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Modeling the biodegradation kinetics of aromatic and aliphatic volatile pollutant mixture in liquid phase

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HIGHLIGHTS

- Biodegradation of complex mixtures of VOCs was evaluated.
- Different combination of MEK, MIBK, toluene, o-xylene and ethyl benzene were used.
- A general mixed-substrate biodegradation model was developed.
- Model incorporates self inhibition and various interactions between compounds.
- Model predicted biodegradation of mixtures of similar/dissimilar VOCs was satisfactory.

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ABSTRACT

Volatile Organic Carbon (VOC) emissions from industries typically consist of a mixture of compounds of different chemical properties. The biodegradation kinetics of individual VOCs often get affected in the presence of other VOC species. In the present study, biodegradation kinetics of different multiple substrate mixtures of common industrial ketones viz. methyl ethyl ketone (M) and methyl iso-butyl ketone (B); and mono-aromatic VOCs such as toluene (T), ethyl benzene (EB) and o-xylene (X) were studied. Acclimatized aerobic bacterial consortium was used for the biodegradation study. A general mixed-substrate biodegradation model was developed which can describe the biodegradation kinetics of common industrial VOCs when present as a mixture, incorporating biokinetic parameters obtained from single substrate biodegradation studies. This model also employs a parameter for interaction effect, which may be obtained from biodegradation studies with binary mixtures. Three types of basic inhibitions, possible in the biodegradation of any mixture i.e. (i) self-substrate inhibition, (ii) interactive inhibition among VOCs of similar chemical nature and (iii) inhibition due to dissimilar VOC species, are considered in the general model. The performance of the proposed model was evaluated using the experimental data obtained from a previously published work, as well as from relevant data reported in the literature. High *E*-values obtained consistently for the simulations indicated good performance of the proposed model. This general model can be used for simulating the biodegradation of mixtures of similar/dissimilar VOCs and may be helpful in the optimal design of biological systems treating multiple VOCs.

1. Introduction

Industrial VOC emissions consist of compounds of different chemical nature. Paint manufacturing and application processes are among the major source of industrial VOC emissions. Though exact chemical constituents of these emissions may vary among different paint industries, the predominant components are aliphatic ketones such as methyl ethyl ketone, mono aromatic compounds such as toluene (T) and some low molecular weight alkyl alcohols such as butyl or propyl alcohol etc. Five VOC species i.e. methyl ethyl ketone (M), methyl iso-butyl ketone (B), toluene (T), ethyl benzene (EB) and o-xylene (X) account for 75–80% of the total VOC load in these emissions. These compounds also constitute major part of the VOC emission from ink, glue and rubber manufacturing units. Most of the above mentioned industries generally have a proper wastewater treatment facility, with activated sludge process being the most common technique adopted. However, these VOCs being volatile in nature, unlike other wastewater pollutants, tend to escape from the aeration tank to the atmosphere. A treatment technique which can combine both wastewater and air emission treatment such as rotating biological contactors may be the appropriate choice in the coming future with stricter VOC emission norms [1].

There have been a number of scientific studies on the biodegradation of mixtures of VOCs of similar chemical nature, such as

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aliphatic ketones and common monoaromatic VOCs. Biodegradation of compounds such as benzene, T, and EB has been reported by previous researchers [2,3]. Performances of biotrickling filter and biofilter for different VOC mixtures were reported earlier [4,5]. Uninhibited biodegradation kinetics of toluene and benzene with specific *Pseudomonas* strains was studied by Reardon et al. [6]. All these studies reported how the presence of one particular VOC species affects the biodegradation of other VOCs present in the mixture [7,8]. A proper knowledge on how constituents of different VOCs, commonly present in industrial VOC emissions, interact with each other is critical for optimized design of biological treatment systems [9,10]. However, studies on the biodegradation kinetics of VOCs of different chemical nature are limited.

Studies by Monod on microbial growth kinetics highlighted the non-linear pattern of microbial growth [11]. Subsequent works of Haldane and Levenspiel [12,13] emphasized the inhibitory effect of high substrate concentration on microbial growth rate. The microbial growth kinetics derived by Haldane from his earlier more generalized inhibition model [14], assumed the formation of inactive enzyme substrate complexes at high substrate concentration as the main cause of observed substrate inhibition. A different mechanism through which substrate inhibition may affect the rate of microbial growth was described by Edwards in 1970 [14]. However, this model was not applicable to all cases universally. Alagappan and Cowan [15] reported in detail how the intrinsic toxicity of solvents such as toluene can affect the biodegradation. They explained how toxicity of common industrial organic solvents such as methanol and toluene is closely related to the cell wall toxicity. Currently, several multiple substrate bio-kinetic models are available which can describe the biodegradation kinetics of common environmental pollutants [2]. Among the common multiple substrate biodegradation models, competitive inhibition of substrates of similar chemical nature such as methanol and ethanol or M and B were reported in literature [16,17]. Non-competitive and uncompetitive inhibition models for compounds of chemical, structural or alosteric similarity are also reported [18,19]. So far, a general model frame work which incorporates (i) self inhibition (ii) inhibition among chemically similar substances and (iii) inhibition and interaction among chemically dissimilar substances in a complex mixture of pollutants is not available.

