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Naphthalene Mass Transfer from a Non-Aqueous Phase Liquid (NAPL) in Rotating Baffled and Bead Mill Bioreactors

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Abstract: Rotating bead mill and baffled bioreactors have earlier been shown to provide excellent mass transfer and bioremediation rates for naphthalene particulates. In this study, the mass transfer rates of naphthalene and methylnaphthalenes from NAPL into water in both the bead mill and baffled bioreactors are reported. The values of K_La ranged between 1.0 h^{-1} and 42 h^{-1}, similar to values observed with suspended PAH particulates, increasing with bead loadings up to 50% by volume, bead size up to 5.0 mm, rotation rate up to 50 RPM, oil loading up to 72 mL (7.2% volume fraction) and naphthalene loading up to 1000 mg/L (based on the water phase). Baffled bioreactors provided similar volumetric mass transfer coefficients as bead mill bioreactors, but without the loss of working volume due to the presence of solid beads.

Keywords: Baffled bioreactor; Bead mill bioreactor; Naphthalene; NAPL; Volumetric mass transfer coefficient

INTRODUCTION

Oil spills at sea or on land are commonplace in modern society (1). These can be catastrophic spill events such as the Exxon Valdez accident in 1989 (at sea) or the 2007 Burnaby, Canada pipeline rupture (on land); or they can be due to long term leakage at refineries or other types of oil production or utilizing facilities. In the USA, it is estimated that 83 large

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scale spills (each approximately 8000 m^3) occur each year. Perhaps fortunately, much of the mass of the oil does not dissolve into water and so separation by physical means is possible. However, water soluble components in oil can enter groundwater, ocean water, lakes, and rivers and cause detrimental effects to plants, animals, birds, aquatic life, and humans. Crude oils contain both simple and complex polycyclic aromatic hydrocarbon (PAH) molecules that are known to be either highly toxic or carcinogenic. In most crude oils, naphthalene and its methylated derivatives represent a significant fraction of the water-soluble PAH compounds (2,3), whereas larger PAH molecules can decompose with time into smaller, more water-soluble fragments including naphthalenes (4). Naphthalene has relatively high water solubility (31 mg/L at 25°C) and toxicity (5). Solubility enhancers including surfactants are sometimes used to increase the removal of small PAH molecules from NAPL, but this leads to further processing in order to recover the surfactants from the concentrated PAH molecules (6).

In-situ treatment methods of NAPL polluted waters suffer from slow reaction rates and low efficiencies. Treatment of NAPL contaminated waters using ex-situ treatment bioreactors always involves the presence of an immiscible NAPL phase in the treatment vessel. The partitioning of the contaminants between the NAPL and aqueous phases plays a key role in the rate at which the water can be treated. In previous work, using suspended PAHs, we investigated mass transfer rates of naphthalene and methylnaphthalenes in both rotating bead mill and baffled bioreactors and showed that high loadings of PAHs could be quickly dissolved and bioremediated in these vessels (7,8). Treatment rates approached the highest values reported in the literature for other, more complex bioreactor design. Other researchers have investigated mass transfer of organics from NAPL into water in reaction vessels. Mukherji and Weber found that mass transfer limited biodegradation of naphthalene only when biofilms were formed at the interface of NAPL and water in bioreactors where the NAPL and water phases were completely segregated (9). On the other hand, Chu et al. developed a model that inferred bioreactions near the interface enhance the rate of dissolution of water soluble compounds from NAPL (10). Ramaswami et al. measured the overall mass transfer coefficients as water flowed past globules of coal tar containing naphthalene, and found maximum values of around 1.0 h^{-1} (11). However, if the coal tar was imbibed in small silica beads, they reported the overall mass transfer coefficient increased to just over 150 h^{-1} in the same flow experiments.

In this work, we report on mass transfer rates of naphthalene and methylnaphthalenes dissolved in an oil in both bead mill and baffled bioreactors. Pump oil, insoluble with water, was used to simulate the NAPL phase and was artificially contaminated by dissolving naphthalene or methylnaphthalenes at concentrations up to their solubility limits in the oil (at room temperature this was found to be 61900 mg/L for naphthalene).

