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NATURAL PROCESSES FOR TREATMENT OF ORGANIC CHEMICAL WASTE

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ABSTRACT. Anaerobic filters and combination anaerobic filter/vascular aquatic plant systems were used to remove and biologically degrade phenol and m-cresol from contaminated river water. The common reed (*Phragmites communis*) and cattail (*Typha latifolia*) were grown on top of two separate anaerobic filters. Starting with approximately 100 mg/l phenol solutions, the *P. communis*, *T. latifolia*, and plant-free anaerobic filter systems removed 93%, 83%, and 60%, respectively, of the phenol during the first 24 hours of exposure. The *P. communis* and plant-free anaerobic filters removed 69% and 58% of m-cresol from 100 mg/l solutions after 24 hours. The results indicated that the phenol and m-cresol were rapidly adsorbed on the filter surfaces and then assimilated and/or metabolized. Accurate determinations of the organics were made using gas chromatography. The corresponding TOC, BOD_5, and COD of each sample were also reported.

Dr. Wolverton has been a Senior Research Scientist with the National Aeronautics and Space Administration (NASA) at the National Space Technology Laboratory in Mississippi for the past ten years. Prior to employment with NASA he directed a research program with the Department of Defense studying the environmental effects from hazardous and toxic substances. He has a B.S. degree in chemistry and a Ph.D. degree in Environmental Engineering.

Since employment with NASA, Dr. Wolverton has directed a research program utilizing vascular aquatic plants and microorganisms for treating domestic sewage and chemical wastewater. This pioneering research has demonstrated potential for closed ecological life support systems for space applications in addition to numerous earthly applications in wastewater treatment and the recycling of plant biomass into food, feed and fertilizer. He has received several patents, published over fifty technical papers in this field, and provided consultant services to numerous state, federal and private organizations.

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Man, like all other animals, depends upon a symbiotic relationship between green plants and microorganisms for his existance on earth. Photosynthesizing plants produce and regulate the oxyen required to support life, in addition to utilizing and controlling the concentration of carbon dioxide and other gaseous chemicals produced by man, animals, and

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microorganisms during their metabolic processes. Plants in conjunction with microorganisms also recycle man's waste and produce his food. These fundamental facts have been known and taken for granted by man for hundreds of years. What man has not known, but is beginning to realize, is that natural biological processes involving the symbiotic relationship between certain plants and microorganisms can also be used to correct environmental imbalances caused by industrial development and environmental abuse, if carefully manipulated. The harnessing of natural biological processes is essential for man's future health and economical growth.

The disposal of hazardous chemical waste by deep well injection and improper land fill operations in the United States is slowly contaminating ground water supplies from which a large part of the population receives their drinking water. Surface water contamination from accidents and improperly treated waste discharged into major river systems has been a problem in the U.S. for many years. A good example is the Mississippi River which is contaminated with industrial chemicals and is still used as drinking water for thousands of people.

During the past seven years NASA has conducted research at the National Space Technology Laboratories (NSTL) in Mississippi on the utilization of biological processes for the efficient and economical treatment of domestic and chemical wastewater generated at NSTL (Wolverton and McDonald, 1977, 1979; Wolverton, 1979; McDonald and Wolverton, 1980). The vascular aquatic plants used in the first studies were floating species. The two major species were the water hyacinth (*Eichhornia crassipes*) and duckweed (*Lemna* sp. and *Spirodela* sp.). This research was highly successful and led to the installation of simple, cost effective wastewater treatment systems at NSTL and developments and communities in Florida, Texas, and California.

Recently an advanced natural wastewater treatment process has been developed by NASA which combines anaerobic microbial filter technology originally noted by Young and McCarty (1969) with the vascular plant wastewater treatment technology to produce an efficient hybrid system (Wolverton, 1981). This system uses rooted, cold-tolerant plants such as the common reed (*Phragmites communis*) growing on the surface area of a microbial rock filter bed. The microbial filter-reed system has advantages over the floating aquatic plant systems in that wastewater is only exposed to the atmosphere after treatment, higher chemical concentrations can be tolerated because of the high surface microbial filter, and the system can be used in colder climates and estuarine environments with higher salt concentrations because of the salt- and cold-tolerant characteristics of reeds.

