

## Applicability comparison of different kinetic/diffusion models for 4-nitrophenol sorption on *Rhizopus oryzae* dead biomass

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Nitrophenols represent one of the most challenging classes of pollutants requiring removal from wastewater streams due to their non-biodegradability and toxicity. The applicability of *Rhizopus oryzae* dead biomass as an alternative “eco-friendly” sorbent for 4-nitrophenol (4-NP) removal from aqueous phase was investigated in this study. The effect of initial sorbate concentration and adsorbent mass on the kinetics of adsorption were evaluated. The experimental kinetic results were analyzed by series of rate/mass transfer equations: pseudo-first, pseudo-second order model, Bangham’s model, intra-particle diffusion model, and Elovich kinetic equation. Probably, 4-NP sorption on the dead biomass was mainly limited by chemisorption, but the role of intraparticle diffusion could not be neglected. The highest extend of 4-NP uptake determined in the recent study was 94 %.

**Keywords:** *Rhizopus oryzae* dead fungi, adsorption, 4-nitrophenol, kinetics

### INTRODUCTION

Nitrophenols are the organic compounds that appear very frequently in the wastewater of the almost all heavy chemical industries. Mononitrophenols can be classified as compounds exhibiting moderate to high toxicity in the aquatic compartment [1]. 4-Nitrophenol (4-NP) could enter the environment during its production and use in high-temperature coal conversion, as an intermediate in the manufacture of parathion, methyl parathion and N-acetyl-p-amino-phenol. It is also found in suspended particulate matter in the atmosphere, originating mostly from secondary photochemical reactions in the air [2].

Among the processes used for the treatment of wastewaters rich in phenolic compounds, solid phase adsorption has been widely applied, and efficiency of various adsorbents have been reported in the literature [3, 4]. A number of scientific investigations proved the high adsorption activity of various biopolymers (unmodified/modified chitosan, lignine, etc) towards phenols, chlorophenols and dyes [5–7].

*Rhizopus oryzae* are saprophylic micro-organisms, which belong to the *Rhizopus fungi*

group. Their cell walls consist mainly of chitin and chitosan. The mechanism of biosorption is quite complicated. Both living and dead biomasses exhibit biosorption capacity; performance of living biomass in binding metal ions depends not only on nutrient and environmental status, but also on cell age. The application of live biomass has some disadvantages: live cells systems are sensitive to the toxicity of the pollutants and to the working conditions (pH, temperature). Dead biomass is produced by physical (heating, autoclave treatment, and vacuum drying), chemical (treatment with acids, alkali and other organic and inorganic substances) and mechanical (mechanical grinding) methods [8, 9]. In addition it can be easily regenerated and reused. The role of different functional groups (i.e. amino, carboxyl, hydroxyl, phosphate) and cell wall components (chitin, chitosan, glucan, phosphomannan) of *Rhizopus oryzae* during rhodamine B adsorption was examined. Chemical group modification studies demonstrated that the carboxyl and amino groups were mainly responsible for the binding of rhodamine B on *Rhizopus oryzae* biomass. The adsorption capacity of the cell wall components with respect to rhodamine B followed the order: phosphomannan > chitosan > chitin ~ glucan [10].

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The aim of this study was to investigate the applicability of *Rhizopus oryzae* as an alternative “eco-friendly” adsorbent for 4-nitrophenol removal from aqueous phase and to evaluate the adsorption mechanism. The applicability of five kinetic/mass transfer models: pseudo-first order, pseudo-second order, Elovich kinetic models, Bangham’s equation and the intraparticle diffusion model, was examined on the basis of comparative estimation of the corresponding rate parameters, equilibrium capacity, and correlation coefficients.

EXPERIMENTAL

Adsorbate

4-Nitrophenol (4-NP) (Merck, 99 %), without further purification, was used as a sorbate in the investigations. Its physicochemical characteristics are presented in Table 1.

