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Project Summary

Removal of Phenolic Compounds From Wood Preserving Wastewaters

Bruce K. Wallin, Arthur J. Condren, and Roy L. Walden

Laboratory and pilot-scale studies were undertaken to develop economically feasible technologies for the treatment of wastewaters from wood preserving operations. Of prime concern was the removal of phenol and its chlorinated derivatives, in particular, pentachlorophenol. Screening analysis of the wastewater indicated that pentachlorophenol was the only chlorinated derivative consistently present in concentrations of approximately 100 mg/l.

Treatment technologies investigated for the treatment of these wastewaters included:

1. adsorption;
2. biological oxidation;
3. chemical oxidation;
4. coagulation;
5. extraction; and
6. pH adjustment.

Each of the above, alone or in combination, was capable of yielding a measurable reduction in the concentration of total phenols and pentachlorophenol in the untreated wastewater.

Two technologies yielded consistently high levels of treatment:

1. pH adjustment of the wastewater, followed by adsorption with bentonite clay and final polishing by the polymeric adsorbant, XAD-4; and

2. pH adjustment of the wastewater, followed by extraction with a mixture of #2 fuel oil and a co-solvent such as still bottoms from amyl alcohol production.

Total annual operating costs for systems treating a typical 10,000 gpd of wastewater were calculated to be \$40,000 and \$23,600, respectively, for the two aforementioned technologies.

This report was submitted in fulfillment of Contract No. 68-03-2605, Work Directive No. 2, Parts 1 and 5, by the Edward C. Jordan Co., Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 20, 1978 to May 20, 1980, and work was completed as of May 20, 1980.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research report that is fully documented in a separate report of the same title (see Project Report ordering at back).

Introduction

The U.S. Environmental Protection Agency has been involved in extensive investigations of toxic compounds being discharged from industrial facilities. Primary emphasis has been on the 65 "priority" pollutants, which are contained in the Settlement Agreement of

1976 and in the Clean Water Act of 1977 (PL 95-217). Phenolics and their chlorinated derivatives are a part of this group and are commonly found in the wood products industry's wastewater streams.

The initial objective of this study was to evaluate the treatability of 2,4,6-trichlorophenol, parachlorometacresol, 2-chlorophenol, 2,4-dichlorophenol, and pentachlorophenol in the wood products industry's wastewater. The wood preserving industry was selected for this program because wastewater from wood preserving facilities is usually low in volume but high in concentrations of chlorinated phenolics. A chemical screening of the wastewater revealed that it had a high organic content, but more significantly, it contained pentachlorophenol in concentrations exceeding 100 mg/l. The program's focus then shifted primarily to pentachlorophenol to the virtual exclusion of all else, since only trace levels of other chlorinated phenolics were found.

In conjunction with the treatability aspect, the program was intended also to explore atypical pretreatment schemes that would reduce chlorinated phenolics, namely pentachlorophenol, in typical wood preserving wastewater to levels at which the wastewater could be discharged to a POTW without causing an upset. Owing to constraints imposed by time and financial resources, it was not the objective of this program to investigate all aspects of each treatment scheme (e.g., residual catalyst after PCP removal, toxicity of the removal concentration, adsorptive capacity of the regenerated resin). The objective here was also not to improve the phenol-contaminated wastewater to drinking water quality, nor was it within the bounds of the study to make any conclusions concerning the toxicity of the residual pentachlorophenol concentration in the wastewater that would be discharged to the POTW.

The physical/chemical properties of pentachlorophenol, as distinguished from those of phenol, were important in considering the pretreatment systems which would be capable of reducing concentrations to an acceptable level. Pentachlorophenol consists of a benzene ring (C₆H₆) with all six hydrogen sites substituted by one hydroxyl group (OH) and five chlorine atoms (Cl₅). The resulting compounds, C₆Cl₅OH, is mildly acidic, boils at 309°C, and is soluble in 50°C water at 30 mg/l. Oils or emul-

