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Review

# Treatment of spent metalworking fluids

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**Abstract**

Metalworking fluids (MWFs) are widely used for cooling and lubricating during the machining process. The worldwide annual usage is estimated to exceed $2 \times 10^9$ l and the waste could be more than ten times the usage, as the MWFs have to be diluted prior to use. For UK industry the disposal cost is estimated to be up to £16 million per year. Used MWFs cause high levels of contamination and rancid odours due to the presence of complex chemicals, biocides, etc., so that their treatment and final disposal must be handled carefully. Conventionally this has been done by combined physical and chemical methods but, with tightened legislation, these routes are no longer acceptable. Now, biological treatment is being increasingly adopted as it seems to offer an alternative with the potential for significant cost saving. However, there are significant difficulties in operating bioreactors, such as maintenance of the stability of the microbial communities present in activated sludge plants (ASP). In order to resolve these problems, four major areas need to be considered: (1) the composition of the spent MWF and its inherent biodegradability, (2) the recalcitrant compounds existing in waste MWFs and their impact on microbes, (3) the nature of the microbial consortia and means of optimising it, e.g, temperature and the practical design of the bioreactor and (4) the requirements for nutrient supplements and optimal control conditions. The potential importance of understanding the microbial community has been studied by the use of molecular biological techniques such as polymerase chain reaction (PCR), denaturing gradient gel electrophoresis (DGGE), fatty acid methyl ester (FAME) and fluorescent in situ hybridization (FISH). The application of attached biofilm bioreactors and thermophilic aerobic technology (TAT) has also been studied. This review describes recent advances in each of these areas.


*Keywords:* Metalworking fluids (MWFs); Biological; Wastewater; Treatment; Molecular techniques; Thermophilic

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## 1. Introduction

Metalworking fluids (MWFs) have been used in industry since ancient Egyptian times (BP, 1969), but their formulation and the study of their mechanism in use has only been investigated during the last two centuries. MWFs can be divided into two main types, oil based and water based. The oil-based MWFs can then be classified into two categories, namely straight oils and soluble oils, and the water-based MWFs can also be divided into two, synthetics and semi-synthetics (Wilbert, 1973; Foltz, 2002). The latter type of MWF is currently the main group used in engineering applications and has resulted in increased amounts of organic chemicals being present in the MWF wastewater. In fact, the complexity of the composition of waste MWF streams has created immense difficulties for the waste disposal companies which deal with this type of waste, according to relevant reports and personal conversations with several waste disposal providers (Sutton et al., 1985; Sutton and Mishra, 1994; Spoors, 2003). Therefore, this review paper attempts to compare many of the methods used in spent MWF treatment and to provide an insight into the key areas for future research.

Before considering the details of treatment methodology, a review of the latest legislation requirements is essential in order to understand the standards to be met. First of all, the European Union demands that MWF manufacturers and suppliers provide products that are both safe to use and ecologically acceptable during their production and use (BLF, 2003). Legislation regarding the regulation of MWFs relates not only to health and safety but also to environmental concerns. In the UK, health and safety matters are monitored by the Health and Safety Executive (HSE) and environmental issues are policed by the Environment Agency (EA). Particular attention has been paid by the environmental authorities to used MWF disposal. The European Union Water Directive (2000/60/EC) has also prioritised substances and identified actions to be taken in order to minimise the impact on the environment. Furthermore, the European Union Directive (2000/76/EC) has addressed the problem of waste from incineration and provided an even stricter framework aimed at reducing the negative effect on the environment. The key pollutants to be reduced are nitrogen oxides ($NO_x$), sulphur dioxide ($SO_2$), hydrogen chloride (HCl) and heavy metals. (European Union, 2000a, b). Consequently it limits the amount of spent MWFs being disposed off by means of incineration. In other words, an alternative and cost effective option has to be identified and applied. The tightening legislation relating to MWF disposal has forced all industries to review their effluent treatment processes or waste disposal options to meet the targets. In the USA, MWF users who generate 10–100 $m^3$ are required to treat their process discharge on site (Burke, 1991).

Faced with all the tightening regulation, there have been many discussions regarding used MWF treatment including chemical, physical and biological methods (Sutton et al., 1985; Viraraghavan and Mathavan, 1990; Kim et al., 1989, 1992a, b, 1994; Aki and Abraham, 1998; Portela et al., 2001; Ji et al., 2004). In the early 1990s, the dominant disposal methods were chemical and physical processes; e.g., adding chemicals (lime, alum, sodium aluminate, etc.) or polymers, and using ultrafiltration and evaporation (Burke, 1991). Few biological treatments were employed. Although MWF treatment plants have existed for a long time, many of them are not suitable to treat current spent MWFs because most of the treatment plants were designed to deal with oil-based MWFs. (Sutton et al., 1985; Kim et al., 1994). Modifications have been made to improve these plants, so that they can be used for biological treatment. Otherwise, plants using a type of hybrid process involving combinations of biological and physical processes are also in use (DTI, 1998; Thomas, 2001). Recently, genetic engineering has also been employed to specify certain species that can enhance overall treatment performance (Van der Gast et al., 2004a).