MATERIALS AND METHODS

Chemicals

Analytical grade naphthalene, 2-methylnaphthalene, and 1,5-dimethylnaphthalene were supplied by Sigma Aldrich. The oil was VWR No.19 vacuum pump oil, cat. no. 54996-082, which is refined from crude oil. Several important properties of this fluid, both pure and containing dissolved naphthalene and methylated naphthalenes, were measured: density using an Anton Paar Model DMA 35 densitometer; viscosity using a Brookfield model DV-1 cone and plate viscometer and surface tension using precision bore glass tubing. The data is listed in Table 1. Reverse osmosis quality water was used for the aqueous phase.

Analytical

Analyses of naphthalenes were performed by spectrophotometry, using a Shimadzu Model UV-Mini 1240 spectrophotometer, at optimum UV wavelengths for each compound (naphthalene at 276 nm, 2-methlynaphthalene at 220 nm, and 1,5-dimethlynaphthalene at 224 nm). Measurements of naphthalene concentrations in the water phase were made by transfer of the sampled water into a quartz cuvette and comparing the absorbance to previously prepared calibration curves. For measurements of naphthalene in the oil phase, 100 μL samples of oil were extracted using 10 mL of ethanol, diluted further in ethanol if necessary,

Table 1. Measured physical properties of pure pump oil and pump oil containing naphthalene solutes, 22°C

Chemical solute	Concentration (mg/L)	Density (kg/m^3)	Viscosity (mPa-s)	Surface tension ($\times 10^3$, N/m)
None	0	852	120	23
Naphthalene	61900	861	66	21
2-methylnaphthalene	58500	877	85	22
1,5-dimethylnaphthalene	58500	878	107	22

Standard errors of density, viscosity and surface tension measurements are ±2 kg/m^3, ±1.2 mPa-s, and 0.001 N/m, respectively.

and then the ethanol solution was transferred to a quartz cuvette, and the absorbance was measured at the same wavelengths as for the water samples. The same calibration curves could be used to determine the naphthalene concentrations in ethanol as were used for naphthalene in water.

Apparatus and Procedures

All experiments were carried out in Pyrex brand, 2.0 liter glass bottles (No. 1395, ID = 12.0 cm, height = 26 cm). As shown in Fig. 1, some of these bottles were fitted with four stainless steel baffles, held securely, and equidistant around the inside circumference and measuring 1.3 cm in width and 13.5 cm in length. Borosilicate glass beads of 1.0, 3.0, and 5.0 mm diameter were provided by Potters Industries, Moose Jaw, Canada. All experimental runs were performed on a Bellco Biotechnology roller apparatus (model 7622-S0003) with the rotational speed controlled between 0 and 50 RPM. Experiments were carried out at room temperature (22.0 ± 1.0°C). Teflon caps were placed over the bottle openings to allow for sampling through a small hole placed in the middle of the cap.

To begin experiments, water and glass beads (if used) were placed in the glass bottles to give a total working volume of 1.0 liter. The bottles were then capped and placed horizontally on the Bellco roller apparatus. The required volume of naphthalene contaminated oil was injected into the bottle through the sampling port using a glass hypodermic syringe fitted with a long stainless steel needle. The rotation was immediately commenced after injection of the contaminated oil. Samples were taken by a reverse procedure, briefly stopping the rotation of the bottle and withdrawing an aqueous sample using a clean glass needle and syringe, and then rotation was quickly resumed. Water samples were placed directly

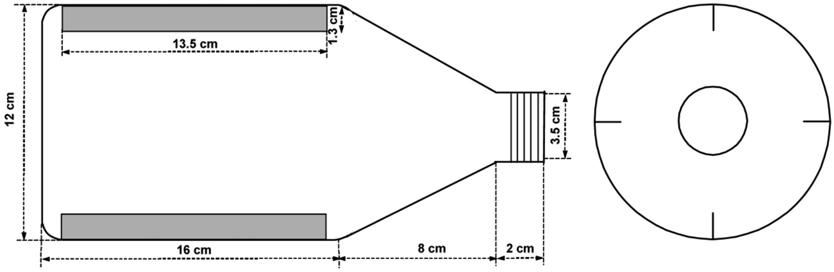

Figure 1. Schematic (side and top views) of bottle equipped with stainless steel baffles.

into a quartz cuvette and optical density was measured. The investigated variables included: the bead loading (0 to 50% by volume), bioreactor rotation speed (0 to 50 RPM), NAPL loading (0 to 7.2% by volume), concentration of PAH in the NAPL (50 to 1000 mg/L), bead size (1.0 to 5.0 mm diameter), type of PAH (naphthalene, monomethylnaphthalene, and dimethylnaphthalene), and baffles instead of beads located inside the rotating bioreactor.

