Increased Biofilm Activity in BGAC Reactors

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In bioreactors systems granulated activated carbon (GAC) was proven to be an advantageous biofilm carrier over inert media with similar physical properties (nonadsorbing carbon) under conditions of pollutant partial penetration in the biofilm. Results from laboratory experiments using atrazine degrading bacteria (Pseudomonas ADP*) and modeling assuming GAC adsorption/desorption mechanism, showed higher atrazine degradation rate resulting in better effluent quality in the biofilm granulated activated carbon (BGAC) reactor. Increased biofilm activity due to the double flux of substrate from the bulk liquid and from the GAC can explain the better performance of the BGAC reactor.*
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Introduction

For the past 30 years, numerous researchers have investigated the use of GAC as a carrier for biofilm in reactor systems. Biofilm covered GAC is reported to have the following advantages: (1) the rough surface of the particles containing macropores with wide channels provides excellent shelter from fluid shear forces for colonization of microorganisms[1,2], and (2) due to its adsorptive properties, GAC has the ability to attenuate high or toxic incident influent concentrations of pollutant while maintaining constant effluent quality. The gradual desorption of shock loads at nontoxic concentrations allows for pollutant biodegradation[3-6]. In addition, the microorganisms in biofilm reactors where GAC is used as the carrier (BGAC) have an additional potential advantage of increased activity due to double flux of substrate: from the liquid phase (bulk solution) and from the GAC solid phase (desorption). The mechanism of substrate adsorption onto GAC followed by diffusion through the porous media and desorption onto the adjacent biofilm layer can provide higher biomass activity due to increased biofilm surface area exposed to the substrate. However, this advantage of the GAC takes place only under conditions of substrate diffusion limitations (that is, when the deeper layers of the biofilm do not receive substrate from the bulk solution), since only then the additional source of substrate from the GAC is beneficial. This observation would explain the contradicting reports regarding biofilm activity in BGAC vs. nonadsorbing carrier reactors[3, 7-9].

Using a preadsorbed ^{14}C-radiolabeled substrate, the internal mass transfer of substrate from the GAC to the biofilm was shown by Spietel et al.[10]. In addition, the interconnection of micropores was proved by Radovic et al.[11] using a CO_2 adsorption experiment. These observations show that adsorbates can migrate from one adsorption site of the GAC to another. Generally, film diffusion and intra-particle diffusion account for the adsorption rate in GAC. Migration of adsorbates can occur by desorption followed by pore transport to a new site and also by migration of an adsorbed molecule to an adjacent adsorption site on pore wall surface, a transport motivated by the surface concentration gradient and available sorption energy[12].

Previous results in our laboratory[13] showed that under normal BGAC fluidized-bed reactor operational conditions, which includes excess biomass removal by mechanical means, a patchy biofilm coverage with exposed areas of GAC or areas covered with only very thin biofilm develops. This patchy structure can explain adsorption of substrate to biofilm covered GAC even under conditions of partial substrate penetration to the biofilm. The objective of this article is to prove the advantage of BGAC reactors vs. nonadsorbing carrier, at conditions of diffusion limitation using modeling and experimental tools.

Mathematical models of BGAC reactors have been developed in the past[9,10,14,15]. However, in all of these models the biofilm layer was assumed to fully cover the bulk-exposed area