It seems that there are many treatment technologies relating to the disposal of spent MWFs, but there is relatively little known about the effects of different compositions on disposal methods, the need for supplement requirements in treatment, the comparative performance of different dominating microorganisms, etc. Therefore, the purpose of this review is to: (1) summarise the compositions of MWFs listed in the literature, (2) outline the variable microbial communities existing in both MWFs and in treatment systems, (3) describe possible safety, health and environmental impacts, (4) compare different types of reactors being used in treating spent MWFs and (5) list relevant advantages and disadvantages of each disposal method.

## 2. Development of treatment processes

MWFs are commonly used as coolants and lubricants in machining processes to increase productivity, prolong tool life, prevent corrosion, etc.; therefore there is a wide

range of industrial users. A number of studies have been carried out for treating the waste MWFs and these are presented in Table 1. The majority of these studies were carried out by Sutton et al. (1985), Sutton and Mishra (1994) and Kim et al. (1989, 1992a, b, 1994). Both authors did their work in conjunction with the motor industry. The possible reason for this could be the massive amount of usage in the automotive industry, which ranges from 76 to 2839 $m^3$/day (Sutton and Mishra, 1994). Sutton et al. (1985), appear to be the first to employ a fluidised bed reactor and demonstrate its advantages. Fluidised bed operation is generally believed to be capable of dealing with higher volumes of influent and providing a vast surface area for microbial growth (Sutton et al., 1985; Fogler, 1999). Two types of carrier have been used in the study of waste MWF treatment, namely sand and granular activated carbon (GAC), as they both provide not only surface area for biological growth, but also adsorption capacity. The latter was observed by Kim et al. (1989) but subsequent treatment of the exhausted GAC was not discussed and its toxicity could be significant. In addition, these studies by Kim et al. (1992a, b) appear to be the first to investigate whether aerobic or anaerobic conditions are better for waste MWF treatment. All their investigations were carried out with simulated wastewater consisting of eight selected MWFs. Following their studies, they concluded that straight aerobic treatment could remove more than 88% COD, while only 64% could be removed anaerobically. The results indicated that the final effluent from an aerobic process gave a better performance. They also reported that there was up to 35% in

Table 1
MWF waste treatment research organisations and process employed

| System | Source of waste MWFs | Influent COD (mg/l) | COD removal (%) | References |
|---|---|---|---|---|
| Aerobic fluidised bed process with sand as carrier | General Motors, Sandusky, OH | 2101–2306 | 66–81 | (Sutton et al., 1985) |
| Activated sludge suspended-growth process | John Deere Dubuque Works, Iowa | 560–1500 | 70–84 | (Polak, 1986) |
| Aerobic fluidised bed process with sand as carrier | General Motors, Sandusky, OH | N/A | N/A | (Hare et al., 1988) |
| Anaerobic fluidised bed process with GAC as carrier | Simulated waste MWFs | 3300 | 60 | (Kim et al., 1989) |
| Packed bed reactor with peat as the packing[a] | Wascan Technical Institute, Canada | 145.9–715.2 | 64.1 | (Viraraghavan and Mathavan, 1990) |
| Anaerobic fluidised bed process with GAC as carrier | Simulated waste MWFs | 1029–5324 | 68 | (Kim et al., 1992b) |
| Aerobic suspended growth | Simulated waste MWFs | 3200–3600 | 88 | (Kim et al., 1992a) |
| Aerobic, anaerobic, and aerobic/anaerobic with fluidised bed reactor and suspended growth | Simulated waste MWFs | 1029–5324 | 72–100 | (Kim et al., 1994) |
| Aeration-suspended growth | Cutting oil supplied by Indian Oil Co. | 560 | 26–78 | (Deepak et al., 1994) |
| Integrated membrane bioreactor system | Waste MWFs from different industries | 48000–68000 | 95–99 | (DTI, 1998) |
| Aerobic fluidised bed bioreactor with sand as carrier[b] | Supplied by Olin Co. Cheshire, CT | 3000 | >90 | (Schreyer and Coughlin, 1999) |
| Hydrothermal oxidation | Supplied by Brugarolas, Spain | 1700–2882 | 38.7–97.4 | (Portela et al., 2001) |
| | Effluent from metal working processes | 48000 | 85 | (Van der Gast et al., 2004a) |

GAC: granular activated carbon.
N/A: not available.
[a]Specific for oil removal.
[b]With pre-treatment.

the system that was non-biodegradable when using an anaerobic process and a relatively lower percentage under aerobic condition. In fact, aerobic heterotrophs can certainly be expected to be the dominant microorganisms because they are the major degraders for reducing the level of organic compounds in the waste stream. Although the aerobic process seems to be superior to anaerobic operation in used MWF wastewater treatment, the upflow anaerobic sludge bed (UASB) reactor was used to treat linear alkylbenzene sulfonate (LAS), a typical substance used in MWFs as a surfactant, under thermophilic conditions (Mogensen and Ahring, 2002).

