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Applications of Porous Resin Sorbents in Industrial Wastewater Treatment and Resource Recovery

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ABSTRACT: Porous resins have been used to sorb organic residues in industrial wastewaters for over four decades. A survey of literature revealed that these resins have surface areas up to 1500 m²/g, and may be tailor made to selectively sorb certain groups of organic chemicals. Resins may be regenerated, upon saturation, on site at ambient temperature by solvent elution, or by other means such as pH adjustment, microwave, or steam. The organic chemicals are desorbed from the resin, during regeneration, and may be recovered for reuse. This paper reviews literature related to the applications of these porous resin sorbents for the removal and recovery of organic chemicals from wastewater, their syntheses and physicochemical properties, as well as their sorption characteristics and mechanisms. Sorption data scattered in literature are compiled, methods of resin regeneration and recovery of organic chemicals for reuse are discussed, and case studies of full-scale industrial applications in both the United States and China are presented.

KEY WORDS: porous resin, sorption, wastewater treatment, organic pollutant.

1. INTRODUCTION

Toxic and recalcitrant organic pollutants can be effectively removed from wastewater by the sorption process. Activated carbon is the most commonly used sorbent in wastewater treatment, due to its vast surface area and affinity for many organic chemicals. However, activated carbon is costly to regenerate; the process is energy intensive and has a high attrition rate. It also tends to sorb most organic chemicals indiscriminately, making it difficult to selectively recover certain organic chemicals for reuse (Weber and LeBoeuf, 1999).

Ion-exchange resins are ionic polymers. They have been widely used for decades for the removal of ionic species in water and wastewater. Nonionic resins were, however, of little practical use in water and wastewater treatment until the introduction of porous resins in the

1960s (Kunin, 1976). After four decades of development, the porous resins have become effective sorbents not just for industrial wastewater treatment, but also for the recovery of useful organic chemicals from the waste stream for reuse. These resins are physically and chemically stable, and have vast surface area comparable to activated carbon. By the proper adjustment of manufacturing process, pore structure and surface polarity of the resin may be controlled so that certain groups of organic chemicals may be preferentially sorbed. Upon resin regeneration, the organic chemicals are desorbed and may be reused due to their relative purities.

The nonionic resins may be classified into three categories: gel-type, macroporous and hypercrosslinked (Tsyurupa et al., 1995). The gel-type resins have a homogeneous, nonporous structure (Okay, 2000). The polymeric network of the resin may swell in good solvents (Davankov and Tsyurupa, 1989), which are solvents capable of dissolving the monomers (Kunin, 1980), doubling its volume in some cases (Agronaut Technologies, 1998). However, these resins are poor sorbents and thus of little use in water and wastewater treatment. They are excluded from further discussion in this paper.

Macroporous resins were first developed in the 1960s. They are capable of effectively sorbing organic pollutants, due to their porous polymeric matrix (Weber and van Vliet, 1981a). An article written over 25 years ago has reviewed many technical aspects of macroporous resins, including their physical and chemical structures, sorption characteristics, and applications in industrial wastewater treatment (Kunin, 1976). It reported that over 25 organic species might be effectively removed by these resins, including ketones, alcohols, benzenes, phenols, phenylenediamine, aniline, indenes, alkyl benzothiophenes, alkyl naphthalenes, etc.

More recently, hypercrosslinked resin sorbents have gained increasing interest. These sorbents are produced by crosslinking polymers of macroporous resin in a good solvent (Davankov et al., 1969a, 1969b). The crosslinking tightens the structures and modifies the surface properties of the porous polymeric network. As a result, hypercrosslinked resins have sorption characteristics superior to the macroporous sorbents (Streat and Sweetland, 1998a). Hypercrosslinked sorbents have been successfully applied for the removal and recovery of organic pollutants from water and wastewater, including complex organics such as benzene derivatives (e.g., naphthalene and anthracene) and heterocyclic compounds.

One of the advantages of macroporous and hypercrosslinked resin sorbents is the possibility of controlling their resin structure, internal surface area, and pore size distribution. This can be achieved by varying the polymerization conditions, the most crucial of which are the amounts of monomers and pore-forming agent used in the polymerization reaction (Kunin, 1976; Weber and van Vliet, 1981a). Consequently, sorbents may be tailor made for specific applications (Cornel and Sontheimer, 1986a). In addition to water and wastewater treatment, porous resin sorbents have also found applications in solid-phase extraction (Serva Electrophoresis GmbH, 2001), bioseparation (Lothe et al., 1999) and blood purification (He and Ma, 1997).

The porous resin technology has advanced considerably in the past two decades, especially in wastewater treatment and the recovery of valuable chemicals from waste streams. Yet, not a single review paper has been published on this technology since 1976. The objective of this paper is to provide the reader with updated technical information on this technology. Production and physicochemical characteristics of porous resin sorbents, sorption mechanisms and process parameters, resin regeneration, and recovery of sorbed organic chemicals for reuse are discussed. Sorption data scattered in various journal articles,

technical bulletins, product brochures, and websites of manufacturers have been compiled for easy reference. Full-scale case studies from the United States and China are summarized. Scientists and engineers in China have over 30 years of closed door experience in the development and applications of macroporous resin technology. Their vast and valuable experiences in industrial applications have been reported in many Chinese journals, but for the most part remain unknown outside of China.

Readers are reminded that the terminology used in the literature of porous resin sorbents has not been unified so far. This has often caused confusion. The term “macroporous resin sorbents” used in this article may be found in the literature as ‘polymeric resin,’ ‘nonionic polymeric resin,’ ‘macroporous resin,’ ‘macroporous polymeric adsorbent,’ ‘macroporous copolymer,’ ‘organic adsorption polymer,’ ‘synthetic adsorber polymer,’ ‘polymeric sorbent,’ ‘nonionic macroporous polymeric resin,’ ‘macroporous synthetic adsorbent,’ etc. The most common type of macroporous sorbent is styrene and divinylbenzene copolymer, which may be found as ‘polystyrene,’ ‘styrene-divinylbenzene copolymer,’ or simply ‘St-DVB copolymer.’

Similarly, the term “hypercrosslinked resin sorbents” used in this article may be found in the literature as ‘hypercrosslinked copolymer,’ ‘hypercrosslinked polymeric adsorbent,’ ‘hypercrosslinked polymer,’ ‘hypercrosslinked polystyrene sorbent,’ ‘highly crosslinked styrene-DVB polymer,’ ‘Friedel-Crafts modified polystyrene,’ etc.

2. SYNTHESIS AND CHARACTERISTICS OF POROUS RESIN SORBENTS

Macroporous resin sorbents are produced by suspension copolymerization of a monomer and a crosslinking agent (Kunin, 1980). The most common monomer is styrene, followed by acrylate (Kunin, 1976; Weber and van Vliet, 1981a; Mitsubishi Chemical Corporation, 2001; Serva Electrophoresis GmbH, 2001) and vinylpyrindine (Kunin, 1980; Kawabata and Ohira, 1979). The crosslinking agent used in nearly all copolymerization is divinylbenzene. Polymerization takes place in the presence of a pore-forming agent—sometimes referred to as the “diluent,” “diluter” or “precipitator”—which is soluble in the monomer mixture but itself is a poor solvent to the copolymer (Davankov and Tsyurupa, 1989; Okay, 2000). After polymerization, the pore-forming agent is removed from the polymeric network, leaving a porous structure with mechanical stability (Okay, 2000).

