PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

---

September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9
Title: PHYSICAL CHEMISTRY 2014 (Proceedings)
Editors: Ž. Čupić and S. Anić
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” Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 441; **Format**: B5; Printing finished in September 2014.

Text an Layout: “Jovan”

200 - *Coppy priting*

PHYSICAL CHEMISTRY 2014

12th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry

Organized by
The Society of Physical Chemists of
Serbia

in co-operation
*with_*

Institute of Catalysis Bulgarian Academy of Sciences

Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences

Faculty of Physical Chemistry, University of Belgrade, Serbia

Institute of Chemistry Technology and Metallurgy,
University of Belgrade, Serbia

Vinča Institute, University of Belgrade, Serbia

Institute of General and Physical Chemistry, Serbia

Faculty of Pharmacy, University of Belgrade, Serbia

International Organizing Committee

Chairman: *S. Anić (Serbia)*
Vice-chairman: *M. Gabrovska (Bulgaria)*
V. A. Sadykov (Russia)
Members:
N. Cvjetičanin (Serbia), S. N. Blagojević (Serbia), M. Daković (Serbia), T. Grozdić (Serbia), D. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), J. Marković-Dimitrić (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Ostrovski (Serbia), I. Pašti (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), D. Stanisavljev (Serbia), B. Šljukić (Serbia), N. Vukelić (Serbia), V. Vukojević (Sweden)

International Scientific Committee

Chairman: *Ž. Čupić (Serbia)*
Vice-chairmans: *V. N. Parmon (Russia)*
S. Rakovsky (Bulgaria)
Members:
B. Adnađević (Serbia), S. Anić (Serbia), A. Antić-Jovanović (Serbia), G. Bačić (Serbia), A. Kelarakis (Greece), R. Cervellati (Italy), V. Dondur (Serbia), Ivan Gutman (Serbia), S. D. Furrow (USA), K. Hedrih (Serbia), M. Jeremić (Serbia), A. V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), V. Kuntić (Serbia), Z. Marković (Serbia), S. Mentus (Serbia), Š. Miljanić (Serbia), M. Perić (Serbia), M. Plavšić (Serbia), D. M. F. Santos (Portugal), G. Schmitz (Belgium), I. Schreiber (Czech), P. Sevčik (Slovakia), B. C. Simionescu (Romania), N. Stepanov (Russia), D. Todorović (Serbia), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia)

Local Executive Committee

Chairman: *S. Blagojević*
Vice-chairmans: *A. Ivanović-Šašić*

Members:
P. Banković, N. Bošnjaković, J. Dostanić, A. Đerić, A. Ignjatović, A. Jović, N. Jović-Jovičić, D. Lončarević, J. Krstić, J. Maksimović, V. Marković, M. Milenković, S. Maćešić, V. Marković, B. Nedić, N. Potkonjak, D. Ranković, M. Stević, M. Žunić, M. Ristić,

MATHEMATICAL MODELING OF PESTICIDE ADSORPTION ON ACTIVATED HEMP FIBERS

M. Vukčević [1], I. Pajić-Lijaković [1], A. Kalijadis [2], Z. Laušević [2] and M. Laušević [1]

[1]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11001 Belgrade, Serbia (marijab@tmf.bg.ac.rs)*
[2]*Laboratory of Physics, Vinča Institute of Nuclear Sciences, University of Belgrade, P.O.Box 522, 11001 Belgrade, Serbia*

ABSTRACT

Activated carbon obtained by carbonization and activation of waste hemp fibers was used as an efficient, low-cost sorbent for pesticide removal. Data obtained from batch and continuous process of pesticide adsorption was used for development of the mathematical model that describes the phenomenon of pesticide transport through the porous sorbent matrices. Effective diffusion coefficient and the pesticide concentration profile within the activated hemp fibers, obtained as results of proposed model, give the insight in the mechanism and the rate of adsorption process and pesticide transport through the sorbent. A good agreement between model prediction and the experimental data indicates that the proposed mathematical model can be successfully used for optimization and selection of appropriate adsorption process for pesticide removal.