RESULTS AND DISCUSSION

As a measure of the reproducibility of this work, results from four duplicate runs (experiments completely redone) are shown in Figs. 2, 3, 5 and 7, where non-filled symbols represent the duplicate runs of the corresponding filled symbols. The duplicating conditions span different bead loadings, bead sizes, RPMs and naphthalene loadings. It is clear that the experimental data is very reproducible. Using data after time zero

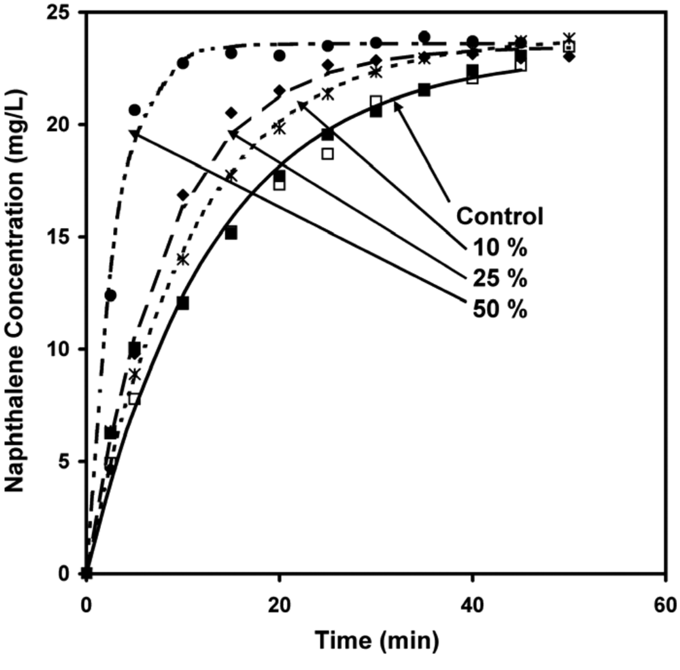

Figure 2. Effect of bead loading on naphthalene transfer from NAPL to water (5.0 mm beads, 50 RPM, 8.08 mL of oil saturated with naphthalene, naphthalene loading based on aqueous phase = 1000 mg/L).

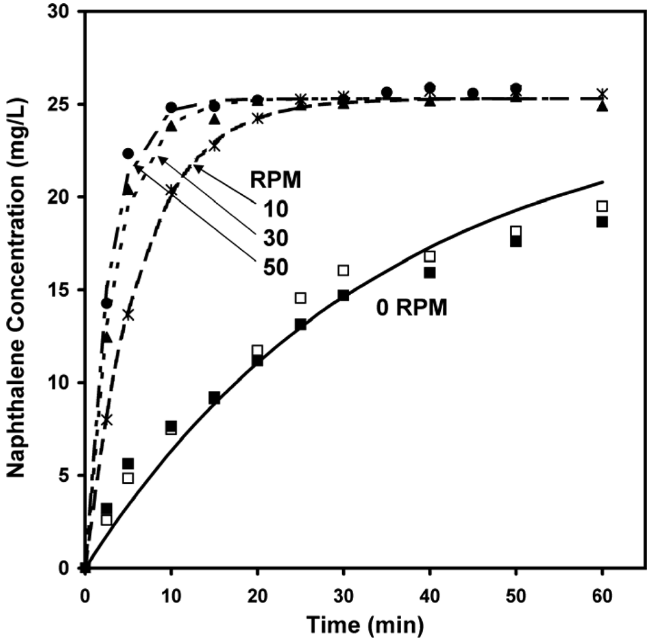

Figure 3. Effect of bottle rotation speed on dissolution of naphthalene from oil (5.0 mm beads, 50% bead loading, 8.08 mL oil saturated with naphthalene, naphthalene loading based on aqueous phase = 1000 mg/L).

and prior to the concentrations reaching 95% of saturation, an absolute average deviation of 5.9% between measured concentration values was determined. As described earlier (8), values of K_La (h^{-1}) were determined by best fit (minimization of the squared error between model and data) of the integrated form of the mass balance equation to the experimental data:

$$C_{WAT} = C^* \times (1 - \exp(-K_L a \times t)) \tag{1}$$

where C_{WAT} is the aqueous phase, dissolved species concentration (mg/L) at some time, t (h), and C^* is the known equilibrium concentration of the dissolved species, described later.

