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# BATCH ADSORPTION IN A FINITE VOLUME RESERVOIR – APPLICATION OF AN APPROXIMATE KINETIC MODEL

## ADSORPCJA W ZBIORNIKU O OGRANICZONEJ OBJĘTOŚCI – ZASTOSOWANIE PRZYBLIŻONEGO MODELU KINETYCZNEGO

Abstract

The paper refers to the kinetics of batch adsorption in a perfect mixing reservoir. Systems with a linear adsorption equilibrium, spherical adsorbent pellets and mass transfer resistance in both phases are considered. An approximate kinetic model, based on approximation with the use of continued fractions, was used in calculations. It was found that the model gives results consistent with the exact solution.

*Keywords*: *adsorption kinetics*, *approximate kinetic equations*

Streszczenie

Artykuł dotyczy kinetyki adsorpcji okresowej w zbiorniku z idealnym mieszaniem. Rozważono układy z liniową równowagą adsorpcyjną, kulistymi ziarnami adsorbentu i z oporami przenoszenia masy występującymi w obu fazach. W obliczeniach wykorzystano przybliżony model kinetyczny oparty na aproksymacji ułamkami łańcuchowymi. Stwierdzono, że model ten daje wyniki zgodne z rozwiązaniem ścisłym.

*Słowa kluczowe*: *kinetyka adsorpcji*, *przybliżone równania kinetyczne*

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Bi  –  Biot number
$C$  –  adsorbate concentration in the fluid phase [kg/m³]
$D_s$  –  solid diffusivity [m²/s]
$K$  –  adsorption equilibrium constant
$L$  –  characteristic linear dimension (radius for a sphere) [m]
$m$  –  mass [kg]
$q_m$  –  adsorbate concentration in solid phase [kg/kg]
$Q$  –  dimensionless concentration of the adsorbate in solid phase
$t$  –  time [s]
$V$  –  volume [m³]
$Y$  –  dimensionless adsorbate concentration in fluid phase

**Greek symbols**

$\alpha$  –  adsorbent load factor
$\eta$  –  dimensionless space coordinate
$\tau$  –  dimensionless time

**Indexes**

0  –  initial value
1  –  pellet surface
–  –  average value

## 1. Introduction

Three different methods are used in order to conduct studies on adsorption kinetics in a liquid phase [1]. These methods are presented in Fig. 1.

In the first method (Fig. 1a), adsorbent pellets are put inside a reservoir containing a solution with the adsorbate. The content of the reservoir is stirred. In the case of the second method (Fig. 1b), the adsorbent is put in a mesh basket attached to a stirrer. The stirrer is rotated and a solution with the adsorbate is introduced into the reservoir. The third method (Fig. 1c) consists of putting an amount of adsorbent into a small column connected with the reservoir that contains the adsorbate. The reservoir is connected to the column by a closed loop. The contents of the loop are circulated and flow through the bed of the adsorbent with such a speed that the adsorption time is much greater than the residence time of adsorbate in the loop. In this way, the flow rate of the solution containing the adsorbate can be controlled so that the heat of the adsorption can be effectively removed and the process can be conducted under isothermal conditions.

In all cases, the saturation of pellets goes together with a reduction of the adsorbate concentration in the solution over time. This results from the finite volume of the solution (reservoir). Hence, the driving force of the process decreases because of two factors: the decreasing concentration of adsorbate in the solution; the increasing concentration
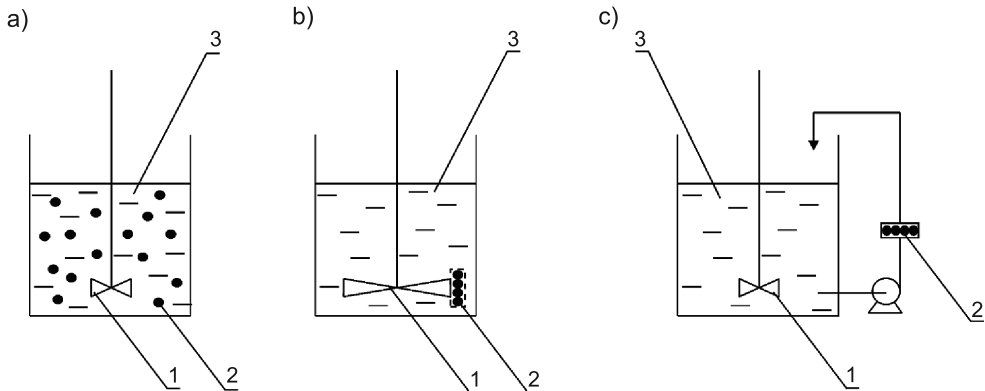
Fig. 1. Studies on adsorption kinetics: 1 – stirrer, 2 – adsorbent pellets, 3 – liquid solution containing an adsorbate

