

INCORPORATING BIODEGRADATION AND ADVANCED OXIDATION PROCESSES IN THE TREATMENT OF SPENT METAL WORKING FLUIDS

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Abstract

The treatment of spent metalworking fluids (MWFs) is difficult due to their complex and variable composition. Small businesses often struggle to meet increasingly stringent legislation and rising costs as they need to treat this wastewater on site annually over a short period. Larger businesses that treat their wastewater continuously can benefit from the use of biological processes, although new MWFs designed to resist biological activity represent a challenge. A three-stage treatment is generally applied with the oil phase being removed first followed by a reduction in COD loading with polishing of the effluent's quality in the final stage. The performance of advanced oxidation processes (AOPs), which could be of benefit to both types of businesses was studied. After assessing the biodegradability of spent MFW, different AOPs were used (UV/H₂O₂, photo-Fenton and UV/TiO₂) to establish the treatability of this wastewater by hydroxyl radicals ($\cdot\text{OH}$). The interactions of both chemical and biological treatments were also investigated. The wastewater was found to be readily biodegradable in the Zahn-Wellens test with 69% COD and 74% DOC removal. UV/TiO₂ reactor was found to be the cheapest option achieving a very good COD removal (82% at 20 min retention time and 10 L.min⁻¹ aeration rate). Photo-Fenton was found

to be efficient in terms of degradation rate, achieving 84% COD removal (1M Fe²⁺, 40M H₂O₂, 20.7 J.cm⁻², pH 3) and also improving the wastewater's biodegradability, followed by UV/H₂O₂ (40M H₂O₂, 34.5 J.cm⁻², pH 9). UV/H₂O₂ process was the most effective in removing recalcitrant COD post-biological treatment stage.

Keywords: biodegradation, H₂O₂, photocatalysis, photo-Fenton, UV

1. Introduction

Metalworking fluids (MWFs) are widely used in manufacturing industries for the lubrication and cooling of metal tools within machining processes. MWFs remove small metal chips, reduce the friction between work pieces, optimise tool life, provide protection against corrosion and improve the finished quality of the manufactured products [1]. Worldwide over 2,000,000 m³ is used annually although the wastewater volume could be ten times higher due to the dilution of the MWFs prior to use. In the UK industry alone, over 400,000 m³ of spent MWFs are produced annually with the disposal costs estimated to range between £8 and £16 million per year [2]. The average disposal cost per 1 m³ of spent MWFs is £20 - £40, however this cost will be significantly higher for smaller businesses (£40 - £80).

There are two main categories of MWFs; oil based (straight oils and soluble oils) and water based (synthetic and semi-synthetic fluids) with a single product containing up to 60 different components and more than 300 different substances known to be used in MWFs [3]. In Europe, the tightening legislation regarding the waste disposal (European Union Water Directive, 2000/60/EC) and the waste from incineration (European Union Directive, 2000/76/EC) has lead manufacturing industries to consider treating their wastes on-site prior to disposal. The development and growing use of water soluble MWFs with enhanced cooling characteristics has resulted in difficulties during the wastewater treatment leading to increased process complexity and costs. Conventional chemical and physical methods are most commonly used during the treatment of spent MWFs and depending on the level of treatment required; one, two or three stages are generally applied [4]. Solids and the oil phase are removed during the primary

stage with the secondary stage being used to reduce the volume and COD loading. Further, tertiary treatment is often required to polish the effluent quality in order to meet the increasingly stringent limits.

New emphasis has been put into developing and enhancing the biological treatment option with promising results [5]. Although previous studies suggested that 10-15% of COD in spent MFWs is aerobically non-biodegradable and this is even higher for anaerobic systems, recently, COD removals reaching 96 and 97% were reported [6,7]. Variable effluent quality and the use of new, enhanced and biocide containing products represent a challenge for biological treatment but the main disadvantage is the need to operate these systems on a continuous basis which makes them unsuitable for smaller businesses. There is a strong need to develop an effective system which could be used by smaller companies on an on/off basis as well as improve the biological treatment efficiency for larger businesses.

Both of these challenges could be addressed by the introduction of advanced oxidation processes (AOPs) into the treatment flow sheet. AOPs have the potential to remove recalcitrant and toxic compounds and improve the biodegradability of the wastewater due to the generation of non-selective and highly oxidising $\cdot\text{OH}$ radicals. The processes of concern here include indirect photolysis (UV/ H_2O_2), photo-Fenton (UV/ Fe^{2+} / H_2O_2) and heterogeneous photocatalysis (UV/ TiO_2) and involve a number of different $\cdot\text{OH}$ forming mechanisms. During UV/ H_2O_2 , the radicals are mainly produced by H_2O_2 photolysis. By adding Fe^{2+} into the system, the production can be enhanced through the formation of photoactive $[\text{Fe}(\text{OH})^{2+}]$ complex [8]. Different mechanism plays a role in the UV/ TiO_2 system where the photoactivation of TiO_2 leads to a generation of electron (e^-) – hole (h^+) pairs which subsequently interact with water and dissolved O_2 to produce $\cdot\text{OH}$ as well as other radicals ($\cdot\text{OH}_2$, $\cdot\text{O}_2$) [9]. Organics adsorbed on TiO_2 can also directly react with the generated h^+ . AOPs have been previously applied for the treatment of industrial wastewaters and wastewaters containing highly toxic and recalcitrant compounds [10, 11, 12]. They have also been reported to significantly enhance the biodegradability of recalcitrant compounds such pesticides and pharmaceuticals as well as remove the recalcitrant organics post-