Van der Gast and colleagues have also carried out a series of waste MWF treatment studies (Van der Gast and Thompson, 2004; Van der Gast et al., 2001, 2002, 2003a, b, 2004a). In their work, the indigenous bacterial communities have been identified. Also comparisons of the overall performance among activated sludge from municipal sewage works, indigenous communities and bacterial consortia have been made. They proved that introducing specific bacterial consortia was more effective. The technique of bacterial inoculation is named bioaugmentation, which is where additional organisms are added to enhance the treatment level when the existing microorganisms are not degrading the pollutant satisfactorily (Goldstein et al., 1985; Kaplan and Kitts, 2003).

The majority of the studies listed above attempt to identify the detailed composition of MWFs. However, MWFs are proprietary products and manufacturers' material safety data sheets (MSDS) normally give very little information for evaluating the impact of end-of-pipe treatment. Waste MWFs can be straight machining oils (non-emulsifiable), emulsifiable oil metalworking fluids, semi-synthetic metalworking fluids, synthetic metalworking fluids, strong alkaline cleaners, mild alkaline cleaners and mineral solvent emulsion cleaners (Burke, 1991); but these names do not assist our understanding of the precise compositions. An understanding of the composition of MWFs is important for the design of waste MWF treatment routes, particularly in biological processes. Table 2 presents the known compositions of different types of MWF. From the composition, identification of the main sources of carbon, nitrogen, sulphate, hydrogen and phosphate can be made and it can also help us decide the requirement for supplements. In addition, knowledge of the type of biocide present in the system is essential for a biological operation, as suppression of this activity would be the first step in ensuring a positive environment for the microorganisms. There is a wide range of biocides used in MWFs and typically they are metallic or chlorinated organic compounds designed for use as a preservative, but other compounds are also used (Rossmoore, 1981).

It also appears that MWFs can also be classified by the additives present, which mainly consist of emulsifiers, biocides, lubricating agents, pressure additives, anti-foam agents, corrosion inhibitors and metal passivators (Byers, 1994). Their individual properties can be used to measure MWF performance as well, e.g., lubricating, cooling, corrosion inhibition and surface finish functionalities (Greeley and Rajagopalan, 2004). The substances listed in Table 2 can also be briefly classified by functionality. For example, chemicals used as lubricating additives would be from the oil category, e.g., mineral oil, petroleum oil, etc., and in order to eliminate mist forming, ester base oils or ester molecules have been used. Alkanolamines are widely known as corrosion inhibitors but other amines and fatty acids are also used. Some of the latest anti-corrosion additives now have anti-wear properties too. In addition, boric acid is also widely used in water-mix MWFs as an additive for corrosion protection, pH buffering and hard water compatibility (BLF, 2003). Substances derived from alcohols or alcohols themselves are the main components in emulsifiers. Phosphate esters and sulphurised esters are mainly used as pressure additives. MWF bases are usually paraffins and chlorinated or sulphonated paraffins (Uniqema, 2003).

MWFs play a major part in machining processes and offer considerable benefits. However, the impact of using MWFs on safety, health and environment is also significant, including harmful vapours in the workplace environment either directly from the compounds or by thermal degradation, toxic hazardous substances from synthetic MWFs and increased sludge production due to the difficulty of waste oil disposal. Other significant health effects reported include occupational allergic contact dermatitis directly linked to alkanolamineborates (Sandin et al., 1990; Bruze et al., 1995), cancer risks associated with MWF exposure (Calvert et al., 1998), a correlation between pneumonitis hypersensitivity and *Mycobacterium* contamination (Moore et al., 2000) and even stroke mortality has increased among workers exposed to MWFs (Park, 2001). In addition to the toxicity of chemical substances, there are some pathogenic bacteria found in MWF samples, e.g., *Pseudomonas aeruginosa* and *Klebsiella pneumoniae* (Chazal, 1995). Despite these significant effects from waste MWFs and in-used MWFs, very few studies have been carried out directly related to toxicity in the environment.

## 3. Biology of MWF

There are a variety of microbial communities existing in MWFs, leading to many interactions that influence their quality or disposal treatment. Although significant interest in the microorganisms existing in MWFs began