of adsorbate in the pellets. An extreme case is when the volume of the solution is infinitely large. In this case, the adsorbate concentration in the solution does not change over time.

For adsorption in a finite volume reservoir, the adsorbent load factor is the main parameter. It is defined in the following way:

$$\alpha = \frac{VC_0}{m_s q_{m0}} = \frac{V}{m_s K} \tag{1}$$

where:

$V$ – the volume of the solution,

$C_0$ – initial concentration of the adsorbate in the solution;,

$m_s$ – mass of adsorbent pellets,

$q_{m0}$ – concentration of adsorbate in pellets in equilibrium with $C_0$,

$K$ – adsorption equilibrium constant ($= q_{m0}/C_0$).

When the solution volume is infinite, then $\alpha \to \infty$.

The aim of this work is to analyze the suitability of the application of the approximate kinetic model for adsorption in a finite volume reservoir. The results obtained on the basis of the approximate model presented in [2] and [3] were compared with the results of the exact analytical solution. Adsorption systems with linear equilibrium are considered in the paper. The presented analysis refers to spherical pellets.

## 2. Computation expressions

### 2.1. Equation of adsorption and diffusion

It is convenient to present the equation of adsorption and diffusion in the dimensionless form with the use of dimensionless quantities. The dimensionless concentration of the adsorbate in the pellet is defined in the following way:

$$Q = \frac{q_m}{q_{m0}} \tag{2}$$

The average concentration is defined analogically:

$$\bar{Q} = \frac{\bar{q}_m}{q_{m0}} \tag{3}$$

where:

$\bar{q}_m$ – concentration averaged over pellet volume.

The dimensionless space coordinate $\eta$ is introduced:

$$\eta = \frac{x}{L} \tag{4}$$

and the dimensionless time $\tau$:

$$\tau = \frac{D_s t}{L^2} \tag{5}$$

Symbol $D_s$ in the foregoing definitions denotes solid diffusivity, and $L$ – characteristic linear dimension (radius for a sphere). The equation of diffusion and adsorption has the form:

$$\frac{\partial Q}{\partial \tau} = \frac{\partial^2 Q}{\partial \eta^2} + \frac{2}{\eta} \cdot \frac{\partial Q}{\partial \eta} \tag{6}$$

For pellets that do not contain the adsorbate, the initial condition has the form:

$$\tau = 0, \quad Q = 0 \tag{7}$$

One of the boundary conditions refers to the symmetry of the pellet:

$$\eta = 0, \quad \frac{\partial Q}{\partial \eta} = 0 \tag{8}$$

The boundary condition for pellet surface takes the form:

$$\eta = 1, \quad \frac{\partial Q}{\partial \eta} = \text{Bi}[Q_1^* - Q_1] \tag{9}$$

The value of $Q_1^*$ is the solid dimensionless adsorbate concentration in equilibrium with the actual bulk concentration in liquid phase, $Q_1$ is a dimensionless concentration on the pellet surface, and Bi – Biot number.

## 2.2. Adsorbate balance in the fluid phase

When the reservoir with fluid and adsorbent pellets has finite volume, concentration of adsorbate in the solution changes during adsorption. Not only a balance equation for the adsorbate in solid phase, but also a balance equation in fluid phase should be taken into account in the model of the process. The equation has the form:

$$\frac{dY}{d\tau} = -\frac{1}{\alpha} \cdot \frac{d\bar{Q}}{d\tau} \tag{10}$$

where the dimensionless concentration in the fluid phase is defined in the following way:

$$Y = \frac{C}{C_0} \tag{11}$$

The initial condition for the fluid phase:

$$\tau = 0, \quad Y = 1 \tag{12}$$

The solution to equation (10) with initial conditions (7) and (12) have the form:

$$\alpha(1 - Y) = \bar{Q} \tag{13}$$

For $\tau \to \infty$, the concentrations of adsorbate in the pellet and the fluid are in equilibrium. According to the definition of dimensionless concentration, the following relationship is valid for linear equilibrium:

$$Q^* = Y \tag{14}$$

It results from equations (13) and (14) that:

$$\lim_{\tau \to \infty} Y = \lim_{\tau \to \infty} \bar{Q} = \frac{\alpha}{1 + \alpha} \tag{15}$$

