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Application of Acute Bioassays in Evaluating the Treatment of Coal Liquefaction Wastewaters

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Many processes involved in the conversion of coal to gaseous and liquid synthetic fuels produce aqueous wastes containing relatively high concentrations of phenols, ammonia, and sulfide, as well as a myriad of other organic and inorganic species (Singer et al. 1978; Tsai et al. 1982). The bulk of these contaminants must be removed from the wastewater prior to reuse or discharge to the aquatic environment. Previous investigations have demonstrated the applicability of conventional treatment technologies in controlling the wastewater generated during coal gasification and liquefaction (Luthy 1981; Drummond et al. 1982). It can be concluded from these studies that no single treatment operation is capable of removing all of the hazardous compounds present in these complex wastewaters. Therefore, it is important that the design of a coal conversion facility includes an environmental control program that incorporates a variety of wastewater treatment operations.

This paper presents results of acute bioassays performed on untreated coal liquefaction process wastewater and the wastewater following a series of treatment steps. The objective of this study was to determine the applicability of acute toxicity tests in evaluating the effectiveness of an integrated wastewater treatment strategy and selected treatment unit operations in reducing the contaminants present in the wastewater. In addition, the relative contribution of the major organic and inorganic components to the total acute toxicity of the wastewater was examined.

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The wastewater examined in this study was obtained from the 200-ton-per-day H-Coal liquefaction pilot plant located in Catlettsburg, Kentucky. This wastewater was generated during the liquid product separation and fractionation steps of the conversion process. Kentucky number 9 coal was used as the feedstock.

MATERIALS AND METHODS

Acute toxicities to Daphnia magna (< 24 hrs. old) were determined for the untreated and treated H-coal wastewater according to procedures developed by the Environmental Protection Agency (1978). Testing was performed in an environmental chamber at 20 $\pm$ 0.5°C under a 12-hour light/12-hour dark lighting regime. Serial test dilutions were prepared on a volume percent basis with spring water. The spring water had an average pH of 8.1; total alkalinity of 210 mg/L (as $CaCO_3$); and total hardness of 235 mg/L (as $CaCO_3$). Standard methods (1980) were employed for all chemical analyses except as indicated. Median effective concentrations (EC_{50}s) and 95 percent confidence limits were calculated using a computerized version of the Litchfield and Wilcoxon (1949) log-probit method. Relative toxicities, defined as the acute toxicity of the individual treatment operation effluents relative to the acute toxicity of the untreated wastewater, were also determined.

Bioassays were conducted on the untreated H-Coal process wastewater and the wastewater after each step of an integrated treatment train maintained and operated at the U.S. Department of Energy's Pittsburgh Energy Technology Center (Drummond et al. 1984). The treatment train consisted of dissolved-gas stripping, solvent extraction, biochemical oxidation, and activated-carbon adsorption. In addition, a sample of the raw wastewater was assayed after undergoing laboratory wet-air oxidation.

RESULTS AND DISCUSSION

Acute toxicities and gross chemical characteristics of the untreated and treated wastewater are shown in Table 1. A progressive reduction in acute toxicity was noted following each treatment step of the integrated treatment train (Figure 1). A reduction in acute toxicity was also recorded after wet-air oxidation of the untreated wastewater. The complete treatment sequence resulted in a greater than 99% decrease in acute toxicity, from a 48-hr EC_{50} of 0.03% for the raw wastewater to a 48-hr EC_{50} of 64.0% for the activated-carbon-column effluent. The decrease in acute toxicity following treatment reflects the significant reductions in the inorganic and the organic components of the wastewater. As evidenced in Table 1, total ammonia, sulfide, phenols, chemical oxygen demand (COD), and total organic carbon (TOC) each decreased by more than 98%.

Table 1. Acute toxicity and chemical characterization of treated and untreated H-Coal wastewater

Treatment operation	48-hr EC_{50} (%)	Concentration in mg/L				
		4-AAP Phenols	Total organic carbon (TOC)	Chemical oxygen demand (COD)	Total ammonia	Sulfide
Untreated	0.03	9150	11030	51900	5500	3900
Dissolved-gas stripping	0.12	9100	10090	34600	200	$\leq$ 10
Solvent extraction	2.55	50	890	2580	180	$\leq$ 10
Biochemical oxidation	53.0	$\leq$ 1	140	340	110	$\leq$ 10
Activated-carbon	64.0	$\leq$ 2	5	15	100	$\leq$ 10
Wet-air oxidation[a]	0.32	235[b]	2555	5300	4450	--

[a]Not a component of the integrated treatment train.
[b]Determined by liquid chromatography.

