



Politechnika Rzeszowska
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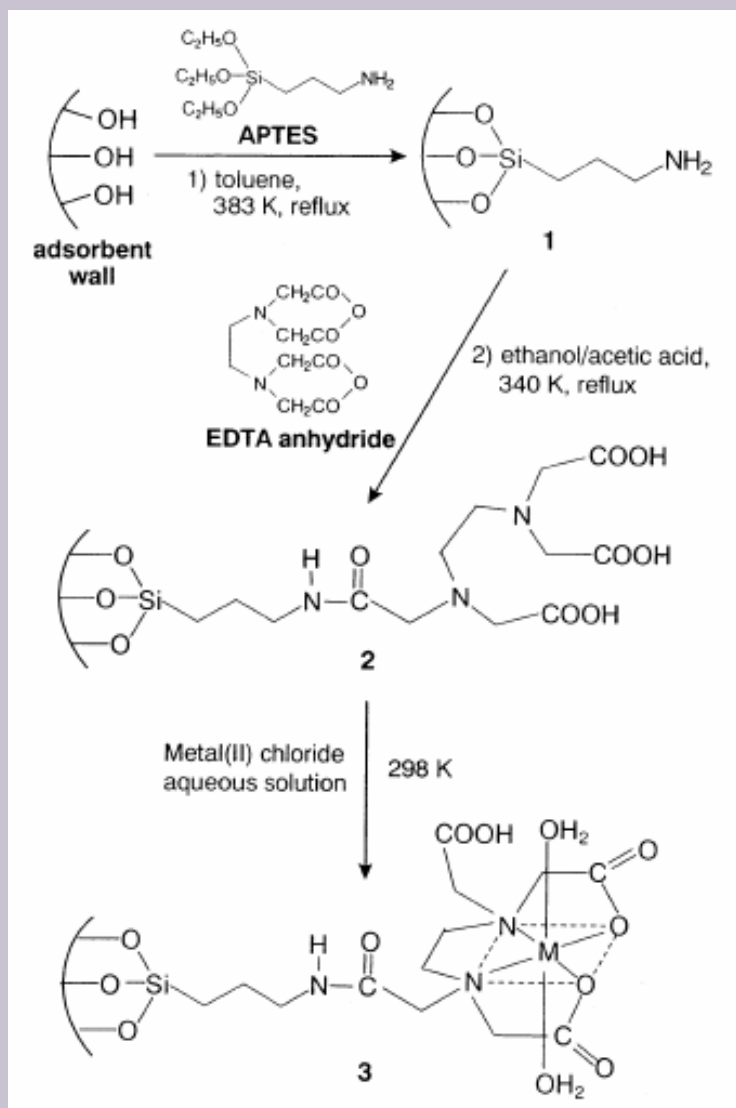


MODELING OF SORPTION EQUILIBRIUM IN TWO-COMPONENT SYSTEMS

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Yaroslav Gumnitsky

Experimental part

Schematic diagram for the synthesis of silica gel modified with EDTA



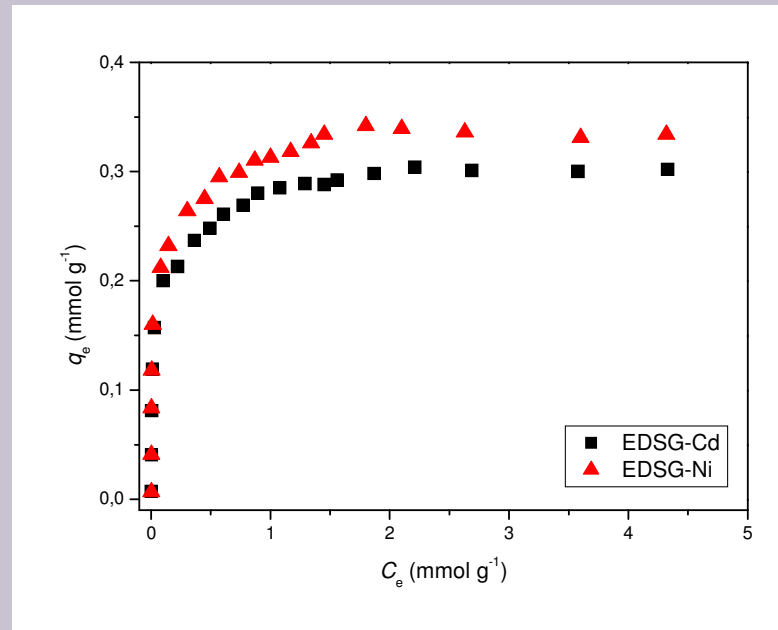
Chemicals and equipment:

- Silica gel (SG);
- Ethylenediaminetetraacetic acid (EDTA),
- Aminopropyl-triethoxysilane (APTES),
- Double deionized water obtained from SG Ultra Clear Basic (0.055 $\mu\text{S}/\text{cm}$);
- Acetic acid 100%,
- Absolute ethanol;
- ICP-OES (iCAP 6300, Thermo Electron Corporation, USA);
- Rotary shaker type ST5 (CAT M.Zipperer GmbH, Staufen, Germany);
- Drying oven, Termaks model TS8000)

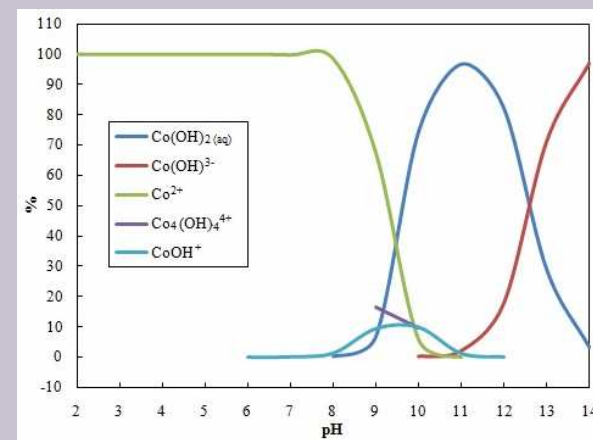
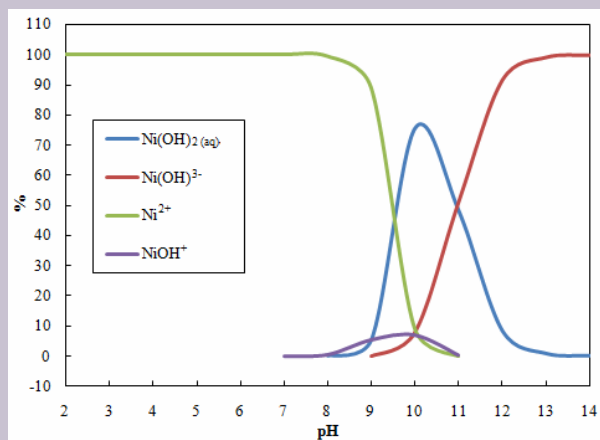
Properties	Silica gel LiChroPrep®		
Diameter (μm)	5-20	40-63	63-200
Pore volume (g/cm^3)	0.84	0.90	0.84
Surface area (m^2/g)	540	580	540

