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Kinetics of BTEX degradation in a packed-bed anaerobic reactor

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Abstract

The ever-increasing diversity of industrial activity is responsible for the discharge of compounds that are toxic or difficult to degrade into the environment. Some of the compounds found in surface and ground waters, usually deriving from the contamination of oil-based products, are benzene, toluene, ethylbenzene and xylenes (BTEX). To remove these compounds from contaminated water, a bench-scale horizontal-flow anaerobic immobilized biomass reactor, containing anaerobic biomass from various sources immobilized in polyurethane foam matrices, was employed to treat a synthetic substrate composed of protein, carbohydrates and BTEX solution in ethanol, as well as a BTEX solution in ethanol as the sole carbon source. The reactor removed up to 15.0 mg/l of each BTEX compound over a hydraulic detention time of 11.4 h. A first-order kinetic model fitted the experimental data well, showing correlation coefficients higher than 0.994. The apparent first-order coefficient values, k_1^{app}, ranged from 8.4 ± 1.5 day^{-1} for benzene to 10.7 ± 1.4 day^{-1} for *o*-xylene in the presence of ethanol, protein and carbohydrates, and from 10.0 ± 2.0 day^{-1} for benzene to 13.0 ± 1.7 day^{-1} for *o*-xylene in the presence of ethanol. The BTEX degradation rates estimated here were 10- to 94-fold higher than those found in reports on microcosm studies.

Abbreviations: A – cross-sectional area of the reactor; BTEX – benzene, toluene, ethylbenzene and xylenes; C – BTEX concentration at a given l/D *position;* C_r – residual BTEX concentration; D – diameter of the reactor; HAIB – horizontal-flow anaerobic immobilized biomass reactor; HDT – hydraulic detention time; k_1^{app} – apparent first-order coefficient; l – given position along the reactor length; L – length of the reactor; Q – liquid flow rate; R_{obs} – overall BTEX conversion rate; v_s – liquid superficial velocity; ε – bed porosity

Introduction

Benzene, toluene, ethylbenzene and xylenes are monoaromatic hydrocarbons commonly found together in crude oil and oil products such as gasoline. These compounds are also produced as bulk chemicals for industrial use as solvents and starting materials for the manufacture of pesticides, plastics and synthetic fibers (Harwood & Gibson 1997). They are important contaminants present in surface and ground waters, which usually originate from the leakage of underground petroleum storage tanks; spills at oil production wells, refineries, pipelines and distribution terminals; and industrial wastewaters.

Under proper conditions, microorganisms are able to degrade all of the BTEX compounds (Grbic-Galic & Vogel 1987; Heidrich et al. 2004; Kazumi et al. 1997; Nales et al. 1998; Phelps & Young 1999; Weiner & Lovley 1998) and the use of bioreactors for water decontamination can be a feasible alternative.

Pump-and-treat bioremediation by means of anaerobic reactors can provide suitable results for BTEX removal. This theme has been addressed in some bench-scale research projects with promising results for full-scale application (Chaudhuri & Wiesmann 1996; de Nardi et al. 2002). The scale-up and design of anaerobic bioreactors for BTEX removal requires reliable data on degradation rates for each compound, thus making the understanding of BTEX degradation kinetics essential. Nevertheless, data on the dynamics of BTEX removal in anaerobic bioreactors are scarce in the literature (Chaudhuri & Wiesmann 1996).

Most of the existing knowledge about the anaerobic degradation of aromatic hydrocarbons derived from microcosm studies or classical enrichment cultures. Microcosms are constructed by placing samples collected from the area under study in sealed vessels. If conditions are altered so as to encourage the growth of a specific organism aiming at its isolation, the microcosms are referred to as enrichment cultures (Johnson et al. 2003; Phelps & Young 2001). Column studies are carried out with sediment or aquifer material to simulate field conditions (Haag et al. 1991; Kuhn et al. 1985; Langenhoff et al. 1996; Weiner et al. 1998; Zeyer et al. 1986).

However, kinetic data obtained in microcosms or columns are not suitable for designing anaerobic reactors. The dynamics of the process, the transport phenomena, the hydrodynamic pattern, the diversity, structure and arrangement of the microorganisms are completely different in such engineered environments. Therefore, kinetic expressions that represent BTEX degradation in anaerobic reactors must be determined directly from bioreactor data.

This study aimed to estimate the kinetic parameters of the biochemical degradation of BTEX for immobilized cells in a packed-bed anaerobic bioreactor.

