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Modeling the effect of the presence of microorganisms on the mass transfer of phenanthrene from an aqueous solution to a sediment

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Microorganisms present in a solution-sorbent system can affect the mass balance of a pollutant by degrading the pollutant in the solution. A recent study suggested that once a biofilm is present on a sorbent then diffusion kinetics through this biofilm should be considered. In the present study, the effect of the presence of microorganisms in a solution-sorbent system is studied through the use of experimental results and a model simulating the coupled processes of diffusion-limited-sorption and biodegradation. Three types of reactors were employed, in triplicates. One reactor type (NSA) contained 8g of sediment and 100 μg/L phenanthrene in 120 mL synthetic groundwater, the other reactor type (SA) contained sediment, phenanthrene in synthetic ground water and 200 mg/L sodium azide as biocide, and the third reactor type (Blank) contained only phenanthrene in synthetic groundwater and sodium azide. All solutions were sterilized before mixed with phenanthrene and/or the sediment. The solution phase measurements were performed under aseptic conditions frequently (every 1-10 days) up to 90 days. Batch tests with pulverized sediment and different phenanthrene initial concentrations were performed to determine the phenanthrene sorption equilibrium constants. Blank reactors demonstrated that no significant losses of phenanthrene were observed when no sediment was added to the reactor. Plate counting with bacteriological agar containing only phenanthrene as the carbon source revealed that the numbers of microorganisms capable of degrading phenanthrene were significantly higher in NSA reactors (thousand colonies per 100 μL) compared to SA reactors (less than hundred colonies per 100 μL). Using the Freundlich isotherm model, the following constants were obtained through the equilibrium batch tests: Kfr = 30 L/Kg and N=0.73. A numerical model (INTRAPAR) was used to simulate diffusion limited non-linear sorption in order to determine the intraparticle diffusion coefficient (Da=10^{-11} cm^2/s) for the kinetic results from the SA reactors. This intraparticle diffusion coefficient value is in agreement with values determined in the literature for this kind of sediments. The SA reactor results were also simulated with the model that couples diffusion limited sorption and biodegradation (BIO-INTRAPAR) assuming no biodegradation. This was done in order to determine the appropriate mass transfer term included in the model that was equal to kf = 3 10^{-7} cm/s. Then, all these constants (Kfr, N, kf, Da) determined from independent experiments were used as model inputs for the coupled model (BIO-INTRAPAR) to determine the biodegradation constants for the results from the NSA reactors. Later data in the kinetic curve obtained for reactors NSA (i.e. for 25-90 days) were successfully predicted by the input constants that were determined independently and one of the different biodegradation rate constant values tested (k1 = 0.0003 1/hr). This biodegradation rate constant results in a half-life time of 96 days that is within the range of 28-126 days found in the literature for phenanthrene. Sensitivity analyses presented that changing the diffusion coefficient or the biodegradation rate did not result into better predictions for the early kinetic data (i.e. for 4.5-25 days). Only changing the mass transfer coefficient (kf= 5 10^{-8} cm/s) resulted in successful fit of the early kinetic data and the rest of the kinetic curve (i.e. for 4.5-90 days). This study can be considered as a first indication that the presence of microorganisms not only results in the biodegradation of pollutants in solution but can also cause a decrease of the mass transfer of the pollutants from the solution to the sorbent phase. If this mass transfer decrease is not taken into consideration then the model predicts lower concentrations in the solution at early times than those concentrations actually measured.