INTRODUCTION

One of the methods used to deal with purification of water contaminated by pesticides is adsorption on activated carbon. In the recent years there is a growing interest in utilizing the use of low-cost and abundantly available lignocellulosic materials as precursors for the preparation of activated carbons. In our previous work [1], short hemp fibers obtained as a waste from textile industry were used as a carbon precursor. Activated hemp fibers, obtained by carbonization and activation of waste hemp fibers, were successfully applied as a sorbent in solid-phase extraction procedure for the pesticides analysis in water samples. In this work, effectiveness of activated hemp fibers (ACh) as a sorbent for pesticide removal from polluted water was tested through the sorption of dimethoate, nicosulfurone and carbofuran, in batch and continuous flow process. In order to describe the process of pesticide adsorption on activated hemp fibers, we have extended and upgrade our previously developed mathematical model [2].

EXPERIMENTAL

Activated hemp fibers (sample ACh129) were obtained by carbonization at 1000 ^{o}C and activation at 900 ^{o}C, using KOH as an activating agent [1]. Adsorption of pesticides on the ACh129 was performed from the aqueous solution of pesticide mixture in batch system, with constant shaking, and in continuous flow system, with flow rate of 1 ml/min. Initial concentration of each pesticide in the mixture was 25 mg/dm^3. The pesticides concentration after adsorption was determined by liquid chromatography-tandem mass spectrometry (LC-MS/MS).

RESULTS AND DISCUSSION

Mathematical model is based on pesticides mass balance equations for two phases: the liquid solution and the fixed bed under batch and continual flow conditions. Model is based on Fick's second low, and considers the adsorption of pesticides, from the pesticide mixture solution, on the activated hemp fibers. Based on morphological analysis, made by scanning electron microscopy, and activated hemp fiber textural characteristics [1], for the model consideration fibers were presented as a cylinder, consisting of the non-porous core region (radius R_{core}) and porous annular region ($\Delta R = R_f$ - R_{core}, ΔR is annular region width and R_f is fiber radius) where pesticide adsorption occurs.

Model prediction for the decrease of pesticide concentration in the solution, during adsorption in the batch process, is well fitted with the experimental data (Figure 1). Pesticides balance equation is formulated, as shown in the literature [2], and it was solved analytically by Fourier's dividing of the variables and using Baseless functions. The general solution of the model balance equation determines the pesticide concentration profiles within the annular porous region of the activated fibers (Figure 2). Profile of pesticides reaches its equilibrium relatively fast and after 5 minutes the pesticide concentration through the porous annular region of fiber is constant.

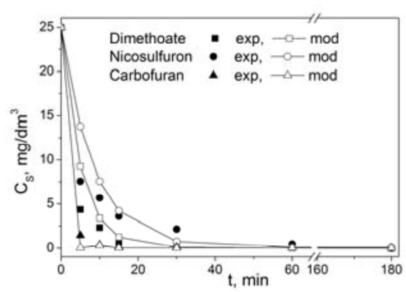

Figure 1. Pesticide concentration in the solution as a function of the adsorption time

The model parameter which represents the specific rate of pesticide concentration change, λ_i^2, effective diffusion coefficient, $D_{e\,i}$, and equilibrium concentration of pesticide within the ACh129, along with experimentally obtained equilibrium pesticide concentrations are presented in Table 1. For purpose of comparison, equilibrium concentration of pesticide within the commercial activated carbon C_{AC}, is also presented in Table 1.

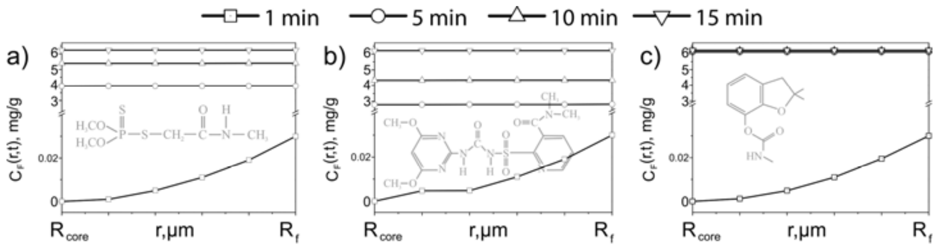

Figure 2. Concentration profile of dimethoate (a), nicosulfuron (b) and carbofuran (c) within the annular region of the ACh129

