Bioremediation of trace organic compounds found in precious metals refineries' wastewaters: A review of potential options

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Abstract

Platinum group metal (PGM) refining processes produce large quantities of wastewater, which is contaminated with the compounds that make up the solvents/extractants mixtures used in the process. These compounds often include solvesso, β-hydroxyxime, amines, amides and methyl isobutyl ketone. A process to clean up PGM refinery wastewaters so that they could be re-used in the refining process would greatly contribute to continual water storage problems and to cost reduction for the industry. Based on the concept that organic compounds that are produced biologically can be destroyed biologically, the use of biological processes for the treatment of organic compounds in other types of waste stream has been favoured in recent years, owing to their low cost and environmental acceptability. This review examines the available biotechnologies and their effectiveness for treating compounds likely to be contained in precious metal extraction process wastewaters. The processes examined include: biofilters, fluidized bed reactors, trickle-bed bioreactors, bioscrubbers, two-phase partitioning bioreactors, membrane bioreactors and activated sludge. Although all processes examined showed adequate to excellent removal of organic compounds from various gaseous and fewer liquid waste streams, there was a variation in their effectiveness. Variations in performance of laboratory-scale biological processes are probably due to the inherent change in the microbial population composition due to selection pressure, environmental conditions and the time allowed for adaptation to the organic compounds. However, if these factors are disregarded, it can be established that activated sludge and membrane bioreactors are the most promising processes for use in the treatment of PGM refinery wastewaters.

1. Introduction

There is a severe paucity of information in public literature regarding the newer wastewater management techniques being introduced by the precious metals industry, because the development of new methods and the practice of importing existing methods from the treatment of other types of wastewater are generally not published. This review attempts to address this gap in public literature by reviewing techniques which are not currently or not widely used in metal industry wastewater treatment, but which would be applicable. Many of the volatile compounds named in the review are used in the solvent extraction of metals such as iridium, gold, palladium and platinum and are therefore found in the aqueous effluents of the extraction processes, hence any information regarding their biological breakdown is relevant to the wastewaters generated by the metal industry.

Solvent extraction technology has been used in hydrometallurgy since the 1950s to extract uranium, base metals and precious metals (Sole et al., 2005). The technology has been developed over decades and has been widely applied for the extraction of the platinum group metals (PGMs) since the early 1980s (Sole et al., 2005). Innovations in the technology have made it possible to extract PGMs of <99.99% purity (Fauconnier, 2005).

During solvent extraction of metals, an extractant is mixed with a diluent to promote various aspects of the extraction process (Hudson, 1982). The extractant is an active substance capable of forming a coordination-covalent bond with metal in the aqueous phase to give a complex that is soluble in the diluent. The extractant must form an electrically neutral species with the metal because only these are extracted. The products of the extraction stage comprise the solution of the metal in the organic solvent and the aqueous extraction raffinate (Hudson, 1982). The solution of the metal can be purified by treatment

with a fresh aqueous phase in order to remove any residual impurities. The resulting solution is then stripped of the metal for further processing, and the organic solvent is re-circulated back into the extraction process.

The reagents used for PGMs extraction are a mixture of solvents and extractants, which include high molecular weight aromatic fluids (such as Solvesso 100®) as the main diluent. Extractants such as β-hydroxyxime, amines and amides are used for the ion exchange extraction of palladium, platinum and iridium, respectively. Methyl isobutyl ketone (MIBK) is used for the solvent extraction of gold. In certain cases, such as with MIBK, the solvent may contain no diluent (Hudson, 1982). Refineries recycle their solvents until no solvent *per se* is left for disposal (Fauconnier, 2005). However, PGM refining processes produce large quantities of wastewater, contaminated with the compounds that make up the solvents/extractants mixtures.

Solvesso 100® is a mixture of mainly polyalkylated benzenes. The main compounds which make up the mixture and their proportions are listed in Table 1 (Stoffels et al., 1998). These compounds belong to eight-, nine-, 10- and 11- chain carbon (C_8, C_9, C_{10} and C_{11}) aromatic monocyclic hydrocarbons, with C_9 compounds making up 91% of the mixture. The main C_9 compounds are 1,2,4-trimethylbenzene (35%) and 1-methyl-3-ethyl benzene (18.8%). Aliphatic hydrocarbons (alkanes, alkenes, etc.) amount to 0.9% of the mixture.

