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11. CB - PROTECTION: DIFFERENT MATERIALS AS ECOLOGICAL FILTERS

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Changes in nature that are the consequences of men's work, are bigger and bigger every day, and they start to be a threat to the whole human race.

Military forces have been struggling with the issue of chemical and biological warfare for decades. Terrorist's attacks or accidents with chemical or biological agents can be the ecological bombs today and in the future.

Simulation modeling methods and techniques and their possible use in ecological modeling are presented in this work.

Because of that, different substances are investigated and described as the filters for danger chemical agents that can be used in laboratory or industrial scale. We measured few parameters that are important for the simulation modeling.

To control the entering parameters and to get the output simulation method we used one of the standard packages for discrete simulation, Service model v4.2 (ProModel Corporation), while for continuous control of the processes we used Extend v4 (Imagine That, Inc.).

INTRODUCTION

Military forces have been struggling with the issue of chemical and biological warfare for decades.

Attack of the Tokyo subway with the nerve agent sarin in March 1995 suddenly put the spotlight on the danger to civilians from chemical and biological attacks.

Terrorists' attacks or accidents with chemical or biological agents can be the ecological bombs today and in the future.

There is no way to prepare in an optimal fashion for a terror incident. There is too low an incidence to justify the enormous financial outlay it would take to optimally prepare every community for every possible incident. Also, there is a huge gap between detection technology and therapy. There are many biologic agents, and certainly many chemical agents for which there are no known treatments.

So, simulation modeling methods and techniques and their possible use in ecological modeling are presented in this work. Different substances are investigated and described as the filters for danger chemical agents that can be used in laboratory or industry scale.

The model for the simulation of absorption of paraoxon and DBS (dibutyl sulfide) on activated charcoal, ZA, SiO_2, TMAZ, ZSM-5 (with different kations) and Al_2O_3 are shown on Figure 1.

For both chemical agents, there are defined the specific rules about absorption of them, through the model Equation, in which it is written the rule/ the possibility for the absorption of every specific material.

To make "the real" picture of the process of the absorption, for every material, the influence (the dependence) of the absorption through the time (which is specific for every absorbing material) is counted, as the entering process.

This is fulfilled with the model for generating the values by the process of accidental numbers through "the best fitted distribution".

In this model we used empirical distributions. Used tool is Stat: Fit from the simulation pocket Service Model v4.2. Empirical distributions are written in the model built in Extend v4. As the started values of the simulation experiment, initial value of the concentration of paraoxon (or DBS, or any other agent) in water were taken. This value is constant. So, this constant and generic value of the dependence of absorbency in time are the entering parameters for the simulation model which transform through the Equation to the output values of the concentration of paraoxon or DBS.

EXPERIMENTAL

Zeolites (ZA (Fluka), Klinoptilolite (IRB) and ZSM-5 (prepared by me, by the procedure described before)) and some other materials as SiO_2 (AnalytiCals, Carlo Erba), Al_2O_3 (neutral, 70-230 mesh ASTM, Merck) and activated charcoal (Riedel- de Haën AG) were used as adsorbents for DBS and paraoxon.

To study the process of absorption of DBS and paraoxon on ZA, klinoptilolite, ZSM-5, SiO_2, Al_2O_3 and activated charcoal, 2.0 g of solid (5.0, 7.5 and 10.0 g) were put into the reaction vessel containing 25.0 mL of DBS solution (10^{-4} M) or paraoxon solution (2×10^{-4} M) in water.

The moment the solid was added to the solution was taken as the zero time of absorption ($t_{ab} = 0$).

At various times after the process of absorption of DBS or paraoxon started (1,2,5,10, 20, 30, 40, 60 and 120 min), suspensions were drawn off for analysis, and centrifuged.

To determine the concentration of unabsorbed DBS in solution (or absorbed on different materials), the tytrimetric reaction with $AgNo_3$, or iodometric reaction were applied. The sorption of paraoxon was measured colorimetricaly (benzidine reagent, 420 nm). A spot test reaction, which produces a yellow color when an aqueous alkaline peroxide solution is added to a nerve gas (or an imitator) in the presence of an oxidizable amine base such as benzinidine, was first described by Schönemann in 1944.

Zeolite ZSM-5 was synthesized with three different cations (K, Na and NH_4).

RESULTS AND DISCUSSION

All "as made" samples of ZSM-5 zeolites (Na-, K- and NH_4-ZSM-5), using as starting materials in absorption studies, were fully crystalline powders, having an MFI structure, as revealed by X-ray difractometry.