The physical descriptions of macroporous resins varied from ‘hard, durable, insoluble spheres’ for Amberlite XAD (Kunin, 1976), to ‘round plastic balls’ and ‘tough beads with high crush strengths’ for Dowex Optipore (The Dow Chemical Company, 2001), to ‘spherical particle, and inside it, there exist effective fine pore structures’ for Diaion and Sepabeads (Mitsubishi Chemical Corporation, 2001). As compared to activated carbon, which has a typical life of 10–20 cycles of regeneration, resin sorbents are highly durable. Sreat and Sweetland (1998a) reported that there was no apparent degradation of resin sorbents observed after two years and 1300 cycles of operation for the recovery of phenol from wastewater. Dow Chemical (2001) also reported that less than 5% of annual adsorbent replacement was required for a fluidized-bed sorption operation. Full-scale experience by one of the authors (Zhang) in China also confirms that the useful life of these resins can be over five years with more than 2000 cycles of regeneration.

Macroporous resin sorbents have surface areas comparable to those of activated carbon. The surface areas of polystyrene-divinylbenzene resin are reported as 750 m²/g for Amberlite XAD-4 (Kunin, 1976), 800 m²/g for Dowex Optipore V502, and 1200 m²/g for Sepabeads SP700 (The Dow Chemical Company, 2001). The pore diameter of polystyrene-divinylbenzene resins was as small as 6 nm, and the pore volume varies from 10 to 90% (Kunin, 1976). Commercial macroporous resin sorbents have an average pore diameter of less than 100 nm (Kunin, 1976; The Dow Chemical Company, 2001; SERVA Electrophoresis GmbH, 2001).

Between the two most common macroporous resins, polystyrene-divinylbenzene resins are nonpolar and thus hydrophobic, whereas polyacrylate-divinylbenzene resins are relatively polar and hydrophilic. Figures 1 and 2 illustrate the respective chemical structures of these two resins (Kunin, 1976). The polystyrene-divinylbenzene resins are mechanically less stable than the polyacrylate-divinylbenzene resins, probably due to the lesser reactivity between divinylbenzene and styrene in the copolymerization process (Davankov et al., 1974; Tsyurupa et al., 1974).

Hypercrosslinked resins are produced by further crosslinking macroporous resins swelling in a good solvent (Davankov et al., 1969a and 1969b). Bifunctional crosslinking agent is added to the swelling resin or produced *in-situ* (Tsyurupa et al., 1995). Using polystyrene-divinylbenzene resins as an example, the crosslinking is achieved by the methylene bridges created by the Friedel-Crafts reaction of chloromethyl groups (Veverka and Jerabek, 1999). As compared to the macroporous predecessors, hypercrosslinked resin sorbents exhibit more uniform pore size distribution with improved sorption capacity and physical strength (The Dow Chemical Company, 2001).

Surface area of hypercrosslinked resin sorbents is mostly over 800 m²/g. Some resins have surface areas over 1000 m²/g, including 1000–1500 m²/g for Hypersol-Macronet (The Purolite Company, 2001c) and 1100 m²/g for Dowex Optipore V493 and L493 (The Dow Chemical Company, 2001). The hypercrosslinked network exhibits a very low packing density with increased free volume and a highly developed inner surface (Tsyurupa et al., 1995).

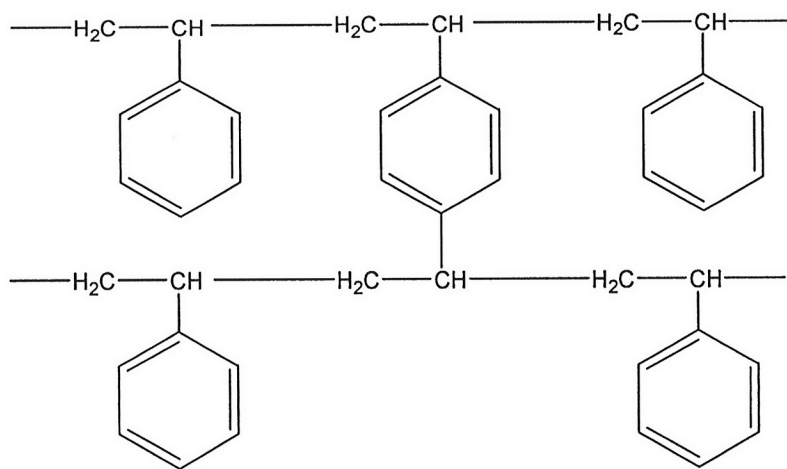


FIGURE 1. Structure of polystyrene-divinylbenzene resins, such as Amberlite XAD-2 and XAD-4 (Kunin, 1976).

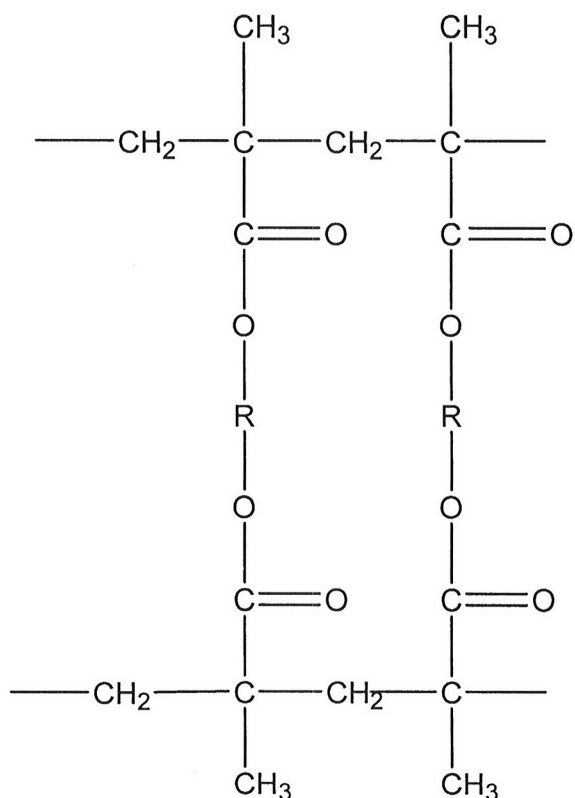


FIGURE 2. Structure of polyacrylate-divinylbenzene (Amberlite XAD-7) (Kunin, 1976).

Hypercrosslinked resins consist of oxygen- and chlorine-containing functional groups, which are by-products residues of the crosslinking reaction. The presence of these polar functional groups on the surface of polystyrene-divinylbenzene copolymers results in an increase of surface polarity and hydrophilicity, and may enhance the sorption of polar sorbates (Trochimczuk et al., 2001).

Table 1 lists the twenty porous resin sorbents available commercially by eleven manufacturers. Thirteen of these resins are macroporous, five hypercrosslinked and two unspecified.

3. SORPTION CHARACTERISTICS

Porous resins sorb organic chemicals by two mechanisms: adsorption by the pore surface and absorption by the swelling polymer matrix.

