

Innovations in separations technology for the recycling and re-use of liquid waste streams

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Abstract

As the costs of wastewater disposal increase more emphasis is being placed upon the recovery and recycling of valuable chemicals contained within these streams. In this article, we review three separations technologies that facilitate such recycling. Solvent extraction is an established technique for recovery of heavy metals and other pollutants and is most useful in large and medium scale operations when solute concentrations are high. Membrane technology is a more recent development that can be used in conjunction with extraction solvents to extend the range of conditions under which such processes are viable. Finally, adsorption and ion-exchange processes provide the means for extracting valuable contaminants when the concentrations of such solutes are low. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Companies are increasingly being forced both by regulatory and cost pressures to reduce the amount and environmental sensitivity of the liquid waste they produce. This has led to a focus on their ability to clean up this waste and return or recycle a significant proportion. The use of recycled waste streams often also has the additional cost benefit of reducing the raw material requirement, thus again reducing costs. A ‘closed cycle’ process is the ultimate objective, whereby all waste streams are recycled and the only output from the process is saleable product.

Wastewater streams have traditionally been treated by a combination of physico-chemical processes such as flocculation, precipitation and filtration, and biological processes such as activated sludge and biofilm processes. Such treatments are usually effective in reducing organic pollutants to a level suitable for disposal into public sewerage or natural waterways. However, they often fail to reduce the concentration of heavy metals below permissible limits. Further, these technologies usually do not provide the selectivity necessary to create valuable product streams suitable for recycle or re-use, and as a consequence the by-product sludge can itself become a disposal problem.

Separation processes provide the means for approaching these latter objectives. The wastewater stream is fraction-

ated into two or more liquid phases that are either process recyclable, saleable or waste. In this paper, we focus on three technologies that can achieve such fractionation. Solvent extraction is an established process for reducing solute concentrations in aqueous streams. Membrane-based processes extend and improve this technology, making it accessible over a wider range of process conditions. Finally, adsorption and ion-exchange technology finds application at lower solute concentrations, when the solvent-based processes become less attractive. Each of these technologies is discussed in more detail below.

2. Solvent extraction

The most established separations technology for wastewater recycling is solvent extraction. This process is principally used for large-scale operations where the concentrations of contaminants are high (see Fig. 1). Solvents are becoming increasingly selective, allowing specific molecules to be separated from the aqueous phase while others are retained. However, the capital outlay for such equipment can be expensive, large volumes of organic extractants are required and performance is often limited by hydrodynamic constraints such as flooding and entrainment. There is also the potential for cross-contamination of the aqueous stream with the organic solution.

A major commercial application of this technology has been in the selective removal of heavy metal ions from

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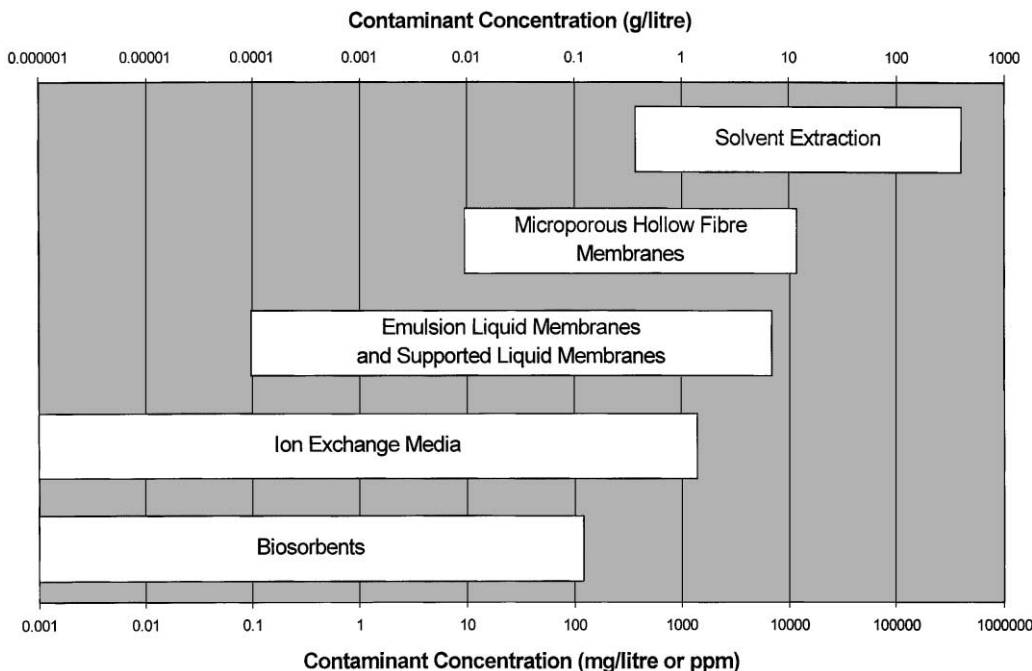


