Recent advances in ion exchange materials and processes for pollution prevention

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Abstract  Even though ion exchange technology is mature and widely employed in industry, new applications, approaches, and materials are emerging at a rapid pace. This article summarizes recent advances in ion exchange technology abstracted from presentations made at the Trends in Metal Adsorption Workshop held on May 5–6, 1998 in Cincinnati, OH co-sponsored by the United States Environmental Protection Agency (U.S. EPA), the American Institute of Chemical Engineers (AIChE), the Council for Chemical Research, and the United States Department of Energy (U.S. DOE). Additional information was obtained from reviews of U.S. EPA sponsored pollution prevention projects, panel discussions and workshops, user surveys, and the authors’ discussions with practitioners in industry. The objectives of this article in the context of ion exchange applications were: (1) to review advances and applications of ion exchange; (2) to present an overview of commercially available ion exchange technology; and (3) to highlight areas for further research. Many of the advances discussed achieve improvement in ion exchange performance through the use of alternate support matrices or through the combination of technologies such as membranes or electric fields with ion exchange.

Introduction

The recovery of metals by ion exchange (IX) from rinse streams and the maintenance of process solutions in the metal finishing and printed circuit board industries is important not only as a means of achieving compliance with existing regulations, but also as a means of improving competitiveness. Many of the metals or metal salts used in these industries are valuable, and their recovery minimizes waste treatment costs and future liability. The metal finishing industry (v.s.) alone consists of more than three thousand job shops and more than eight thousand “captive” metal finishing operations within larger manufacturing facilities (Cushnie 1994). Although ion exchange, as well as many other innovative chemical, electrochemical, and membrane-based technologies, are widely used in these industries (Hartinger 1994), there still remains a need to develop, validate and improve ion exchange or sorption based separation technologies. This paper is not intended as a critical review but as an overview of emerging and recently commercialized ion exchange technologies and applications for the recovery of metals. And while it is recognized that ion exchange technology is employed in a wide variety of industries including the food and beverage industry as well as the drug industry, the primary discussion of this article will focus on new IX technologies and applications for rinse water recovery, process metal recovery, and bath maintenance found in the metal finishing industry. The presented material is based in-part on reviews of Environmental Protection Agency (EPA) sponsored pollution prevention projects, panel discussions and workshops, user surveys and the authors’ discussions with practitioners in the industry. The objectives of this article in the context of ion exchange applications in the metal finishing industry are: (1) to review advances and applications of ion exchange; (2) to present an overview of commercially available ion exchange technology; and (3) to highlight areas for further research.

In recent years the EPA has been inviting industries to work voluntarily with the EPA to improve regulations and to develop new technologies. EPA’s Common Sense Initiative (CSI), started five years ago, is one such program that works with volunteering companies and non-governmental organizations in identifying barriers to environmental improvement and suggesting ways to remove those impediments. Another highly focused program is the Design for the Environment (DfE) Printed Wiring Board Project. This multi-stakeholder program has brought together government, suppliers and public interest groups to identify high-risk activities and provide a comparative evaluation of alternatives (Hart 1997). More recently, the Environmental Technology Verification Program (ETV) has been established by the EPA to provide users of environmental technology with independently acquired performance data and operational information on new pollution prevention (P2) technologies (USEPA 1998). The CSI, Emerging Technology verification Program (ETV), EPA and DOE Small Business Innovative Research (SBIR) programs all encourage the development of new technologies to reduce pollutant emissions. In August 1997, the CSI unveiled National
Performance Goals for the metal finishing industry. These goals were: Improved Resource Utilization (Smarter Goals); Reduced Hazardous Emission (Cleaner Goals); Increased Economic Payback; and Decrease Compliance Costs (Cheaper Goals). The ETV program will verify innovative technologies designed to improve industry performance and achieve cost-effective pollution prevention. It is hoped that the verification results will generate confidence in innovative pollution prevention technologies and enhance their deployment in metal finishing operations. Some of the technologies necessary to meet these goals are available but do not meet the economic goals of the majority of metal finishers (payback <1 to 3 years depending on company size). Additional technology development is necessary to lower the cost of innovative IX technology.