Table 2
Summary of different metalworking fluid compositions

| Type of MWFs | Composition | References |
|---|---|---|
| 1. Synthetic | Ethanolamines, Polyglycols, chlorinated or sulphonated paraffins, mineral oil | (Baker et al., 1983) |
| | Polyglycols, glycol ether, alcohol amine salts, little or no oil | (Sutton et al., 1985) |
| | Alkanolamine, emulsified oil | (Polak, 1986) |
| | Sodium O, O-diethyl dithiophosphate, methyldiethanolamine (MDEA) | (Sherburn and Large, 1999) |
| | 2-amino-2-ethyl-1, 3-propanediol (AEPD), 2- (2-aminoethoxy) ethanol | (Geier et al., 2003) |
| | Ethanolamine; 2-aminoethanol, *N,N′*-methylenebismorpholine | (Castrol, 2002a) |
| 2. Semi-synthetic | Triethanolamine (1800–2100 mg/l), sodium sulphonate (500–600 mg/l), 2-ethoxyethanol (80–100 mg/l) | (Schreyer and Coughlin, 1999) |
| | Alcohol ethoxylate phosphate ester, polysulphides, di-tert-dodecyl, alcohol, C11-14-iso, C13-rich, sodium sulphonate, 1-[2-(allyloxy)-2-(2,4-dichlorophenyl]-1H-imidazole, *N,N′*-methylenebismorpholine | (Castrol, 2002b) |
| 3. Not stated whether synthetic/semi-synthetic | Petroleum oil (1–5%), petroleum sulphonates(0.1–0.5%), linoleic acid (<0.1%),oleic acid | (Foxall-VanAken et al., 1986) |
| | Fatty acids, alkanolamines, alcohols, polyglycols, amino acids, carboxylic acids, surfactants containing sulphur, chloroalkanes, triazoles, triazines | (Kim et al., 1989; Kim et al., 1994) |
| | Triethanolamine, cyclohexanamine, benzotriazole, indole, heptanoic acid | |
| | Decanoic acid, hexadecanoic acid, 9-octadecenoic acid | (Kim et al., 1994) |
| | Mineral oil, sulphonated products, emulsifying agents | (Deepak et al., 1994) |
| | Alkanolamineborates, ethanolamines | (Bruze et al., 1995) |
| | Boric acid | (BLF, 2003) |
| | Mineral oil (89%), nonyl phenol 10 MEO (3.5%), fatty acids (3.0%) | |
| | Nonyl phenol 4 MEO (2.7%), ethoxylated alcohols (1.8%) | (Portela et al., 2001) |
| | Benzotriazole (16%), amine propoxylate (54%), propylene (8%), formaldehyde-based biocide, benzotriazole, dodecanedioic acid, lauric acid, sebacic acid, amine propoxylate, glycerin, propylene glycol | (Van der Gast et al., 2003a, b) |
| 4. Cleaners | Silicic acid, dipotassium salt, ethanolamine; 2-aminoethanol, alcohol, C8-10, ethers with polyethylene-polypropylene, glycol monobenzyl ether, sodium hydroxide, silicic acid, sodium salt, alcohol, C11-14-iso-, C13-rich | (Castrol, 2003) |

in the mid-20th century, most of the investigations focused on MWF deterioration and epidemiologic studies for health and safety. Baker et al. (1983) were the first to examine bacterial communities existing in activated sludge systems for treating waste MWFs. Knowledge of biodiversity in the microbial mixtures used for wastewater treatment is important in terms of determining their potential function in biodegradation. Methods used in identifying bacterial cells within the references cited in this paper are discussed below.

Traditionally, identification of bacterial isolates has been achieved by a cultivation approach but it is believed that less than 1% of the population present in the environment is isolated and identified by means of culture-based techniques (Amann et al., 1995; Van der Gast et al., 2001; WS Atkins Environment, 2000). Recent developments in biomolecular analytical techniques have enhanced the approach to understanding the diversity of the microbial population in environmental samples. PCR–DGGE is a molecular approach to the

analysis of the genetic diversity, and is based on the separation of PCR-amplified 16S rDNA fragments by polyacrylamide gels containing a linear gradient of denaturant (7 M urea with 40% formamide at 50–65 °C) (Lapara et al., 2000a, b; Van der Gast and Thompson, 2004; Van der Gast et al., 2001, 2002, 2003a, b). The molecular-based techniques involve extracting DNA from the environmental samples, PCR amplification of a sequence of the DNA, and then DGGE separation of DNA fragments. The DGGE pattern obtained provides a rapid indication of biodiversity. By excising, re-amplifying, cloning and sequencing specific DNA fragments, the components of the microorganisms can be identified (Lapara et al., 2000a). Fluorescence in situ hybridisation (FISH) is another method to identify bacteria. The technique involves the binding of complementary oligonucleotide probes (with fluorescent label) to a target sequence in the host ssDNA. Gene probe is a single-stranded sequence of DNA and can be designed specifically for the RNA of certain bacteria. Through hybridisation, the identification and quantification of desired cells can be achieved by epifluorescence microscopic detection. The advantage of PCR–DGGE and FISH is that the methods are cultivation-independent, which means that the environmental microbial samples do not need to be cultured. The techniques enable us to assess the extent of the microbial diversity without being limited to the culturable microbes.

