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Project Summary

Application of Adsorptive/ Absorptive Resins and Membranes for Toxic and Hazardous Waste Reduction

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A study was undertaken to assess the use of membrane separation and ion exchange/adsorption resins for reducing or eliminating toxic and hazardous wastes in the metal finishing and munitions manufacturing industries. Data were gathered by means of a literature review and personal interviews with leading researchers in the field.

The study examined the capabilities of adsorptive and ion exchange systems using conventional resins, and it also evaluated the newer ion selective and macroreticular non-ionic resins. Similar evaluations were made for the membrane separation processes based on the use of conventional size exclusion, ion exchange film-type membranes, and experimental liquid membranes.

The process streams and operations involved in the metal finishing and munitions manufacturing industries were studied in detail. All of the important chemical species normally found in aqueous solutions throughout the plants were identified. Also documented are other chemical and physical characteristics of these streams such as the pH, suspended solids, and the presence of strong oxidizing or reducing agents.

The treatment problems encountered in the two industries are quite different, since the species to be removed from the metal finishing wastes are primarily ionic, whereas the wastes from the munitions industry contain mostly non-ionic, nitrated organic compounds. Both the membrane separation and ion exchange/adsorption resin systems are evaluated relative to the specific characteristics of the hazardous materials to be removed.

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

Introduction

This study was conducted to assess the state of the art of commercially available and developing technologies for reducing or eliminating hazardous materials from liquid wastes generated in the metals finishing and munitions manufacturing industries. The study examines membrane separation systems and ion exchange/adsorption resin systems for purifying these industrial wastewaters.

Toxic and Hazardous Wastes in the Metal Finishing Industry

The metal finishing industry uses more than 100 surface finishing and fabricating processes that require aqueous application and removal of metals. Wastewaters from metal finishing processes contain heavy metal cations that may be toxic and anions that are also a potential hazard to the environment. In addition to the ionic species, organic molecules used as brighteners, cleaners, and chelating agents are also present and can complicate the wastewater treatment process. Potential pollutants in metal finishing wastes are listed in Table 1.

Hazardous Wastes in the Munitions Industry

The common explosives produced by the munitions industry contain nitro groups attached to a wide variety of organic structures, which can be aromatic (benzene ring type), heterocyclic (rings containing non-carbon atoms), or aliphatic (straight or branched chains). The munitions industry also produces nitrated organic compounds of mercury and lead that are used as primers for explosives or propellants. Typical hazardous wastes from Army munitions operations are as follows:

RDX	(Hexahydro-1,3,5-trinitro-1,3,5-triazine)
HMX	(Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)
TNT	(Trinitrotoluene)
DNT	(Dinitrotoluene)
NT	(Nitrotoluene)
TAX	(1-Acetyl-1,2,3,4,5,6-hexahydro-3,5-dinitro-1,3,5 triazine)
SEX	(1-Acetyl-1,2,3,4,5,6,7,8-octahydro-3,5,7-trinitro-1,3,5,7-tetraazocine)
PETN	(Pentaerythritol tetranitrate)
Tetryl	(N-Methyl-N,2,4,6-tetranitrobenzenamine)

Nitroglycerin

Nitrocellulose

Nitroguanidine

PRIMERS

Lead Styphnate Pb ($C_6HN_3O_8$)

Lead Azide N_6Pb

Mercury compounds

Two particular effluents from the manufacture and processing of TNT (trinitrotoluene) and TNT-containing ordnance constitute a significant problem. Red water is a darkly colored solution that results from selite processing of TNT to remove unwanted isomers and byproducts. This solution can be concentrated and used as an additive in the paper industry or disposed of by incineration. Further washing of the partially purified TNT produces the more dilute and lighter colored solution termed "pink water." Pink water is also produced as a result of general cleaning and washing operations throughout the plant when the carrying stream has a neutral or alkaline pH and is exposed to sunlight. LAP (load, assembly, and pack) plants, where artillery shells are cleaned by steam and repacked with fresh explosives, also produce pink water. This waste stream contains RDX and HMX, two heterocyclic nitrated explosives, as well as TNT.

The wastewaters encountered in these two industries are quite different in physical and chemical characteristics and also in the type of hazard they present relevant to the general population and to the environment. In metal finishing, the species to be removed are ionic and amenable to treatment based on either ion exchange or membrane-type separation techniques. The munitions wastewaters contain mostly non-ionic, nitrated organic compounds that have so far resisted ion exchange treatment. The various organic compounds encountered should be able to be concentrated through the use of reverse osmosis or even ultrafiltration membrane systems, since these separation techniques are based on size discrimination. Removing organics from aqueous streams with adsorptive materials such as activated carbon is quite common, and resin systems with high adsorption capacities, such as those with macroreticular resins, should have the potential for treating munitions wastes.

Table 1. *Potential Pollutants in Metal Finishing Wastes*

Cations (Valence)	*Anions (Valence)*	*Other Materials*
Cr (+3 +6)	Cr_2O_7 *(-2)*	*Organics*
Cu (+1 +2)	*CN (-1)*	*Brighteners*
Ni (+2 +3)	SO_4 *(-2)*	*Cleaners*
Sn (+2 +4)	BF_4 *(-1)*	*Chelates*
Pb (+2 +4)	*Cl (-1)*	*Detergents*
Au (+1 +3)	S_2O_8 *(-2)*	
Ag (+1)	P_2O_7 *(-4)*	
Zn (+2)		
NH_4 *(+1)*		
Cd (+2)		

Use of Membrane Separation Systems

Osmotic membranes have been a laboratory curiosity since the 1920's, but practical membranes were not commercially available until the 1960's. The full report evaluates the classic thin-skinned polymeric membranes used in ultrafiltration and reverse osmosis systems today, and it examines dynamic inorganic membranes. The full report also evaluates processes that use ion exchange membranes, such as electrodialysis and Donnan dialysis. Finally, the full report considers potential applications of an emerging liquid membrane technology that uses both supported and emulsion liquid membranes.

