

# Biological granulated activated carbon fluidized bed reactor for atrazine remediation

M. Herzberg, C.G. Dosoretz, S. Tarre, M. Beliavski and M. Green

Faculty of Civil and Environmental Engineering, Technion, Haifa 32000, Israel (E-mail: [herzberg@tx.technion.ac.il](mailto:herzberg@tx.technion.ac.il); [carlosd@tx.technion.ac.il](mailto:carlosd@tx.technion.ac.il); [shelly@tx.technion.ac.il](mailto:shelly@tx.technion.ac.il); [agmgreen@tx.technion.ac.il](mailto:agmgreen@tx.technion.ac.il))

**Abstract** To show that an adsorbing biofilm carrier (GAC) can be advantageous for atrazine bioremediation over a non-adsorbing carrier, fluidized bed (FB) reactors were operated under atrazine limiting concentrations using *Pseudomonas* sp. strain ADP as the atrazine degrading bacteria. The following interrelated subjects were investigated: 1) atrazine adsorption to GAC under conditions of atrazine partial penetration in the biofilm, 2) differences in atrazine degradation rates and 3) stability of atrazine biodegradation under non-sterile anoxic conditions in the GAC reactor versus a reactor with a non-adsorbing biofilm carrier. Results from batch adsorption tests together with modeling best described the biofilm as patchy in nature with covered and non-biofilm covered areas. Under conditions of atrazine partial penetration in the biofilm, atrazine adsorption occurs in the non-covered areas and is consequently desorbed at the base of the biofilm substantially increasing the active biofilm surface area. The double flux of atrazine to the biofilm in the GAC reactor results in lower effluent atrazine concentrations as compared to a FB reactor with a non-adsorbing carrier. Moreover, under non-sterile denitrification conditions, atrazine degradation stability was found to be much higher (several months) using GAC as a biofilm carrier while non-adsorbing carrier reactors showed sharp deterioration within 30 days due to contamination of non-atrazine degrading bacteria.

**Keywords** Atrazine; biofilm; degradation; GAC; *Pseudomonas* ADP; reactor

## Introduction

Atrazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine ( $C_8H_{14}ClN_5$ ), is a widely used herbicide in agriculture. High concentrations of both atrazine and nitrate frequently occur in groundwater of intensive agricultural areas (Burkart and Kolpin, 1993; Giovanni, 1996) and therefore, their simultaneous removal is attractive. While nitrate bioremediation is a well established technology, atrazine is a recalcitrant compound that is commonly removed by adsorption to activated carbon columns.

Recently, Mandelbaum *et al.* (1993, 1995) isolated and characterized a bacterium degrading atrazine at rates several orders of magnitude higher than previously reported making economic biological treatment feasible (Crawford *et al.*, 1998; Vink and van der Zee, 1997). The bacterium, *Pseudomonas* sp. strain ADP (*P.ADP*), has a constitutive hydrolytic pathway for atrazine detoxification, consisting of six different enzymes encoded by six genes located on a 108-kb plasmid (Martinez *et al.*, 2001; de Souza *et al.*, 1998). The bacterium can utilize the herbicide as its sole nitrogen source under aerobic conditions with citrate as the carbon source and electron donor. A potentially suitable carrier for cultivating *P.ADP* for atrazine biodegradation in a fluidized bed (FB) reactor is granulated activated carbon (GAC) as the carrier for the biofilm under aerobic and anoxic conditions.

The use of GAC as a carrier in biofilm reactors (commonly referred to as BGAC) has been investigated by numerous researchers. One possible, though controversial, advantage of the BGAC is a reported higher specific bacterial activity as compared to inert media, attributed to substrate desorption from the GAC (Hanaki *et al.*, 1997). In BGAC reactors, the microorganisms comprising the biofilm have two potential sources of substrate (where substrate in this paper refers to the pollutant atrazine): the liquid phase and the sorbed

phase. Under conditions of substrate partial penetration in the biofilm, substrate desorption from GAC can result in a higher specific activity due to an increase in the active biofilm surface area.