Table 1
Composition of Solvesso 100® (Stoffels et al., 1998)

Component	Percentage (%)
C_8 aromatics	
Ethylbenzene	0.1
p-Xylene	0.6
m-Xylene	0.7
o-Xylene	1.0
Total	2.4
C_9 aromatics	
Isopropylbenzene	0.7
n-Propylbenzene	4.6
1-Methyl-3-ethylbenzene	18.8
1-Methyl-4-ethylbenzene	8.7
1-Methyl-2-ethylbenzene	7.3
1,3,5-Trimethylbenzene	9.2
1,2,4-Trimethylbenzene	35.0
1,2,3-Trimethylbenzene	6.7
Total	91.0
C_{10} aromatics	
t-Butylbenzene	0.1
I-Butylbenzene	0.3
n-Butylbenzene	0.1
1-Methyl-2-isopropylbenzene	0.1
1-Methyl-3-isopropylbenzene	0.2
1-Methyl-4-isopropylbenzene	0.1
1-Methyl-3-*n*-propylbenzene	0.9
1-Methyl-2-*n*-propylbenzene	0.2
1-Methyl-4-*n*-propylbenzene	0.1
1,3-Diethylbenzene	0.1
1,4-Diethylbenzene	0.3
1,2-Diethylbenzene	0.1
1,4-Dimethyl-2-ethylbenzene	0.3
1,3-Dimethyl-4-ethylbenzene	0.3
1,2-Dimethyl-4-ethylbenzene	0.4
1,3-Dimethyl-2-ethylbenzene	0.1
1,2-Dimethyl-3-ethylbenzene	0.5
1,2,4,5-Tetramethylbenzene	0.1
1,2,3,5-Tetramethylbenzene	0.1
Indane	0.5
Total	4.9
C_{11} aromatics	
1,3-Diethyl-5-methylbenzene	0.3
1-Methyl-3-*terc*-butylbenzene	
terc-Pentylbenzene	
Other C_{11} alkylbenzenes (not identified)	0.1
Total	0.8
Total amount of aromatics	99.1
Aliphatics	0.9

Methyl isobutyl ketone is a keto hydrocarbon derivative and has an aqueous solubility of 19 g l^{-1} (Yalkovsky and Dannenfelser, 1992), allowing it to be used for liquid–liquid extraction (Hudson, 1982). It has a variety of alternative names: isobutyl methyl ketone, isopropylacetone, 4-Methylpentan-2-one and 4-Methyl-2-pentanone.

Amines are a class of nitrogenous organic derivatives of ammonia (NH_3) in which one or more of the hydrogen atoms (H) has been replaced by an alkyl group, e.g., methylamine (CH_3NH_2), used as solvent, fuel additive and dyeing and staining agent (Porteous, 2000). Silica-based ion exchangers containing (poly)amine groups as the functional group have also been shown experimentally to possess very high selectivity for PGMs as no detectable amounts of nickel, copper and iron were adsorbed even though these base metals were present in the tested effluent alongside the PGMs (Kramer et al., 2001). Chemically, amines can be divided into primary, secondary and tertiary with one, two or three alkyl and/or aryl groups substituting for H atoms on the ammonia molecules. If only alkyl groups are present in an amine molecule, then these are called aliphatic amines. If aryls groups are sole substituents, then we refer to aromatic amines. Mixed amines are encountered when alkyls and aryls are both present in the same amine.

Primary amines are obtained by the action of NH_3 on alcohols or chloro-derivatives of hydrocarbons (Sharp, 1990). Secondary amines are used extensively in various industrial applications, such as in synthesis of optical brighteners, pharmaceuticals, crop protection, dyes and in solvents mixtures (Bae et al., 2002). Many amines have powerful pharmacological and sensory effects on the mind and the body. For example, epinephrine (adrenaline), the hormone released into the bloodstream during fearful situations is an amine. Caffeine and nicotine are also amines (Umland and Bellama, 1996). Secondary amines can be converted biologically and chemically to *N*-nitrosamines, which are known mutagens and carcinogens (Enzamann et al., 1995) hence it is important that they are removed from wastewaters.