Table 1. Physicochemical properties of 4-NP [11]

Molar mass, kg kmol <sup>-1</sup>	Density, g cm <sup>-3</sup>	Solubility, g/100g H <sub>2</sub> O	Molecular volume, nm <sup>3</sup>	pKa	Effective molecular diameter, nm	λ <sub>max</sub> , nm
139.11	1.270*	1.7	0.191	7.08	0.813	228

\* 20 °C

Adsorbent

*Rhizopus oryzae* used in the recent study as a sorbent was supplied by the International Mycological Institute in Surrey, Great Britain, in the form of IMI strain 266680. The microorganisms were isolated from a soil in Sri Lanka. malt extract was inoculated by a standard sterile method. Three

ceramic granules were added to each of the batch. The spores dried at low temperature were reactivated and cultivated in malt extract (17 g dm<sup>-3</sup> malt extract and 3 g dm<sup>-3</sup> mycological peptone, dissolved in distilled water at pH 5.4±0.2) incubated at 32°C for and 3 days in a platform shaker at 175 rpm. The reactors with malt extract to limit the microorganisms threadlike growth. The biomass obtained was precisely washed out consecutively with maternal lye and distilled water and then dried in an oven at 50°C. The dried biomass was ground in a hammer mill and screened. The fraction used in the recent investigations was 0.15 – 0.50 mm.

Kinetic studies

The kinetic experiments were conducted in a standardized batch adsorber with a two-bladed impeller with a Heidolph RZR 2100 motor [12]. The kinetic experiments were carried out at initial 4-NP concentrations c<sub>o</sub> 5, 10, 15, 20 mg dm<sup>-3</sup>, masses of adsorbent w 1, 2 g, agitation rate n 200 rpm.

SPECORD UV-VIS, Carl Zeiss Jena, spectrophotometer was used for concentration determinations at the corresponding wavelength (λ 228 nm). The working temperature was 19±2 °C and pH 6.1±0.2. The pH was measured using a LHP 403T TACUSSEL pH-meter. Blanks containing no adsorbate and replicates of each adsorption point were used for each series of experiments.

Table 2. Kinetic and mass transfer models

Model		
Pseudo-first order kinetic model [13]	$\frac{dq_t}{dt} = k_1(q_e - q_t)$ (1)	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$ (2)
Pseudo-second order kinetic model [14]	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ (3) $\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t$ (4)	$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t$ (5)
Elovich kinetic model, [15, 16]	$\frac{dq}{dt} = \alpha \exp(-\omega \cdot q)$ (6) $q_t = \frac{1}{\omega} \ln(\alpha \cdot \omega) + \frac{1}{\omega} \ln t$ (7)	$q_t = A + B \cdot \ln t$ (8) $A = \frac{1}{\omega} \ln(\alpha \cdot \omega)$ (9) $B = \frac{1}{\omega}$ (10)
Bangham’s equation [17]	$\log \left[ \log \left( \frac{c_o}{c_o - q_t \cdot m} \right) \right] = \log \left( \frac{k_o \cdot m}{2.303 \cdot V} \right) + \sigma \cdot \log t$ (11)	
Intraparticle diffusion model [18]	$q_t = k_i t^{0.5}$ (12)	

## RESULTS AND DISCUSSION

*Kinetics modeling*

In order to investigate the mechanism of 4-NP sorption on *Rhizopus oryzae*, the applicability of the pseudo-first order, pseudo-second order, Elovich kinetic models, Bangham's equation and the intraparticle diffusion model were examined. The non-linear and linear forms of the models applied are resented in Table 2.

*Effect of initial sorbate concentration*

The experimental kinetic curves presenting the effect of initial nitrophenol concentration in the liquid phase ( $c_0$ ) on the kinetics of its adsorption on *Rhizopus oryzae* are displayed in Fig. 1. Obviously, the system reached equilibrium approximately 50 min after the beginning of the sorption process. The highest extend of 4-NP removal attained was 94 %.

According to the experimental data, the equilibrium adsorption capacity ( $q_{exp}$ ) increased directly proportionally (from 7.99 to 19.72 mg g<sup>-1</sup>) with the increase of  $c_0$ . The values of the regression coefficients  $R_1^2$  и  $R_2^2$ , calculated by the pseudo-first

