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Removal kinetics of acetone and MIBK from a complex industrial wastewater by an acclimatized activated sludge

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Abstract

Removal rates of acetone and methyl isobutyl ketone (MIBK) were determined singularly and in combination in batch experiments employing an acclimatized activated sludge from a pilot system treating an organic chemical manufacturer industrial wastewater, as well as during the course of operation of the pilot system. Both acetone and MIBK removals were described by first-order removal kinetics. Acetone, as a single substrate, was biodegraded at a rate of 1.7 day^{-1}. MIBK was biodegraded, during the single-substrate experiments, at an observed rate of 2.23 day^{-1}. Relative to the control (no spike) experiments, acetone removal was augmented by a factor of 3 during the acetone spike, with an observed biomass-specific removal rate of 0.0023 L/mg VSS day. MIBK removal during an MIBK spike was also enhanced by a factor of 2, and the greatest biomass-specific removal rate of MIBK was observed during the acetone spike of 0.0019 L/mg VSS day. The observed rates were approximately 3 orders of magnitude greater than the observed rates in the pilot scale system. MIBK exerted a synergistic effect on the acetone-removal rate while acetone exerted an inhibitory impact on the MIBK-removal rate.

Keywords: Industrial wastewater; Acetone; MIBK; Activated sludge; Biodegradation kinetics; Extant; Intrinsic

1. Introduction

The fate of specific organic chemicals during biological treatment is of great importance. Determining if the compound would be biodegraded, volatilized, or sorbed onto sludges is vital to properly design treatment systems. In general, there is substantial information regarding the effectiveness of biological degradation of a variety of industrial effluents, but these are based upon the typical surrogate parameters such as COD, BOD, and TKN. The presence of volatile organic compounds (VOC) can present additional challenges.

It has been reported by several authors [1–5] that acetone is a readily biodegradable substrate. Gaudy et al. [6] and Young et al. [2] reported many years ago that acetone could be readily biodegraded by conventional activated sludges in laboratory testing. Eliosov et al. [7] also investigated acetone removal from two different municipal treatment works activated sludges and found substantial removal. Bhattacharya et al. [8] observed that the removal of acetone in a spiked toxic cocktail with other volatile organic compounds (VOC) in a pilot scale-activated sludge system. Yet, despite the overwhelming reports of acetone biodegradation, there is contradictory evidence to these reports. Robinson et al. [9] documented that an industrial-activated sludge treatment system was unable to biodegrade acetone, which was used at the site. Gerhold and Malaney [10] found that acetone was resistant to biological removal during laboratory testing using three different activated sludges. Acetone was also reported to act as an inhibitor of biochemical processes [11,12]. Zwiener and Frimmel [13] observed that acetone was not biodegraded during the course of experimentation with a study using an activated sludge, oxic biofilm reactor, and an anoxic biofilm reactor.

What is of interest is the impact of mixtures of these VOC and others, and the effect upon biodegradation. The wide disparity in the biodegradability of specific organics in the literature can be attributed in part to the wastewater complexity (i.e. the presence of other substrates) which may exert synergistic or inhibitory effects. Yet, despite the information regarding the biodegradation of VOCs in mixtures, there is a lack of specific kinetic data (i.e. biokinetic coefficients) [14,15]. The purpose of

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Nomenclature

C	liquid chemical concentration ($M L^{-3}$)
ΔC	concentration difference across the film ($M L^{-3}$)
D	coefficient of molecular diffusion of chemical in the film ($L^{-2} t^{-1}$)
DI	de-ionized water
GC	gas chromatography
HRT	hydraulic retention time (t)
K	first-order exchange constant ($L t^{-1}$)
k	maximum biomass-specific substrate-biodegradation rate ($M_s M_x^{-1} t^{-1}$)
K_L	overall mass-transfer coefficient for the liquid phase ($L t^{-1}$)
K_{ow}	octanol/water partition coefficient
K_s	Monod half-velocity substrate concentration ($M_s L^{-3}$)
K_v	volatilization rate constant (t^{-1})
MDL	method detection limit
MIBK	methyl isobutyl ketone
MLTSS	mixed liquor total suspended solids ($M_x L^{-3}$)
MLVSS	mixed liquor volatile suspended solids ($M_x L^{-3}$)
MSD	mass selective detection
N	flux ($M L^{-2} t^{-1}$)
P/H	liquid phase concentration in equilibrium with the gas phase concentration in accordance with Henry's Law constant ($M L^{-3}$)
sTKN	soluble total Kjeldahl nitrogen ($M_N L^{-3}$)
S	substrate concentration ($M_s L^{-3}$)
S_0	initial substrate concentration ($M_s L^{-3}$)
SRT	solids retention time (t)
t	time (t)
TKN	total Kjeldahl nitrogen ($M_N L^{-3}$)
TSS	total suspended solids ($M_x L^{-3}$)
VOC	volatile organic compounds
VSS	volatile suspended solids ($M_x L^{-3}$)
X	biomass concentration ($M_x L^{-3}$)
z	film thickness (L)

this study was to evaluate and determine kinetic coefficients for the removal of acetone and MIBK from a complex industrial wastewater, which contained significantly greater concentrations of these VOCs, on the order of mg/L, compared to those reported in previous studies.