3.1. Sorption of Resins

Unlike activated carbon, macroporous and hypercrosslinked resin sorbents have high degrees of selectivity. It has become possible to tailor make resin sorbents for the sorption

TABLE 1. Commercially available resin adsorbents

Type	Resin Adsorbent	Monomers	Manufacturer
Macroporous	Amberlite XAD-2 & -4	Styrene-divinylbenzene	Rohm and Haas
Macroporous	Amberlite XAD-7, -7HP & -8	Acrylic ester	Rohm and Haas
Macroporous	Amberlite XAD-12, -16 & -1600	Divinylbenzene	Rohm and Haas
Macroporous	Duolite XAD 761	Phenolic	Rohm and Haas
Macroporous	DIAION [®] HP-20 & -21	Styrene	Mitsubishi Chemical
Macroporous	DIAION [®] HP2MG	Methacrylic ester	Mitsubishi Chemical
Macroporous	Duolite ES-861	Styrene-divinylbenzene	Rohm and Haas
Macroporous	SEPABEADS [®] SP-825, -850, -70 & -700	Styrene	Mitsubishi Chemical
Macroporous	SEPABEADS [®] SP-207	Brominated aromatic	Mitsubishi Chemical
Macroporous	SERDOLIT [®] PAD-I, -II, & -III	Styrene-divinylbenzene	SERVA Electrophoresis GmbH
Macroporous	SERDOLIT [®] PAD-IV	Acrylic copolymerisate	SERVA Electrophoresis GmbH
Macroporous	Wofait EP61 & Y77	Styrene-divinylbenzene	Chemie AG Bitterfeld
Macroporous	Wofait EP62 & Y59	Acrylic ester-divinylbenzene	Chemie AG Bitterfeld
Hypercrosslinked	CHA-101 and -111	Styrene-divinylbenzene	Zhengxing Chemical
Hypercrosslinked	DOWEX OPTIPORE L493	Styrene	Dow Chemical
Hypercrosslinked	H-103	Styrene-divinylbenzene	Nankai University
Hypercrosslinked	Hypersol-Macronet MN-200 & -250	Styrene	Purolite International
Hypercrosslinked	Styrosorb	Styrene	Biochrom
Unspecified	Lewatit EP63	Styrene-divinylbenzene	Bayer AG
Unspecified	LiChrolut EN	Ethylvinylbenzene-divinylbenzene	Merck

of specific groups of organic chemicals. This may be achieved by controlling the functional groups, pore structure and internal surface area in polymerization (Kunin, 1976; Cornel and Sontheimer, 1986a).

The early generation of macroporous sorbents had lower sorption capacity than activated carbon (McGuire and Suffet, 1978; Suffet et al., 1978). However, van Vliet and Weber (1981) found that macroporous sorbents were superior to activated carbon for the removal of concentrated organic pollutants at over 1000 mg/L, including phenol, p-chlorophenol, p-toluenesulfonate, carbon tetrachloride and dodecylbenzenesulfonate. For the sorption of trichloroethene and chloroform (Browne and Cohen, 1990), the slopes of the Freundlich adsorption isotherms for the macroporous resin sorbents were steeper than the corresponding slopes for activated carbon. This suggests that resin sorbents would have higher adsorption capacity than activated carbon at increased concentrations, as observed in the sorption of diuron in drinking water (Frimmel et al., 1999). Similarly, Streat and Sweetland (1998b) found that, as compared to activated carbon, hypercrosslinked resin sorbent had only one-third of pesticide sorption capacity at low concentrations, but the slopes of the Freundlich isotherm were three times steeper. This suggests weak interactions between resins and pesticides, which favor the recovery of pesticides during resin regeneration.

Hypercrosslinked sorbents in general have higher sorption capacity than macroporous sorbents. Hypersol-Macronet MN-200 was reported to have a concentration ratio of 120,000 in treating a wastewater containing 0.1 mg/L of pesticides (Streat and Sweetland, 1998d). Azanova and Hradil (1999) found that two hypercrosslinked resins, Lewatit EP63 and a homemade resin, had higher surface areas and over three times higher sorption activity towards phenol and other organic compounds than two macroporous sorbents, Amberlite XAD-4 and ethylene-dimethacrylate polymer. Tsyurupa et al. (1995) also found that hypercrosslinked resin Styrosorb had significantly higher sorption capacities in many cases than two macroporous resins, Amberlite XAD-2 and XAD-4. Similarly, Xu et al. (1999) found that two hypercrosslinked resins, CHA-101 and CHA-111, had higher sorption capacity for four naphthalene derivatives than the macroporous resin, Amberlite XAD-4. The superior sorption capacity of hypercrosslinked resins was attributed to their high surface area, uniform pore structure, adequate pore size and the partial polarity of the polymeric network.

3.2. Adsorption by Molecular Interactions

Adsorption of organics may be attributed to several types of molecular interactions, including hydrophobic interaction, hydrogen bonding, ionic attraction and complex formation (Streat and Sweetland, 1998b). The binding energies of hydrophobic interaction and hydrogen bonds are relatively weak. Organic chemicals adsorbed from such interactions can be easily desorbed and recovered for reuse.

3.2.1. Hydrophobic Interaction

Streat and Sweetland (1997) reported that the hypercrosslinked Hypersol-Macronet resins adsorbed phenols and chlorophenols by hydrophobic interaction, the binding energy of which was weaker than that of activated carbon. Azanova and Hradil (1999) found that hydrophobic interaction was the binding mechanism for adsorption by Amberlite XAD-4,

Lewatit EP 63 and several home-made hypercrosslinked polystyrene-divinylbenzene resins. The enthalpies of adsorption of phenol were determined as 11.06 kcal/mol and 5.30 kcal/mol for XAD-4 and Lewatit EP 63, respectively.

3.2.2. Hydrogen Bond

Amberlite XAD-7 resin exhibited higher adsorption capacities than XAD-4 resin towards phenol and 4-chlorophenol. This was attributed to the hydrogen bonding capability of the former resin (Juang et al., 1999). Judging from the enthalpy of adsorption data, XAD-7 had a stronger affinity with both solutes than XAD-4. The adsorption of aniline, N-methylaniline and N,N-dimethylaniline by Amberlite XAD-7 was also attributed to the formation of hydrogen bonds (Payne, 1990). In addition, Maity et al. (1991) showed that the degrees of adsorption for phenols, alcohols and aromatic amines, increased with the strength of the hydrogen bond between the organic chemicals and the resin.

3.2.3. Complex Formation

The phenol adsorption capacity of polyvinylpyridine-divinylbenzene copolymer was attributed to the molecular interaction between the pyridyl group of the copolymer and phenol (Kawabata and Ohira, 1979). The pyridyl group takes away a proton from phenol and forms a complex with the phenoxy anion.

3.2.4. Combined Interactions

Adsorption is often governed by more than one type of molecular interaction. Based on the adsorption isotherms, Juang and Shiau (1999) found that adsorption of phenol and chlorophenol by the macroporous Amberlite XAD resins was affected by the resin's hydrophobicity, number of active sites and pore size distribution. Judging from the apparent enthalpy of adsorption, the adsorption of phenols onto Amberlite XAD resins is likely a hybrid of physical and chemical adsorptions. The adsorption of phenols by macroporous resins was found as a physicochemical phenomenon. Streat and Sweetland (1998b), on the other hand, found that the adsorption of pesticides, including simazine, chlorotoluron, isoproturon and diuron, appeared to be controlled by both hydrophobic interaction and hydrogen bonding.

By comparing the adsorption of five organic chemicals, Weber and van Vliet (1981b) concluded that hydrophobic interaction played the key role in the adsorption of macroporous Amberlite XAD resins. The reversible nature of such interaction enables an effective desorption of the organic chemicals upon solvent elution. As a result, Amberlite XAD resins have been widely used for analytical applications, as well as for the recovery of valuable organic chemicals from waste streams.