Both phospholipid fatty acid (PLFA) analysis and fatty acid methyl ester (FAME) analysis are chemotaxonomic techniques, based on analysis of bacterial fatty acid originating from the cells, and provide a distinctive profile entirely unique to one strain (Lonon et al., 1999; Van der Gast et al., 2001, 2003a, b, 2004a). In other words, it allows the characterization and identification of the bacteria in mixed cultures. The differentiation between PLFA and FAME is that PLFA analysis only analyses phospholipid fatty acids originating from the cell membrane whilst FAME analysis covers all fatty acids present in the microbial cell. The analytical procedures involve harvesting bacterial isolates, fatty acid extraction and gas/liquid chromatography (GLC). The profiles generated from GLC are then compared with the microbial identification database (Microbial Identification System/MIS) to determine the strains or their relatedness. The advantage of this technique is that it is able to detect and identify bacteria and fungi although it is limited to the culturable microbes, as this technique requires microorganism extraction prior to the analysis.

Real-time PCR provides a more sensitive technique for direct cultivation-independent detection and quantification of environmental microbial samples by monitoring the fluorescence emitted during the reaction as an indicator of amplicon product (Khan and Yadav, 2004). The techniques involve extracting DNA, PCR amplifying a sequence of DNA, and measuring the flourescence intensity.

Researchers, who have attempted to isolate cultures from in-use MWFs or from waste MWF treatment, have found *Pseudomonas* to be the main species with more than seven species present. Among the seven, *P. fluorescens, P. putida* and *P. stutzeri* were frequently isolated/detected from MWFs. Chazal (1995) also stated that the first two species are the major part of the indigenous microflora in MWFs. Several papers have characterised the microorganism components with respect to the kind of bacteria present and the presence of soluble protein in cell-free supernatants or in lipid extracts of pelleted cells from fluids. A summary of the bacterial groups observed in related MWF systems is presented in Table 3 and it appears that there are more than 30 genera existing in either waste or in-use MWFs. As these bacteria are present in both in-use and waste MWFs, they may well actually contribute to breaking down organic compounds within bioreactors in spent MWF treatment. As such, Baker et al. (1983) investigated the bacterial distribution present in activated sludge reactors used for the degradation of MWFs. He reported that four bacteria, *Acinetobacter*, *Alcaligenes*, *Flavobacterium* and *Pseudomonas* existed in the local plant, and these were also reported to exist in waste MWFs. This proves that the indigenous MWF communities could enhance the biodegradation of waste MWFs, providing correct conditions to enrich these species were present. For example, another dominating genus in waste MWFs is *Acinetobacter* and species of this genus are important as natural degraders of a variety of hydrocarbons in the soil (Foxall-VanAken et al., 1986; Mattsby-Baltzer et al., 1989; Cloete and Muyima, 1997). Presumably, species of *Acinetobacter* could be used to form a bacterial consortium for degrading wasted MWFs. A series of studies using constructed bacterial consortia for the purpose of degrading used MWF has been done by Van der Gast and Thompson (2004), Van der Gast et al. (2001, 2002, 2003a, b, 2004a) According to Van der Gast et al. (2004a), a bacterial consortium composed of *Clavibacter michiganensis*, *Methylobacterium mesophilicum*, *Rhodococcus erythropolis* and *P. putida* has been successfully applied to treat wasted MWFs and are 30–40% more effective than other biological treatments (Van der Gast et al., 2004a). Although the performance of the constructed consortium was more effective as reported by Van der Gast and Thompson (2004) and Van der Gast et al. (2004a), the potential difficulty of maintaining a stable bacterial consortium in a dynamic environment needs to be addressed.

Along with these microorganisms found in waste MWFs and in-used MWFs, there are a variety of microbes found in petroleum land treatment units and