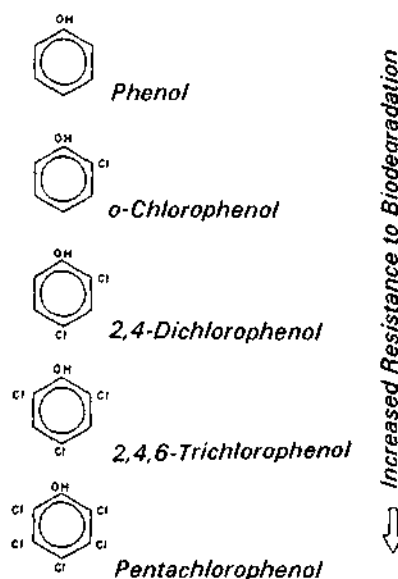


Figure 1. Phenolic resistance to biodegradation (2).

sions in wastewater can provide a "carrier" effect, allowing pentachlorophenol to far exceed its normal solubility in water. Table 1 summarizes the physical properties of several phenolic compounds. Figure 1 presents phenolic structures for several compounds.

A review of available literature assisted the investigators in identifying treatment techniques for investigation. Investigations were divided into two phases: preliminary bench-scale treatability studies and an evaluation of batch treatment techniques.

Unlike phenol, which is quite

unstable and easily oxidized either chemically or biologically, pentachlorophenol is stable and resistant to oxidation. In some instances, though, when wastewater containing pentachlorophenol in concentrations which a biomass can tolerate is run through a biological treatment system, pentachlorophenol is adsorbed onto the biofloc. Disposal of the sludge, now laden with pentachlorophenol, then presents a hazardous waste problem. Alkylinization of the sludge, a relatively common practice, would more than likely release the pentachlorophenol into the environment. If the sludge were incinerated, 2,3,7,8-tetrachlorodibenzo-p-dioxin, a thermal degradation product of pentachlorophenol, could be released into the atmosphere.

These rather ominous prospects make such treatment techniques as solvent extraction and batch polymeric resin adsorption, two schemes investigated during this study, more appealing from the standpoint of avoiding the creation of a hazardous waste problem while improving water quality.

In the preliminary bench-scale studies the investigators traveled to a wood preserving facility on the west coast to evaluate treatment technologies, described in the literature, designed to lower pentachlorophenol concentrations. Treatment schemes tested included pH reduction, acid cracking, chemical coagulation, chemical oxidation, ultrafiltration, resin adsorption, and solvent extraction.

After conducting the preliminary bench-scale studies, the investigators reported to representatives of the EPA,

Table 1. Physical Properties of Several Phenolic Compounds

Compound	Boiling Point °C	Solubility in H ₂ O mg/l @ 25°C	K _a x 10 ¹⁰
Phenol	182	93,000	1.1
o-Chlorophenol	173	28,000	77.0
m-Chlorophenol	214	26,000	16.0
p-Chlorophenol	220	27,000	6.3
2,4-Dichlorophenol	210	4,500	Large
2,4,6-Trichlorophenol	246	900	Very Large
Pentachlorophenol	309	30(50°C)	Very Large
o-Cresol	191	25,000	0.63
m-Cresol	201	26,000	0.98
p-Cresol	202	23,000	0.67
p-Chloro-m-Cresol	196	insol.	Unknown
2,4,6-Trichloro-m-Cresol	265	sl. sol.	Unknown

K_a = thermodynamic acid dissociation constant

At this time, mid-course corrections were suggested. It was suggested that the program emphasis be shifted to focus on only those pretreatment systems that would both lower pentachlorophenol concentrations to levels acceptable for discharge to a POTW and be economically feasible for wood preservers.

To meet the revised criteria, pretreatment schemes had to be both efficient and economically feasible, which essentially eliminated from consideration the more elaborate treatment technologies (e.g., reductive degradation, electrochemical oxidation, ion exchange, rotary vacuum filtration with activated carbon). The effectiveness of these cannot be denied, but the cost of installing and operating any one of them makes it economically impractical for wood preservers.

Batch treatment systems were set up at the southern facility to provide some indication of which methods were cost effective. Technologies tested at the southern facility included batch biological treatment, chemical and polymeric coagulation, resin adsorption, acid cracking, bentonite clay, solvent extraction, and filtration. As at the west coast facility, a combination of these were tested. The size of the batch treatment reactors ranged from several liters to 50 gallons, depending on the pretreatment system being tested.