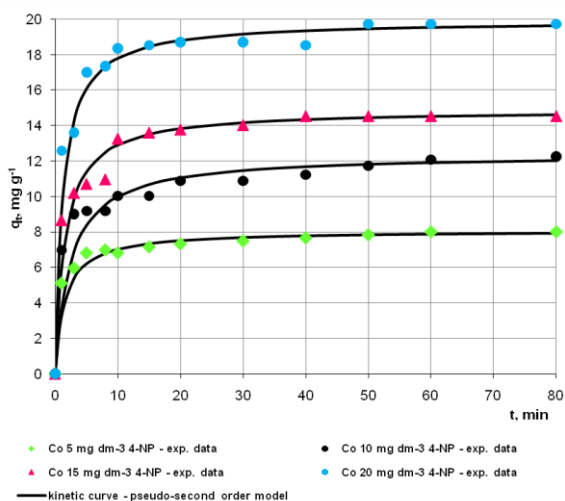
and pseudo-second order kinetic models (Table 3) proved better applicability of the second-order model. The latter conclusion was unambiguously ascertained as by the nearly analogous modes of the experimental and model kinetic curves, juxtaposed on Figure 1 as  $q_t$  vs  $t$ , so by the nearly equal values of the experimental ( $q_{exp}$ ) and the calculated by the second-order model ( $q_2$ ) equilibrium sorption capacities (Table 3). The observed direct relationship between the values of the initial sorption rate ( $h$ ) and  $c_0$  values could, probably, be due to the greater number of organic molecules that attack the active sites of the sorbent, as well as to the decreased mass transfer resistance they had to overcome.

The proven applicability of this model signified the role of chemisorption as probably one of the basic rate limiting mechanisms during 4-NP adsorption on the biomaterial studied.

The kinetic data were also analyzed using the Elovich equation. The corresponding model parameters ( $\omega$ ,  $\alpha$ ) determined along with the correlation coefficients ( $R_E^2$ ) were given in Table 3.

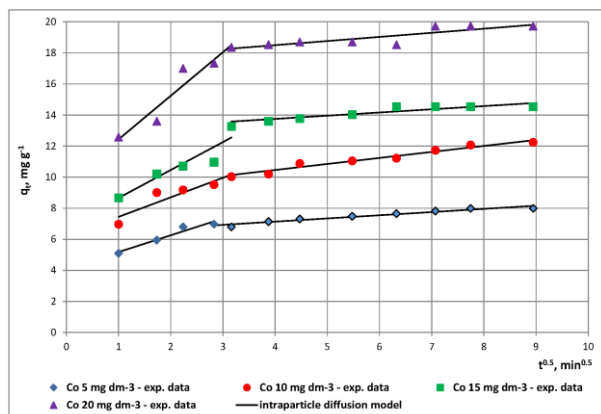
**Table 3.** Values of the kinetic and diffusion parameters characterizing 4-NP sorption on *Rhizopus oryzae* - effect of initial sorbate concentration

Pseudo-first order model	$k_1, \text{min}^{-1}$	$q_{e1}, \text{mg g}^{-1}$	$q_{exp}, \text{mg g}^{-1}$	$R_1^2$	
5 mg dm <sup>-3</sup>	0.0481	1.98	7.99	0.9320	
10 mg dm <sup>-3</sup>	0.0465	4.33	12.24	0.9314	
15 mg dm <sup>-3</sup>	0.0894	5.28	14.54	0.8790	
20 mg dm <sup>-3</sup>	0.1375	7.26	19.72	0.8865	
Pseudo-second order model	$k_2, \text{g mg}^{-1} \text{min}^{-1}$	$q_{e2}, \text{mg g}^{-1}$	$q_{exp}, \text{mg g}^{-1}$	$h, \text{mg g}^{-1} \text{min}^{-1}$	$R_2^2$
5 mg dm <sup>-3</sup>	0.0817	8.09	7.99	5.3504	0.9994
10 mg dm <sup>-3</sup>	0.0336	12.39	12.24	5.1593	0.9979
15 mg dm <sup>-3</sup>	0.0435	14.88	14.54	9.6432	0.9995
20 mg dm <sup>-3</sup>	0.0418	19.92	19.72	16.5837	0.9992
Bangham's equation	$k_0, \text{dm}^3 \text{g}^{-1}$	$\sigma$		$R_B^2$	
5 mg dm <sup>-3</sup>	2.7500	0.2495		0.9725	
10 mg dm <sup>-3</sup>	1.6167	0.1875		0.9653	
15 mg dm <sup>-3</sup>	1.2409	0.1760		0.9145	
20 mg dm <sup>-3</sup>	1.4422	0.1423		0.8521	
Elovich model	A	B	$\omega, \text{g mg}^{-1}$	$\alpha, \text{mg g}^{-1} \text{min}^{-1}$	$R_E^2$
5 mg dm <sup>-3</sup>	5.3838	0.6319	1.5826	3167.8980	0.9544
10 mg dm <sup>-3</sup>	7.2288	1.1364	0.8800	657.8480	0.9678
15 mg dm <sup>-3</sup>	8.7751	1.4885	0.6718	540.8047	0.9162
20 mg dm <sup>-3</sup>	13.3240	1.6302	0.6134	5778.8980	0.8630
Intraparticle diffusion model	$k_{i1}, \text{mg g}^{-1} \text{min}^{-0.5}$	$k_{i2}, \text{mg g}^{-1} \text{min}^{-0.5}$		$R_{i1}^2$	$R_{i2}^2$
5 mg dm <sup>-3</sup>	0.4810	0.2055		0.9451	0.9421
10 mg dm <sup>-3</sup>	1.8599	0.8619		0.8835	0.8333
15 mg dm <sup>-3</sup>	1.2593	0.2056		0.9023	0.8103
20 mg dm <sup>-3</sup>	2.8069	0.2647		0.9185	0.7598