One-component isotherm

Equilibrium data of Ni(II) and Co(II) sorption on EDSG, pH=3

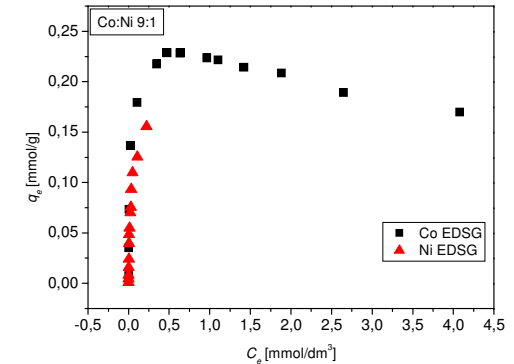
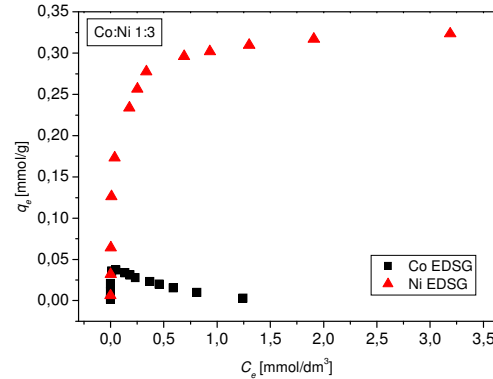
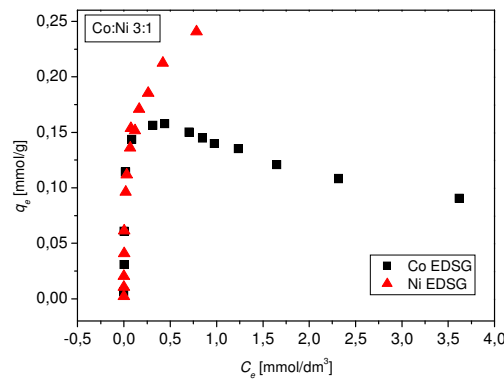
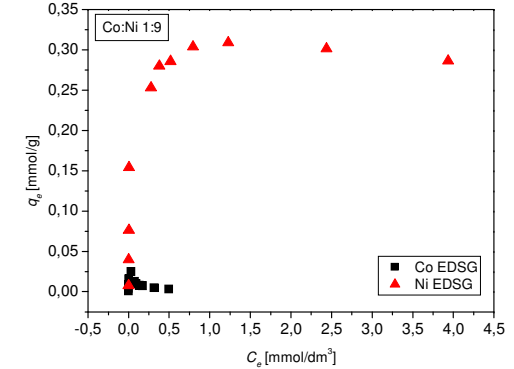
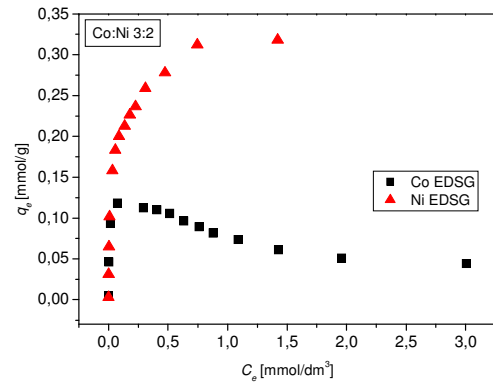
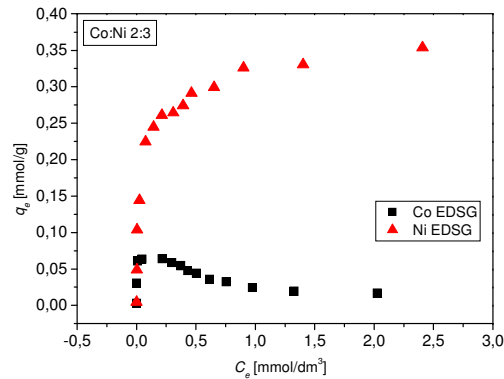
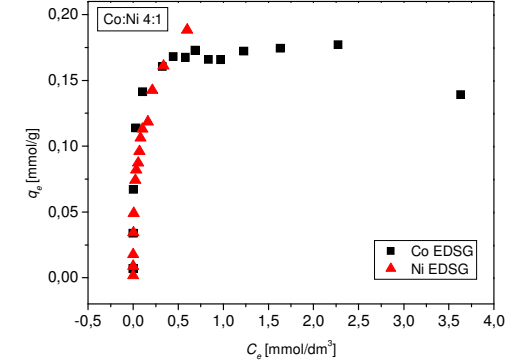
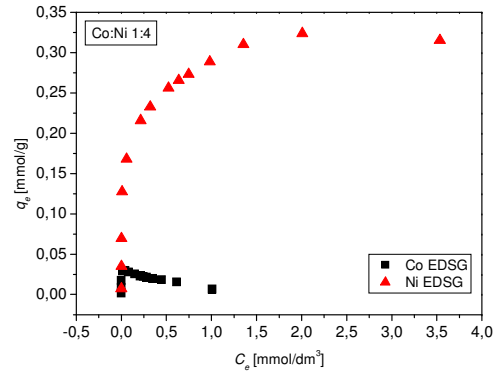
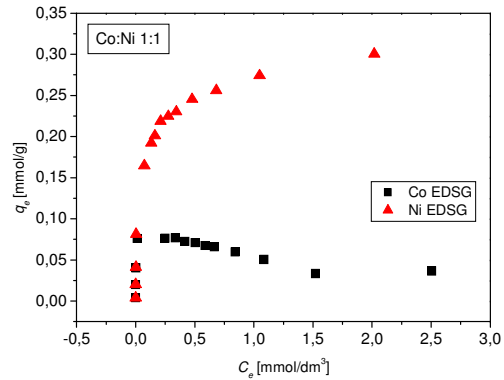


Distribution of various Ni(II) and Co(II) species as a function of pH



Two-component isotherm

Under constant mass ratio of Co:Ni ions: 1:1, 1:3, 3:1, 2:3, 3:2, 1:4, 4:1, 1:9, and 9:1



Modeling part

BiLangmuir model

$$q_e = \frac{q_{m,1}K_1C_e}{1 + K_1C_e} + \frac{q_{m,2}K_2C_e}{1 + K_2C_e}$$

where $q_{m,1}$ and $q_{m,2}$ are the maximum adsorption capacities of two different adsorption sites: (1) APTSG and (2) EDSG, respectively. K_1 and K_2 are energies of the adsorption related to adsorption sites (1) APTSG and (2) EDSG, respectively.