Amides are also a class of organic compounds manufactured by replacing one, two or three of the H atoms of NH_3 by an acyl, e.g. acetamide (CH_3CONH_2), manufactured from acetic acid (CH_3COOH) and NH_3, is widely used as complexing agents for the selective extraction of precious metals. Primary ($RCONH_2$), secondary (($RCO)_2NH$) and tertiary (($RCO)_3N$) amides are obtained by the replacement of one, two or three H atoms as in amines but with an acyl. The amides are generally crystalline solids soluble in alcohol and ether, and some are also soluble in water.

The precious metal refineries usually store the water used in the PGMs extraction process (wastewaters) in reservoirs. A method to clean these wastewaters so that they could be used to replace potable water supplies in the refining process wherever possible would greatly help resolve the continual dirty water storage problems and lead to clean water purchase cost reduction.

Nearly all hydrocarbons are of natural origin, or can be chemically synthesized directly from natural hydrocarbons (Widdel and Rabus, 2001). They are naturally formed by long-term geochemical reactions of buried biomass or as metabolites in living organisms and, therefore, anthropogenic activities have not introduced hydrocarbons as novel compounds, but instead led to an increase in their accumulation in the environment (Widdel and Rabus, 2001). The presence of hydrocarbons in the biosphere throughout the history of life may explain why microorganisms have acquired pathways to make use of these compounds as growth substrates (Widdel and Rabus, 2001). McCarty (1991) suggested that the question is not whether *in situ* biological degradation is successful, but how to best exploit this natural process in the few cases where it is too slow to

meet bioremediation requirements. Engineered biological treatment processes have been used for over a century for degradation of organic chemicals that are unwanted and may otherwise pollute the environment, including municipal and industrial wastewater treatment plants, anaerobic sludge treatment facilities, soil farming, oxidation ponds and sanitary landfills. In general, these engineered processes take advantage of the concept of microbial infallibility. This concept suggests that organic compounds that are produced biologically can be destroyed biologically (McCarty, 1991).

The use of biological processes for the treatment of organic compounds in waste streams has been favoured in recent years, owing to their lower cost and environmental acceptability. These technologies would be widely used if proved effective. Susceptibility to biodegradation varies with the type and size of the hydrocarbon molecule (Atlas and Bartha, 1997); *n*-alkanes of intermediate chain length (C10–C24) are degraded most rapidly. Short chain alkanes are toxic to many microorganisms and very long chain alkanes become increasingly resistant to biodegradation. Branched alkanes are more resistant to biological degradation than straight-chain alkanes. Such a resistance is affected by the position, size and stereochemistry of the branches. In general, they are resistant to degradation when branches are located near or at the end of the molecule, because most degradation starts externally by terminal oxidation (Kunihiro et al., 2005). Aromatic compounds, especially those of the condensed polynuclear type, degrade more slowly than alkanes (Atlas and Bartha, 1997). Nitrogenous compounds, including nitrogenous heterocyclic compounds and organic amines are usually hardly biodegradable or even non-biodegradable in activated sludge processes (Yi et al., 1994). They accumulate in the waste sludge, leading to potential pollution problems during sludge disposal. Biodegradation of quaternary ammonium salts decreases with the number of non-methyl alkyl groups and replacement of a methyl group in a quaternary amine with a benzyl group can decrease biodegradability further (Swisher, 1987).

