Supplementary Materials: The Influence of Salt Anions on Heavy Metal Ion Adsorption on the Example of Nickel

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Formulas and Fittings of the isotherms

The adsorption efficiency in percentage of nickel was calculated according to the following equation:

adsorption efficiency in % =
$$\frac{(C_0 - C_f)}{C_0} \cdot 100$$
 (1)

where C_0 and C_f are the initial and final nickel concentration in mg L⁻¹, respectively.

The amount of nickel adsorbed on the surface of chitosan flakes at equilibrium Q_e was calculated using the mass balance equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}$$
⁽²⁾

where C_0 and C_e (mg L⁻¹) are the initial and equilibrium concentrations of nickel ions, respectively. V (L) is the volume of the solution with the adsorbate and m (g) is the mass of the adsorbent.

Langmuir isotherm model is based on several assumptions that include the following:

- 1. a homogeneous surface,
- 2. adsorption takes place at a fixed number of definite localized sites,
- 3. all sites are equivalent and have the same energy,
- 4. at each site only one molecule is able to adsorb and
- 5. no interaction between adsorbed molecules takes place.

When the surface is saturated by a monomolecular layer of adsorbate the maximum adsorption is reached. The Langmuir isotherm is given by the following equation[1]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where C_e (mg L⁻¹) is the equilibrium concentration of nickel, q_e (mg g⁻¹) is the equilibrium nickel concentration in the solid phase, q_m (mg g⁻¹) is the maximum amount of adsorption and K_L (L mg⁻¹) is the Langmuir adsorption equilibrium constant. The favorability of the adsorption is given by the dimensionless separation factor R_L which is given by equation (4)[2–4]:

$$R_{L} = \frac{1}{1+K_{L}C_{0}} \tag{4}$$

where C_0 (mg L⁻¹) is the initial nickel concentration and K_L is the Langmuir constant. R_L indicates whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Freundlich adsorption isotherm model is a relationship between the amounts of ions (nickel) adsorbed per unit mass on adsorbent (q_e) and the concentration of the ions (nickel) at equilibrium (C_e). It is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface with the assumption that different sites with several adsorption energies are involved (heterogeneous surface), which lead to multilayer adsorption. Interactions between adsorbed molecules are considered. The more molecules are absorbed, the more difficult is the sorption of additional molecules. The Freundlich model is represented by equation (5)[5]:

$$q_e = K_F C_e^{1/n_F}$$
(5)

where $q_e (mg g^{-1})$ and $C_e (mg L^{-1})$ have the same destination as in Langmuir equation, $K_F (mg^{1-1/n}L^{1/n}g^{-1})$ is the Freundlich constant and n_F is a dimensionless constant. K_F is related to the bonding energy and represents the adsorption capacity. A larger K_F means higher adsorption capacity of the adsorbent. The constant n_F depicts the adsorption intensity and the degree to which an adsorption process is favorable, respectively. A value of n_F less than 1 means poor adsorption. When n_F is between 1 and 2 a moderately difficult adsorption takes place and a value of n_F between 2 to 10 good adsorption should be observed.[6]

Langmuir-Freundlich isotherm model is also known as sips model and was selected for further analysis. It is essentially a Freundlich isotherm, which approaches at high concentrations a maximum value. Langmuir-Freundlich isotherm is given by equation (6)[7–9]:

$$q_{e} = \frac{Q_{m}(K_{LF}C_{e})^{n_{LF}}}{1 + (K_{LF}C_{e})^{n_{LF}}}$$
(6)

where K_{LF} (L mg⁻¹) is the Langmuir-Freundlich constant and n_{LF} is the dimensionless Langmuir-Freundlich heterogeneity constant that ranges from 0 to 1 as frequently described in literature. The Langmuir-Freundlich equation trends to the Langmuir isotherm, when the heterogeneity parameter n_{LF} is set to unity and at very low concentrations reduces to the Freundlich isotherm.