Although this new system was developed for domestic sewage, it is demonstrating great potential in chemical waste treatment and drinking water applications. Two organics, phenol and m-cresol, were selected for study. Phenol is one of the most important industrial organic chemicals in use today. It is used in the manufacture of phenolic resins, epoxy resins, herbicides, and nylons. It is also an important industrial and pharmaceutical solvent. m-Cresol is a phenolic compound which is used as a disinfectant, an intermediate for synthetic resins, a solvent for enamel and paints, and in reclaiming rubber. Phenols were chosen as a starting point in this area of study because they have become a major contaminant in the Mississippi River.

Recent events concerned with the discharge of large quantities of phenol into the Mississippi River north of New Orleans and subsequent contamination of the city's drinking water demonstrated the need for efficient, inexpensive means of removing phenol and other toxic and undesirable chemicals from contaminated drinking water.

EXPERIMENTAL SYSTEM DESCRIPTION

The experimental system shown in Figure 1 consisted of a metal trough, 50.5 cm W × 298 cm L × 30.5 cm D. The bottom 16 cm of the trough was filled with 2.5–7.5 cm diameter railroad rocks covered with 5 cm deep of 0.25–1.3 cm diameter pea gravel. The common reed (*Phragmites communis*) was grown on top with its roots extending down through the rock filter. Two other identical troughs were also studied. One trough contained cattail (*Typha latifolia*) instead of reed, and the other trough was kept free of plants in order to assess the microbial activity of the rock filter alone. The cattail trough was used only in the phenol study. The three troughs had been matured for eight months with domestic sewage. Therefore a high anaerobic microbial population had been well established on the rock surfaces prior to this study.

The experimental troughs were maintained in a greenhouse. The minimum and maximum temperatures during the study period were 26° and 37°C, respectively.

Fifty-seven liters of water obtained from the East Pearl River at NSTL was added to each trough. Phenol or m-cresol was added to the water and a sample removed prior to introducing it into the troughs. Samples were removed by a bottom outlet at one end of each trough. At the end of each batch study period, final samples were removed, the troughs drained completely, and a new experiment started immediately.