2. Materials and methods

2.1. Acclimatized biomass

Fig. 1 displays the pilot scale system set up. The pilot scale-suspended growth activated sludge was fed the effluent from an existing aerobic thermophilic bacterial consortium that was used to treat the organic chemical manufacturer wastewater. The influent wastewater was characterized by containing varying concentrations of acetone and MIBK. Samples of

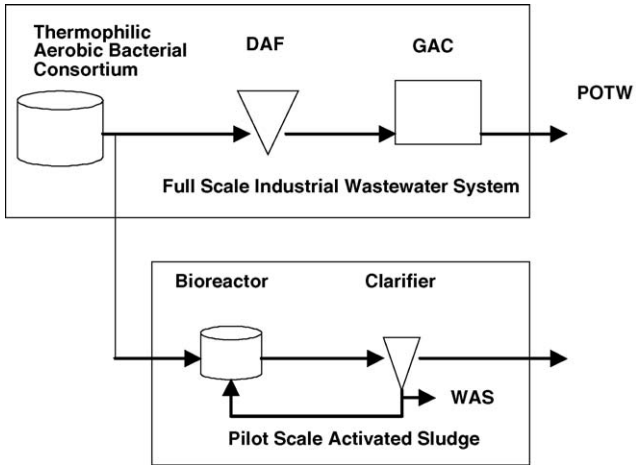

Fig. 1. Flowsheet for full scale and pilot scale wastewater treatment systems.

acclimatized biomass were taken directly from the return activated sludge of the operating pilot scale-activated sludge system [16,17].

2.2. Chemical reagents

Chemical grade reagents of acetone and MIBK were utilized. Stock solutions were made using de-ionized (DI) water to final concentrations of acetone of 396 mg/L and MIBK of 80 mg/L which were utilized as the spikes for the volatilization and single-substrate experiments.

2.3. Volatilization experiments

Two-hundred and fifty millilitres of Erlenmeyer flasks were filled with 100 mL of DI water and inactive biomass (i.e. active biomass that was subjected to a biocide and confirmed inactive by continuously measuring the oxygen-uptake rate until the oxygen-uptake rate was measured to be zero). The samples were then spiked with a stock solution of acetone, stoppered with a foam plug, and placed on an orbital shaker set to rotate at 200 rpm. At intervals of 15 min, the orbital shaker was halted, and samples were quickly removed and sampled for biomass and VOC concentrations in the liquid phase. The shaker was restarted and the sampling program continued until all samples were taken. A similar experiment was conducted with the exception that MIBK was used instead of acetone. All samples were stored in 40 mL VOC vials with no headspace and refrigerated at 4 °C prior to analysis.

2.4. Biodegradation experiments

2.4.1. Pilot scale VOC removal

The influent and effluent of the pilot scale-activated sludge system were sampled weekly and stored in 40 mL VOC vials with no headspace. The samples were stored at 4 °C before undergoing analysis in accordance with US EPA 1624 [18].

2.4.2. Laboratory removal

These were set up similar to the volatilization experiments with the exception that acclimatized biomass from the pilot scale-activated sludge system was used instead of DI water. The initial and final mixed liquor total suspended solids (MLTSS) in the flasks were measured. The acclimatized, active biomass samples were measured for the initial concentrations of each VOC and were found to be at the method detection limits (MDL) of 10 μg/L for acetone and 5 μg/L for MIBK prior to commencing the experiments. For the multiple-substrate experiments, four separate systems were set up using 90, 225, 450, and 900 mL of the return activated sludge from the aforementioned pilot scale system and topped up to 1800 mL with the influent wastewater. Then to determine the impact of the background organics upon the removal rate of the specific VOC, pure VOC was pipetted directly into the system, resulting in the measured initial VOC concentrations of acetone in the acetone spike in the range of 220–270 mg/L and 210–430 mg/L of MIBK in the MIBK spike. Sampling was conducted by withdrawing the mixed liquor directly from the system and storing in a 40 mL VOC vial, with no headspace. All samples were stored at 4 °C prior to undergoing analysis in accordance with US EPA 1624 [18]. A control experiment was also conducted were neither acetone nor MIBK were spiked to compare the removal rates.

