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Confirmation of Monod Model for Biofiltration of Styrene Vapors from Waste Flue Gas

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ABSTRACT

Background: The objective of this research was to investigate the kinetic behavior of the biofiltration process for the removal of styrene.
Methods: A three stage compost based biofilter was inoculated with thickened activated sludge. The reaction order rate constants were obtained from continuous experiments and used as the specific growth rate for the Monod equation.
Results: The measured concentration profiles show a linear dependence on the bed height in the biofilter at higher loadings, such as 75 and 45 g m^{-3} h^{-1}. This is the condition of reaction limitation for a reaction with zero-order kinetics. From the experimental data, maximum elimination capacity (EC_{max}) was estimated to be 44, 40 and 26 g m^{-3} h^{-1} at empty bed retention times (EBRTs) of 120, 60 and 30 s, respectively. However, at lower loadings, the measured concentration profile of the biofilter is one of exponential increase, which is the condition of both reaction and diffusion limitations for a reaction with zero-order kinetics. Maximum elimination capacities found from the experimental results were the same as Monod model predictions. Both the experimental results and the model predictions showed the influence of EBRT on the removal rate of styrene, particularly for the highest loading rate.
Conclusion: In terms of the practical applications of the proposed models have the advantage of being simpler than Monod kinetics and Monod kinetics requires a numerical solution.
Keywords: Biofiltration, Styrene, Monod Model

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Introduction

Styrene ($C_6H_5CH=CH_2$) is a colorless-to-yellowish, viscous liquid with a distinctive, sweetish, pungent odor. Worker exposure to styrene, probably through inhalation and\or skin absorption, may be wide-spread in a number of industries and operations, including styrene or polystyrene production and the manufacture of other styrene-containing polymer resins, plastics and rubber products; the fabrication of reinforced-polyester plastic composites; and the use of products containing styrene, such as paints,

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adhesives, metal cleaners and varnishes. The highest exposure of workers to styrene has been reported to exceed 20 ppm infrequently, usually during the occasional leakage of reactors and other equipment [1, 2]. Measurements of styrene in indoor air samples in fiberglass manufacturing units in Washington State have shown concentrations greater than 100 ppm [3]. The International Agency for Research on Cancer (IARC) has classified styrene in group 2A, probably carcinogenic to humans, due to the evidence of its carcinogenicity in experimental animals and a lack of sufficient evidence for humans [1].

For more than several decades, biofiltration has been considered to be an environmentally friendly and highly efficient approach for the removal of organic and inorganic pollutants from waste gas streams with high flow rates and low concentrations [4]. Biofiltration works by the passage of a polluted and humidified air stream through a packing material in which microorganisms are immobilized within a biofilm attached to the bed-packing material. Contaminants are transferred to the biofilm and biodegraded as carbon and/or energy sources by the microorganisms in the biofilm. The solid and moisturized bed material provides a nutrient source and a matrix for the attachment of the microorganisms used in the biofiltration process [5].

Many studies of biofilter modeling have been conducted under steady-state and dynamic conditions for single and mixed volatile organic carbons (VOCs) [5-8]. However, the modeling of styrene as a sole carbon source is rarely studied [8]. The microkinetic model of Ottengraf and van den Oever remains the most commonly used model for establishing other models [9]. Biological degradation can be described using the Monod model. The Monod kinetic expression is the most commonly used to determine the kinetic parameters of many macro- and micro-kinetic models formulated for the removal of VOCs by biofiltration systems [10]. In addition, the kinetics of biological systems without any inhibitory substrates can be described by the Monod equation. Zilli et al. [11] performed a macrokinetic and quantitative microbial analysis in a bench-scale biofilter treating styrene-laden waste gases. They used a peat packed biofilter inoculated with pure culture of *Rhodococcus rhodochrous*. The results showed zero-order macrokinetic with respect to styrene concentration, and the maximum removal rate was found to be 63 g m^{-3} h^{-1} for an inlet concentration of 0.80 g m^{-3}. Jorio et al. [12] developed a new mathematical model to describe the performance of a biofilter treating styrene at a steady state using a specific activated consortium of microbial species, EVB 110. In this study, a maximum elimination capacity of 50 g m^{-3} h^{-1} was obtained at an input styrene concentration of about 2.7 g m^{-3}. Das et al. [13] studied the removal of styrene from a simulated air-styrene mixture through the microbial route using *Pseudomonas putida* in a bench scale biofilter. They found that a Monod-type reaction model was appropriate to explain the growth kinetics of the microorganisms.