Fig. 1. Solute concentration ranges for separation technologies.

wastewater streams. A water insoluble metal-complexing agent in a non-polar organic solvent is contacted with the waste stream and the metal ions transfer into the organic phase. This loaded organic phase is then further contacted with a second aqueous strip phase. The metal ions transfer back into this aqueous stripping solution which is returned as recycle to the industrial process.

Heavy metals can be present in wastewater as either cations or anions. Cations are usually extracted into an organic diluent by acidic or chelating extractants. Thus, for example, aromatic oxime molecules, known commercially as LIX84, LIX984N, LIX860 (Cognis) and Acorga P50 (Avecia) extractants may be used to remove Cu(II) or Au(I) [1–7] whereas organophosphates such as 2-ethylhexylphosphonic acid mono-ethylhexyl ester (HEH(EHP)), mono(2-ethylhexyl) phosphoric acid (H₂MEHP), di(2-ethylhexyl) phosphoric acid (D2EHPA) or di(2-ethylhexyl) di thio phosphoric acid (DTPA) have been used to remove Pb, Cd, Zn(II), Ni, Co, Cr(III), Ag(I) and rare earth metal species [7–13].

Metal anions can be extracted by ion-pair formation with long chain alkyl amines in an organic diluent, as long as salts or acids are present in the aqueous feed [14]. Suitable metal-complexing agents include tri-*n*-octylamine (TOA) for the removal of Cr(VI) and Hg(II) [1,5] and methyl tricaprylyl ammonium chloride (Aliquat 336) for Cr(VI) removal [15–18].

For wastewater with low concentrations of metal ions, such technology is limited by the need for high aqueous to organic phase ratios. This leads to high organic losses through entrainment in the aqueous phase. For mixer-settler

units, such entrainment is typically in the range of 100–200 ppm, while in column operation this can be reduced to 10–50 ppm depending on the system. This presents a significant cost to the process and the contamination of the aqueous stream with organics can also cause problems. At high phase ratios, in excess of 20:1, as used in some of these processes, the performance of column contractors is reduced because of increased axial dispersion, resulting in larger and more expensive equipment.

Other instances where solvent extraction processes can be applied to wastewater treatment include the use of a tertiary amine, tris(2-ethylhexyl) amine (TEHA) or a phosphine oxide mixture (CYANEX 923) for the recovery of mineral acids from hydrometallurgical process waste streams [19–22]. The recovery of acetic acid and furfural from sulfite wood pulping waste liquors, using trioctylphosphine oxide (TOPO) has also been commercialised [23].

3. Membrane technology

A membrane is a semi-permeable barrier through which only selected chemical species may diffuse. Ho and Sirkar [24] provide a good overview of membrane processes.

Historically, membrane technology has had wide application in wastewater treatment and desalination through reverse osmosis. In this process, a pressure difference across a membrane is used to overcome the osmotic pressure gradient. The smaller water molecules are literally pushed through the semi-permeable membrane while the larger solute species retained. Cellulose acetate membranes are the

most common, used in either a spiral wound, hollow fibre, tubular or plate-and-frame configuration.

