ORGANIC SOLVENTS REMOVAL FROM WASTEWATERS WITH A METHODS OF ADSORPTION AND SELECTIVE ADSORPTION (LIQUID CHROMOTOGRAPHY)

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Abstract The mathematical model of chromatographic separations of two-component mixtures is developed for the heterogeneity of the adsorbent surface with variable composition of mobile phase and its adequacy is tested in the real process.

Key words: Liquid chromatography; Solvent; Wastewater; Adsorption.

INTRODUCTION

Purification of sewage which is contaminated by multi-component organic substances is complicated because of their similarity. In such cases the purification takes few steps according to each pollutant, but it is almost impossible to receive a clean sewage and to classify each pollutant that have very similar physical and chemical characteristics without using complicated schemes. That is why the process of liquid chromatography can be very efficient, since it allows not only to purify the sewage from mix of pollutants but also to receive clean solvents that can be used in the technological process.

In liquid chromatography it is important to study the conditions of adsorption with variable composition of mobile phase and it is used for improving the process of chromatographic separation. For heterogeneous surface of the adsorbent the model of multi-component adsorption is complicated because it creates the competition between molecules on each of the adsorption centers (Ruthven, 1989; Suzuki, 1990). In this case the multi-component adsorption can be described as IAS model, separate for each adsorption; the total adsorption is a sum of adsorbed components on every active place (Ruthven, 1989). In heterogenic adsorption model (HIAS) the adsorbent surface is presented with consideration of an activity of the adsorption centers. Such approach requires sequence of regulated parameters and also a calculation of energy on the adsorption surface.

The main task is to check a correspondence of the model to the components-pollutants of sewage, to determine the possibility to forecast the equilibrium for binary system according to the pollutants in the presence of few active centers (that are a heterogeneous surface of adsorption).

Analysis of the last investigations and publications
Processes of chromatography are modeled on base of certain assumptions and are described with mathematical models.

Modified model of bi- Langmuira isotherm can be used for calculation of two-place heterogeneous surface. The isotherm is shown as an equation:

$$q_A^* = \frac{q_{A1}^\infty \cdot K_1 \cdot x_A^m \cdot \gamma_A^m}{1 + K_1 \cdot x_A^m \cdot \gamma_A^m} + \frac{q_{A11}^\infty \cdot K_{11} \cdot x_A^m \cdot \gamma_A^m}{1 + K_{11} \cdot x_A^m \cdot \gamma_A^m} \tag{1}$$

Variable mobile phase composition for normal phase systems depends on the conditions of linear isotherm and is described on base of the theoretical model of adsorption [3-6]. In these models the

adsorption on a polar adsorption surface is explained as a competition between molecules of the solution and a modificator in the centers of adsorption.

The modified model of Unilan isotherm is used for calculation of the adsorption processes of heterogeneous surface with taking into consideration the activation energy. In Unilan equation the total active surface is used (Suzuki, 1990). The activation energy is described as:

$$f(E) = \begin{cases} \dfrac{1}{E_{max} - E_{min}} & for \ E_{min} < E < E_{max} \\ 0 & for \ E < E_{min} \ or \ E_{max} \end{cases} \qquad (2)$$

Modified Unilan equation for non-ideal mobile phase can be expressed through integral dependence:

$$q_A^* = \int\limits_{-\infty}^{+\infty} \frac{q_A^\infty \cdot K \cdot x_A^m \cdot \gamma_A^m}{1 + K \cdot x_A^m \cdot \gamma_A^m} f(E) dE \qquad (3)$$

$$q_A^* = \frac{q_A^\infty}{(2h)} \ln\left(\frac{1 + q_A^\infty \cdot K \cdot x_A^m \cdot \gamma_A^m \cdot \exp(h)}{1 + K \cdot x_A^m \cdot \gamma_A^m \cdot \exp(-h)}\right) \qquad (4)$$

where $K = K_0 \exp(\overline{E}/RT); \ \overline{E} = (E_{min} + E_{max})/2; \quad h = \dfrac{E_{max} - E_{min}}{2RT}$.

Parameter h defines the heterogeneity of the surface and for the homogenous surface $h = 0$.

For mathematical modeling of equilibrium between the component concentration in mobile and stationary phase it is important to forecast a differentiated mass equilibrium for one and i component in the mobile phase (Myers, 1983; Valenzuela et al, 1988; Guiochon et al, 1994; Guiochon et al, 2003):

$$\frac{\partial c_i^m}{\partial t} + F \frac{\partial \Gamma_i^*}{\partial t} + \omega \frac{\partial c_i^m}{\partial z} = D_a \frac{\partial^2 c_i^m}{\partial z^2} \qquad (5),$$

where $\omega = u/\varepsilon_t$ - speed in the thinnest cut; ε_t - total porosity of the column; D_a - dispersion coefficient, connected with the efficiency of the column, $N = \omega L/2D_a$; c_i^m - component concentration the the mobile phase; t, z – coordinates of time and space, Γ_i^* - additional adsorption in equilibrium with c_i^m .