Competitive BiLangmuir model

$$\left\{ \begin{array}{l} q_{e1} = \frac{q_{m,1,1}K_{1,1}C_{e1}}{1 + K_{1,1}C_{e1} + K_{2,1}C_{e2}} + \frac{q_{m,1,2}K_{1,2}C_{e1}}{1 + K_{1,2}C_{e1} + K_{2,2}C_{e2}} \\ q_{e2} = \frac{q_{m,2,1}K_{2,1}C_{e2}}{1 + K_{1,1}C_{e1} + K_{2,1}C_{e2}} + \frac{q_{m,2,2}K_{2,2}C_{e2}}{1 + K_{1,2}C_{e1} + K_{2,2}C_{e2}} \end{array} \right.$$

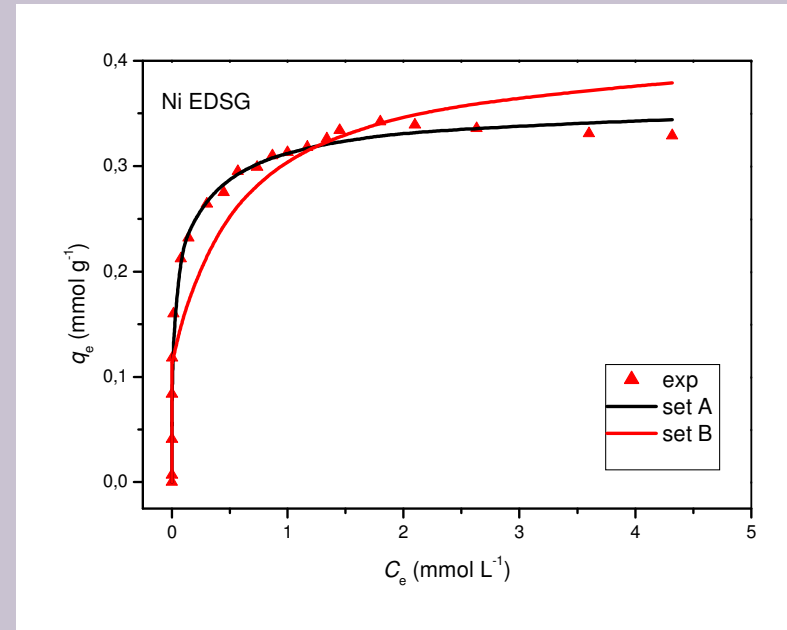
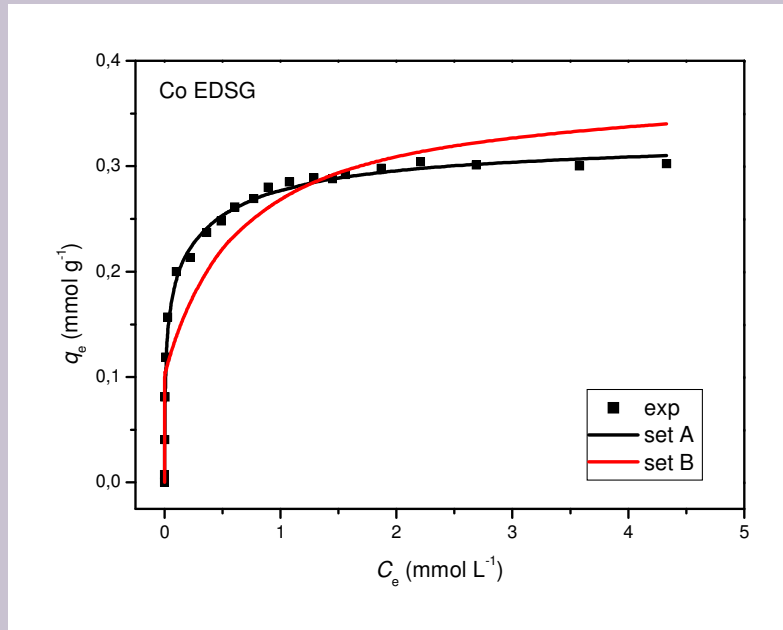
Estimation procedure

Nonlinear regression method based on the Levenberg-Marquardt algorithm. The isotherm parameters were determined by minimizing the Sum of the Squares of the Errors function

$$\sum_{i=1}^n (q_{e,\text{exp}} - q_{e,\text{calc}})_i^2$$

The relationship between experimental and theoretically predicted points was assessed by the coefficient of determination (R^2), standard deviation (σ), and mean error (ME).

