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Biodegradation of coal slurry transport wastewater organics

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SUMMARY

Activated sludge was successful in reducing the levels of dissolved organic carbon (DOC) in coal slurry wastewaters. DOC removal by the activated sludge ranged from 61% to 97% with a large percentage (21–41%) of this DOC being completely metabolized to CO_2. Second order kinetic constants (k_2) developed for DOC removal ranged from $1.39 \cdot 10^{-4}$ to $2.30 \cdot 10^{-1}$ liter $\cdot$ day^{-1} $\cdot$ (mg of sludge)$^{-1}$, providing evidence that biological treatment was an effective mechanism for reducing the pollution potential of the slurry wastewaters. After treatment with activated sludge a residual DOC remained in the wastewater and data from ultrafiltration studies indicated that this residual carbon was of MW > 1000. The activated sludge preferentially removed the lower (MW < 1000) molecular weight compounds and the higher molecular weight DOC was more resistant to biological attack. However, extended acclimation (greater than 1 month) enabled the activated sludge to remove the higher molecular weight DOC from the slurry wastewaters.

INTRODUCTION

The transport of coal through pipelines to power plants, shipping facilities and, potentially, coal conversion industries is an economically acceptable alternative for bulk coal transportation. In the future, slurry pipelines may become the preferred method of coal transport. Although there is currently only one operative pipeline, the Black Mesa Pipeline, eight additional pipelines have been proposed for construction in the United States. These pipelines would span approximately 7500 kilometers and require approximately 120 million gallons of coal slurry per day for the annual transport of 175 million tons of coal [30].

Very little attention has been given to the potential water pollution problems resulting from the coal slurry pipeline technology. Although deterioration in transport water quality has been reported, these studies focused primarily on the solubilization of inorganic compounds from the coal into the transport water [20]. In contrast, there is a paucity of information concerning the contamination of

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transport water by the organic compounds indigenous to the parent coal. Leaching of carbonaceous material during slurry transport would result in the deterioration of the transport water and may affect the reuse potential of this wastewater. Reid et al. [22,23] reported significant concentrations of organic carbon solubilizing from the coal into the transport water during slurry preparation and simulated pipeline transport. The majority of this dissolved organic carbon (DOC) was operationally defined as fulvic acids [6]. Structural analysis of the fulvic compounds by gas chromatography/mass spectrometry revealed that these compounds were comprised primarily of substituted aryl subunits connected by aliphatic bridges [23].

The environmental impact and health effects of discharging untreated slurry wastewater have yet to be determined and may not be feasible without first reducing the organic contamination. Biochemical oxygen demand (BOD) measurements ranging from 7 to 250 mg $\cdot$ liter^{-1}, have been reported for some slurry wastewaters, indicating that the wastewater's DOC may be susceptible to microbial attack [21,22]. The purpose of this investigation was to assess the viability of utilizing activated sludge for reducing the slurry wastewater's organic contamination. This included the development of kinetic rate constants to describe this process and determining the fate of specific classes of organics comprising the slurry wastewater's DOC.

MATERIAL AND METHODS

Coal storage and slurry wastewater preparation

The conditions for coal storage and the preparation of coal slurry wastewater have been reported elsewhere [22]. Basically, Wyodak coal was ground to 50 mesh and slurry formulated as a 50:50 mixture (w/w) of surface dry coal with distilled water. Slurries were allowed to mix up to 14 days followed by centrifugation to achieve coal-water separation and filtration of the supernatant through glass fiber filters and 0.4 μm membrane filters to remove coal fines. All slurry wastewaters were utilized immediately or were stored at 4°C and used within 1 week of preparation.

Activated sludge

Activated sludge samples were collected from aerobic treatment tanks located at the Knoxville Municipal Waste Treatment facility. Once collected the sludge was immediately transported to the laboratory. Acclimation of the activated sludge was accomplished by the fill and draw technique [5,26] utilizing the coal slurry wastewater (pH 7.0–7.2) as the feed stock (sole carbon and energy source).