The Gibbs free energy change (ΔG^0) was calculated by the following equation[10]:

$$\Delta G^0 = -RT \ln(K_C) \tag{7}$$

where R is the universal gas constant with 8.314 J mol⁻¹ K⁻¹, T is the temperature (K) and K_c the equilibrium distribution constant. The constant K_c can be calculated by

 $K_{\rm C} = C_{\rm S} / C_{\rm e} \tag{8}$

where C_e is the equilibrium concentration (mg L⁻¹) and C_S is the amount sorbed on solid at equilibrium.

The Pseudo-first-order rate equation is given as[1]:

$$\log(q_e - q_t) = \log(Q_e) - \left(\frac{k_1}{2.303}\right)t$$
(9)

where q_e is the maximum adsorption capacity (mg g⁻¹), q_t is the adsorption capacity at time t (mg g⁻¹) and k_1 (min⁻¹) is the pseudo-first-order rate constant of the adsorption. The rate constant k_1 and q_e were calculated from the slope $\left(-\frac{k_1}{2,303}\right)$ and intercept (logq_e) of the linear plots of log(q_e - q_t) versus t.

Pseudo-second-order equation is given by the following equation[11]:

$$\frac{\mathrm{t}}{\mathrm{q}_{\mathrm{t}}} = \frac{1}{\mathrm{k}_{2}\mathrm{q}_{\mathrm{e}}^{2}} + \left(\frac{1}{\mathrm{q}}\right)\mathrm{t} \tag{10}$$

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where $q_e (mg g^{-1})$ and $q_t (mg g^{-1})$ have the same destination as in pseudo-first-order equation. $k_2 (g mg^{-1} min^{-1})$ is the pseudo-second-order rate constant of the adsorption. By the plot of t/q_t versus t, which should give a straight line when pseudo-second-order kinetics are applicable, q_e and k_2 can be determined from slope $(\frac{1}{q_e})$ and intercept $(\frac{1}{k_2q_e^2})$, respectively.

Intra-particle diffusion model is given by the following equation[12]:

$$q_t = k_i t^{1/2} + C$$
 (11)

where q_t (mg g⁻¹) is the amount adsorbed at time t (min), k_i (mg g⁻¹ min^{-1/2}) is the intra-particle diffusion rate constant and C (mg g⁻¹) is the intra-particle diffusion constant and related to the thickness or resistance of the boundary layer in the adsorption process. If intra-particle diffusion was involved in adsorption process, the linear plot of q_t vs t^{1/2} give a straight line and if rate-limiting step was only intra-particle diffusion, the line will pass through the origin.[11]

Experimentally determined adsorption capacities and equilibrium parameters

Table S1. Experimentally determined adsorption capacities and equilibrium parameters given by the Langmuir, Freundlich and Langmuir-Freundlich models of the adsorption of nickel on chitosan in presence of sulfate or nitrate anions.

	Langmuir				Freundlich				Langmuir-Freundlich			
	qm,exp	qm	KL	RL	R ²	KF	NF	R ²	qm	Klf	n lf	R ²
	mg g-1	mg g-1	L mg ⁻¹			$mg^{1-1/n}L^{1/n}g^{-1}$			mg g-1	L mg ⁻¹		
Ni ²⁺ (SO ₄ ²⁻)	81.9	87.90	0.016	0.033-0.946	0.979	10.894	3.41	0.892	81.92	1.41*10-2	3.475	0.991
Ni ²⁺ (NO ₃ -)	21.2	24.60	0.006	0.097-0.981	0.963	1.9735	2.876	0.995	74.34	1.21*10-4	0.422	0.996

Comparison EDX spectra



Figure S1. Comparison of the EDX spectra of natural chitosan surface (black line) with chitosan surfaces loaded with nickel sulfate (red line) and nickel nitrate (blue line).



Streaming potential – pH measurements

Figure S2. Streaming potential-pH-profile of the chitosan flakes.

Adsorption capacity of nickel

Table S2. Adsorption capacities for nickel (a.d. = adsorbent dose; aN,N'-di(carboxymethyl)dithiocarbamate, boxidized multiwall carbon nanotubes; csilica gel modified by triethylenetatraaminomethylenephosphonic acid).