Adsorption of DBS on ZA reached the maximum after about 30 minutes after the reaction started. The efficacy of ZA as the adsorbent depends on the mass used in the reaction, especially in first five minutes. When the time of reaction on the use of some chemical agent is important, this fact can't be ignored.

Figure 2 shows the absorption of DBS on silica (a) and charcoal (b) on 2.0 g, 5.0 g , 7.5 g and 10.0 g.

It is seen that the amount of adsorbent has less influence on the efficiency of adsorption than it is noticed with ZA.

Adsorption of DBS on silica is much faster than on activated charcoal. During the first five minutes more than 50 % of DBS were adsorbed on silica, and about 40 % on activated charcoal. The maximum of adsorption for silica is between 76 and 85 % (76 % using 2.0 g, 81- 82 % for 5.0 and 7.5 g and 85 % using 10.0 g).

Adsorption of DBS on alumina shows that there is no difference in adsorption using 5.0, 7.5 or 10.0 g of adsorbing material, and that 2.0g of that material for the concentration that was used is not enough.

Figure 3 shows the adsorption of DBS on 2.0 g of different adsorbing materials (ZA, klinoptilolite (TMAZ), activated charcoal, silica and alumina.

Adsorption of paraoxon on different materials also depends on the amount of adsorbent, but only after it is reached the plateau of adsorption.

Adsorption of paraoxon on ZSM-5, silica and activated carbon is especially fast in first few minutes (from 50 % for activated carbon to 70 % for ZSM-5), what makes these adsorbents very efficient for adsorption of paraoxon.

Using ZA or klinoptilolite, the plateau of adsorption is reached much slower and with the fewer efficacies. Main reasons for that is probably that the total surface is less for those adsorbents, because of the particle size.

Figure 4 shows the adsorption of paraoxon on 10.0 g of different adsorbing materials.

CONCLUSIONS

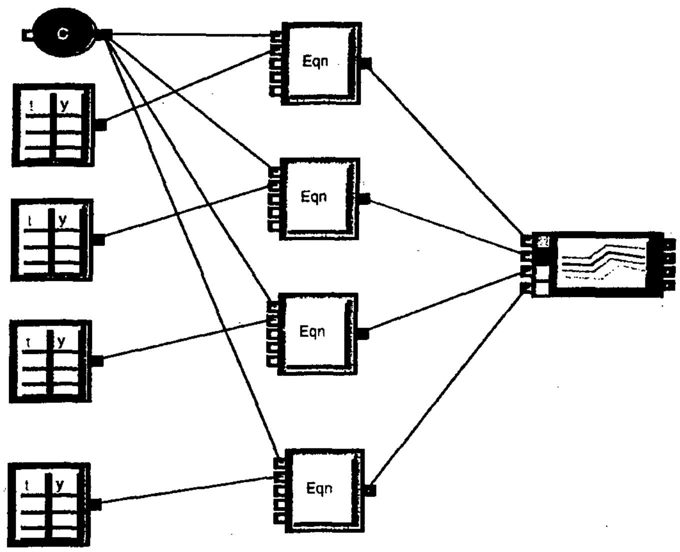
- With some materials (ZA, Al_2O_3) there is a great difference in adsorption of DBS and Paraoxon, depending on used mass of adsorbing materials.
- With the others there is almost no difference in the amount of used materials (especially charcoal, SiO_2 and klinoptilolite)
- Adsorption of DBS is especially small using Al_2O_3, and especially great when using SiO_2)
- There is almost no difference in the adsorption of POx on different amounts of ZA
- There is great difference in adsorption of POx on ZSM-5 at different temperatures (20, 30, 37 and 45 ^{0}C)
- For all materials except for ZA adsorption is quick in first few minutes, and in that time it is adsorbed almost 60 % (or even more) of the toxic material.
- About the model, after the model is made, its evaluation must confirm the possibility of its use in the real system. Evaluation is confirmed with statistical tests (hi square Kolmogorov- Smirnov test or Anderson- Darling test). Using this model it can be predicted in any time the concentration of the chemical agent in the solution and the amount of the agent that is absorbed. Comparing all adsorbents, it is possible to get the information which absorbing material is the most efficient. Beside that, the simulation experiments can be done even for the chemical agents for whom experimental adsorption measurements were not done.
- Also, it can be predict the most useful combination of adsorbing materials (in percentage).