2.5. Single-solute chemical analysis

Samples for the single-solute VOC concentrations were transferred to gas chromatography (GC) vials and allowed to sit for at least 15 min to ensure compounds in solutions were in equilibrium with the concentrations in the headspace. The samples then underwent headspace analysis in a GC with a split/splitless inlet, mass selective detection (MSD) and a DB-5 column (30 m × 250 μm, 0.2 μm film thickness). The initial oven temperature was 40 °C and the initial time of 2.5 min. The oven ramp temperature was 40 °C/min with a final oven temperature of 280 °C. The inlet temperature was 150 °C and the split ratio was 2:1 with a 50 μL injection volume. A helium flow of approximately 1.6 mL/min was used. The MSD parameters used were a MSD transfer line heater temperature of 300 °C, MS quad temperature of 150 °C, and the MS source temperature of 220 °C with tuning set to the standard spectral autotune. Prior to analysis of the volatilization and biodegradation single-solute samples, stock solutions of acetone and MIBK were run through the system and calibration curves generated to correlate the peak area versus concentration data.

2.6. Total suspended solids

Total suspended solids (TSS) were determined by vacuum filtering a pre-measured volume of sample through a pre-weighed Whatman No. 5 filter paper. The filter paper was then placed in an oven to dry overnight to constant weight.

3. Results and discussion

3.1. Overall system performance

Table 1 displays the results obtained from the operational performance of the pilot scale-activated sludge system. The results shown here indicate that the activated sludge system experienced loadings ranging from 0.3 to 14.8 g acetone/kg volatile suspended solids VSS day, and MIBK loadings ranging from 0.67 to 5.3 g MIBK/kg VSS day. As shown, substantial removal of acetone and MIBK was observed throughout the course of the activated sludge operation. This is even more remarkable given the variability in the influent wastewater concentrations throughout the course of the study. This is highlighted in Fig. 2, which displays the measured influent and effluent concentrations of the pilot scale system. The system consistently exhibited virtual complete removal of acetone and MIBK. It was previously determined that biodegradation was the primary pathway of the VOC removal accounting for the bulk of the acetone and MIBK disappearance (approximately 90% by mass) and volatilization accounting for approximately 10% by mass, of the VOC removal from this system [16]. These results clearly demonstrated that the biological sludges in this system were acclimatized to the wastewater matrix and had been able to biodegrade acetone and MIBK. It must be additionally noted that this complex wastewater did not only comprise of the readily biodegradable VOC such as acetone and MIBK, but also varying concentrations of aniline, 2-mercaptobenzothiazole, diphenylamine, and toluene were also present [17]. The characterization of this wastewater revealed that only 36% of the influent wastewater-dissolved organic carbon concentration could be accounted for by the total VOC and semi-volatile organic compounds [17], that highlights the complexity of this wastewater matrix.

Table 1
Operating conditions of the pilot scale-activated sludge system

Operating stage	HRT days	SRT days	Average acetone loading g acetone/kg VSS day (no. of samples)	Average acetone effluent (μg/L)	Average MIBK loading g MIBK/kg VSS day (no. of samples)	Average MIBK effluent (μg/L)
1	5.4	31.4	14.4 ± 7.6 (5)	10 ± 1	2.1 ± 1.6 (5)	5 ± 0
2	4.3	20.6	5.8 ± 7.0 (9)	10 ± 0	1.8 ± 1.5 (9)	5 ± 0
3	3.0	19.7	1.4 ± 1.9 (4)	15 ± 9	0.67 ± 0.60 (4)	5 ± 0
4	2.7	14.5	2.3 ± 2.0 (4)	14 ± 6	2.4 ± 1.6 (4)	5 ± 0
5	2.2	13.4	0.3 ± 0.5 (5)	11 ± 2	1.1 ± 0.9 (5)	6 ± 2
6	1.9	17.2	12.7 ± 2.6 (5)	10 ± 0	4.4 ± 3.1 (5)	5 ± 0
7	2.3	6.3	14.8 ± 7.9 (6)	636 ± 720	5.3 ± 3.7 (6)	49 ± 42