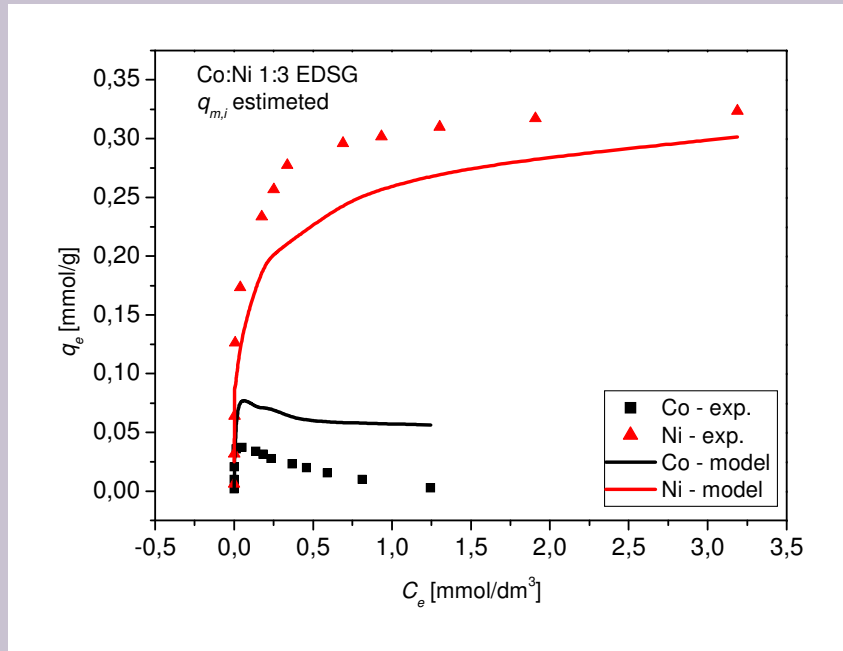
Modeling of one-component equilibrium



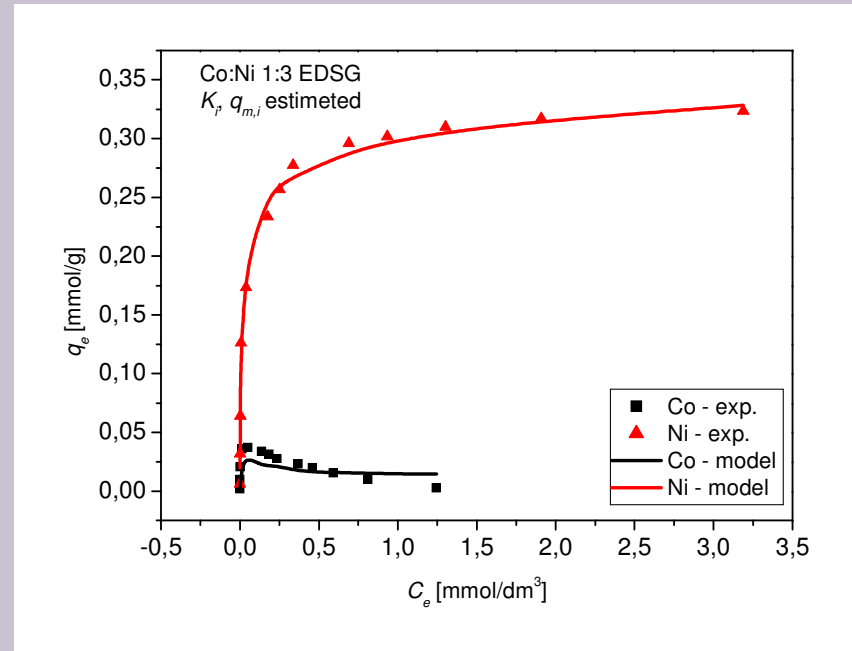
Guess value	ion	$q_{m,exp}$ mmol/g	q_{m1} mmol/g	K_{BiL1} L/g	q_{m2} mmol/g	K_{BiL2} L/g	R^2	σ	ME %
A			0.3	1.0	0.3	1.0			
	Co	0.302	0.132	1.883	0.193	110.671	0.9962	0.009	20.827
	Ni	0.329	0.142	2.328	0.215	118.205	0.9869	0.019	46.605
B			0.1	1.0	1.0	1.0			
	Co	0.302	0.102	$1.75 \cdot 10^9$	0.274	1.568	0.9161	0.040	79.447
	Ni	0.329	0.111	$1.67 \cdot 10^9$	0.303	1.750	0.9153	0.046	93.546