Equilibrium theory in the process of chromatography is expressed by an ideal model which takes into consideration the balance between compound concentrations in mobile and stationary phase and neglects all the axis dispersion and kinetic effects.

The simplest model is introduced in Golshan-Shirazi et al (1988) for calculation of adsorption equilibrium in binary system (solution-modifier). It is called "Langmuira competitive isotherm". If coefficients of "solution-modifier" isotherm are known, then coefficients of the competitive "solution-modifier" isotherm can be determined, providing that modifier concentration is known.

In heterogeneous adsorption model (HIAS) developed in Golshan-Shirazi et al (1988), the adsorbent surface is presented with taking into consideration the activity of adsorption centers. Such approach requires the whole range of regulated parameters and also calculation of energy on the adsorption surface.

Aim of the work. Aim of this work is to calculate the mathematical model of technological process of chromatographic separation of two-component organic solvents which are present in sewage and to carry out an experimental investigation of the process as well as to prove the mathematical adequacy of the model to the real process.

MATHEMATICAL MODEL OF THE PROCESS

For mathematical modeling of the equilibrium between component concentration in mobile and stationary phases it is important to forecast the differentiated mass equilibrium for one and i component in the mobile phase using the equation (5).

Additional adsorption for the mix of mobile phase components in the in the adsorption column and inert phase is expressed by the equation:

$$\Gamma_A^* = q_A^* - q_A^* \cdot x_A^m = q_A^*(1 - x_A^m) \tag{6}$$

For the solution with insignificant concentration $\Gamma_i^* \cong q_i^*$.

The calculation in molar particles is calculated using the equation:

$$\frac{\partial x_i^m}{\partial t} + F \frac{\partial \Gamma_i^*}{\partial t} \cdot \frac{M^m}{\rho^m} + \omega \frac{\partial x_i^m}{\partial z} = D_a \frac{\partial^2 x_i^m}{\partial z^2} \tag{7}$$

where M^m i ρ^m - is an equivalent molar mass and density of the mobile phase; $M^m = f(x_i^m), \ \rho^m = f(x_i^m)$.

For description of the chromatographic process the Danckwerts-type conditions are used, where:

$t > 0; \quad z = 0$

$$u(x_i, F(t) - x_i^m(t,0)) = -D_a \frac{\partial x_i^m(t,0)}{\partial z} \tag{8}$$

where $x_i, F(t)x$ - determines the profile of sample impulse.

Then it is received:

$$x_i, F(t) = \begin{cases} x_{i,F} \ for \ t \in [0, t_p] \\ 0 \quad for \ \ t > t_p \end{cases} \tag{9}$$

Study of the additional adsorption was carried out with application of impulse method. Mathematical analysis is based on the principles of classic equilibrium theory.

Equilibrium theory is described as an ideal model which considers the balance between component concentration in mobile and stationary phases and neglects the axis dispersion and kinetic effects. Ideal model for i standard component can be calculated according to the dependence:

$$\frac{\partial x_i^m}{\partial t} + \left(\frac{\omega}{1 + F(d\Gamma_i^* / dx_i^m)(M^m(x_i^m) / \rho^m(x_i^m))} \right) \frac{\partial x_i^m}{\partial z} = 0 \tag{10}$$

Time when the impulse starts is expressed as:

$$t_{\Gamma i}(x_i^m) = t_{\Gamma 0}\left(1 + F \frac{d\Gamma_i^*}{dx_i^m} \frac{M^m(x_i^m)}{\rho^m(x_i^m)} \right) \tag{11}$$

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where $t_{\Gamma 0} = \dfrac{L}{\omega}$ - time before the impulse occurred (so to say, a dead-time of the column), when L is the column height.

The dependence (11) can be used for calculation of the additional adsorption of the $i = A$

$$\Gamma_A^* = \int_0^{x_A} \left(\frac{t_\Gamma/t_{\Gamma 0} - 1}{F} \right) \frac{\rho^m(x_i^m)}{M^m(x_i^m)} dx_A \tag{12}$$

or

$$\Gamma_A^* = \int_0^{x_A} \left(\frac{t_\Gamma/t_{\Gamma 0} - 1}{F} \frac{\rho^m(x_i^m)}{M^m(x_i^m)} dx_A \right) \tag{13}$$

In equation (12) i (13), Γ_A^* - is an additional adsorption which corresponds to the adsorbent volume (for example, mol/(cm^3 of the adsorbent).