In the present work, the kinetic behavior of the styrene biodegradation rate was investigated in a compost based biofilter inoculated with mixed culture of activated sludge for the first time. The Monod equation was used to describe the kinetics of the biofilter, and the zero- and first-order reaction rates were validated to obtain reliable full scale design concepts as well as reduce the time and cost of experimentation at the pilot scale.

Materials and Methods

A same-size, three-stage, downward flow, and bench-scale biofilter was used to eliminate styrene vapors from a laden gas stream produced by an air compressor (Fig. 1). The biofilter column was constructed from galvanized iron with an inner diameter of 8 cm and an effective bed height of 120 cm. The simulated waste gas stream was prepared by passing compressed air through a granular activated carbon canister to capture residual oil and particles. The air

stream was then sparged through a 15-L water container equipped with a heated element to adjust the gas stream temperature and humidification. The pollutant vapor was prepared by introducing a low-flow air stream into a container receiving drops of styrene from a burette. The water content of the bed material was maintained at 60-65% throughout the study period. The bed media were prepared by mixing yard waste compost and shredded high-density plastics (PVC) with sizes between 1.5 and 1.0 cm as a bulking agent to produce a volumetric ratio of about 25:75 (25% compost and 75% PVC) compost-bulk agent with an overall porosity of 54%.

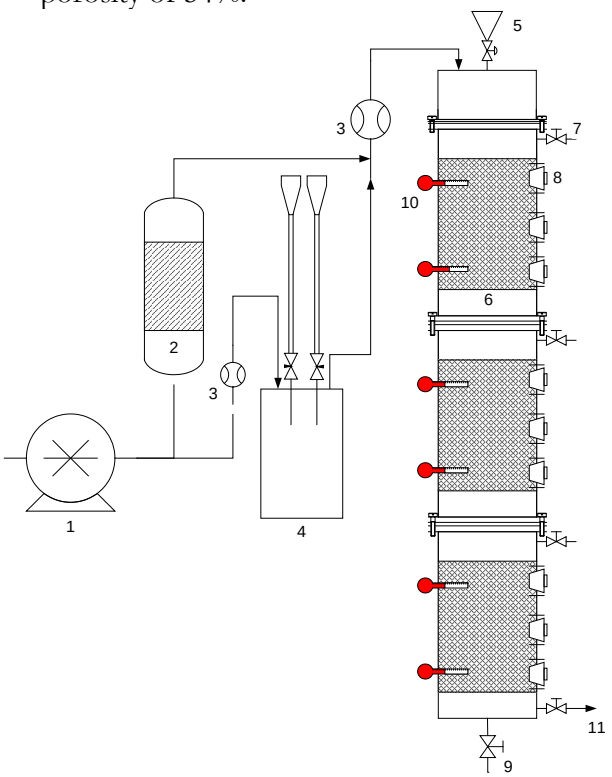

Fig. 1: Schematics of the biofilter system (1-compressor, 2-humidifier, 3-air flowmeter, 4-styrene injector, 5-nutrient inlet, 6-biofilter bed, 7-gas sampling port, 8-bed sampling port, 9-leachate outlet, 10-thermometer, 11-clean air outlet)

Table 1 presents the physical properties and elemental analysis of the yard waste compost used in the biofilter media. When preparing the packing medium, the yard waste compost was screened to reject large objects, and thickened, activated sludge obtained from a municipal wastewater treatment plant was added to the mixture to increase the microbial density and improve the homogeneity of the compost particles and bulking agents. Nutrients and buffering solutions were added to the bed medium according to the quantity of inlet carbon to maintain the C:N:P ratio around 100:5:1. The nutrient solution had the following composition (per liter of tap water): 0.694 g KH_2PO_4; 0.854 g K_2HPO_4; 1.234 g $(NH_4)_2SO_4$; 0.46 g $MgSO_4.H_2O$; 0.176 g $CaCl_2.2H_2O$; 0.001 g $FeSO_4.7H_2O$; and a 5 ml trace element solution consisting of 60 mg l^{-1} H_3BO_3; 40 mg l^{-1} $CoCl_2.6H_2O$; 20 mg l^{-1} $ZnSO_4.7H_2O$; 6 mg l^{-1} $MnCl_2.4H_2O$; 6 mg l^{-1} $NaMoO_4.2H_2O$; 4 mg l^{-1} $NiCl_2.6H_2O$; and 2 mg l^{-1} $CuCl_2.2H_2O$ with an overall pH around 6.9 ± 2 [14].

