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Treatment of waste metalworking fluid by a hybrid ozone-biological process

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HIGHLIGHTS

- ▶ Ozone pre-treatment favours biodegradation of recalcitrant metalworking fluid wastewater.
- ▶ Monoethanolamine, triethanolamine and benzotriazole were degraded by ozone.
- ▶ Novel hybrid treatment achieved 72% reduction of recalcitrant COD.

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ABSTRACT

In metal machining processes, the regulation of heat generation and lubrication at the contact point are achieved by application of a fluid referred to as metalworking fluid (MWF). MWFs inevitably become operationally exhausted with age and intensive use, which leads to compromised properties, thereby necessitating their safe disposal. Disposal of this waste through a biological route is an increasingly attractive option, since it is effective with relatively low energy demands. However, successful biological treatment is challenging since MWFs are chemically complex, and include biocides specifically to retard microbial deterioration whilst the fluids are operational. In this study remediation of the recalcitrant component of a semi-synthetic MWF by a novel hybrid ozone-bacteriological treatment, was investigated. The hybrid treatment proved to be effective and reduced the chemical oxygen demand by 72% (26.9% and 44.9% reduction after ozonation and biological oxidation respectively). Furthermore, a near-complete degradation of three non-biodegradable compounds (viz. benzotriazole, monoethanolamine, triethanolamine), commonly added as biocides and corrosion inhibitors in MWF formulations, under ozonation was observed.

1. Introduction

Metalworking fluids (MWFs) are employed in a variety of metal cutting and processing operations, primarily to reduce the heat produced and the friction caused by contact of the tool on the work piece. In-use MWFs become operationally exhausted process waste when their functional properties are compromised, thereby necessitating their safe disposal. The treatment and disposal of these operationally exhausted fluids is challenging due to their high pollution load (chemical oxygen demand) and toxicity. The commonly employed methods to remediate these wastewaters consist primarily of coagulation, membrane separation, incineration or disposal into landfills; all of which are energy intensive and unsustainable options. Disposal of this waste through a biological route is an attractive option, since it is cost-effective, with a relatively low energy demand. However, a suitable treatment process requires evaluation since exhausted MWFs are chemically complex and contain environmentally hazardous biocides which are added specifically to retard bio-deterioration whilst the fluids are operational.

MWFs are composed of a complex mixture of various organic compounds and operate in extreme environments. Alkaloamines (such as monoethanolamine (MEA), triethanolamine (TEA)) and benzotriazole (BTA) are common additives found in MWF formulations. The amines are well known corrosion inhibitors and provide a valuable source of reserve alkalinity; in addition, they possess antimicrobial properties. The antimicrobial effect of ethanolamines is suggested to be due to their surface-active properties which cause damage to the bacterial cell membrane [1]. Alkanolamines include both amino and hydroxyl functional groups. Because of the amine functionality, they are basic compounds with acid dissociation constant (pK_a) values in the higher pH range (>7); for example, the pK_a values for MEA and TEA are 9.68 and 7.7, respectively [1,2]. Biodegradation of alkanolamines proceeds by hydrolysis to

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Table 1
Metalworking Fluid Wastewater Characteristics. Values in parenthesis indicate standard deviation of measured values.

Wastewater characteristics	pH	SS (mg L^{-1})	COD (mg L^{-1})	BOD_5 (mg L^{-1})	BOD_5/COD	TOC (mg L^{-1})	T–N (mg L^{-1})
	7.32 (0.04)	905 (35.9)	3100 (328.1)	395 (71)	0.127 (0.021)	675 (37.1)	278 (72.4)

ammonium and acetaldehyde [3]. For the complete degradation of these amines, ammonium hydrolysed from MEA and TEA needs to be nitrified to nitrite and nitrate [4], and in some situations nitrogen removal by a denitrification step may be required to comply with effluent discharge standards.

Benzotriazole (BTA) belongs to a class of high production volume chemicals which are added as corrosion inhibitors and biocides in metalworking fluid formulations. BTA contains a five-membered ring with three nitrogen atoms, directly bonded to one another as substituents on a benzene ring. It is a weakly basic compound arising from the association of a hydrogen atom with two of the nitrogen atoms, thus it has two acid dissociation constants: pK_{a1} ~0.4 and pK_{a2} ~8.2–8.8 [5]. It forms a thin complexing film on metallic surfaces, hence protecting the underlying metal from corrosion [6,7]. In addition, BTA is a commonly employed biocide in metalworking fluids, where it imparts significant microbial toxicity and is resistant to microbial degradation [8]. Several unsuccessful attempts to isolate organisms that can degrade benzotriazole as a C or N source have been reported [6,9–11]. In addition to being non-biodegradable, BTA is also an effective inhibitor of nitrification of nitrogenous compounds; in this respect it is applied extensively in agriculture alongside nitrogen fertilizers [12,13].

