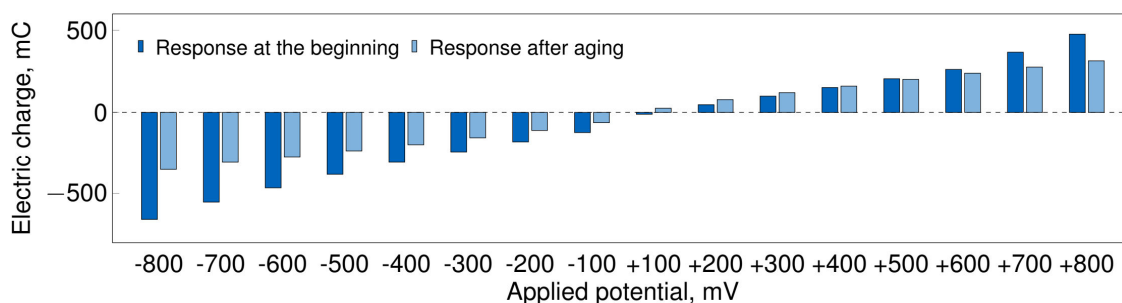
A characteristic number to describe the quality of the conductive particle packed bed is the specific resistance  $\rho$ , which is defined as

$$\rho = \frac{U_{app}}{I_{mean}} \frac{A_{Col}}{l_{Col}}. \quad \text{Eq S2}$$

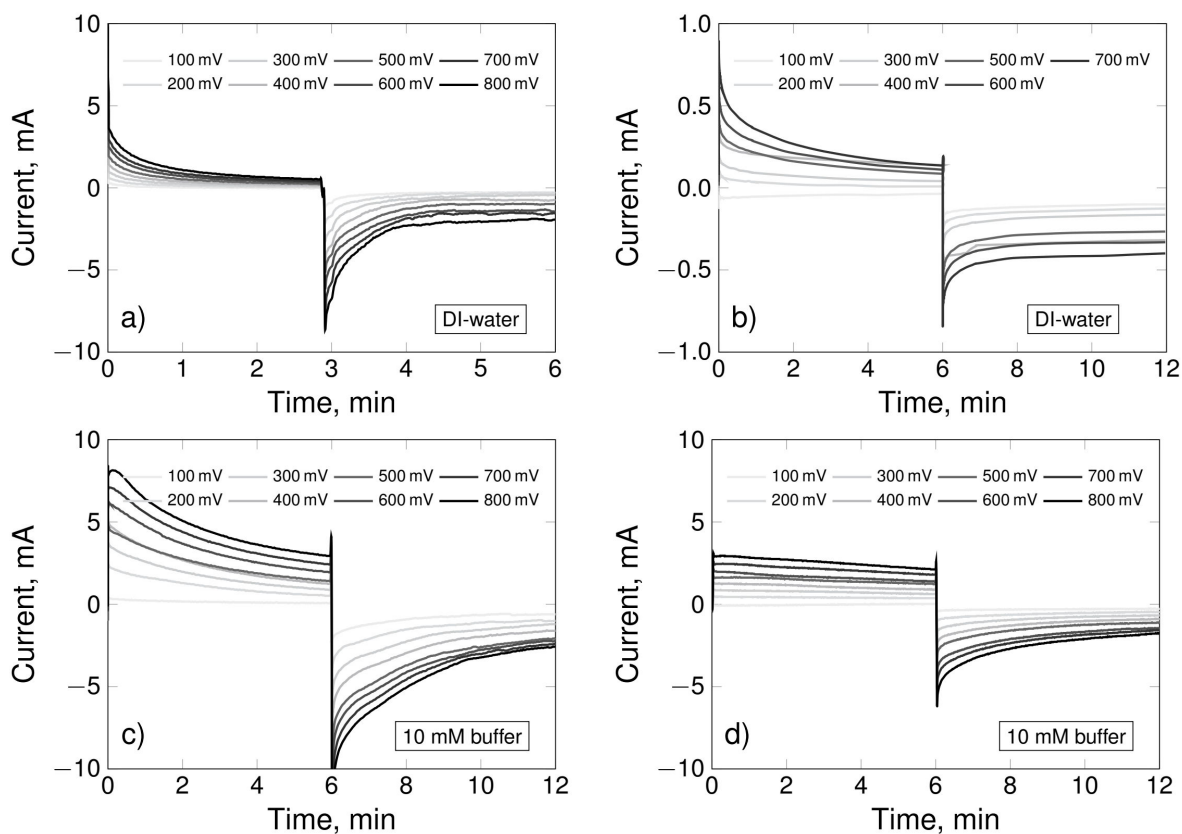
Here,  $U_{app}$  is the applied potential in mV,  $I_{mean}$  is the mean current in mA,  $A_{Col}$  is the cross-sectional area of the column in mm<sup>2</sup> and  $l_{Col}$  is the length of the packed bed in m.