Mathematical	Adsorption	NT:2+14	Expe	- Dof		
waterial	capacity, q	IN1 ² Salt	\mathbf{pH}_0	a.d. (g/L)		ket.
Activated red mud	160 mg/g	NiSO4	5.0	n.a.	20-25°C 600 s	[13]
Activated carbon from apricot waste	101.01 mg/g	NiNO ₃	5	70	1 h	[14]
Chitosan flakes 90% da Biolog®	81.9 mg/g 1.39 mmol/g	NiSO4	6.0	5.0	25 °C, 24 h	current study
Chitosan/ceramic alumina	78.10 mg/g	NiSO4	4.0	n.a.	25 °C 24 h	[15]
Activated carbon from coirpit	62.5 mg/g	NiSO4	5.0	0.4	30 °C 40 min 288 K,	[16]
PSDC ^a	0.97 mmol/g	n.a.	5.0	1	303 K, 318 K, 24 h	[17]
Blast furnace slag	0.95 mmol/g 55.75 mg/g	NiCl ₂	4.20	1.0	25 °C 240 min	[18]
Parthenium	54.35 mg/g	NiSO ₄	5.0	1	12 h 20°C	[19]
Activated carbon from peanut hull	53.65 mg/g	NiSO4	6.5	0.85	24 h	[20]
Chitosan/magnetite	52.55 mg/g	NiSO4	4-6	0.1	120 min RT	[21]
Activated carbon from almond husk	30.769 mg/g	NiSO4	5.0	5	20 °C 10 min	[22]
PEI-Silica gel	28.25 mg/g	NiNO ₃	5.5	3.0	2 h	[23]
Peat	28.26 mg/g	n.a.	4.5	4.0	25 °C 3 h	[24]
Blank alginate beads	25.6 mg/g	NiNO3	5.0	2.5	25 °C	[25]
Na-bentonite	24.2 mg/g	n.a.	6.0	2.5	22°C 6 h	[26]
Chitosan flakes 90% da Biolog®	21.2 mg/g 0.36 mmol/g	NiNO ₃	6.0	5.0	25 °C, 24 h	current study
Chitosan/cellulose	13.21 mg/g	n.a.	5.30	2	12 h 25 °C	[27]
Clinopttilolite rock (Ukraine)	13.03 mg/g	NiNO ₃	6.2	60	24 h	[28]
Baker`s yeast	11.4 mg/g	NiSO ₄	6.75	1	24 h	[29]
Grape stalks waste	0.1818 mmol/g	NiCl ₂	6.0	10	25 °C	[30]
MWCNT ^b	9.43 mg/g	NiNO3	6.55	0.75	303 K	[31]

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Chitosan/cotton fibers	7.63 mg/g	n.a.	6.5	4	25 °C	[32]
Begasse fly ash	6.49 mg/g	NiCl ₂	6.0	10	30 °C 5 h	[33]
Ca-bentonite	6.32 mg/g	n.a.	6.0	10	22°C 6 h	[26]
Modified activated carbon	5.81 mg/g	NiSO4	5.0	50	25 °C 200 min	[34]
GH-T-Pd ^c	0.0964 mmol/g	n.a.	5	2	25 °C 24 h	[35]
Chabazite	4.50 mg/g	n.a.	3 - 6	5	24 h	[36]
bentonite	0.0736 mmol/g	NiNO ₃	3.0	25	60 min 303 K	[37]
Chitosan/alginate beads	2.40 mg/g	n.a.	5.0	0.05	24 h, 25 °C	[38]
Raw Kaolinite	1.669 mg/g	NiSO4	n.a.	n.a.	298 K 2 h	[39]
Fly ash (seyitomer)	1.160 mg/g	NiNO ₃	8.0	25 mg/l	20 °C 120 min	[41]
Bagasse fly ash	1.12 mg/g	NiNO ₃	6.5	10	30°C 80 min	[40]
Fly ash (Afsin-elbistan)	0.987 mg/g	NiNO ₃	8.0	25 mg/l	20 °C 120 min	[41]
Clinoptilolite	0.48 mg/g	NiCl ₂	5-7	10 - 40	1 mL / min.	[42]
Silica gel	0.0076 mmol/g	n.a.	4.0- 5.45	10	25 °C 4 h	[43]

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