

**Sorption of Aromatic Amines in Engineered and Natural Systems:  
Development of a Time-Dependent Multiparameter Model**

by

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## ABSTRACT

The environmental persistence of hydrophobic organic contaminants (HOCs) has resulted in a number of studies to both describe and predict fate and transport of these chemicals in the environment. One such chemical is benzidine. A known human carcinogen, benzidine has been used in the textile industry for the production of benzidine based dyes. While its use has been halted in the United States, Japan, and Europe, benzidine-based dyes are still manufactured in both India and China.

When released to the environment, benzidine can follow a number of sorption pathways. In this study, an equilibrium-derived multi-parameter model (MPM) incorporating partitioning, cation exchange, and covalent bonding was developed and tested. The model was based on four fitting parameters ( $K_1$ ,  $K_2$ ,  $K_3$ ,  $\alpha$ ) which were determined through regression analyses of benzidine sorption data to lake sediments collected from Lake Macatawa (Holland, MI). High correlations were found between the model and sorption data. The fitting parameters were found to be reasonably correlated with total organic carbon (TOC) in the sediment, and applications of the model to other Lake Macatawa sediments with similar TOC values resulted in acceptable predictions of benzidine sorption.

In order to test the parameter dependence on various system parameters, two synthetic resins were chosen. The Amberlite XAD-4 resin, a cross-linked aromatic polymer, provided a hydrophobic domain for benzidine uptake to occur. The structurally similar Amberlite IR-120 resin, through its sulfonate functional groups, provided a means for cation exchange of the protonated benzidine molecule. Additionally, experiments were carried out in sodium citrate/citric acid systems buffered

to pH values of 3.0, 3.9, 5.9, and 6.5 as well as in DI water in order to bracket the two  $pK_a$  values of benzidine and ensure varying degrees of benzidine protonation. The sorption experiments ranged in time from six hours to 56 days for the XAD-4 resin and from six hours to 14 days for the IR-120 resin, respectively.

Nonlinear uptake occurred for both resins under all conditions. The XAD-4 resin was described with the dual mode model. Results indicated that the nonlinear hole filling process was the predominant mechanism for benzidine uptake by the resin. A linear partitioning term was also applied to the data. Despite the errors associated with this application, a positive trend ( $r^2 = 0.60$ ) was found when relating the partition coefficient with time. An attempt was made to relate the result back to natural systems in order to predict partition coefficients in natural systems based on time and TOC. However, the outcome was not acceptable due primarily to the linear fitting of nonlinear data sets.

Further studies with the IR-120 cation exchange resin allowed for the use of the MPM, modified by removal of the covalent bonding term. The two term model, consisting of partitioning and cation exchange, was able to successfully model the uptake of benzidine by this resin. The model parameters were also correlated with high statistical significance to the pH of the system and the equilibration time. In particular, a three-dimensional regression allowed for the concurrent use of pH and time to predict the cation exchange coefficient ( $K_3$ ).

The resulting time-dependent correlations were applied to benzidine sorption data gathered previously. Using only the system pH, equilibration time, and soil TOC from these systems, parameters were calculated and the modified MPM applied. The

result was an overestimation of sorption for sandy loam and sandy type soils and an underestimation for the silty-clay type soil. The underestimation was a result of poor data. The overestimations were expected, as the parameters were calibrated using resins with much higher sorptive capacities than natural soils and sediments. The sorption behavior was only overestimated by one order of magnitude, lending support to the assertion that, once properly calibrated, this model can be used as a predictive tool for the sorption behavior of benzidine and possibly other aromatic amines.