Materials and methods

A bench-scale horizontal-flow anaerobic immobilized biomass (HAIB) reactor was assayed, filled with 5 mm-side cube polyurethane foam matrices (23 kg/m^3 density and 95% porosity) for biomass attachment. The HAIB reactor consisted of a 100 cm-long (L) glass tube with a 5 cm-diameter (D), resulting in a L/D ratio of 20, and a total volume of 1995 ml. Samples were taken from five intermediate ports, four of which were located 20 cm from each other and the fifth one 5 cm from the outlet. Each reactor was also equipped with a gas collector system (Figure 1). The anaerobic conditions in the reactor were ensured by flushing N_2 into the affluent before BTEX addition and by maintaining the affluent reservoir connected to a gas bag with N_2.

The reactor was inoculated with a mixture of sludge taken from up-flow anaerobic sludge blanket (UASB) reactors treating paper recycling wastewater, domestic sewage and poultry slaughterhouse wastewater. The hydraulic detention time (HDT) was 11.4 h and the temperature was kept constant at 30 ± 1 °C.

Kinetic data of BTEX degradation were obtained by feeding the reactor either with BTEX solution in ethanol added to synthetic substrate or BTEX solution in ethanol as the sole carbon source. Ethanol was mixed in as a co-solvent since Brazilian gasoline contains, on average, 45% (v/v) of aromatic compounds and 20% (v/v) of ethanol used as a gasoline additive.

In the acclimation phase, the reactor was fed with synthetic substrate (Table 1) to promote the suitable development and adhesion of biomass in the packed bed.

After this phase, the BTEX solution in ethanol was added to the influent stream and the lipids were suppressed. BTEX concentrations were gradually increased for 65 days. Kinetic tests were

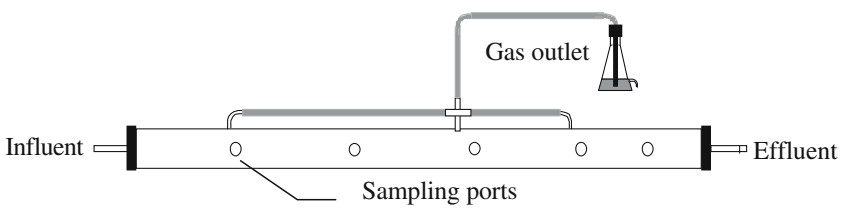

Figure 1. Scheme of the bench-scale HAIB reactor.

Table 1. Composition of the synthetic substrate

Constituent	% of COD	Source	Concentration
Protein	50	Meat extract	208 mg/l
Carbohydrates	40	Sucrose (20%)	36 mg/l
		Commercial starch (60%)	112 mg/l
		Cellulose (20%)	41 mg/l
Lipids	10	Soybean oil (emulsified with 3 detergent drops/l)	0.056 ml/l
Mineral salts	–	Solution of NaCl (50 g/l), $MgCl_2 \cdot 6H_2O$ (1.4 g/l) and $CaCl_2 \cdot 2H_2O$ (0.9 g/l)	5.0 ml/l

carried out with BTEX concentrations of about 5.0 and 10.0 mg/l. The reactor was then fed with the BTEX solution in ethanol (approximately 12.0 mg/l of each compound) as the sole carbon source, together with micro- and macronutrients (Table 2) for 20 days (de Nardi et al. 2005).

Kinetic models were adjusted to the experimental data of BTEX concentration taken along the length of the reactor (Table 3). The sampling ports were located at a length to diameter (l/D) ratio of 4, 8, 12 and 16. The profiles for each concentration under study were obtained at regular 2-day intervals.

The kinetic parameters were estimated from the mass balance in the heterogeneous reactor, considering a first-order kinetic model, plug-flow reactor (de Nardi et al. 1999) and steady-state condition:

$$R_{obs} = k_1^{app} \cdot (C - C_r) = \frac{-\varepsilon \cdot v_s}{D} \frac{d(C - C_r)}{d(l/D)} \quad (1)$$

In Equation (1), R_{obs} is the overall BTEX conversion rate ($M \cdot L^{-1} \cdot T^{-1}$), k_1^{app}, the apparent first-order coefficient (T^{-1}); ε, the bed porosity; v_s, the liquid superficial velocity ($L \cdot T^{-1}$); D, the diameter of the reactor (L); l, a given position along the reactor length (L); C, the BTEX concentration at a given l/D position ($M \cdot L^{-3}$) and C_r, the residual BTEX concentration ($M \cdot L^{-3}$). The residual concentration was inserted into the model since the BTEX concentrations did not reach zero in any of the experiments, making it necessary to normalize the first-order model. In general, the value of C_r is zero, a value to be attained when the length of the reactor tends to infinite ($l \to \infty$). However, in this case, C_r assumed values different from zero, depending on the compound.