The relative toxicity of the untreated wastewater and treated effluents is presented in Figure 2. These results further highlight the concomitant reduction in acute toxicity associated with each treatment step reduction in the inorganic and the organic contaminants present in the wastewater.

The first step of the integrated treatment train, dissolved-gas stripping, was responsible for a significant reduction in the total ammonia present in the wastewater (Table 1). The acute toxicity to many aquatic organisms of total ammonia (NH_3 + NH_4^+), however, is attributed to its un-ionized (NH_3) component (Willingham 1976; Parkhurst et al. 1981). Therefore, in order to evaluate the toxic contribution of total ammonia, un-ionized ammonia concentrations were calculated for the untreated wastewater and the treated effluents at their respective EC_{50} dilutions and pH as described by Parkhurst et al. (1981) (Table 2).

As presented in Table 2 the un-ionized ammonia concentration calculated at the 48-hr EC_{50} dilutions of the untreated wastewater and the wastewater following the final treatment step, activated-carbon adsorption, were 0.10 mg/L and 2.45 mg/L, respectively. These values compare favorably with the 48-hr EC_{50} un-ionized ammonia concentrations for untreated hydrocarbonization (HCZ) wastewater and an ammonia solution calculated at 25°C and at pH 8.2 by Parkhurst et al (1981). They reported un-ionized ammonia concentrations at the 48-hr EC_{50} dilution to *D. magna* of 0.17 mg/L and 2.08 mg/L, respectively, for the HCZ effluent and the ammonia solution.

A further examination of Table 2 shows that the calculated un-ionized ammonia concentration decreased after dissolved-gas stripping and then proceeded to increase after each successive step of the integrated treatment train. The initial decrease in the calculated un-ionized ammonia concentration was the result of the substantial reduction in total ammonia (Table 1). The subsequent increases, however, were due to the significant decreases in phenols, TOC, and COD. These results strongly suggest that the acute toxicity of the un-ionized ammonia component is influenced by the organic contaminants present in the wastewater. Thus, it would appear that as the organic compounds are effectively removed, the contribution of un-ionized ammonia to the acute toxicity of the treated wastewater will become more apparent. Further toxicity testing of the major components of the wastewater, however, would be necessary in order to accurately define the relationship between the organic contaminants and un-ionized ammonia.

The largest reductions in acute toxicity were recorded after solvent extraction of the wastewater and after biochemical oxidation. The effluents from the solvent extraction column and the biological reactor were over twenty times less toxic

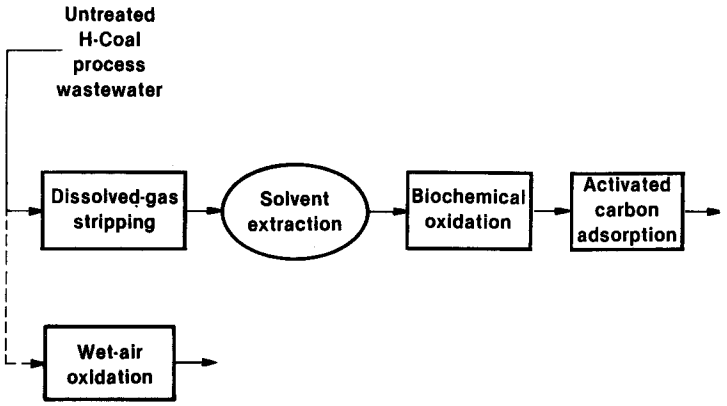

Figure 1. Integrated wastewater treatment train.