Modeling of two-component equilibrium

Two-parameters estimated



Four-parameters estimated

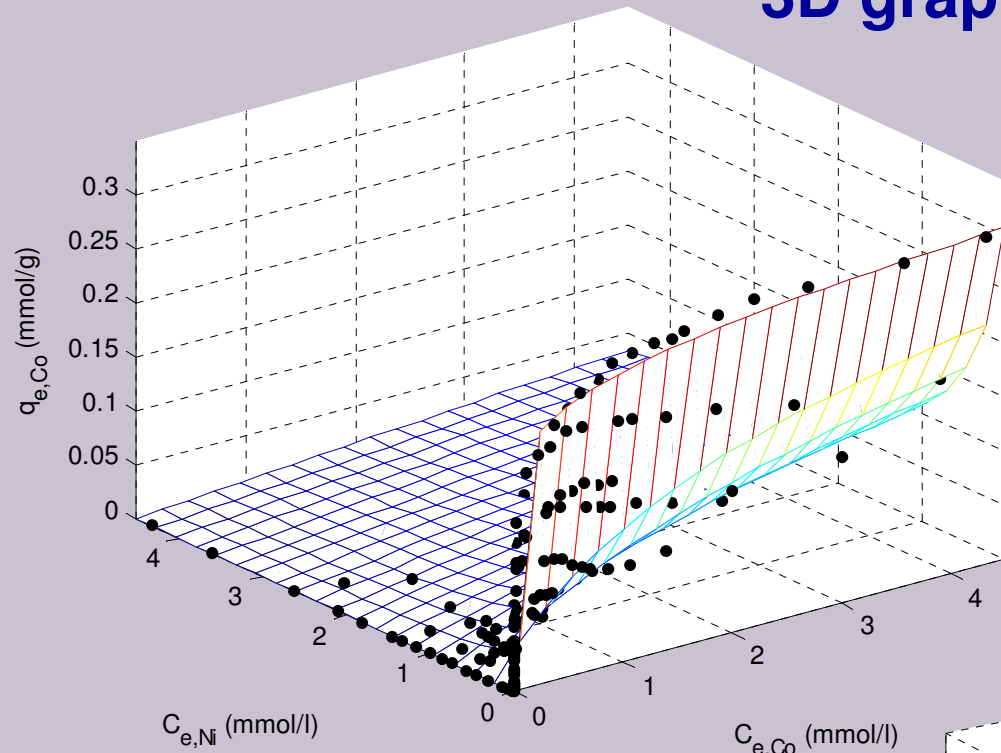


q_{mCo1} (mmol/g)	q_{mCo2} (mmol/g)	K_{BiLCo1} (L/g)	K_{BiLCo2} (L/g)	q_{mNi1} (mmol/g)	q_{mNi2} (mmol/g)	K_{BiLNi1} (L/g)	K_{BiLNi2} (L/g)	R^2	σ	ME (%)
n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	n.e.	0.7639	0.074	138.983
0.047	0.158	n.e.	n.e.	0.220	0.238	n.e.	n.e.	0.8565	0.060	110.941
0.099	0.238	0.529	70.084	0.098	0.229	13.907	492.982	0.9864	0.018	106.953

