

СЕКЦІЯ 6

ХІМІЯ ДОВКІЛЛЯ ТА ЕКОТОКСИКОЛОГІЯ. ПРОБЛЕМИ ЗМІН КЛІМАТУ ТА БІОСФЕРИ. КОНТРОЛЬ ЗА АТМОСФЕРНИМИ ВИКИДАМИ У СВІТЛІ КІУТСЬКОГО ПРОТОКОЛУ

UDC 532.5: 519.688

Roman Petrus, Jolanta Warchol (Polska, Rzesov)
Miroslav Malovanyy, Yaroslav Gumnitsky (Ukraine, Lviv)

MODELING OF SORPTION EQUILIBRIUM IN TWO-COMPONENT SYSTEMS

1. Introduction

Mesoporous silica-based adsorbents have been increasingly attracting the attention of researchers over the last decades due to their large, easy-to-modify surface areas. Immobilization of active chemical groups results in a substantial increase of binding capacity of silica gels for variety of metal ions and opens up a possibility to achieve effective alternatives for conventional sorbents. Preliminary modification is usually done by a simple silylating agent such as (3-aminopropyl)triethoxysilane (APTES). After that an increase of the organic chain with a variety of organic molecules, such as EDTA-anhydride, is possible. [1].

Practical application of the modified silica gel requires multi-component equilibrium models that are able to describe quantitatively the partitioning of one or more ions as a function of solution composition. Recently reported results demonstrated that the biLangmuir model could be used to represent one-component adsorption equilibrium of Co(II) and Ni(II) ions on EDTA-modified silica gel (EDSG) [2]. This model correlates well with the experimental finding considers the coexistence of two different adsorption groups on the sorbent surface: APTES groups having a low affinity toward metal ions and EDTA groups with high affinity. However, the validation of the model parameters cannot be totally proven by nonlinear regression. It is frequently observed that the initial value of the parameters (the initial guess) may not converge to a global minimum during the optimization process [3]. Consequently, even for a small residual error, the isotherm equation can yield an unacceptable match of the data and highly biased parameters [4]. Therefore, the aim of this work was to examine model sensitivity to an initial guesses of estimated parameters and to investigate the competitive adsorption by using the extended biLangmuir model.

2. Experimental part

Silica gel type LiChroPrep® as well as all chemicals used in this study (analytical grade) were supplied by Merck. Surface functionalized silica gel was synthesized by reacting EDTA-anhydrides with aminopropyl-modified silica gels in ethanol/acetic acid solution.

Adsorption of Ni(II) and Co(II) by modified silica gel (EDSG) were studied at ambient temperature using batch experiments. A contact time of 50 h and the adsorbent dose of 2 g/L were used. Agitation was conducted with a rotary shaker (CAT M.Zipperer GmbH, Staufen, Germany). The initial metal concentration in one- and two-component systems were varied from 1 to 300 mg/L to generate a relatively evenly spaced distribution of ions along the adsorption isotherm. To obtain the competitive effect of Co(II) and Ni(II) adsorption, the initial concentration of both metal ions was varied so as to maintain the 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. The pH of each solution was adjusted to the value of 3.0 by using 0.1 M HNO₃.

After each adsorption test, the adsorbent was separated from the solution using a 0.45 μm polypropylene syringe filter. The metal contents were analyzed by an inductively coupled plasma optical atomic emission spectrometer (ICP-OES) (iCAP 6300, Thermo Electron Corporation, USA). The amount of metal ions adsorbed per unit mass of modified silica gel (mg/g) was calculated as follows:

$$q_e = \frac{(C_i - C_e)}{M} V \quad (1)$$

where C_i and C_e (mg/L) are the initial and the equilibrium ion concentrations, respectively, M (g) represent the weight of the adsorbent, and V (L) is the volume of the solution.

3. Modeling part

The biLangmuir model assumes the coexistence of two kinds of active sites associated with monolayer adsorption ($q_{m,1}$ and $q_{m,2}$) that behave independently and have different stabilities of the adsorbed complexes formed between sites and metal ions (K_1 and K_2) [5]:

$$q_e = \frac{q_{m,1} K_1 C_e}{1 + K_1 C_e} + \frac{q_{m,2} K_2 C_e}{1 + K_2 C_e} \quad (2)$$

where $q_{m,1}$ and $q_{m,2}$ are the maximum adsorption capacities of two different adsorption sites: (1) APTES and (2) EDTA, respectively. K_1 and K_2 are energies of the adsorption related to adsorption sites (1) APTES and (2) EDTA, respectively. In the case of two component systems, the extended BiLangmuir model is given as:

$$q_{e1} = \frac{q_{m,1,1} K_{1,1} C_{e1}}{1 + K_{1,1} C_{e1} + K_{2,1} C_{e2}} + \frac{q_{m,1,2} K_{1,2} C_{e1}}{1 + K_{1,2} C_{e1} + K_{2,2} C_{e2}} \quad (3)$$