The present study attempts to understand biodegradation kinetics of chemically dissimilar VOC mixtures viz. aliphatic ketone and mono-aromatic VOC mixtures. A generic model was developed to describe the biodegradation of systems, incorporating three types of basic inhibitions possible in such a mixture: (i) substrate inhibition of individual VOC species, (ii) interactive inhibition which may or may not be competitive among VOCs of similar chemical nature and (iii) inhibition due to dissimilar VOC species present in the mixture. The model performance was evaluated over several combinations of such mixtures with satisfactory results. The performance of the proposed model was also evaluated using the data from three earlier studies on biodegradation of mixtures of chemicals of different chemical nature available in literature.

2. Materials and methods

2.1. Enrichment of microbes

An acclimatized microbial culture was prepared by using target chemical/s i.e. M, B, T, EB and X, as the sole carbon source. The culture was initially acclimatized with MEK and subsequently with toluene [20,21]. To begin the enrichment process, activated sludge was collected from the nearby sewage treatment plant (Nesapakkam, Chennai, Tamil Nadu). The culture was acclimatized with the target pollutants in minimal salt medium (MSM). Composition of MSM used in the present study is as follows (quantities of chemicals are given in g/L in parentheses): K_2HPO_4 (0.8), KH_2PO_4 (0.2), $CaSO_4{\cdot}2H_2O$ (0.05), $MgSO_4$ – $7H_2O$ (0.5), $(NH_4)_2SO_4$ (1.0), $FeSO_4$ (0.01) in distilled water. After the addition of all the salts, pH of the MSM was 6.7.

2.2. Analytical procedures

2.2.1. Measurement of cell density in liquid phase

Growth of microbes was monitored in terms of optical density (OD), which was measured by turbidimetric measurement using a spectrophotometer at 540 nm. A standard curve was made by plotting the OD values of samples of known bacterial concentration. Bacterial concentration was obtained by filtering known volume of these solutions through 0.45-μm filter paper followed by measuring the corresponding weight of the dried cells [2]. Corresponding absorbance was measured at 540 nm using a UV–Vis spectrophotometer (Techcomp, UK).

2.2.2. Gas chromatographic analysis

Perkin Elmer Clarus 500 gas chromatograph with flame ionization detector (GC-FID) was used for analyzing residual VOC concentrations in liquid samples. The GC was equipped with an auto sampler, an on-column, split/split less capillary injection system, and a capillary column (Perkin Elmer Elite (PE)-624, 30 m × 0.53 mm × 0.5 mm film thickness). A temperature ramp of 50 °C to 140 °C was used with temperature rise of 5 °C per min. Injector and detector temperature were maintained at 190 °C and 300 °C, respectively. Nitrogen was used as the make-up and carrier gas at flow rates of 60 and 1.0 mL/min, respectively [2]. Standard graphs for different solvents were prepared individually by injecting known amounts of respective compound into a sealed reagent bottle equipped with Teflon septum as per the standard method. The aqueous samples were extracted with n-Hexane (1:1 ratio) for the analysis. Liquid samples were then transferred to GC vials and was analyzed by GC-FID [20].

2.3. Batch biodegradation studies

Serum bottles of 125 mL capacity sealed with silicone/Teflon septum and aluminum crimps were kept in a BOD orbital shaking incubator (REMI, India) at 150 rpm at 30 °C, during the batch experiments. Each serum bottles contained fifty milliliters of sterile MSM. Before the addition of organic solvents, the serum bottles were purged with pure oxygen for 1–2 min to ensure the overhead space (75 mL) contains pure oxygen. Liquid samples (5 mL each) were withdrawn at discrete time intervals. Two milliliter of each sample was centrifuged (REMI, India) in a closed Eppendorf centrifuge tube of 2 mL capacity at 10000 rpm for 2 min in order to remove microbes. Supernatant was then utilized for GC-FID analysis. Rest 3 mL of each sample was used for measuring optical density. Ten milliliter of pure oxygen was injected in the headspace of the serum bottle at each sampling interval. An equilibration time of 4 h after the addition of the solvents was given to attain stable initial concentrations, which was then followed by an additional equilibration time of 10 min after the addition of inoculum. The initial concentrations were observed at the end of the second equilibration period. All the batch studies were conducted under aerobic conditions (dissolved oxygen levels remained above 3 mg/L) and without any pH control (pH remained in the range of 6.2–6.9). The theoretical oxygen demand, the actual oxygen supplied and the theoretical carbon di-oxide production for various batch systems were calculated (given in Appendix-1). Purpose of conducting various batch degradation studies and corresponding details are presented in Table 1. GC–MS analysis of the gas samples and liquid were carried out to confirm mineralization as well as to look-out for possible metabolites once the reactor attained steady