ANALYTICAL PROCEDURES

All samples were analyzed according to *Standard*

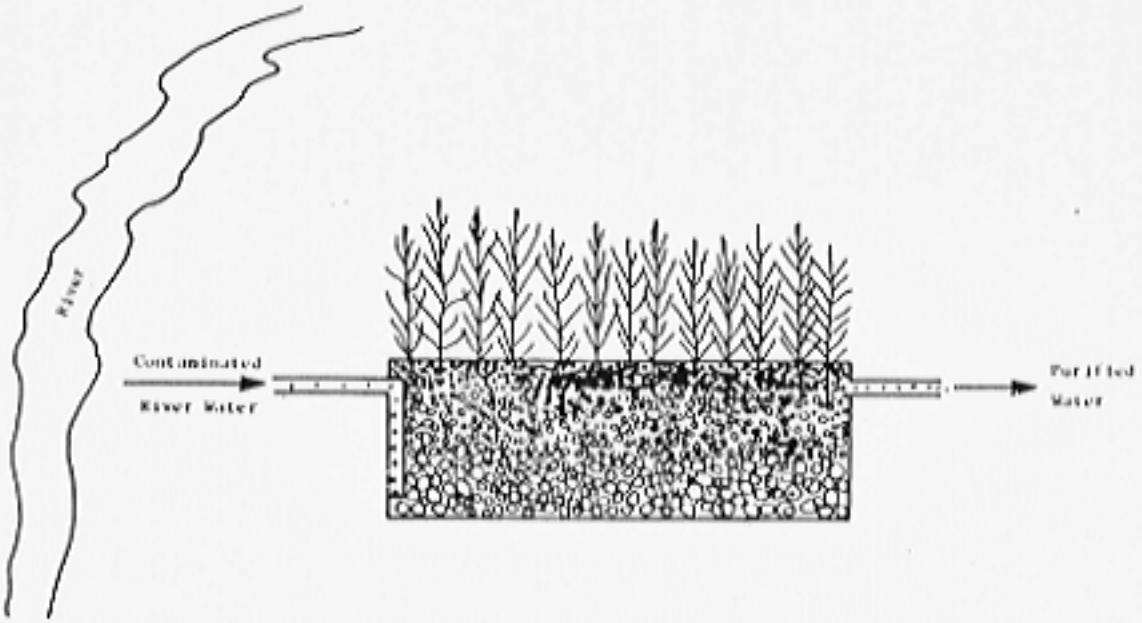

FIGURE 1. Hybrid water purification cell containing microbial rock filter and rooted aquatic plants.

Methods (1975) for total organic carbon (TOC) using the infrared-combustion method, 5-day biochemical oxygen demand (BOD_5) using a DO membrane probe, and chemical oxygen demand (COD) using the dichromate reflux method. Phenol and m-cresol were analyzed with a Varian Model 2100 gas chromatograph using a 1.8 m × 3.3 mm stainless steel column packed with 5% free fatty acid on 60/80 mesh Chromosorb W and a flame ionization detector. The injection temperature was 200°C, the column temperature 165°C, and detector temperature 250°C. The nitrogen carrier gas flow was maintained at 30 ml/min. The phenol and m-cresol retention times were 2.4 and 3.8 minutes, respectively.

RESULTS AND DISCUSSION

The results organized in Table 1 are the mean of five consecutive phenol experiments. The concentrations are not corrected for water loss due to evaporation or evapotranspiration. The phenol removal patterns for each experimental trough is graphically compared in Figure 2. During the first 24 hours, the anaerobic filter alone removed 60% of the initial 100 mg/l phenol. With *T. latifolia* in the system, 83% was removed after 24 hours. The *P. communis* system removed 93% during the first 24 hours. Wolverton and McKown (1976) had previously reported that a 100 mg/l phenol solution in river water would naturally lose only 3% of the phenol after 24 hours if allowed to sit undisturbed without any treatment. In the Wolverton and McKown (1976) study, *Eichhornia crassipes* in phenol-contaminated river water removed 18% and 84% in 24 and 48 hours, respectively. The large initial drop of the phenol concentration in the river water is probably due to rapid adsorption of the phenol when fresh solutions are added followed by microbial degradation. The filters did not display saturation and phenol bleeding during any of the five phenol or three m-cresol experiments. Wolverton and McKown (1976) found that *E. crassipes* removed and metabolized phenol to other

TABLE 1
Mean Concentrations Remaining at Sampling Times for Phenol Study.

	Concentration (mg/l)			
Exposure Time (hr)	Phenol	TOC	BOD_5	COD
W/P. communis				
0	104	57	148	308
24	7	14	15	45
48	4	6	9	33
W/T. latifolia				
0	101	63	142	312
24	17	17	36	101
48	7	18	22	48
Filter w/o plants				
0	100	59	159	286
24	40	39	57	108
48	28	28	53	97
W/o filter or plants (Wolverton and McKown, 1976)				
0	100	–	–	–
24	97	–	–	–
48	84	–	–	–

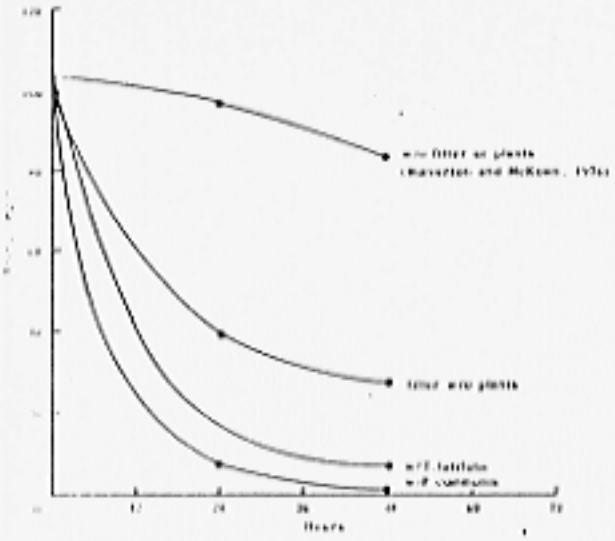

FIGURE 2. Phenol removal from contaminated river water.