biological stage [8,13]. Further, UV/TiO₂ proved to be a very economical and effective method in treating biological effluent of dying wastewater [14]. However the treatment of high organic load and complex waste such as spent MWFs has not been widely reported to the best of our knowledge.

Aims and scope

The scope of this study was to investigate the applicability of UV based AOPs (UV/H₂O₂, photo-Fenton and UV/TiO₂) in the treatment of MWF wastewater. This study was conducted with the main aim of developing low chemical treatment solution for smaller businesses which can be operated on an ON-OFF basis. A potential of using AOPs to enhance the biodegradation of spent MWFs was also addressed.

A semi-synthetic MWF was pre-treated using ultrafiltration (UF) to remove the emulsified oil and the biodegradability of the resulting effluent was studied. The potential of direct photolysis, UV/H₂O₂, UV/Fe²⁺/H₂O₂ and particularly UV/TiO₂ process to treat the UF permeate was investigated with the possibility of combining biodegradation and AOPs to enhance the final effluent quality.

2. Materials and Methods

2.1. Reagents and solutions

The wastewater used in this study was the UF permeate of a semi-synthetic spent MWF obtained from a machining facility in the UK. The principal characteristics of the wastewater were as follows: COD 14055 mg.L⁻¹, BOD₅ 4460 mg.L⁻¹ (non-seeded) and 5880 mg.L⁻¹ (seeded), TOC 4600 mg.L⁻¹, TN 1690 mg.L⁻¹, TP < 0.5 mg.L⁻¹, alkalinity (as CaCO₃) 3480 mg.L⁻¹, conductivity 4.78 mS.cm⁻¹ and pH 9. Unless otherwise stated, the spent MWF was diluted to a COD of 1000 mg.L⁻¹ with deionised water prior use. For AOP experiments, hydrogen peroxide (H₂O₂) was analytical grade and purchased as a stabilised 35% (wt.) solution from Fisher Scientific UK Ltd. (Loughborough, UK). Ferrous sulphate heptahydrate, FeSO₄ · 7 H₂O (EA West, Grimsby, UK) was used in the photo-Fenton experiments. Titanium dioxide (Aeroxide[®] TiO₂ P 25) with a specific surface area of 50 ± 15 m².g⁻¹, anatase to rutile ratio of 80:20 with

an average primary particle size of 21 nm was purchased from Lawrence Industries (Tamworth, UK). For pH adjustments, 0.5M sulphuric acid (H₂SO₄) and 1M sodium hydroxide (NaOH), both purchased from Fisher Scientific UK Ltd. (Loughborough, UK) were used. The manganese oxide (MnO₂) powder, used for removing the residuals of peroxide, was laboratory reagent grade and purchased from VWR (Lutterworth, UK). All the chemicals used to prepare the mineral solution for the biodegradation test (OECD, 1992) were of analytical grade and purchased from Fisher Scientific UK Ltd. (Loughborough, UK).

2.2. *Biological degradation of the spent MWF*

The biodegradability of the MWF was assessed with the standardised Zahn-Wellens/EMPA test no. 302B [15] in 5L cylindrical glass reactors and kept in the dark. Solutions were aerated and mixed with compressed air diffused through a porous air sparger and were saturated with dissolved oxygen (~9 mg.L⁻¹). The inoculum was obtained from a pilot plant treating sewage at Cranfield University. A concentration of 1 g.L⁻¹ dry matter was used in all the reactors. Diethylene glycol with an initial COD of 1010 mg.L⁻¹ was used as the reference compound for monitoring the activity of the sludge. The MWF was tested at two initial CODs, 412 and 988 mg.L⁻¹. All the blanks, controls and test samples were run in duplicate to ensure reproducibility of results. The solutions pH values were monitored daily and held between 7 and 7.5 to ensure optimum conditions. 60 ml of each sample were filtered through glass micro fiber filter of pore size 1.3 μm prior the analysis. Degradation percentage (D_t) was calculated using equation $D_t = [1 - (C_t - C_B) / (C_A - C_{BA})] \times 100$ where C_t and C_A represent the COD of the test sample at a time t and at 3h respectively; C_B and C_{BA} represent the COD in the blank at a time t and at 3h respectively.