The liquid superficial velocity (v_s) was calculated according to Equation (2):

$$v_s = \frac{Q}{\varepsilon \cdot A} \quad (2)$$

In Equation (2), Q is the liquid flow rate ($L^3 \cdot T^{-1}$) and A is the reactor's total cross-sectional area (L^2).

The reactor's cross-sectional area was 19.95 cm^2 and a bed porosity of 0.4 was adopted, as previously estimated (Zaiat et al. 2000). The liquid superficial velocity was kept constant at 8.8 cm/h throughout the experiment.

Equation (1) can be integrated, resulting in Equation (3):

$$(C - C_r) = (C_0 - C_r) \cdot e^{\frac{-k_1^{app} \cdot D}{\varepsilon \cdot v_s}(l/D)} \quad (3)$$

The apparent first-order coefficient values k_1^{app} were obtained for each BTEX compound by Equation (3), using the Levenberg–Marquardt non-linear regression method (Microcal Origin 5.0® software).

Table 2. Composition of micro and macronutrients

Constituent	Concentration (mg/l)	Constituent	Concentration (mg/l)
$NiSO_4 \cdot 6H_2O$	1.0	$KHPO_3$	8.5
$FeSO_4 \cdot 7H_2O$	5.0	K_2HPO_3	21.7
$FeCl_3 \cdot 6H_2O$	0.5	Na_2HPO_3	33.4
$CaCl_2 \cdot 2H_2O$	47.5	$NaHCO_3$	800.0
$CoCl_2 \cdot 6H_2O$	0.08	Urea	250.0
SeO_2	0.07		

Table 3. Average BTEX concentration along the length of the reactor

Compound	$l/D=0$	$l/D=4$	$l/D=8$	$l/D=12$	$l/D=16$
Synthetic substrate + BTEX solution in ethanol (≅5 mg/l)					
Benzene	5.6	2.6	2.4	2.1	1.8
Toluene	5.1	2.0	1.8	1.7	1.5
Ethylbenzene	4.9	1.6	1.5	1.3	1.3
o-Xylene	4.9	1.8	1.7	1.5	1.5
Synthetic substrate + BTEX solution in ethanol (≅10 mg/l)					
Benzene	10.6	4.9	4.5	4.4	4.1
Toluene	10.4	4.3	3.9	3.9	3.6
Ethylbenzene	10.0	3.6	3.1	3.1	2.7
o-Xylene	10.9	4.1	3.7	3.7	3.5
BTEX solution in ethanol (≅12 mg/l)					
Benzene	14.7	6.8	6.1	6.0	5.8
Toluene	12.9	5.1	4.6	4.5	4.4
Ethylbenzene	11.8	4.2	4.1	3.9	3.7
o-Xylene	12.2	4.8	4.7	4.4	4.3

The first-order kinetic model presupposes that the concentration of the substrate will reach zero when the length of the plug-flow reactor tends to infinite. However, in environmental systems and in bioreactors applied to wastewaters or contaminated waters treatment, this behaviour is rarely observed, since the substrate or contaminant concentration tends to a constant value, forming a plateau. So, in this case, the first-order kinetic model should be modified to fit such behaviour, previously observed by several researchers. According to Pavlostathis & Giraldo-Gomez (1991), the nature of C_r is not completely elucidated and it seems to be related to thermodynamic conditions and microbial species present in the reactor. Moreover, the residual concentration was inserted into the model since the BTEX concentrations did not reach zero in any of the experiments, making it necessary to normalize the first-order model.

The BTEX concentrations were determined by a static headspace gas chromatography method. Gas chromatography was performed on a 6869 HP gas chromatograph, with a 30 m×0.53 mm i.d. HP-1, film thickness of 2.65 μm (crosslinked methylsiloxane) fused-silica capillary column, equipped with a flame ionization detection (FID) system. H_2 was used as carrier gas. Injector and detector port temperatures were 250 and 300 °C, respectively; oven temperature 70 °C (hold 3 min), rate 4 °C/min to 110 °C (hold 3 min). Late-eluting compounds were removed by increasing the temperature to 220 °C for 5 min. Synthetic air (300 ml/min), H_2 (30 ml/min) and N_2 (30.8 ml/min) as make-up gas were set for best FID function. The split ratio was 40.