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of the carrier. Assuming full biofilm coverage of the GAC at low bulk substrate concentration conditions, adsorption of substrate to the GAC cannot take place because of mass transfer limitations resulting in substrate partial penetration to the biofilm. At these conditions the GAC acts as an inert media as soon as the pre-adsorbed substrate is exhausted and the model will fail to show the potential advantage of substrate double flux to the biofilm. In this article, we present a conceptual model of a GAC (adsorption - desorption model) with a patchy biofilm coverage, which allows for substrate adsorption even under conditions of partial penetration, thus providing an additional route for mass transfer of the substrate (pollutant) by a mechanism of adsorption-desorption. The pollutant is assumed to first be adsorbed to the GAC in the nonbiofilm covered areas, diffuses through the GAC pores and is subsequently desorbed to the inner biofilm layers that would otherwise not be exposed to the pollutant. For the purpose of proving the advantage of BGAC reactor vs. nonadsorbing carrier reactor, two models were compared: one which is based on a double flux simulating the BGAC reactor, and the other simulating the nonadsorbing carrier reactor[14]. The two models are identical (including the assumption of partial coverage of the biofilm on the carrier) except for the inclusion of substrate adsorption, diffusion through the porous media and desorption in the GAC model only. In addition, two lab scale fluidized bed (FB) continuous reactors were operated using *Pseudomonas* ADP (*P* ADP), a fast atrazine degrading bacteria, with citrate as the main carbon and energy source. In one FB reactor, GAC was used as a biofilm carrier while in the other, a nonadsorbing carbon carrier ("baker product" - particles taken from the GAC process of manufacturing before the activation stage) with the same surface area available for biofilm growth was used. The results from the experimental reactors were compared to the BGAC model and to the model of a biofilm on a nonadsorbing carrier.

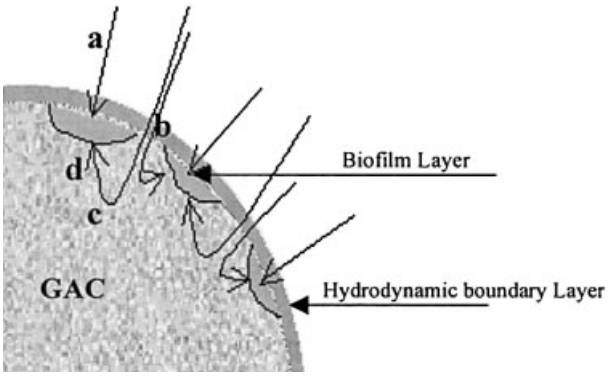

Figure 1. Typical slice of BGAC in the BGAC reactor with suggested atrazine mass transfer pathways: (a) Atrazine convective mass transport through the hydrodynamic boundary layer, followed by diffusion and degradation in the biofilm layer; (b) adsorption of atrazine to the GAC, (c) Intraparticle diffusion of atrazine in the GAC particle; and (d) desorption of atrazine from the GAC to the adjacent biofilm layer followed by diffusion and degradation in the biofilm layer.

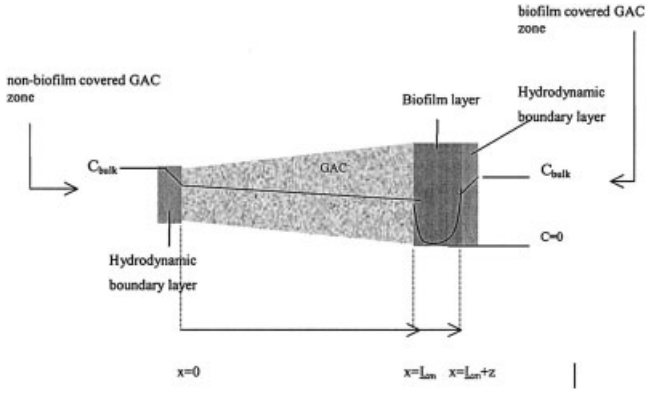

Figure 2. Modeled slice of BGAC and atrazine concentration profile (z - biofilm depth, Lm - average migration distance).

Dual flux of the substrate in the BGAC model

For simplicity, a one-dimensional(1-D) model was used to prove the advantage of the BGAC double flux mechanism. The BGAC model includes three interfaces: (1) Biofilm-bulk liquid, (2) GAC-bulk liquid, and (3) GAC-biofilm. A representation of the BGAC is shown in Figure 1, and a theoretical modeled slice of the BGAC is shown in Figure 2. The model is based on nonsteady state material balance continuity equations solved by a finite difference numerical solution. It involves diffusive mass transfer through the biofilm with Monod's kinetics for the biological reaction. Adsorption and diffusion of the adsorbed substrate through the porous media, was described using the homogeneous surface diffusion (HSD) model[12]. Under conditions of substrate partial penetration in the biofilm adsorption was assumed to occur only on areas not covered by biofilm. The model input variables are the influent and biomass concentration being analyzed during the experimental period. The state variables are the effluent (bulk) and the adsorbed concentration of the limiting substrate (atrazine). The model describes transient conditions resulting from a sharp decrease in the influent concentration. Measured and model calculated concentrations in the effluent and adsorbed to the GAC were used to describe the transient period until a new steady state was achieved. The model solution for effluent and adsorbed concentration was compared to the experimental analysis.