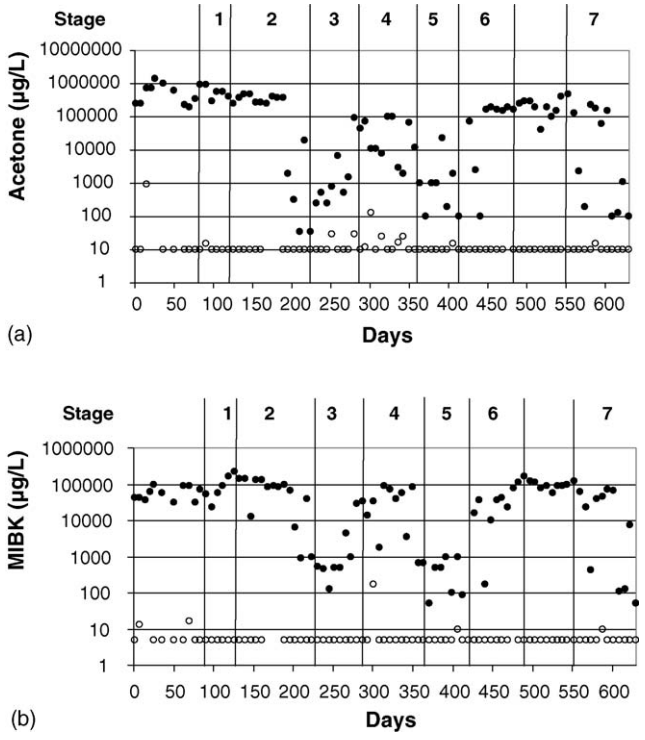

Fig. 2. Influent (●) and effluent (○) acetone, and MIBK concentrations during the operation of the pilot scale-activated sludge system.

In review of Table 1, the loadings to the system observed here are greater than those that would be experienced in a pulp mill, as described by Barton et al. [19] with 2.6 g acetone/kg VSS day and 0.13 g MIBK/kg VSS day. It should be further noted that in the pulp mill effluent investigation by Barton et al. [19], methanol comprised the single largest contaminant, with acetone being approximately 3% of the initial methanol concentration, and MIBK being less than 1% of the initial methanol concentration. Methanol is a known readily biodegradable material to the extent that it is commonly used as a carbon substrate for denitrification processes [20].

The breakthrough of acetone and MIBK observed in the pilot scale system, as displayed in Table 1, coincided with the operation of the system at significantly short solids retention time (SRT) of 6.3 days. During this operating stage, the loss of nitrification was observed, as evidenced by the comparability of the measured effluent ammonia and soluble total Kjeldahl nitrogen (sTKN) concentrations of 45 and 82 mg/L, respectively, to the influent ammonia and sTKN concentrations of 42 and 109 mg/L.

3.2. Single-solute removal

3.2.1. Acetone removal

Fick's first law of diffusion can be utilized to describe the flux of volatile compounds across the air–water interface. The equation may be presented as follows:

$$N = K\Delta C \tag{1}$$

where N is the flux (g/cm^2 s), $K = D/z$, the first-order exchange constant (cm/s), D the coefficient of molecular diffusion of chemical in the film (cm^2/s), z the film thickness (cm), and ΔC the concentration difference across the film (g/cm^3).

Since the atmospheric concentration of the chemical is low, the transfer coefficient is independent of the value of the Henry's law constant, so the gas phase can be disregarded in the overall mass-transfer rate, thus allowing Eq. (1) to be modified at steady state to be:

$$N = K_{\mathrm{L}}\left(C - \frac{P}{H}\right) \tag{2}$$

where K_{L} is the overall mass-transfer coefficient for the liquid phase (cm/s), C the liquid chemical concentration (g/cm^3), and P/H the liquid-phase concentration in equilibrium with the gas-phase concentration in accordance with Henry's Law constant (g/cm^3), and upon integration gives the concentration at any time (t):

$$C = C_0\,\mathrm{e}^{-K_{\mathrm{v}}t} \tag{3}$$

where K_{v} is the volatilization rate constant. Thus, a plot of $\ln(C/C_0)$ versus time would result in a straight-line relationship with the slope being equivalent to the rate of volatilization (K_{v}) for this set of experiments.

As mentioned earlier, volatilization of acetone was determined from both DI water and inactive biomass matrices, and the results were subjected to statistical analysis, which determined that there was no significant difference between these two media at the 99.9% confidence level using the student t-test. Acetone has a very low octanol/water partition coefficient, K_{ow}, of 0.575 [21]. The observation that acetone is not greatly adsorbed onto suspended solids found here is in agreement with the reports in the literature [6,8,15,16]. The data obtained were used to describe the volatilization of acetone from this experiment, with a first-order rate (K_{v}) constant of 0.58 day^{-1} ($r^2 = 0.66$, data not shown).