$$q_{e2} = \frac{q_{m,2,1}K_{2,1}C_{e2}}{1 + K_{1,1}C_{e1} + K_{2,1}C_{e2}} + \frac{q_{m,2,2}K_{2,2}C_{e2}}{1 + K_{1,2}C_{e1} + K_{2,2}C_{e2}} \quad (4)$$

where $q_{m,1,1}$ and $q_{m,1,2}$ are the maximum adsorption capacities of the component 1 on adsorption sites (1) APTES and (2) EDTA, respectively and $K_{1,1}$ and $K_{1,2}$ are adsorption energies related to the adsorption of the component 1 on adsorption sites (1) APTES and (2) EDTA, respectively. Accordingly, $q_{m,2,1}$, $q_{m,2,2}$, $K_{2,1}$ and $K_{2,2}$ are corresponding parameters related to the adsorption of component 2. The equilibrium constant were obtained by fitting experimental data to the model by using a nonlinear regression method based on the Levenberg-Marquardt algorithm [6]. The isotherm parameters were determined by minimizing the Sum of the Squares of the Errors (ERRSQ) objective function across the concentration range studied:

$$\sum_{i=1}^n (q_{e,exp} - q_{e,calc})_i^2 \quad (5)$$

where n is the number of experimental data points, $q_{e,exp}$ and $q_{e,calc}$ are experimental and the calculated equilibrium concentration in solid phase, respectively. The relationship between experimental and theoretically predicted points was assessed by the coefficient of determination (R^2), standard deviation (σ), and mean error (ME).

4. Results and discussion

4.1. Modeling of one-component equilibrium

The search for an appropriate set of initial model parameters, which converges the optimization procedure to the global minimum, was started with a random value of model parameters. Next the value of each of them was changed one at a time (0.0001, 0.001, 0.01, 0.1, 1.0, etc.), keeping the values of the others constant. The border range of optimization was from 1×10^{-10} to 1×10^{10} . This procedure was repeated until the objective function achieved the lowest value. Table 1 summarizes the BiLangmuir model sensitivity for two different sets of initial parameter guesses: set A relates to guess value of $q_{m,1}$, K_1 , $q_{m,2}$, K_2 equal to 0.3, 1.0, 0.3, 1.0 respectively, where $q_{m,1}$ and $q_{m,2}$ correspond to the experimentally obtained values of maximum adsorption capacity (q_m); set B relates to random value of $q_{m,1}$, K_1 , $q_{m,2}$, K_2 equal to 0.1, 1.0, 1.0, 1.0, respectively. A comparison of the value of the statistical tests (R^2 , σ , ME) identified that use of the experimentally obtained value of maximum adsorption capacity (q_m) as an initial guess (set A) allowed to achieved better approximation of the experimental points. As can be seen in Fig.1, the optimization procedure may converge to a local minimum, which gives an unacceptable match of equilibrium data if a poor initial guess is used.

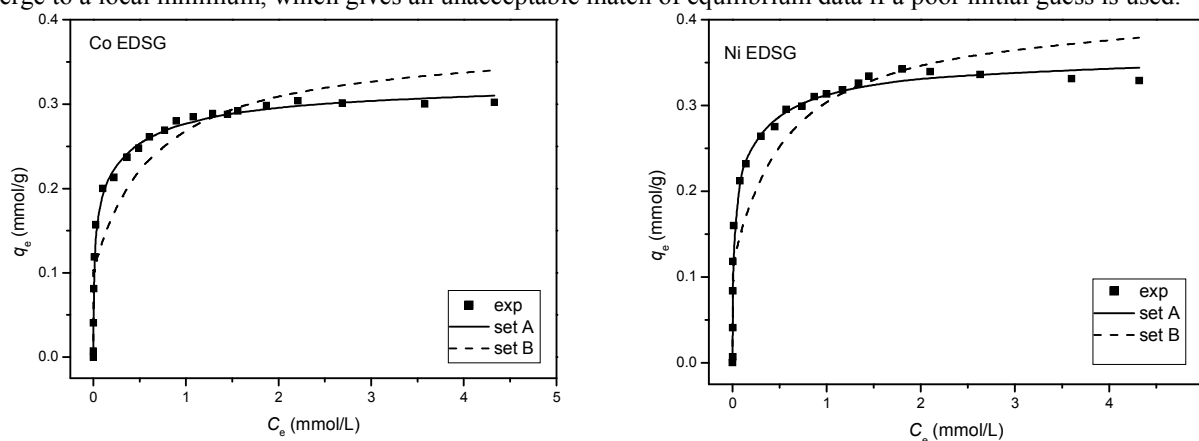


Fig.1 Comparison between the model and experimental data for one-component systems.

Table 1. BiLangmuir constants for the one-component systems.