Table 1: Physicochemical properties of the spent yard waste compost

Variables	Quantity (unit)
Bulk density (dry)	0.456 (g cm^{-3})
Bulk density (wet)	0.883 (g cm^{-3})
Moisture content (w/w)	52 (%)
Total phosphorus (P_2O_5)	1.0 (%)
Total nitrogen (as N)	4.7 (%)
Total carbon	25 (%)

The gas phase concentrations of styrene were determined via gas chromatography (model SRI 110 Inc. USA). The gas chromatograph (GC) was equipped with a flame ionization detector and a 30 m stainless steel capillary column (GM 6210). The GC operating conditions for styrene were as follows: a temperature schedule with an injector at 200 ºC, an oven with an initial temperature of 100 ºC and a ramp of 40 ºC per min to reach a final temperature of 220 ºC with a holding time of 0.1 min and a detector at 230 ºC. N_2 was used as a carrier gas at a flow rate of 8 ml min^{-1}, H_2 as a makeup gas at a flow rate of 25 ml min^{-1} and O_2 with a 6 ml min^{-1} flow rate. Because an online GC was not available in our lab, samples were collected in 5-L Tedlar bags by connecting the bag port to a tube that was connected to the biofilter sampling ports.

The inlet and outlet streams, including the area between the biofilter sections, were sampled. Gas samples of 1 ml containing styrene were withdrawn from the Tedlar bags using a 2-ml gas-tight syringe (Series A-2, VICI, Inc.); they were injected immediately into the GC unit to determine the concentration of styrene. Inlet and outlet concentrations were reported, representing the average of two sequential samples. Unknown samples were determined using a calibration curve that was prepared from peaks observed for known concentrations of styrene by introducing known volumes of styrene into a 5-L sealed Tedlar bag. For example, to prepare a 5-L Tedlar bag containing 100 ppmv styrene at 25 ºC, that should be spiked into the bags with a volume of 2.3-L.

The biodegradation kinetics of styrene was estimated by measuring the removal rates along the biofilter column operating under continuous conditions. This technique is based on the removal rate of VOC in each particular section divided by the retention time in that section and requires that the removal rate be independent of the VOC concentration. In other words, the removal process should be zero-order (or nearly zero-order). Such conditions usually exist in the top sections of the biofilter where the concentration of the substrate is high. The zero-order rate constant was obtained from continuous experimentation, and it was used as the specific growth rate for the Monod equation. The half saturation constant in the Monod kinetic expression was then estimated by fitting the experimental results to the removal of low concentrations of styrene over the entire biofilter.

Results

Biofilter performance at start up

An analysis of the axial styrene concentration profile along the biofilter column showed lower performance for all sections until about 35 days after start up (Fig. 2). After about two months, the biofilter reached a steady-state condition, and styrene outlet concentration decreased along the biofilter column regularly, indicating the acclimation of the microorganisms to the new substrate. Other experiments conducted with pasteurized media under similar conditions have also confirmed styrene biodegradation. The breakdown of styrene occurred after about 3 h of operation, and no styrene removal was observed for 30 days of continuous monitoring.