Oxygen uptake

The rate of oxygen utilization by the activated sludge was measured for three separate molecular weight fractions isolated from the Wyodak slurry wastewater's DOC (MW > 5000, MW 5000–1000 and MW < 1000). Oxygen uptake was monitored using a YS1 Model 53 Biological Oxygen Monitor (Yellow Springs Instrument Co., Yellow Springs, OH). All samples were run in triplicate. The basic procedure involves adding 1.0 ml of activated sludge to the Oxygen Monitor followed by the addition of 2.0 ml of slurry wastewater of the appropriate molecular weight fraction. An oxygen probe was used to monitor the amount of oxygen consumed over a 5–10 min period. Prior to inoculation the sludge was washed twice with phosphate-buffered saline (PBS) and stored for 48 h at 4°C. Approximately 1 h before use, the sludge was equilibrated to room temperature.

DOC removal and determination of kinetic constants

Both first and second order kinetic constants were determined for biologically mediated DOC removal from the coal slurry wastewaters. These constants were determined for batch reactors by monitoring the removal of DOC during the respirometer studies. Aliquots were removed from the respirometer during the course of biochemical oxygen demand (BOD) tests and the concentration of DOC was determined.

First order kinetics of DOC removal were described by the following equation:

$$-d[\mathrm{DOC}]\mathrm{d}t = k_1\,[\mathrm{DOC}]$$

where k_1 represents the first order kinetic constant.

The k_1 was determined by plotting the $\log_{10}$ [DOC] remaining at time (t) versus t. The slope of the line was taken to be k_1. For comparative purposes all first order kinetic constants were normalized to the activated sludge concentration (i.e., dry weight) and these values were taken to be the second order kinetic constant (k_2) [14]. Substrate removal rates were also determined for the semi-continuous reactors. Duplicate fill and draw reactors were prepared with the activated sludge and the slurry wastewater. Two separate sets of reactors were prepared, each with a different biomass concentration. The activated sludge was acclimated to the slurry wastewater for 1 month prior to the experiment. The biomass concentration remained constant and there was no sludge wasting during the course of the investigation. The rate of substrate utilization was viewed on the basis of a mass balance approach which is the same as that reported for a completely mixed activated sludge treatment plant [27].

Molecular weight determinations using ultrafiltration

The molecular weight distribution of the DOC contained in the coal slurry wastewater was determined before and after each respirometer study. Aliquots of the slurry wastewater were removed and then filtered through a prewashed 0.4 μm Nucleopore filter (Pleasonton, CA) to remove particulates and activated sludge. Ultrafiltration was then performed using Amicon YM ultrafiltration membranes (Amicon Corp. Lexington, MA) and an Amicon Model 52 stirred cell with an operating pressure of 40 psi (nitrogen). The filtrate from the slurry wastewater which passed through the membranes was recovered and analyzed for DOC concentration. By employing the use of YM 2 and YM 5 membranes the slurry wastewater DOC could be classified into three distinct molecular weight fractions: MW > 5000, MW 5000–1000 and MW < 1000.

Analytical

The BOD for the slurry wastewaters was determined using the E/BOD electrolytic respirometer system (Oceanography International, College Station, TX) [29]. Phosphate buffer (1.0 ml $\cdot$ liter^{-1}) was added to the slurry wastewater, adjusted to a pH of 7.0–7.2, and then inoculated with activated sludge. Bacterial levels in the activated sludge ranged from $1.0 \cdot 10^7$ to $1.0 \cdot 10^8$ bacteria $\cdot$ ml^{-1} as determined by direct microscopic counts. Oxygen consumption was then monitored over a 6–20-day period. The Thomas graphical method [28] was used to determine the velocity rate constant (k) and the BOD_{20} (L) computed with the following equation:

$$Y_t = L\,(1 - 10^{-kt})$$

DOC determinations were performed using a Beckman Model 915 Total Organic Carbon Analyzer (Beckman Instruments, Fullerton, CA) with direct injection capabilities. Prior to DOC analysis the activated sludge was removed by centrifugation. The slurry wastewater was then acidified and the acidified sample was purged for 5 min with compressed gas (nitrogen).

Carbon dioxide respired by the activated sludge was determined at the termination of each respirometer study. An alkali trap was removed from the E/BOD respirometer and carbon dioxide levels were determined by injecting an aliquot of the alkali trap into a 0524-HR Carbon Analyzer (Oceanography International, College Station, TX).