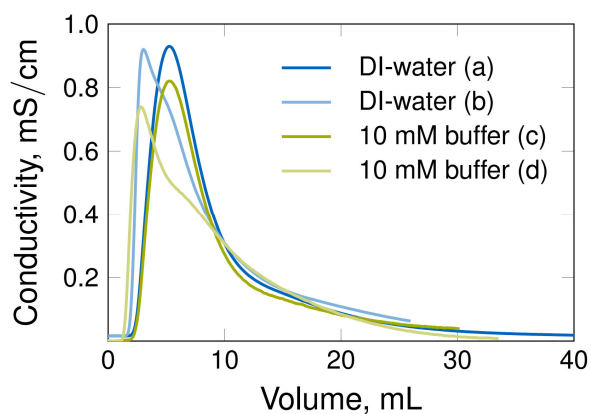
**Figure S9:** Tracer experiment to describe the packed bed quality at the beginning of the column life and after several experiments (1 M NaCl, 1 mL/min, 50  $\mu$ L, DI-water). The information of this tracer corresponds to the chronoamperometry experiments of column A (see Figure 4).



**Figure S10:** The electric charge of a CNT-K electrode (column A) at different applied potentials corresponds to the area under the current profiles of the chronoamperometry measurements used in Figure 4. The aging effect of the column is represented here as well.

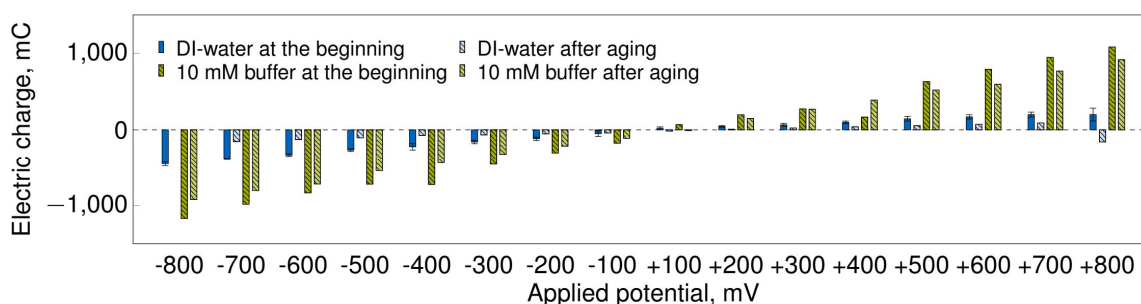


**Figure S11:** Additional chronoamperometry experiments to visualize the water and buffer influence on resistance and EDL rearrangement time using column B. a) Column response at the beginning using DI-water, b) Column response after aging using DI-water (the same column after more than 250 working hours), c) Column response at the beginning using 10 mM phosphate buffer, d) Column response after aging using 10 mM phosphate buffer (the same column after more than 250 working hours). Flow rate is 1 mL/min.

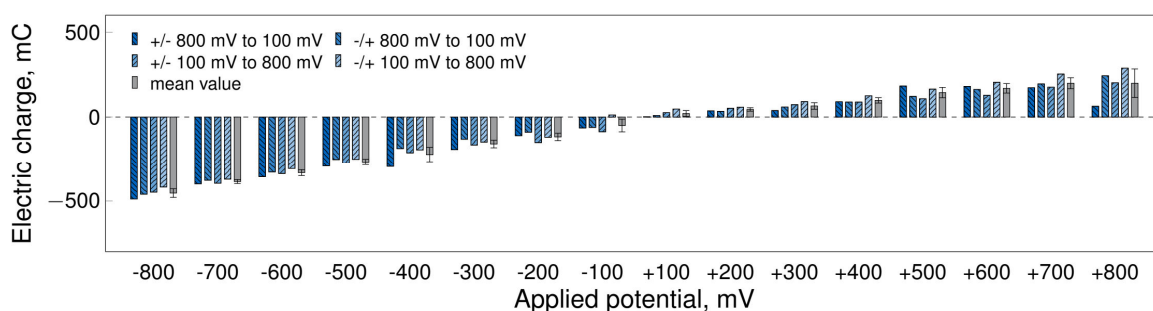


**Figure S12:** 1 M NaCl tracer experiment to analyse the quality of the packed bed chromatographically (column B). a) Column response at the beginning using DI-water, b) Column response after aging using DI-water (the same column after more than 250 working hours), c) Column response at the beginning using 10 mM phosphate buffer, d) Column response after aging using 10 mM phosphate buffer (the same column after more than 250 working hours). Flow rate is 1 mL/min.



