

Kinetics of multi-site-occupancy adsorption at the solid/solution interfaces. The absolute rate theory approach*

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The kinetic approach based on the absolute rate theory and the model of a two-site-occupancy adsorption has been proposed to describe the kinetics of sorption of solute at the solid/solution interfaces. The obtained general kinetic equation reduces to the popular empirical formulas (i.e. the Lagergren equation and the pseudo-second order equation) depending on the values of physical and technical parameters which characterize the adsorption system. here, for the case when the adsorption kinetics is governed by the rate of surface reactions. The features of this general equation are shown by presenting some simple model investigations, and its applicability is tested by presenting the analysis of some experimental data reported in literature.

1. INTRODUCTION

The adsorption process at the solid/solution interface is probably the most commonly applied physical phenomenon in the industrial purification of wastewaters. During this process the sorbent and the solution are in contact only

* This article is dedicated to Professor Emil Chibowski on the occasion of his 65th birthday.

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for a limited period of time. Thus, the knowledge about the rate at which the sorption process takes place in a given system is one of the most important factors in designing adsorption systems. According to the commonly accepted views, there are essentially four stages in the adsorption process [1]:

1. Transport of adsorbate from the bulk of the solution to the external liquid film surrounding particles of the adsorbent.
2. Movement of adsorbate across the external liquid film to the adsorbent surface.
3. Migration of adsorbate within the pores of the adsorbent by intraparticle diffusion.
4. Adsorption on the solid surface viewed as a kind of chemical reaction.

In order to investigate the mechanism of adsorption process, various kinetic models have been proposed. Numerous kinetic models have described the reaction order of adsorption systems based on the solution concentration. These include the Lagergren equation and the pseudo-second order equation.

At the end of 19th century, Lagergren presented the empirical rate equation for the adsorption of ocalic and malonic acids onto charcoal [2]. This equation is probably the earliest known one describing the rate of adsorption. Moreover, it has been one of the most widely used kinetic equations until now. It can be written as follows:

$$\frac{d\theta(t)}{dt} = k_1(\theta_e - \theta(t)), \quad (1)$$

where θ is the fractional coverage of adsorption sites at the time t , θ_e is the equilibrium surface coverage, i.e. $\theta_e = \theta(t \rightarrow \infty)$ and k_1 is a constant. The values of θ_e and k_1 parameters can be determined by applying the commonly accepted procedure, based on the following linear regression:

$$\ln(\theta_e - \theta(t)) = \ln \theta_e - k_1 t. \quad (2)$$

Equation (2) is the integral form of equation (1), obtained by assuming the boundary condition $\theta(t = 0) = 0$. In spite of its common use, until very recently the Lagergren equation (2) has remained only a useful empirical formula. In 2004 Azizian proposed the first theoretical interpretation of this equation, based on the classical fundamental ART approach (Absolute Rate Theory) [3]. Later, in 2006 Rudziński and Płaziński proposed their first interpretation based on the new fundamental SRT approach to adsorption/desorption kinetics (Statistical Rate Theory) [4]. Also, in 2007 Rudziński and Płaziński presented a theoretical analysis, according to which the Lagergren equation should be treated as a

general formula, describing adsorption kinetics in the systems which are not far from equilibrium [5].

The common use of the Lagergren equation led also to reveal deviations in many cases from the behaviour predicted by equation (2). In 1984 a pseudo-second order equation for adsorption at the solution/solid interface was introduced by Blanchard et al. [6]. According to this equation, the rate of adsorption is expressed as:

$$\frac{d\theta(t)}{dt} = k_2(\theta_e - \theta(t))^2, \quad (3)$$

where k_2 is another constant. The integral form of this equation, obtained with the boundary condition $\theta(t=0) = 0$, can be written as follows:

$$\frac{t}{\theta(t)} = \frac{1}{\theta_e}t + \frac{1}{k_2\theta_e^2}, \quad (4)$$

which has commonly been applied in the analysis of experimental data. Recently, the number of papers has been rapidly growing in which better applicability of the pseudo-second order kinetic equation than the Lagergren equation is demonstrated. The pseudo-second order kinetic equation has always been associated with the model of two-site-occupancy adsorption, however, no further explanation based on this ground has been given. One of the aims of this paper is to propose the first theoretical interpretation of the Lagergren and the pseudo-second order equations based on the two-site-occupancy adsorption model and the fundamental ART approach.