In earlier work the presence of beads in the rotating bottle was found to dramatically increase the overall volumetric mass transfer coefficient of solid naphthalene particles (8). In that study, at a rotational speed of 50 RPM and a naphthalene loading of 1000 mg/L, K_La increased from 1.4 h^{-1} to 23 h^{-1} as bead loading was increased from 0 to 50%. Figure 2 shows that, similar to the earlier study, at 50 RPM the rate of naphthalene

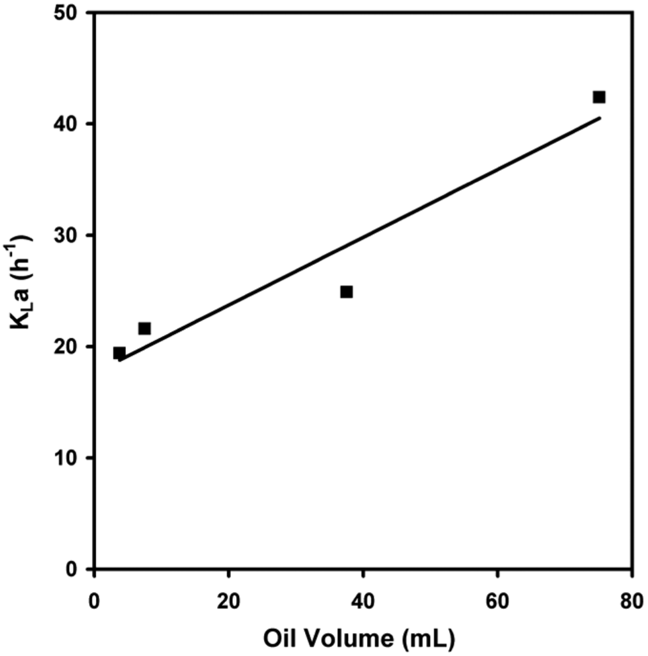

Figure 4. Effect of increasing oil volume on the overall volumetric mass transfer coefficient (5.0 mm beads, 50 RPM, 50% bead loading, saturated naphthalene in oil).

transfer from NAPL into the aqueous phase increased when the bead loading increased (control represents no beads or baffles inside the bottle). The overall mass transfer coefficient increased steadily: 4.6, 5.5, 7.2, and 20.4 h^{-1} at bead loadings of 0, 10, 25, and 50% by volume, respectively. It is seen that the K_La values are similar for naphthalene particulates and naphthalene dissolved in NAPL, indicating the interfacial areas and mass transfer resistance mechanisms are similar in both cases. It is reported that fine particulate and NAPL mass transfer rates are similar (12). This suggests that the major limiting factor for mass transfer in both cases is a film in the water phase.

Rotation rate of the bioreactor also greatly affected the overall volumetric mass transfer coefficient. Figure 3 shows that for a stationary system (0 RPM), representing pure diffusion of naphthalene from NAPL into a motionless water phase, the mass transfer rate was slowest with an overall volumetric mass transfer coefficient of only 1.7 h^{-1}. With a 50% bead loading, K_La continuously increased as the speed of rotation increased: 9.5, 17.6, and 22.0 h^{-1} at rotation rates of 10, 30, and