REFERENCES

1. D. E. Vaughan, *Coprehensive Supramolecular Chemistry*, V. 7, Ed. G. Alberti and T. Bein (1996) 379-392.
2. D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, J. Wiley & Sons, New York (1974).
3. R. B. R. Schönemann, US Department of Comerce, *PB 119887* (1944).
4. B. Gehauf, J. Epstein, G. B. Wilson, B. Witten, S. Sass, V. E. Bauer, W. H. C. Ruggeberg, *An. Chem.*, 29 (2) (1957) 278-283.
5. A. Čižmek, B. Subotić, R. Aiello, F. Crea, A. Nastro, *Zeolites*, 14 (1994) 182-189.
6. A. Čižmek, B. Subotić, I. Šmit, A. Tonejc, R. Aiello, F. Crea, A. Nastro, *Microporous Materials*, 8 (1997) 159-169.

KEY WORDS

Chemical and biological warfare agents, terrorist's attack, modelling



Symbols (icons) that are used:

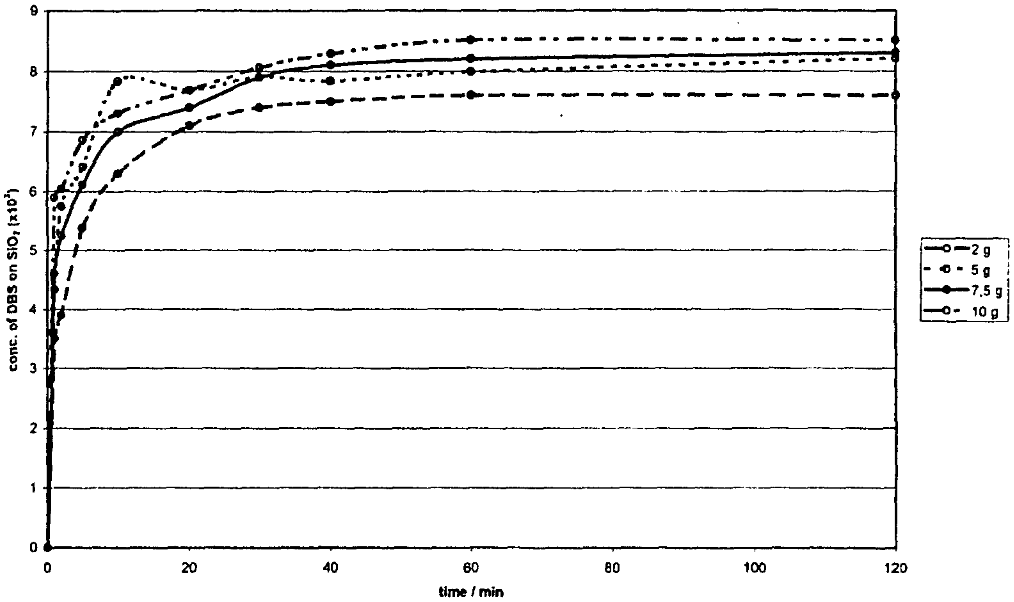

-Constant


-Input Data

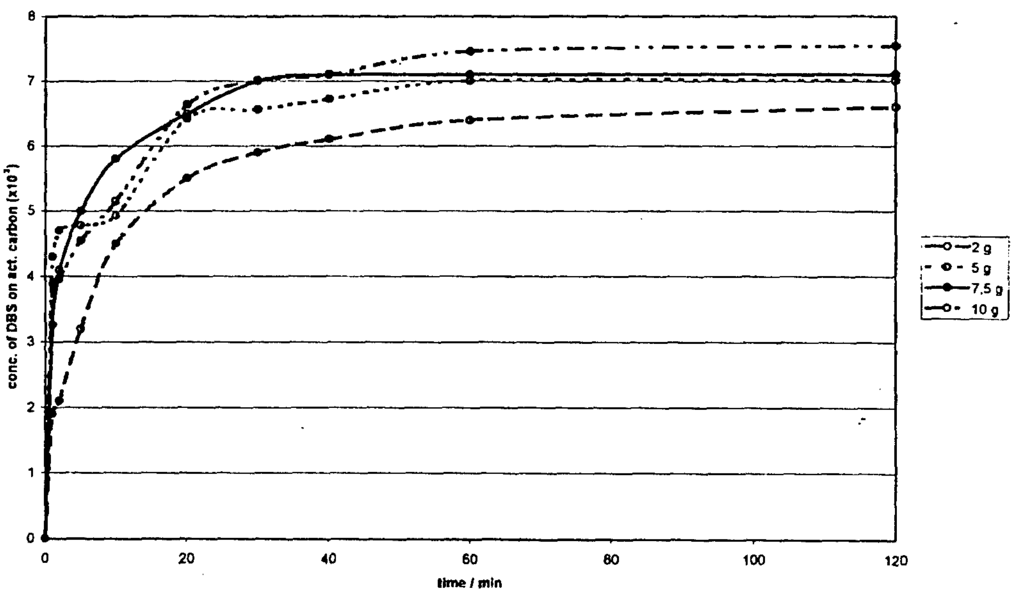

-Equation


-Plotter

Figure 1. Shematic presentation of the model



(a)