The microbial biomass in the activated sludge was determined by dry weight measurements. Cellular carbon was estimated as 50% of the dry weight [16]. Acridine orange direct cell counts (AODC) were performed by the method of Hobbie et al. [11] with minor modifications which included homogenization of the activated sludge prior to staining.

RESULTS AND DISCUSSION

BOD and DOC removal

The activated sludge consumed significant concentrations of oxygen when it was incubated in the presence of Wyodak slurry wastewater. Oxygen consumption resulted primarily from the biological oxidation of the DOC present in the wastewater. The BOD_{20} for the four experiments ranged from 52 to 216 mg · liter^{-1} (Table 1). Four separate experiments were performed using fresh slurry wastewater, since the DOC decreased upon storage of the wastewater at 4°C.

Although BOD_5 (5-day test) values are normally reported for wastewaters, longer incubation times (1 week or more) were required, since additional DOC removal occurred by the activated sludge. The longer incubation and resulting BOD_{20} (20-day test) more accurately reflects the potential for biologically mediated DOC removal. Velocity rate constants (k) determined by the Thomas Graphical method, ranged from 0.08 to 0.11 day^{-1} with an average of 0.10 ± 0.01 day^{-1}. Determining the k values from the oxygen demand allows one to evaluate whether biological treatment is a viable alternative for reducing the pollution potential of a specific wastewater. Coal slurry wastewaters have been shown to contain elevated levels of salts and heavy metals [20] which could be detrimental to the activated sludge and interface with biological treatment. However, the k values determined for the Wyodak slurry wastewaters compare favorably with other velocity rate constants reported for wastewaters which are amenable to biological treatment. Typically k values of 0.10 to 0.15 day^{-1} have been reported for primary and secondary effluent [8].

Concomitant with the oxygen demand, an average 61% reduction in the slurry wastewater's DOC was noted (Table 1) after activated sludge treatment. The removal of soluble organic material from solution by activated sludge is thought to be a two-stage process: adsorption followed by metabolism [1,13]. The first step is hypothesized to be a physical process, while the later step is enzymatically mediated [18]. However, adsorption of the DOC onto activated sludge was insignificant. As seen in Fig. 1, removal of slurry wastewater DOC required a viable activated sludge population. There was no removal of DOC from the slurry wastewater by sludge treated with biocidal levels of $HgCl_2$. In contrast, the DOC decreased by 50% of the initial concentration when the activated sludge remained viable. The failure of the slurry wastewater DOC to adsorb onto mercury-treated activated sludge was not surprising. Hydrophobic molecules are the most susceptible compounds to removal by adsorption, and the soluble organic material in the slurry wastewater has been characterized as polar, water-soluble polymers of moderate but variable molecular weight originating from the humic and fulvic acids present in the parent coal [22,23].

The BOD test is an indirect measurement of the pollution potential of a wastewater; however, compounds other than organic carbon can contribute to the oxygen demand of the slurry wastewater [4,9]. In this investigation there was not a direct relationship between BOD_{20} (20-day) and the concentration of organic material in the wastewater. This lack of correlation between oxygen consumed and the initial DOC is exemplified by comparing the results obtained for experiments Nos. 1 and 4

Table 1

DOC removed and BOD constants for Wyodak coal slurry transport wastewater

Experiment	Initial DOC (mg of carbon · liter^{-1})	BOD_{20} (mg · liter^{-1})	k_1 (day^{-1})	DOC removed (%)	BOD_{20}/DOC
1	114	78	0.09	51	0.68
2	298	216	0.10	74	0.72
3	197	108	0.11	59	0.54
4	142	52	0.08	61	0.35
Mean	188 ± 81[a]	113.5 ± 72.1	0.10 ± 0.01	61 ± 10	0.57 ± 0.16

[a] One standard deviation.

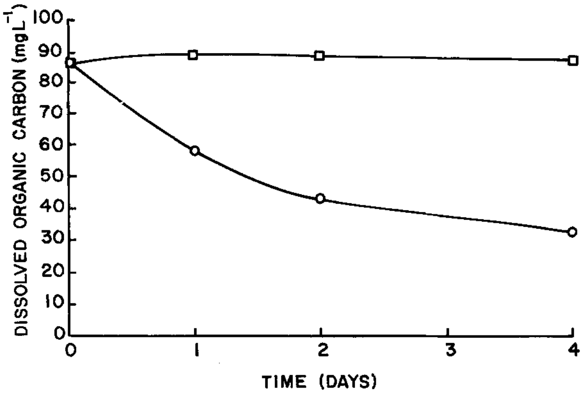

Fig. 1. Kinetics of DOC removal from Wyodak slurry wastewater by activated sludge. Biomass levels were determined by AODC and are recorded as bacteria · ml^{-1}. ○, $6.43 \cdot 10^7$; □, mercury-killed cells, $6.89 \cdot 10^7$.