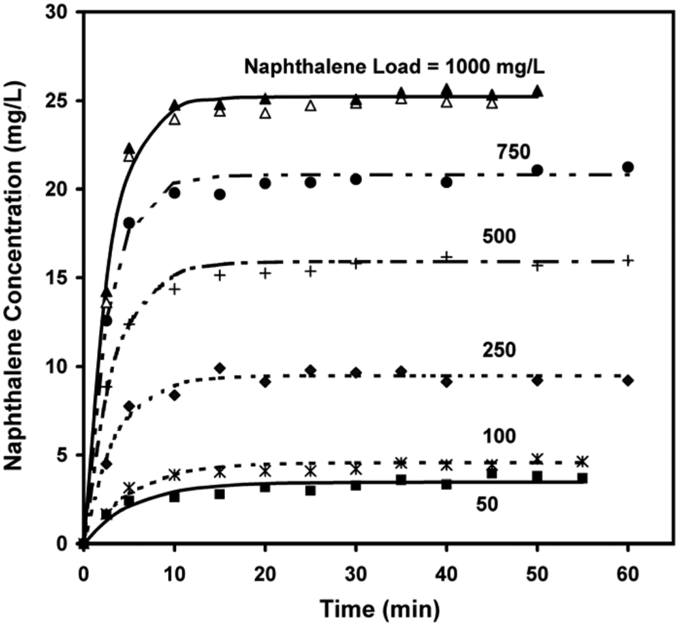

Figure 5. Effect of naphthalene loading in oil on mass transfer of naphthalene into the water phase (5.0 mm beads, 50 RPM, 50% bead loading, 8.08 mL oil, naphthalene loadings based on the water phase concentrations).

50 RPM respectively. This increase in volumetric mass transfer coefficient was expected, since increased turbulence is generated by improved mixing of beads, water, and oil at higher rotation rates. The final operating condition (50 RPM) was a duplicate run when compared to the final operating condition of the bead loading experiments shown previously in Fig. 2. The 10% difference in the values of the best fit parameter, K_La, represents the typical scatter of that variable when it was best fit to individual experimental runs.

Figure 4 demonstrates the effect of oil loading on the mass transfer rate in the rotating bioreactor. As expected, the overall volumetric mass transfer coefficient increased with increase in oil loading, V_{OIL}, due to the larger interfacial areas. Over the oil loading range studied (8 to 75 mL), K_La appeared to increase linearly such that:

$$K_La = 17.6 + 0.305 \times V_{OIL} \tag{2}$$

where V_{OIL} is in mL. The standard error of the intercept and slope were 2.6 and 0.060, respectively. Equation (2) cannot be extrapolated beyond the measured limits of V_{OIL}, since it is clear that at zero oil volume K_La

must be zero. A maximum experimental value for K_La of $42\,h^{-1}$ was reached. During these series of experiments, it was noted that higher saturation concentrations of naphthalene in the water phase were reached as the oil loading was increased, due to the partitioning effect of naphthalene between the oil and water phases. As a result, a series of experiments were performed to quantify the partitioning phenomenon and to determine whether variation in the naphthalene loading by changing the quantity of naphthalene dissolved in a constant volume of oil would affect the mass transfer rate. Figure 5 shows that, as expected, the saturated water phase concentrations increased as the naphthalene loading was increased in the oil. There was also a noticeable increase in the rate of naphthalene mass transfer as the naphthalene concentration in the oil was increased. The overall volumetric mass transfer coefficient increased from $11.2\,h^{-1}$ at a loading of 50 mg/L (based on the water phase concentration) to $21.2\,h^{-1}$ at a loading of 1000 mg/L. This suggests there was some mass transfer resistance occurring inside the oil phase. The relationship between equilibrium concentration of naphthalene in the oil and water phases was closely modeled by the following best fit empirical equation (curve

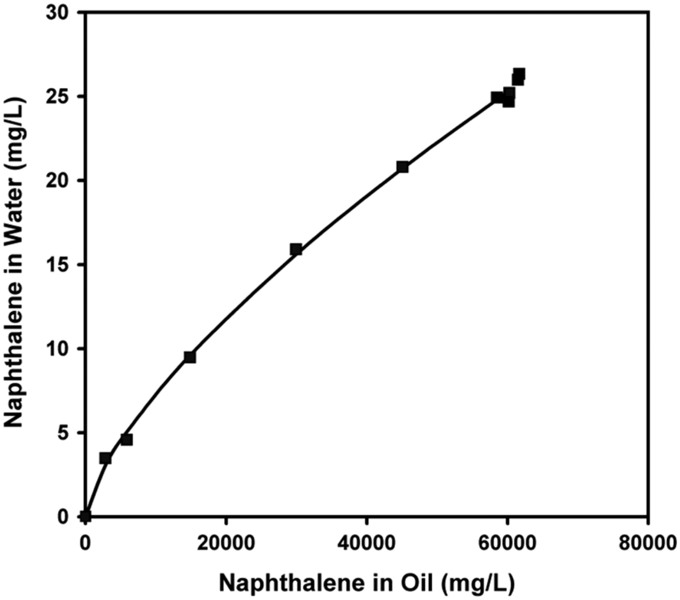

Figure 6. Partitioning of naphthalene between water and NAPL (VWR No. 19 vacuum pump oil, curve represents Equation (3)).

on Fig. 6):

$$C_{WAT} = 0.0123 \times C_{OIL}^{0.694} \tag{3}$$

where concentrations are in mg/L. The standard errors of the coefficients were 0.0015 and 0.012, respectively. The pump oil in this study was capable of containing much more naphthalene than the coal tar oil used by Ramaswami et al. (11).