The mechanism of adsorption-desorption in the GAC porous media has been discussed by various researchers (Dovantzis, 1986; Chang and Rittmann, 1987b; Ehrhardt and Rehm, 1989; Hanaki *et al.*, 1997). However, their findings are contradictory and no decisive conclusions can be drawn. The reason for the controversy probably stems from the differing operational conditions of the BGAC reactor in each case. Only under conditions of mass transfer limitations prevailing in the biofilm can an alternative flux from the carrier to the biofilm be advantageous. Moreover, organic pollutant concentrations are usually very low (ppb) and if they are used as the sole energy source for the bacteria, only a very thin biofilm will develop. Under these conditions, the advantage of GAC as an additional source of substrate will be insignificant. If another energy source is available and the pollutant is not essential for bacterial growth, biofilm thickness will not depend on the pollutant's concentration and substrate limitations within the thicker biofilm are possible.

GAC is characterized by a very irregular surface with many holes, ridges and crevices. The removal of excess biomass from a fluidized bed (FB) reactor to ensure steady state conditions and to prevent bioparticle washout is performed regularly by mechanical means. As a result, a patchy-like biofilm coverage of GAC can develop where the biofilm resides mainly in sheltered areas. The incomplete coverage can allow for substrate adsorption to GAC even at low substrate concentrations in the presence of thicker biofilms.

If indeed substrate adsorption to GAC under conditions of partial penetration in the biofilm do exist, then a BGAC reactor, in comparison to a reactor with a non-adsorbing carrier, should show a higher biodegradation rate by the increase in active biofilm surface area resulting from an adsorption-desorption mechanism. Furthermore, due to atrazine desorption from the GAC, a favorable microenvironment for the atrazine degrading bacteria may provide higher atrazine degradation stability. To show the advantage of a BGAC FB reactor for atrazine remediation as opposed to other biofilm reactors, this paper investigates three main subjects that are interrelated: 1) atrazine adsorption to GAC under the condition of atrazine partial penetration in the biofilm, 2) the existence of a double flux of atrazine in the biofilm (from both the bulk and the GAC particle), resulting in a higher atrazine degradation rate, and 3) increased stability of atrazine biodegradation in a reactor operating under non-sterile anoxic conditions.

## Materials and methods

### Chemicals

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

### Bacterial strain and growth media

The atrazine degrading bacterium *Pseudomonas* sp. strain ADP was used (Mandelbaum *et al.*, 1995). The liquid growth medium was prepared according to Mandelbaum *et al.* (1993).

### Fluidized bed reactors (FBRs)

Two 2.5 litre fluidized bed reactors were constructed from clear PVC tubing (50 mm diameter). The columns were filled with 700 g carrier, the first column with non-adsorbing carbon particles from the Calgon-Chemviron production process ("Baker product") and the second column with Calgon-Chemviron F400 GAC. The "Baker product" and GAC have the same physical characteristics. The carrier was fluidized by recirculating the fluid in the

reactor with an influent to recirculation ratio of 1:40. During start-up the reactors were inoculated with *P. ADP* pre-grown in sterile batch media and under the following selective enrichment conditions: atrazine as a sole nitrogen source, citrate as the electron donor and the carbon source, and oxygen as the terminal electron acceptor. During different stages of the research study, the reactors were operated either under aerobic conditions with atrazine as the sole nitrogen source, or under anoxic conditions, i.e. nitrate as the terminal electron acceptor. The nitrate daily load was between 0.45 to 4.6 g/l (as N) and the citrate load was according to a 5.1:1 weight ratio of citrate to N-NO<sub>3</sub> (Katz *et al.*, 2000). Phosphate was added as KH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> at 0.05 g/l each. The daily atrazine load was between 100 mg/l reactor/day and 1 mg/l reactor/day with the corresponding influent atrazine concentrations: 5–25 mg/l and 1.0–0.08 mg/l. The hydraulic retention time varied between 2 and 4 hours. A constant biomass concentration of about 2 mg protein/g carrier was maintained on the non-adsorbing carbon and on the GAC by daily removal of excess biomass. The reactors were operated under non-sterile conditions.