Basic model assumptions.

The following assumptions were made for modeling mass balance in the two models:

BGAC and Baker product model's assumptions

- All the particles are identical and homogeneous.
- The biofilm is homogeneous with constant density and mass-transfer coefficient.
- Mass transfer through the biofilm is diffusion limited governed by Fick's law.
- Biofilm exists only on the external surface area of the particle.
- The same hydrodynamic boundary layer mass-transfer coefficient *kf* was defined for the particle-bulk and biofilm-bulk interfaces[13].
- Biofilm coverage on the particles is incomplete.

Table 1. Main Parameters in the Two Models

Dry biofilm density	ρ_b [g VSS/cm^3]	0.038
Wetted particle density	ρ_p [g/cm^3]	1.2
Biofilm diffusion coefficient	D_b [cm^2/sec]	$3 \cdot 10^{-7}$
Intra-particle diffusion coefficient*	D_s [cm^2/sec]	$2.5 \cdot 10^{-9}$
Film diffusion coefficient	k_f [cm/sec]	$2.5 \cdot 10^{-3}$
Monod's maximal atrazine specific degradation rate	d_{max} [mg/day/g VSS)]	2000
Monod's half saturation coefficient	K_s [mg/l]	1
Biofilm coverage fraction	f_c	0.6–0.85
Average substrate migration distance*	L_m [cm]	0.05

*For the BGAC model only.

BGAC model's assumptions

- The typical distance that one atrazine molecule passes (from adsorption site to desorption into the biofilm) was termed as the average migration distance and taken to be the average radius of the particles used in the experiment. The coordinate for bulk liquid-GAC interphase was determined as zero, and GAC-Biofilm layer was determined as *Lm*.
- Atrazine inside the particle (beyond the interface) is defined as adsorbed and the adsorption is completely reversible.
- The intraparticle diffusion of the adsorbate is constant and governed by Fick's law.
- An instantaneous equilibrium exists between the adsorbed concentration and the solute concentration in the GAC-bulk, and in the GAC-biofilm interfaces expressed by Freundlich isotherm.

Parameters determination.

The main parameters used in the model are given in Table 1. Biofilm density (ρ_b), atrazine diffusion coefficients in the biofilm (D_b), and in the GAC (D_s), film diffusion coefficient (k_f) and biofilm coverage fraction (f_c), were determined by Herzberg et al.[13]. Monod's coefficients for atrazine degradation by *P* ADP, were determined by Katz et al.[16]. The value for the wetted particle density of the GAC (ρ_p) is given by the GAC manufacturer (Calgon Chemviron), and the value for the average substrate migration distance (L_m) was determined arbitrarily as the particle radius.

Dual flux BGAC model's equations

Biofilm density (ρ_b), biofilm coverage fraction (f_c) and measured biofilm concentration (X_b) were used to calculate biofilm depth (z) according to Eq. 1, where V_p is the typical particle volume, ρ_p is the wetted particle density, and d_p is the particle's dia.

$$z = \frac{\rho_p \cdot V_p \cdot X_b}{\pi \cdot d_p^2 \cdot f_c \cdot \rho_b} \tag{1}$$

The nonsteady state mass transport equation for the adsorbed atrazine in the GAC according to the HSD model is the following

$$\frac{\partial q(x,\,t)}{\partial t} = D_s \cdot \left(\frac{\partial^2 q(x,\,t)}{\partial x^2} \right) \tag{2}$$

where q is the adsorbed substrate concentration, and D_s is the average pore diffusion coefficient.