The next series of experiments were conducted to determine the degree of biodegradation of acetone by an acclimatized activated sludge. As mentioned elsewhere [16,17] and shown above, the activated sludge utilized as seed had a demonstrated ability to biodegrade acetone and MIBK down to the MDL of 10 μg/L for acetone and 5 μg/L for MIBK. The return activated sludge TSS in the pilot scale system at the time of the biodegradation studies was 5430 mg/L and the VSS:TSS ratio for the system was 0.7 while the acetone and MIBK concentrations in the initial seed sludge were at their respective MDLs.

At the time that the biomass seed was taken from the pilot scale-activated sludge system, the influent concentration and loading of acetone was 140 mg/L and 21 g acetone/kg VSS day.

Biodegradation is commonly described by expressing the Monod equation [22] as:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\frac{kSX}{K_{\mathrm{S}} + S} \tag{4}$$

where S is the substrate concentration in mg/L, t the time, k the maximum substrate-utilization rate in mg/L day, X the biomass in mg/L, and K_{s} the Monod half-velocity substrate concentration in mg/L.

When the substrate concentration is significantly less than the saturation constant (i.e. $K_s \gg S$), Eq. (4) takes the form of:

$$\frac{dS}{dt} = -\frac{kSX}{K_s} = K'SX \quad (5)$$

where $K' = k/K_s$, and this is a first-order rate with respect to substrate and biomass concentrations. This form of the equation has been demonstrated in the literature to accurately reflect the removal of VOCs such as acetone and MIBK [6,19,23–25]. It is interesting to note that Urano and Kato [24] and Robinson et al. [9] both report acetone as following first-order biodegradation kinetics at high initial acetone concentrations on the order of 100 mg/L and up to 630 mg/L, respectively. This is substantially greater than both the K_s value of 1.13 mg/L found in the CHEMDAT8 [26] database used by the USEPA for the modeling of acetone in municipal-activated sludge systems, and the K_s value of 0.75 mg/L. Wilkinson and Hamer [27] reported for a continuous flow reactor using biomass from a pilot plant-activated sludge treating a petrochemical manufacturing wastewater.

Eq. (5) is further modified when the biomass (X) value remains constant, thus becoming Eq. (6):

$$\frac{dS}{dt} = -K'SX = K''S \quad (6)$$

where: $K'' = K'X$, and upon integration, Eq. (6) takes the form:

$$S = S_0\, e^{-K''t} \quad (7)$$

Table 2 presents the calculated removal rates during the single-solute biodegradation experiments. It is necessary to state that the results displayed in Table 2 are the combined volatilization and biodegradation of the single solutes from the system. Thus, the first-order biodegradation rate could be calculated by subtracting the observed volatilization from the first-order removal rate, resulting in a calculated acetone biodegradation rate of 1.7 day^{-1} (2.3–0.58 day^{-1}). The rate of biodegradation of acetone from this study was found to be greater than that found by Gaudy et al. [6] who reported a biodegradation rate of 0.65 day^{-1} from a laboratory study evaluating an activated sludge treating a synthetic wastewater with acetone as the sole carbon source. The findings here are within the observed rates reported by Rathburn et al. [28] for the bacterial degradation of acetone in water at 25 °C of 0.79–7.9 day^{-1}. It should be noted that the MLTSS from the active biomass samples was monitored to ensure that the biomass concentration remained constant, thus allowing for the utilization of Eqs. (3) and (4) without the consideration of biomass variation. The initial MLTSS was 5355 mg/L and the measured MLTSS during the acetone spike are displayed in Table 3. These results validate the assumption of constant biomass concentration (X) during the experiment.

Table 2
Removal rates during single-solute experiments of acetone and MIBK using the acclimatized biomass

Contaminant spike	Rate order	Removal rates (day^{-1})	r^2
Acetone	First	2.3	0.96
MIBK	First	2.95	0.63

Table 3
Measured biomass-suspended solids during the single-solute experiments of acetone and MIBK using the acclimatized biomass

Time (min)	Acetone MLTSS (mg/L) (average ± S.D.)	MIBK MLTSS (mg/L) (average ± S.D.)
0	5355 ± 106	5355 ± 106
15	5157 ± 95	5387 ± 130
30	5140 ± 52	5493 ± 181
45	5193 ± 67	4807 ± 110
60	5243 ± 25	4887 ± 12
120	5287 ± 59	5020 ± 111
240	–	4980 ± 72

3.2.2. MIBK removal

Similarly for MIBK, again DI water and inactive biomass was spiked to evaluate the impact of volatilization upon MIBK. Again, statistical analysis (student t-test) was performed to compare the volatilization data from the two media and was found not to be significantly different ($P = 0.001$). Based upon this finding, the average of the volatilization rates from the two media was used to calculate the volatilization rate of removal of MIBK, using a first-order fit. The resultant first-order rate of MIBK volatilization was observed to be 0.72 day^{-1} ($r^2 = 0.86$, data not shown). At the time that the biomass seed was taken from the pilot scale-activated sludge system, the influent concentration and loading of MIBK was 10 mg/L and 1.5 g MIBK/kg VSS day.