#### **Batch adsorbing experiments**

Four 250 ml columns filled with either washed virgin GAC (dry weight 100 g) or with GAC covered with a non-atrazine degrading biofilm were used in the batch adsorption experiments. A non-atrazine degrading biofilm was used in order to differentiate between adsorption and biodegradation, i.e. using an atrazine degrading biofilm would interfere with the adsorption experiments. Virgin GAC particles were meshed between 0.8 and 1.2 mm. The columns were connected to a 100-litre tank containing buffered tap water with 19–25 mg/l atrazine. A high recirculation rate between the feeding tank and the GAC column ensured completely mixed conditions. The atrazine concentration in the bulk solution and adsorbed to the GAC was measured periodically.

#### **Analytical methods**

High atrazine concentrations (>0.2 ppm) were extracted and analyzed by HPLC according to Katz *et al.* (2000). 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 measurable HPLC levels (<0.2 ppm). Adsorbed atrazine was extracted from 20 mg of a dried (105°C) and pulverized sample of BGAC with 20 ml of ethyl acetate. An aliquot sample of 0.4 ml of ethyl acetate was evaporated to dryness and atrazine re-dissolved in 1.6 ml acetonitrile. The acetonitrile sample was injected into an HPLC.

#### **ELISA (enzyme linked immuno sorbent assay)**

The amount of chlorohydrolase (the first enzyme in the atrazine hydrolytic degradation pathway) was determined by ELISA applying an antigen against atrazine chlorohydrolase (Katz *et al.*, 2001). Biofilm was separated from the carrier by vortex (5 min in PBS+0.1% Tween 80). Cell disruption was done by incubation of the biofilm in 0.5 mg/ml lysozyme and 1% NP-40. The protein concentration was analyzed according to the Bradford method (1976) using Bio-Rad's protein assay reagent. Protein samples were diluted in coating buffer (0.05M carbonate-bicarbonate buffer, pH 9.6) to a final concentration of 0.1, 0.2, 0.5 and 1 mg/l protein. The assay was also conducted on a pure culture of *P.ADP*. The amount of chlorohydrolase in the biofilm extracted protein was calculated as a fraction of the pure culture reading.

#### **Model equations and numerical solution**

A detailed description of the homogeneous surface diffusion model developed is given elsewhere (Herzberg *et al.*, 2003a). A finite differential numerical solution was applied using MATLAB technical computing language (The MatWorks, Inc. v.5.2).

## Results and discussion

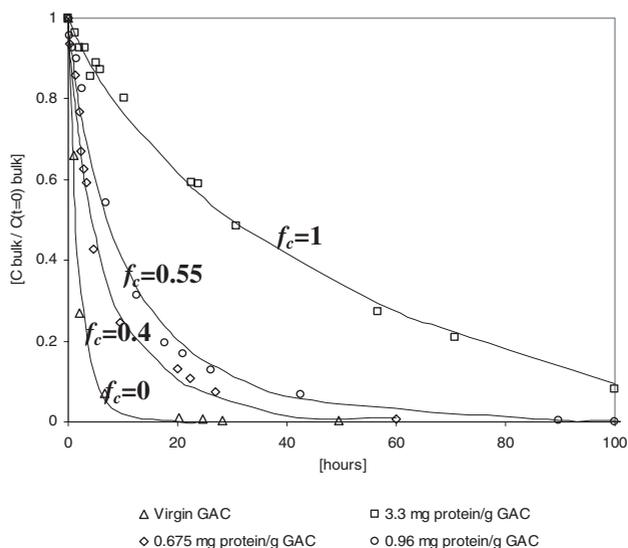
To show that BGAC is an advantageous reactor for atrazine remediation as opposed to other biofilm reactors, the aforementioned aspects were investigated: 1) atrazine adsorption to GAC under conditions of atrazine partial penetration in the biofilm, 2) higher atrazine degradation rates due to double flux of atrazine in the biofilm, and 3) increased stability of atrazine biodegradation under non-sterile anoxic conditions.