Namkung and Rittmann (1987) used a general fate model to show that biodegradation was the main mechanism for the removal of non-chlorinated volatile organic compounds (VOCs) including toluene, benzene, ethyl benzene and methylene chloride. Kemp et al. (2000) later showed minimal VOC losses due to abiotic mechanisms and significant biodegradation for eight compounds, including toluene and 1,3,5-trimethylbenzene; degradation of the aromatic compounds was particularly rapid. Biological processes have been used for the treatment of organic compounds contaminating groundwater ((Höhener et al., 2003), (Aulenta et al., 2005), (Ohlen et al., 2005) and (Rike et al., 2003)); waste gas (Hekmat et al., 2004); wastewaters (Freitas dos Santos and Livingston, 1995); and in various laboratory prepared VOCs mixtures ([Collins and Daugulis, 1999], [Bustard et al., 2000] and [Hamed et al., 2004]). This review examines the available biotechnologies and their effectiveness for the treatment of pollutants likely to be contained in precious metal refinery wastewaters. The processes examined comprise: biofilters, trickle-bed bioreactors (TBBs), fluidized bed reactors (FBRs), bioscrubbers, two-phase partitioning bioreactor (TPPBs), membrane bioreactors (MBRs) and activated sludge (AS). Anaerobic digestion was not considered, since various recent studies on degradation of azo-dyes have shown that although anaerobic systems are effective to degrade azo-dyes, they are unable to degrade the aromatic amines resulting from the dyes' cleavage (van der Zee and Villaverde, 2005). The PGM refiners' wastewaters are contaminated with amines, which makes anaerobic processes unsuitable to fully treat these wastewaters.

2. Biotechnologies for treating wastewaters containing organic solvents and extractants

Examples of the processes included here and their removal efficiencies for various compounds are listed in Table 2.

Table 2
Performance of processes for treating volatile organic compounds

Process	Compound name	Initial concentration (mg m^{-3})	Removal efficiency (%)	Reference
FBR[a]	1,2,4-Trimethylbenzene	0.220	99	Ohlen et al. (2005)
	1,3,5-Trimethylbenzene	0.065	99	Ohlen et al. (2005)
	m/p-Xylene	1750	98	Ohlen et al. (2005)
	o-Xylene	170	98	Ohlen et al. (2005)
	Ethylbenzene	650	98	Ohlen et al. (2005)
FBR	Phenols, N-heterocycles, aromatic amines	125–1000 mg l^{-1} as DOC[p]	59–69	Koch et al. (1991)
TBB[b]	Solvesso 100®	120 000 h^{-1}	67	Hekmat et al. (2004)
Biofilter CFB[c]	MEK[k]	106 000 h^{-1}	>99	Moe and Li (2004)
Biofilter SBB[d]	MEK	106 000 h^{-1}	>99	Moe and Li (2004)
Biofilter SBB	MEK	380 000 h^{-1}	>99	Moe and Li (2004)
Biofilter SBB	MEK	760 000 h^{-1}	83	Moe and Li (2004)
Biofilter	Amines	Not specified	65	Cruz and Buitrón (2001)
Biofilter	BTEX[l]	>200	>90	Abumaizar et al. (1998)
AS[e]	Acetone	220–270	B/D	Quesnel and Nakhla (2006)
AS	MIBK[m]	210–430	B/D	Quesnel and Nakhla (2006)
AS	VOCs mixture	681 g d^{-1}	89	Escalas et al. (2003)
AS	BTEX	15–17 g l^{-1} MLSS d^{-1}	>99	Bielefeldt et al. (1997)
AS	Trimethylamine	168 g kg^{-1} MLSS d^{-1}	99	Fukuyama et al. (1986)
CFAS[f]	Methyl diethanolamine	40 l day^{-1}	>96	Fürhacker et al. (2003)
UASB[g]	Benzidine	Not specified	46	Işik and Sponza (2003)
CSTR[h]	Benzidine	238	91	Işik and Sponza (2003)
TPPB[i]	Benzene gas	340	95	Davidson and Daugulis (2003)
MBR[j]	DCE[n] aqueous	1000 mg l^{-1}	94.5	Freitas dos Santos and Livingston (1995)
ICALB[o]	p-Xylene and naphthalene	15 mg l^{-1} h^{-1}	100	Kermanshahi pour et al. (2005)

[a] Fluidized bed reactor.
[b] Trickle bed bioreactor.
[c] Continuous flow bioreactor.
[d] Sequencing batch bioreactor.
[e] Activated sludge.
[f] Continuous flow activated sludge.
[g] Upflow anaerobic sludge blanket reactor.
[h] Completely stirred tank reactor.
[i] Two-phase partitioning bioreactor.
[j] Membrane bioreactor.
[k] Methyl ethyl ketone.
[l] Benzene, toluene, ethylbenzene, xylene.
[m] Methyl isobutyl ketone.
[n] 1,2-Dichloroethane.
[o] Immobilized cell airlift bioreactor.
[p] Dissolved organic carbon; B/D below detection limit.