Nanofiltration is an emerging technology that combines such pressure filtration with the use of a negatively charged membrane. The more negatively charged multivalent anions and higher molecular weight organics are retained while monovalent salts pass through the membrane. Such an approach has been applied to the recovery and re-use of dairy [25,26], tanning [27,28], sugar [29,30] and textile [31–33] industry effluents. Fouling and energy costs remain the major barrier to large-scale application of this technology.

With both reverse osmosis and nano-filtration, the membrane operates primarily through size exclusion and so the selectivity for specific metal ions is limited. Much greater selectivity in wastewater treatment can be obtained by combining the physically selective permeability of membranes with the chemically selective separation provided by the solvent extraction process. In this instance, a membrane is placed between a waste stream and a suitable solvent, and mass transfer of selected chemical species occurs across this barrier.

3.1. Emulsion liquid membranes

The concept of a permeable barrier for use in solvent extraction was first proposed by Li [34] in the 1960s in the form of an emulsion liquid membrane (ELM). Ho and Li [35] provide a good review of this technology.

An emulsion liquid membrane is formed by first encapsulating an aqueous ‘receiving’ or strip phase within a hydrophobic membrane liquid. This emulsion is then further dispersed within the continuous aqueous feed phase (see Fig. 2). The resulting system is thus a water/oil/water double emulsion. Oil/water/oil systems are also possible.

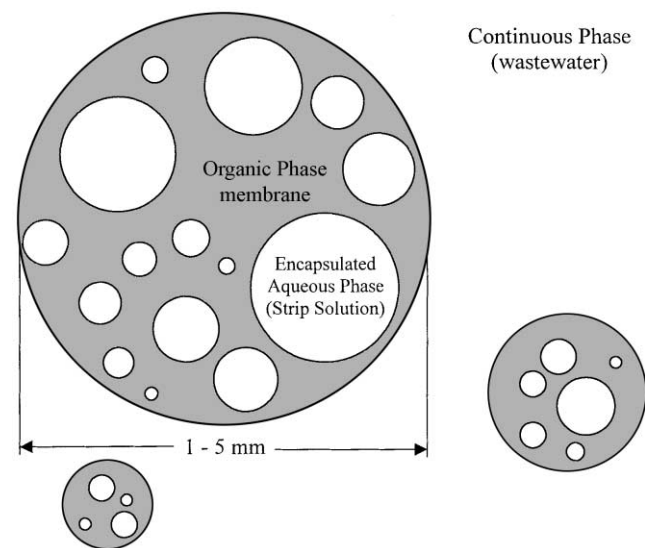


Fig. 2. Schematic diagram of an emulsion liquid membrane (developed from Cahn and Li [39]).

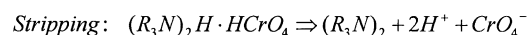
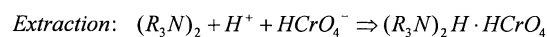
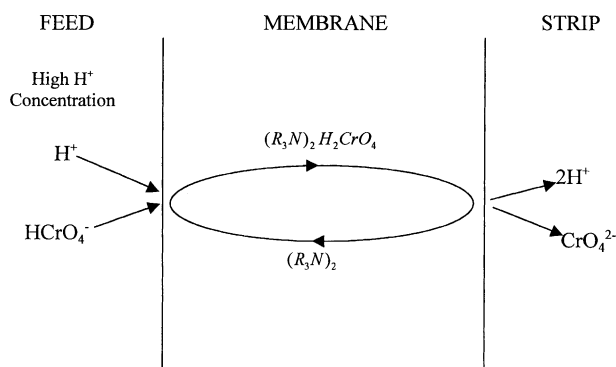


Fig. 3. Mechanism for facilitated transport of Cr(VI) and H^+ using a tertiary amine carrier (see Youn et al. [127]).

Mass transfer occurs between the outer continuous phase and the internal encapsulated phase. Once mass transfer is complete, settling is used to separate out the external phase, followed by breakage of the internal emulsion system. Operation can be completed within mixer-settler type units or in continuous countercurrent columns [36–39].