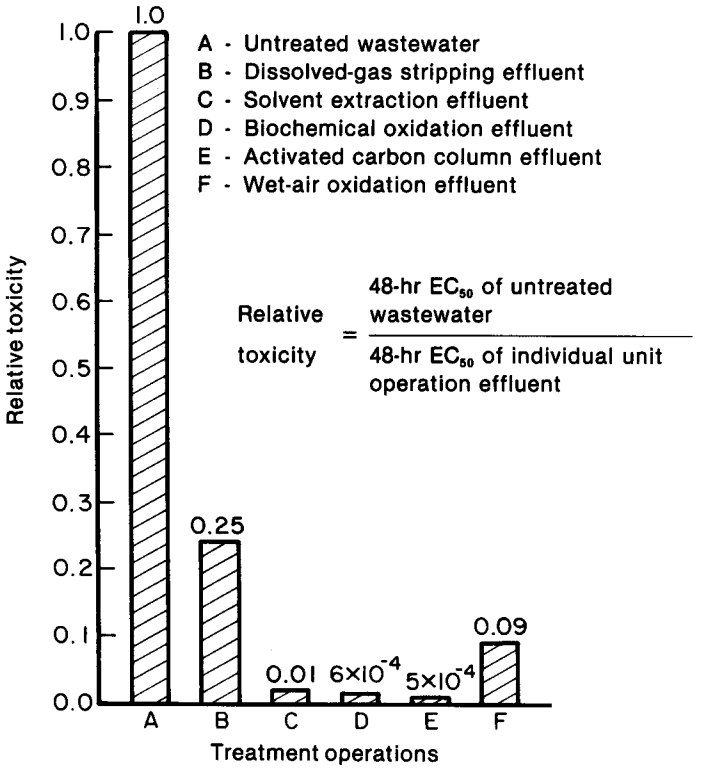

Figure 2. Relative toxicities of treated and untreated H-coal wastewater.

Table 2. Calculated un-ionized ammonia (NH_3) concentrations for the untreated and treated H-Coal wastewater

Treatment operation	pH at the 48-hr EC_{50}	(NH_3 + NH_4^+) at the 48-hr EC_{50} (mg/L)	Calculated NH_3 at 48-hr EC_{50}[a] (mg/L)
Untreated	8.2	1.65	0.10
Dissolved-gas stripping	8.1	0.25	0.01
Solvent extraction	7.8	4.59	1.11
Biochemical oxidation	7.7	58.3	1.14
Activated-carbon adsorption	8.0	64.0	2.45
Wet-air oxidation	7.8	14.2	0.35

[a]The un-ionized ammonia concentrations were calculated at 20°C and a pKa of 9.4 for NH_3.

than their respective influents (Table 1). These acute toxicity reductions were associated with significant decreases in the wastewater's organic contaminants. However, it should be noted that ammonia and sulfide had been removed previously from the wastewater during dissolved-gas stripping. This reduction in the inorganic compounds undoubtedly contributed to the large decrease in the acute toxicity of the solvent-extracted and biochemically-oxidized effluents.

The results obtained in this testing program are interesting with respect to the relative component contributions to acute toxicity reported for other coal conversion wastewaters. Parkhurst et al. (1979) concluded that organic compounds such as phenols were the major contaminants of untreated HCZ wastewater that were toxic to D. magna, while inorganic compounds, predominately ammonia, were responsible for the toxicity of the wastewater following biological treatment. Conversely, Daphnia pulicaria, when exposed to raw underground coal gasification wastewater, were relatively insensitive to phenols. The principle toxic constituent of this wastewater was ammonia (DeGraeve et al. 1980).

Because of the apparent chemical interactions it is difficult to definitively quantify the contribution to acute toxicity of the major constituents of the wastewater based only on the effectiveness of the individual treatment operations in removing specific contaminants. An examination of the 48-hr EC_{50} values and chemical characteristics of the treated effluents, however, has afforded some degree of insight into the relative impact the major components have on acute toxicity. As discussed, the overall decrease in acute toxicity was due to significant reductions in both the inorganic and the organic contaminants present in the untreated wastewater, although the organics, specifically phenols, may play a more dominant role.

The impact on the acute toxicity of the wastewater of both the organic and the inorganic compounds is further evidenced in light of the acute-toxicity and contaminant reductions associated with the dissolved-gas-stripped and wet-air-oxidized effluents. Each of these treatment operations was performed on the untreated wastewater. As can be seen in Table 1, dissolved-gas stripping removed the bulk of the total ammonia and sulfide from the wastewater but had little impact on the organic components and resulted in a 48-hr EC_{50} of only 0.12%. Wet-air oxidation, on the other hand, appreciably reduced phenols, TOC, and BOD. The 48-hr EC_{50} of the wet-air oxidized effluent, however, was only 0.34% and probably reflects the high total ammonia remaining in the wastewater. The relatively small reductions in acute toxicity recorded after either of these two unit operations emphasize the importance of an integrated treatment program that removes

both the inorganic and the organic contaminants from the wastewater.

The use of aquatic bioassays in determining the acute toxicity of coal gasification and liquefaction conversion wastewaters and their major components is well documented (Parkhurst et al. 1979; Brand et al. 1980; DeGraeve et al. 1980). In addition, our investigation has demonstrated the applicability of these tests in assessing the effectiveness of a given wastewater treatment strategy and the individual treatment operations in reducing contaminant concentrations. The incorporation of an acute bioassay program as a complement to more traditional chemical and physical analysis, therefore, can provide valuable information for the successful control and mitigation of complex coal conversion wastewaters.

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