EXPERIMENTAL WORK

For the experiments a liquid chromatograph HPLC LaChom MERCK was used. The experiment was carried out with saturation of the column by polar solvent (ethyl acetate or isopropan). Height and diameter of the column are 250mm and 4 mm respectively, and it is filled with silica LiChrospher® Si 60 with pores diameter 60 $\overset{o}{A}$ and particles size 5 $\mu м$ (producer: Merck, Darmstadt, Germany). In order to determine the adsorption isotherm the column was adjusted to each concentration of the standard mixture, so to say to the horizontal line on the detector, which characterizes the adsorbent saturation of a certain concentration by mobile phase component, the impulse contained a slight excess of the concentration. There ware investigated two-component mixtures: "ethyl acetate – hexane", "C5 – hexane" and "isopropan – hexane".

Calculation of isotherm model for 2-component mixtures. The received data $t_r = f(C)$ were used for co-modification of the isotherm model. The first derivative from the isotherm equation for diffusion peak is connected to the time of peak in an ideal model according to the equation:

$$t_r(C) = t_0 \left(1 + F \frac{dq^*}{dx} \left(\frac{M_e}{\rho_e} \right) \right) \tag{14}.$$

In order to calculate the mass equilibrium of the model there was used a coefficient of concentration re-calculation between activity coefficient and concentration in mole particles. The value of density of mobile phase, which characterizes of moll mass, was calculated according to the equation:

where $\qquad \rho_e = \sum_{i=1}^{N} \rho_i \bar{x}_i \ ; M_e = \sum_{i=1}^{N} M_i x_i \tag{15},$

where: $\bar{x}_i$ - mass part of the component in the mobile phase.

In order to receive the optimal equation of sorption isotherm of the system "C5 – hexane" such isotherm models were used: bi Langmuira, Totha та Unilan.

As a result of the calculation, the following dependences were received:

Bi-Langmuira isotherm:

$$q_{C5}^{*} = \frac{b_{I}\,\Gamma_{I}^{\infty}\,\gamma_1 x_1}{(1-x_1)\gamma_3 + b_{I}\,\gamma_1\,x_1} + \frac{b_{II}\,\Gamma_{II}^{\infty}\,\gamma_1\,x_1}{(1-x_1)\gamma_3 + b_{II}\,\gamma_1\,x_1} \tag{16}.$$

Unilan isotherm:

$$q_{C5}^{*} = \frac{\Gamma_{C5}^{\infty}}{(2h)}\,\ln\!\left(\frac{(1-x_1)\gamma_3 + b_1\,x_1\,\gamma_1\exp(h)}{(1-x_1)\gamma_3 + b_1\,x_1\,\gamma_1\exp(-h)}\right) \tag{17}.$$

Totha isotherm:

$$q_{C5}^{*} = \frac{\Gamma_{C5}^{\infty}\,x_1\,\gamma_1}{\left[b_1 + (x_1\,\gamma_1)^h\right]^{\frac{1}{h}}} \tag{18}.$$

The results isotherm models calculations and the calculated parameters of the equations are presented in the Table 1.

All the suggested isotherms have accuracy ±0.05%. The model of Totha isotherm is not taken into consideration because constant equations do not have physical significance. The comparison of presented data shows that the most correct model is Unilana, which was used for the following data processing.

For calculation of the optimal equation of sorption isotherm for systems "isopropan – hexane" and "ethyl acetate – hexane" the following isotherm models were chosen: Unilan, Langmuira.

Langmuira isotherm:

$$q_{m}^{*} = \frac{\Gamma_{m}^{\infty}\,b_2\,\gamma_2\,x_2}{b_2\,\gamma_2\,x_2 + (1-x_2)\gamma_3} - \Gamma_{m}^{\infty}\,x_2 \tag{19}.$$

Unilan isotherm:

$$q_{m}^{*} = \frac{\Gamma_{m}^{\infty}}{(2h_2)}\,\ln\!\left(\frac{(1-x_2)\gamma_3 + b_2\,x_2\,\gamma_2\exp(h_2)}{(1-x_2)\gamma_3 + b_2\,x_2\,\gamma_2\exp(-h_2)}\right) - \Gamma_{m}^{\infty}\,x_2 \tag{20}.$$

Optimized parameters of the isotherm model for modificator of the solution are presented on the Figures 2 and 3.

Both suggested models have accuracy ±0.02%.

CONCLUSION

The suggested mathematical model can be used for evaluation of the adsorption process on the heterogeneous surface of the solution providing that there are different solvents with the known adsorption equilibrium. The successful experimental check showed the correspondence of forecast model for double equilibrium of two-component solution.

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