3.3. Absorption by Resin Swelling

Resins tend to swell in good solvents. Resin swelling has been reported as a key factor in the absorption by both hypercrosslinked and macroporous resins (Gusler et al.,

1993). The swelling of resin increases the volume of the polymer phase and, thus, the absorption capacities of organic chemicals (Tsyurupa et al., 1995). Swelling may be affected by hydrogen bonding of polar organic chemicals and the macroporous resins, such as Amberlite XAD-8 (Maity et al., 1991) and XAD-12 (Garcia and King, 1989). Hydrogen bonding results in a lower free energy, a proportional decrease in the elastic entropy of deformation, and consequently a greater degree of swelling. Swelling makes the active sites at the interior of the resin matrix more accessible to the sorbate, and the swollen matrix is considered as a pseudo-homogeneous phase, which comprises the polymer, solute and solvent (Anasthas and Gaikar, 2001).

Sorption of various organic chemicals by the macroporous Amberlite XAD-4 resin was attributed to absorption by resin swelling (Simpson et al., 1993; Azanova and Hradil, 1999). Cornel and Sontheimer (1986a) also found that the sorption of a homemade macroporous polystyrene-divinylbenzene resin was governed jointly by the adsorption of the organic chemicals onto the pore surface as well as by the absorption resulting from resin swelling. They further classified absorption by swelling into two categories: absorption by latent pores and absorption by the gel regions. Cornel and Sontheimer (1986a) found that sorption of p-nitrophenol by polystyrene-divinylbenzene resins was more apparent for resins of low surface area, and concluded that sorption of organic chemicals by polystyrene-divinylbenzene resins was to a large extent due to the swelling of the gel regions. On the other hand, other researchers (Garcia and King, 1989; Gulser et al. 1993) found that sorption by macroporous resins, such as Amberlite XAD-12, was primarily due to pore filling rather than swelling. Results of Browne and Cohen (1990) and Juang et al. (1999) also suggested that absorption by swelling took place after most pore volume had been saturated.

Davankov and Tsyurupa (1989, 1990) found that sorption of organic chemicals by the hypercrosslinked polystyrene was also partly due to absorption by the swelling resin matrix. As compared to macroporous resins, hypercrosslinked resins have tighter polymeric networks and they also swell more in a good solvent (Simpson et al., 1996a). Sorption of organic chemicals by hypercrosslinked polystyrene-divinylbenzene resins was attributed jointly to the adsorption onto pore surface as well as to the absorption by the polymer matrix (Tsyurupa et al., 1995).

3.4. Factors Affecting Sorption of Organic Chemicals

The sorption efficiency of organic chemicals by porous resin sorbents is dependent upon a number of factors. These include the characteristics of (a) organic chemicals, such as molecular weight, molar volume, solubility, polarity, etc. (van Vliet and Weber, 1981; Weber and van Vliet, 1981a and 1981b); (b) sorbents, such as surface area, pore size distribution, porosity, polarity, etc.; and (c) operating conditions, such as temperature, pH, flow rate, feed concentration, ionic strength, the presence of other organic and inorganic species, etc. Some of these factors are discussed below:

3.4.1. Pore Size

Pore size distribution affects a resin's adsorption capacity. Organic chemicals that are larger than the pore openings cannot be adsorbed by the active sites inside the pores (Browne

and Cohen, 1990). This was observed in the adsorption of phenols by the hypercrosslinked Hypersol-Macronet sorbent (Streat and Sweetland, 1997) and the adsorption of large pesticides, such as atrazine (Streat and Sweetland, 1998b).

It was reported that the Wofatit EP 62 and Y 59 resins adsorbed more aliphatic amines than the EP 61 and Y77 resins, because the latter resins contained pores of smaller size (Heitzsch et al., 1994). Aliphatic amines are capable of forming micelles and vesicles with diameters of 3 to 15 nm and ≥ 30 nm, respectively, in aqueous solutions, and they are thus favorably adsorbed by the former resins, which have larger pore openings.

3.4.2. Temperature and pH

Heitzsch et al. (1994) found that macroporous Wofatit resins adsorbed more aliphatic amines at elevated temperatures. This was attributed to the increased hydrophobicity of amines resulting from the dehydration of ethoxy groups, and the lesser tendency for amines to form micelles and vesicles at elevated temperatures. They also found that the adsorption efficiency of aliphatic amines on macroporous resins increased with increasing pH. This was attributed to the de-protonation of the amines, leading to better adsorption onto the hydrophobic sorbent.

The breakthrough capacities for phenol adsorption by polyvinylpyridine-divinylbenzene and polystyrene-divinylbenzene resins were almost unaffected by pH below 7.0, but decreased drastically at pH above 8.5 (Kawabata and Ohira, 1979). On the other hand, the breakthrough capacities for adsorption of ϵ -caprolactam by Amberlite XAD-4 and crosslinked poly(hydroxystyrene) resins were unaffected by pH (Kawabata and Taketani, 1980). And yet, the breakthrough capacity for the adsorption of 2-aminonaphthalene-1-sulfonate by Lewatit EP63 resin increased at lower pH (Frimmel et al., 1999).

Doulia et al. (1997) investigated the influence of pH on the efficiency of adsorption of atrazine onto three macroporous Amberlite XAD resins. They found that at low pH the adsorption of atrazine decreased with increasing polarity of the resins. The polystyrene divinylbenzene resin tended to adsorb more atrazine than the more polar polyacrylate-based resin. At high and intermediate pH values, on the other hand, the polar polyacrylate-based resin was more effective for the retention of atrazine. The optimal pH for the adsorption of atrazine by polyacrylate resin was pH 11. They also found that adsorption of atrazine increased with decreasing ionic strength.

Feng et al. (1999) reported that the sorption of 2-hydroxy-3-carboxylic-naphthalene by hypercrosslinked resin NDA-708 was strongly affected by the pH of the wastewater. Sorption increased at low pH, probably due to the increased insolubility of naphthalenes. Sorption capacity of the resin decreased with increasing temperature, especially at greater than 50°C. The optimal sorption conditions were 50°C, pH 1–2, and a flow rate of 5–9 BV/h (BV: bed volume).

Zhang et al. (1987) reported that the optimal conditions for the sorption of sorbic acid by hypercrosslinked H-103 resin were pH 3.0 and a flow rate of 6–8 BV/h. Pan et al. (1999) found optimal conditions for the sorption of phenyl acetic acid in wastewater by hypercrosslinked NDA-999 resin to be pH 2.5–3.0 and a flow rate of 1.0–1.5 BV/h.

3.4.3. Flowrate and Feed Concentration

Streat and Sweetland (1998c) found that sorption of humic and fulvic acids by hypercrosslinked MN-100, MN-150 and MN-200 resins decreased with increasing flow rate. Juang and Chang (1995), however, found that flow rate had little effect on the breakthrough curve for citric acid sorption by the XAD-4/EIR (extractant-impregnated resin) system, but had a greater effect on the breakthrough curve for citric acid sorption by the XAD-2/EIR system. The breakthrough curve for citric acid sorption by the XAD-4/EIR system had a steeper slope at lower feed concentrations of citric acid.

Heitzsch et al. (1994) found that the sorption capacity of aliphatic amines decreased drastically at a linear flow rate over 3 m/h, and was independent of the amine concentration in the feed solution.

3.4.4. Presence of Other Species

The presence of inorganic salts appears to have little effect on the sorption of organic chemicals. Sodium chloride and sodium sulfate did not affect the breakthrough capacities for the sorption of phenol by polyvinylpyridine-divinylbenzene and polystyrene-divinylbenzene resins (Kawabata and Ohira, 1979). Similarly, the chloride salts of sodium, potassium, calcium and magnesium also did not affect the sorption of ϵ -caprolactam by Amberlite XAD-4 and crosslinked polyhydroxystyrene resins (Kawabata and Taketani, 1980).

