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Supplementary material

SUPPLEMENTARY MATERIAL TO

Chromium(VI) removal from aqueous solutions using a polyethylenimine–epichlorohydrin resin

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THE RESIN

The non-crystalline spherical particles of the resin had an average diameter of 80 μm and specific surface area of 0.410 $m^2 g^{-1}$. The resin was found to be stable up to *ca.* 180 °C.

The XPS examination of the resin showed the existence of both ternary (nitrogen binding energy (BE) 399.2 eV) and quaternary (BE: 401.4 eV) amino-groups in the relation 45 to 55 %.[1–3] These groups can justify the anion-sorption properties of the material. The quaternary amine groups can exchange anions over the whole pH range, whereas the ternary ones show, because of their protonation, a higher metal uptake capacity at low pH values. A small number of COO^--groups (*ca.* 8 %) were also observed by XPS. Additional information about the characterization of the resin is given in a previous publication.[4]

Influence of the resin on the chromates solution pH

The equilibrium pH (pH_{equil}) of the investigated Cr-solutions as a function of the equilibrium concentration (c_{equil}) is shown in Fig. S-1.

The following reactions can lead to an increase of pH_{equil}:[5]

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \leftrightarrow 2\ Cr^{3+} + 7\ H_2O \quad (S\text{-}1)$$

$$CrO_4^{2-} + 8\ H^+ + 3\ e^- \leftrightarrow Cr^{3+} + 4\ H_2O \quad (S\text{-}2$$

$$HCrO_4^- + 7\ H^+ + 3\ e^- \leftrightarrow Cr^{3+} + 4\ H_2O \quad (S\text{-}3)$$

$$H_2CrO_4 + 6\ H^+ + 3\ e^- \leftrightarrow Cr^{3+} + 4\ H_2O \quad (S\text{-}4)$$

$$CrO_4^{2-} + 4\ H_2O + 3\ e^- \leftrightarrow Cr(OH)_{3(s)} + 5\ OH^- \quad (S\text{-}5)$$

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During Cr uptake, a change in the color of the resins (from yellowish to black) at all pH values was observed.

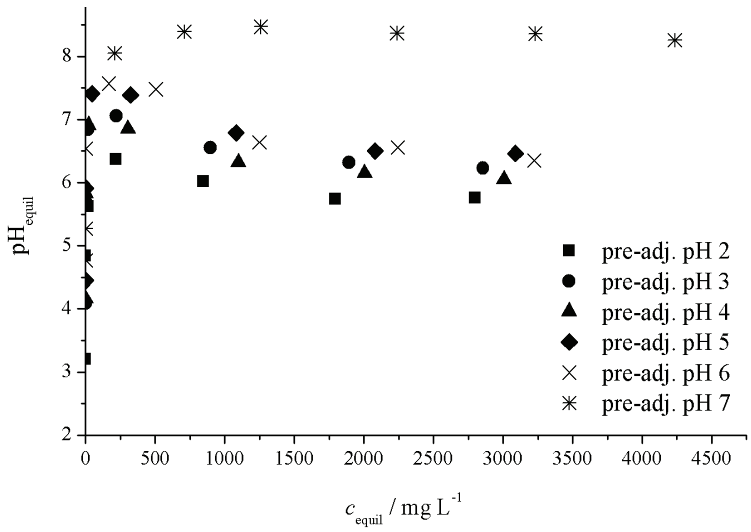

Fig. S-1. Equilibrium pH of Cr(VI) solution *vs.* c_{equil}.

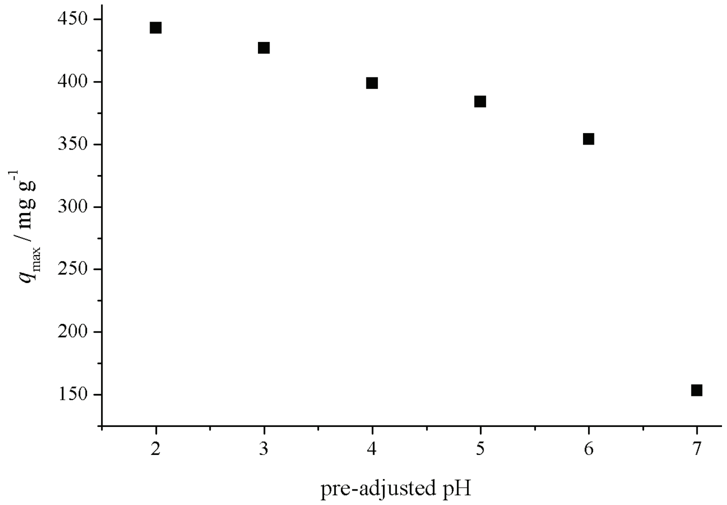

Fig. S-2. Experimental maximum sorption capacity, q_{max}, from solutions of different pre-adjusted pH values.

