



NATO Science for Peace and Security Series - C:  
Environmental Security

# Recent Advances in Adsorption Processes for Environmental Protection and Security

Edited by  
José Paulo Mota  
Svetlana Lyubchik

 Springer



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# Recent Advances in Adsorption Processes for Environmental Protection and Security

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**Series C: Environmental Security**

# Recent Advances in Adsorption Processes for Environmental Protection and Security

*Edited by*

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## PREFACE

The NATO Advanced Research Workshop on *Recent Advances in Adsorption Processes for Environmental Protection and Security* was held during, September 9–12, 2006, at Hotel Salyut, Kiev, Ukraine. There were 45 participants from 12 NATO countries, 8 Eligible Partner and Mediterranean dialog home and one key speaker from Switzerland. We hope that everyone went home with excellent memories and new ideas to enhance environmental protection and security through adsorption science and technology.

The purpose of the Workshop was to bring together researchers and engineers working in adsorption-related fields, to share knowledge on the latest advances on adsorption processes for environmental security and protection, as well as to cross-link and disseminate to the scientific community the main results and achievements of recent NATO SfP projects on environmental security and protection.

Topics covered by the Workshop include recent theoretical and experimental developments on environmental adsorption, adsorption processes, as well as synthesis and tailoring of novel adsorbents, including the assessment of materials and processes.

The invited lectures provided a comprehensive report on adsorption and colloids, carbon materials and adsorbents for various industrial applications, and ecological safety and antiterrorism. Because rapidly developing areas in nanotechnology for fine chemistry, air quality, and environmental protection, are based on the synthesis and modification of the adsorbents, special attention was given to synthesis and chemical tailoring of porous materials to achieve desired properties as adsorbents and separation media.

We hope that the Workshop helped to intensify the cooperation between scientists from NATO countries, USA, Central Europe and FSU countries, and to shorten the gap between Partner/Mediterranean Dialogue countries and NATO countries with respect to environmental protection and security standards. Finally, we also hope that the Workshop opened a forum for discussion on possibilities for further improvements and areas still lacking critical knowledge and expertise.

We would like to express our gratitude to the members of the local organizing committee for all their hard work to make this Workshop a success. The Workshop would not have been possible without the generous financial support from the NATO Science for Peace and Security Programme.

José Paulo Mota  
Svetlana Lyubchik



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# EXTENSION OF DUBININ'S THEORY TO ADSORPTION FROM AQUEOUS SOLUTIONS

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**Abstract.** Adsorption of sparingly soluble organics from aqueous solutions, by activated carbons, can be described within the framework of Dubinin's theory by using a modified Dubinin–Radushkevich–Kaganer (DRK) equation, where relative pressures are replaced by relative concentrations. With respect to the descriptions based on the Langmuir model and similar expressions, this approach has the advantage that it allows predictions on the basis of simple physico-chemical properties of the solid and of the adsorbate. Preliminary experiments indicate that in the case of dilute binary mixtures, the model of independent coadsorption, based on the DRK equation, applies. However, more experimental evidence is needed to confirm this potentially very useful approach in filtration technology.

**Keywords:** Dubinin's theory; adsorption; aqueous solutions; binary mixtures

## 1. Introduction

The removal of sparingly soluble organics from aqueous solutions is a relatively important topic, in particular for the purification of drinking

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water by activated carbon. So far, a variety of theoretical models have been proposed, which can reproduce accurately the experimental data.<sup>1,2</sup>

However, a major shortcoming in the use of Langmuir- or Freundlich-based approaches is the fact that predictions are difficult, and even impossible in many cases, due to the complexity of the parameters used in these expressions. It is therefore necessary to find alternative descriptions, which provide a tool for quantitative or at least semi-quantitative predictions in filtration technology.

Active carbons are very efficient adsorbents and the adsorption of vapours is well described by Dubinin's theory,<sup>3,4</sup> which uses relatively simple parameters and allows predictions over relatively wide pressure and temperature ranges. As shown in detail elsewhere,<sup>5-7</sup> for relative concentrations  $c_{eq}/c_s < 0.01-0.05$  (submonolayer conditions) adsorption of sparingly soluble species such as phenol and its derivatives can be described by the modified Dubinin-Radushkevich-Kaganer (DRK) equation.

$$N_a(T;p) = N_{am} \exp[-(A/E_s)^n] \quad (1)$$

where

$$A = RT \ln(c_s/c_{eq}) \text{ and } n \sim 2-4 \quad (2)$$

In the case of sparingly soluble species,  $N_{am}$  corresponds to the monolayer capacity of the walls of the micropores and not to the filling of these pores, as opposed to adsorption from the vapour phase. This means that the sorptive capacity of a microporous carbon is often smaller in the case of adsorption from dilute aqueous solutions, than from the vapour phase. This point is clearly illustrated by the adsorption of phenol from both phases.<sup>8</sup>

It appears that the principle of temperature invariance observed by Dubinin for micropore filling also applies here, as parameters  $n$  and  $E_s$  are practically constant over a range of 20°–30°.

One can also introduce specific scaling factors (surface affinity coefficients  $\beta_s$ ) for  $E_s$ , to correlate the adsorption of different species relative to a reference solute (benzene or phenol). These properties are reflected in the logarithmic plot (Figure 1) for the adsorption of various phenolic compounds from aqueous solutions, at different temperatures and on three different activated carbons, with  $n = 4$ . As shown in the case of the DRK equation<sup>9</sup> (adsorption of vapours by non-porous solids), exponent  $n$  is related to the heterogeneity of the surface and it appears that for certain systems  $n = 3$  (or even 2) also provides a good fit.

As observed for adsorption from the vapour phase, the characteristic adsorption energy  $E_s$ , depends on both the adsorbent and the adsorbate. It appears that in the case of aqueous solutions of phenol,<sup>5-7</sup>  $E_s$  is practically equal to the characteristic energy of adsorption of benzene vapours  $E_o$ ,