2. THEORY

Absolute Rate Theory (ART) is one of the most widely used approaches for description and theoretical interpretation of adsorption/desorption kinetics. The classical ART approach, combined with the model of localized ideal adsorption, offers the well-known simple expression for the rate of adsorption, expressed here as a change of the surface coverage θ with the time t :

$$\frac{d\theta}{dt} = K_1c(1-\theta)^s - K_2\theta^s, \quad (5)$$

where K_1 and K_2 are some temperature-dependent constants, s is the number of adsorption sites involved in an elementary adsorption/desorption process

(reaction) and c is the solute concentration in the bulk phase. For the sake of convenience, equation (5) can be rewritten to the following form:

$$\frac{d\theta}{d\tau'} = \kappa'(1-\theta)^s - \theta^s, \quad (6)$$

in which $\kappa' = K_1 c / K_2$ and τ' is the dimensionless time, defined as $\tau' = K_2 t$. Accepting κ' as a surface-coverage-independent constant is reasonable only when the solute concentration does not change throughout the kinetic experiment, i.e. c is not a function of θ . Generally, there are two situations which one may face in the course of a kinetic experiment:

- Case 1. The “volume dominated” system. The number of the solute molecules in the bulk phase dominates that of the adsorbed molecules in the experiment to such an extent that the bulk concentration does not practically change during that kinetic experiment. It also means that the solute concentration c can be identified with the initial concentration $c^{(in)}$ and with the equilibrium solute concentration $c^{(e)}$.
- Case 2. The “solid dominated” system. In the course of a kinetic experiment significant changes in the solute concentration are observed.

When the second possibility (Case 2) occurs, the solute concentration c is the following function of the surface coverage:

$$c = c^{(in)} - \frac{\theta N_m}{V}, \quad (7)$$

where V is the volume of solution and N_m is the monolayer capacity.

Thus, when assuming the changes in the bulk concentration of solute c in the course of experiment, one can propose a more general form of equation (5):

$$\frac{d\theta}{d\tau'} = \kappa(\lambda - \theta)(1-\theta)^s - \theta^s, \quad (8)$$

where $\lambda = c^{(in)} V / N_m$ and the κ parameter can be defined now as: $\kappa = K_1 N_m / K_2 V$. Let us note that the λ parameter shows how significant deviations of the adsorption system from the behavior described as Case 1 are, i.e. with the increasing value of λ , the decline of solute concentration in the bulk phase becomes greater. Accordingly, the range of possible values of λ parameter is: from θ_e (this is when all the sorbate is removed from the solution during the

kinetic experiment) to infinity (when there are no changes in solute concentration in the bulk phase, i.e. this is the “volume dominated” system).

When equilibrium is reached, i.e. $d\theta/d\tau'=0$ and while the rate of adsorption is expressed by equation (5) (Case 1), the following adsorption isotherm equation is obtained:

$$\kappa' = \frac{\theta_e^s}{(1-\theta_e)^s}, \quad (9)$$

in which θ_e is the equilibrium surface coverage, i.e. $\theta_e = \theta(\tau' \rightarrow \infty)$. When equation (8) is applied (Case 2), one obtains:

$$\kappa = \frac{\theta_e^s}{(\lambda - \theta_e)(1 - \theta_e)^s}. \quad (10)$$

Introducing relation (9) to equation (6) one can obtain the rate of adsorption as a function of the equilibrium surface coverage θ_e :

$$\frac{d\theta}{d\tau} = \theta_e^s(1-\theta)^s - \theta^s(1-\theta_e)^s. \quad (11)$$

While in the case of rate equation (10) and equilibrium adsorption isotherm (6):

$$\frac{d\theta}{d\tau} = (\lambda - \theta)(1 - \theta)^s \theta_e^s - (\lambda - \theta_e)(1 - \theta_e)^s \theta^s. \quad (12)$$

In both equations (11) and (12) τ is the dimensionless time, but in equation (11) it is defined as: $\tau = \tau'/(1-\theta_e)^s$ while in equation (8) we have $\tau = \tau'/(\lambda - \theta_e)(1 - \theta_e)^s$.