2.3. *Photochemical degradation of the spent MWF*

2.3.1. Collimated beam apparatus

A Wedeco AG bench scale collimated beam (CB) apparatus (Herford, Germany) fitted with four 30W monochromatic low pressure mercury lamps (emitting at 254 nm) was used for UV-C irradiation. 250 ml of test solutions was placed in a Petri dish at 22 cm from the light source and stirred with a magnetic

stirrer. UV irradiance was determined to be 19.2 W.m^{-2} by uridine actinometry [16]. The lamps were allowed to warm up for 10 min to ensure consistent light output before irradiating the test solutions.

2.3.2. Photocatalytic reactor

An annular, plug flow, single path reactor which operates in continuous mode (Water Innovate, Cranfield, UK) of following dimensions; $d_i = 52 \text{ mm}$ and $l = 270 \text{ mm}$ was equipped with a medium pressure lamp (0.6 kW; Hanovia, Slough, UK) housed in a quartz sleeve. The distance between the external surface of the sleeve and the internal wall of the reactor was 2.5 mm. The spent MWF was mixed with TiO_2 in a 20 l container and the resulting slurry was pumped into the vertically positioned reactor at its base with aeration achieved through a diffuser situated underneath the reactor inlet. There was no recirculation and the treated effluent was collected and filtered ($1.2 \mu\text{m}$) prior to analysis. The reactor was equipped with a cooling jacket in order to avoid overheating.

2.3.3. Experimental Procedures

Initial AOP experiments were conducted in the CB apparatus. For the UV/ H_2O_2 experiments, peroxide was added to the test MWF solutions at different initial concentrations (1, 4 and 8 g.L^{-1}) as based on Schuch et al. (2000) and pH was adjusted prior to UV irradiation. For the photo-Fenton experiments, ferrous sulphate from a stock solution (68.08 g.L^{-1} of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, pH adjusted to 1.5 to avoid any precipitation) was added straight after H_2O_2 . Initial pH was then adjusted to 3. To compare photo-Fenton with UV/ H_2O_2 , ferrous ions were added at a concentration of 0.165 g.L^{-1} in order to achieve $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio of 1:10 and 1:40 at H_2O_2 concentrations of 1 and 4 g.L^{-1} respectively. In the case of UV/ TiO_2 experiments, pH was adjusted after TiO_2 addition and irradiation was started after dark adsorption equilibrium was reached. Preliminary dark adsorption tests were conducted to identify the optimum TiO_2 dose ($0.5\text{-}15 \text{ g.L}^{-1}$) as well as the adsorption equilibrium period (0-24h). The effluent (initial COD of 988 mg.L^{-1}) from the biodegradation study was centrifuged, filtered and then stored in a cold room. Thereafter, optimised AOPs were applied to further reduce the COD of the biodegraded effluent. In all AOP experiments, fresh test solutions were prepared before irradiation under each UV dose investigated.

After irradiation, solutions containing any solids (TiO₂ or iron precipitates) were filtered prior to analysis. Those containing residuals of H₂O₂, which is known to interfere with COD measurements, were treated with MnO₂ powder and then filtered [10].

Further UV/TiO₂ experiments were carried out in the photocatalytic reactor at a flow rate of 8.5, 17, 34, 170 and 340 ml min⁻¹ resulting in a retention time of 20, 10, 5, 1 and 0.5 minutes respectively. A range of air flow rates (0 - 20 l min⁻¹) was tested to insure sufficient mixing of the treated solution inside the reactor chamber. The first effluent sample was collected after at least one retention time had passed from the start of the experiment and further 2 samples were collected at one minute intervals.

2.4. Analysis

The dissolved organic carbon (DOC) was determined with a Shimadzu 5000A analyser (Shimadzu, Milton Keynes, UK). COD measurements were performed using Spectroquant® cell test kits purchased from VWR (Lutterworth, UK) with a NOVA 60 spectrophotometer (Merck, Nottingham, UK). Carbonaceous BOD was measured on seeded and non-seeded samples (spent MWF only) according to the blue book standard methods [17]. Final effluent from Cranfield University sewage works was used as the seed to provide additional source of microorganisms. Residual H₂O₂ was determined qualitatively with colorimetric Merckoquant® peroxide test strips purchased from VWR (Lutterworth, UK).