As shown in Table 2, the overall removal of MIBK from this experiment was observed to be 2.95 day^{-1}. The net biodegradation rate of MIBK from this system was determined by subtracting the volatilization rate from the overall rate with a net biodegradation rate of MIBK to be 2.23 day^{-1} (2.95–0.72 day^{-1}). Barton et al. [19] reported a first-order MIBK biodegradation rate of the order of 0.010 L/mg VSS day. However, there is no listing of the MLVSS used in those experiments, so the actual first-order rate biodegradation constant cannot be elucidated. No other biodegradation rates for MIBK could be obtained by the authors.

The utilization of MIBK did not affect a significant change in the biomass concentration, as demonstrated in Table 3. The variability of the biomass concentrations (i.e. the range of 4807–5493 mg/L) is within 10%, which is within the expected analytical error.

3.3. Multiple-substrate kinetics

The impact of multiple substrates on the acclimatized activated sludge was then evaluated. Table 4 displays the initial VSS and VOC along with the final VOC concentrations measured during the multiple-substrate experiments. Varied amounts of initial mixed liquor VSS (MLVSS) were used to determine the impacts of the multiple substrates and their removal from this system. The data of Table 4 highlights that MIBK removal rates during the batch experiments were generally larger than the acetone-removal rates at comparable biomass concentrations. While it is evident that MIBK was more volatile than acetone, with a first-order volatilization rate coefficient of 0.72 day^{-1}

Table 4
Measured conditions during the multiple-substrate experiments with spikes of acetone and MIBK

Parameter	Acetone spike				MIBK spike			
	1	2	3	4	1	2	3	4
Initial VSS (mg/L)	5903	3926	2937	2344	4552	2716	1797	1247
Initial acetone (mg/L)	220	230	250	270	55	55	58	58
Initial MIBK (mg/L)	25	42	55	59	430	210	330	270
Final acetone (mg/L)	0.010	0.010	0.330	1.100	0.01	0.14	0.68	0.98
Final MIBK (mg/L)	0.005	0.005	0.012	0.017	0.005	0.53	0.16	0.35
Acetone first-order removal rate (day^{-1}) (r^2)	10.6 (0.97)	4.2 (0.79)	2.0 (0.84)	3.2 (0.86)	8.4 (0.99)	6.2 (0.997)	2.6 (0.77)	2.5 (0.78)
MIBK first-order removal rate (day^{-1}) (r^2)	8.7 (0.82)	7.5 (0.89)	6.2 (0.75)	2.4 (0.31)	11.2 (0.996)	8.4 (0.98)	8.6 (0.69)	7.5 (0.72)

versus 0.58 day^{-1} for acetone, the observed differences in overall removal rates between MIBK and acetone were much greater than would be attributed to volatilization, clearly suggesting that MIBK was more readily biodegraded by the sludges than acetone. As such, the results were normalized against the MLVSS. The data obtained from these experiments were fitted with a first-order removal rate with respect to biomass. Fig. 3 displays the overall acetone removal while utilizing the complex feedstock containing spikes of acetone, MIBK, and the control (i.e. no spike of acetone or MIBK) as a function of MLVSS.

Acetone removal was enhanced by the presence of MIBK and additional acetone, as demonstrated in Fig. 3, with the biomass-specific first-order removal coefficient approximately doubling in the MIBK spike, and tripling during the acetone spike, both relative to the control experiment. Comparison of the first-order acetone-removal rates of Table 4 indicate that at comparable biomass concentrations, the acetone-removal rate in the MIBK spike was greater than during the acetone spike, thus emphasizing the synergistic effect of MIBK on the acetone biodegradation rate in the range of 210–430 mg MIBK/L.