It is worth mentioning that in the case of one-site-occupancy model of adsorption, i.e. for $s = 1$, the general equation (11) becomes the Lagergren equation (1) in which the k_1 constant is enclosed in the dimensionless time. According to such a theoretical interpretation (which was originally given by Azizian [4]), the applicability of the Lagergren equation is limited only to those systems in which the solute concentration in bulk phase is constant during the experiment (“volume dominated” system).

In the case $s = 2$, i.e., when one molecule occupies two adsorption sites, equation (7) can be solved with the boundary condition $\theta(\tau = 0) = 0$ to yield:

$$\theta(\tau) = \frac{\theta_e}{\theta_e + (1 - \theta_e) \coth[(1 - \theta_e)\theta_e \tau]} \quad (13)$$

It can be easily shown that when the kinetic isotherm is expressed by equation (9) and the equilibrium surface coverage is close to unity:

$$\lim_{\theta_e \rightarrow 1} \theta(\tau) = \frac{\tau}{1 + \tau} \quad (14)$$

The above expression can be rewritten to the following form:

$$\frac{\tau}{\theta(\tau)} = \tau + 1, \quad (14a)$$

which is identical with the classical integral form of the pseudo-second order equation (4) for $\theta_e = 1$ and the constant k_2 enclosed in the dimensionless time τ . Also, while the equilibrium surface coverage is close to 0.5, we obtain the expression:

$$\lim_{\theta_e \rightarrow 0.5} \theta(\tau) = 0.5 - 0.5e^{-\tau/2}, \quad (15)$$

which is another form of Lagergren equation (2) written for $\theta_e = 0.5$; the constant k_1 is enclosed in the dimensionless time τ .

$$\ln(0.5 - \theta(t)) = \ln 0.5 - \tau/2. \quad (15a)$$

Similar simple theoretical analysis can not be performed for the more general rate equation (12). This is because there are no analytical solutions of differential equation (12) for the case $s = 2$ (i.e. two-site-occupancy adsorption model, considered here). Thus, we have made a simple model investigation of equation (12) features, based on the numerical solutions. The main aim of these investigations was to see whether the integral form of equation (12) can serve as a linear representation for the functions $\theta(t)$ calculated from the Lagergren equation (i.e. representation (2)) or the pseudo-second order equation (i.e. representation (4)). For the sake of clarity we also had to take into account the following essential fact: namely, adsorption times monitored in different experiments may differ by several orders of magnitude, depending on the physical nature of an adsorption system. Thus, we have decided to study the

behaviour of θ as a function of the reduced time $\tau/\tau_{0.9}$, where $\tau_{0.9}$ is the time when the surface coverage θ reaches the value $\theta = 0.9\theta_e$. The results of our model investigations are shown in Figures 1 and 2.