The presence of fulvic acid reduced the sorption capacity of pesticides by hypercrosslinked MN-100, MN-150 and MN-200 resins. This was likely caused by the clogging of pore openings by the large fulvic acid molecules (Streat and Sweetland, 1998c). Similarly, the presence of natural organic matter (NOM) also reduced the breakthrough capacity for the sorption of diuron and 1-naphthol by Lewatit EP63 and LiChrolut EN resins (Frimmel et al., 1999).

Garcia et al. (1999) analyzed the effluent from a bed packed with macroporous Duolite ES-861 resin treating a wastewater containing phenol and m-cresol. Results showed that the resin preferentially adsorbed m-cresol, which could displace phenol previously adsorbed by the resin.

3.5. Resin Regeneration and Resource Recovery

Thermal regeneration of activated carbon is an energy-intensive process. It is often conducted off site and has an attrition rate of 5–10% each time. Porous resin sorbents, however, are normally regenerated on site at ambient temperature with very little attrition (The Dow Chemical Company, 2001). The sorbed organic chemicals may be recovered for reuse upon resin regeneration. Means of resin regeneration, including solvent elution, pH adjustment, microwave, and steam, are discussed below.

3.5.1. Solvent Elution

Complete regeneration of resin sorbents can be readily achieved on site at ambient temperature using polar solvents (Streat and Sweetland, 1998d). Solvents, such as methanol,

ethanol, isopropanol and acetone, are excellent solvents for the elution of most organic chemicals from the resins (Crook et al., 1975; Carlyle, 1982). In many cases, about three BV of solvent are used in cascade for resin regeneration. Organic chemicals desorbed from the resins may be directly recycled to the production process, or recovered by distillation from the eluted solution (Carlyle, 1982).

The choice of solvent used for the resin generation is dictated by practical considerations, such as cost, availability, desorption efficiency, and feasibility of direct recycle to the production process (Carlyle, 1982).

Streat and Sweetland (1998d) studied the regeneration of resins saturated with five pesticides. They found that 99.95% of pesticides were recovered by 3.2 BV of ethanol. The breakthrough profile of the regenerated column for the pesticides was identical with the virgin resin. The eluted pesticides could be either recovered by distillation, or disposed of by incineration. The recovered solvent was recycled after filtration.

Bohra et al. (1994) also used ethanol to regenerate a series of Amberlite resins laden with phenyl ethyl alcohol, linalool and eugenol. Typically, 95% of the organic chemicals were recovered by 12 BV of solvent. Heitzsch et al. (1994) used methanol to regenerate macroporous Wofatit sorbents laden with aliphatic amines. Nearly all the amines were eluted by 2.5 BV of methanol after rinsing the resin first with 2 BV of deionized water. Methanol was recovered from the mixture by distillation. Frimmel et al. (1999) used isopropanol to regenerate Lewatit EP 63 sorbent laden with hydrophilic organic compounds. It took 40–60 BV of isopropanol to completely desorb diuron and naphthol, and 10 BV to desorb 2-aminonaphthalene-1-sulfonate and natural organic matter.

Phenol was completely eluted from macroporous Amberlite XAD-2 and XAD-4 resins in a continuous flow column by 3.4 BV and 3.2 BV of methanol, respectively (Kawabata and Ohira, 1979). Complete elution of ϵ -caprolactam from both hypercrosslinked poly(hydroxystyrene) resin and Amberlite XAD-4 was achieved in a continuous flow column by only 2 BV of methanol (Kawabata and Taketani, 1980).

3.5.2. pH Adjustment

Since macroporous resins are nonionic, organic chemicals may be desorbed from the resins when the chemicals become ionized due to a pH change. Phenol may thus be recovered from spent resins at high pH by the addition of sodium hydroxide, whereas aniline may be recovered at low pH by the addition of hydrochloric acid (Carlyle, 1982). Citric acid was completely recovered from tri-*n*-octylamine(TOA)-impregnated resins by 0.1N acidic or sodium carbonate solutions (Juang and Chang, 1995).

3.5.3. Steam

Steam was used to recover ethylenedichloride from resin sorbents treating effluents of vinyl chloride production. The process was effective due to the low boiling point of ethylenedichloride (Carlyle, 1982). Steam was also used to regenerate DOWEX OP-TIPORE L493 sorbent, which was used to remove methylene chloride and chloroform from concentrated hydrochloric acid (33–35%). The organic residues were recovered from the condensed steam while the sorbent was regenerated to its full sorption capacity for

continued use. Similarly, steam was also used to regenerate resin which was used to sorb benzene and chlorobenzene from a concentrated hydrochloric acid stream (32%) (Hellmig, 1987).

Resin regeneration by steam is usually conducted at 95–120°C (The Purolite Company, 2001d, 2001e). The steam consumption was 0.8–1.2 kg per liter of sorbent.

3.5.4. Microwave

Microwave has been used to regenerate resin sorbents used in water, wastewater and landfill leachate treatment (American Purification, Inc., 2001). The advantages of microwave treatment over steam were claimed as lower energy consumption, less time required, and more uniform heating.

3.5.5. Attrition upon Regeneration

Porous resin sorbents are highly durable. Streat and Sweetland (1998a) claimed that the resin sorbent had no apparent degradation after two years of operation treating a phenol-laden wastewater over 1300 cycles of regeneration. Dow Chemical (2001) also claimed that less than 5% of resin sorbent needed to be replaced annually for a fluidized-bed operation. Full-scale experience by one of the authors (Zhang) in China also confirms that the useful life of these resins is over five years with more than 2000 cycles of regeneration.

4. APPLICATIONS IN WATER AND WASTEWATER TREATMENT

4.1. Organic Compound Removed

Table 2 is a compilation of literature data on 49 individual organic species that had been effectively removed from waste streams using porous resin sorbents. Table 3 lists waste streams containing mixed organic pollutants that have been treated by porous sorbents.

Porous resin sorption was also proven to be an effective process for the decontamination of dilute pharmaceutical effluents (Lunn et al., 1994). One gram of Amberlite XAD-16 was able to decontaminate 20–200 mL of effluent.

4.2. Organic Chemicals Recovered

Since porous resin sorption is a reversible process, valuable organic chemicals in the waste stream removed by the resin may be desorbed under proper conditions for recovery. Table 4 lists organic chemicals that have been recovered from waste streams of full-scale production plants. In some of these cases, the recovered organic chemicals were directly recycled to the manufacturing process without distillation or other means of purification.

TABLE 2. Individual organic pollutants removed by resin adsorbents

Organic Chemical	Concentration	Resin Adsorbents	References
Acetone	Throughout the aqueous solubility range	Amberlite XAD-2 & -4	Simpson et al., 1993
2-Aminonaphthalene-1-sulfonate	0.09–10 mg/L	Lewatit EP63 & LiChrolut EN	Frimmel et al., 1999
Aniline	2–10 mmol/L; 50–524 mmol/L	Amberlite XAD-4, Lewatit EP63, hypercrosslinked resin Sample 390 & ethylene dimethacrylate polymer	Azanova & Hradil, 1999
Aniline	Not mentioned	Amberlite XAD-7	Payne, 1990
Atrazine	30–500 mg/L	Amberlite XAD-2, XAD-4 & XAD-7	Doulija et al., 1997
Benzene	0.015–0.17 mmol/L	Amberlite XAD-4, Lewatit EP63, hypercrosslinked resin Sample 390 & ethylene dimethacrylate polymer	Azanova & Hradil, 1999
Benzene	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16; Dow XUS 43493, XUS 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
Benzene	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993
Benzoic acid	8–25 mmol/L	Reillex-425; Amberlite XAD-4, XAD-8, XAD-16 & XAD-12	Gusler et al., 1993
ϵ -Caprolactam	2000 mg/L	Amberlite XAD-2 & XAD-4; crosslinked poly(hydroxystyrene) resin	Kawabata & Taketani, 1980
Carbon tetrachloride	Not mentioned	Amberlite XAD-2, XAD-4 & XAD-8	Weber & Van Vliet, 1981a
Carbon tetrachloride	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
Carbon tetrachloride	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993
Chlorobenzene	0.05–5 mmol/L	Reillex-425, Amberlite XAD-4, XAD-8, XAD-16 & XAD-12	Gusler et al., 1993

