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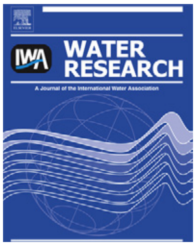

A novel hybrid nano zerovalent iron initiated oxidation – Biological degradation approach for remediation of recalcitrant waste metalworking fluids

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ABSTRACT

Disposal of operationally exhausted metal working fluids (MWF) through a biological route is an attractive option, since it is effective with relatively low energy demands. However, it is enormously challenging since these fluids are chemically complex, including the addition of toxic biocides which are added specifically to retard bio-deterioration whilst the fluids are operational. Nano-sized elemental iron represents a new generation of environmental remediation technologies. Laboratory scale batch studies were performed to test the degradation ability of a semi-synthetic metalworking fluid (MWF) wastewater (which was found to be resistant to initial bacterial treatment in specifically established bioreactors) by employing a novel hybrid approach. The approach was to combine the synergistic effects of nano zerovalent iron (nZVI) induced oxidation, followed by biodegradation, specifically for the remediation of recalcitrant components of MWF effluent. Addition of nZVI particles to oxygenated wastewater resulted in oxidation of organic contaminants present. Our studies confirmed 78% reduction in chemical oxygen demand (COD) by nZVI oxidation at pH 3.0 and 67% reduction in neutral pH (7.5), and 85% concurrent reduction in toxicity. Importantly, this low toxicity made the nZVI treated effluent more amenable for a second stage biological oxidation step. An overall COD reduction of 95.5% was achieved by the novel combined treatment described, demonstrating that nZVI oxidation can be exploited for enhancing the biodegradability of a recalcitrant wastewater in treatment processes.

1. Introduction

Metalworking fluids (MWFs) are extensively used in machining operations as both lubricant and coolant. Water-soluble semi-synthetic MWFs are used in approximately 80–90% of applications of the estimated 2 billion litres of MWFs consumed worldwide every year (Rao and Srikant, 2006; Cheng et al., 2005). The formulations of MWF are chemically complex consisting of base mineral oil (hydrogenated petroleum distillates of naphthenic or paraffinic nature), emulsifiers and surfactants (petroleum sulphonates and ethoxylate products), corrosion inhibitors (e.g., fatty acid salts, sulphonates, amines, amides, borates, silicates, phosphates and nitrates), extreme pressure agents and anti-weld agents (sulphur, chlorine, and phosphorus chemical compounds), foam inhibitors, biocides (phenolic derivatives such as

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chlorinated phenols, aliphatic derivatives (hydrazine), aldehydes, formaldehyde release biocides (triazine, isotiazolines) and organosulphur nitrogen compounds), friction reduction agents and alkaline reserve compounds (sodium hydroxide and ethanolamines) (Muszynski et al., 2009; van der Gast et al., 2003; Connolly et al., 2006). The exact chemical composition of the formulation, however, is difficult to ascertain due to the fact that the manufacturers of MWF never disclose the exact composition, since this is proprietary information. Furthermore, the composition of the formulation changes temporally and spatially with use. Worldwide annual usage of MWF is over 2,000,000 m^3 and the waste volume could be as high as ten times the usage as a consequence of the dilution of MWFs prior to its usage (Cheng et al., 2005).

MWF becomes less effective after use because of thermal degradation and contamination by microorganisms, and therefore they must be replaced periodically and the spent liquid has to be disposed safely. Until recently, most of the waste MWF has been disposed either by incineration or into landfills (van der Gast et al., 2003; Connolly et al., 2006). Incineration of such wastes are associated with evolution of nitrogen oxides (NO_x), sulfur dioxide (SO_2) and hydrogen chloride (HCl) and disposal into landfills result in contamination of the soil and potential leaching of toxic compounds to the underground water table. The 2000/76/EC and EA 2004 Directives issued by the European Union and Environmental Agency in UK (EA) impose strict framework for the disposal of these wastes (Cheng et al., 2005). These regulations have created a growing interest in the development of environmentally benign and sustainable disposal methods for the MWF wastewater.