Table 3
Partial list of bacteria isolated from in-use MWFs and spent MWFs

| Organism | Identification method | Location | References |
|---|---|---|---|
| *Mycobacterium immunogenum*, *Pseudomonas fluorescens* | Genus-specific real-time PCR assays | In-used MWFs | (Khan and Yadav, 2004) |
| *Alcaligenes xylosoxydans*, *Bacillus pumilius*, *B. sphaericus*, *B. marinus*, *B. oleronius*, *B. licheniformis*, *Brevibacterium brevis*, *Brevibacterium lyticum*, *Brevundimonas diminuta*, *Cellulomonas flavigena*, *Clavibacter michiganensis*, *Comamonas acidovorans*, *Comamonas testosteroni*, *Curtobacterium flaccumafaciens*, *Gordona rubropertinctus*, *Methylobacterium mesophilicum*, *M. radiotolerans*, *Nocardia globerula*, *Enterococcus faecium*, *P. putida*, *P. saccharophilia*, *Ralstonia pickettii*, *Rhodococcus erythropolis*, *Stenotrophomonas maltophilia* | PCR–DGGE, FAME | Wasted MWFs | (Van der Gast et al., 2001, 2002, 2003a, b, 2004a; Van der Gast and Thompson, 2004) |
| *Proteobacteria* and, high G+C Gram + bacteria | FISH | Wasted MWFs/In-use MWFs | (Van der Gast et al., 2001, 2003a, b, 2004a) |
| *Ochrobactrum anthropi*, CDC Group B-1/B-3, *Alcaligenes faecalis ss faecalis*, *Tetragenococcus halophilus*, *P. glathei*, *Streptococcus pneumoniae*, *Staphylococcus hominis*, *Corynebacterium halophilus*, *Staphlococcus auricularis*, *P. pseudoalcaligenes Comamonas terrigena*, *Citrobacter freundii*, *Serpens flexibilis*, *Xanthomonas oryzae*, *Micrococcus* sp. *P. dimuta*, *Straphylococcus* sp. *Comamonas testosteroni*, *P. fragi* | Culture-based techniques, PLFA analysis | In-use MWFs | (Lonon et al., 1999) |
| *Aeromonas*, *Pseufomonas*, *Flavobacterium*, *Bacillus* | Culture-based techniques | Wasted MWFs | (Sherburn and Large, 1999) |
| *Salmonella* spp., *Shigella* spp., *Vibrio* spp., Gram (+) cocci, *P. aeruginosa*, *P. putida*, *P. fluorescens*, *Klebsiella pneumoniae* | Culture-based techniques | | (Chazal, 1995) |
| *P. pseudoalcaligens*, *P. stutzeri*, *Shewanella putrefaciens*, *Aerococcus viridans*, *Enterobacter agglomerans*, *K. pneumoniae*, *K. oxytoca*, *Proteus vulgaris*, *E. coli*, *Citrobacter diversus*, *Citrobacter freundii*, *Serratia* spp., *A. viridans*, *Morganella morganii*, *Corynebacterium* spp., *Streptococcus* spp., fungi, yeast *Candida* spp., Mould *Fusarium* spp. | Culture-based techniques and GC analysis of 3-hydroxylauric acid for *Pseudomonas* spp. determination | In-used MWFs | (Mattsby-Baltzer et al., 1989) |
| *Acinetobacter calcoacetucus* subsp. *Anitratus* subsp. *Lwoffi*, *Acinetobacter haemolyticus*, *P. putida*, *P. stutzeri*, *P. alcaligenes*, *P. putrefaciens*, *P. cepacia*, *Alcaligenes denitrificans* | Culture-based techniques | Wasted MWFs | (Foxall-VanAken et al., 1986) |
| *Acinetobacter*, *Aeromonas*, *Alcaligenes*, *Caulobacter*, *Corynebacterium*, *Hyphomonas*, *Flavobacterium*, *Listeria*, *Microcyclus*, *Noraxella*, *Pseudomonas*, *Seliberia*, *Sphaerotilus*, *Spirosoma* | Culture-based techniques | | (Baker et al., 1983) |

oil fields. *Flavobacterium*, *Pseudomonas*, *Azoarcus 2*, *Azoarcus 1*, *Alcaligenes*, *Microbacterium*, *Bacteroides*, *α-Proteobacteria*, *Rhodanobacter* and *Thermononas* have been found in petroleum land treatment units and *Flavobacterium* was found to be the most abundant when the degrading performance was at a relatively high level (Kaplan and Kitts, 2003). A thermophilic bacterium strain C2 was also found to be able to transform crude oils to lighter hydrocarbons in an oil field located in East China (Hao et al., 2004).

## 4. Pragmatic design and operational considerations

The treatment plants for waste MWF treatment have generally consisted of flow equalization, gravity separation of free oil, chemical emulsion breaking, flocculation, dissolved air flotation and clarification/filtration for oil removal, when oil-based MWFs were the main type used (Sutton et al., 1985). However, oil removal has become of relatively low importance in MWF disposal processes since synthetic and semi-synthetic MWFs have gradually replaced oil-based MWFs. Organic matter removal is now the main task in MWF waste treatment. Although biological treatment is extensively considered as being able to offer the most cost-effective option for organic matter removal (DTI, 1998, 2000), there are many different approaches to it (Burke, 1991; Aki and Abraham, 1998; DTI, 1998; Portela et al., 2001). Table 4 provides a review of existing used MWF waste disposal methods. The capacity of each method listed was not stated in all studies. Brief estimates of evaporation, ultrafiltration and chemical treatment were done by Burke (1991) and were 25–3000, 50–15,000 and 50–1,000,000 gallons per day, respectively. For the reverse osmosis system, capacity varies with design and can normally deal with 100,000 gallons per day (Lin, 2004).