As well as reducing the complexity of the solvent extraction process, a liquid membrane can be used to improve both the mass transfer rate and selectivity through either facilitated or coupled transport. With facilitated transport a carrier molecule binds to the diffusing species on one side of the membrane, carries it across to the other side and then, owing to the alternate chemical environment, releases it (see Fig. 3). Conversely, coupled transport allows a species to be pumped ‘uphill’ against its own concentration gradient as a consequence of an existing concentration gradient of a second species. Such a process is illustrated in Fig. 4 for the ‘uphill’ transport of copper ions. These transport mechanisms vastly improve the mass transfer flux that can

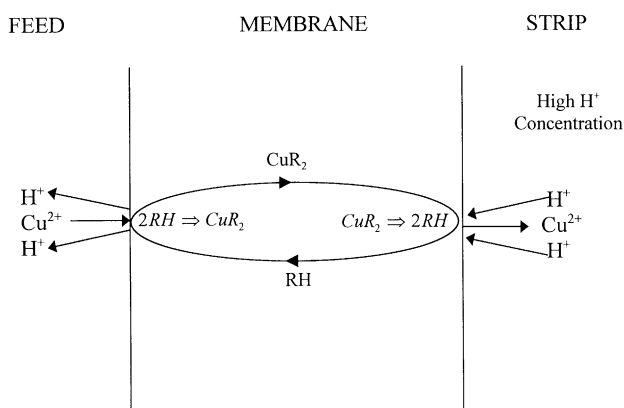


Fig. 4. Mechanism for coupled transport of copper through a liquid membrane.

be achieved in a liquid membrane and allow extraction to proceed to solute levels that would be otherwise impossible to achieve by equilibrium limited processes.

A further advantage of ELM processes is the creation of very large surface area to volume ratios. Large interfacial areas can be achieved in units that occupy significantly less floor space and cost significantly less than the traditional solvent extraction columns. This advantage has led to the commercialisation of this technology for the extraction from wastewater of phenols [39,40], cyanide [35] and zinc [41].

Pilot scale studies have also been conducted on the use of such technology for the removal of heavy metal cations such as zinc, cadmium, chromium, copper, lead, palladium and mercury from wastewater [11,12,16,36,42–52]. Research has been conducted into the removal of alkali metal cations such as Na^+ , K^+ , Li^+ and Cs^+ [52–55], radioactive fission products, such as Cs-137, Sr-90, Ce-139 and Eu-152 [56] and the removal of anions, such as chlorides, sulfate, selenium, phosphate and chromate [47,52,54,57]. Wang and Bunge [58] and Terry et al. [59] consider the simultaneous extraction of organic acids and phenols whereas Baird et al. [60] consider multi-solute extraction of amines from wastewaters.

The extraction of ammonia from wastewater has been given considerable attention [61–71]. While such an ELM process has been found to be technically feasible, it is not usually economically advantageous, as the ammonia is recovered as an inexpensive ammonium salt rather than the more valuable hydroxide solution NH_4OH [24]. However, a pilot plant of 4 tonne/day capacity using rotating disc columns has recently been installed in China to reduce ammonia levels from 0.8 to 1.5 g/l in a metal production plant [72].

ELMs provide efficient mass transfer in small and medium size applications, particularly when feed concentrations are fairly low (see Fig. 1). However, issues of emulsion stability and membrane leakage have limited their commercial potential. The thin membranes are prone to leakage or rupture and the inner phase can suffer from swelling instability. Current research has been directed at increasing emulsion stability without significantly reducing the extraction rate, for example, through the use of bi-functional surfactants which act as both emulsifiers and extractants [73]. Long