2.5 Cost analysis

Power consumption has been assessed using modified Electrical Energy per Order (E_{EO}) based on a relationship (Equation 1) developed by Bolton, where P is the rated power in kW, t is the irradiation time in min, V is the volume of water treated in litres, C_{inf} = the influent and C_{eff} = the effluent COD concentration in mg l⁻¹[18]. Although based on a 90% removal, where this was not achieved, the maximum removal values obtained here were used. The cost of chemicals added was as follows: H₂O₂ (35%) £270 per ton, FeSO₄ · 7 H₂O £70 per ton [10], H₂SO₄ (98%) £55 per ton and electricity £0.04 k/Wh. Cost of TiO₂ addition was not considered since the catalyst can be reused.

$$E_{EO} \text{ (kWh m}^{-3}\text{)} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_{inf}}{C_{eff}}\right)} \quad \text{Equation 1}$$

3. Results

3.1. Biological degradation of spent metalworking fluids

The biodegradation of spent MWF was investigated at two different initial concentrations (COD_i = 412 and 988 mg.L⁻¹) and in both cases the COD began to decrease from the start of the experiment with over 50% removed after 4 days leading to 68-69% removal after 20 days (Figure 1). This indicates that the microbial population has reached the maximum rate at the lower concentration. In both cases, just over 30% of the initial COD remained in the treated solution. The BOD₅/COD data indicate that the initial biodegradability of the MWF (BOD₅/COD ~0.35) was higher than the biodegradability of the reference compound; hence the faster COD decrease for the MWF. The reference compound, diethylene glycol showed very low biodegradation rate during the first few days corresponding to an initial BOD₅/COD ratio of 0.02 which increased to 0.21 after 6 days leading to an increase in COD removal which was then completed within 11 days. In terms of DOC, 50% were biodegraded in both MWF samples within four days with a maximum removal observed after 11 days of 74% and 66% for the higher and lower strength solutions respectively. Overall, the level of biodegradation achieved here indicates biocompatibility of this wastewater [15].

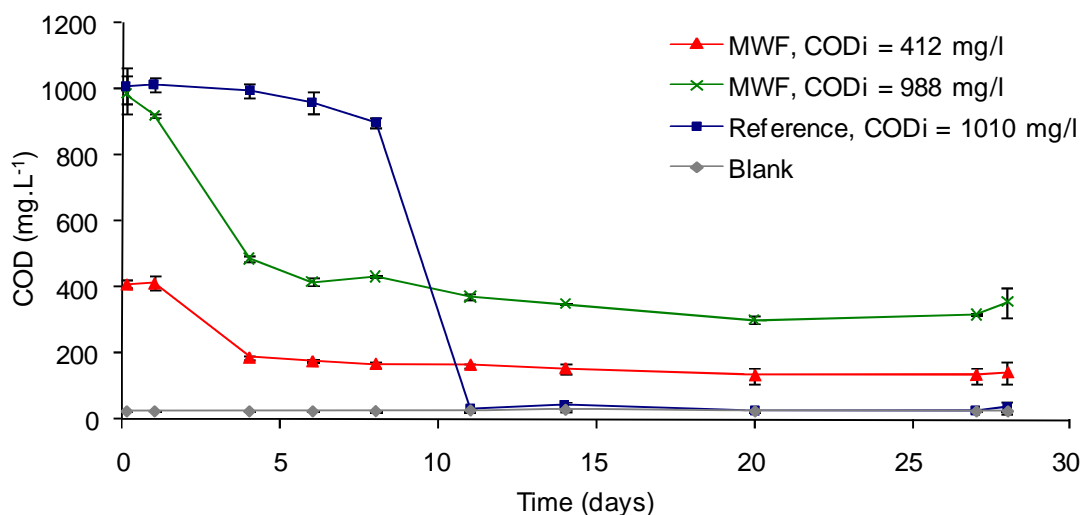


Figure 1. COD removal versus time in the Zahn-Wellens tests.

The results from other studies investigating the biodegradation of spent MWFs vary depending on the origin and type of the wastewater and the treatment conditions but generally, under optimised conditions high COD removals can be achieved. Most of these studies looked at aerobic degradation of various simulated (freshly mixed MWFs) or spent MFWs. To illustrate, Hilal *et al.* [5] obtained over 90% COD removal in optimised aerobic reactor with specifically developed bacterial consortium, Anderson *et al.* [6] achieved over 96% COD reduction during a treatment of simulated semi-synthetic MWF in an membrane biological reactor (MBR) and Cheng *et al.* [7] achieved 97% removal during thermophilic aerobic treatment of spent MWF at 50°C. Largely, this type of waste is suitable for biological treatment however, as mentioned previously such treatment does not represent solution for smaller businesses.

3.2. Treatment of spent MWF with AOPs

Treatment of spent MWFs with direct photolysis depends on the presence of UV absorbing organics. The molar absorbance coefficient of MWF sample (with a COD of 100 mg.L⁻¹) was measured at 41.9 l.cm⁻¹ at 254 nm (wavelength used for the UV treatment in this study). However, photolysis did not reduce COD or TOC (results not shown) for UV doses of up to 34.5 J.cm⁻² (corresponding to 5h irradiation).