Chlorobenzene	Throughout the aqueous solubility range	Home-made Friedel-Crafts modified polystyrene	Simpson et al., 1996a
Chlorobenzene	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
Chlorobenzene	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993
Chloroform	Saturated aqueous solution	Amberlite XAD-2, XAD-4 & XAD-8 & Reillex-425	Browne & Cohen, 1990
Chloroform	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
Chloroform	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993
2-Chlorophenol	50.0 mg/L	Hypersol-Macronet MN-100, MN-150 & MN-200	Streat & Sweetland, 1997
3-Chlorophenol	50.0 mg/L	Hypersol-Macronet MN-100, MN-150 & MN-200	Streat & Sweetland, 1997
4-Chlorophenol	Not mentioned	Amberlite XAD-2, XAD-4 & XAD-8	Van Vliet & Weber, 1981
4-Chlorophenol	100–3000 mg/L	Amberlite XAD-4, XAD-7 & XAD-16	Juang et al., 1999
4-Chlorophenol	Not mentioned	Amberlite XAD-2, XAD-4 & XAD-8	Weber & Van Vliet, 1981a
4-Chlorophenol	1–32 mmol/L	Amberlite XAD-4 & XAD-7	Juang & Shiau, 1999
4-Chlorophenol	50.0 mg/L	Hypersol-Macronet MN-100, MN-150 & MN-200	Streat & Sweetland, 1997
m-Cresol	<200 mg/L	Duolite ES-861	Garcia et al., 1999
p-Cresol	Not mentioned	Amberlite XAD-7	Maitly et al., 1991
2, 4-Dichlorophenol	Not mentioned	Custom-made polystyrene resins polymerized by Bayer A. G.	Cornel & Sontheimer, 1986a; 1986b
Diuron	0.09–10 mg/L	Lewatit EP63 & LiChrolut EN	Frimmel et al., 1999
Dodecylbenzenesulfonate	Not mentioned	Amberlite XAD-2, XAD-4 & XAD-8	Weber & Van Vliet, 1981a

(Continued on next page)

TABLE 2. Individual organic pollutants removed by resin adsorbents (*Continued*)

Organic Chemical	Concentration	Resin Adsorbents	References
Ethanol	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
Eugenol	1300 mg/L	Amberlite XAD-2, XAD-4 & XAD-7	Bohra et al., 1994
Hexane	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
2-Hydroxy-3-carboxylic-naphthalene	Not mentioned	Home-made NDA-708	Feng et al., 1999
Isoproprurion	2000 mg/L	CHA-101	Zhang et al., 1993
Lecitin	Not mentioned	Polysorb 40/100, Amberlite XAD-4 & Styrosorb 2	Tsyurupa et al., 1995
Linalool	1000 mg/L	Amberlite XAD-2, XAD-4 & XAD-7	Bohra et al., 1994
Methanol	Not mentioned	Custom-made polystyrene resins polymerized by Bayer A. G.	Cornel & Sontheimer, 1986a; 1986b
Methanol	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993
N,N-dimethylaniline	Not mentioned	Amberlite XAD-7	Payne, 1990
N-methylaniline	Not mentioned	Amberlite XAD-7	Maitty et al., 1991
N-methylaniline	Not mentioned	Amberlite XAD-7	Payne, 1990
Naphthalene	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
1-Naphthol	0.09–10 mg/L	Lewatit EP63 & LiChrolut EN	Frimmel et al., 1999
1-Naphthol	200–1000 mg/L	Amberlite XAD-2, XAD-4, XAD-7 & XAD-8	Xu et al., 1997
1-Naphthol	200–1000 mg/L	CHA-101 & CHA-111	Xu et al., 1999
2-Naphthol	200–1000 mg/L	Amberlite XAD-2, XAD-4, XAD-7 & XAD-8	Xu et al., 1997
2-Naphthol	200–1000 mg/L	CHA-101 & CHA-111	Xu et al., 1999
1-Naphthylamine	200–1000 mg/L	Amberlite XAD-2, XAD-4, XAD-7 & XAD-8	Xu et al., 1997
1-Naphthylamine	200–1000 mg/L	CHA-101 & CHA-111	Xu et al., 1999

2-Naphthylamine	200–1000 mg/L	Amberlite XAD-2, XAD-4, XAD-7 & XAD-8	Xu et al., 1997
2-Naphthylamine	200–1000 mg/L	CHA-101 & CHA-111	Xu et al., 1999
Nitrobenzene	639 mg/L	CHA-111	Zhang et al., 1997
4-Nitrophenol	Not mentioned	Custom-made polystyrene resins polymerized by Bayer A. G.	Cornel & Sontheimer, 1986a
Oleic acid	Not mentioned	Polysorb 40/100, Amberlite XAD-4 & Styrosorb 2	Tsyurupa et al., 1995
Phenol	<200 mg/L	Amberlite XAD-4	Hand et al., 1999
Phenol	2–10 mmol/L; 50–524 mmol/L	Amberlite XAD-4, Lewatit EP63, home-made hypercrosslinked resin Sample 390, home-made ethylene dimethacrylate polymer	Azanova & Hradil, 1999
Phenol	Not mentioned	Amberlite XAD-2, XAD-4 & XAD-8	Weber & Van Vliet, 1981a
Phenol	Not mentioned	Amberlite XAD-7	Maity et al., 1991
Phenol	615–850 mmol/L	Reillex-425, Amberlite XAD-4, XAD-8, XAD-16 & XAD-12	Gusler et al., 1993
Phenol	100–3000 g/m ³	Amberlite XAD-4, XAD-7 & XAD-16	Juang et al., 1999
Phenol	3000–3500 mg/L	Amberlite XAD-2 & XAD-4	Kawabata & Ohira, 1979
Phenol	<200 mg/L	Duolite ES-861	Garcia et al., 1999
Phenol	1–32 mmol/L	Amberlite XAD-4 & XAD-7	Juang & Shiau, 1999
Phenol	50.0 mg/L	Hypersol-Macronet MN-100, MN-150 & MN-200	Streat & Sweetland, 1997
Phenylacetic acid	3705 mg/L	Home-made NDA-999	Pan et al., 1999
Phenylbutanol	Not mentioned	Amberlite XAD-7	Maity et al., 1991
Phenyl ethyl alcohol	8000 mg/L	Amberlite XAD-2, XAD-4 & XAD-7	Bohra et al., 1994
Sodium p-nitrophenolate	960–5156 mg/L	H-103	Zhang et al., 1989
Sorbic acid	100–1100 mg/L	H-103	Zhang et al., 1987
Tetrahydrofuran	Not mentioned	Custom-made polystyrene resins polymerized by Bayer A. G.	Cornel & Sontheimer, 1986a
Toluene	1–4 mmol/L	Reillex-425, Amberlite XAD-4, XAD-8, XAD-16 & XAD-12	Gusler et al., 1993

(Continued on next page)

TABLE 2. Individual organic pollutants removed by resin adsorbents (*Continued*)

