# Equilibrium versus Nonequilibrium Treatment Modeling in the Optimal Design of Pump-and-Treat Groundwater Remediation Systems

Karen L. Endres[1]; Alex Mayer[2]; and David W. Hand[3]

**Abstract:** The present work proposes that the incorporation of granular activated carbon (GAC) treatment model that accounts for nonequilibrium adsorption into the optimal design of pump-and-treat systems will result in more realistic costs and better-engineered remediation systems. It was found that, when nonequilibrium GAC adsorption effects are considered, the predicted cost of optimal remediation strategies increases consistently when compared to costs obtained assuming equilibrium GAC adsorption, for a wide range of cleanup goals. This finding implies that when simpler equilibrium models are used for GAC adsorption, cleanup costs will be underestimated. GAC treatment costs are shown to be particularly sensitive to the degree of mass transfer limitations in the aquifer–contaminant system, especially when nonequilibrium GAC adsorption is accounted for. Time-varying pumping rates are shown to produce more efficient remediation solutions; the increase in efficiency is even more pronounced when nonequilibrium GAC adsorption is accounted for. Further results show that the optimal remediation designs can be significantly more efficient when the number of GAC adsorber units is selected through optimization.

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## Introduction

Pump-and-treat (PAT) technologies have become common for groundwater remediation. Optimization of these systems has primarily focused on design of the hydraulic components of the system; however, the treatment component of the remediation often comprises the majority of the total cost (e.g., Culver and Shoemaker 1997; Culver and Shenk 1998; Aksoy and Culver 2000). A common treatment for removing dissolved organic contaminants is adsorption by granular activated carbon (GAC). The primary expense associated with GAC treatment of contaminated groundwater is the cost of replacing the GAC as its capacity for removing contaminants is exhausted. The GAC treatment process typically has been modeled by assuming equilibrium between the contaminant in the aqueous and solid phases. The equilibrium assumption allows the use of simple algebraic models of GAC usage that depend on a limited number of GAC-contaminant properties.

[1]Dept. of Civil and Environmental Engineering, Michigan Technological Univ., 1400 Townsend Dr., Houghton, MI 49931; formerly, Graduate Student.

[2]Professor, Dept. of Geological and Mining Engineering and Sciences, Michigan Technological Univ., 1400 Townsend Dr., Houghton, MI 49931 (corresponding author). E-mail: asmayer@mtu.edu

[3]Professor, Dept. of Civil and Environmental Engineering, Michigan Technological Univ., 1400 Townsend Dr., Houghton, MI 49931.

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However, it is well known that the process of adsorption onto GAC is complex and that mass transfer limitations can be significant (e.g., Sontheimer et al. 1988). The use of equilibrium methods to predict carbon usage has been shown to be inadequate by several investigators (e.g., Crittenden et al. 1987a,b; Hand et al. 1984, 1989, 1997; Jarvie et al. 2005). Crittenden et al. (1987a) discussed the importance of considering mass transfer in performed GAC usage rate calculations. Hand et al. (1989) showed that equilibrium calculations used to calculate GAC usage rates for dichloroethene and trichloroethene for several empty bed contact times (EBCTs) significantly overpredicted the adsorption capacity as compared to GAC usage rates obtained from pilot plant data and mass transfer model predictions. They attributed the failure of the equilibrium model to predict the GAC usage rates to mass transfer limitations in the adsorption of contaminants to the carbon. Jarvie et al. (2005) demonstrated that using an equilibrium approach to model GAC adsorption can greatly underestimate the rate of carbon usage by comparing models that account for nonequilibrium and equilibrium behavior. They modeled groundwater treatment scenarios with a range of chemical types and concentrations, EBCTs, and influent flow rates, target effluent concentrations, and background groundwater compositions containing natural organic matter. They found that the equilibrium approach underestimated carbon usage by a factor of 2–10 without the effects of natural organic matter and up to 20 times when natural organic matter was considered.

Operational costs for a GAC groundwater treatment system are based primarily on the GAC usage rate, given that once breakthrough of the contaminant occurs in the treatment system, the GAC must be replaced. With equilibrium modeling of the GAC system, the replacement rate is based on the assumption that the entire adsorptive capacity of the GAC is exhausted at the time of breakthrough. Residence time in the adsorption unit does not need to be considered. However, when nonequilibrium processes are