(b)

Figure 2. Adsorption of DBS on silca (a) and charcoal (b) on 2.0g, 5.0g, 7.5g and 10.0g

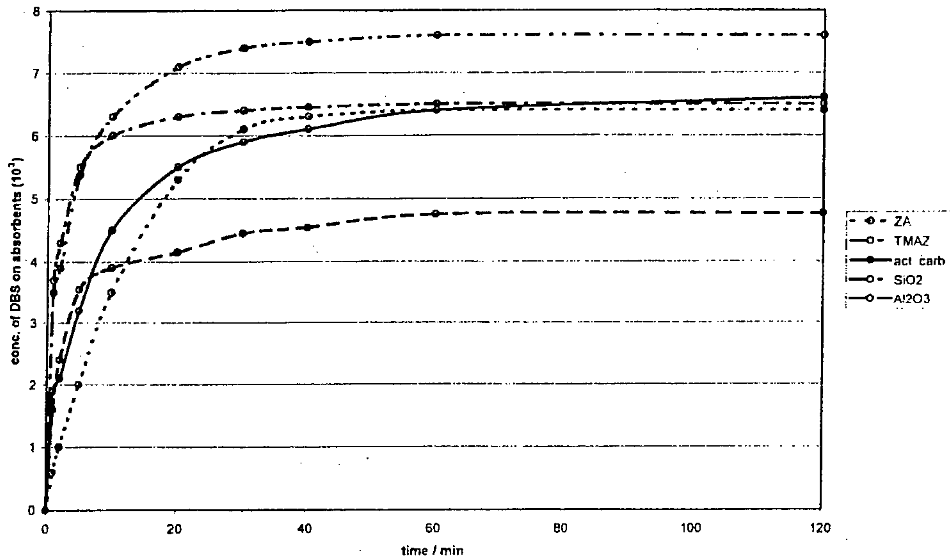


Figure 3. Adsorption of DBS on 2.0 g of different adsorbing materials (ZA, klinoptilolite (TMAZ), activated charcoal, silica and alumina.

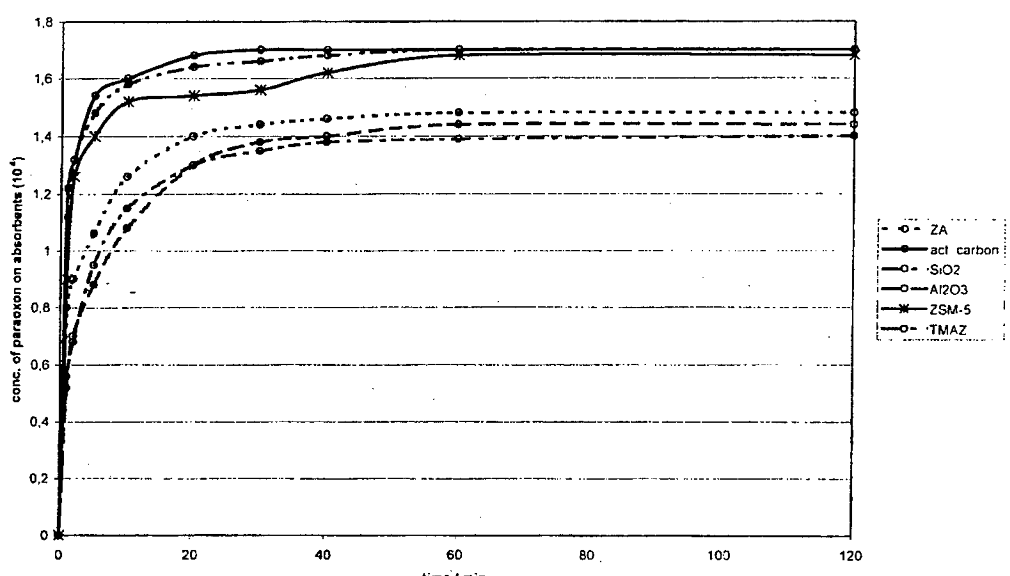


Figure 4. Adsorption of paraoxon on 10.0 g of different adsorbing materials.