(Table 1). Although BOD_{20} was higher for study No. 1 than for study No. 4 (78 vs. 52 mg · $liter^{-1}$), the initial DOC was lower for study No. 1 (114 vs. 142 mg · $liter^{-1}$).

Kinetic parameters were developed to provide more accurate predictions of biologically mediated removal of the DOC from slurry wastewaters. Factors controlling microbial transformation rates are poorly understood but are assumed to be enzymatically mediated and should follow Michaelis-Menten type kinetics [12]. Under non-saturation conditions, at substrate concentrations less than k (half saturation constant), substrate removal is a first order process with respect to substrate concentration [15,19]. In this investigation DOC removal was determined to be pseudo-first order with respect to the DOC concentration.

First order kinetic constants for DOC removal were determined for four separate experiments and these values are presented in Table 2. A linear decrease in the $\log_{10}$ DOC concentration occurred with time, and this linear relationship was demonstrated by the high values obtained for the coefficient of variation (r^2) (Table 2) for these four studies. The k_1 varied about 2.5-fold (0.020 to 0.049 day^{-1}, Table 2). However, when the k_1 values were normalized to the biomass concentrations the difference in the second order kinetic constants (k_2) was reduced to less than 25% ($1.74 \cdot 10^{-4}$ vs. $2.30 \cdot 10^{-4}$ liter · day^{-1} · (mg of $sludge)^{-1}$) (Table 2).

The removal of the DOC from the slurry wastewater was shown previously to be a biologically mediated process, since no organic material was removed from the wastewater by a mercury-killed activated sludge population. However, the fate of the DOC could not be determined by simply monitoring DOC removal. To examine the interaction of the DOC and the activated sludge more closely, carbon material balance was calculated from the data on initial and final DOC concentrations, cellular carbon, and respired carbon. As seen in Table 3, 61% to 97% of the DOC removed could be accounted for as biomass accumulated or respired as carbon dioxide. The slurry wastewater provided a source of readily oxidizable carbon for the activated sludge, since net carbon dioxide respired ranged from 21% to 41% of the total DOC removed. The

Table 2

First and second order rate constants for removal of DOC from slurry wastewaters

n.d., not determined.

Wyodak sample	k_1 (day^{-1})	r^2	Dry weight (mg · $liter^{-1}$)	k_2 liter · day^{-1} · (mg of $sludge)^{-1}$
1	0.020	0.95	115	$1.74 \cdot 10^{-4}$
2	0.028	0.94	161	$1.74 \cdot 10^{-4}$
3	0.044	0.98	n.d.	n.d.
4	0.049	0.97	213	$2.30 \cdot 10^{-4}$
Mean	0.035	0.96	163	$1.93 \cdot 10^{-4}$

Table 3

DOC respired and accumulated into biomass during respirometer studies

Wyodak sample	Net DOC removed[a]	Biomass		Respired CO_2		Percent of DOC removed in biomass plus respired
		net accumulation	percent of total DOC removed	net CO_2 respired[a]	percent of total DOC removed	
1	29.0	7.2 ± 0.6	25	10.3 ± 1.4	36	61
2	111.0	34.0 ± 1.5	31	44.6 ± 0.7	40	71
3	57.9	27.5 ± 4.1	47	24.0 ± 1.7	41	88
4	44.1	33.5 ± 2.1	76	9.2 ± 0.7	21	97

[a] All values recorded as mg of carbon present.

results from these experiments provide unequivocal evidence that slurry wastewater DOC provides a carbon and energy source for the growth and metabolism of the activated sludge.