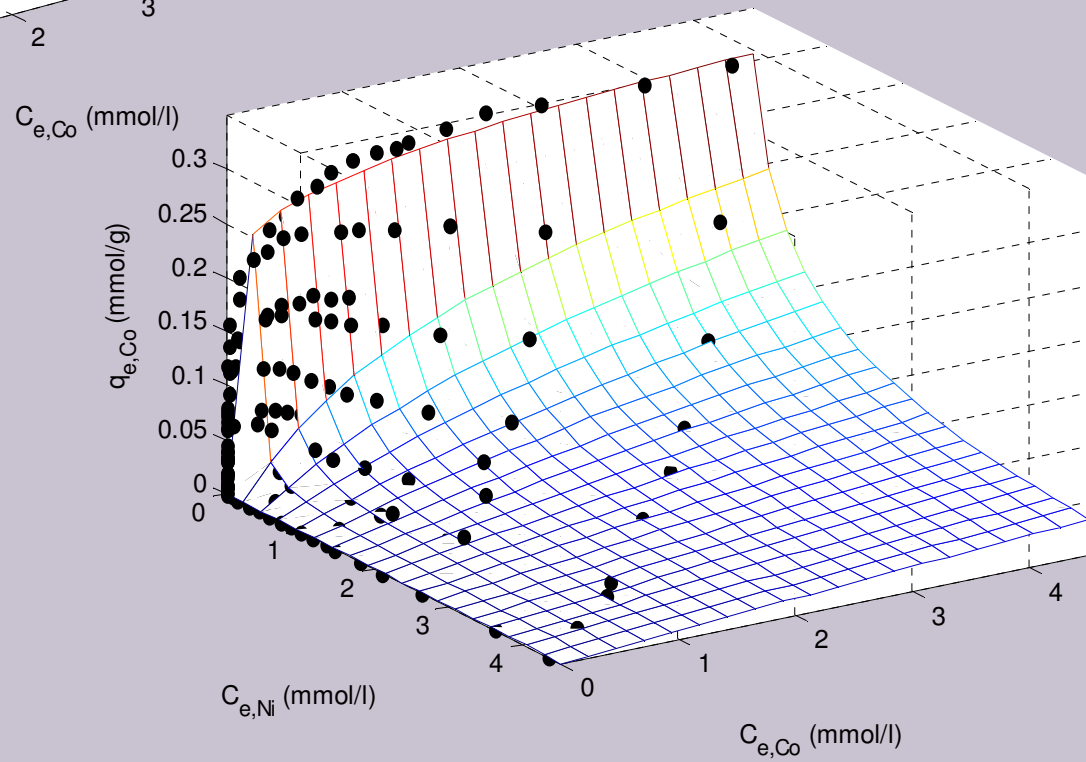
n.e. non estimated

Co EDSG

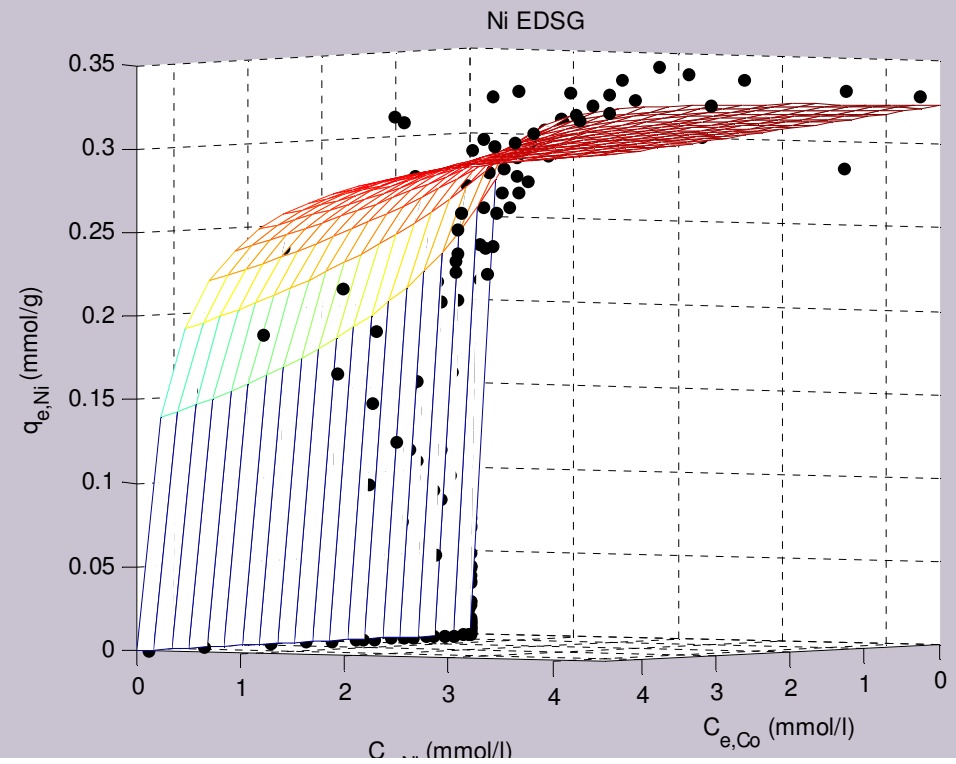
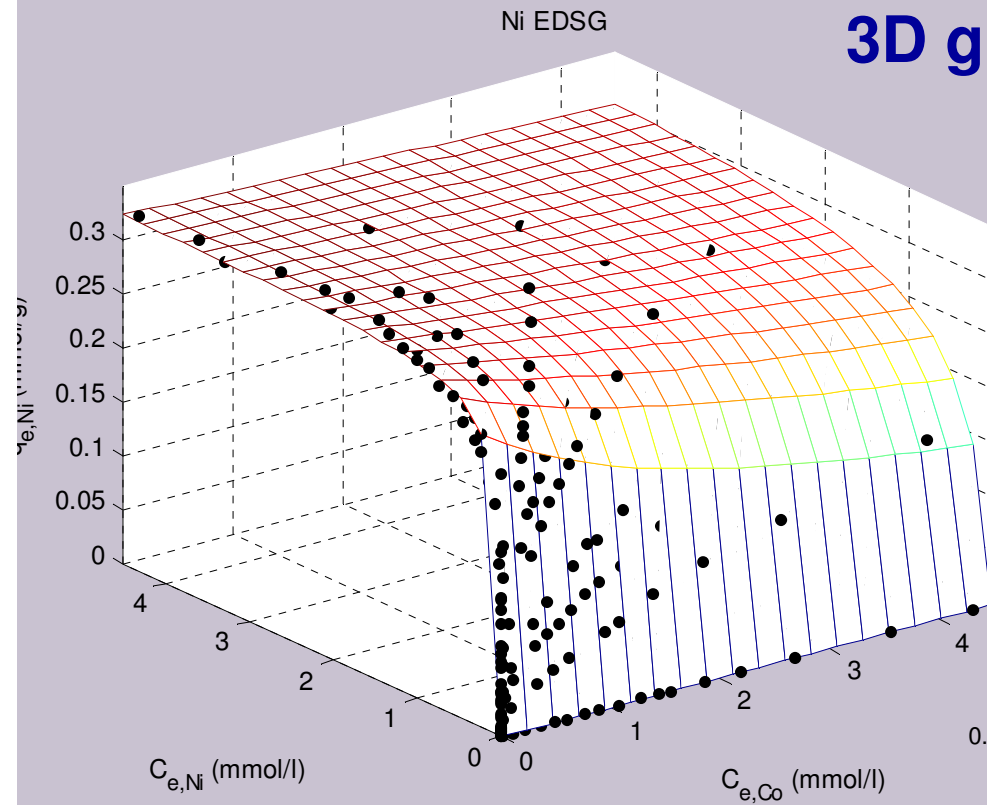
3D graphs