Results and discussion

Data on the reactor's performance under different experimental conditions were presented previously by de Nardi et al. (2005). Organic matter removal efficiencies varying from 96% to 99% and BTEX removal efficiencies ranging from 75% to 99% were achieved at HRTs over 11.4 h.

The adjustment of the kinetic expression to the experimental data presented correlation coefficients higher than 0.994 for all the profiles. Because the $(m+p)$-xylenes were not separated by the gas chromatography method, the meaning of the kinetic constant is different from that obtained for individual compounds. As the coefficient embodies the intrinsic kinetic coefficients for both compounds and the mass transfer fluxes, such value cannot be compared to the apparent coefficients obtained for a specific compound. Therefore, this value was not considered in order to avoid any misinterpretation.

The values of the apparent first-order coefficients k_1^{app} were the same at the different concentrations of BTEX solution in ethanol and synthetic substrate (Table 4). Nevertheless, the residual

concentrations C_r of BTEX increased as the influent concentrations varied (Table 5).

The BTEX apparent kinetic constants, estimated with BTEX solution in ethanol as the sole carbon source, were about 18% higher than the ones estimated in the presence of the other carbon sources (Table 4). Thus, the presence of other organic sources seemed unsuitable for BTEX biodegradation. Edwards & Grbic-Galic (1994) observed that the degradation of toluene and *o*-xylene was inhibited by the addition of organic substrates such as acetate, propionate, methanol, acetone, glucose, amino acids, fatty acids, peptone and yeast extract in microcosm studies.

o-Xylene displayed the highest degradation kinetic constant and benzene presented the lowest constant value. The kinetic constants of toluene and ethylbenzene showed similar values in the presence of the other carbon sources. However, the ethylbenzene degradation constant was higher than the one found with toluene in the absence of other carbon sources.

The overall conversion rates R_{obs} were calculated from Equation (1) and their analyses provide a comprehensive understanding of the kinetic behaviour of each compound. The rates were higher for BTEX solution in ethanol than those observed in the presence of synthetic substrate,

Table 4. Apparent first-order coefficients values (k_1^{app}) obtained for each compound

Compound	k_1^{app} (day^{-1})	
	Synthetic substrate + BTEX solution in ethanol[a]	BTEX solution in ethanol[b]
Benzene	8.4 ± 1.5	10.0 ± 2.0
Toluene	9.7 ± 1.1	11.3 ± 1.0
Ethylbenzene	9.8 ± 1.2	12.7 ± 0.2
o-Xylene	10.7 ± 1.4	13.0 ± 1.7

[a]Average of 4 observations.
[b]Values concerning a profile and parameter error.

Table 5. Residual concentration values (C_r) obtained for each compound

Compound	C_r (mg/l)[a]		
	Synthetic substrate + BTEX solution in ethanol (≅5 mg/l)	Synthetic substrate + BTEX solution in ethanol (≅10 mg/l)	BTEX solution in ethanol (≅12 mg/l)
Benzene	2.1 ± 0.3	4.3 ± 0.03	5.9 ± 0.2
Toluene	1.7 ± 0.1	3.8 ± 0.02	4.5 ± 0.04
Ethylbenzene	1.4 ± 0.01	2.9 ± 0.03	3.9 ± 0.1
o-Xylene	1.6 ± 0.03	3.6 ± 0.03	4.5 ± 0.1

[a]Values concerning a profile and parameter error.

Table 6. Overall degradation rate of each compound

Compound	R_{obs}* (mg/l day)	
	Synthetic substrate + BTEX solution in ethanol	BTEX solution in ethanol
Benzene	47.9	41.0
Toluene	60.1	62.2
Ethylbenzene	69.6	77.5
o-Xylene	68.5	71.5

*The overall reaction rate was calculated assuming an influent concentration of 10 mg/l of each compound.