The previous BOD analyses and DOC removal kinetic determinations were conducted using batch reactors (E/BOD respirometer). Such analyses may suffer from the lack of steady state maintenance of the microbial community during prolonged incubations. Consequently, kinetic parameters describing removal of DOC during biological treatment may not realistically predict process efficiency. For this reason fill and draw reactors (semi-continuous system) were employed to develop kinetic parameters for DOC removal from Wyodak slurry wastewaters. Furthermore, two different concentrations of activated sludge were used to examine the effects of the biomass concentrations on the kinetics of DOC removal.

Initial substrate concentrations in the reactors ranged from 90 to 250 mg of carbon · liter^{-1}. Fig. 2 displays the linear relationship between DOC removal rates and the concentration of DOC in the semi-continuous reactors. A 2-fold difference was observed in the k_1 (slope) between the two reactors (0.27 vs. 0.49 day^{-1}, Fig. 2) but this difference disappeared when the first order kinetic constants were normalized to the biomass concentrations. The resulting second order constants were $1.47 \cdot 10^{-4}$ and $1.39 \cdot 10^{-4}$ liter · day^{-1} · (mg of sludge)$^{-1}$ (Fig. 2).

The difference in reactor designs between the fill and draw and the batch reactors would be expected to affect the activity of the activated sludge. For the batch reactors, potentially toxic metabolic end products and nutrient depletion should occur, reducing the overall metabolic activity of the microorganisms. In the fill and draw reactors clarified supernatant is wasted on a bidaily basis and replenished with fresh feed stock. Microbial activity would be expected to be higher under these conditions. The k_1 for the batch reactors varied from 0.020 to 0.049 day^{-1} and from 0.27 to 0.49 day^{-1} for the semi-continuous system. This difference is over 10-fold for the two reactor designs and renders

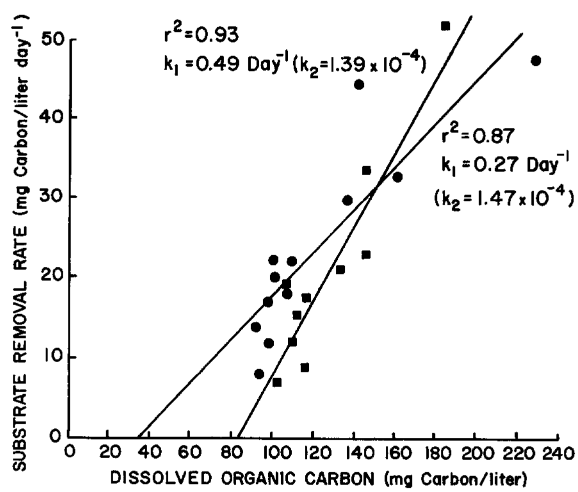

Fig. 2. Rate of DOC removal by an activated sludge population in a semi-continuous (fill and draw) reactor. Each observation represents the average value from duplicate reactors. (k_2 second order rate constants first order in substrate and biomass.) Biomass: ■, 3525 mg · l^{-1}; ●, 1836 mg · l^{-1}.

direct comparison between k_1 values for the different systems difficult. When the results were normalized to the biomass concentration, the second order kinetic constants then became comparable between the two systems. The mean value of the second order kinetic constants for the batch culture (respirometer) studies was $1.93 \cdot 10^{-4}$ liter $\cdot$ day^{-1} $\cdot$ (mg of sludge)$^{-1}$ (Table 2). This difference was only 25% from the average k_2 determined for the fill and draw reactors ($1.43 \cdot 10^{-4}$ liter $\cdot$ day^{-1} $\cdot$ (mg of sludge)$^{-1}$. Similar rate constants developed for the different reactors further support the interpretation that the differences in the k_1 values were due primarily to the total biomass. These results reinforce the importance of accounting for biomass concentrations in developing kinetic parameters for predicting biological treatability.