The nonsteady state mass transport equation for atrazine in the biofilm is described in Eq. 3, where D_b is the average biofilm diffusion coefficient, C_b is the substrate concentration in the biofilm, X_b is the biofilm concentration, m_p is the typical mass of the particle, v_b is the biofilm volume on a typical particle, d_{max} is the maximal specific degradation rate of atrazine, and K_s is Monod's half saturation coefficient

$$\frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial x^2} - \frac{d_{\max} \cdot (X_b \cdot m_p / v_b) \cdot C_b}{K_s + C_b} \tag{3}$$

The fluxes from the GAC and into the biofilm in the GAC-biofilm interface are given by Eqs. 4 and 5 in the GAC and biofilm layers accordingly

$$G_{GAC}\,(x = L_m,\, t) = D_s \cdot \rho_p \cdot \left(\frac{\partial q}{\partial x} \right) \tag{4}$$

$$G_{Biofilm}\,(x = L_m,\, t) = D_b \cdot \left(\frac{\partial C_b}{\partial x} \right) \tag{5}$$

The nonsteady state mass-transfer equation in the GAC-biofilm interface in terms of adsorbed concentration q on the interface is given in Eq. 6

$$\frac{\partial q}{\partial t}\,(x = L_m,\, t) = \frac{\partial G}{\partial x} \tag{6}$$

Except for the case of the GAC-biofilm interface ($x = L_m$) where a specific development of a numerical expression was required[17] due to different depth in the biofilm and in the GAC, all the rest of the numerical expressions were regular according to finite difference method with constant intervals for Δx_q and Δx_b values for the depth interval in the GAC slice and in the biofilm layer, respectively[18].

Boundary conditions

Equation 7 describes the flux from the bulk solution to the GAC at the GAC-bulk interface where no accumulation is assumed

$$\rho_p \cdot D_s \cdot \frac{\partial q}{\partial x}\,(x = 0,\, t) = k_f \cdot (C_r - C\,(x = 0,\, t)) \tag{7}$$

C_r is the atrazine bulk concentration in the reactor, $C(x=0,t)$ is the concentration of the adsorbate in the liquid phase adjacent to the GAC surface, and k_f is the mass-transfer coefficient in the hydrodynamic boundary layer.

Equation 8 describes the flux to the GAC through the biofilm covered area at the Biofilm-Bulk interface. The mass boundary layer is assumed to form instantaneously and a constant mass-

transport coefficient was determined elsewhere[13] (no accumulation is assumed):

$$D_b \cdot \frac{\partial C_b}{\partial x}(x = L_m + z, t) = k_f \cdot ((C_r - C_b(x = L_m + z, t)) \quad (8)$$

Equation 9 assumes an instantaneous equilibrium between the adsorbed concentration on the GAC surface, and the solute concentration adjacent to the surface in the interfaces GAC-bulk and GAC-biofilm[12]. The equilibrium is expressed by the Freundlich isotherm with 1/n and K as Freundlich isotherm's constants

$$q(x = (0, L_m), t) = K \cdot C(x = (0, L_m), t)^{1/n} \quad (9)$$

This equilibrium is assumed only at the interfaces where $x = 0$ and $x = L_m$ in Eqs. 6 and 7.

Atrazine mass balance equation for the whole BGAC reactor is given in Eq. 10, where Q is the influent flow rate, C_{in} is the atrazine influent concentration, and A is the total surface area of the bioparticle exposed to the bulk liquid. f_c describe the fraction of the particle covered by biofilm[13]

$$V \cdot \frac{dC_r}{dt} = Q \cdot C_{in} - Q \cdot C_r - f_c \cdot A \cdot k_f \cdot (C_r - C(x = L_m + z, t)) - (1 - f_c) \cdot A \cdot k_f \cdot (C_r - C(x = 0, t)) \quad (10)$$

Materials and Methods

Chemicals

Atrazine (94% technical grade) was kindly supplied by Agan chemicals, Ashdod, Israel. All other reagents were of reagent grade or higher.

Bacterial strain and growth media

The atrazine degrading bacterium *P.* ADP was used as the inoculum to all the reactors. The liquid growth medium was prepared according to Mandelbaum et al.[19].