Figures 7 and 8 demonstrate the effects of bead size and the type of naphthalene on mass transfer rates, respectively. Larger glass beads enhanced the turbulence and mixing in the rotating bioreactor, thereby increasing the overall volumetric transfer coefficient from 10.7 to 21.2 h^{-1} as the bead size increased from 1.0 to 5.0 mm. However, Fig. 8 shows that the type of naphthalene (monomethyl, dimethyl or pure naphthalene) had no measurable effect on the overall volumetric mass transfer coefficients, with a best fit value of 18.6 ± 1.1 h^{-1} for all three cases. According to the theory of Wilke and Chang for diffusion

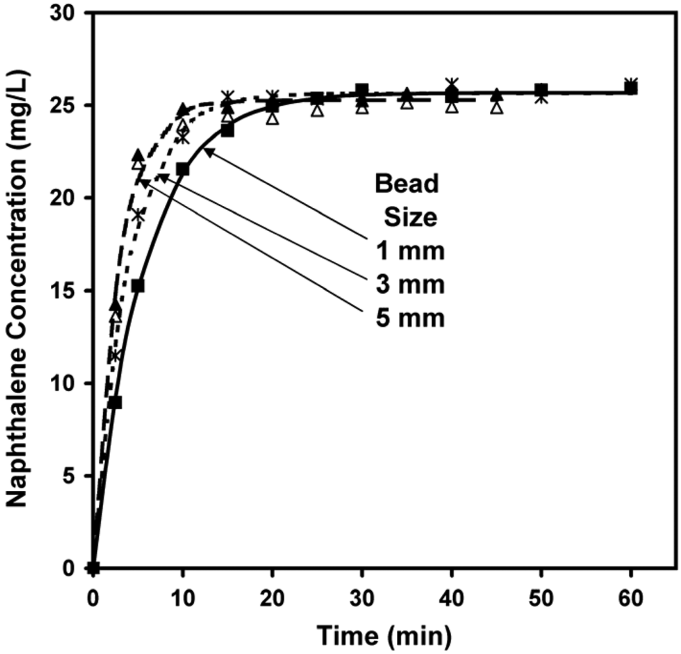

Figure 7. Bead size effects on the mass transfer of naphthalene from oil into water (50 RPM, 50% bead loading 8.08 mL of oil saturated with naphthalene, 1000 mg/L naphthalene loading).

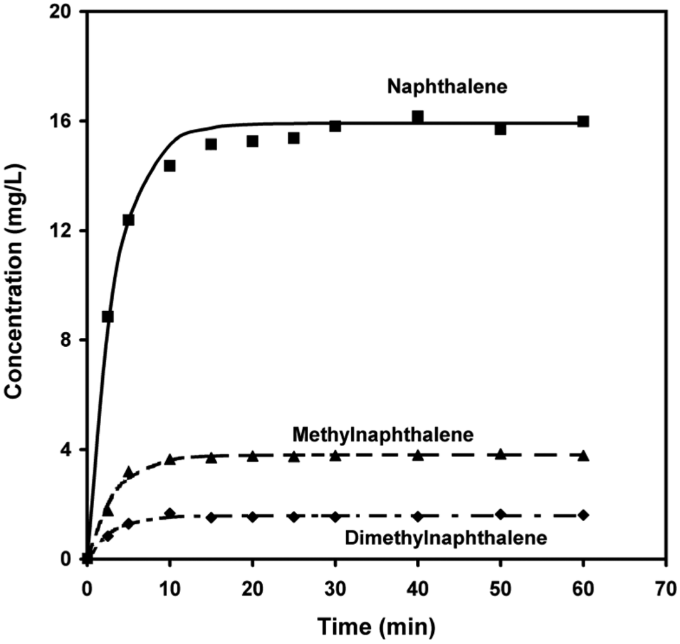

Figure 8. Mass transfer of methylnaphthalenes in the rotating bioreactor (5.0 mm beads, 50 RPM, 50% bead loading, 8.08 mL oil, 500 mg/L naphthalene loadings).