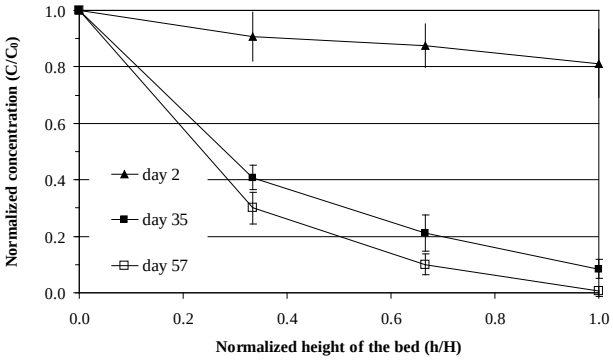

Fig. 2: Evaluation of biofilter performance at the start-up period

Overall biofilter performance

Fig. 3 presents the removal efficiency of styrene versus different superficial gas flow rates (U_S) of 35.8, 71.6 and 143.2 m h^{-1}. It appears that the effect of retention time exists for the entire range of styrene inlet concentrations. At an EBRT of 120 s corresponding to a superficial gas flow rate of 35.8 m h^{-1}, the removal of styrene was about 100% for inlet concentrations ranging from 0.18 to 1.5 g m^{-3} but decreased to 60% as the inlet concentration increased from 1.5 to 2.6 g m^{-3} because the excess concentration inhibited the performance of the biofilter. At a lower EBRT of 60 s corresponding to a gas flow rate of 71.6 m h^{-1}, removal efficiency decreased from 93% to 43% for styrene inlet concentrations varying from 0.47 to 1.6 g m^{-3}. Similarly, at a gas flow rate of 143.2 m h^{-1} or an EBRT of 30 s, any changes in inlet concentration ranging from 0.2 to 0.9 g m^{-3} reduced the biofilter removal efficiency sharply from 80% to 25%. An analysis of the results show that for constant inlet con-

centrations, removal efficiency decreased when the gas flow rate was increased.

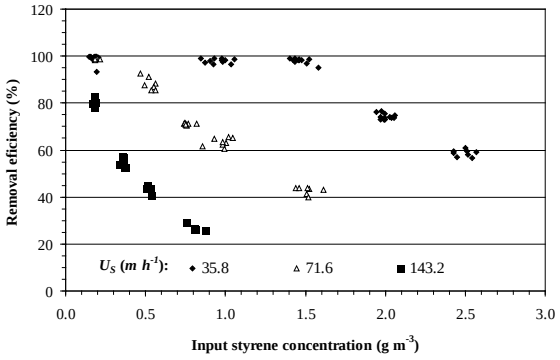

Fig. 3: Removal efficiency of styrene versus different empty bed retention time

Model development

The substrate consumption rate can be described by the Monod equation when no inhibitory effects are observed [15]. According to this equation, the styrene utilization rate (r_{su}), which supports biomass growth in the biofilm, can be expressed as follows:

$$-\frac{dC}{dt} = r_{su} = \frac{\mu_m}{Y}\frac{X.C}{K_s + C} \qquad (1)$$

where μ_m is the maximum specific growth rate (g new cells/g cells.d), Y is the biomass yield coefficient (g/g), C is the concentration of styrene in the biofilm (g/m^3), X is the biomass concentration (g/m^3) and K_s is the half saturation constant (g/m^3).

For this steady-state model, the kinetics parameters (μ_m, X and Y) are assumed to be constant throughout the reactor and unchanging with time. When the substrate is being used at its maximum rate, the bacteria also grow at their maximum rate. The maximum specific growth rate of the bacteria is thus related to the maximum specific substrate utilization rate as follows:

$$k = \frac{\mu_m}{Y} \qquad (2)$$

where k is maximum specific substrate utilization rate (g/g.d) and is summarized as the styrene utilization rate constant as follows:

$$r_m = k.X \qquad (3)$$

where r_m is the substrate utilization rate constant for styrene (g/m^3.h). Therefore, Equation (1) can be rewritten as follows:

$$-\frac{dC}{dt} = r_m \frac{C}{K_s + C} \qquad (4)$$

When the substrate concentration is much smaller than the value of K_S (i.e., when $C<<K_S$), by defining the new constant $k_1=r_m/K_S$, Equation (4) can be simplified to a first-order reaction rate as follows:

$$-\frac{dC}{dt} = k_1 C \qquad (5)$$

where k_1 is the first-order reaction rate constant (h^{-1}) when the rate of reaction is proportional to the substrate concentration. Integrating Equation (5) with the boundary condition $C=C_0$ at $t=0$ gives

$$-\int_{C}^{C_0}\frac{dC}{C} = k_1\int_{t}^{0}dt \rightarrow Ln\frac{C}{C_0} = k_1 t \qquad (6)$$

By plotting LnC/C_0 versus t, a straight line should be obtained and the first-order reaction constant k_1 can be determined from the slope of the line found from a linear regression of the data points (Fig. 4).