Organic Chemical	Concentration	Resin Adsorbents	References
Toluene	0.17–3.76 mmol/L	Amberlite XAD-4, Lewatit EP63, home-made hypercrosslinked resin Sample 390, home-made ethylene dimethacrylate polymer	Azanova & Hradil, 1999
[-0.25pt] Toluene	Throughout the aqueous solubility range	Home-made Friedel-Crafts modified polystyrene	Simpson et al., 1996a
Toluene	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493, XU 43502 & home-made Friedel-Crafts modified polystyrene	Simpson et al., 1996b
Toluene	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993
p-Toluene(sodium)-sulfonate	Not mentioned	Amberlite XAD-2, XAD-4 & XAD-8	Van Vliet & Weber, 1981
p-Toluenesulfonate	Not mentioned	Amberlite XAD-2, XAD-4 & XAD-8	Weber & Van Vliet, 1981a
Tributylphosphate	Not mentioned	Polysorb 40/100 & Styrosorb 2	Tsyurupa et al., 1995
Tributylphosphate	Not mentioned	Custom-made polystyrene resins polymerized by Bayer A. G.	Cornel & Sontheimer, 1986a
Trichloroethene	Saturated aqueous solution	Amberlite XAD-2, XAD-4 & XAD-8 & Reillex-425	Browne & Cohen, 1990
Trichloroethene	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
Trichloroethene	Not mentioned	Custom-made polystyrene resins polymerized by Bayer A. G.	Cornel & Sontheimer, 1986a
Trichloroethene	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993
n-Valeric acid	5 g/L	Styrosorbs 1 (XDC), Styrosorbs 1BP & Amberlite XAD-2	Tsyurupa et al., 1995
p-Xylene	Throughout the aqueous solubility range	Amberlite XAD-2, XAD-4 & XAD-16, Dow XUS 43493 & XU 43502; Friedel-Crafts modified polystyrene	Simpson et al., 1996b
p-Xylene	Throughout the aqueous solubility range	Amberlite XAD-2 & XAD-4	Simpson et al., 1993

TABLE 3. Mixed organic pollutants removed by resin adsorbents

Mixed Organic Pollutants in Wastewater	Resin Adsorbent	References
Ethoxylated aliphatic amines	Wofatit EP61, EP62, Y59 & Y77	Heitzsch et al., 1994
Humic substances	Lewatit EP63 & LiChrolut EN	Frimmel et al., 1999
Pollutants discharged from olive oil mill	Duolite XAD 761	Zouari, 1998
Pesticides, including simazine, chlorotoluron, isoproturon, atrazine & diuron	Hypersol-Macronet MN-100, MN-150 & MN-200	Streat & Sweetland, 1998b
Petrol	Amberlite XAD-4 & MT-43	Tsyurupa et al., 1995
Pharmaceuticals chemicals, including amoxicillin, ampicillin, bleomycin, carmustine, cephalothin, dacarbazine, lomustine, metronidazole, norethindrone, streptozocin, sulfamethoxazole & verapamil	Amberlite XAD-2, XAD-4, XAD-7 & XAD-16	Lunn et al., 1994
Space station wastewaters from shower, hand-wash, humidity condensate, urine distillate, oral hygiene, wet shave, animal condensate & equipment off-gasing water streams	Amberlite XAD-4	Hand et al., 1999

4.3. Case Studies—USA

Porous resin sorbents have been used with industrial wastewater for the removal of recalcitrant toxic organic chemicals in order to protect the biological treatment process downstream or to recover valuable residues for reuse. Most of the literature is based on bench-scale results. Technical reports on full-scale industrial applications in the United States are still scarce. Information on individual case studies can be found in the literature published by the resin manufacturers, including technical bulletins, product brochures, and homepages and reports available on the Internet.

4.3.1. Pretreatment for Biological Processes

Resin sorption has been used as a pretreatment process to remove toxic and recalcitrant organic pollutants to protect the downstream biological wastewater treatment process. This exemplified in the two following examples. First, Amberlite XAD-2 was used to remove about 25% of COD and 33% of toxic chemicals from pulp mill hemp black liquors prior to the final treatment in anaerobic reactors (Kortekaas et al., 1995). Second, phenolic sorbent Duolite XAD 761 was used to remove over 60% of COD from an olive oil mill prior to the anaerobic treatment of effluent (Zouari, 1998).

TABLE 4. Organic compounds recovered from wastewaters by resin adsorbents

Recovered Organic	Production Effluent	Resin Adsorbent	References
Phenol	Bisphenol-A	Amberlite series	Carlyle, 1982
Phenol	Cumene hydroperoxide	Amberlite series	Carlyle, 1982
Phenol	Phenol-formaldehyde	Amberlite series	Carlyle, 1982
2,4-Dichlorophenoxy acetic acid	Pesticide	Amberlite series	Carlyle, 1982
Dichlorophenol	Pesticide	Amberlite series	Carlyle, 1982
2,4-Chloro-2-methylphenoxy	Pesticide	Amberlite series	Carlyle, 1982
Propionic acid	Pesticide	Amberlite series	Carlyle, 1982
p-Chloro-o-cresol	Pesticide	Amberlite series	Carlyle, 1982
4,2-Methylphenoxy acetic acid	Pesticide	Amberlite series	Carlyle, 1982
Dichloraniline	Pesticide	Amberlite series	Carlyle, 1982
Ethylenedichloride	Vinyl chloride	Amberlite series	Carlyle, 1982
Chloroform	Pharmaceutical	Hypersol Macronet TM	The Purolite Co., 2001a
Isoproturon	Isoproturon	CHA-101	Zhang et al., 1993
Sodium p-nitro-phenolate	p-nitrophenyl ether	H-103	Zhang et al., 1989
2-Hydroxy-3-carboxylic-naphthalene	2-Hydroxy-3-carboxylic-naphthalene	NDA-708	Feng et al., 1999
Phenylacetic acid	Phenylacetic acid	NDA-999	Pan et al., 1999

4.3.2. Phenol Recovery (Carlyle, 1982)

Phenol in waste streams was effectively recovered from resin sorbents by solvent elution. In two bisphenol-A production plants, phenol at concentrations up to 10,000 mg/L was recovered from the effluent using Amberlite sorbent. Acetone was used to regenerate the resins. The resin adsorption and regeneration were carried out in vessels separated from the production process. In another plant producing cumene hydroperoxide, phenol at 6,000–8,000 mg/L was also recovered using Amberlite sorbent from the waste stream, which also contained acetone, sodium sulfate and residual cumene. In this case, the adsorption process used to recover this phenol was of the ‘integrated’ type. The adsorbent was regenerated with acetone from the main process.

4.3.3. Pesticide Recovery (Carlyle, 1982)

Pesticides, including 2,4-dichlorophenoxy acetic acid, dichlorophenol, 2,4-chloro-2-methylphenoxy propionate, p-chloro-o-cresol, 2,4-methylphenoxy acetate and

dichloraniline, were recovered using Amberlite sorbents from the wastewater of four production plants, as listed in Table 4. These pesticides of phenolic or phenoxy acid nature have very low solubilities in aqueous medium, and were all effectively removed. In all cases, methanol, a better solvent to these pesticides than acetone, was the solvent used for resin regeneration.