## 2.3. Exact kinetic model

The results of numerical calculations were compared with results obtained from the analytical solution of the system of equations (6) and (10) with conditions (7), (8), (9) and (12). In this case, the analytical solution was given by Huang and Li [4]. The expression has the form:

$$Y = 1 - \frac{1}{1+\alpha}\left[1 - \sum_{i=1}^{\infty} \frac{6\mathrm{Bi}^2(1+\alpha)\exp(-\mu_i^2\tau)}{\left(\frac{9}{\alpha} + \alpha\mu_i^2 + 9\right)\mathrm{Bi}^2 - (6+\alpha)\mu_i^2\mathrm{Bi} + \alpha\mu_i^4}\right] \tag{16}$$

where $\mu_i$ are consecutive positive roots of the algebraic equation:

$$\frac{\tan\mu}{\mu} = \frac{3\mathrm{Bi} - \alpha\mu^2}{(\mathrm{Bi}-1)\alpha\mu^2 + 3\mathrm{Bi}} \tag{17}$$

Values of the roots $\mu_i$ depend on the parameter $\alpha$ and also on the Biot number. In order to determine the location of the first few roots for different combinations of the values of $\alpha$ and Bi, graphs of functions $y_1$ and $y_2$ presented in Fig. 2 were plotted. These functions are defined in the following way:

$$y_1 = \tan\mu \tag{18a}$$

$$y_2 = \frac{(3\text{Bi} - \alpha\mu^2)\mu}{(\text{Bi} - 1)\alpha\mu^2 + 3\text{Bi}} \tag{18b}$$

The graph of function $y_2$ depends not only on the parameter $\alpha$, but also on Bi. The abscissas of the intersections of functions $y_1$ and $y_2$ correspond to the solutions of equation (17), because the equality $y_1 = y_2$ is equivalent to this equation. Values of the first six roots of equation (17) are presented in Table 1.

Table 1

**Values of solutions to equation (17)**

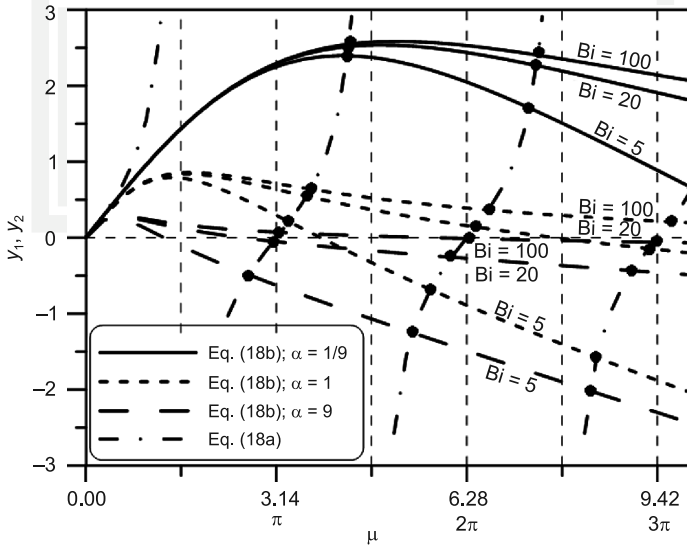| $\alpha$ | Bi | $\mu_1$ | $\mu_2$ | $\mu_3$ | $\mu_4$ | $\mu_5$ | $\mu_6$ |
|---|---|---|---|---|---|---|---|
| 1/9 | 5 | 4.3172 | 7.3235 | 10.0032 | 12.3015 | 14.8172 | 17.6935 |
| | 20 | 4.3344 | 7.4383 | 10.4685 | 13.4484 | 16.3765 | 19.2553 |
| | 100 | 4.3385 | 7.4596 | 10.5306 | 13.5867 | 16.6374 | 19.6864 |
| | ∞ | 4.3395 | 7.4645 | 10.5437 | 13.6133 | 16.6831 | 19.7565 |
| 1 | 5 | 3.3499 | 5.6845 | 8.4194 | 11.3837 | 14.4323 | 17.5171 |
| | 20 | 3.6411 | 6.4247 | 9.2826 | 12.2069 | 15.1802 | 18.1894 |
| | 100 | 3.7100 | 6.6329 | 9.6322 | 12.6749 | 15.7411 | 18.8207 |
| | ∞ | 3.7264 | 6.6814 | 9.7156 | 12.7927 | 15.8924 | 19.0049 |
| 9 | 5 | 2.6872 | 5.3866 | 8.3144 | 11.3398 | 14.4105 | 17.5049 |
| | 20 | 3.0939 | 6.0318 | 9.0156 | 12.0243 | 15.0532 | 18.0992 |
| | 100 | 3.2116 | 6.2736 | 9.3664 | 12.4680 | 15.5733 | 18.6807 |
| | ∞ | 3.2410 | 6.3353 | 9.4599 | 12.5928 | 15.7291 | 18.8672 |