Pesticide concentration within the ACh129 obtained as a model prediction are well correlated with the ones obtained experimentally. Higher extent of resistance to the nicosulfuron and dimethoate transport is shown through the lower values for both specific rate of concentration change and effective diffusion coefficient. Due to the fact that the structure of pesticides plays an important role in adsorption, the steric hindrance caused by nicosulfurone high molecular weight and chemical structure may be the reason of its slower adsorption on the ACh129 surface. Due to the aromatic structure of carbofuran, dispersion forces between the π electron density of the graphene layers on the ACh and the aromatic ring of the adsorbate should be expected, and therefore the faster adsorption. On the other hand, adsorption of dimethoate is not forced by mentioned π-π interactions, due to the absence of aromatic ring, which induce slower adsorption.

Table 1. Model parameters that describes the pesticide transport through the porous matrices of ACh129 during batch adsorption

Pesticide	M (g/mol)	λ^2 (min^{-1})	D_e / D_0	C_{Feq},*mod* (mg g^{-1})	C_{Feq},*exp* (mg g^{-1})	C_{AC}, (mg g^{-1})
D	229	0.20	0.065	6.234	6.232	6.001
N	410	0.12	0.045	6.210	6.215	5.407
C	221	0.80	0.265	6.222	6.228	5.746

* D-dimethoate, N-nicosulfuron, C-carbofuran

For continual flow system, balance equation of the pesticide concentrations in the hemp fibers is similar as for the batch process, while the balance equation for solution is considered within two regimes. In the Regime I, the pesticide inflows $Q\ C_{S0\ i}$ are totally adsorbed by the fibers and the outer flows are $Q\ C_{Si}(t) \approx 0$, while in the Regime II, only partial adsorption of the pesticide inflows are achieved.

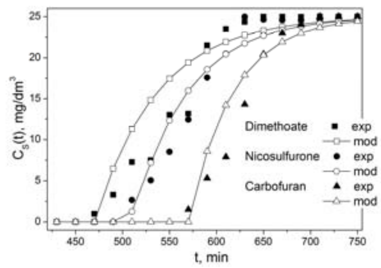

Figure 3. Continual process of pesticide adsorption on ACh129

The pesticide concentrations in out flow solution, for continual flow process, in the Regime II were calculated using developed mathematical model, while in the Regime I these concentrations were $C_{S0i}(t)\approx 0$. The relative error of 5% was obtained between the model prediction and experimental data (Figure 3). Using this mathematical model, the breakthrough time (t_B) and the pesticides concentration on the ACh129 at the breakthrough point ($C_F(t_B)$) (Table 2), can be determined.

Table 2. The ACh129 adsorption capacity at breakthrough time

Pesticide	t_{Bi}, min		$C_{Fi}(t_B)$, mg/g	
	experiment	model	experiment	model
Dimethoate	472	473	24.69	23.64
Nicosulfuron	499	512	25.74	25.59
Carbofuran	567	575	28.95	28.74

CONCLUSION

Activated hemp fibers have proven to be an efficient low-cost sorbent for pesticides removal. Effective diffusion coefficient and the pesticides concentration profile through the ACh129, obtained by developed mathematical model, show that mechanism of pesticide transport was influenced by the pesticide structure. Proposed mathematical model enables the deeper insight into the multi-scale phenomena of the pesticides transport through the porous matrices, which is essential for designing the filters for pesticide removal.

ACKNOWLEDGMENT

The authors wish to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support through the projects No 172007 and No 45006.

REFERENCES

[1] M. Vukcevic, A. Kalijadis, M. Radisic, B. Pejic, M. Kostic, Z. Lausevic, M. Lausevic, Chem Eng J 2012, 211-212, 224-232.

[2] M. Vukčević, B. Pejić, A. Kalijadis, I. Pajić-Lijaković, M. Kostić, Z. Laušević, M. Laušević, Chem Eng J 2014, 235, 284-292.