4.3.4. Ethylenedichloride Recovery (Carlyle, 1982)

Ethylenedichloride at concentrations ranging 4000–8000 mg/L was recovered by Amberlite sorbents from the wastewater of two plants producing vinyl chloride. The removal was highly effective due to the affinity of ethylenedichloride to the sorbents. The volumetric adsorption capacity was 200kg ethylenedichloride/m³-sorbent. The consumption of steam for resin regeneration was less than 1 ton/m³-sorbent. The process consumed only 10–20% of steam needed for the conventional steam stripping process, and produced an effluent of superior quality containing less than 0.1 mg/L of residual ethylenedichloride, as compared to 10 mg/L or more for steam stripping.

4.3.5. Chloroform Recovery (The Purolite Company, 2001a)

Chloroform was recovered for reuse from the wastewater of a pharmaceutical plant using Hypersol MacronetTM sorbent. Chloroform was effectively removed at concentrations as high as 350 mg/L and its concentration in the retention was up to 100 g/L-resin. The recovery system consisted of two columns (2.2 m in diameter each) in series for adsorption and one column of same size for regeneration. An additional stripper column was used for resin regeneration and chloroform recovery. The recovery process saved the plant \$170,000 in the first year of operation in terms of chloroform savings and waste management.

4.3.6. Methyl Tertiary Butyl Ether Removal (Melin, 1999)

Wastewater containing methyl tertiary butyl ether and other gasoline constituents was treated using Dowex L-493 and Amborsorb 563 resins. There was no detectable residual ether and other constituents after two weeks of operation. The resins were regenerated with steam, which concentrated methyl tertiary butyl ether by a factor of 250. Over 90% of methyl tertiary butyl ether was recovered.

4.3.7. Reuse of a Textile Dyeing Effluent (The Purolite Company, 2001b)

A textile dyeing wastewater was first treated by the conventional biological process, followed by settling and filtration. The filtrate was then further treated by resin adsorption at 4 BV/h in two columns packed with the Macronet resin. The treated effluent retained salts required in the dyeing process, and was recycled for reuse in order to reach the goal of zero effluent discharge. The cost of Macronet resin for treating each m³ of effluent was

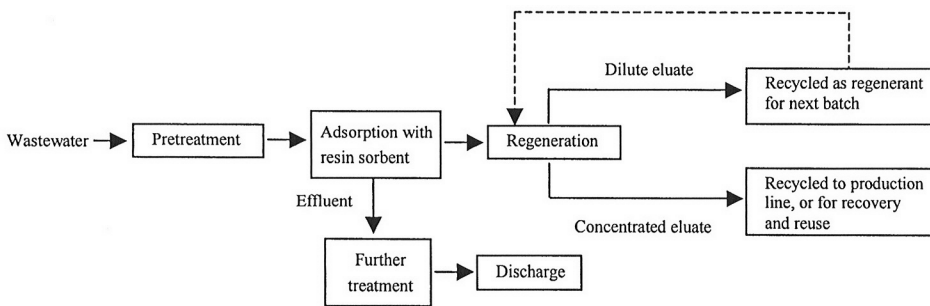


FIGURE 3. Flow diagram of a typical resin sorption/regeneration system.

about \$0.036. This treatment process saved the plant over \$225,000, and the installation paid for itself in two years.

4.4. Case Studies—China

China has three decades of experience in the development of macroporous resin sorbents. A flow diagram for a typical resin sorption/regeneration system is illustrated in Figure 3. Due to various reasons, little has been reported outside of China. The following summarizes several case studies in China of resource recovery in full-scale plants.

4.4.1. 2-Hydroxy-3-carboxylic-naphthalene Recovery (Feng et al., 1999; Chen et al., 2000a)

Wastewater generated from the production of 2-hydroxy-3-carboxylic-naphthalene was treated using resin sorbent NDA-708. The wastewater contained about 3000 mg/L of COD, and 1000 mg/L of residual 2-hydroxy-3-carboxylic-naphthalene and 2-naphthol. The sorption process removed 99.5% of naphthalenes and 98.5% of COD from the wastewater. The treated effluent met the national emission standard after pH adjustment, and was discharged directly into the receiving water. The 2-hydroxy-3-carboxylic-naphthalene and 2-naphthol sorbed by the resins were recovered and recycled directly to the production process without further treatment. This process has been used in five plants in China treating an annual total of 450,000 m³ of effluent, and has recovered 350 tonnes of 2-hydroxy-3-carboxylic-naphthalene and 2-naphthol.

A plant of Ditong Chemicals in Suzhou producing 1300 tons of 2-hydroxy-3-carboxylic-naphthalene a year generated 150 m³ of waste effluent daily. In 1998, the effluent was treated by resin adsorption using NDA-708. The process recovered annually 50 tons of 2-naphthol and 5 tons of 2-hydroxy-3-carboxylic-naphthalene, saving the plant RMB 0.6M in 1999 and RMB 0.75M in 2000. The plant has doubled its production capacity in 2002, and the resin adsorption process has saved RMB 1.5M annually.

The same process was also applied in another plant (Xinshun Chemical) in Shanghai in 1999, resulting in the annual recoveries of 90 tons of 2-naphthol and 10 tons of 2-hydroxy-3-carboxylic-naphthalene from an effluent with a daily flow rate of 420 m³, saving the plant

RMB 1.1M in 2000. The plant has increased its production capacity by 50% in 2002, and the adsorption process is likely to save RMB 1.5M annually.

4.4.2. Sodium p-nitrophenolate Recovery (The State Bureau of Petroleum and Chemical Industry, 1998)

Over 99.5% of residual sodium p-nitrophenolate was removed from the production effluent using resin sorbent CHA-111. About 5 kg of p-nitrophenol was recovered from each m³ of effluent when the resin was regenerated by dilute caustic solution. Over six plants in China were using this process. A plant of Jinlong Chemical in Changshu with an annual production capacity of 7000 tons of sodium p-nitrophenolate started using this treatment technology in 1998. The process resulted in an annual saving of RMB 0.44M in 2001.

4.4.3. Phenylacetic Acid Recovery (Pan et al., 1999; Chen et al., 2000b)

The NDA-999 resin was used to treat an effluent containing 3.5-3.7 kg/m³ of residual phenylacetic acid, plus benzyl alcohol and benzaldehyde. The spent resin was regenerated in two steps. It was first treated with caustic solution. The eluted solution containing sodium phenylacetate was directly recycled into the production process. The spent resin was then further treated with methanol to remove benzyl alcohol and benzaldehyde. After recovering methanol by distillation, the precipitates were disposed of by incineration. Over 99% of phenylacetic acid was recovered from the waste stream. One plant using this process is in operation in China.

4.4.4. Phenol Recovery (Shi and Wang, 1994)

Aqueous effluents of coke production containing 1500–2200 mg/L phenol and the waste gases were both treated with XH303 resin sorbent. Two plants in China have been using this process for 6 and 13 years, respectively. Phenol has been effectively removed from both air and water effluents. Industrial-grade phenol has been recovered as product.

5. SUMMARY

Synthesis, characteristics and sorption mechanisms of macroporous resin resins were discussed in this review paper. Sorption data scattered throughout the literature were compiled, followed by discussion of case studies of full-scale industrial applications in the United States and China. Through such a thorough review of the literature, it is clear that porous resin sorbents offer a number of advantages in wastewater treatment. The network property, pore structure and functional groups of resins may be tailor made to certain degrees for the sorption of certain groups of organic chemicals. As a result, the selectively sorbed

organic chemicals may be recovered for reuse upon resin regeneration. The porous resin sorbents have high degrees of tolerance towards acidity, alkalinity, heat, and concentrated organic as well as inorganic salts in the wastewater. They are highly durable with a reported annual attrition rate of less than 5%. The sorption facilities are simple and compact, and the process is easy to operate and energy efficient.

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