Fig. 2. Location of solutions to equation (17)

## 2.4. Approximate kinetic model

In order to describe transient mass (also heat) transfer, it is useful to use such an approximation that consists in elimination of a space coordinate in a body (pellet). The process is described with an ordinary differential equation and the resulting expression is called the approximate kinetic equation. The approximate model used in this paper is based on the use of the Laplace transformation for the diffusion equation, rearrangement of the solution to form a continued fraction and truncation of the obtained expression to such a number of terms that ensures the required accuracy. Such a model was presented for the first time by Lee and Kim [2] for systems without external resistance to mass transfer, and the model for systems with resistance in both phases was presented in work by the authors of this paper [3]. The considered approximate model refers to the basic shapes of pellets: infinite slab, infinite cylinder and sphere.

The main advantage of approximate kinetic equations is the fact that they are ordinary differential equations (not partial equations). This results in the reduction of the calculation time when compared to the exact calculations. This is important when a kinetic equation is solved repeatedly in a complex procedure.

In order to determine the adsorbate concentration in the pellet as a function of time with the use of the approximate kinetic equation, the following system of equations must be solved [3]:

$$\dot{\mathbf{x}} = \mathbf{d}^{-1}\mathbf{A}\mathbf{x} + \mathbf{d}^{-1}\mathbf{b}Q_1^* \tag{19}$$

where vectors $\dot{\mathbf{x}}, \mathbf{x}$ and $\mathbf{b}$ are defined in the following way:

$$\dot{\mathbf{x}} = \begin{bmatrix} \dot{x}_1 & \dot{x}_2 & \dots & \dot{x}_n \end{bmatrix}^T \tag{20}$$

$$\mathbf{x} = \begin{bmatrix} x_1 & x_2 & \dots & x_n \end{bmatrix}^T \tag{21}$$

$$\mathbf{b} = \begin{bmatrix} 3 & 3 & \dots & 3 \end{bmatrix}^T \tag{22}$$

Elements of matrix $\mathbf{A}$ are defined as:

$$A_{ij} = -p_i q_j \quad \text{for} \quad j > i \tag{23a}$$

$$A_{ij} = -p_j q_j \quad \text{for} \quad j < i \tag{23b}$$

$$A_{ij} = -p_i q_i \quad \text{for} \quad j = i \tag{23c}$$

where $p_i$ and $q_i$ have the forms:

$$p_i = 2i^2 + i \tag{24}$$

$$q_i = 4i + 1 \tag{25}$$

$$d_{ij} = \frac{q_j}{\text{Bi}} \quad \text{for} \quad j \neq i \tag{26a}$$

$$d_{ij} = 1 + \frac{q_j}{\text{Bi}} \quad \text{for} \quad j = i \tag{26b}$$

The number of equations (19) is the order of approximation; the higher the order is, the higher the accuracy of the approximation.