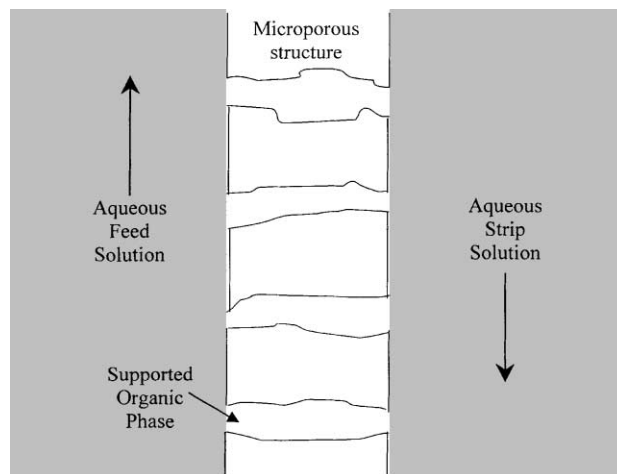


Fig. 5. Schematic of a supported liquid membrane.

chain polymers can also be added to the membrane phase to impart elasticity to the membrane [74]. The extent of elasticity is a strong function of temperature and the stability can thus be reversed for de-emulsification following extraction through simple heating.

3.2. Supported liquid membranes

An alternate approach to the problems of emulsion stability has been to immobilise the organic liquid phase within a porous structure [75–77] (see Fig. 5). This solvent is placed in the pores of a microporous membrane material prior to service by a soaking procedure. The extraction and stripping operations then proceed simultaneously by passing the feed and the stripping solution across either side of this membrane. Again, facilitated or coupled transport can be used to aid selectivity.

These supported liquid membranes (SLMs) are usually manufactured as a series of small diameter microporous hollow membrane fibres (MHF), typically 240 μm in internal diameter (see Gabelman and Hwang [78]). The solvent soaked fibres are bundled together into a module arrangement which, while much smaller in size, is not dissimilar in design to the traditional shell and tube heat exchanger (see Fig. 6). The feed and strip solutions then pass respectively

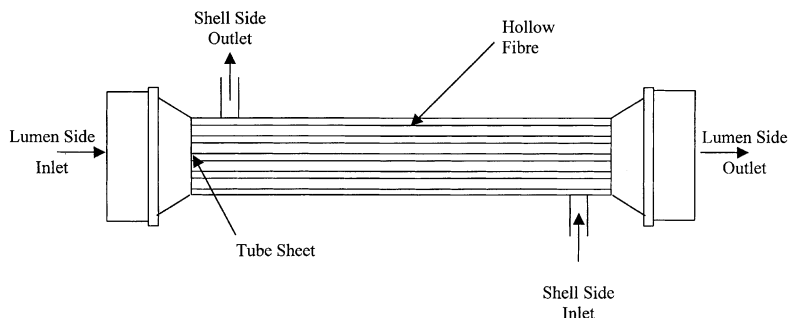


Fig. 6. Schematic of a parallel flow microporous hollow fibre membrane module.

through either the shell or lumen sides of the bundle. Supported liquid membranes can also be prepared in a flat sheet arrangement (FS-SLMs).

The SLM technique has received much attention in the literature [7,13,15,79–86]. In particular, the possibility of utilising such technology for the treatment of low level radioactive wastewater with crown ether or calix-crown extractants has been extensively studied [87–95]. Such an approach has the advantage of self-containment and limits the amount of the expensive extractant that is required.

However, while often studied, few industrial applications of SLMs have been successfully implemented. Commodore Separation Technologies installed such technology at the Port of Baltimore in 1998 for the removal of 500–1000 ppm of Cr(VI) from groundwater. The effluent water was to contain less than 0.05 ppm Cr(VI), suitable for direct discharge into Chesapeake Bay [96]. However, it appears that environmental standards could not be attained and the equipment has now been removed [97].

The lack of commercial success lies primarily with the lack of long term stability of the membrane [95,98,99]. The organic liquid in the membrane gradually dissolves into either of the contacting phases, or conversely, water enters the membrane phase, progressively wetting the support pores [100]. Research has been directed at improving this stability through alternate membrane materials [91–103], configurations [104] and operating conditions [105,106], re-impregnation techniques [107,108], coated SLMs [109,110] and gelation of SLMs [111–114]. Kilambi et al. [95] have recently patented an approach whereby stability is enhanced through control of the dielectric constant of the membrane liquid.