**Fig. 1.** Experimental and pseudo-second order model kinetic curves for 4-NP adsorption on *Rhizopus oryzae* - effect of initial sorbate concentration.

Elovich equation was used successfully to describe second-order kinetics assuming that the actual solid surfaces are energetically heterogeneous [19]. The analyses of the results outlined an inversely proportional relationship between  $c_o$  and the values of the parameter -  $\omega$ , which is related to the extent of surface coverage and the activation energy for chemisorption. Consequently, the number of active sites available for adsorption was reduced due to the larger number of sorbate molecules at higher initial concentrations. Fig. 2 presented graphically the intraparticle diffusion model applied to the investigated system.



**Fig. 2.** Intraparticle diffusion model applied for the system 4-NP - *Rhizopus oryzae* - effect of initial sorbate concentration.

The plots consisted of only two linear sections, presuming the presence of macro- and transitional pores in the sorbent structure. The diffusion in them characterized with specific rate parameters,  $k_{i1}$  and  $k_{i2}$ , respectively (Table 3). The calculated values of  $k_{i1}$  were higher than that of  $k_{i2}$ . The reason could be as circumscription of the available vacant space for

diffusion in them, so of pore blockage. The values of the correlation regression coefficients characterizing the applicability of the intraparticle diffusion model ( $R_{i1}^2$ ,  $R_{i2}^2$ ) were lower than that of  $R_2^2$ , but commensurable with  $R_1^2$ . Actually, the three models stated above could describe the proposed sorption process to a definite extend, but they could not predict the high rate of adsorption during the first minutes of the process. Probably, the initial stages were controlled by external mass transfer or surface diffusion, followed by chemical reaction or a constant-rate stage, and diffusion causing gradual decrease of the process rate. The initial steep section of the plots associated with a sharp increase of the nitrophenol concentration was indicative of a rapid initial external mass transfer or chemical interactions between functional groups of the organic molecules with those of the biomaterial. After saturating the external solid particles surface, the molecules began to enter them in order to find new vacant active sites. The sorption of 4-NP molecules inside the pores of *Rhizopus oryzae*, however, increased the diffusion resistance and led to a decrease in the process rate.

The effect of initial sorbate concentration on the values of the second-order model parameters  $q_2$ ,  $k_2$  and  $h$  was examined by plotting the linear relationships between them and  $c_o$ :

$$q_2 = \frac{c_o}{A_q c_o + B_q} \quad (13)$$

$$k_2 = \frac{c_o}{A_k c_o + B_k} \quad (14)$$

$$h = \frac{c_o}{A_h c_o + B_h} \quad (15)$$

The values of the coefficients  $A_q$ ,  $B_q$ ,  $R_q^2$ ,  $A_k$ ,  $B_k$ ,  $R_k^2$ ,  $A_h$ ,  $B_h$  and  $R_h^2$  were calculated by linear regression analyses and presented in Table 4.

The substitution of  $q_2$  and  $h$  values in eqn. (13) and (15) and then in eqn. (5), allowed working out the pseudo-second rate law rendering an account of the effect of initial nitrophenol concentration:

$$q_t = \frac{c_o t}{0.0086c_o + 1.3006 + (0,0272c_o + 0.5196)t} \quad (16)$$

Eqn. (16) is a generalized model for prediction of the adsorption capacity during 4-NP sorption on *Rhizopus oryzae* at various initial concentrations with time. The kinetic data for 4-NP adsorption on *Rhizopus oryzae* were analyzed by using the Bangham's equation to examine if pore diffusion