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	1.75×10^9	0.274	1.568	0.9161	0.040	79.447
	Ni	0.329	0.111	1.67×10^9	0.303	1.750	0.9153	0.046	93.546

4.1. Modeling of two-component equilibrium

The adsorption fitting parameters for the extended biLangmuir model are depicted in Table 2. The three-dimensional Fig. 2(a) demonstrates that the applied model could be successfully used for the prediction of the adsorption behavior of Co(II) and Ni(II) from two-component mixtures on the EDSG. However, a quite big mean error (ME) values (Table 2) made the model applicability a bit doubtful. To have a deeper insight into the quality of the model fit, single sets of two-component adsorption data were presented in two-dimensional graph (Fig. 2(b), as an example). The calculated curves clearly show the deviations from the experimental points. Obviously, this effect originated from the presence of relatively strong ion interactions that were able to change the behavior of isotherm model in a qualitative way. It was

further confirmed by ME values that represent the average of absolute difference between experimental and modeling data.

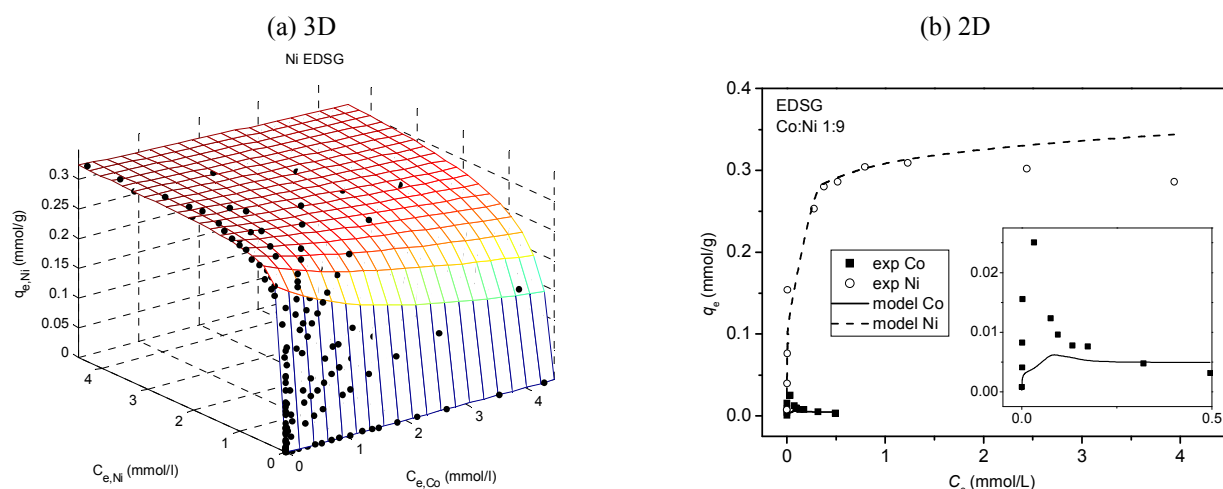


Fig.2 Comparison between the model and experimental data for two-component systems. (a) 3 Dimensional, (b) 2 Dimensional

Table 2. BiLangmuir constants for the two-component systems.

q_{mCo1}	q_{mCo2}	K_{BiLCo1}	K_{BiLCo2}	q_{mNi1}	q_{mNi2}	K_{BiLNi1}	K_{BiLNi2}	R^2	σ	ME
mmol/g		L/g		mmol/g		L/g				%
0.099	0.238	0.529	70.084	0.098	0.229	13.907	492.982	0.9864	0.018	106.953

5. 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.

1. Jal P.K., Dutta R.K., Sudarshan M., Saha A., Bhattacharyya S.N., Chintalapudi S.N., Mishra B.K., Talanta 2001, 55, 233–240.
2. Repo E., Kurniawans T.A., Warchoń J.K., Sillanpaa M.E., J. Hazard. Mat., 2009, 171(1-3), 1071-1080.
3. Seferlis P., Hrymak A.N., Computers Chem. Eng., 1996, 20, 1177–1200.
4. Kumar K.V., Sivanesan S., J. Hazard. Mater., 2005, B126, 198–201.
5. Guiochon G., Felinger A., Shirazi D.G., Katti A.M., Fundamentals of preparative and nonlinear chromatography. Elsevier, NY, 2006.
6. Marquardt, D.W., J. Soc. Ind. Appl. Math., 1963, 11 (2), 471–475.

УДК 66.074.5:551.588.74

Дерейко Х. О. (Україна, Львів), Długogorski В.-Z. (Australia, Newcastle),
Мальований М. (Україна, Львів)

ЗАСТОСУВАННЯ МЕТОДОЛОГІЇ ОЦІНЮВАННЯ ЖИТТЄВОГО ЦИКЛУ ДЛЯ АНАЛІЗУ ПРОЦЕСІВ УЛОВЛЕННЯ ДІОКСИДУ ВУГЛЕЦЮ

Останнім часом турботи щодо кліматичних змін на Землі набувають все більшої актуальності. Відомо те, що кліматичні зміни викликані головним чином викидами парникових газів, серед яких найбільшої уваги заслуговують викиди діоксиду вуглецю. Основною причиною утворення викидів CO₂ є спалювання палива для забезпечення світових енергетичних потреб. Приблизно 86 % глобального використання енергії та 75 % антропогенних викидів CO₂ є похідними спалювання викопного палива [1]. Зокрема, Австралія є однією з країн,