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Hybrid biological, electron beam and zero-valent nano iron treatment of recalcitrant metalworking fluids

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Hybrid approaches for the remediation and detoxification of toxic recalcitrant industrial wastewater were investigated. The focus was waste metalworking fluid, which was selected as a representative model of other waste streams that are toxic, recalcitrant and that require more sustainable routes of safe disposal. The hybrid approaches included biodegradation, electron beam irradiation and zero-valent nano iron advanced oxidation processes that were employed individually and in sequence employing a factorial design. To compare process performance operationally exhausted and pristine metalworking fluid were compared. Sequential hybrid electron beam irradiation, biological, nanoscale zero-valent iron and biological treatment lead to synergistic detoxification and degradation of both recalcitrant streams, as determined by complementary surrogates and lead to overall improved COD removal of 92.8 ± 1.4% up from 85.9 ± 3.4% for the pristine metalworking fluid. Electron beam pre-treatment enabled more effective biotreatment, achieving 69.5 ± 8% ($p = 0.005$) and 24.6 ± 4.8% ($p = 0.044$) COD reductions.

1. Introduction

There are many effluents of industrial origin that are chemically mixed, recalcitrant in nature and potentially toxic making them exceptionally challenging in terms of sustainable end-of-pipe treatment. Added to this environmental protection legislation such as the EU Water Directives (2000/60/EC, 2000/76/EC) are increasingly stringent in terms of post-treatment standards. Consequently, there is an increasing urgent requirement to develop and apply technologies that are efficient, cost effective and sustainable. Metalworking fluids (MWFs) were selected for this study since they are formulated specifically to resist premature biodeterioration and thus provide a good model representative of other recalcitrant effluents generated by many industries to assess and develop more sustainable waste treatment methods. They are chemically complex yet defined and consist of base mineral oils, emulsifiers and surfactants, corrosion inhibitors, extreme pressure agents, friction reducing agents, foam inhibitors and biocides (Jagadevan et al., 2012), making subsequent treatment challenging. Their exact chemical composition is typically proprietary information. Furthermore, the extreme conditions of heat and pressure during their deployment leads to chemical changes which make monitoring of the exact chemical composition MWF effluent impractical. Consequently in this study, the process efficiency of several approaches for their treatment was monitored by assaying the aggregate effects on individual component oxidations using a combination of established measures including chemical oxygen demand (COD) and toxicity bioassays (Muszynski et al., 2007), which reflect the general metabolic health of bacteria.

Since MWFs are a hazardous waste, disposal is tightly regulated by local and international legislation (Rodriguez-Verde et al., 2014). Traditionally, spent metalworking fluids have been treated using chemical treatment, evaporation or ultrafiltration (Connolly et al., 2006), but recent advances in our laboratory showed that biological treatment of MWFs is a promising cost and energy effective treatment option (Jagadevan et al., 2011), in particular if combined with advanced oxidation processes (AOPs) such as Fenton's reagent (Jagadevan et al., 2011) and various UV-based AOPs (MacAdam et al., 2012). Biological treatment processes commonly used in

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wastewater treatment are not able to degrade complex organic chemicals (Haji-Saeid et al., 2012) and biocides. Even specifically designed MWF biotreatment processes benefit from some degree of chemical enhancement to inactivate biocides and facilitate biodegradation (Jagadevan et al., 2011). AOPs have been successfully used as pre-treatment of industrial wastewaters to improve their biodegradability before biological treatment (Rizzo, 2011). Their effectiveness is due to the formation of highly reactive species, such as hydroxyl radicals, which enable the degradation of organics and inorganics. However, relying solely on AOPs is energy and cost intensive and biological treatment has the potential to serve as a complement (Oller et al., 2011).

One particularly effective AOP to complement biological treatment is nanoscale zero-valent iron (nZVI), which has previously been reported to reduce toxicity and improve COD removal of a MWF (Jagadevan et al., 2012). nZVI has been used in environmental remediation for over 20 years (Tratnyek and Matheson, 1994). It can be produced economically, has low toxicity in the environment and presents a high reactivity, ideal for treating a wide range of chemical pollutants through various sorption, precipitation and reduction pathways (Crane and Scott, 2012). However, further research into simultaneous removal of multiple contaminants is needed (Guan et al., 2015).