3.3. Other membrane designs

As problems with liquid membrane stability remain unresolved, attention has turned in recent years to alternative membrane designs. In hollow fibre containing liquid membranes (HFCLMs) [1,115–119] two sets of hollow fibres are packed together into the shell side of a single microporous hollow fibre permeator. The organic phase is contained in the spaces between these fibres (shell side). The aqueous feed solution is then passed through the lumen of one set of fibres while the aqueous strip solution is passed through the lumen of the other set. Each aqueous–organic phase interface is immobilised at the pore-mouths of the respective fibre by the hydrophobic or hydrophilic nature of the membrane material and by the maintenance of the correct phase pressure conditions. The organic liquid membrane pressure is set independently by the membrane liquid reservoir, which automatically replaces any membrane liquid lost to the feed and strip solutions.

This configuration enhances the area available for mass transfer per unit volume compared with traditional solvent extraction equipment and can reduce the potential for organic phase entrainment significantly. It does however,

increase the diffusional resistance because of the need for the solutes to diffuse through a stationary organic phase. Circulating the organic phase through the permeator shell side to enhance turbulence can reduce this resistance. Recent studies [120] show that this gives identical mass transfer performance to the simpler MHF permeators described below.

HFCLM membranes have been considered for the extraction of both organic pollutants such as phenol [115,116] and heavy metals such as Cu(II), Cr(VI) and Au(I) [117–119].

Wienczek and co-workers consider an alternative design for copper extraction whereby an emulsion liquid membrane is contained within a hollow fibre contactor [43,121]. The aqueous wastewater feed is placed on the shell side of the contactor, while the solvent/stripping phase emulsion flows through the lumen. They claim that such an arrangement allows for simultaneous extraction and stripping without the emulsion stability problems of ELM technology. The absence of high shear rates minimises leakage of the internal phase and the physical separation of the two aqueous phases reduces emulsion swelling rates. They find that good extraction can be accomplished even without the use of surfactant, leading to the possibility of substantially reduced de-emulsification costs.

In the simplest case of membrane-based solvent extraction, two separate MHF permeators are used for the respective extraction and stripping operations. Such hollow fibre membrane units have been used for experimental and pilot scale studies on the extraction of metals such as gold, copper, chromium, iron, zinc, molybdenum and actinides from aqueous waste streams [5,79,120,122–126]. The use of MHF technology for the separation of dilute electroplating rinse waters into a reusable rinse water and recyclable plating chemicals is identified as a particularly promising application [127,128]. For example, Ortiz and co-workers [129,130] have shown that the Cr(VI) concentration in the wastewaters from a galvanic plating process can be reduced from 50 to 1 mg/l in a pilot plant with a capacity of 250 l/h. Similarly, several authors report the extraction of organic pollutants [131–135]. Zander et al. [136,137] use a gas-filled membrane in contact with a stripping oil as an effective means of removing volatile organic contaminants from wastewater.

MHF permeators provide large interfacial areas per unit volume (up to $6000 \text{ m}^2/\text{m}^3$ [78]). Such membranes are also better able to handle particulates, and liquids of comparable density difference. As the two phases do not require mixing, the hydrodynamic problems of flooding and entrainment inherent in traditional solvent extraction are avoided. For example, as already discussed, conventional dispersive extractors are particularly inefficient at high aqueous to organic phase ratios. Seibert and Fair [138] show that under phase ratios of 40:1 to 80:1 extractor height can be reduced by a factor of 10 if a membrane contactor is used. Further, such systems are easier to operate, requiring less operator input than the traditional solvent extraction columns. They are thus most suitable for smaller installations where capital and labour costs must be minimised.