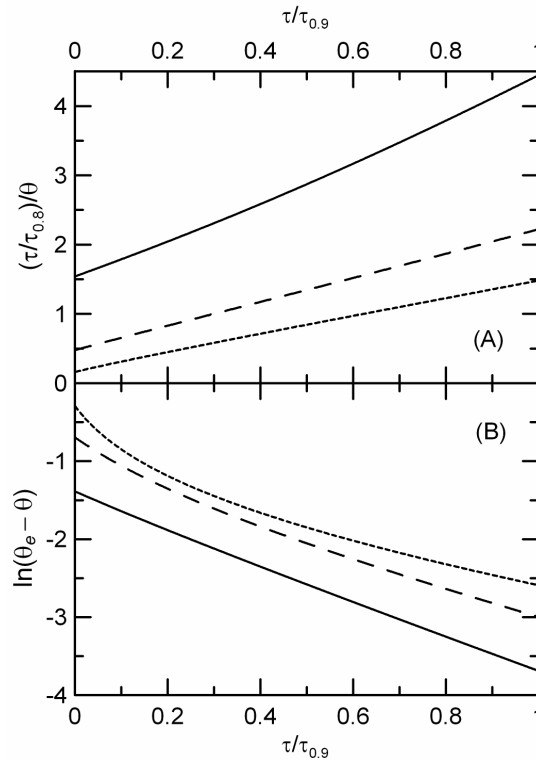


Fig. 1. Kinetic isotherms $\theta(\tau/\tau_{0.9})$, drawn as the pseudo-second order plots (A) and the Lagergren plots (B), calculated from equation (12), for $s = 2$, and the three values of the equilibrium surface coverage: $\theta_e = 0.25$ (—), $\theta_e = 0.5$ (- - -), $\theta_e = 0.75$ (.....). The calculations were performed for the case when $\lambda = \theta_e + 0.1$.

Looking at Figure 1, one can see a quite good linearity of the pseudo-second order plots, not only for the higher values of equilibrium surface coverages (here $\theta_e = 0.75$) as it is predicted by equation (13). Moreover, all the kinetic isotherms presented in Figure 1 were calculated by assuming that the adsorption system is “solid dominated”, i.e. for low values of λ parameter. Thus, on the grounds of the approach presented here, the applicability of the pseudo-second order equation seems to be independent of the value of technical parameter λ . When considering applicability of the Lagergren equation for the case of the “solid

dominated” system, the conclusion can be drawn that decreasing of the θ_e value results in improvement of the linearity of the Lagergren plots.

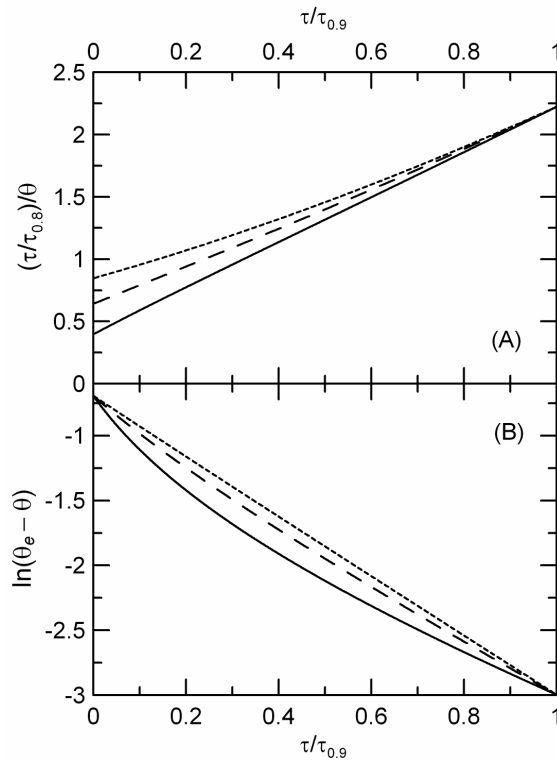


Fig. 2. Kinetic isotherms calculated from equation (12), and drawn as the pseudo-second order plots (A) and the Lagergren plots (B) for $s = 2$ and the equilibrium surface coverage $\theta_e = 0.5$. The three values of the λ parameter were assumed: $\lambda = 0.51$ (—), $\lambda = 1$ (- - -), and $\lambda = 10$ (.....).

Figure 2 shows how the value of technical parameter λ affects the behaviour predicted by the Lagergren and the pseudo-second order equations. One can see again the good applicability of the pseudo-second order equation for both “solid” and “volume” dominated adsorption systems. However, the best linearity is obtained while assuming the lowest value of λ parameter. The Lagergren plots, presented in panel (B) are in agreement with equation (13), i.e. the best linearity is obtained for the case of “volume dominated” system when the general kinetic equation (12) reduces practically to equation (13) and, next, because the assumption $\theta_e = 0.5$ was made, to the Lagergren equation (15a). This simple model investigation suggests that generally, the applicability of the pseudo-

second order equation is better than that of the Lagergren equation. This statement finds its confirmation in many experimental reports [7].