**Table 4.** Values of the empirical parameters for  $q_2$ ,  $k_2$  and  $h$  regarding  $c_0$ 

$A_q$ , g mg <sup>-1</sup>	$B_q$ , g dm <sup>-3</sup>	$R_q^2$	$A_k$ , mg g min <sup>-1</sup>	$B_k$ , mg <sup>2</sup> g dm <sup>3</sup> min <sup>-1</sup>	$R_k^2$	$A_h$ , g mg min <sup>-1</sup>	$B_h$ , g dm <sup>3</sup> min <sup>-1</sup>	$R_h^2$
0.0272	0.5196	0.8877	25.98	-29.225	0.9291	0.0086	1.3006	0.0164

**Table 5.** Values of the kinetic and diffusion parameters characterizing 4-NP sorption on *Rh. oryzae* - effect of adsorbent mass.

Pseudo-first order model	$k_1$ , min <sup>-1</sup>	$q_{e1}$ , mg g <sup>-1</sup>	$q_{exp}$ , mg g <sup>-1</sup>	$R_1^2$	
1 g	0.0465	4.33	12.24	0.9314	
2 g	0.0573	0.94	7.23	0.8650	
Pseudo-second order model	$k_2$ , g mg <sup>-1</sup> min <sup>-1</sup>	$q_{e2}$ , mg g <sup>-1</sup>	$q_{exp}$ , mg g <sup>-1</sup>	$h$ , mg g <sup>-1</sup> min <sup>-1</sup>	$R_2^2$
1 g	0.0336	12.39	12.24	5.1593	0.9979
2 g	0.8715	7.26	7.23	12.6743	0.9999
Bangham's equation	$k_0$ , dm <sup>3</sup> g <sup>-1</sup>	$\sigma$	$R_B^2$		
1 g	1.6167	0.1875	0.9653		
2 g	1.7456	0.1139	0.9526		
Elovich model	A	B	$\omega$ , g mg <sup>-1</sup>	$\alpha$ , mg g <sup>-1</sup> min <sup>-1</sup>	$R_E^2$
1 g	7.2288	1.1364	0.8800	657.8480	0.9678
2 g	5.9809	0.3177	3.1476	4.7630.10 <sup>7</sup>	0.9375
Intraparticle diffusion model	$k_{i1}$ , mg g <sup>-1</sup> min <sup>-0.5</sup>	$k_{i2}$ , mg g <sup>-1</sup> min <sup>-0.5</sup>	$R_{i1}^2$		$R_{i2}^2$
1 g	1.8599	0.8619	0.8835		0.8333
2 g	0.6883	0.1521	0.9999		0.9457

was the only controlling step in the adsorption process or not. The experimental data modeled by eqn. (8) did not yield a desired linear fit in the double logarithmic plot. This indicated that the adsorption kinetics was not limited only by pore-diffusion. The values of the Bangham's equation parameters  $k_0$  and  $\sigma$  along with the correlation coefficients ( $R_B$ ) were presented in Table 3. The highest values of the three parameters estimated at  $c_0$  5 mg dm<sup>-3</sup>, seemed logical as the number of organic molecules competing for vacant active sites inside the sorbent pores was the lowest, consequently the obstacles, due to pore blockage, they had to overcome were reduced. According to the results, it could be concluded that both film and pore-diffusion played a significant role to different extend during the different stages of the sorption process.

#### Effect of adsorbent mass

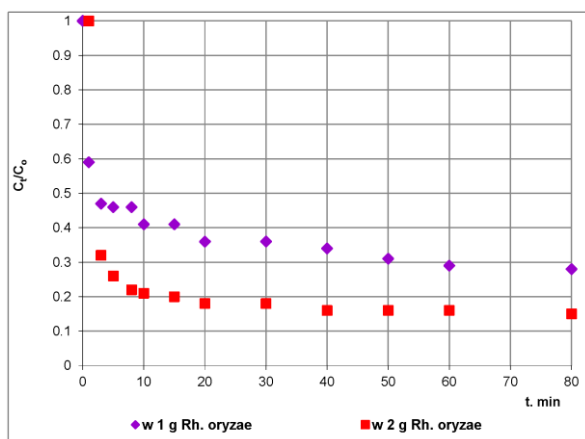
The effect of adsorbent mass on the kinetics of 4-NP adsorption on *Rhizopus oryzae* was tested in the present investigations. The experimental kinetic curves (Fig. 3) displayed an outlined direct relationship between adsorbent quality and the extent of nitrophenol uptake from its model solutions. The latter statement was logical as the greater amount of adsorbent is related to larger number of vacant active sites for the organic molecules sorption. The sorption rate in the initial stages of the process was the highest. The system

reached equilibrium, indicated by the horizontal section of the kinetic curves, approximately 40-50 min after the beginning of the process. The highest adsorption capacity attained was  $q_e$  12.24 mg g<sup>-1</sup>.