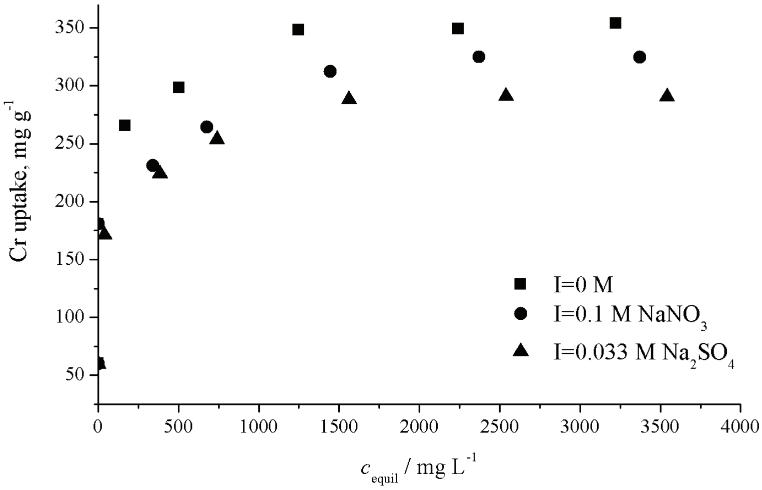

Fig. S-3. Isotherms for Cr(VI)-removal by the resin from aqueous solutions of pre-adjusted pH 6 in the presence of background electrolytes.

TABLE S-I. Adsorption isotherm models (q_{equil} and c_{equil}: equilibrium concentration of Cr(VI) in solid and liquid phase, respectively; q_{max}: the maximum sorption capacity in mg g^{-1}; K: the equilibrium constant; n and m: parameters characterizing the system heterogeneity)

Isotherm model	Equation
Langmuir (L)	$q_{equil} = q_{max}Kc_{equil}/1 + Kc_{equil}$
Redlich–Peterson (RP)	$q_{equil} = q_{max}Kc_{equil}/1 + (Kc_{equil})^n$
Langmuir–Freundlich (LF)	$q_{equil} = q_{max}(Kc_{equil})^n/1 + (Kc_{equil})^n$
Toth (T)	$q_{equil} = q_{max}Kc_{equil}/[1 + (Kc_{equil})^n]^{1/n}$

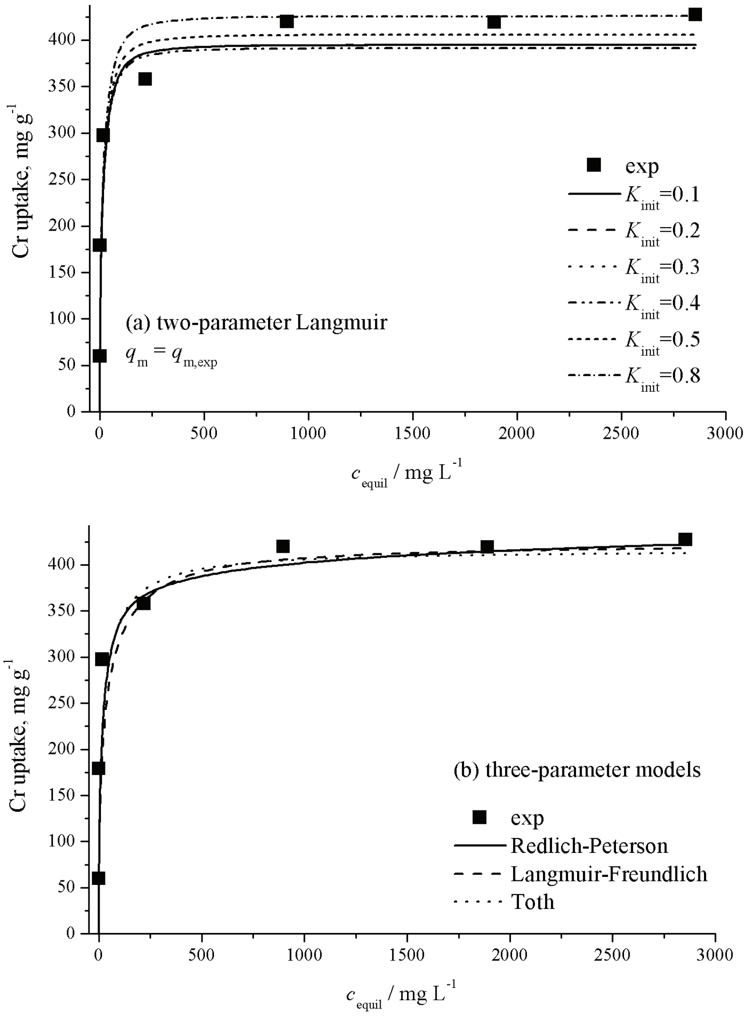

Fig. S-4. Experimental (symbols) and calculated (lines) isotherms for Cr(VI) sorption from aqueous solutions pre-adjusted pH 3 by the resin: a) the sensitivity of the Langmuir model to an initial guess of the estimated parameter *K* ($q_{init,max}$ was set equal to $q_{e,max}$ = 427.05 mg g^{-1}); b) three-parameter models.