The second order kinetic constants for the removal of slurry wastewater DOC compare favorably with those developed by other investigators [5,19,25]. Paris et al. [19] examined the transformation of phenols and substituted phenols by pure cultures of *Pseudomonas putida*. The second order kinetic constants for these data normalized to liter $\cdot$ day^{-1} $\cdot$ (mg of biomass)$^{-1}$ ranged from $2.25 \cdot 10^{-5}$ to $8.00 \cdot 10^{-4}$ liter $\cdot$ day^{-1} $\cdot$ (mg of bacteria)$^{-1}$. Since these values were determined for pure culture, they may not be directly applicable for comparison with those developed for a mixed microbial community such as activated sludge. However, Sayler and coworkers [25] determined second order kinetic constants for the mineralization of aromatic compounds under batch culture conditions using acclimated activated sludge. The average k_2 values for the mineralization of phenol and toluene by activated sludge were $2.12 \cdot 10^{-4}$ and $3.50 \cdot 10^{-4}$ liter $\cdot$ day^{-1} $\cdot$ (mg of bacteria)$^{-1}$, which ranged very close to the average value determined for the removal of the DOC from Wyodak slurry wastewater under batch culture conditions ($1.93 \cdot 10^{-4}$ liter $\cdot$ day^{-1} $\cdot$ (mg of sludge)$^{-1}$; Table 2). The magnitude of the kinetic constants in this investigation is very close to kinetic constants determined for those systems in which biodegradation was successful. Thus biological treatment by activated sludge provides a viable alternative for reducing the carbon load of the coal slurry wastewater.

DOC molecular weight distribution

Removal of all organic contaminants from the slurry wastewater was not achieved. A residual concentration of carbon remained after biological treatment (an average of 33 mg of carbon $\cdot$ liter^{-1}, data not shown). Further evidence that a fraction of the DOC in the slurry wastewater was resistant to biological attack was provided by the BOD/DOC ratios (Table 1). The mean ratio observed in this investigation was 0.57 ± 0.16, and the ratios are considerably lower than those reported for wastewater routinely treated with activated sludge. For example, BOD/TOC (total organic carbon) values ranging from 1.26 to 1.44 have been reported for settled influent and domestic sewage [2,3]. The BOD/TOC ratio for biologically treated industrial and domestic wastewater routinely ranges from 0.2 to 0.7. Such reduced ratios (0.35 to 0.68; Table 2) indicate that slurry wastewater contains a fraction of non-biodegradable or slowly biodegradable organic material.

The nature of the recalcitrant organic material was further elucidated using ultrafiltration analysis. The DOC in Wyodak slurry wastewater was fractionated by ultrafiltration before and after each respirometer study. Three different molecular weight classes were examined: MW $>$ 5000, MW 5000–1000, and MW $<$ 1000. Table 4 represents a summary of the percentage of DOC removed from each of the three fractions. For the four respirometer studies there was an average of 61% $\pm$ 10 (Table 1) reduction of the initial DOC. Greater than 80% (Table 3) of the total DOC removed was from the MW $<$ 1000 fraction.

There was a net removal of 19.0 ± 16.4% from the MW 1000–5000 fraction; however, the percentage removed was far less than observed for the MW $<$ 1000 fraction. One reason for the lower removal of DOC in the mid-range organic fractions is that the physical size of the organic compounds render them less susceptible to uptake and metabolism. An alternate, but equally plausible, explanation is that the removal rate of the mid-range DOC was com-

Table 4

Relative molecular weight distribution and removal of Wyodak slurry DOC following biological treatment

Respirometer study	MW > 5000 (%)	MW 5000–1000 (%)	MW < 1000 (%)
1	−21.5[a]	+8.4	+113.0
2	+4.0	+36.0	+60.0
3	−20.0	+29.6	+90.6
4[c]	+27.6	+2.0	+70.5
Mean	−2.5 ± 23.2[b]	+19.0 ± 16.4	+83.5 ± 23.4

[a] Negative sign indicates net gain in DOC and each value represents the percent of total DOC removed.

[b] ± one standard deviation.

[c] Acclimation time was greater than 1 month for study 4 and 5–7 days for studies 1, 2 and 3.

parable to the MW < 1000 fraction, but this could have been masked by conversion of part of the MW > 5000 material to the mid-range DOC class.

Less straightforward results were observed in the higher molecular weight (MW > 5000) fraction. In this fraction there was an overall 2.5% gain in DOC for the four experiments, although this average is somewhat misleading. For respirometer studies 1, 2, and 3 there was little reduction in the MW > 5000 class. In contrast, there was a 27.6% reduction in the MW > 5000 fraction for study 4. This reduction can be attributed to the increased acclimation time of the activated sludge. In experiment 4 the activated sludge was maintained in the presence of the slurry wastewater as the sole carbon source for over 1 month, while for studies 1, 2, and 3 the acclimation period was reduced to only 5–7 days.