FB Reactors

Two fluidized-bed reactors, each with a 2.5 L column, were filled with 700 g carrier: one with nonadsorbing carbon particles ("Baker product", Calgon-Chemviron), and the other with GAC F400 (Calgon-Chemviron). The particles were meshed between 0.8 and 1.2 mm and washed with deionized water. The carrier was fluidized by recirculating the fluid in the reactor with an influent to recirculation ratio of 1 to 50. During startup, the reactors were inoculated using *P.* ADP grown in sterile batch media and operated aerobically under selective enrichment conditions with atrazine (20-25 mg/L) as a sole nitrogen source and citrate as the sole carbon and energy source (200-250 mg/L). Phosphate was added as KH_2PO_4 and Na_2HPO_4 at 50 mg/L each. The reactors were operated at influent loading rate of 10 mL/min and under nonsterile conditions. At the end of the startup, a constant biofilm concentration of 2 mg protein/g GAC was maintained by daily removal of excess biomass by mechanical brushing of the bioparticles.

Adsorption isotherm for atrazine

Different volumes (0.25-1.0 L) of buffered atrazine solution (25 mg/L, pH = 7.2) were mixed at 25°C with different amounts of GAC particles until equilibrium was reached (7–14 days). Freundlich model for atrazine adsorption was found to give the best fit to the experimental results as was also reported by others using atrazine, and the same type of GAC (20, 21, 22) Freundlich isotherm coefficients of 1/n = 0.18 and K = 79.4 $[(L/mg)^{0.18}(mg/g)]$ were observed.

Analytical Methods

High atrazine concentrations (>0.2 ppm) were extracted from the influent and effluent streams and analyzed by HPLC according to Katz et al.[16]. Low atrazine concentrations (<0.2 ppm) were extracted using solid phase extraction (SPE) cartridges with 500 mg C18 (J&W Scientific) in order to concentrate atrazine to the HPLC measurable level (>0.2 ppm).

Adsorbed atrazine was extracted with 20 mL of ethyl acetate, following drying (105 °C) and grinding of 20 mg BGAC sample. An aliquot of 0.4 mL of ethyl acetate was evaporated to dryness and atrazine redissolved in 2 mL acetonitrile. The acetonitrile sample was injected to HPLC.

Atrazine was extracted and analyzed by reverse phase HPLC, according to Katz et al.[23]

Biofilm protein concentration was determined by Bradford procedure[24]: mild hydrolysis of 1 g carrier in 10 mL of 2 M NaOH for 10 min at 60°C, followed by diluting the sample 1:25 in distilled water, and using the Bio-Rad reagent. A constant ratio of a volatile suspended solids (VSS) /Protein concentration of 10:1, was observed in a FBR operating under identical conditions and with the same bacteria, using sintered glass beads as the biofilm carrier. This ratio was used for model calculations (VSS as an indicator for biomass concentration in biofilm reactor systems can only be used with inert carrier, while GAC volatilized at high-temperatures).

Model's numerical solution

A finite difference numerical solution was applied using MATLAB® technical computing language (The MatWorks, Inc. version 5.2).

Results and Discussion

Experimental results

At the end of the start up period, atrazine adsorbed concentration was 45 mg/g and the effluent concentrations were 0.08 and 0.15 mg/L in the BGAC and Baker product reactors, respectively, and the biofilm concentration was similar in both reactors: 2 mg protein/g carrier. At this stage, atrazine influent concentration was reduced drastically from 20 mg/L to 0.7-1 mg/L (flow rate of 10 mL/min, with the corresponding retention time of 4 h). These operation conditions guaranteed atrazine partial penetration to the biofilm. The experimental results are shown in Figure 3a. After a transition period which lasted 10 days for the baker reactor and much longer period of 60 days for the GAC reactor due to desorption and biodegra-