The NRC’s National Materials Advisory Board (NMAB) recently convened a panel to study industrial separations in primary process industries (Munns 1998). Sponsored by the Department of Energy (DOE) Office of Industrial Technology (OIT), the study focused on the identification of separation issues within “Industries of the Future” (i.e., aluminum, chemical, glass, forest products, steel, metal casting.) The panels mission was to: review current and planned OIT research; assess current programs tasked with identifying future research and development opportunities; and suggest criteria for the identification and coordination of separations research. In a more narrowly focused effort U.S. EPA’s Office of Research & Development (ORD) in conjunction with AIChE, the Council for Chemical Research and the U.S. DOE sponsored a “Trends in Metal Adsorption Workshop” in Cincinnati, Ohio on May 5–6, 1998. ORD’s National Risk Management Research Laboratory’s Sustainable Technologies Division hosted the workshop to exchange information and to explore new developments in metals adsorption for recycle/recovery. The invited speakers and attendees representing industry, academia, and government participated in technical presentations and discussions covering new chemistries, new applications, and new physical forms for adsorbent materials.

The most common applications of ion exchange in the metal finishing industry are (1) process water deionization or softening; (2) rinse water recovery; (3) recovery of metals from rinse water; (4) final effluent polishing to ensure compliance; and (5) bath purification. In order to avoid the permitting process entirely and to ensure compliance with increasingly strict local, state, and federal regulations, more and more metal finishers are moving towards closed-loop, zero discharge processes. A generic “closed loop” metal finishing process is illustrated in Fig. 1. To achieve zero or near-zero discharge: A) water must be recycled; B) metals or metal salts must be recycled “in-process” or recovered; and C) contaminants must be removed from the process bath. The reversible nature of ion exchange and sorption processes make them particularly suited to these applications. A recent survey of metal finishers indicated that over 80% of the industry use deionized or softened water for rinsing (Cushnie 1994). This application of ion exchange technology is mature and is generally more cost effective than competing technologies such as reverse osmosis (RO).

Ion exchange materials (IEMs) contain electrically charged sites. At these sites, benign (usually sodium or hydrogen for cation exchange materials and chloride or hydroxide for anion exchange materials) ions are replaced by the target metal species. Three key factors determine the effectiveness of the ion exchange process: selectivity for the target metal ion, the number of active sites (capacity) available for exchange, and the regenerability of the ion exchange material. Regeneration allows the same ion exchange material to be used over and over again, and the target metal ions to be concentrated 100–10,000 times in the regeneration effluent. It is the ability to separate and purify as well as to concentrate that gives ion exchange the cost advantages in many applications.

**Fig. 1.** Generic metal finishing process identifying in-process pollution prevention opportunities

**Ligands and ion exchange materials**

*Existing commercial ion exchange materials*

There are a wide variety of ion exchange materials (IEMs) available from many manufacturers (Isacoff 1998; Meyers 1998). The most common IEMs are ion exchange resins (IERs) manufactured as polymeric beads, having particle sizes ranging from 0.3 to 1.2 mm, that reversibly exchange ions in solutions. This reversibility allows IERs to be regenerated and reused, resulting in substantial cost savings over non-recyclable metals removal systems. Although the variety of IEMs available in the marketplace is large, the variety of chemistries or functional groups that are commercially available has not until recently been very large. IERs typically have one of four functionalities: strong acid cations (SAC), weak acid cations (WAC), strong base anions (SBA), and weak base anions (WBA). Alternatively, chelating resins have ligands that can selectively bond with certain types or classes of metal cations. Ligand is the chemical term for an electron pair donor (Lewis base) that forms a bond with a metal cation that is a Lewis acid. The ligands may be in addition to or in place of conventional ion exchange sites. The two main configurations of IERs are gelular and macroreticular. Gelular resins make use of micropores...