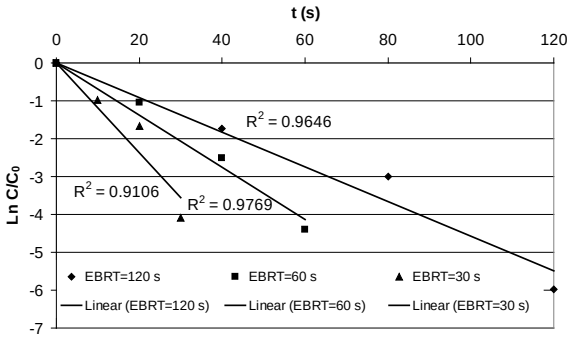

Fig. 4: Graphical analysis of the determination of the first-order reaction rate constant (C_0 < 0.5 g m^{-3})

When the substrate concentration is much larger than the value of K_S (i.e., when $C>>K_S$), by defining the new constant $k_0=r_m/K_S$, Equation (4) can be simplified to a zero-order reaction rate as shown below:

$$-\frac{dC}{dt} = k_0 \qquad (7)$$

where k_0 is the zero-order reaction rate constant (g/m^3.h) when the rate of reaction is independent of substrate concentration. Integrating Equation (7) with the boundary condition C=C$_0$ at t=0 gives

$$-\int_{C}^{C_0} dC = k_0 \int_{t}^{0} dt \rightarrow$$

$$C_0 - C = k_0 t \qquad (8)$$

If C_0-C is plotted against t, a straight line should be obtained from a linear regression of the data points, and the slope k_0 is the maximum elimination capacity of the biofilter for styrene (Fig. 5).

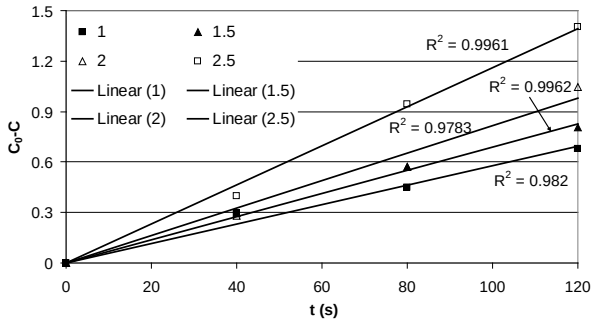

Fig. 5: Graphical analysis of the determination of the zero-order reaction rate constant (EBRT=120 s)

Table 2 shows the results of the linear regressions and the first- and zero-order reaction rate constants at different styrene input concentrations and individual EBRTs.

Table 2: The results of linear regression for first- and zero-order reaction rates

First-order reaction rate C_0 = 0.5 g m^{-3}		**Zero-order reaction rate *EBRT* = 120 s**	
EBRT (s)	k_1 (h^{-1})	C_0 ($g\ m^{-3}$)	k_0 or Maximum elimination capacity ($g\ m^{-3}\ h^{-1}$)
		1	20.79
30	-106.6	1.5	24.75
60	-123.7	2	29.36
120	-164.9	2.5	41.75

As shown in Fig. 6, the maximum elimination capacity, which is the maximum value estimated from the Monod model expression, was found to be about 77.7, 54.1 and 51.1 g m^{-3} h^{-1} at EBRTs of 120, 60 and 30 s, respectively, whereas the maximum elimination capacities were as low as those shown by the experimental data depicted in Table 2. The half saturation constants (K_S) achieved for EBRTs of 120, 60 and 30 s were 1.46, 0.49 and 0.47 g m^{-3}, respectively, when the treatment of styrene shifted from a first-order reaction to a zero-order metabolic process.