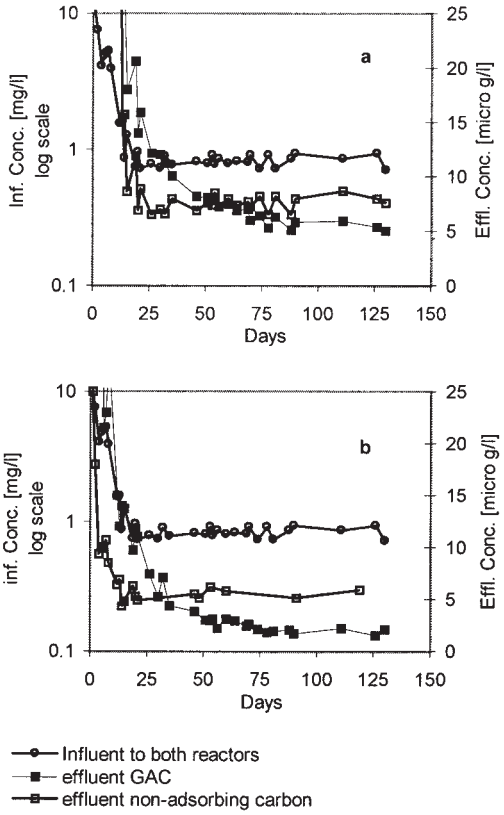

Figure 3. Influent and effluent concentration in the GAC and baker product reactors (model (a) vs. experimental (b) results).

dation of atrazine from the preadsorbed GAC, the effluent concentration was stabilized on 2 μg/L in the BGAC reactor vs. 5-6 μg/L in the nonadsorbing carbon reactor. These results from reactors with similar physical characteristics of the carriers and the same operation conditions except for the adsorption/desorption ability show the advantage of the adsorbing carrier (GAC) over the nonadsorbing carrier under conditions of diffusion limitations.

Model results

Figure 3b shows the results from the two models: One for the adsorbing carrier with the corresponding adsorption/desorption mechanism, and the other for the nonadsorbing carrier reactor, with substrate flux only from the bulk. As was already mentioned the two experimental reactors were fed with the same influent concentration and this concentration was used as input data for the model. In addition, the measured biofilm concentration in the experimental reactors was also used as an input to the model.

The models' results show that under identical operation conditions better effluent quality is achieved in a BGAC reactor vs. a nonadsorbing carrier reactor: 5 vs. 8 μg/L, respectively. Despite the double flux assumed in the BGAC reactor, which can result in an apparent two fold increase in biofilm surface area, the difference in degradation rate between the two reactors was relatively small (few μg/L multiplied by the influent flow rate under steady-state conditions). This is typical of biofilm reactor systems due to decreased substrate penetration depth into the biofilm and lower specific degradation rate at the lower substrate concentrations. However, this small difference can be important under conditions of stringent effluent quality requirements. The differences between the model and the experimental results for the same reactor (either BGAC or Baker product) resulted from too low biological removal coefficients used in the model - as evidenced by sensitivity analysis runs (results not shown). In addition, sensitivity analysis of the adsorbate migration distance (L_m) showed only a minor effect on the model results.

The adsorbed atrazine concentration in the BGAC reactor (experimental and model results), and the measured biofilm concentration in the two reactors are shown in Figure 4. As could be expected, reducing the influent atrazine concentration resulted in a significant decrease in adsorbed atrazine concentration: from 45 to 28 mg atrazine/g GAC. This decrease contributed atrazine to the BGAC reactor in a daily amount equivalent to 20 times the daily influent loading rate during the first 50 days of reactor's operation. The higher atrazine load in the GAC reactor (feeding + desorption of preadsorbed atrazine) resulted in higher biofilm concentration as compared to that of the "baker product" reactor (atrazine was the sole nitrogen source while nitrogen was the growth limiting rate).

In order to evaluate the effect of the higher biomass concentration relative to the effect of the double flux on the BGAC effluent quality (both inherent characteristics of the adsorbing carrier) the two models were extended to include an additional 250 days beyond the 150 days of the actual reactors operation. During this time an influent atrazine concentration of 0.8 mg/L was used as input data for both reactors, similar to the influent concentration during most of the experimental period (Figure 3a, day 10-127). An equal biofilm concentration of 1.2 mg protein/g carrier (measured concentration on the BGAC after 130 days) was assumed for the two reactors. The model results showed steady-state concentrations of 4 and 8 μg/L for the BGAC and Baker product reactors, respectively (Figure 5). These results indicate that the difference in biofilm concentration in the reactors was not the reason for the higher effluent quality observed in the BGAC reactor.