It can be seen in Table 4 that a further consideration of the end products generated from the treatment process is required. For example, an air emission permit will be needed for evaporation processes, and an incineration procedure will be essential when the final treatment is linked to membrane separation or a filtration-related process. The design of the combination process listed in Table 4 combines a biological process, an ultrafiltration system and a number of modules arranged in sequence. For example, a waste holding tank acted as a reservoir and an equilibration tank, followed by a pre-filter to remove particulate matter. The pre-filter is a coalescer separator allowing re-use of oily waste from the oil-rich effluent. There is a pre-treatment tank in which the waste was emulsified to aid biological treatment. Then the next stage was the aerobic biotreatment plant itself, and finally the ultrafiltration unit for removing residual particles and oil

Table 4
Comparison of MWF waste disposal methods

| Method | References |
|---|---|
| *Physical Treatment* | |
| Evaporation | (Burke, 1991; MILACRON, 2000) |
| Membrane separation | |
| Microfiltration | (Burke, 1991) |
| Ultrafiltration (UF) | (Burke, 1991; MILACRON, 2000) |
| Reverse osmosis (RO) | (Burke, 1991; MILACRON, 2000; Lin, 2004) |
| Peat adsorption | (Viraraghavan and Mathavan, 1990) |
| *Chemical Treatment* | |
| Use of inorganic chemicals | (Burke, 1991; MILACRON, 2000) |
| Use of cationic/anionic organic compounds | (Burke, 1991; MILACRON, 2000; Yoshio and Masanori, 2001) |
| Hydrothermal oxidation | (Aki and Abraham, 1998; Portela et al., 2001) |
| *Biological Treatment* | |
| Aerobic activate sludge | (Polak, 1986; Kim et al., 1992a, 1994; Deepak et al., 1994; van der Gast et al., 2003a) |
| Anaerobic activate sludge | (Kim et al., 1992b) |
| Aerobic sand fluidised bed reactor (FBR) | (Sutton et al., 1985; Hare et al., 1988; Schreyer and Coughlin, 1999) |
| Anaerobic granular activated carbon (GAC) FBR | (Kim et al., 1989, 1994) |
| Reed wetland | (Ji et al., 2004) |
| *Combination process* | |
| Activated sludge process plus ultrafiltration membrane technology | (DTI, 1998) |

droplets (DTI, 1998, 2000; Thomas, 2001). Filtration technology has developed rapidly in the last 10 years and is employed in residential drinking water, as well as in industrial wastewater treatment. Generally, filtration can be classified by the pore dimension, such as ultrafiltration, microfiltration, etc., and can also be catalogued by the type of filtration materials, e.g., activated carbon, ceramic blocks, etc. (Lin, 2004). In waste MWF treatment, filtration processes are applied as a pre-treatment or a post-treatment for biological degradation. When the filtration precedes the use of biological treatment, the function is mainly to eliminate the oil content. Alternatively, it is to retain the bio-solids in the system. Sludge, as a by-product, from the biological process will require further treatment, and either incineration or landfill could be the last stage. It should be borne in mind that there are many limitations in disposing off sludge to landfill sites and therefore, sludge elimination will be a vital issue in biological processes.

With regard to biological wastewater treatment processes, carbon, nitrogen, phosphorus and sulphur are critical from the viewpoint of bacterial growth. From the composition of MWFs listed in Table 2, it can be seen clearly that there is sufficient carbon, nitrogen, sulphur, etc. Actually, in Kim's research, the enrichment of ammonia in MWFs significantly interfered with the COD analysis when chloride was present (Kim et al., 1994). As for phosphorous, it seems relatively absent and a supplement would improve the efficiency. According to Schreyer and Coughlin (1999), a phosphorous supplement has improved the growth of microorganisms and the overall treatment performance. Therefore, the level of phosphorous present in the treatment of spent MWF streams should be considered either by adding it as a supplement or by combining other waste streams to enhance the overall efficiency. Within the references cited in this paper, only Schreyer and Coughlin (1999) and Cheng et al. (2004) pointed out that additional phosphate directly enhances the overall treatment efficiency. In Schreyer's study (Schreyer and Coughlin, 1999), the supplementation of phosphorous was accomplished by replacing phosphoric acid with a portion of sulphuric acid in the breaking MWF emulsion stage, whilst in Cheng's work (Cheng et al., 2004), additional phosphate was added at the beginning of the treatment process according to the data generated from the industrial site where the activated sludge was collected. On the industrial scale, the additional phosphate is added empirically on a daily basis. In terms of carbon source supplements, Foxall-VanAken et al. (1986) also pointed out that with fatty acids as the sole carbon source, there is a more positive effect on strain growth than with the naphthenic petroleum oil components as the sole carbon sources.

Reactor temperatures in the studies mentioned in this paper ranged from 15 to 40 °C and according to Deepak et al. (1994), the COD was reduced as temperature increased from 15 to 30 °C. Cheng (Cheng et al., 2004) also increased temperature to 40 °C and found the COD removal rate was effectively double that at 30 °C. This brings us to thermophilic technology, which emerged in the early 1950s (Lapara and Alleman, 1999). Several studies have been carried out in thermophilic operation since, but there have not been many of these systems implemented at full scale, which may be due to the inconsistent results (Couillard et al., 1989; Konopka et al., 1999; LaPara et al., 2000a, b, c, 2001b; Suvilampi et al., 2003). This is most likely because under thermophilic conditions, many physico-chemical parameters, which are affected by higher temperature, need to be taken into account either in the reactor design or operational conditions. These physico-chemical parameters include viscosity, surface tension, gas–liquid solubility, diffusivity, and solid–liquid solubility. The first three parameters decrease with temperature and conversely, the last two factors increase with temperature (Lapara and Alleman, 1999; Lapara et al., 2001a). Moreover, the narrower range of bacterial communities within the thermophilic category could reduce the consistency of the bioreactor (Lapara et al., 2002).