The maximum observed acetone-removal rate of 0.0023 L/mg VSS day occurred during the acetone spike, is approximately 1 order of magnitude less than the average removal rate reported by Barton et al. [19] of 0.011 L/mg VSS day treating the pulp mill effluent. The differences are attributed to the fact that in the present work, the pilot scale-activated sludge system was operating at a hydraulic retention time (HRT) of 4.3 days, and the solids retention time (SRT) was 19.7 days, which are substantially longer than the 4 h HRT and 6.7 day SRT that was used for the pulp mill experiment. The Barton et al. [19] work would then have been operating with a significantly reduced decay coefficient as the biomass would not undergo endogenous respiration to the same degree as in the present work. This would then imply that the Barton et al. [19] study would have had a much greater active fraction of biomass, whereas the active fraction of the biomass in this study would have been significantly lower. Additionally, the pulp mill influent experiments were operated at 30 °C, where the present work was performed at room temperature of approximately 20 °C. Furthermore, the influent wastewater used in the present work has been reported to contain substantial amounts of VSS [16,17] that may not contribute to active biomass. However, it should be mentioned that the influent VSS of the wastewater utilized in the present work does not contribute a significant BOD fraction. For example, at the time the seed for the multiple-substrate experiment was taken from the pilot system, the influent VSS was 1260 mg/L, with a total BOD of 1780 mg/L and the soluble BOD of 1490 mg/L. Thus, the influent particulate BOD of 290 mg/L is comprised of 1260 mg VSS-L, indicating that there is a very small contribution to BOD, being attributed to VSS. These conditions were typical of the influent wastewater. Accordingly, the accumulation of the high influent VSS as a result of the long SRT in the system inevitably reduces the active biomass fraction.

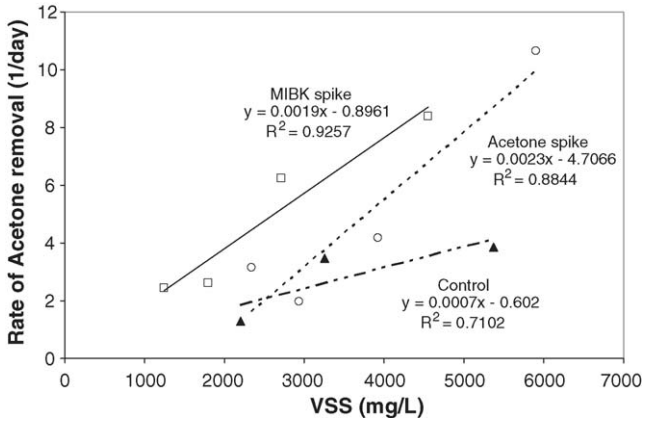

Fig. 3. First-order acetone-removal rate during acetone spike (◯), MIBK spike (□), and control experiments (▲) as a function of initial mixed liquor suspended solids.

Fig. 4 displays the MIBK results during the control, acetone, and MIBK spikes performed. As was observed previously, the presence of excessive MIBK resulted in an increased removal rate, approximately double of that observed in the control. Acetone enhanced the MIBK removal by approximately three times the control experiment. However, as noted from the data in Table 4 and Fig. 4, by comparison of MIBK-removal rates from the MIBK and acetone spikes, the MIBK-removal rate was inhibited by acetone concentrations of 220–270 mg/L. This may be explained by the relatively slower acetone biodegradability observed in this study relative to MIBK. Similar to acetone, the observed removal rate of MIBK, with a maximum of

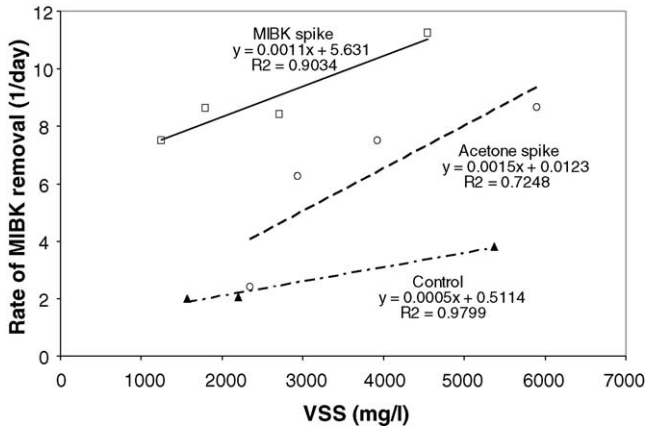

Fig. 4. First-order MIBK-removal rate during acetone spike (◯), MIBK spike (□), and control experiments (▲) as a function of initial mixed liquor suspended solids.

0.0019 L/mg VSS day, which also occurred during the acetone spike, is approximately 1 order of magnitude lower than the Barton et al. [19] reported average of 0.010 L/mg VSS day. The other aforementioned reasons listed earlier regarding the differences in the acetone-removal rates also apply in this situation.