Average dimensionless concentration of adsorbate in an adsorbent pellet after time $\tau$ is defined by the following equation [2]:

$$\bar{Q} = \mathbf{q}\mathbf{x} \tag{27}$$

where:

$$\mathbf{q} = [q_1 \quad q_2 \quad \cdots \quad q_n] \tag{28}$$

Substituting $Q_1^* = Y$ into (19) and considering equation (13) one gets:

$$\dot{\mathbf{x}} = \mathbf{d}^{-1}\mathbf{A}\mathbf{x} + \mathbf{d}^{-1}\mathbf{b}\left(1 - \frac{\bar{Q}}{\alpha}\right) \tag{29}$$

After transformation, it was obtained that:

$$\dot{\mathbf{x}} = \mathbf{d}^{-1}\left(\mathbf{A} - \frac{1}{\alpha}\mathbf{b}\mathbf{q}\right)\mathbf{x} + \mathbf{d}^{-1}\mathbf{b} \tag{30}$$

The following initial condition is required to solve the system of equations (30):

$$\tau = 0, \quad \mathbf{x} = 0 \tag{31}$$

This condition refers to the pellet that does not contain the adsorbate at the beginning of the process. As a result of solving system (30), a vector function $\mathbf{x}(\tau)$ is obtained. On the basis of relation (27) the scalar function $\bar{Q}(\tau)$ is determined.

The algorithm was as follows. Elements of matrix $\mathbf{A}$ and vectors $\mathbf{b}$, $\mathbf{q}$ and $\mathbf{d}$ were determined for given values of Bi and $n$. Then the system of equations (30) with initial condition (31) is solved. Finally, the function $\bar{Q}(\tau)$ was obtained from formula (27).

## 3. Results of calculations

Comparison of results obtained with the use of the approximate and exact kinetic models for adsorption in a finite volume reservoir with mass transfer resistance in both phases is presented in Fig. 3a, b and c. Solid lines refer to the approximate model. Dots denote values found with the use of the exact solution. The figures present results for different values of parameter $\alpha$.

Concentrations in the fluid phase decrease, while in the pellets, they increase. After some time, the system reaches equilibrium and the dimensionless concentrations become equal to each other. Values of dimensionless equilibrium concentrations in both phases depend on the values of $\alpha$. For instance, for Fig. 3a that refers to $\alpha = 1/9$, it is easy to calculate from formula (15) that for $\tau \to \infty$, it is $Y = \bar{Q} = \dfrac{1/9}{1 + 1/9} = 0.1$.

It can be seen from the figures that the greater value the Biot number has, the faster the system reaches equilibrium. It results from this fact that for a given value of diffusivity

in a pellet, a smaller value of external resistance corresponds to greater Bi. The reduction of the external resistance, while the internal one is constant, results in the decrease of the total resistance to mass transfer.

It can also be seen from these figures that the approximate model gives results very similar to the exact results. Some deviations can be observed only for a high Biot number, a low adsorbent load factor and short adsorption times.
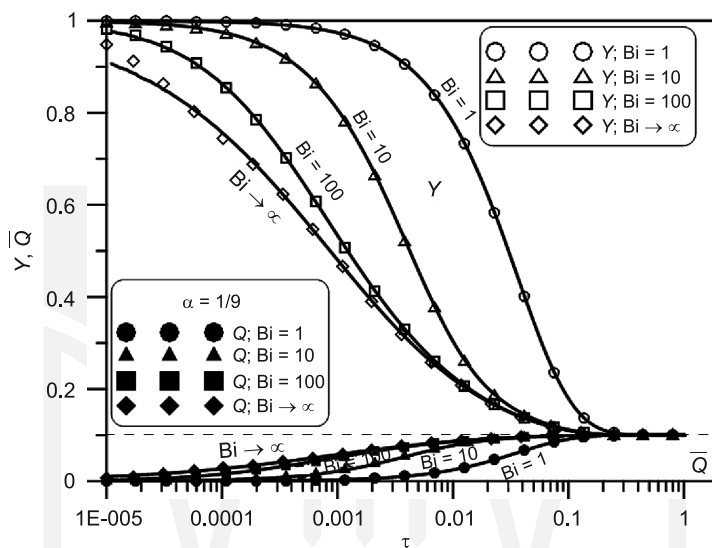