Control experiments with 4 g.l^{-1} of H_2O_2 in the absence of irradiation showed that no degradation occurred in the dark (Figure 2a). At the maximum UV dose studied here, 34.5 J.cm^{-2} and initial H_2O_2 concentration of 4 g.l^{-1} , the COD removal was 89% with $\sim 1 \text{ g.l}^{-1}$ of residual H_2O_2 in solution indicating that higher UV dose could have further increased COD removal. Reducing initial H_2O_2 concentration to 1 g.l^{-1} lowered the COD removal at 34.5 J.cm^{-2} to only 65%. No additional benefit was observed when the initial H_2O_2 concentration was increased to 8 g.l^{-1} achieving COD removal of 85% at 34.5 J.cm^{-2} . It is known that H_2O_2 can potentially act as a scavenger of $\cdot\text{OH}$ radicals if present in sufficient amounts [19]. Lowering the pH from 9 to 5 also proved to be counter-productive and a significantly reduced COD removal of 71% was achieved at pH 5 with a UV dose of 34.5 J.cm^{-2} and 4 g.l^{-1} of H_2O_2 .

A pH of 3 was selected for the Fenton's reagent (FR) studies since it is widely known that Fenton processes have better efficiencies in acid conditions [20]. Control experiments with only Fe^{2+} (coagulation) or $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (dark Fenton) showed poor degradation (Figure 2b) but the combination of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ at molar ratio of 1:40 and UV ($0.165 \text{ g.L}^{-1} \text{ Fe}$, $4 \text{ g.L}^{-1} \text{ H}_2\text{O}_2$ and 20.7 J.cm^{-2}) gave a maximum COD removal of 84% not notably increasing with further irradiation (85% at 34.5 J.cm^{-2}). The equivalent TOC removals were 75 and 76% respectively. The initial degradation rate under these conditions was faster than for UV/ H_2O_2 (4 g.L^{-1} , pH 9) with pseudo-first order initial rate constant of 0.62 h^{-1} and over 50% of both COD and TOC removed in less than 1 hour of UV irradiation (6.9 J.cm^{-2}). In comparison, double the UV dose was required to achieve the same removal with UV/ H_2O_2 with the initial rate constant of 0.34 h^{-1} . $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio of 1:10 ($0.165 \text{ g.L}^{-1} \text{ Fe}$, $1 \text{ g.L}^{-1} \text{ H}_2\text{O}_2$) did achieve poorer removals reaching a plateau at 52% of COD removed (13.8 J.cm^{-2}). Higher UV dose did not increase removal significantly (56% at 34.5 J.cm^{-2}) and the final TOC removal at this UV dose was also much lower (45%) in comparison to the higher H_2O_2 concentration.

UV/ TiO_2 process is effectively a 'chemical free' way of generating $\cdot\text{OH}$ radicals as the TiO_2 catalyst can be recycled and therefore offers an effective alternative to the above investigated processes. In order to

identify the optimum treatment conditions, the effect of lowering the pH was again investigated with the treatment studied at pH 9 and pH 5. Initial dark adsorption tests conducted at pH 9 and initial COD of 1052 mg.L^{-1} identified 10 g.L^{-1} as the optimum TiO_2 dose and 10 minutes as sufficient adsorption period but desorption was observed over longer periods. At pH 5 and 10 g.L^{-1} of TiO_2 , dark adsorption equilibrium was reached within 30 min. At an initial COD concentration of 1050 mg.L^{-1} removal of 34% was observed for a UV dose of 34.5 J.cm^{-2} with a similar removal observed at pH 5 (Figure 2c). The initial zero order rate constant was $64.6 \text{ mg.L}^{-1}.\text{h}^{-1}$. It has been reported previously that the UV/ TiO_2 process is rather limited at high COD concentrations as a high organic load will saturate the TiO_2 surface as well as reduce the photonic efficiency leading to photocatalyst deactivation [21]. Therefore the effect of lowering the initial concentration of the MFW was studied here and by reducing the initial COD concentration to 589 mg.L^{-1} , the final removal increased to 66% at the maximum dose studied (34.5 J.cm^{-2}). This is a significant improvement, however in comparison to the other AOPs studied here even at half the COD loading; the removal achieved is still much lower.