3. ANALYSIS OF EXPERIMENTAL DATA AND CONCLUSIONS

A variety of experimental data has been reported in literature on the sorption kinetics. The most frequently studied systems are those connected with the sorption of pollutants from aqueous solutions by various low-cost sorbents. While looking for a particular system to be subjected to our theoretical analysis, we focused our attention on the papers in which both kinetics and equilibrium sorption isotherms were reported.

As an example we present here the analysis of the data published by J.W. Lee, W.G. Shim, J.Y. Ko, and H. Moon, on sorption of 2-chlorophenol onto hydrophobic resin, XAD-1600, without ion-exchange functional groups [8]. The equilibrium adsorption isotherm measured in this system can be fairly well correlated by the equilibrium isotherm equation (9) rewritten here to the form useful for the analysis of experimental data:

$$N_e = \frac{N_m \sqrt{Kc^{(e)}}}{1 + \sqrt{Kc^{(e)}}} \quad (16)$$

in which N_e is the amount adsorbed at equilibrium, K is some constant and N_m is the monolayer capacity. The correlation of experimental adsorption isotherm by the above equation is shown in Figure 3. The fact of good agreement between equation (16) and the measured data speak in favor for applicability of two-site-occupancy adsorption model and allows us to use the kinetic expressions (12) and (13) in further analysis of kinetic data.

When analyzing the description of the kinetic experiment given by Lee et al. and looking at Figure 6 in their original paper [8], one can conclude that the reported adsorption system can not be treated as a "volume dominated" one. This is because the changes of solute concentration reach 50% of its initial value. Thus, when analyzing the reported experimental kinetic isotherm, we have applied equation (12) first. The values of the amount adsorbed corresponding to the given initial solute concentration were reported by Lee et al. as well as the technical parameters of the system, i.e. initial solute concentrations, volume of solution and mass of the applied sorbent. We have also used the value of the monolayer capacity N_m , determined by using the best-fit of the measured equilibrium adsorption isotherm presented in Figure 3. Thus, the only unknown parameter was the constant K_2 , enclosed in the dimensionless time τ , appearing

in equation (12). The results of applying our best-fit procedure are shown in Figure 4 and the obtained values of parameters are collected in Table 1.

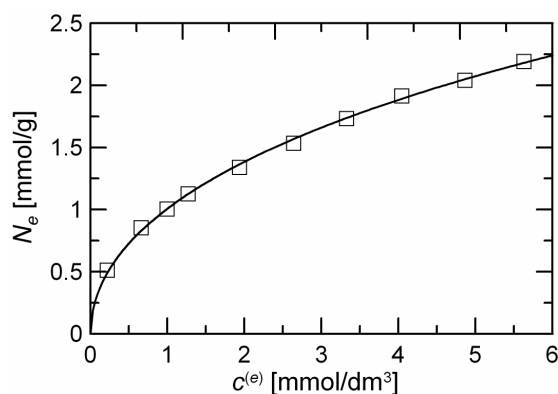


Fig. 3. Equilibrium adsorption isotherm of 2-chlorophenol by XAD-1600 resin. The squares ($\square \square \square$) are the data recorded by Lee *et al.*, while the solid line (—) is the theoretical isotherm (16) calculated by accepting the following values of best-fit parameters: $K = 0.007807$ L/mmol and $N_m = 14.43$ mmol/g.

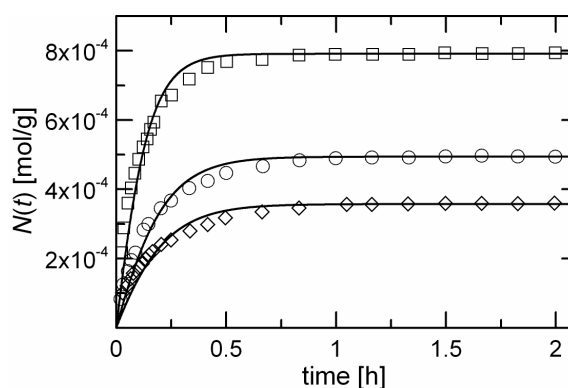


Fig. 4. The results of applying best-fit procedure for the kinetic experimental isotherms of 2-chlorophenol sorption by XAD-1600 resin, reported by Lee *et al.* for the three initial solute concentrations: 0.3 mmol/L (\diamond), 0.5 mmol/L (\circ) and 1 mmol/L (\square). The solid lines (—) are the theoretical kinetic isotherms calculated from equation (13). Here, $N(t)$ is the amount adsorbed at time t . All calculations were performed by using the parameters collected in the first four columns of Table 1.