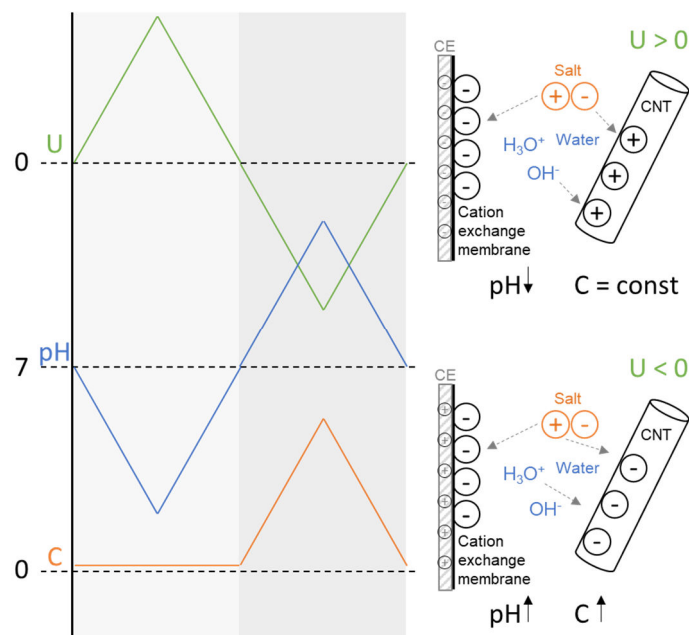


**Figure S13:** The electric charge of a CNT-K electrode (column B), determined from experiments with DI-water and 10 mM phosphate buffer as mobile phase (1 mL/min). Several periods in the column lifetime are examined. The data correspond to the current/potential diagram in Figure 5 or related chronoamperograms in **Figure S11**



**Figure S14:** Electric charge from several chronoamperometry measurements. The potential variation was applied in different ways from low to high potential and by varying the sign of the applied potential to confirm the reproducibility of the measurement series. The single experiments are printed in blue, the mean values in grey. The experiment was performed in column B using DI-water as mobile phase (1 mL/min).

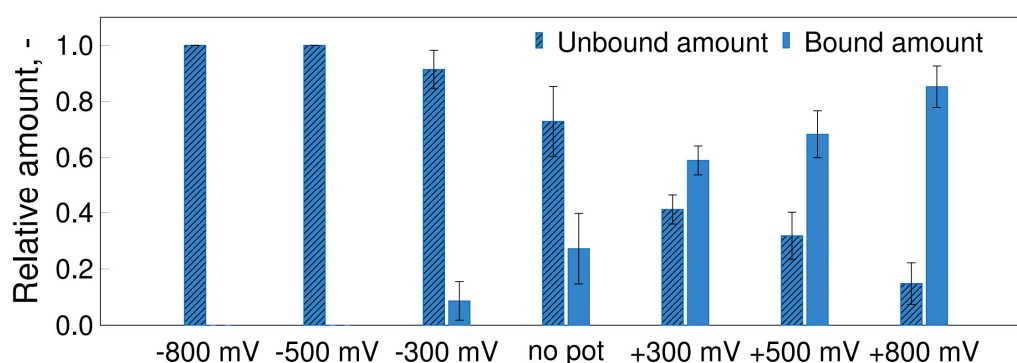
### The potential influence on pH and conductivity