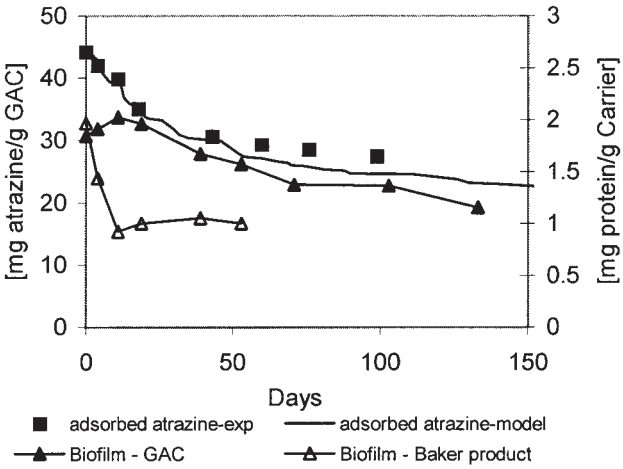

Figure 4. Biofilm concentration in both reactors (measured) and adsorbed atrazine concentration in the BGAC reactor (model and experiment).

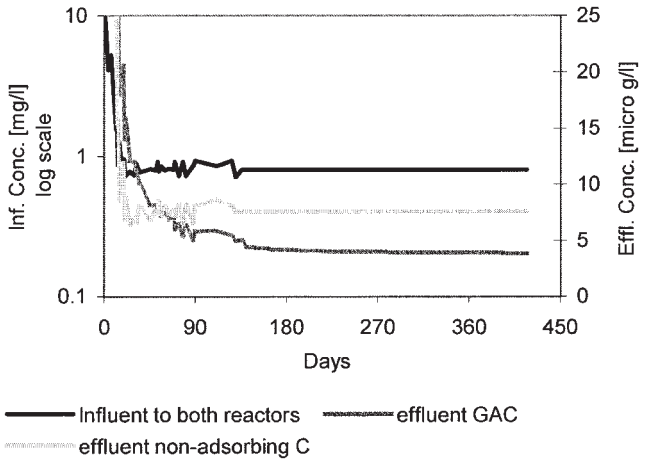

Figure 5. Model results of the BGAC reactor vs. inert carrier for a period of 400 days.

The results presented in this article prove the advantage of a BGAC reactor vs. nonadsorbing carrier reactor. Model and experimental results showed that under conditions of substrate partial penetration in the biofilm, typical to treatment systems where effluent requirements are stringent (2 and 0.1 μg/L atrazine, according to the EPA and the EC standards), higher biofilm activity is achieved. The higher biofilm activity results from the additional source of substrate from the GAC to the adjacent base biofilm layer.

Notation

ρ_b = dry biofilm density, g VSS/cm^3
ρ_p = wetted particle density, g/cm^3
A = total surface area of the bioparticles exposed to the bulk liquid, cm^2
C_b = biofilm atrazine concentration, mg/L
C_r = atrazine bulk concentration, mg/L
D_b = average dry biofilm diffusion coefficient, cm^2/s
D_s = average pore diffusion coefficient, cm^2/s
d_{max} = monod's maximal atrazinr specific degradation rate, mg/day/g VSS
d_p = particle's diameter, cm
f_c = biofilm coverage fraction
G_q = flux of adsorbed atrazine, mg/cm^2/s
K = freundlich isotherm coefficient, (l/mg) $^{1/n}$(mg/g)
k_f = film layer coefficient, cm/s
K_s = Monod's half saturation coefficient, mg/L
L_m = average substrate migration distance, cm
m_p = typical mass of an average size particle g
n = freundlich isotherm coefficient
q = adsorbed substrate concentration, mg/g
t = time coordinate, sec
V = liquid volume of the FB reactor, l
ν_b = biofilm volume on a typical particle, cm^3
V_p = typical particle volume, cm^3
x = distance coordinate, cm
X_b = biofilm concentration, g VSS/g GAC
Z = biofilm depth, cm

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