The experimental data were modeled by the pseudo-first order, pseudo-second order, Elovich kinetic models, Bangham's equation and the intraparticle diffusion model, to determine the prevailing mechanism/s during 4-NP sorption on the biomaterial and to examine the effect of adsorbent mass on the models kinetic and diffusion parameters (Table 5). The high values of the correlation coefficients ( $R_2^2 > 0.9979$ ) and the approximately equal values of the calculated and experimentally obtained equilibrium adsorption capacities ( $q_2$ ,  $q_e$ ) (Table 5), calculated by the pseudo-second order model compared to the values of the parameters obtained by applying the first order equation (Table 5), proved the better applicability of the second order model. Thus, chemisorption could be accepted as one of the basic rate limiting mechanisms during 4-NP sorption on *Rhizopus oryzae*.

The above stated conclusion regarding the mechanism of the proposed sorption process was confirmed by the analyses of the applicability of Bangham's model, assuming pore diffusion as the major rate limiting mechanism, and Elovich kinetic equation based on the hypothesis of chemisorption. The values of Bangham's and Elovich equation parameters:  $k_0$ ,  $\sigma$ , A, B,  $\omega$  and  $\alpha$ , along with the

regression coefficients ( $R_B^2$  and  $R_E^2$ ) were presented in Table 5. The values of  $R_B^2$  and  $R_E^2$  were commensurable but lower than  $R_2^2$ . Consequently, probably 4-NP sorption on the dead biomass was mainly limited by chemical interactions between the organic molecules and some functional groups of *Rhizopus oryzae*, but the role of intraparticle diffusion could not be neglected.



**Fig. 3.** Experimental kinetic curves of 4-NP adsorption on *Rhizopus oryzae* - effect of adsorbent mass.

The analyses of the results outlined a direct relationship between  $w$  and the values of the parameter  $\omega$ , related to the extent of surface coverage and the activation energy for chemisorptions, as the larger adsorbent amount defined greater active sites available for adsorption.

As the values of  $R_{i1}$  are higher than those of  $R_1$  and lower than  $R_2$  (Table 5), an explicit conclusion whether chemisorption or intraparticle diffusion was the general rate controlling mechanism during 4-NP sorption on *Rhizopus oryzae* could not be withdrawn, i.e. either of the proposed processes could dominate during the different sorption stages.

The adsorbent loading increased when its mass was decreased, as unit sorbent mass got into contact with larger number of organic molecules. Moreover, the rate of intraparticle diffusion decreased at higher sorbent mass as indicated by the lower values of the rate coefficients ( $k_{i1}$ ,  $k_{i2}$ ), characterizing the experimental series with  $w$  2 g *Rhizopus oryzae*, when compared to that with  $w$  1 g sorbent (Table 5). Probably, the latter was due to the larger external surface area available for adsorption, followed by a sharp drop of 4-NP concentration in the liquid phase and respectively, reduction of the process driving force.

The conclusions of our scientific team, regarding the mechanism of the sorption process investigated were sustained by analyses of the adsorbate and adsorbent nature. As mentioned above, chitin and

chitosan are the basic components of *Rhizopus oryzae* cell walls. Chitosan characterized with well distinguished hydrophilic properties due to the presence of a polar amino group in its structure. As a result it expands in aqueous media and its active sites responsible for the formation of H-bonds become more easily accessible. According to Uzun and Guzel, 4-NP adsorption on chitosan was controlled by both physical and chemical adsorption [5, 6]. The pKa value for the 4-NP is 7.15, i.e. its aqueous solution characterized with low pH. The O-H bond could be easily destroyed, while the  $\text{NO}_2$ -group supports the resonance stability of the molecular structure through delocalization of the negative charge. The amino group of the chitosan is positively charged in the acidic 4-NP solution. Consequently, a chemical interaction between the negatively charged molecule and the positive charge of the biopolymer could take place.