### Atrazine adsorption to GAC under conditions of atrazine partial penetration in the biofilm

Atrazine adsorption to GAC under conditions of partial penetration in an atrazine degrading biofilm can only occur in non-covered areas of the particle. In order to show that biofilm free areas exist on BGAC particles, adsorption kinetics were studied in batch experiments using GAC covered with different concentrations of a non-atrazine degrading biofilm (see Materials and methods). A homogeneous surface diffusion model (HSDM) (Weber and Smith, 1987; Furuya *et al.*, 1996) incorporating an additional biofilm layer where atrazine mass transfer occurs (Chang and Rittmann, 1987b) was used for data analysis. The model was modified to include partial biofilm coverage of the GAC.

Model parameter values, including hydrodynamic boundary layer mass transfer coefficient ( $k_p$ ), average pore diffusion coefficient ( $D_s$ ), average biofilm diffusion coefficient ( $D_b$ ), biofilm average density ( $r_b$ ), and biofilm coverage fraction ( $f_c$ ), were determined using sensitivity analysis on model and experimental results. Experimental and model adsorption results for the batch tests are given in Figure 1.

The results show that adsorption was strongly affected by the biofilm concentration. Using the sensitivity analysis it was found that only changes in the coverage fraction ( $f_c$ ) could give a good agreement between experimental and model results. Studying different values for the biofilm diffusion coefficient as well as biofilm density, hydrodynamic boundary layer mass transfer coefficient and average pore diffusion coefficient did not yield a satisfactory correlation (Herzberg *et al.*, 2003a). Epifluorescence microscopic pictures of DAPI (4',6'-diamidino-2-phenylindole) stained GAC particles used in the batch experiments revealed a patchy-like structure of the biofilm, and also confirmed that a greater area of biofilm coverage was observed with samples having higher biofilm concentrations.



**Figure 1** Experimental and model results for batch adsorption tests on GAC particles with different biofilm concentrations (lines for model results, symbols for experimental results). Biofilm coverage ( $f_c$ ) was determined by the model

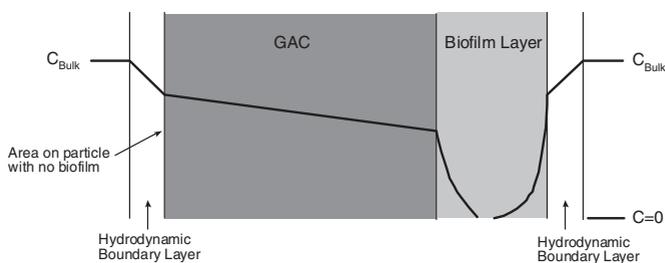
### Higher atrazine degradation rate due to double flux of atrazine in the biofilm

Establishing the patchy-like nature of the biofilm coverage and that atrazine adsorption occurs mainly in the non-covered areas of the GAC particles allows for concurrent atrazine desorption at the base layer of the biofilm, even under conditions of atrazine partial penetration in the biofilm. Under conditions of partial penetration, concurrent atrazine desorption may result in higher biofilm activity due to an increase in active biofilm surface area. To describe this phenomenon, a typical slice of the BGAC particle (Figure 2) consisting of both atrazine degrading biofilm areas and non-covered biofilm areas was defined and the total mass balance of atrazine in the reactor was modeled using a finite differential numerical solution (Herzberg, 2003).

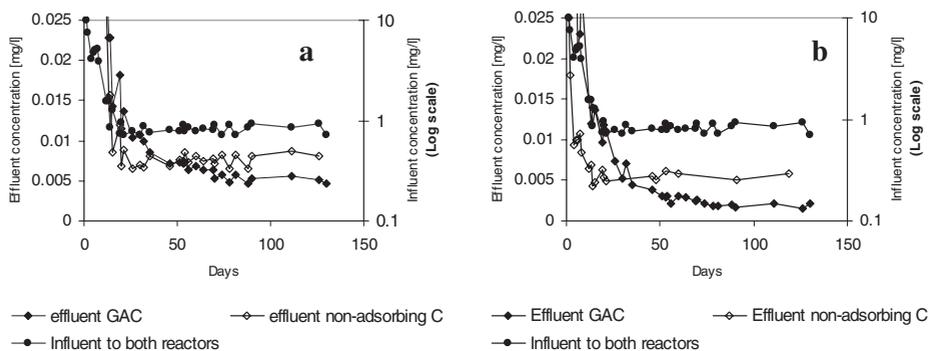
For model verification and comparison purposes, two fluidized bed reactors for atrazine degradation were operated: one with GAC as the carrier for the *P.ADP* biofilm and the other with non-adsorbing carbon (“Baker product”) as a carrier with the same physical characteristics as GAC. The reactors were operated under aerobic conditions with citrate as the electron donor and atrazine as a sole nitrogen source and at limiting atrazine concentrations (a deep biofilm with partial atrazine penetration). An equal biofilm concentration of 1.9 mg protein/g carrier was observed in both reactors at the beginning of the operation.