2.1. Biofilters

Biofiltration units are packed-bed microbial systems packed with support materials including polyurethane, peat, heather, bark, compost, soil or a combination, to which degrading microorganisms attach as a biofilm. Biofilters are commonly used to treat airborne VOC pollution. Air containing gaseous pollutants is first humidified to facilitate microbial activity and then pumped through the packing media, where the pollutants are sorbed by the filter material and degraded by the biofilm microbes. Compounds in the air stream provide a source of carbon and energy for the biomass, while the moisture added is used to supply other nutrients (e.g. nitrogen, phosphorus and potassium) to the biofilm (Burgess et al., 2001). The specific

performance of a biofilter is relatively low, owing to the low density of microbes present as a mixed culture, although removals were reported of up to 99% for methyl ethyl ketone (MEK) gas concentration of 106 mg m^{-3} using continuous-flow and sequencing batch biofilters (Moe and Li, 2004) and of >90% for benzene, toluene, ethylbenzene and o-xylene (BTEX) gas concentration >200 mg m^{-3} (Abumaizar et al., 1998). Efficiency of biofiltration for organics removal can be improved when combined with a specific bacterial inoculum (examples are given in Table 3). Lee et al. (2002) showed >90% removal of MEK and other ketones, including MIBK, at initial concentrations of around 500 ppmv, using a biofiltration system inoculated with a liquid culture of *Pseudomonas* sp. strain KT-3 and attached to polyurethane as the solid support. They reported that the maximum removal rate was 690 g m^{-3} h^{-1}. Biofiltration processes designed for waste gas biodegradation could be adapted to treat volatile organics in liquid phase, such as in evaporation dams, by sprinkling the wastewater through the top of the biofilter, instead of water sprinkled to moisten the packing material used in the conventional system for waste gases treatment.

Table 3
Removal efficiencies of different organic compounds in biotechnological systems with microbial inoculation

Reactor type	Microorganism	Compound	Initial concentration (mg m^{-3})	Removal efficiency (%)	Reference
Biofilter (polyurethane)	*Pseudomonas* sp. strain KT-3	MEK[d]	500	>90	Lee et al. (2002)
TPPB[a]	*Alcaligenes xylosoxidans* Y234	Benzene	340	95	Davidson and Daugulis (2003)
TPPB	*Pseudomonas* sp. ATCC 55595	Toluene	50	100	Collins and Daugulis (1999)
RBC[b]	Mixed culture	Trichloroethelyne	0.0039 d^{-1}	99.9	Brar and Gupta (2000)
Vials (20 ml)	*Rhodococcus* sp. strain TMP2	Pentadecane	0.125% v/v	66	Kunihiro et al. (2005)
Vials (20 ml)	*Rhodococcus* sp. strain T12	Pentadecane	0.125% v/v	67	Kunihiro et al. (2005)
TBB[c]	Proteobacteria – β subclass	Solvesso 100®	400 g m^{-3} h^{-1}	60	Stoffels et al. (1998)

[a] Two-phase partitioning bioreactor.
[b] Rotating biological contactor.
[c] Trickle-bed bioreactor.
[d] Methyl ethyl ketone.

2.2. Trickle-bed bioreactors

Similarly to biofilters, in TBBs the microorganisms are immobilized in a biofilm, which covers the surface of a packing material of the trickle-bed column. Waste gases enter the column continuously from the top, while a re-circulating mineral salt solution flows co-currently with gas downward through the column (Hekmat et al., 2004). Biodegradation of the organic compounds occurs mainly via aerobic oxidation by the mixed population of microorganisms. Trickle-bed bioreactors have proved to be effective processes for waste gas treatment. This is especially the case for relatively low pollutant concentrations of around 1 g m^{-3} of waste gas (Hekmat et al., 2004). Hekmat et al. (2004) conducted a laboratory-scale study on the degradation of Solvesso 100® using TBB (Table 2). With an input rate of Solvesso 100® of 120 g m^{-3} h^{-1}, steady-state removal of 67% was achieved. Hekmat et al. (2004) reported TBB were previously shown to be suitable for the treatment of VOCs such as dichloromethane (Diks and Ottengraf, 1991), toluene ([Arcangeli and Arvin, 1992], [Moller et al., 1996] and [Pedersen et al., 1997]) and polyalkylated benzenes (Hekmat and Vortmeyer, 1999). This process designed for waste gases treatment could also be adapted to treat volatile organics in the VOCs in liquid waste streams, such as evaporation dams water, by either preparing the mineral salt solution with the wastewater or by mixing the wastewater with the mineral salt solution used in the conventional system for waste gases treatment.