The present investigations proved the high efficiency (94 %) of *Rhizopus oryzae* as an alternative adsorbent for 4-NP removal from aqueous phase and revealed the mechanism of the separation process at laboratory scale. Due to the harmful effects of these organic compounds and the urge for sustainable development for the natural water resources at global scale, however, the wastewaters containing them must be treated before being discharged to receiving natural water bodies. Consequently, the future perspectives of the applicability of the proposed “eco-friendly” adsorbent for industrial purposes include large-scale investigations of our scientific team with real wastewaters containing mononitrophenols and/or contaminated natural waters.

## CONCLUSIONS

The mechanism of 4-NP adsorption on *Rhizopus oryzae* from aqueous medium on the basis of kinetic studies was investigated. As the theoretical kinetic curves predicted by the pseudo-second order model displayed an extremely high degree of correlation with the experimental data, the rate-limiting step might be chemical adsorption or chemisorption involving valency forces through exchange of electrons between the sorbate and the sorbent. The laboratory studies proved the high efficiency (94 % uptake extend) of *Rhizopus oryzae* dead biomass as an alternative adsorbent for removal of the toxic and recalcitrant organic contaminant 4-NP from aqueous phase, and outlined its future applicability in large-scale wastewater treatment technologies.

## NOMENCLATURE

$c_e$	equilibrium adsorbate concentration in the liquid phase, $\text{mg dm}^{-3}$
$c_o$	initial adsorbate concentration in the liquid phase, $\text{mg dm}^{-3}$
$d_p$	particle diameter, mm
$h$	initial adsorption rate, $\text{mg g}^{-1} \text{min}^{-1}$
$K_1$	Bangham's model equilibrium constant for the first layer adsorption
$K_2$	Bangham's equilibrium constant for multilayer adsorption
$k_i$	intraparticle diffusion rate constant, $\text{mg g}^{-1} \text{min}^{-0.5}$
$k_o$	Bangham's equation parameters, $\text{dm g}^{-1}$
$k_1$	rate constant of pseudo-first order sorption, $\text{min}^{-1}$
$k_2$	rate constant of pseudo-second order sorption, $\text{g mg}^{-1} \text{min}^{-1}$
$m$	adsorbent concentration, $\text{g dm}^{-3}$
$n$	agitation rate, rpm
$q_e$	the equilibrium sorbate concentration in the solid phase, $\text{mg g}^{-1}$
$q_t$	the sorption capacity at equilibrium and at time t, $\text{mg g}^{-1}$
$R$	the universal gas constant ( $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$ )
$R^2$	correlation coefficient
$T$	temperature, K
$t$	time, min
$V$	solution volume, $\text{dm}^3$
$w$	adsorbent mass, g
$\alpha$	the initial adsorption rate in Elovich equation, $\text{mg g}^{-1} \text{min}^{-1}$
$\lambda$	maximum absorbance wavelength, nm
$\sigma$	Bangham's equation parameter, ( $\sigma < 1$ )
$\omega$	parameter in Elovich model related to the extent of surface coverage and the activation energy for chemisorption, $\text{g mg}^{-1}$

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## СРАВНЯВАНЕ НА ПРИЛОЖИМОСТТА НА РАЗЛИЧНИ КИНЕТИЧНИ/ДИФУЗИОННИ МОДЕЛИ ЗА СОРБЦИЯ НА 4-НИТРОФЕНОЛ ВЪРХУ МЪРТВА БИОМАСА *RHIZOPUS ORYZAE*

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(Резюме)

Нитрофенолите представляват един от най-предизвикателните класове замърсители, изискващи отстраняване от водни потоци, поради тяхната трудна биоразградимост и токсичност. В тази публикация е изследвана приложимостта на мъртвата биомаса *Rhizopus oryzae* като алтернативен „еко-сорбент“ за отстраняване на 4-нитрофенол (4-NP) от водна среда. Оценен е ефектът на началната концентрация на сорбата и масата на адсорбента върху кинетиката на адсорбция. Резултатите от изследване на кинетиката са анализирани чрез серия от скоростни/масопреносни уравнения: модели от псевдо-първи и псевдо-втори порядък, модел на Бангам, модел за вътрешна дифузия и кинетичното уравнение на Елович. Вероятно, сорбцията на 4-NP върху мъртвата биомаса се лимитира главно от хемисорбция, но не трябва да се пренебрегва ролята на вътрешната дифузия. Най-високата степен на отстраняване на 4-NP, постигната в това изследване, е 94 %.