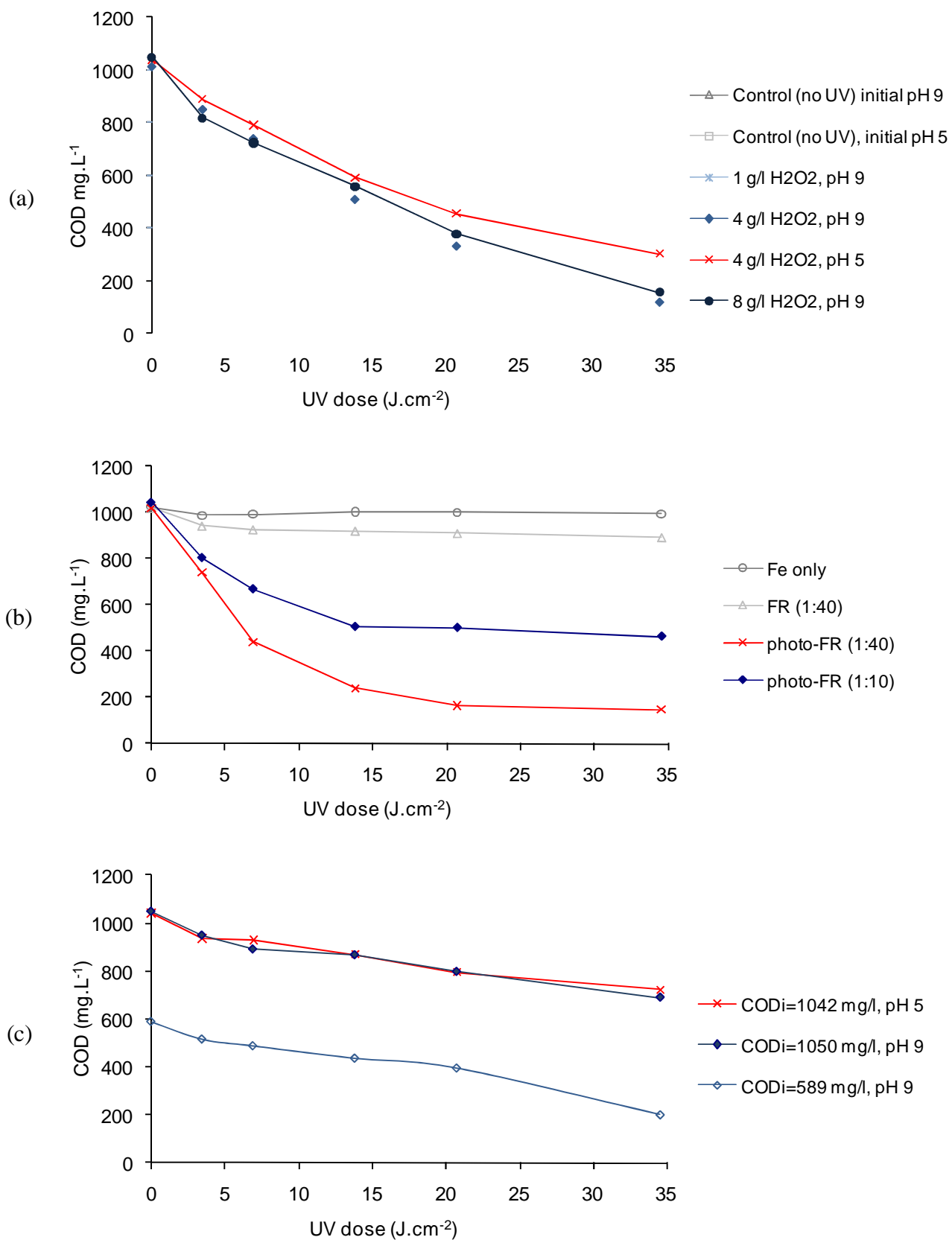


Figure 2. COD removal with (a) UV/H₂O₂, (b) photo-Fenton and (c) UV/TiO₂ (10 g.L⁻¹) in the CB apparatus under different experimental conditions.

As mentioned previously, CB apparatus was used to conduct all UV utilising experiments in order to control the UV dose delivered throughout this study. However, this system appeared to have limitations when used for the photocatalysis. Despite mixing, it was not always possible to avoid the settlement of TiO_2 particles in the periphery of the container, inevitably leading to poor activation of the catalyst. Additional experiments were conducted using a photocatalytic reactor to increase the catalyst activation and promising results have been obtained with the COD removal increasing with longer retention time and higher aeration rate (Figure 3). Apart from enhancing the catalyst mixing the aeration also leads to the formation of a superoxide radical which further increases the process efficiency. The maximum removal of 82% was observed at a retention time of 20 minutes and an aeration rate of $20 \text{ L}\cdot\text{min}^{-1}$. There is an indication in the literature that this process can be applied in more challenging conditions and it was reported being used in the treatment of industrial wastewater [22]. Further, Muruganandham and Swaminathan [23] reported a complete decolourisation of a reactive yellow azo dye by UV/ TiO_2 ($4 \text{ g}\cdot\text{L}^{-1}$) after 60 minute-treatment in photo-reactor equipped with eight 8W medium pressure UV lamps set in parallel and emitting 365nm of peak wavelength.

