

A NEW RATE MODEL FOR THE OXIC REMOVAL OF PHENOL AND o-CRESOL BY GRANULATED ACTIVATED CARBON: I. BATCH STUDIES

K.F. Loughlin , A. I. Fatehi and N. Abuzaid[#]*

*Department of Chemical Engineering and the Research Institute[#], King Fahd University
of Petroleum & Minerals, Dhahran-31261, Saudi Arabia.*

Introduction

Phenolic compounds, on adsorption in granular activated carbons(GAC) in the presence of oxygen, react to form dimers and trimers etc. which are irreversibly adsorbed(1,2). The driving force for the transport of the organics into the GAC is the chemical potential and the flux is observed to be a dual mechanism of surface diffusion and pore diffusion(3). In a previous presentation, we reported the adsorption of the phenolic compounds only when oxygen is absent(4). Here we extend the results to include the presence of oxygen.

Experimental

The same apparatus was used as reported earlier(4) with the exception that the liquid phase could consist of water plus the dissolved organic with (oxic) or without oxygen (anoxic), and was neutralized with a buffer to a pH of 7.0 Samples of the liquid phase were analyzed periodically for the organic. Unfortunately the dissolved oxygen was not measured except initially.

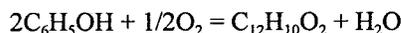
Theoretical

We assume a finite bath system, constant temperature, isotropic adsorbent particles with uniform pores and no preferential pore direction, dilute solution having constant molecular diffusivity and mass transfer coefficient, and organic diffusion by a combined surface and pore diffusion mechanism. The surface diffusion driving force is the chemical potential gradient

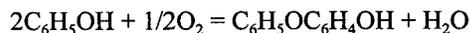
and the relationship expressing the diffusion coefficient for the adsorbed species is given by Darken's relation

$$D_{is} = D_{is0} \frac{\partial \ln C_A}{\partial \ln q_A}$$

In the oxic system, oxygen diffuses by a surface mechanism only. The phenol and oxygen react in the adsorbed phase to form significant quantities of two dimers, identified as 2,2-dihydroxy--1,1-biphenyl and 4 phenoxyphenol, and a trimer. We assume that the reaction products and phenolic compounds compete for adsorption sites as has been observed by Rajeshwari and Ghosh(5) in the case of phenol and microbial cells coadsorption. For modeling purposes, we assume dimers only are created to make the problem tractable for solution. The reaction step is assumed to be the creation of either 2,2-dihydroxy-1,1-biphenyl compound



or the formation of 4 phenoxyphenol by



Both equations may be represented as follows



where A is phenol, B is oxygen C is the dimer and D is water. The pure and multicomponent isotherms are assumed to follow the Langmuir-Freundlich form.

With these assumptions the mass balances for phenol and oxygen are:

$$\frac{\partial q_A}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \left[\varepsilon \frac{D_{AP}}{\rho_p} \frac{\partial C_A}{\partial q_A} + D_{AS} \right] \frac{\partial q_A}{\partial r} \right\} + R_A$$

$$\frac{\partial q_B}{\partial t} = \frac{D_{BS}}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \frac{\partial q_B}{\partial r} \right\} + R_B$$

The rate of reaction is postulated to be the Langmuir-Hinshelwood form based on the principle that it involves two adsorbed species (Laidler):

$$R_C = k_r \theta_A \theta_B$$

Hence the fraction of sites occupied can be deduced as

$$\theta_C = \frac{C_C}{C_{sat}}$$

We may then define a pseudo equilibrium term for the Langmuir-Freundlich equilibrium as follows:

$$k_C C_C^{1/nc} = \frac{\theta_C}{1 - \theta_A - \theta_B - \theta_C}$$

For the reaction rate expression given then

$$R_A = \gamma_A / \gamma_C R_C M_A / M_C$$

$$R_B = \gamma_B / \gamma_C R_C M_B / M_C$$

where γ_i are the stoichiometric coefficients, positive for products, negative for reactants, and zero for inerts.

The general isotherm expression is

$$\theta_i = \frac{q_i}{q_{sat}} = \frac{k_i C_i^{1/ni}}{1 + k_A C_A^{1/na} + k_B C_B + k_C C_C^{1/nc}}$$

Initial conditions :

$$q_A = q_C = 0.0, \quad q_B = q_{BO}; \quad C_A = C_{AO}$$

$$C_B = C_{B0}, \quad C_C = 0.$$

Boundary conditions :

$$\left. \frac{\partial q_A(0,t)}{\partial r} \right|_{r=0} = 0; \quad \left. \frac{\partial q_B(0,t)}{\partial r} \right|_{r=0} = 0$$

$$V(C_{AO} - C_A) = \int_0^t \left(-4\pi r^2 n \rho_p D_{Aeff} \cdot \left. \frac{\partial q_A}{\partial r} \right|_{r=r_s} \right) dt$$

$$V(C_{B0} - C_B) = \int_0^t \left(-4\pi r^2 n \rho_p D_{BS} \cdot \left. \frac{\partial q_B}{\partial r} \right|_{r=r_s} \right) dt$$

where

$$D_{Aeff} = \varepsilon \frac{D_{AP}}{\rho_p} \frac{\partial C_{AP}}{\partial q_A} + D_{AS}$$

Results and Discussion

The equations given above, have been normalized and are presently being solved using the orthogonal collocation method. The experimental results for phenol for oxic and anoxic phenol adsorption data is presented in Figure 1. The oxic uptake is slower than the anoxic. From these curves we expect to report the reaction rate constant.

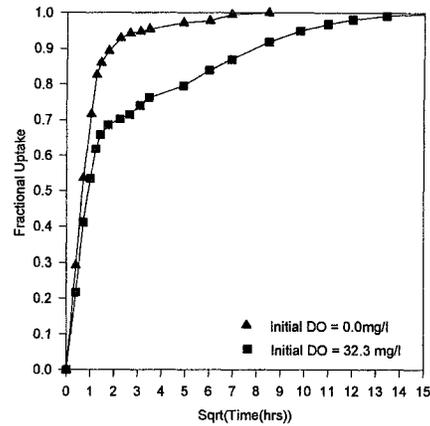


Figure 1. Effect of DO on Phenol Uptake at 21°C

Acknowledgments

The authors wish to acknowledge the support of King Fahd University of Petroleum & Minerals during this work.

References

1. Osei-Twum, E.Y., Abuzaid, N.S., and Nakhla, G., Bull. Environ. Contam. Toxicol. 1996, 56, 513.
2. Vidic, R.D. and Suidan, M.T., AWWA 1992, 3 101.
3. Ekhaton, O., MS thesis, King Fahd University of Petroleum & Minerals, 1996.
4. Loughlin, K.F., Fatehi, A.I., and Abuzaid, N., in Carbon '97 (ext. Abstr. 23rd Biennial Conf. Carbon), Pennsylvania, Pa, 1997.
5. Rajeshwari, K.V., and Ghosh, P., J. Microb. Biotechnol., 1995, 10, 59.