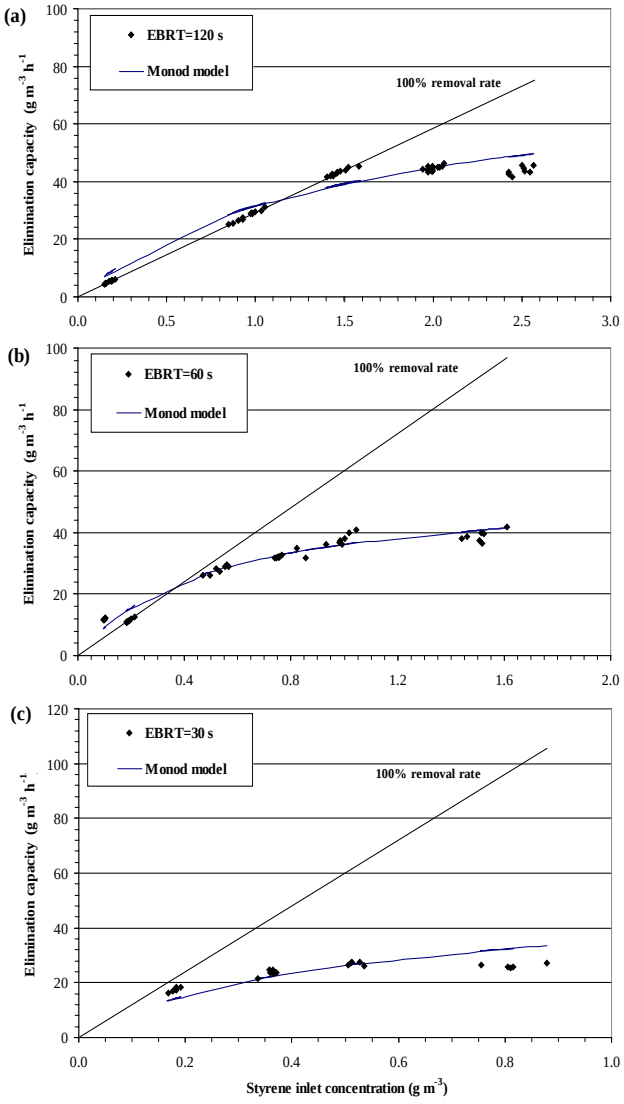

Fig. 6: Overall comparison of the experimental data and the model predictions for the elimination capacity of styrene at different inlet concentrations and various EBRTs

Discussion

The biofilter reached a steady-state condition after about two months. Microbial degradation is the only mechanism that achieves styrene removal [11]. An evaluation of the biofilter performance at individual empty bed retention times showed that, excess inlet concentrations inhibited the performance of the biofilter. However, Jorio et al. [12] reveled that an increase of styrene inlet concentration enhanced the transfer rate of styrene into the biofilm such that more microorganisms could participate in biodegradation.

The Monod equation gives close to zero-order kinetics at high styrene concentrations. Moreover, the zero-order (diffusion-limited) kinetics were always concentrat-ion-dependent and, therefore, could not predict the experimental results at higher concentrations where the process became independent of styrene concentration. Considering the results, it may be concluded that the biodegradation of styrene in the biofilter and across the entire range of concentrations cannot be explained by simple zero- or first-order kinetics. According with the results reported by Zilli et al. [11], although zero-order diffusion-limited kinetics was able to predict the outcome of the process at relatively low styrene concentrations, they could not explain the process under all operating conditions.

The effect of retention time on the removal rate of styrene in the biofilter was also studied using the Monod equation (with parameters estimated from continuous experiments). Both the experimental results and the model predictions indicate the influence of EBRT on the removal rate of styrene, particularly for the highest loading rate. At loading rates up to 30 g m^{-3} h^{-1}, this influence was not seen because the biofilters were near or at 100% of their maximum removal efficiencies, regardless of an EBRT of 30 s.

The maximum elimination capacities estimated using the Monod model expression were the same as the results found from the experimental data. An EBRT of 120 s provides more time to partition the substrate into the biofilm, and zero-order kinetics appear to prevail at inlet concentrations almost above 0.5 g m^{-3}. This is consistent with the results suggested in modeling studies of other hydrophobic and hydrophilic compounds, and the model has been shown to be a reaction with first-order kinetics at an inlet concentration lower than 0.5 g m^{-3}[8, 12, 16]. The Monod kinetic model, on the other hand, can determine whether the removal rate depends on concentration, as long as the kinetic parameters are properly estimated.

Conclusion

In terms of the practical applications of the proposed models, zero-order diffusion-limited kinetics has the advantage of being simpler than Monod kinetics. Zero-order models can be solved analytically, and they can provide an exact solution, whereas Monod kinetics requires a numerical solution. Therefore, zero-order diffusion-limited kinetics can be used for the quick analysis and prediction of biofilter behavior, as long as the biofilter is operating at relatively low concentrations.

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