The DOC in the higher molecular weight fractions (MW > 5000 and MW 1000–5000) appeared to be more slowly transformed or were completely resistant to removal. However, this fraction may not contain the same organic components that were present in the initial slurry wastewater. There are numerous reports which indicate that the higher molecular weight compounds in biologically treated wastewater effluents can be direct byproducts of microbial metabolism [7,10,24]. Indeed, in this investigation the net increases in DOC of the MW > 5000 class, observed in respirometer studies 1 and 3, was likely caused by microbial metabolism. Although removal of some of the MW > 5000 fraction can be attributed to the metabolic activity of the activated sludge, the pattern of DOC removal suggests that the slurry wastewater DOC becomes more recalcitrant to removal as the molecular weight of the DOC increases. A corollary to this hypothesis is that the organic compounds in the lower molecular weight fractions should stimulate greater microbial activity. To determine which of the molecular weight fractions had the greatest stimulatory effect on the activated sludge, the following experiment was performed. The DOC in each of four inclusive molecular weight classes (MW > 5000, MW < 5000, MW > 1000 and MW < 1000) and raw Wyodak slurry wastewater were added to activated sludge. The rate of oxygen utilization was monitored in order to assess microbial activity. The results of these experiments are presented in Table 5. Raw Wyodak slurry wastewater stimulated the highest rate of oxygen utilization (15.8 $\mu g \cdot ml^{-1} \cdot h^{-1}$) while the MW > 5000 fraction exhibited only endogenous respiration rates (0 $\mu g \cdot ml^{-1} \cdot h^{-1}$) (Table 5). The MW < 5000 fraction stimulated activity greater than any of the four enriched fractions (14.7 $\mu g \cdot ml^{-1} \cdot h^{-1}$). The rate of oxygen uptake by the MW < 1000 fraction was 13.8 $\mu g \cdot ml^{-1} \cdot h^{-1}$ and approached 90% of the activity exhibited by the raw slurry wastewater. These results are in agreement with the previous

Table 5

Oxygen uptake by the activated sludge using different molecular weight fractions of Wyodak slurry wastewater

Molecular weight fractions	DOC (mg of carbon $\cdot$ liter^{-1})	Oxygen uptake (mg $O_2 \cdot ml^{-1} \cdot h^{-1}$)
MW > 5000	107	0
MW > 1000	104	2.6
MW < 1000	110	13.8
MW < 5000	102	14.7
Raw coal slurry water	118	15.8

experiments in that the MW < 1000 fractions of the Wyodak slurry wastewater were the most susceptible to microbial attack.

The results of this investigation demonstrate that conventional biological treatment is effective in reducing the DOC load of coal slurry transport wastewater. This removal is initially accomplished by preferential removal of the lower molecular weight organic material. The preferential removal of lower molecular weight organic material is characteristic of activated sludge treatment and similar observations have been reported by others for the effluent from sewage treatment plants [17] and bench-scale, activated sludge reactors [10]. The unavailability of the higher molecular weight compounds to the microorganisms could explain the recalcitrant nature of the higher molecular weight DOC. The increased size of the molecules may prohibit their transport and prevent their subsequent removal. Alternately, without prolonged acclimation the microorganisms present in the activated sludge may not develop the enzymatic capacity necessary for the metabolism of these larger organic compounds which are apparently fulvic polymers [23].

A qualitative description of the slurry wastewater's DOC has recently been reported by Reid and coworkers [23]. The organic constituents were classified as largely polar, fulvic type compounds. Gas chromatography-mass spectrometry analyses of the oxidized and methylated slurry wastewater's fulvic compounds revealed the presence of five distinct classes of compounds: (1) benzenecarboxylic acid esters; (2) methoxybenzenecarboxylic acid esters; (3) furan carboxylic acid esters; (4) aliphatic debasic acid esters; (5) aliphatic forbasic acid esters [23]. However, the non-fulvic organics found in the wastewater were primarily aliphatic in nature [23]. Future work should identify which classes of compounds are susceptible as well as recalcitrant to biological removal. Furthermore, alternative bioreactor designs including fixed film processes need to be examined for potentially more efficient removal of the high-MW DOC which would contribute to a reduced impact of wastewater discharge and perhaps greater flexibility in reuse applications of the process wastewater.

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