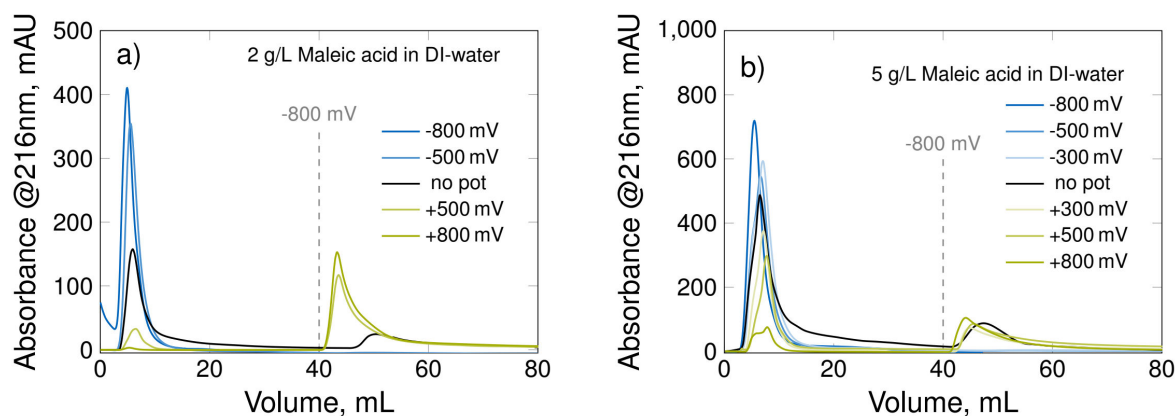
**Figure S15:** Scheme of a cyclic voltammetry experiment using DI-water with weak conductivity as mobile phase.

The influence of a potential gradient on the pH-value or the mobile phase conductivity is illustrated in **Figure S15**. While the potential gradient is positive, the pH value decreases while the conductivity of DI-water ( $C < 0.02$  mS/cm) remains constant. However, if the potential gradient turns negative, the pH value and the conductivity increase. The pH value depends on the presence of oxonium and hydroxyl ions, which adsorb or desorb at the CNT surface, depending on the sign of the applied potential difference (oxonium ions are retained by a negative charged surface, hydroxyl ions by a positive one). The conductivity development is probably due to the higher specific surface conductance of oxonium ions, which do also impact the conductivity of the mobile phase.

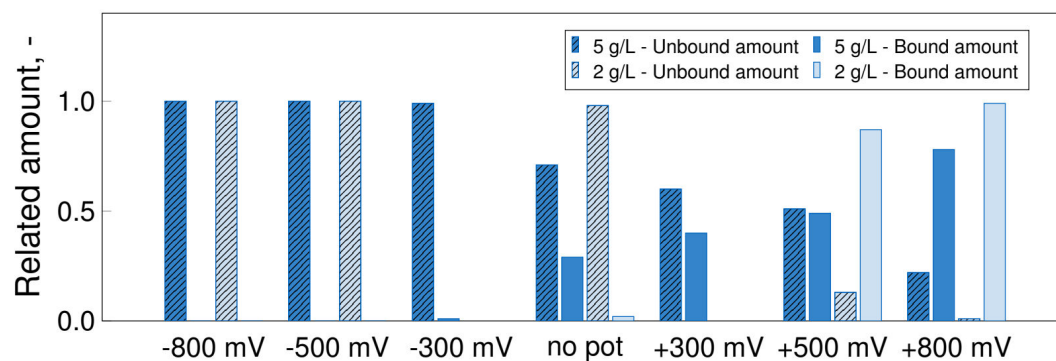
### Potential influence on the column capacity



**Figure S16:** Relative amount of maleic acid in potential-step experiments using DI-water as mobile phase and three independent PCC columns (5 g/L, 50  $\mu$ L, 1 mL/min, 216 nm). The adsorption phase shows the percentage of the unbound amount (shaded bars), executed at different potentials (see x-axis). The elution phase was induced after 30 mL by a potential switch to -800 mV and represents the bound amount (bar bars).



**Figure S17:** Potential-step experiments to compare the absorbance values at the column outlet for different initial concentrations of maleic acid in DI-water (1 mL/min, 216 nm). The experiment was executed at different potentials applied during the adsorption phase (see legend); the elution was repeated each time with a potential switch to -800 mV (horizontal mark). The experiment was performed in a column C with 2 g/L and 5 g/L maleic acid in DI-water and a potential switch at 40 mL



**Figure S18:** Relative amount of maleic acid in potential-step experiments using DI-water as mobile phase and 2 g/L (light blue) and 5 g/L (dark blue) injection concentration (1 mL/min, 50  $\mu$ L, pH = 7.2, 216 nm). The adsorption phase shows the percentage of the unbound amount (shaded bars), executed at different potentials (see x-axis). The elution phase was induced after 40 mL by a potential switch to -800 mV and represents the bound amount (bar bars). The experiment was performed in a column C.