Thermophilic aerobic treatment for waste MWFs can be still with potential, as it provides the possibility of eliminating pathogenic bacteria. There is a high possibility of harbouring pathogens in waste MWFs because of its extent of microbial communities, and it has been proved that those pathogens can directly harm human health. Although a UV disinfection process can be used for disinfection (Johnson and Phillips, 2002), it could be more cost effective to use an all-in-one process, which includes both biodegradation of pollutants and elimination of pathogens. Therefore, a further investigation into the disposal of spent MWFs under thermophilic conditions may be worthwhile.

In addition to temperature, pH is also an important factor that needs to be considered when operating a bioreactor. Among those studies discussed here, the pH ranged from 6 to 8.5. As high pH helps biocide activity (Rossmoore, 1981; Sandin et al., 1990), alkaline compound formations in the treatment process have to be limited. To our knowledge, the investigation carried out by Van der Gast and Thompson (2004) is the only study relating to the effects of pH control over waste MWF treatment and their results showed that the optimal pH range for biological treatment is between 6 and 7. It is important to note that in this study, a specific bacterial consortium was reinoculated to the bioreactor for waste MWF treatment. Therefore, whether the optimal pH range is

the same with an undefined microbial mixture will need to be considered.

Although investigations into either suspended growth or attached growth-activated sludge systems have been taken into account in waste MWF treatment, attempts to directly compare the two operations to waste MWF treatment have not been made. Among these studies, fluidised bed reactors were the only type of attached growth-activated sludge system used with sand and GAC as carriers (Table 1). The selection of carriers directly affects the overall performance of wastewater treatment and recent developments in carriers have provided other alternatives, such as polypropylene beads (Harris et al., 2001), polyurethane foam (Peng et al., 1997) and ceramic particles (Peng et al., 1999). Over all the biological treatments, the influent COD concentration varied from 1000 to 1,337,000 mg/l, which corresponded to organic loadings from approximately 2400 to 16,800 mg COD/day (Schreyer and Coughlin, 1999; Hilal et al., 2005). The treatment efficiency in terms of COD removal ranged form 60% to 99%. Most of the influent was simulated wastewater and most of the studies were operated on a batch control basis. In other words, the hydraulic retention time (HRT) is equal to the sludge retention time (SRT). Whilst the operation is continuous, HRT ranged from 3 h to 28 days in the reference cited in this paper. Another important factor for treatment facility design is food and microorganism (F/M) ratio. The F/M ratio for conventional activated sludge systems ranges from 0.2 to 0.5 whilst for waste MWF treatment, it is from 0.63 to 0.22 (Polak, 1986), depending on the character of the waste streams. The source of activated sludge or microorganisms employed for waste MWF in this review paper included sludge originating from domestic and industrial wastewater treatment plants and selective bacterial consortia.

Very little is known concerning the biodegradation kinetics of MWFs. As mentioned above, Deepak et al. (1994) seem to be the only ones who have evaluated the effect of temperature change on biodegradation kinetics in a waste MWF treatment system. For mixed culture systems like MWFs, a more detailed investigation into the kinetics may assist the actual operation. For example, fatty acids would be the primary carbon source in waste MWF biological disposal processes and thus, a slowdown in biodegradation rate could be expected once the carbon source is switched to the oil components. Therefore, from an intrinsic kinetic point of view, the biodegradation reaction could be from first order, gradually slowing down and tending towards zero-order reaction. In order to optimise/stabilise waste MWF treatment operation, an insight into the biodegradation mechanism to determine which is the limiting stage would assist the understanding.

## 5. Conclusions

Metalworking fluids (MWFs) have proved to be effective materials for improving machining processes, but in the concept of sustainability, care has to be taken in treating waste MWFs, as well as seeking an overall improvement in their management, such as the use of recycling procedures for increasing usage efficiency. Technology for the latter would most likely be a combination of reverse osmosis and solvent extraction. For biological treatment, the predominant bacterial types found in used MWFs and in the used MWF biological treatment plants have been determined and their contribution to biodegradation in treatment regimes has been shown to be significant. Issues needing further investigation are:

1. determination of the effect of thermophilic condition control on MWF treatment efficiency for sludge and pathogenic bacteria elimination,
2. determination of the effect of employing the biological fluidised bed reactor (BFBR), using types of carrier on the overall treatment efficiency and on the optimisation of operation conditions,
3. determination of the ratio of bioadsorption and biodegradation in MWF biological treatment for further sludge disposal consideration and
4. determination of the effect of changes in influent constituents on the bacterial community structure.

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