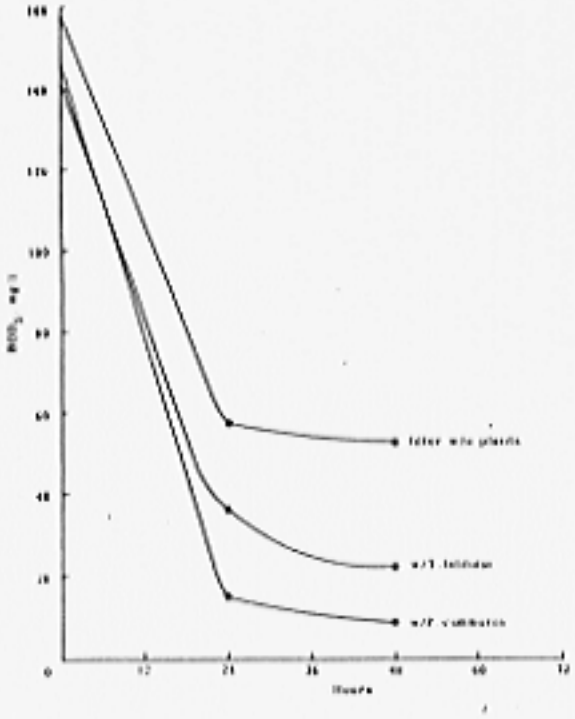

FIGURE 4. BOD_5 removal from phenol contaminated river water.

compounds. Seidel (1966) also found that bulrush (*Scirpus lacustris*) could remove phenol. However these experiments demonstrated that *S. lacustris* did not fully metabolize the phenol. Instead a portion was lost through evapotranspiration.

The TOC, BOD_5 and COD data for phenol graphed in Figures 3-5 respectively, reflected the loss of phenol. However the concentrations of these parameters remained slightly higher than would be expected based only on the remaining phenol concentrations. This suggested that most of the phenol is totally assimilated by the microflora and/or plants, and that a small portion is degraded into simpler organics which are still present in solution after 48 hours.

Following the phenol experiments, three consecutive m-cresol experiments were performed using the same *P. communis* and plant-free anaerobic filter systems. The means of three experiments are shown in Table 2. These three experiments were monitored

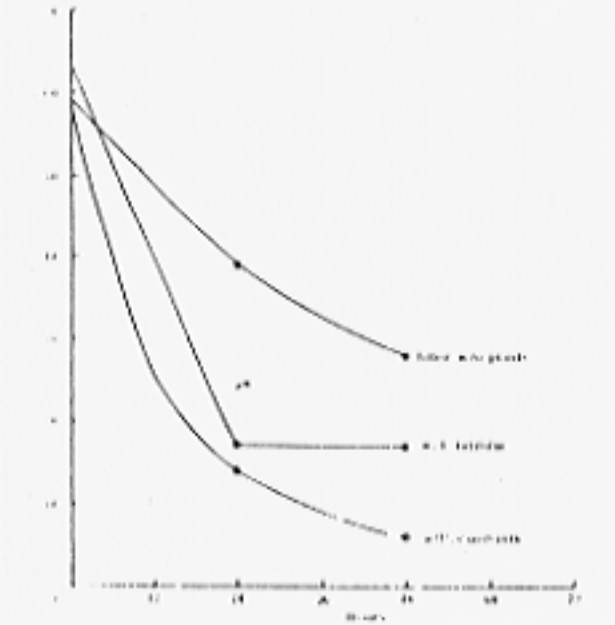

FIGURE 3. TOC removal from phenol contaminated river water.