A comparison of the substrate-removal rates from the single- and multiple-substrate studies is warranted. Using the biomass-specific removal rates for acetone and MIBK removal during their respective spikes in the multiple-substrate experiments, as shown in Figs. 3 and 4, and the single-solute experiment initial VSS of 3800 mg/L would result an expected removal rate of acetone of 4.0 day^{-1} and MIBK-removal rate of 9.8 day^{-1}, both of which are significantly greater than what was reported earlier in Sections 3.2.1 and 3.2.2 of 2.3 and 2.95 day^{-1}, respectively. While superficially this may be interpreted that the complex wastewater matrix contained constituents that exerted synergistic effects on biokinetics, scrutiny of the seed sludge provides the genuine rationale for this disparity. The seed sludge used for the multiple-substrate studies was during operating stage 2, when the pilot system was performing well while seed sludge for the single-substrate studies was during operating stage 7, at an SRT of 6.3 days, when both acetone and MIBK were breaking through. Furthermore, this period was characterized by the loss of nitrification.

It is of particular importance to compare the kinetics derived from the mixed-substrate studies with the removal rate observed in the pilot system at the time of these studies. For acetone, using the biomass-specific removal rate of 0.0023 L/mg VSS day and knowing that operating stage 2 MLVSS was 7750 mg/L; this translates to a removal rate of approximately 18 day^{-1} (g acetone/g VSS day), which is much greater than the pilot plant observed removal rate of approximately 6 g acetone/kg VSS day, as shown in Table 1. The same observation is also pertinent for MIBK. While it can be argued that volatilization in the bench-scale kinetic studies was much greater than in the pilot system, the net rate of biodegradation delineated from the difference between the spiked systems and the controls was still about 3 orders of magnitude greater than that observed in the pilot system.

The reasoning for the large observed differences in the removal rates is as follows. First-order removal kinetics best described the removal of the VOC in this study in the μg/L range, which was observed in the control experiments. This is to be expected since the Monod kinetics would reduce to first-order when $K_s \gg S$. However, the first-order kinetics best described that the single- and multiple-substrate experiments results with initial acetone concentrations ranging from 220 to 396 mg/L and MIBK initial concentrations ranging from 80 to 430 mg/L. K_s values of such magnitudes (i.e. ≫396 mg/L acetone and ≫430 mg/L MIBK) are characteristics of slowly biodegradable contaminants, which contradicts most of the literature. While the disparity in K_s values for the same contaminants in different published reports may span orders of magnitude as demonstrated by comparative data compiled by Nakhla [29] who demonstrated the large discrepancies of kinetic parameters such as K_s ranging from a low of 0.08 mg/L to a high of 16.9 mg/L for benzene, toluene, and xylene treatment; it is very rare that the same biomass exhibits 3 orders of magnitude difference in K_s values. Alternatively, it is possible that there are different biokinetic coefficients based upon the ambient conditions of the system. This concept of the existence of multiple K_s values for a given system and contaminant (i.e. extant and intrinsic kinetic parameters), has been described by Grady et al. [30].

Extant kinetic parameters represent the kinetic capabilities of the biomass obtained from the bioreactor as it existed in the bulk system. Since treatment systems are designed to affect high removal efficiencies, the ambient-substrate concentrations in the bioreactor are very low, consistent with the low μgL levels of this study. On the other hand, the intrinsic parameters are reflected during the acetone and MIBK spike experiments, where the biomass is exposed to very high substrate concentrations.

4. Summary and conclusions

A pilot scale-activated sludge system was operated to determine its effectiveness in further treating the effluent from an existing thermophilic, aerobic bacterial consortium pretreating an organic chemical manufacturer's wastewater. Samples from this pilot scale-activated sludge system were utilized as seed biomass to determine the specific removal rates of acetone and MIBK, in both single-substrate and multiple-substrate experiments, as there is an apparent lack of this information in the literature. The following conclusions can be drawn from these experiments:

- The pilot scale-activated sludge system had an inherent stability, and was extremely effective at removing acetone and MIBK down to the method detection limits of 10 and 5 μg/L, respectively.
- Both single-substrate and multiple-substrate batch kinetics at initial concentrations on the order of several 100 mg/L conformed to the first-order kinetic model with respect to substrate concentration.
- The first-order biodegradation rate during the single-substrate acetone experiment was 1.7 day^{-1}, which is comparable to the literature results.

- The first-order biodegradation rate during the MIBK single-substrate experiment was 2.23 day^{-1}.
- While the MIBK spike did in fact enhance the acetone removal, both relative to the control and acetone spike, acetone exerted an adverse impact on the MIBK-removal rate. The largest acetone biomass-specific removal rate was determined to be 0.0023 L/mg VSS day, and the largest MIBK biomass-specific removal rate was determined to be 0.0019 L/mg VSS day.
- The observed removal rates from the multiple-substrate experiments were approximately 3 orders of magnitude greater than the corresponding rates observed in the pilot scale system. The concept of the biomass having extant and intrinsic kinetic parameters explains these dramatically different observed removal rates.

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