2.3. Fluidized-bed reactors

Unlike biofilters and TBBs, which use microbial cultures immobilized on the surface of inert support materials, FBRS employ fluidized particles as a biofilm carrier for aerobic removal of organic compounds (Koch et al., 1991). Sand or activated carbon have been the most frequently used biofilm carriers. Fluidized-bed processes were used in the past for the degradation of recalcitrant compounds containing phenols such as dichlorophenols and dichloromethane (Koch et al., 1991). An airlift-loop FBR was used by Koch et al. (1991) to compare the effectiveness of sand and activated carbon as biofilm carriers for the removal of a mixture of 22 phenols, N-heterocycles and aromatic amines as sole carbon sources, which together gave a dissolved organic carbon (DOC) concentration varying between 125 and 1000 mg l^{-1}. Their results showed DOC removal in the sand to be constant (59–69%), while that in the activated carbon decreased during operation to a final value of 39%. Ohlen et al. (2005) determined the decomposition efficiency of various VOCs, including halogenated aliphatics, in groundwater using a pilot scale pure-oxygen aerated FBR. They achieved 99% decomposition for 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene from the initial concentrations of 220 and 65 µg l^{-1}, respectively (Table 2). They also used a two-stage version of the process to avoid competitive inhibition when degrading chlorinated compounds. In the two-stage FBR the cell growth compartment is separated from the chlorinated compounds degradation compartment. An anaerobic version of this biological treatment process was used for the treatment of textile wastewater (Georgiou and Aivasidis, 2006). In their study, the FBR was used for decolouration of the wastewater and transformation of the non-biodegradable azo-reactive dyes to the degradable aromatic amines that were then degraded aerobically. Special porous carriers and immobilised anaerobic methanogenic bacteria were utilised. The high concentration of active microbial mass that can accumulate on the carriers is expected to achieve wastewater decolouration at very low hydraulic retention times (HRT). Full decoloration was achieved at an HRT of 6 h.

2.4. Bioscrubbers

In a bioscrubber, the pollutant is absorbed in an aqueous phase in an absorption tower. The aqueous phase containing the dissolved compound is then treated in a separate AS unit. The effluent of this unit is circulated over the absorption tower in a co- or counter-current direction to the gas stream, which results in excellent cleaning of highly soluble pollutants. The pollutants are dissolved and degraded by the naturally occurring microorganisms in the AS unit (Kennes and Thalasso, 1998). Bioscrubbers have several advantages over media-based filtration. The process is more easily controlled because pH, temperature, nutrient balance and removal of metabolic products can be altered in the liquid (Smet et al., 1998). One disadvantage of the bioscrubber is that the pollutant must be dissolved into the liquid phase during its short residence time in the absorption column, so it is best suited to contaminants with high aqueous solubility (Herrygers et al., 2000), which is a major drawback in the treatment of many air pollutants and odourants which are highly volatile and exhibit low aqueous solubilities. Obviously, this would not be a problem if the process were going to be used to treat a liquid phase waste stream.