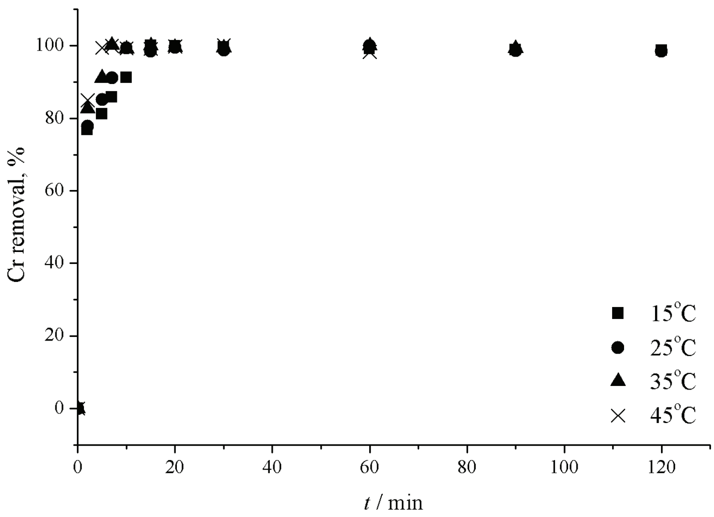

Fig. S-5. Time dependence of chromium removal onto the resin at different temperatures.

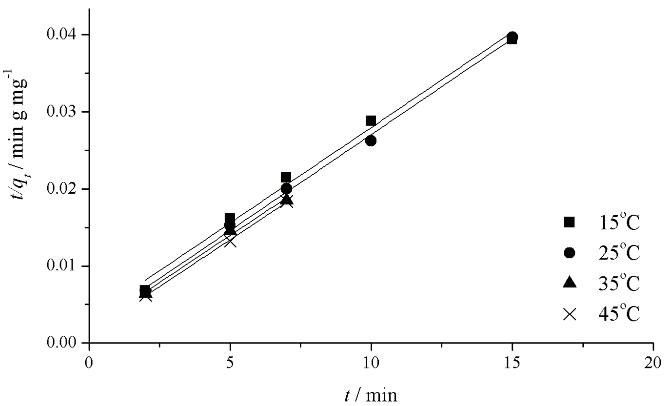

Fig. S-6. Pseudo-second order sorption kinetics of Cr(VI) onto the resin at various initial temperatures.

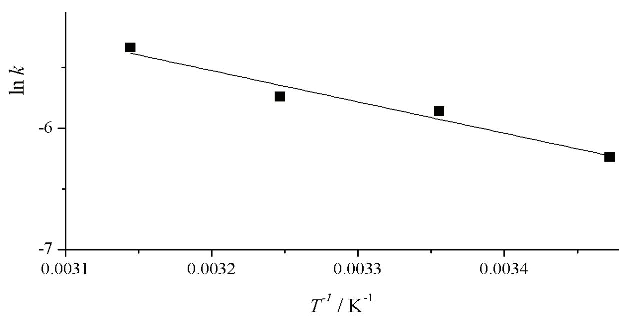

Fig. S-7. Plot of ln k against temperature for Cr(VI) sorption onto the resin.

TABLE IV. A comparison of sorption capacity for the Cr(VI)-sorption by selected sorbents reported in the literature

Sorbent	pH	Sorption capacity, mg g^{-1}	Ref.
Pterocladia capillacea	1	12	6
Surfactant-modified montmorillonite	3	18	7
Resin Lewatit MP 64	5	20.8	8
Resin Lewatit MP 500	6	21.3	8
Amberlite IRA96 ion-exchange resin	3	23.9	9
Dowex 1×8 ion-exchange resin	3	28.1	9
Untreated *Coriolus versicolor*	2	44.2	10
Ethylenediamine-modified cross-linked magnetic chitosan resin	2	51.8	11
Chemically modified *Sargassum sp.*	2	58.4	12
Ethylenediamine (EDA)-functionalized magnetic polymers	2.5	61.4	13
Aakaganeite (b-FeO(OH))	5.5	80	14
Chitin	2	101.2	15
Rhizopus arrhizus	2	108.9	16
Anion-exchange resin D314	4.5	120.5	17
Chitosan coated with poly-3-methyl thiophene	2	127.6	18
Stabilized iron nanoparticles	1	131.6	19
	3	123.4	
	5	96.2	
	7	112.4	
Staphylococcus xylosus	1	143	20
Anion-exchange resin D301	4.5	152.5	21
Anion-exchange resin D354	4.5	156.2	22
Tannery residual biomass	2	217	23
Fe-crosslinked chitosan complex	4.7	295	24
Polyethylenimine modified aerobic granules sludge	5.2	348.1	25
Aerobic granules functionalized with polyethylenimine	5.5	401.5	26
Polyethylenimine–epichlorohydrin resin	2	443	This work
Chitosan grafted with acrylic acid	4	518	27
Chitosan	4	655	27
Chitosan grafted with acrylamide	4	935	27

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