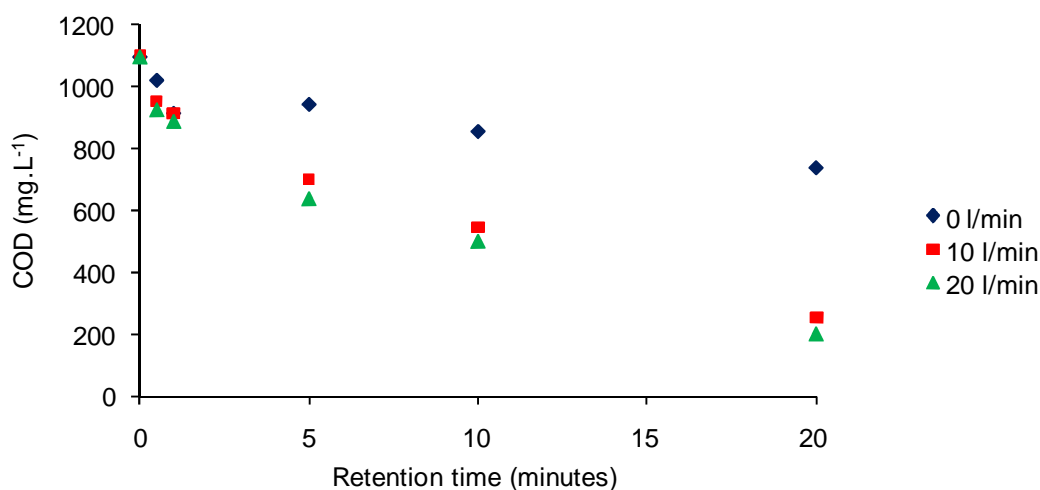


Figure 3. The effect of various retention time and different mixing conditions on COD removal in the photocatalytic reactor; retention time of 20 minutes is equivalent to 0.2 kWh.

To put the use of AOPs into a context here is quite hard as the literature on the treatment of spent metalworking fluids by these processes is very limited. Generally, it is assumed that high organic load wastewater will be too expensive to treat by any AOP due to the amount of chemicals or energy needed to achieve significant removals. Miller and Anderson [24] reported only 19% COD removal during UV/H₂O₂ treatment of MWF wastewater of similar organic strength (COD = 1390 mg.L⁻¹). However, others investigating the treatment of high organic load industrial wastewater reported much more promising results. For illustration, Azbar *et al.* [10] obtained 85% COD reduction for a dye effluent with a COD of 930 mg.L⁻¹ in 90 minutes with UV/H₂O₂ process where the peroxide concentration was 300 mg. L⁻¹. Comparing these to the current results, it is clear that the semi-synthetic spent MWF is treatable by 'OH radicals produced during the UV/H₂O₂ process, although significant levels of energy are required to achieve this. Number of studies used the photo-Fenton process to degrade wastewaters containing highly toxic organic compounds. Galvão *et al.* [25] achieved 99% mineralisation in wastewater contaminated with diesel at Fe²⁺: H₂O₂ molar ratio of 1:500. They also found a similar trend when comparing photo-Fenton with UV/H₂O₂ with the photo-Fenton being much faster at reducing the organic content. Here, initial first order rate constants (0.62 h⁻¹ for photo-Fenton and 0.34 h⁻¹ for UV/H₂O₂) at the optimum conditions highlight faster degradation rates for photo-Fenton but with a similar maximum COD removal achieved (85% in comparison with 89% for UV/H₂O₂) although at a much lower UV dose. For photo-Fenton a plateau was reached after UV doses of 13.8 and 20.7 J.cm⁻² for ratios of 1:10 and 1:40 respectively. These plateaux corresponded to the depletion of H₂O₂ from the solutions. Although the removal was similar for UV/H₂O₂ and photo-Fenton processes, the latter has a clear advantage in the lower energy requirement. However, the chemicals required to lower the pH during the photo-Fenton process and to adjust it back afterwards should be considered. The main advantage of the UV/TiO₂ process is that no chemicals are required and it was previously found to be very effective in removing colour and COD from high organic load wastewater [14]. Although not very successful here in removing COD during the CB trials, high removals were achieved in the photocatalytic reactor, although at much higher power input (0.6kW).

The effectiveness of an AOP to remove the organics depends on the rate of $\cdot\text{OH}$ formation and the availability of $\cdot\text{OH}$ to react with the target organic compound [26]. Under the conditions used in this study, lower amounts of $\cdot\text{OH}$ were likely to be produced during the UV/ H_2O_2 treatment than during the photo-Fenton process. In UV/ H_2O_2 system at pH 9, the production of $\cdot\text{OH}$ radicals by H_2O_2 photolysis is reduced as H_2O_2 also undergoes decomposition to H_2O and O_2 . Further, HO_2^- anion formed under these conditions scavenges both, $\cdot\text{OH}$ and H_2O_2 [27]. In UV/ Fe^{2+} / H_2O_2 system, additionally to the above mentioned photolysis, Fe^{2+} ion forms under acidic conditions the most photoactive ferric iron - water complex, $[\text{Fe}(\text{OH})_2]^{2+}$ leading to a significant and fast production of $\cdot\text{OH}$ radicals [8]. In UV/ TiO_2 system, apart for radicals ($\cdot\text{OH}$, $\cdot\text{OH}_2$, $\cdot\text{O}_2$) produced by the interaction of $e^- - h^+$ pairs with dissolved water and O_2 , organic pollutants adsorbed on the TiO_2 can also directly react with h^+ . However, if the photons are unable to reach the TiO_2 particles, neither h^+ nor $\cdot\text{OH}$ can be formed leading to poor treatment efficiency.