coefficients in liquids and the penetration theory of Higbie (12), it was expected that the overall mass transfer coefficients would be about 5% and 9% smaller for monomethylnaphthalene and dimethynaphthalene, respectively, compared to naphthalene. It may be that the scatter of the experimental data prevented the observation of this phenomenon. Figure 8 does demonstrate, however, that increasing the number of methyl groups attached to the naphthalene structure significantly lowered the solubility of the molecule. Naphthalene partitioned to a water concentration of 15.9 mg/L, monomethylnaphthalene reached 3.8 mg/L while dimethylnaphthalene reached only 1.6 mg/L, all at the same loading in the oil (58,500 mg/L in the oil phase).

Finally, although beads clearly improve mass transfer in the rotating bioreactor, they also occupy significant volume inside the bioreactor, thereby reducing the volume available for bioremediation to take place. Figure 9 demonstrates that four baffles, equally spaced around the outer circumference of the rotating bioreactor, provided overall volumetric mass transfer coefficients of 6.5, 17.5, and 21.2 h^{-1} at rotation rates of 10, 30, and 50 RPM, respectively. These values are very similar to the

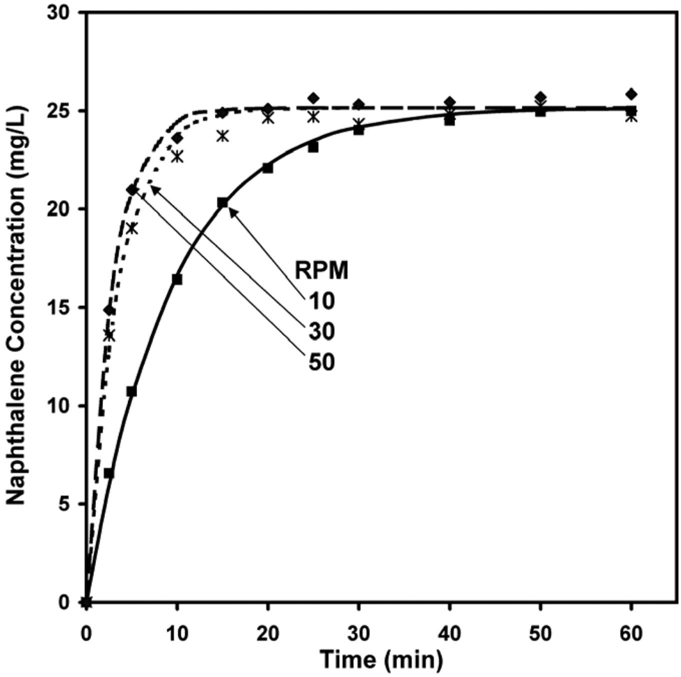

Figure 9. Mass transfer of naphthalene using baffles in the roller bioreactor in lieu of beads (50 RPM, 16.16 mL oil saturated with naphthalene, 1000 mg/L naphthalene loading).

mass transfer rates observed with a 50% bead loading at the same rotation rates. But in the case of baffles, mass transfer enhancement is achieved without consuming a significant volume of the bioreactor, so that more volume is available for the bioreaction fluid. Thus, it is seen that the rotating baffled bioreactor has the potential to provide twice the productivity for treating contaminated NAPL compared to a rotating bead mill bioreactor containing 50% bead loading.

CONCLUSIONS

The rotating bead mill and baffled bioreactors were found to provide similar volumetric mass transfer coefficients for naphthalenes partitioning between NAPL and water as had been observed earlier with fine suspended particulates of these chemicals. The chemical structure of the naphthalene compound did not affect the volumetric mass transfer coefficients. The volumetric mass transfer coefficients reached up to 42 h^{-1}, and within the experimental boundaries of this investigation, the optimum operating conditions were 50% bead loading, 5.0 mm beads, 7.2% oil loading, 1000 mg/L naphthalene loading, and 50 RPM. Baffled bioreactors provided equally high volumetric mass transfer rates as the bioreactor with beads under the best operating conditions, while allowing a working volume twice as much as that for the bioreactor with beads.

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