The major disadvantage of these membranes is that they have a limited lifetime before membrane fouling or failure of adhesive bonds necessitates replacement. The cost of periodic replacement must thus be included in any analysis of their economic viability. Like heat exchangers, their performance can also be limited by pressure drop constraints and by shell side bypassing of the contacting fluid.

4. Ion-exchange and adsorption processes

At low solute feed concentrations, the use of solvent extraction or solvent-based membrane processes lose their advantage. Often under these conditions, the loss of solvent into the aqueous wastewater phase through solubility or entrainment is greater than the quantity of solute recovered. In this instance, an alternative technology is required.

The use of a solid matrix for adsorption and ion-exchange of contaminants provides such an alternative. The volume of adsorbent material required increases proportionately with the solute load, so that at higher solute concentrations, equipment size makes such processes economically unfeasible. Applications are typically limited to levels of contaminants in the ppm range (see Fig. 1).

Activated carbon is the most widely used adsorbent for organic impurities in wastewater. Its non-polar surface, and low cost has made it the adsorbent of choice for a range of pollutants such as aromatics and pesticides. However, as it is non-selective, common innocuous organics, typically

present at much higher concentrations than more troublesome hazardous pollutants, may interfere with the removal of the hazardous compounds. Tailored bentonite clays have been trialled as a more selective alternative [139].

Synthetic ion-exchange resins have long been used in commercial scale applications for the softening or demineralisation of water. Again, while effective in reducing ionic contaminant levels to low levels, such resins have traditionally suffered from a lack of selectivity. Research has therefore been directed towards improving this selectivity. Experimental and pilot scale research has targeted the use of new ion-exchange resins and zeolite materials for the selective removal of specific heavy metal cations from wastewater [140–147] and the use of clinoptilolite, another natural zeolite, for the removal of the soluble ammonium content [148–150]. Research is active in the field of radioactive waste stream cleanup [151–153] while Wasay et al. [154] have used impregnated alumina to remove a selection of anions from industrial wastewaters.

4.1. Biosorption

Biosorption is an emerging technology that also attempts to overcome the selectivity disadvantage of adsorption processes [155–157]. In this instance, biological materials, such as chitosan [158–161], marine algae or alginates [161–171], fungi [157] or bacterial biomass [167,170,172] are used as a chelating ion-exchange medium. These biopolymers and their derivatives contain a variety of functional groups,

Table 1
Maximum uptake of heavy metals on selected sorbents recent experimental results

Sorbent origin	Sorbent	Absorbed metal uptake (mmol/g)			Reference
		U	Cu(II)	Pb(II)	
Fungi	<i>Rhizopus arrhizus</i>	0.68			[155]
	<i>Aspergillus niger</i>	0.15			[155]
	Pre-treated <i>Aspergillus niger</i>		3.9		[172]
	Pre-treated <i>Penicillium chrysogenum</i>		4.4		[172]
	Pre-treated <i>Micrococcus luteus</i>		3.8		[172]
Marine algae	<i>Sargassum fuitans</i>	2.4	0.80		[168,171]
	<i>Sargassum vulgare</i>		0.93		[171]
	<i>Sargassum natans</i>			1.22	[157]
	<i>Ascophyllum nodosum</i>			1.31	[157]
	Pre-treated <i>Durvillaea potatorum</i>		1.30	1.55	[165]
	Pre-treated <i>Ecklonia radiata</i>		1.11	1.26	[165]
Yeast	<i>Saccharomyces cerevisiae</i>	0.45			[155]
Cattle bones	Bone char		0.75		[176]
Zeolite	13X zeolite		0.70		[147]
	Australian zeolite			0.08	[165]
Chitin	Chitosan		0.33	0.06	[158]
Rice waste	Quatemized rice husk		1.3	1.6	[174]
Pulp mill waste	Ellagic acid extract		2.7–3.1		[178]
Ion-exchange	Duolite GT-73			1.37	[157]
Resin	Amberlite IR-120			2.14	[157]

which can chelate ionic species of a specific size and charge. Such biomass is thus often much more selective than traditional ion-exchange resins and can reduce heavy metal ion concentrations to ppb levels. The biomass can be immobilised on to an inert framework in order to reduce its fragility under industrial conditions [166,170,173]. A selection of recent experimental results utilising such materials is provided in Table 1.