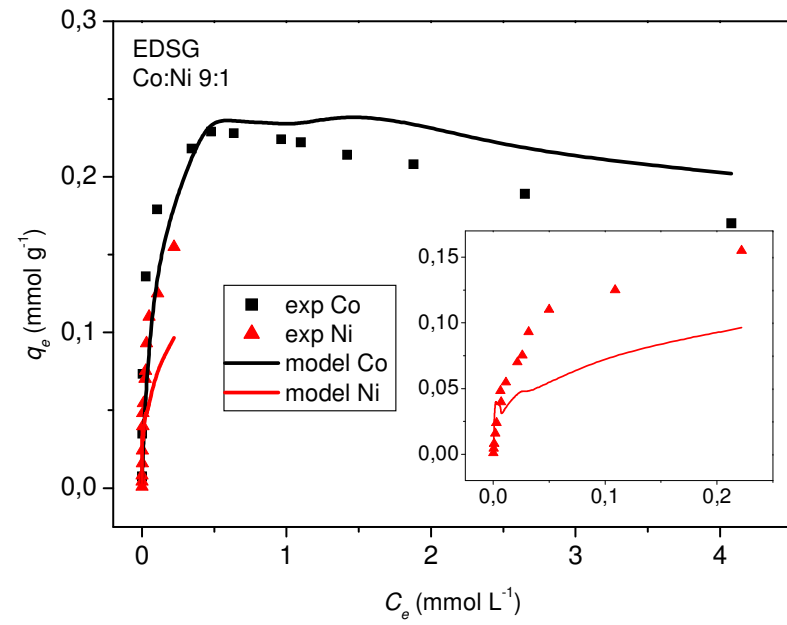
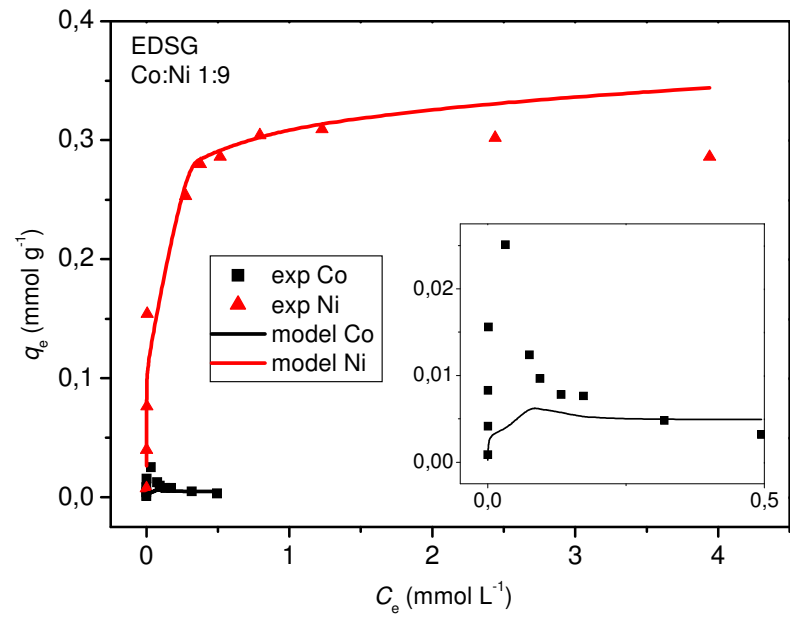
Co EDSG



3D graphs



2D graphs



Conclusions

The validation of the parameter values cannot be totally proven by nonlinear regression and corresponded to the global minimum of the objective function. The best correlation with the experimental data was obtained using initial guesses of maximum adsorption capacities (q_m) corresponding to the experimentally obtained ones.

The application of the extended Bilangmuir model confirmed the coexistence of low- (APTES) and high (EDTA) -energy active sites on sorbent surface that showed an unequal ability for Co(II) and Ni(II) adsorption. However, the overlapping parts of the resulting isotherms presented in the three-dimensional graphs could not provide a useful evaluation of the accuracy of the fit.

Acknowledgements

The authors gratefully acknowledge the State Committee for Scientific Research (Poland) (KBN N N209 760140) for the financial support.