



**PHYSICAL CHEMISTRY 2012**

<sup>11</sup>th International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry

---

Under the auspices of the  
University of Belgrade

---

Proceedings

---

The Conference is dedicated to  
Professor Ivan Draganić

---

September 24-28, 2012  
Belgrade, Serbia

<b>ISBN 978-86-82475-27-9 <i>Volume 1</i></b> <b>ISBN 978-86-82475-28-6 <i>Volume II</i></b>
---

**Title:** PHYSICAL CHEMISTRY 2012 (Proceedings)

**Editors:** S. Anić and Ž. Čupić

**Published by:** Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia

**Publisher:** Society of Physical Chemists of Serbia

**For Publisher:** S. Anić, President of Society of Physical Chemists of Serbia

**Printed by:** “Jovan” Printing and Publishing Company; 200 Copies;

**Number of pages:** 6+ 497; **Format:** B5; Printing finished in September 2012.

**Text and Layout:** “Jovan”

*200- Copy printing*

## CONTENTS

### *Volume 1*

Organizers	V
Committees	VI
Sponsors	VIII
Professor Ivan Draganić	IX
Plenary lectures	1
Chemical Thermodynamics	35
Spectroscopy, Molecular Structure, Physical Chemistry of Plasma	65
Kinetics, Catalysis	137
Nonlinear Dynamics	225
Electrochemistry	301
Biophysical Chemistry, Photochemistry, Radiation Chemistry	337
Radiochemistry, Nuclear Chemistry	
Material Science	415

### *Volume II*

Solid State Physical Chemistry	505
Macromolecular Physical Chemistry	515
Environmental Protection	
Forensic Sciences Pharmaceutical Physical Chemistry	557
Phase Boundaries	667
Complex Compounds	681
General Physical Chemistry	707
Geophysical Chemistry	719
Education, History	731
Food Physical Chemistry	743
Free Topic	783
Index	791

## DIFFUSION-BASED KINETIC MODELING OF TEXTILE DYE ADSORPTION BY POROUS COPOLYMER

Z. Sandić<sup>1</sup>, D. Maksin<sup>2</sup>, N. Jović-Jovičić<sup>3</sup>, B. Ekmešćić<sup>3</sup>, A. Nastasović<sup>3</sup>,  
A. Onjia<sup>2</sup>, A. Popović<sup>4</sup>

<sup>1</sup>*University of Banja Luka, Faculty of Science, 78000 Banja Luka, Mladena Stojanovića 2, Bosnia and Herzegovina*

<sup>2</sup>*University of Belgrade, Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Republic of Serbia*

<sup>3</sup>*University of Belgrade, ICTM, Njegoševa 12, 11000 Belgrade, Republic of Serbia*

<sup>4</sup>*Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Republic of Serbia*

### Abstract

Macroporous glycidyl dimethacrylate and ethylene glycol dimethacrylate copolymer functionalized with diethylene triamine, PGME-deta, was tested as adsorbent for removal of Acid Orange 10 (AO10) and Reactive Black 5 (RB5) from aqueous solutions. Diffusion-based kinetic models (intraparticle diffusion, Bangham and Boyd model) were used for interpretation of experimental data.

### Introduction

The removal of synthetic dyes from the industrial effluents becomes a critical issue. Over  $7 \times 10^5$  t of nearly 100,000 commercially available dyes are produced annually worldwide while 2% of dyes are discharged directly into the environment [1]. Among the most attractive polymeric adsorbents for textile dyes removal from aqueous media are amino-functionalized glycidyl methacrylate (GMA) copolymers [2]. In this paper, kinetic data of textile dyes adsorption onto PGME-deta were interpreted with intraparticle diffusion, Bangham and Boyd model.

### Experimental

PGME-deta (surface area  $53 \text{ m}^2\text{g}^{-1}$ , pore diameter 50 nm, particle size 150-500  $\mu\text{m}$ , amino groups concentration  $5.01 \text{ mmolg}^{-1}$ ) was obtained as described elsewhere [2]. AO10 [CAS: 1936-15-8], and RB5 [CAS: 17095-24-8] were purchased from Alfa-Aesar and used as received. The experiments were carried out at 25 °C, with the initial dye concentration of 30; 50 and 70  $\text{mg L}^{-1}$ ,  $m_{\text{adsorb}}$  of 25.0 mg and  $V=50.0 \text{ mL}$ , at unadjusted pH values of 5.1 for RB5 and 7.4 for AO10. The solution aliquots were withdrawn and the absorbance of supernatant solution was measured using Thermo Electron Nicolet Evolution 500 UV-VIS spectrophotometer (absorption peaks of AO10 and RB5 were at 478 and 597 nm, respectively).