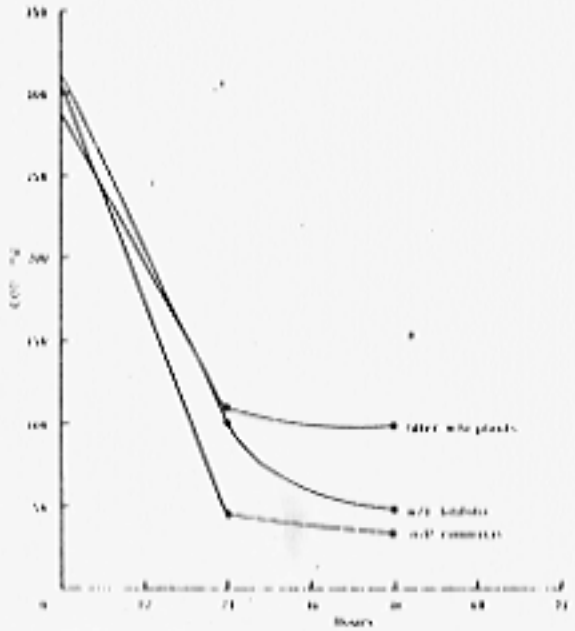

FIGURE 5. COD removal from phenol contaminated river water.

TABLE 2
Mean Concentration Remaining at Sampling Time for m-Cresol Study.

Exposure Time (hr)	Concentration (mg/l) m-Cresol	TOC	BOD_5	COD
W/P. community				
0	94	66	168	262
0.5-1.0	55	46	118	–
24	29	30	56	87
48	14	21	43	68
72	8	15	21	38
Filter w/o plants				
0	86	64	167	269
0.5-1.0	67	54	134	–
24	36	34	62	106
48	22	22	47	84
72	15	21	29	66
W/o filter or plants				
0	94	–	–	–
24	88	–	–	–
72	72	–	–	–

during the first 30-60 minutes of exposure in order to present further evidence of a significant initial adsorption effect. The plant-free anaerobic filter lost 22% and 58% of the initial m-cresol after 0.5–1.0 and 24 hours, respectively. The results of the m-cresol removal is shown in Figure 6. A comparison of the phenol curves in Figure 2 and the m-cresol curves in Figure 6 show that the system does not remove m-cresol as rapidly as phenol. This is probably due to the increased toxicity of m-cresol to the microbial population. The plants did not exhibit any physical signs of stress during the entire series of experiments.

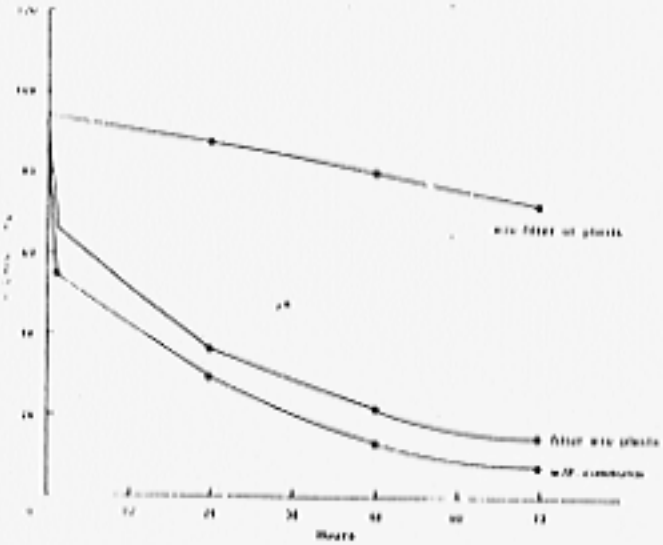

FIGURE 6. m-Cresol removal from contaminated river water.