Summary and Conclusions

Processes for the treatment of wastewaters from two wood preserving facilities were investigated at the laboratory and pilot scale levels. Included were various chemical, physical, and biological operations selected specifically for the removal of phenol and its chlorinated derivatives. Of the treatment technologies investigated, two systems consistently lowered the concentrations of pentachlorophenol in the wastewater from 100 mg/l to less than 1 mg/l.

In the first system, the wastewater was first acidified to a pH of 4.0 ± 0.1 , then bentonite clay was added. A polymeric adsorbant, amberlite XAD-4 was used in the final polishing process. In the second system a mixture of No. 2 fuel oil and a cosolvent (amyl alcohol still bottoms) was used to extract pentachlorophenol from the waste stream. Reductions were consistently in excess

of 99 percent. Since No. 2 fuel oil is used often in the preserving process, as it was at this facility, it is conceivable that a facility could operate this extraction process without incurring any additional chemical expense, except possibly for the cosolvent. Trials with No. 2 fuel oil alone yielded removal efficiencies in the vicinity of 97 percent, which may be high enough to allow the wastewater to be discharged to a POTW. For both systems to function consistently, the wastewater first had to be subjected to free oil separation and flow equalization. The following summarizes the findings of other investigations, based on reductions in total phenol and/or pentachlorophenol concentrations.

pH Adjustment

Lowering the pH of the wastewater with sulfuric acid was found to induce the formation of colloidal material. Subsequent removal of this colloidal material resulted in slight reductions in total phenol concentrations as measured by the modified lowry procedure described in the Project Report. Pentachlorophenol concentrations, however, were consistently reduced from approximately 100 mg/l to less than 20 mg/l.

Biological Oxidation

Biological oxidation was not found to be an effective treatment technique because bioadsorption rather than biotransformation was found to be the primary removal mechanism. Removal rates continued to diminish as the adsorptive capacity of the biomass was approached.

Chemical Oxidation

At high doses, chlorine yielded substantial reductions in the compounds of concern. Hydrogen peroxide, on the other hand, had little effect. The high chemical demand observed precludes the use of chemical oxidation as a viable treatment alternative.

Coagulation

Coagulation with alum, ferric chloride, and/or polymers resulted in modest pollutant reductions. These reductions were not deemed sufficient to justify coagulation as a sole treatment technology.

Applicability of Technologies

In turning now to the applicability of the programs' findings to the wood preserving industry as a whole, it should be understood that the utility of any single pretreatment option is contingent upon both the volume and chemical make-up of the waste stream. Because wood preserving processes are so variant, each facility must be evaluated in terms of its preserving process, its waste stream, and the capital available for investing in a pretreatment system. The systems devised for wood preservers in connection with this study would probably not be transferable to the leather tanning industry or to the paper industry, not because a No. 2 fuel oil - cosolvent mixture would not remove pentachlorophenol from leather tanning or paper industry effluent just as effectively as it would from wood preserving wastewater, but because neither of these industries uses No. 2 fuel oil in its production process (non-combustion) as do some members of the wood preserving industry. The advantage of the fuel oil extraction process is that the pentachlorophenol can be removed from the wastewater without creating an additional waste and without bringing large capital and operating expense to bear on the wood preserver.

Recommendations

If results obtained during these investigations are to be verified, a continuously flowing pilot-scale system must be established. Because this study was done on a quick response basis with limited financial resources, researchers could not investigate all aspects of each pretreatment scheme (e.g., residual catalyst after pentachlorophenol removal, toxicity of removal concentrations, utility or necessity of catalysts other than amyl alcohol still bottoms). Instead, the project provided an overview of the many economically achievable approaches to removing pentachlorophenol from wastewater and identified two systems especially successful in lowering pentachlorophenol concentrations in wood preservers' wastewater to levels that would allow it to be discharged to the POTW without causing an upset.

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Donald L. Wilson and Brian Westfall are the EPA Project Officers (see below). The complete report, entitled "Removal of Phenolic Compounds from Wood Preserving Wastewaters," (Order No. PB 81-172 637; Cost: \$12.50, subject to change) will be available only from:

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