Looking at Figure 4, one can see poor applicability of the kinetic equation (12) to correlate experimental data. This can be explained in the following way. The calculation of the parameter λ may be difficult although it is defined by measurable quantities. The serious difficulty in calculating λ lies in two facts.

1. The volume V , which partially defines λ , may be equal to the geometric volume of solution but it may also be smaller, because not the entire volume of the system can determine the values of equilibrium solute concentration and surface coverage. It is possible that only small part of this volume, closest to the surface, may be practically important in determination of these equilibrium values.
2. Equation (12) does not take into account the flux of solute molecules to the solid surface. For such a case, the solute concentration of these parts of solution which are the closest to the surface can have smaller values than those predicted by simple equation (7); to determine the actual function $c(t)$, a much more complicated procedure has to be applied [9].

Thus, the parameter λ should be rather considered as a parameter which can be treated as the best-fit one. With this assumption, we fitted again the measured kinetic isotherms, using now the two best-fit parameters: λ and K_2 . The results applying this procedure are presented in Figures 5 and 6. The obtained values of parameters are collected in the last two columns of Table 1. One can see now in Figure 5 an excellent agreement between the measured kinetic isotherms and equation (12). This can be especially seen when the time is presented in the logarithmic scale as shown in Figure 6.

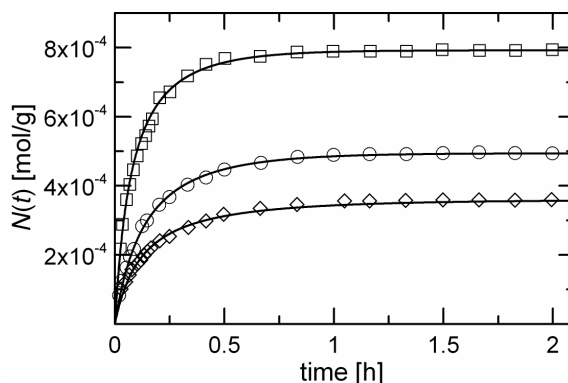


Fig. 5. The results of applying the best-fit procedure for the kinetic experimental isotherms of 2-chlorophenol sorption by XAD-1600 resin, reported by Lee et al. The calculations were now performed by using the best-fit parameters collected in the last two columns of Table 1. All notations are the same as in Figure 4.

Tab. 1. The values of the best-fit parameters used to fit the kinetic isotherms measured by Lee *et al.* The obtained agreement between the theory and the experiment is shown in Figures 4-6.

$c^{(in)}$ [mmol/L]	$N^{(e)}$ [mmol/g] (experimental)	λ (Figure 4)	K_2 [1/h] (Figure 4)	λ (Figure 5)	K_2 [1/h] (Figure 5)
0.3	0.357	0.0478	59	0.0141	375
0.5	0.494	0.0797	27	0.0220	168
0.7	0.791	0.1593	13	0.0341	121

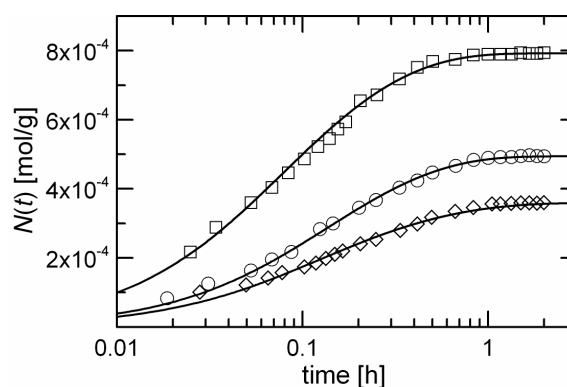


Fig. 6. The measured kinetic isotherms of 2-chlorophenol sorption by XAD-1600 resin, correlated by equation (13) with λ treated as the best-fit parameter. All notations are the same as in Figure 4.