### Results And Discussion

The prediction of the rate-limiting step in the adsorption process is essential for understanding the adsorption mechanism. Our previous studies showed that the adsorption of AO10 and RB5 by PGME-deta obeyed the pseudo-second-order kinetic model, suggesting that the adsorption rate is controlled by both adsorbent

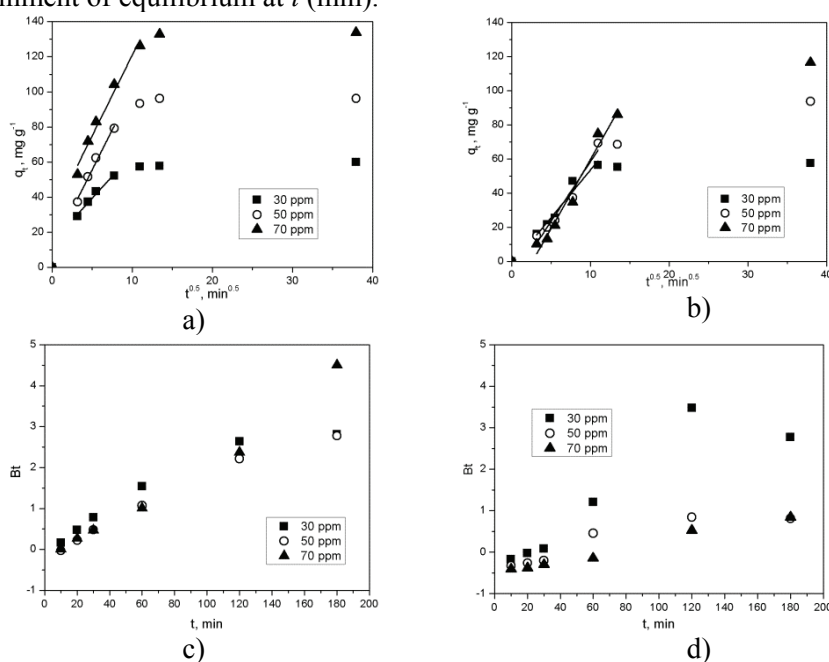
C-19-P

capacity and adsorbate concentration. For further analysis and the assessment of the influence of diffusion on adsorption, kinetic data were analyzed using diffusion-based models given in Table 1.

**Table 1.** Kinetic models.

Kinetic model	Equation	Reference
Intraparticle diffusion	$Q_t = C_{id} + k_{id} \cdot t^{0.5}$	[3]
Bangham	$\log \log \left[ \frac{C_i}{C_i - C_s Q_t} \right] = \log \left[ \frac{k_b C_s}{2.303V} \right] + \alpha \log t$	[4]
Boyd	$Bt = -0.4977 - \ln(1 - F)$	[5]

Where:  $Q_t$  is the amount of adsorbate at time  $t$  ( $\text{mg g}^{-1}$ ),  $C_{id}$ - intercept proportional to the boundary layer thickness ( $\text{mg g}^{-1}$ ),  $k_{id}$  -intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ ),  $t$ -time (min),  $C_i$ -initial adsorbate concentration in solution ( $\text{mg L}^{-1}$ ),  $C_s$  -weight of adsorbent per L of solution ( $\text{g L}^{-1}$ ),  $V$ -solution volume (mL),  $\alpha$  ( $< 1$ ) and  $k_b$  are constants of the systems,  $Bt$  - time constant ( $\text{min}^{-1}$ ),  $F$  - fractional attainment of equilibrium at  $t$  (min).



**Figure 1.** Intraparticle diffusion plots for RB5 (a) and AO10 (b); Boyd plots for RB5 (c) and AO10 (d) using PGME-deta as sorbent.

The intraparticle diffusion model plots did not pass through the origin suggesting that even though the adsorption process involved intraparticle diffusion, it was not the only rate-controlling step. Also, the positive (RB5) and negative (AO10) value of intercept  $C_{id}$  is indicative of some degree of boundary layer control. Bangham's

parameters also confirmed that these sorption processes were at least partly pore diffusion controlled. In a Boyd plot, if a straight line passes through the origin, it indicates that particle-diffusion mechanisms govern sorption processes. If not, they are controlled by film-diffusion. It is evident from the presented data, that under the same conditions, the contribution of intraparticle diffusion in sorption of RB5 in comparison with AO10 on PGME-deta is more notable. Eventhough the Boyd plots for RB5 do not pass through origin, they are approaching straight-line dependance, while for AO10 these plots were neither linear nor passed through the origin, indicating the film diffusion-controlled mechanism is dominant in overall adsorption regardless of initial concentration.