Fig. 3a. Adsorption in a finite volume reservoir for $\alpha = 1/9$
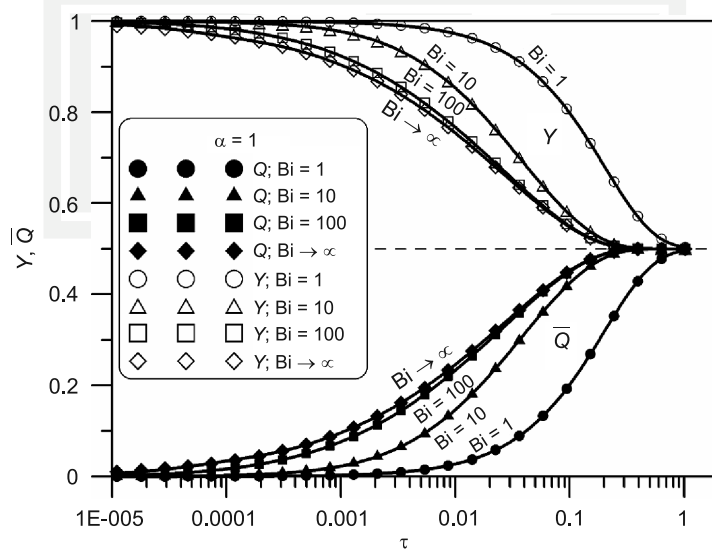


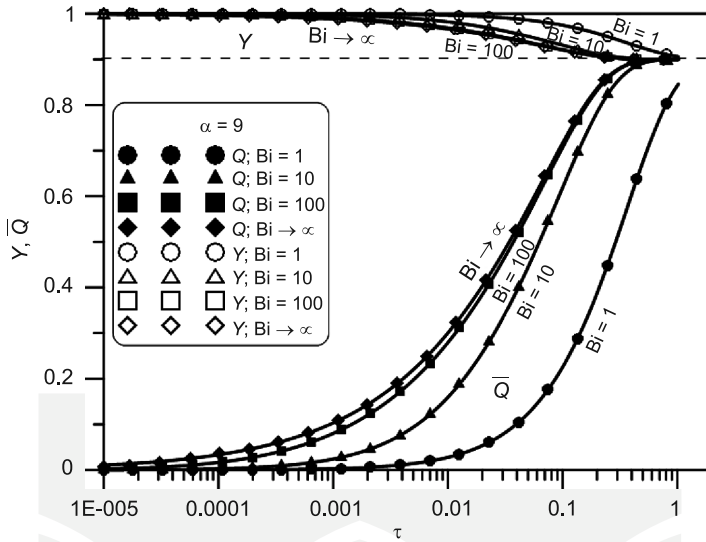Fig. 3b. Adsorption in a finite volume reservoir for $\alpha = 1$

Fig. 3c. Adsorption in a finite volume reservoir for $\alpha = 9$

The agreement between values obtained on the basis of the approximate and exact models confirms that the approximate model based on the continued fractions approximation can be used in the design and modeling of batch adsorption in a reservoir.

## 4. Conclusions

The approximate model for adsorption kinetics based on continued fractions is much more convenient to use than exact models based on solutions in the form of an infinite series. The obtained results do not differ much from the results obtained with the use of the exact methods.

References

[1] Do D.D., *Adsorption Analysis: Equilibria and Kinetics*, ICP 1998.
[2] Lee J., Kim D.H., *Simple high-order approximations for unsteady-state diffusion, adsorption and reaction in a catalyst: a unified method by a continued fraction for slab, cylinder and sphere geometries*, Chemical Engineering Journal, 173, 2011, 644-650.
[3] Kupiec K., Gwadera M., *Approximation for unsteady state diffusion and adsorption with mass transfer resistance in both phases*, Chemical Engineering and Processing, 65, 2013, 76-82.

[4]   Huang T-C., Li K-Y., *Ion-exchange kinetics for calcium radiotracer in a batch system*, Industrial and Engineering Chemistry Fundamentals, 12, 1973, 50-55.
[5]   Crank J., *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975.
[6]   Suzuki M., *Adsorption Engineering*, Elsevier 1990.
[7]   Carslaw H.S., Jaeger J.C., *Conduction of Heat in Solids*, Clarendon Press, Oxford, 1959.
[8]   Petrus R. at al., *Wymiana masy w układzie ciało stałe-ciecz*, OWPR Rzeszów 1998.