2.5. Two-phase partitioning bioreactors

Two-phase partitioning bioreactors are based on the use of a non-biodegradable, non-volatile, non-miscible and biocompatible organic solvent together with the aqueous phase (Muñoz et al., 2003). The process was initially developed to allow the high-yield production of inhibitory products that could then be extracted in situ by the organic solvent. It was then shown that the organic phase could serve to supply a toxic compound at sub-inhibitory levels in the aqueous phase and/or

improve the transfer and degradation of hydrophobic compounds (Muñoz et al., 2003), an approach that has been successfully demonstrated for the degradation of various organic pollutants (Déziel et al., 1999). Two-phase processes consisting of an aqueous phase followed by a second distinct organic phase added to the aqueous medium was used by Hamed et al. (2004) to degrade benzene, toluene and phenol. The addition of a second phase promotes bioconversion of higher concentrations of the compounds and decreased inhibition effects of these aromatic hydrocarbons. *Pseudomonas putida* F1 was added to the aqueous phase. The maximum overall biodegradation rates of benzene, toluene and phenol were 183, 197 and 18 mg l^{-1} h^{-1}, respectively.

2.6. Membrane bioreators

A membrane bioreactor (MBR) process for detoxifying industrial wastewater was described by Livingston (1993). The process employed a silicone rubber membrane to extract the organic pollutant from the wastewater and deliver it to a biomedium where it was biodegraded. Because silicone rubber is an organophilic polymer, it does not allow the diffusion of inorganic species or water into the biomedium. As the organic pollutants diffuse through the membrane into the biomedium, the concentration gradient is maintained by the biological degradation of the pollutants. The MBR has been shown to be particularly useful when dealing with wastewaters which are saline, acidic/alkaline or which have inorganic compositions that otherwise preclude microbial function. Freitas dos Santos and Livingston (1995) compared the performance of a laboratory-scale silicone rubber MBR with that of a completely stirred tank reactor (CSTR) for the degradation of 1,2-dichloroethane (DCE) concentration of 1000 mg l^{-1}. Their results showed removals of 94.5% and 95% for the MBR and the CSTR, respectively. However, 34% of DCE removal in the CSTR was due to air stripping, while only a negligible amount (1.5%) was air stripped in the MBR, showing the superior performance of the MBR process. Ergas et al. (1999) obtained >99% removal of toluene and dichloromethane using a laboratory-scale MBR.

2.7. Activated sludge

The AS process is a suspended growth system comprising a mass of microorganisms constantly supplied with organic matter from the wastewater, and oxygen through aeration (Horan, 1990). Aeration results in the microorganisms being mixed and held in suspension as flocs, under aerobic conditions. The growth of the microorganisms in flocs is responsible for the metabolism and removal of organic matter from the liquid. Typical products of this metabolism are carbon dioxide (CO_2), nitrate (NO_3^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) (Bowker and Burgess, 2001). Continuous addition of wastewater displaces the flocs into a secondary sedimentation tank, where they are able to flocculate and settle. Thus the nature of the floc is important as it determines the separation of sludge from the treated water and hence the efficiency of the overall process. A fraction of the settled sludge is recycled to the aeration tank whilst the remainder is discarded. The result is the ability to control the average time microorganisms will remain in the reactor, called the sludge age (SRT) or mean cell retention time (MCRT). Activated sludge systems have been used to remove odours, sulphurous gases and VOCs waste gaseous streams, both at pilot- and full-scale (Barbosa et al., 2002). Previous pilot-scale studies using AS to degrade organic compounds from waste gases showed 99% removal of trimethylamine (Fukuyama et al., 1981) and BTEX (Bielefeldt et al., 1997). An AS system modified to be used in a dual purpose, for odour treatment, in addition to treating wastewater, consists of transferring the foul air to the aeration basin, through a blower system. The odorous contaminants are dissolved and are then available to be absorbed or adsorbed and biodegraded. The AS process would be ideal for degrading VOCs in a liquid stream such as evaporation dam wastewater.