Electron beam (E-beam) irradiation treatment has been shown to also improve the biodegradability of various waste streams (Han et al., 2012; Rawat and Sarma, 2013). This can be attributed in part at least to radiolytical conversions of biologically resistant pollutants (Getoff, 1986) into smaller, more bioavailable compounds (Han et al., 2012). During E-beam irradiation highly reactive transient oxidising (•OH) and reducing ($e^-_{(aq)}$ & H•) species are formed (Cooper et al., 1992). E-beam treatment has been investigated on a large variety of waste streams (Pikaev et al., 2001; Shin et al., 2002) including oily petroleum waste streams (Duarte et al., 2004a; Pikaev, 2002) and used lubricating oil (Scapin et al., 2007), but to date has not been reported to have been applied to MWFs. Metal removal was found to be high in simulated effluents in the absence of co-contaminating organics (Ribeiro et al., 2004), but required higher doses in the presence of organics (Duarte et al., 2004b). However, to destroy the organics in complex effluents very high irradiation doses were required (Duarte et al., 2004a). Also although effective for metal removal, oily effluents do reliably show alterations of organic compounds (Scapin et al., 2007) or exhibit toxicity reduction by e-beam irradiation on its own even at very high doses (Borrely et al., 2000). This suggests their integration with biological treatment and other AOPs might be an effective treatment route. We therefore tested for synergies between nano iron and e-beam treatment for enhancement of biological treatment.

Each treatment method has their specific strengths and weaknesses, however what has not been reported to date is treatment effectiveness when they are combined as a sequential treatment. Thus the objective of this study was to compare and contrast each treatment technique: biotreatment, nanoscale zero-valent iron and the e-beam individually and when combined in a full factorial sequential order to determine the most effective treatment sequence.

2. Materials and methods

2.1. Wastewater characteristics

Two semi-synthetic metal recalcitrant working fluid waste streams (MWFs) were investigated in this study: A pristine (unused) MWF, diluted to its operating concentration of 5% and an operationally exhausted MWF. The operationally exhausted MWF was obtained from industrial collaborators and is in diluted form. The physico-chemical parameters of the wastewaters are summarised in Table 1.

2.2. Chemicals

All chemicals (iron sulphate ($FeSO_4 \cdot 7H_2O$), ammonium iron sulphate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$), sodium chloride (NaCl), sodium hydroxide (NaOH), sodium borohydride ($NaBH_4$), sulphuric acid (H_2SO_4), and solvents (ethanol, acetone)) used in this study were of analytical grade, obtained from Fisher Scientific, and employed without any further purification and all solutions were prepared using Milli-Q water (resistivity 15 MΩ cm).

2.3. Biological treatment experiments

Aerobic bacterial treatment was carried out at room temperature (293 ± 1 K) in 15 mL fixed-film batch bioreactors, with a working volume of 10 mL, with airflow maintained at 0.4 L min^{-1}. The bioreactor had been inoculated with a five-membered bacterial consortia previously reported to be effective for biological treatment of MWF streams (van der Gast et al., 2003). The acclimatisation period was 21 days to allow the biomass to grow and acclimatise to the metalworking fluid substrate, which is in line with similar studies (Jagadevan et al., 2011).

2.4. Nanoscale zero-valent iron experiments

Nanoscale zero-valent iron particles (nZVI) were synthesised using a borohydride reduction method, which has been previously reported (Dickinson and Scott, 2010). Ferrous iron is reduced to a metallic state using sodium borohydride via the following reaction:

$$2Fe^{2+} + BH_4^- + 3H_2O \rightarrow 2Fe^0 \downarrow + H_2BO_3^- + 4H^+ + 2H_2$$

7.65 g of $FeSO_4 \cdot 7H_2O$ was dissolved in 50 mL of Milli-Q water. The pH was adjusted to 6.8 using a 4 M NaOH solution. The nanoparticle product was isolated through centrifugation and then sequentially washed twice with water, ethanol and acetone (20 mL of each). The nanoparticles were dried in a desiccator under low vacuum (approx. 10^{-2} mbar) for 48 h at 60 °C and then stored until required. All experiments were carried out at room temperature (293 ± 1 K) in 15 mL test tubes. Before use, the nanoparticles were sonicated for 5 min using a probe sonicator at 80 W before being added to the samples under constant stirring and left to react for 1 h before being separated out using centrifugation and magnetic separation and stored for subsequent analysis.

2.5. Electron beam experiments

The samples were irradiated with 6 MeV electrons, provided by a single pulse linear accelerator (E-beam) at the Gray Institute, Department of Oncology, University of Oxford. Irradiation was performed in a batch system using synthetic quartz (QS) cuvettes, supplied by Hellma Analytics at an average dose of 50.1 ± 2.4 Gy per pulse, determined by Fricke Dosimetry. The pulses were delivered at 50 Hz. Fricke Dosimetry is based on the oxidation of ferrous ions

Table 1
Wastewater characteristics. Mean and standard deviation of triplicates (n = 3) are shown in parentheses.

Wastewater	COD (mg/L)	TOC (mg/L)	pH
Operationally exhausted MWF	19,188 (151)	3326 (133)	7.5 (0.1)
Pristine MWF	117,180 (5680)	22,132 (4574)	7.9 (0.5)