After a start-up period with a relatively high atrazine concentration of 25 mg/l, the influent atrazine concentration was reduced to concentrations typical of contaminated groundwater, 700–1,000  $\mu\text{g/l}$ . Following a transient time of higher atrazine effluent concentrations in the BGAC reactor (due to the release of pre-adsorbed atrazine), the atrazine effluent concentration stabilized at 2  $\mu\text{g/l}$  in the BGAC reactor vs. 5–6  $\mu\text{g/l}$  in the non-adsorbing carbon reactor, i.e. better performance of the BGAC as compared to the non-adsorbing carrier reactor. Mass balance calculations for atrazine showed that the amount of atrazine degraded in the BGAC reactor was higher by 2 orders of magnitude than the influent loading rate due to degradation of both influent and pre-adsorbed atrazine. Results from the double-flux model using similar operating conditions also showed the significant advantage of the BGAC reactor and confirmed that the double flux of the substrate is the reason for the higher activity observed in the BGAC reactor. Experimental and model results are given in Figures 3a and 3b.

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. 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 beyond the actual reactors’ operational periods to include an additional period, but here an identical biofilm concentration was assumed for the two reactors (1.2 mg protein/g carrier, which was the measured concentration in the BGAC reactor after 130 days). An influent atrazine concentration of



**Figure 2** Typical concentration profile in a slice of BGAC showing double atrazine flux in the biofilm: from the bulk and from the GAC



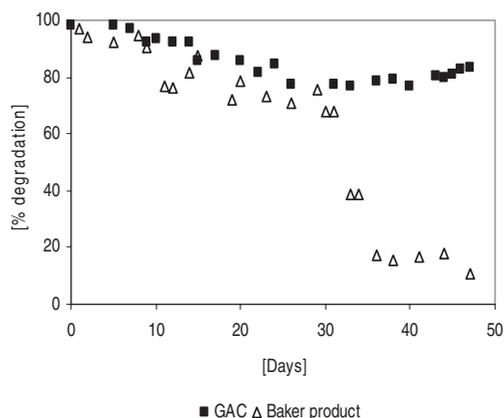
**Figure 3** Model (a) and experimental (b) results of atrazine influent and effluent concentrations in reactors

0.8 mg/l was used as input for both reactors, similar to the influent concentration during most of the experimental period. The model results showed steady state concentration of 4 and 8  $\mu\text{g/l}$  for the BGAC and Baker product reactors respectively. 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 (Herzberg *et al.*, 2003b).

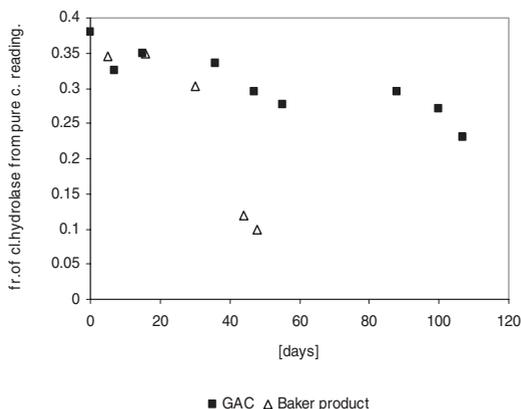
#### Increased stability of atrazine biodegradation under non-sterile anoxic conditions

In contrast to the stable atrazine biodegradation by *P.ADP* observed under aerobic conditions where atrazine was the sole nitrogen source, previous laboratory results under non-sterile conditions using a denitrifying FB reactor showed a gradual decrease in atrazine degradation efficiency with time (within 20–30 days) due to denitrifying bacterial contamination (Katz *et al.*, 1999, 2000, 2001). While in the earlier experiments sintered glass was used as the carrier for the biofilm, the present research study used GAC as a carrier in the anoxic reactor. It was assumed that GAC could provide a favorable microenvironment for the bacteria due to its characteristic adsorption-desorption mechanism (Herzberg *et al.*, 2003c).