Physico-chemical methods such as evaporation, chemical de-emulsification and ultra-filtration have been the favoured options to treat used MWFs (Hilal et al., 2004; Anderson et al., 2009). These treatment methods have several drawbacks such as high energy requirement and membrane fouling resulting in significant costs for such treatments. An alternate potential disposal route is through biological degradation treatment. Biological treatment of waste MWF has been investigated by several researchers (Muszynski et al., 2009; van der Gast et al., 2003; Rabenstein et al., 2009; Kim et al., 1994) and it has been demonstrated that aerobic biological treatment processes can successfully degrade simpler and more bioavailable constituents of the MWF wastewater, leaving behind complex recalcitrant, and potentially toxic organic compounds. These toxic components of the waste typically persist after biological treatments and thus have to be further treated in order to enable safe disposal, which can add additional costs.

MWFs have previously been reported to have been successfully treated by advanced oxidation processes (AOP) (Seo et al., 2007), whereby the waste treatment relies on generation of highly reactive, short-lived and non-selective hydroxyl radicals, which oxidise and mineralise most organic compounds. A major problem in the successful application of AOPs such as photocatalytic oxidation (Hoffmann et al., 1995; Tachikawa et al., 2007), ultrasonic irradiation (Mason, 2003, 2007; Adewuyi, 2005) and Fenton oxidation (Pignatello et al., 2006; Gogate and Pandit, 2004a,b) is the non-uniform irradiation of the catalyst resulting in a substantial loss of the incident energy, addition of large quantities of reagents and operation in an acidic environment, leading to an overall unfavourable economics. Furthermore, the residual hydrogen peroxide contributes additional toxicity to the effluent. In contrast, chemical oxidation technologies such as the application of ozone and hydrogen peroxide exhibit lower rates of degradation as compared to the processes based on the free radicals (Gogate and Pandit, 2004b; Ikehata and El-Din, 2004).

There has been a significant interest in employing zerovalent metals as electron donors to degrade model organic pollutants such as methanol, ethanol, 2-propanol, (Keenan and Sedlak, 2008a) benzoic acid, (Joo et al., 2005) molinate transformation, (Joo et al., 2004) chlorophenol, (Noradoun et al., 2003) and arsenic (III) removal (Kanel et al., 2005) Zerovalent iron (ZVI) is an electron donor, a strong reducing agent, and the spent agent, Fe^{2+} is environmentally innocuous. The main feature of this system is its ability to create *in-situ* reactive oxygen species in aqueous-phase employing less expensive and nontoxic reagents under room temperature and pressure conditions. This reaction is very similar to the Fenton oxidation system, in which the key reaction centres on the generation of hydroxyl radicals, by the decomposition of hydrogen peroxide catalysed by ferrous ions in acid conditions (Pignatello et al., 2006). In addition, relative to the homogeneous Fenton catalysts, the heterogeneous catalysts can treat organic pollutants over a wide range of pH, without the need for extraneous addition of hydrogen peroxide.

What is clear is that none of the above treatment methods, when employed in isolation, are effective for treating wastewaters to an acceptable level of chemical oxygen demand (COD)/toxicity reduction and is certainly not economically viable. Thus, in the present study, a hybrid method combining the synergistic effects of advanced oxidation processes to reduce the toxicity of the effluent, making it amenable for further bacterial treatment in a subsequent biological oxidation step, was investigated. Present study reports the results of employing a novel hybrid approach (zerovalent iron oxidation (nZVI) followed by biological degradation) for treatment of a recalcitrant semi-synthetic MWF wastewater. We found that nZVI oxidation achieved 85% reduction in toxicity (based on bacterial biosensor assessments) with a concurrent increase in the biodegradability. The final reduction in COD was over 95.5% when combined nZVI and biodegradation processes were applied sequentially. The present study, to our knowledge, is the first investigation into determining the feasibility of employing nZVI to reduce the toxicity and enhance biodegradability of a real industrial wastewater on the basis of previous reports.

2. Materials and methods

2.1. *Wastewater characteristics*

The recalcitrant semi-synthetic MWF wastewater samples (Hocut 795-B, Houghton International Inc.) were obtained from Microbial Solutions Limited, Upper Heyford, Oxfordshire, a small company which specialises in biological treatment of MWF effluent. The wastewater samples had been initially treated in an aerobic fixed film batch bioreactor,