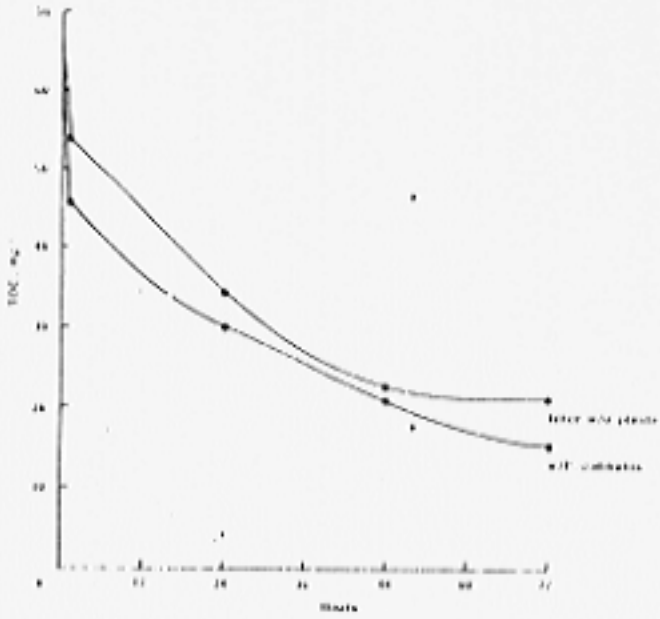

FIGURE 7. TOC removal from m-cresol contaminated river water.

The TOC, BOD_5 and COD data shown in Figures 7–9, respectively, indicate that the m-cresol removal and/or degradation process is similar to that discussed for phenol.

The results presented herein demonstrate that combination anaerobic filter/vascular aquatic plant

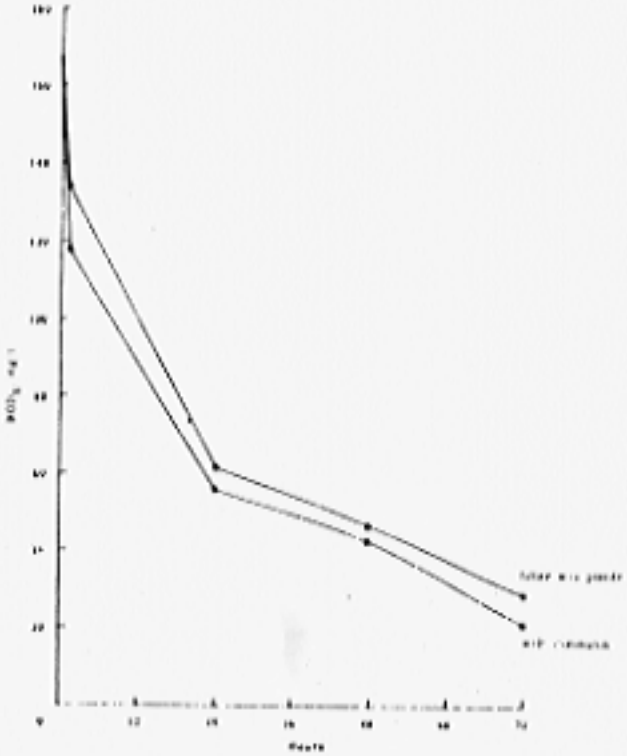

FIGURE 8. BOD_5 removal of m-cresol contaminated river water.

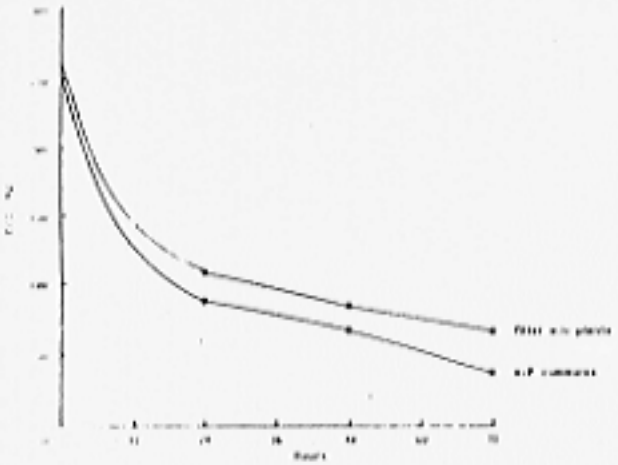

FIGURE 9. COD removal from m-cresol contaminated river water.

systems have great potential in the field of organic chemical waste treatment. This screening process at NSTL has just begun. The methods and procedures are being refined in order to use continuous flow systems to determine minimum retention times before saturation occurs and maximum concentrations which can be tolerated by the system before the microbial population is reduced or the plants display toxic effects.

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