The denitrifying BGAC reactor was operated at both high and low influent atrazine concentrations and results were compared to the fluidized bed reactor with the “Baker product” carrier. The results of the non-adsorbing carrier reactor demonstrated a similar pattern of atrazine degradation as in the sintered glass reactor, i.e. gradual deterioration in atrazine degradation efficiency, reaching a value of only 20% after 30 days. No significant deterioration in atrazine degradation was observed in the BGAC reactor during the entire experimental period of 4 months. For comparison purposes only the first 50 days are presented in



**Figure 4** Atrazine degradation efficiency in the reactors



**Figure 5** Chlorohydrolase fraction in the reactors

Figure 4. In addition, the chlorohydrolase fraction (the first enzyme in the atrazine hydrolytic pathway which was used as a measure of atrazine degradation ability) remained relatively constant in the BGAC reactor during the entire experimental period: between 0.4 and 0.25 after 120 days, as opposed to a sharp decrease in the non-adsorbing carbon reactor to as low as 0.1 after 35 days (Figure 5).

The retention of the atrazine degrading characteristics in the BGAC reactor as opposed to the non-adsorbing carrier reactors can probably be explained by the adsorption-desorption mechanism which characterizes this reactor. In the non-adsorbing carrier reactors under conditions of high biofilm thickness with the consequent substrate partial penetration (for all substrates), the deep layers of the biofilm starve and die, while foreign denitrifying bacteria with higher growth rate penetrate and out-compete *P.ADP*. In contrast, in the BGAC reactor the adsorption-desorption mechanism provides for a microenvironment which preserves the viability of the deep biofilm layers consisting mainly of the original *P.ADP* which were attached to the carrier during the start-up period. In addition, the chances for penetration and growth of non-atrazine degrading bacteria (including *P.ADP* lacking the plasmid) in the deeper layers of the biofilm are lower due to selective pressure favoring atrazine degrading bacteria. The flux of atrazine from the adsorbing carrier provides a nitrogen source and even a small energy source to these bacteria.

## Conclusions

Results from batch adsorption tests and modeling characterized the biofilm coverage of GAC particles as being patchy in nature. In the non-covered biofilm areas atrazine adsorption occurs even under conditions of partial penetration of atrazine in the biofilm. Internal flux of desorbed atrazine from the GAC to the base of the biofilm increases the active biofilm surface area as observed by lower effluent atrazine concentrations in a BGAC reactor as compared to a FBR with non-adsorbing carrier. Moreover, under non-sterile conditions and in the presence of external nitrogen compounds (nitrate), atrazine degradation stability was found to be higher using GAC as a biofilm carrier as opposed to a non-adsorbing carrier reactor that showed drastic deterioration within 30 days due to contamination of non-atrazine degrading bacteria.

## References

- Bradford, M.M. (1976). A rapid and sensitive method for the quantification of microgram quantities of protein utilizing the principle of protein-dye binding. *Anal. Biochem.*, **72**, 248–254.
- Burkart, M.R. and Kolpin, D.W. (1993). Hydrologic and land-use factors associated with herbicides and nitrate in near-surface aquifers. *J. Environ. Qual.*, **22**, 646–656.