Table 7. First-order coefficient values for BTEX compounds

Reference	Condition*	Compound	k_1 (day^{-1})
Aquifer soil microcosms			
Wilson et al. (1986)	M	Benzene	0.004**
		Toluene	0.047**
		Ethylbenzene	0.005**
		o-Xylene	0.005**
Salanitro et al. (1997)	M	Benzene	0.16–0.20
		Toluene, *m*-xylene	0.037–0.17
Hutchins et al. (1991a, b)	NR	Toluene	0.022–1.1
		Ethylbenzene	0.015–0.55
		o-Xylene	0.016–0.018
		(*m* + *p*)-Xylenes	0.067–0.38
Bregnard et al. (1996)	NR	Toluene	0.04**
		Xylenes	0.02–0.04**
Ball & Reinhard (1996)	NR	Ethylbenzene	0.57**
Lovley et al. (1994)	IR	Benzene	0.24**
		Toluene	0.12**
Groundwater microcosms			
Salanitro et al. (1997)	M	Toluene	0.09
Morgan et al. (1993)	NR	Benzene	0.022
		Toluene	0.046
		Ethylbenzene	0.016
		(*m* + *p*)-Xylenes	0.005
Enrichment cultures microcosms			
Edwards & Grbic-Galic (1992)	SR	Benzene	0.20**
Edwards et al. (1992)	SR	Toluene	0.04**
		o-Xylene	0.01–0.02**
Chaudhuri & Wiesmann (1995)	SR	Benzene	0.38–0.46
Natural attenuation			
Essaid et al. (2003)	M	Benzene	0.00065
		Toluene	0.19
		Ethylbenzene	0.00071
		o-Xylene	0.03
		(*m* + *p*)-Xylenes	0.0023
Column studies			
Patterson et al. (1993)	NR	Toluene	3.4
		Ethylbenzene	3.4
	SR	Toluene	3.4
Bioreactors studies			
This work	M	Benzene	8.4–10.0
		Toluene	9.7–11.3
		Ethylbenzene	9.8–12.7
		o-Xylene	10.7–13.0

*NR, SR, IR and M refer to nitrate-, sulfate-, and iron-reducing and methanogenic conditions.
**Calculated first-order (or pseudo-first order) rates taken from graphs published by Salanitro et al. (1997).

except for the benzene removal rate, which decreased by about 14% (Table 6). The overall rates of all the compounds were relatively high when compared with those obtained in the environment.

Volatile solids (VS) contents in the polyurethane foam matrices at L/D ratios of 4 and 16 were 0.55 and 0.19 g/g foam, respectively.

Most kinetic studies of BTEX degradation have been carried out in microcosms containing indigenous soil or groundwater as biomass sources at temperatures ranging from 12 to 24 °C (Table 7). Under such conditions, the BTEX degradation rates are very low. The use of groundwater to determine biodegradation potential may lead to erroneous results because non-native microorganisms are often associated with wells (Thomas & Ward 1989). The BTEX degradation rates, estimated here at a temperature of 30 °C, were 10- to 94-fold higher than those found in microcosm studies using soil samples taken from petroleum-contaminated aquifers (Ball & Reinhard 1996; Hutchins et al. 1991a, b; Lovley et al. 1994; Salanitro et al. 1997). These degradation rates were even higher (125- to 450-fold) when compared with microcosm studies involving ground waters (Morgan et al. 1993; Salanitro et al. 1997). Nevertheless, in a study of BTEX biodegradation in aquifer material using large-scale columns, Patterson et al. (1993) estimated first-order degradation rates of 3.4 day^{-1} for toluene and ethylbenzene. This value is quite similar to the ones found in this work. Shim & Yang (1999) observed that the immobilized cells in the bioreactor had 9- to 75-fold higher BTEX degradation rates than those of free cells in serum bottles.

Packed-bed reactors presented better performance than those attained in microcosms due to high cell density, development of a biomass acclimated to BTEX degradation in the reactor (Shim & Yang 1999), minimization of the liquid-phase mass transfer resistance (Sarti et al. 2001) and a suitable hydrodynamic pattern (Zaiat et al. 1997).

Conclusions

The first-order kinetic model properly represents the anaerobic degradation of BTEX with apparent first-order coefficient values k_1^{app} ranging from 8.4 ± 1.5 day^{-1} for benzene to 10.7 ± 1.4 day^{-1} for *o*-xylene in the presence of ethanol, protein and carbohydrates, and from 10.0 ± 2.0 day^{-1} for benzene to 13.0 ± 1.7 day^{-1} for *o*-xylene in the presence of ethanol.

High overall conversion rates of more than 40 mg/l day were observed for all the compounds, demonstrating the feasibility of the pump-and-treat bioremediation procedure using packed-bed anaerobic reactors.

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