**Table 2.** Kinetic parameters for A10 and RB5 using PGME-deta as adsorbent (pH=unadjusted,  $t=25$  °C).

	RB5			AO10		
$C_i$ , mg L <sup>-1</sup>	30	50	70	30	50	70
$Q_e$ , mg g <sup>-1</sup>	60.00	96.2	133.7	57.5	93.74	116.5
Intraparticle						
$k_{id}$ , mg g <sup>-1</sup> min <sup>-0.5</sup>	4.99	9.08	9.18	5.57	6.99	8.11
$C_{id}$ , mg g <sup>-1</sup>	14.4	10.3	29.2	-2.14	-11.4	-21.2
$R^2$	0.982	0.988	0.978	0.957	0.962	0.974
Bangham						
$k_b \cdot 10^3$ , g <sup>-1</sup>	16.3	8.63	10.2	3.99	2.4	0.68
$\alpha$	0.61	0.72	0.65	0.84	0.79	0.95
$R^2$	0.991	0.998	0.997	0.952	0.932	0.977

### Conclusion

Kinetic data of textile dyes adsorption onto PGME-deta were interpreted with three diffusion-based models: intraparticle diffusion, Bangham and Boyd model. The results suggest that involved intraparticle and film diffusion both play important part in the adsorption process, besides the previously established influence of adsorbent capacity and adsorbate concentration.

### Acknowledgements

This work was supported by the Ministry of Education and Science of the Republic of Serbia (Projects III 43009 and III 45001).

### References

- [1] K. Z. Elwakeel, M. Rekaby, J. Hazard. Mater., 2011, 188, 10-18.
- [2] Z. P. Sandić, A. B. Nastasović, N. P. Jović-Jovičić, A. D. Milutinović-Nikolić, D. M. Jovanović, *J. Appl. Polym. Sci.*, 2011, 121, 234-242.
- [3] G. E. Boyd, A. M. Adamson, L. S. Myers, *J. Am. Chem. Soc.*, 1947, 69, 2836-2848.
- [4] N.Y. Mezenner, A. Bensmaili, *Chem. Eng. J.* 2009, 147, 87-96.
- [5] Y. Qu, C. Zhang, F. Li, X. Bo, G. Liu, Q. Zhou, *J. Hazard. Mater.*, 2009, 169, 146-152.

CIP Volume I

CIP - Каталогизација у публикацији  
Народна библиотека Србије, Београд

544(082)  
621.35(082)  
66.017/.018(082)

MEĐUNARODNA konferencija iz fundamentalne i  
primenjene fizičke hemije (11 ; 2012 ;  
Beograd)

Physical Chemistry 2012 : proceedings.  
#Vol. #1 / 11th International Conference on  
Fundamental and Applied Aspects of Physical  
Chemistry, September 24-28, 2012, Belgrade ;  
[editors S.[Slobodan] Anić and Ž.[Željko]  
Čupić ; organized by Society of Physical  
Chemists of Serbia ... et al.]. - Belgrade :  
Society of Physical Chemists of Serbia, 2012  
(Belgrade : Jovan). - VI, 498 str. : ilustr.  
; 24 cm

"The Conference is dedicated to Professor  
Ivan Draganić" --> nasl. str. - Tiraž 200. -  
Bibliografija uz svaki rad.

ISBN 978-86-82475-27-9  
1. Društvo fizikohemičara Srbije (Beograd)  
a) Физичка хемија - Зборници b)  
Електрохемијско инжењерство - Зборници c)  
Наука о материјалима - Зборници  
COBISS.SR-ID 193432332

CIP Volime II

CIP - Каталогизација у публикацији  
Народна библиотека Србије, Београд

544(082)  
621.35(082)  
66.017/.018(082)

MEĐUNARODNA konferencija iz fundamentalne i  
primenjene fizičke hemije (11 ; 2012 ;  
Beograd)

Physical Chemistry 2012 : proceedings.  
#Vol. #2 / 11th International Conference on  
Fundamental and Applied Aspects of Physical  
Chemistry, September 24-28, 2012, Belgrade ;  
[editors S.[Slobodan] Anić and Ž.[Željko]  
Čupić ; organized by Society of Physical  
Chemists of Serbia ... et al.]. - Belgrade :  
Society of Physical Chemists of Serbia, 2012  
(Belgrade : Jovan). - VI str., 499-782 str. :  
ilustr. ; 24 cm

"The Conference is dedicated to Professor  
Ivan Draganić" --> nasl. str. - Tiraž 200. -  
Bibliografija uz svaki rad. - Registar.

ISBN 978-86-82475-28-6  
1. Društvo fizikohemičara Srbije (Beograd)  
a) Физичка хемија - Зборници b)  
Електрохемијско инжењерство - Зборници c)  
Наука о материјалима - Зборници  
COBISS.SR-ID 193433356