- Chang, H.T. and Rittmann, B.E. (1987a). Mathematical modeling of biofilm on activated carbon. *Environ. Sci. Technol.*, **21**, 273–280.
- Chang, H.T. and Rittmann, B.E. (1987b). Verification of the model of biofilm on activated carbon. *Environ. Sci. Technol.*, **21**, 280–288.
- Crawford, J.J., Sims, G.K., Mulvaney, R.L. and Radosevich, M. (1998). Biodegradation of atrazine under denitrifying conditions. *Appl. Microbiol. Biotechnol.*, **49**(5), 618–623.
- de Souza, M.L., Wackett, L.P. and Sadowsky, M.J. (1998). The *atzaABC* Genes encoding atrazine catabolism are located on a self-transmissible plasmid in *Pseudomonas* sp. strain ADP. *Appl. Environ. Microbiol.*, **64**(6), 2323–2326.
- Dovantzis, K. (1986). *A mathematical model of the interaction between adsorption and biodegradation on granular activated carbon at low substrate concentrations*. Ph.D. thesis. Department of Environmental Sciences and Engineering, University of North Carolina at Chapel Hill.
- Ehrhardt, H.M. and Rehm, H.-J. (1989). Semicontinuous and continuous degradation of phenol by *Pseudomonas putida* P8 adsorbed on activated carbon. *Appl. Microbiol. Biotechnol.*, **30**, 312–317.
- Furuya, E.G., Chang, H.T., Miura, Y., Yokomura, H., Tajima, S., Yamashita, S. and Noll, K.E. (1996). Intraparticle Mass Transport Mechanism in Activated Carbon Adsorption of Phenols. *J. of Environ. Eng.*, **122**(10), 909–916.
- Giovanni, R. (1996). Water quality decreasing in Brittany streams: nitrates and example of two pesticides, atrazine and lindane. *Cybiuim.*, **20**(3), 143–162.
- Hanaki, K., Saito, T. and Matsuo, T. (1997). Anaerobic treatment utilizing the function of activated carbon. *Wat. Sci. Tech.*, **35**(8), 193–201.
- Herzberg, M. (2003). Ph.D. Dissertation, The Technion, Technical Institute of Israel.
- Herzberg, M., Dosoretz, C.G., Tarre, S. and Green, M. (2003a). Patchy biofilm coverage can explain the potential advantage of BGAC reactors. *Environ. Sci. Technol.*, **37**, 4274–4280.
- Herzberg, M., Dosoretz, C.G. and Green, M. (2003b). Modeling and Verification of Increased Biofilm Activity in BGAC Reactors. Submitted for publication to *Environ. Sci. Technol.*
- Herzberg, M., Dosoretz, C.G., Tarre, S., Minz, D. and Green, M. (2003c). Simultaneous removal of atrazine and nitrate using a biological granulated activated carbon (BGAC) reactor. Submitted for publication to *J. Chem. Technol. Biotechnol.*
- Katz, I., Dosoretz, C., Ruskol, Y. and Green, M. (1999). Simultaneous removal of nitrate and atrazine from groundwater. *Wat. Sci. Technol.*, **41**(4–5), 49–56.
- Katz, I., Green, M., Ruskol, Y. and Dosoretz, C. (2000). Characterization of atrazine degradation and nitrate reduction by *Ps. ADP*. *Adv. Environ. Res.*, **4**, 219–224.
- Katz, I., Dosoretz, C., Mandelbaum, R. and Green, M. (2001). Atrazine degradation under denitrifying conditions in continuous culture of *Pseudomonas* ADP. *Wat. Res.*, **35**(13), 3272–3275.
- Mandelbaum, R.T., Wackett, L.P. and Allen, D.L. (1993). Mineralization of the s-triazine ring of atrazine by stable bacterial cultures. *Appl. Environ. Microbiol.*, **59**(6), 1694–1701.
- Mandelbaum, R.T., Allen, D.L. and Wackett, L.P. (1995). Isolation and characterization of a *Pseudomonas* sp. that mineralized the s-triazine herbicide atrazine. *Appl. Environ. Microbiol.*, **61**(4), 1451–1457.
- Martinez, B., Tomkins, J., Wackett, L.P., Wing, R. and Sadowsky, M.J. (2001). Complete nucleotide sequence and organization of the Atrazine catabolic plasmid pADP-1 from *Pseudomonas* sp. Strain ADP. *J. Bacteriol.*, **183**(19), 5684–5697.
- Vink, J.P.M. and van der Zee, S.E.A.T.M. (1997). Effect of oxygen status on pesticide transformation and sorption in undisturbed soil and lake sediments. *Environ. Toxicol. Chem.*, **16**(4), 608–616.
- Weber, W.J. and Smith, E.H. (1987). Simulation and design models for adsorption processes. *Environ. Sci. Technol.*, **21**(11), 1040–1050.