Use of Resin Systems

A wide range of ion exchange/adsorption-type resins have been used in industrial water purification systems over the years. The new types of resins being developed for both ion exchange and adsorption applications are presented in this report. Both microreticular and macroreticular divinylbenzene/polystyrene resins are included. Also examined are chelating and reductive resins that react with the metallic ions. Finally, recently developed ion exchange precoats are examined for potential applicability.

Methods

Sources of Information

A wide range of publications dealing with the separation sciences was reviewed to develop a list of experts from industry, government, and academia who would be knowledgeable in this field. Appropriate trade publications were reviewed to identify companies actively engaged in metal finishing, munitions manufacturing, producing or supplying membranes or membrane separation systems, producing or supplying ion exchange/adsorption resins or treatment systems, or conducting research in these areas.

Evaluation of Information

Information from these sources was compiled to give an overall history and general picture of the state of the art for the different types of membrane separation and ion exchange/adsorption resin systems. The data available on the performance of individual products in the treatment of hazardous wastes from the metals finishing and munitions manufacturing industries were then evaluated Combined information from all of these sources was then assessed to determine the potential of these technologies in the treatment of waste streams from the target industries.

Results

A considerable body of data and technical information was compiled as a result of the literature review, telephone and personal interviews, and visits to various research facilities. The data are presented primarily in the form of tables that describe (1) the characteristics of the various waste streams and plating solutions encountered in the metal finishing and munitions manufacturing industries, and (2) the performance characteristics of specific types of membrane separation systems, membrane materials, commercial membrane modules, ion exchange/adsorption systems, resin materials, and commercially available resin formulations.

The full report presents a complete discussion of data available on the commercial uses of these wastewater treatment technologies and for the treatment of similar aqueous solutions. In addition, the full report reviews and evaluates the results of advanced research projects on the development of new or novel membrane systems and resin formulations that are potentially applicable to the treatment of these wastes. The conclusions and recommendations presented in the report are based on assessment of the accumulated data.

Conclusions

Treatment of Metal Finishing Wastes

Use of Ion Exchange Resin Technology

Ion exchange resin technology is a mature technology for the removal of contaminants from plating solutions, the recovery of precious metals, and the freshening of plating baths for reuse. This technology is being used by both manufacturers and firms that collect and rejuvenate spent solutions from small companies. Research is being performed by private industry and government on process improvements in areas such as producing more highly selective resins and developing better removal and recovery techniques. The economics of using ion exchange technology in the treatment of these wastes varies widely for specific applications, depending on the type of plating system involved, the configuration of rinses, and the configuration of the waste treatment system.

Use of Membrane Technology

Reverse osmosis and ultrafiltration are mature technologies for treating metal finishing wastes. Zero-sludge and reduced-sludge systems are available and are used extensively throughout the industry. Reverse osmosis has a particularly high utilization rate in the treatment of nickel plating wastewaters.

Although zirconium oxide dynamic membranes are commercially available and appear promising, they have not been used to any extent in the treatment of hazardous wastes. The newer membrane separation systems based on liquid and ion exchange membranes, Donnan dialysis, and emulsion liquid membranes are not sufficiently developed to assess their potential for application to the treatment of hazardous wastes.

The economics of using membrane separation systems in the treatment of these wastes generally depends on:

- the amount of water to be treated,
- the fouling index (SDI) of the water to be treated,
- pretreatment requirements for the wastewater before introduction to the membrane separation process, and
- the potential for resource recovery.

Potential savings and capital payback depend on.

- the value of recovered materials,
- the potential for reusing the treated water in the process,
- potential reductions in sewer discharge charges, and
- potential savings in sludge removal and disposl charges.

Electrodialysis and other electrolysis processes have been used to a moderate degree in the treatment of these waste streams. Supported liquid membranes have been demonstrated in the field and show some promise, and the combination of Donnan dialysis with other technologies has demonstrated potential for the treatment of these wastes. However, insufficient data are available at this time to assess the potential economics of these systems in the treatment of metal finishing wastes.

Of the various pollutants from electroplating processes, hexavalent chromium is probably the most difficult material to treat, since it is an anion and a powerful oxidizing agent. Claims of successful treatment have not been fully substantiated by the data available at this time.

Treatment of Munitions Wastes

Use of Ion Exchange/Adsorption Resin Technology

Granular activated carbon (GAC) has been shown to be more cost effective in the treatment of munitions wastes than currently available macroreticular resins. However, recent laboratory studies indicate that the use of these resins in a two-bed system has significant potential for being more cost effective than GAC in the future.

Use of Membrane Technology

Very little effort has been made to apply membrane separation technology to the treatment of wastewaters from the munitions manufacturing industry. Concern over the potential for accumulating dangerous concentrations of explosive materials has been a major impediment to research in this area. Also, very little work has been done on the application of membrane separation technology for treating the unique wastes from military installations. Although the data available indicate mixed results, this technology is considered to have a high potential for the treatment of these wastes in the future.

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The complete report, entitled "Application of Adsorptive/Absorptive Resins and Membranes for Toxic and Hazardous Waste Reduction," (Order No. PB 85-241 776/AS; Cost: $13.00, subject to change) will be available only from:
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