4. SUMMARY

Kinetics of solute adsorption at the solid/liquid interfaces is the essential feature of these systems mainly for their applications in technology of environmental protection. The Lagergren and the pseudo-second order empirical equations are the most widely used expressions to correlate the experimental data on adsorption kinetics. We have shown here that it is possible to find the theoretical origin of these equations on the ground of the classical fundamental ART approach and the model of a two-site occupancy adsorption. Application of this approach makes it also possible to take into consideration the technical conditions under which the kinetic experiment is carried out (mass of adsorbent, volume of solution and its initial concentration). In this way we arrived at a general differential equation (12) describing the rate of adsorption which reproduces very well all the essential features of the observed adsorption kinetics. This was shown by presenting an analysis of exemplary experimental

data found in literature. It can be proved by using the simple model investigation that for certain values of physical and technical parameters, our new general equation reduces to the Lagergren equation or to the pseudo-second order equation.

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CURRICULA VITAE



Władysław Rudziński was born in Poland in 1942. In 1964 graduated from the Faculty of Chemistry of the Maria Curie Skłodowska University in Lublin. In 1979 received his Ph.D. degree in the Department of Theoretical Chemistry at Jagiellonian University in Cracow. Since 1970 he has been back at UMCS University in Lublin, where he organised his research group working on theoretical problems of adsorption. In 1979 his research group received the status of the Department of Theoretical Chemistry. He has been the Head of that Department until now. Since 1999 he has also been the Head of the Laboratory for the Theoretical Problems of Adsorption of the Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences in Cracow. He was also the Chairman of the Committee for Interface Chemistry of the Polish Chemical Society, and served also one year as the President of the Society. Professor Rudziński was a member of the Board of Directors of the International Adsorption Society, and served as a member of the Scientific Committees of such international conferences as the largest world conference on adsorption FOA (Fundamentals of Adsorption), or the Pacific Adsorption Conference. He is also a corresponding member of the European Academy of Arts Sciences and Humanities.

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He organised the six international symposia: *"Effects of Surface Heterogeneity in Adsorption and Catalysis on Solids"-ISSHAC* (Poland, 1992, 1995, 1998, 2001, 2004, 2006), and the Polish-Israeli Symposium *"Current Trends in Interface Chemistry"*, in 2000.

For his outstanding scientific achievements, he was awarded five times by the Polish Ministry of Education and once by the Rector of Maria Curie-Skłodowska University. He was also awarded by the Polish Chemical Society.

Besides many short visits to many Universities of the world, he also paid long-term visits to Queens University (Canada), University of Vienna (Austria), University of Leipzig (Germany), Tohoku University (Japan), CNRS Laboratory at the University of Montpellier (France), Ruhr University in Bochum (Germany), Seoul National University (Korea), Chonnam National University (Korea), CNRS Laboratory in Nancy (France), University of San Luis (Argentina), and National Chung Cheng University (Taiwan).

Main scientific interests: Theoretical description of adsorption of simple ions and of surfactants at oxide/electrolyte interfaces (Special attention focused on enthalpies of adsorption and on effects of surface heterogeneity), equilibria and kinetics of gas adsorption on energetically heterogeneous solid surfaces, (also thermodesorption), and mixed-gas adsorption.



Wojciech Płaziński was born in Krasnystaw in Poland in 1981. Studies of chemistry at the Faculty of Chemistry, Maria Curie-Skłodowska University, in 2000–2005. Scholarship awarded by the Minister for National Education in 2004/2005. He is a member of Polish Chemical Society (since 2004). At present, he is a Ph.D. student at the Department of Theoretical Chemistry at Maria Curie-Skłodowska University in Lublin. His main field of interest is: kinetics and equilibrium of dyes and heavy metal ion adsorption at solid/solution interfaces, kinetics and equilibrium of gas adsorption on solids and modeling of biosorption processes. He published over 10 original papers.