High concentrations of MEA, TEA and BTA are added to MWF formulations to prevent biodeterioration of MWFs. Although the amines are biodegradable in isolation, the presence of BTA co-existing in the MWF formulations is suspected to impart non-biodegradability attributes to the amines, which is most likely to be due to the nitrification inhibition properties of BTA. Several studies have reported reduced biodegradation of alkalomines in MWFs [2,4,14–17].

Ozone is known to be able to facilitate the biodegradability of recalcitrant wastewaters by virtue of its high oxidation potential and is widely employed in water and effluent treatment. Because of its electron rich aromatic structure, ozonation of BTA could be a viable treatment option [5,6,18]. Amines may also be degraded by either gas-induced (molecular) ozonation, hydroxyl free radicals, or by second stage biological oxidation (facilitated by the removal of BTA). In the present study, degradation of three model constituents commonly present in MWFs (MEA, TEA and BTA) under gas-induced ozonation is reported. The role of molecular ozone and hydroxyl free radicals in the reduction of the test pollutants was also investigated. The study demonstrated the complete removal of all three MWF constituents under the influence of ozone and hydroxyl free radicals. We have also explored the feasibility of employing a hybrid treatment combining ozonation with a post bio-degradation step for the treatment of a recalcitrant semi-synthetic MWF wastewater. The final reduction in COD was over 70% when combined processes were applied sequentially. The present study, to our knowledge, is the first investigation of the feasibility of employing ozone to reduce the toxicity and enhance biodegradability of waste metalworking fluid and specific recalcitrant constituents.

2. Materials and methods

2.1. Chemicals and reagents

All reagents used in this study were of analytical grade and employed without any further purification. 1H-Benzotriazole 99% was obtained from Acros Organics, UK, and the two alkanolamines (triethanolamine and monoethanolamine) were procured from Sigma Aldrich, UK. All other chemicals and solvents were supplied by Fisher Scientific, UK. Reagents were prepared using 15 MΩ Milli-Q water.

2.2. Wastewater characteristics

Samples of recalcitrant semi-synthetic MWF wastewater (Hocut 795-B, Houghton International Inc.) were obtained from Microbial Solutions Ltd (Upper Heyford, Oxfordshire, UK), a company which specialises in biological treatment of MWF effluent. Wastewaters were treated biologically in large-scale attached bio-filters by the company, but the final effluent quality did not comply with the prescribed discharge limits due to the persistent residuals. The residual chemical oxygen demand (COD) of the effluent was categorised as being refractory and resistant to treatment by the conventional biological process. The exact composition of the wastewater was difficult to ascertain as the formulation details of MWFs are proprietary information and not available from the manufacturers owing to their commercial sensitivity. The poorly defined composition of the wastewaters made the detailed evaluation of the extent and rate of degradation of specific compounds, and the determination of intermediary components generated by ozonation, very difficult. However, general physico-chemical parameters of the wastewater are summarised in Table 1.

2.3. Experimental set-up and ozone generation

Ozone was produced from air using a TRAILIGAZ ozone generator (Ozotech Burgess Hill, UK), which is capable of producing up to 9 g h^{-1} of ozone. Compressed air was supplied as feed gas for the production of ozone at a rate of 0.550 L min^{-1} (STP). In order to determine the effectiveness of ozone treatment on the degradation of the MWF a model formula was assembled on the basis of the usual concentrations found in semi-synthetic MWF formulations. The composition of the model MWF was as follows: MEA 3500 mg L^{-1} (57.4 mM), TEA 4250 mg L^{-1} (28.5 mM), and BTA 100 mg L^{-1} (0.84 mM). The experiments were performed in laboratory batch column reactors, consisting of 18.5 cm long cylindrical wash bottle with 4 cm internal diameter. The gas containing ozone was bubbled into the liquid by means of a ceramic porous diffuser. The exhaust gas stream exited from the top of the column through a wash bottle containing potassium iodide (KI) solution in order to trap residual ozone, which was determined by the iodometric method [19]. All experiments were performed at room temperature using 100 mL samples, for various reaction times.

2.4. Determination of aqueous ozone

The concentration of ozone in water was measured by the standard indigo method, as described previously [20]. Ozone rapidly and stoichiometrically decolourises indigotrisulphonate, and as it does the absorbance at 600 nm decreases linearly with increasing concentration of ozone. Stock indigo solution was prepared from potassium indigotrisulphonate and phosphoric acid. All experiments were performed under ambient conditions in an environmentally controlled laboratory where the room temperature was 21 ± 1 °C. The applied ozone dose was determined from