3. Discussion

Various laboratory-scale studies have shown the ability of enrichment of specific or mixed microbial cultures to degrade organic pollutants in media-based bioreactors ([Stoffels et al., 1998], [Collins and Daugulis, 1999], [Brar and Gupta, 2000], [Lee et al., 2002], [Davidson and Daugulis, 2003] and [Kunihiro et al., 2005]), with 90–100% removals being obtained for BTEX and different ketones (Table 3). Assuming the organic compounds are present in relatively high, but not inhibitory concentrations, biomass capable of obtaining energy from these compounds will respond with growth (Kemp et al., 2000). This response will, with time, change the rate at which organics are degraded, as there will be a shift in the composition of the biomass. The modified biomass community will have a greater fraction of microorganisms that can deal with the compound and, hence, will have a higher apparent biotransformation rate. An example of this trait in microorganisms was shown by Stoffels et al. (1998), who found a fermentor enrichment and TBB selected for different bacteria capable of degrading aromatic compounds, even though the enrichment was previously adapted to the pollutant (Solvesso 100®) to be removed in the TBB. They found that whereas batch enrichment in the fermentor starting from a complex wastewater sample resulted in an almost pure culture of gamma subclass proteobacteria closely related to *Pseudomonas putida* or *P. mendocina*, the community structure of the TBB inoculated with fermentor enrichment returned to high diversity, with dominance of members of the beta and alpha subclass proteobacteria, which at group level was similar to that in the wastewater sample used to inoculate the fermentor.

Only one laboratory-scale study has shown removal of Solvesso 100® at high concentration (Stoffels et al., 1998) and one TBB study showed removal of low concentrations of 1,3,5-trimethylbenzene, the main component of Solvesso 100® (Ohlen et al., 2005). The findings for this review suggests that although microbial enrichments coupled with media-based bioreactors are effective for removing organic compounds from gaseous and probably liquid waste streams, there have not been reports in the literature of their effectiveness when scaled-up. For example, Davidson and Daugulis (2003) determined that the specific utilization rate of benzene by *Alcaligenes xylosoxidans* Y234 was 0.57 g benzene g cells^{-1} h^{-1}. As long as the ratio of microbial biomass to organic compounds concentration in the wastewater is taken into consideration, microbial enrichment prepared in a fermentor could be used for treatment of PGM processing plant wastewaters, but a pilot-scale trial would be recommended in advance of full-scale application.

There are fewer examples of liquid-based systems than media-based systems for VOCs removal (WEF and ASCE, 1995), although AS diffusion is used as an alternative to more established bioreactors for waste gas treatment, such as biofilters, bioscrubbers and biotrickling filters. Two studies ([Bielefeldt et al., 1997] and [Escalas et al., 2003]) showed effective removals of VOCs in AS processes at full-scale (Table 2). Activated sludge diffusion avoids the problems associated with biofilters, TBRs and MBRs of media plugging, excess biomass accumulation, moisture control and maintaining a correct biofilm thickness (Bielefeldt et al., 1997). Ostojic et al. (1992) compared wet scrubbing, biofiltration and AS for odour control of an off-gas from sludge composting. Wet scrubbing is one of the most popular methods of odour control in the USA, but suffers from recurring problems and averages 70–75% removal efficiencies. Biofiltration, using compost or wood chips averaged around 90–95% removal efficiency and has replaced wet scrubbing at some sites. However, media failure due to humidification can reduce efficiency to 45%. Activated sludge systems were shown to average up to 100% removal efficiency at full-scale, when 2.0–2.5 m depth of mixed liquor suspended solids (MLSS) was maintained. Activated sludge outperformed wet scrubbing for the treatment of a number of odourants, such as alcohols, ketones, aldehydes and acids that persisted after wet scrubbing treatment.

The construction of an AS process dedicated for removing VOCs from PGMs extraction wastewater would probably not be a feasible option, owing to space restrictions, as well as operational costs, but an emerging technology, MBR being more compact could be a more feasible option. Although MBRs have not been widely used at full-scale, pilot-scale examples have proven effectiveness of this system in the removal of organic compounds, such as the highly persistent dichloroethane (Freitas dos Santos and Livingston, 1995).

Any bioremediation technology in use for a waste stream containing a mixture of components is subject to complex problems of toxicity. While metals belong to the list of elements and compounds toxic to micro-organisms, the issue of component toxicity is not specific to this particular wastewater. The toxic effects of whole wastewaters compared with single compounds and the principles of synergistic and competitive interactions in complex mixtures fall outside the scope of this review, but have been discussed extensively in the decade or so since the inclusion of whole effluent toxicity criteria into water quality guidelines in the UK and the USA in some excellent review articles, to which the reader is directed (e.g. [Burton et al., 2000] and [Gotvajn and Zagorc-Koncan, 1998]).

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