The biological material used for these systems is cheap and readily available. Indeed, in some instances it may be possible to recycle a material that is a waste product in itself for use as a biosorption medium [172,174–178]. This makes the use of biosorbents extremely cost-effective.

4.2. Hybrid membrane systems

Other researchers overcome the lack of selectivity inherent in adsorption technology by combining ion-exchange resins with alternate separation processes.

Thus, for example, Draye et al. [91] recommend that strontium be selectively extracted from acidic nuclear waste streams using solvent extraction and then concentrated onto an ion-exchange resin. The overall process reduces the volume of material containing Sr by a factor of 5000 and fixes the soluble species onto an organic incinerable material.

Komatsu et al. [179] propose a combined ion-exchange/solvent extraction system to separate a mixture of alkaline earth metal ions. An organic phase containing 2-thenoyltrifluoroacetone (TTA) and TOPO is added to an ion-exchange system using dihydrogen tetratitanate hydrate. The selectivity of the former solvent is in favour of the smaller metal ions, i.e. $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ whereas for the latter ion-exchange substrate selectivity is reversed, with the larger ions sorbing. By combining the two systems a quantitative separation of Ca^{2+} and Sr^{2+} can be achieved.

Similarly, Wodzki et al. [180] sandwich an organic phase acting as a bulk liquid membrane (BLM) between two ion-exchange polymer membranes. This system is used to extract Zn(II) from wastewaters in an 'uphill' direction, using coupled transport. Kedem and Bromberg [181] and Isono et al. [182] also describe processes that combine solvent extraction with ion-exchange membranes.

5. Conclusions

In this paper, we have discussed three inter-related technologies capable of extracting valuable product streams from wastewater.

Solvent extraction is a well-established process which is economically viable when both solute concentrations and wastewater flowrates are high. It finds particular application to the recovery of metallic species from industrial wastewater. However, as a process it becomes uneconomic when contaminant concentrations are low (<0.5 g/l). Further, traditional solvent extraction columns are difficult to operate

as they are prone to flooding and entrainment, particularly at the high phase ratios required for such applications.

Membrane technology is a more recent development that is capable of extending the conditions under which solvent-based processes are economically viable. In particular, ELM technology has been used in several commercial installations to treat more dilute waste solutions (1–1500 ppm). In this instance, the mass transfer rate and overall selectivity of mass transfer is enhanced through the use of facilitated or coupled transport.

SLMs have the potential to combine the enhanced mass transfer provided by emulsion liquid membranes with the utility of MHF permeators. Further, such units can also be used to limit the amount of organic phase that is required, making the use of expensive extractants more viable. However, as an emerging technology they have had their own operational difficulties, chiefly arising from the instability of the liquid membrane itself.

HFCLMs overcome membrane instability issues by placing two sets of fibres in a solvent filled permeator. However, large-scale studies of these systems are still limited.

Simpler MHF membrane-based processes are useful in situations where the scale of operation is too small to warrant the capital outlay necessary for a dispersive solvent extraction column. These permeators provide very high mass transfer areas per unit volume and eliminate many of the problems associated with two phase mixtures, such as flooding and entrainment. In turn, this makes them easier to operate and thus more suitable when skilled supervision is unavailable. However, the permeators have only a limited life and periodic replacement must be factored into any economic analysis of their application.

In ion-exchange and adsorption processes, a solid matrix replaces the solvent as the medium for mass transfer. This well-established technology finds its value when solute concentrations in the wastewater stream are very low (in the ppm to ppb range). Recent research in this area has focused on the use of novel bi-products, often waste materials in themselves as selective adsorbents for metal ion species. The main attraction of biosorption is its cost effectiveness. Research has also focused on the use of hybrid systems to increase selectivity. These systems combine ion-exchange membranes with solvent extraction processes.

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