3.3. The potential of combining AOPs with biological degradation of spent MWFs

The effect of AOP treatment on the biodegradability of MWFs was studied by monitoring the change in the BOD_5/COD ratio of samples through the AOP treatment. BOD measurements of both seeded and non-seeded samples were unaffected by the UV irradiation and seeded samples depicted a constant BOD_5/COD ratio of 0.42 compared to 0.31 for non-seeded ones. Only the results from the seeded samples are further reported. The effects of the three AOPs (UV/ H_2O_2 , photo-Fenton and, UV/ TiO_2), at their previously determined optimum conditions, on the BOD_5/COD ratio of the treated MWF samples are summarised in Figure 4.

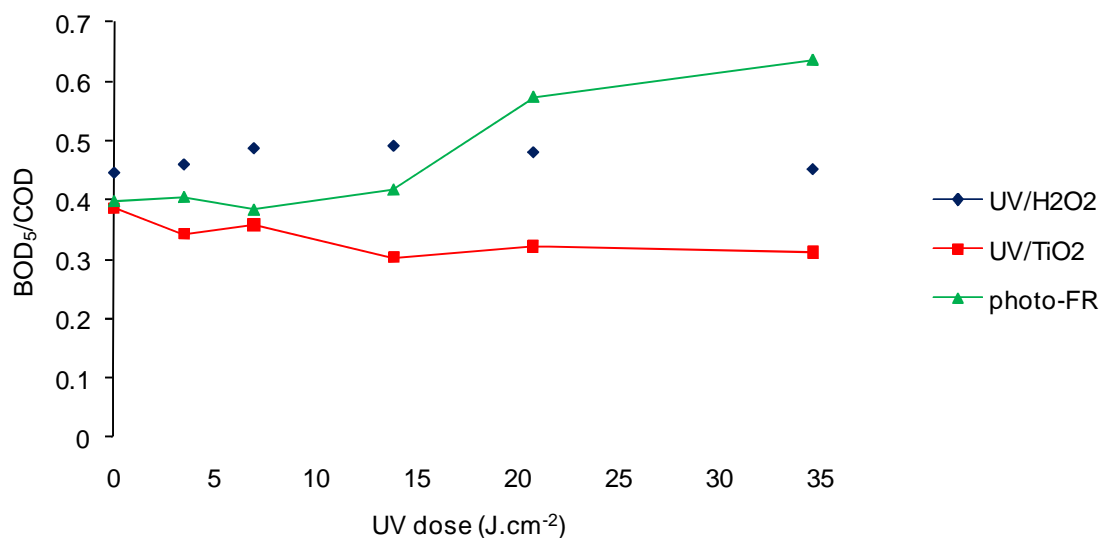


Figure 4. Evolution of biodegradability with applied UV dose (CB) during the AOP treatments: UV/H₂O₂ (4 g.L⁻¹, pH 9), UV/TiO₂ (10 g.L⁻¹, pH 9) and photo-Fenton (0.165 g.L⁻¹ Fe, 4 g.L⁻¹ H₂O₂ and pH 3); seeded samples.

The UV/H₂O₂ and UV/TiO₂ processes did not extend the biodegradability of MWF. UV/TiO₂ treatment actually decreased the BOD₅/COD ratio of the wastewater from 0.39 to 0.30 after applying a UV dose of 13.8 J.cm⁻² but no further change was recorded at higher UV doses. These results are in agreement with those of [28] who reported that a cottonseed wastewater pre-treated with UV/TiO₂ showed only 55% biological COD removal in comparison to 95% for the non-treated effluent. The biodegradability of the MWF marginally increased during the UV/H₂O₂ process from 0.44 to 0.49 at a UV dose of 6.9 J.cm⁻² but a subsequent decrease was observed and the final BOD₅/COD ratio at 34.5 J.cm⁻² applied was 0.45. The only substantial increase of the biodegradability of the MWF wastewater was observed during the photo-Fenton process with the BOD₅/COD ratio increasing by 44% at 20.7 J.cm⁻² and 59% at 34.5 J.cm⁻². Although this increase is significant, it would come at a very high price as the energy required to achieve it is also substantial. Photo-Fenton was previously reported in the literature to enhance the biodegradability of non-biodegradable organic compounds present in industrial effluents [8].

The other option is to remove the compounds resistant to biodegradation after the biological stage and apply the AOP as a fine polishing step. Here, UV/H₂O₂, photo-Fenton and UV/TiO₂ (at the optimal

treatment conditions determined previously) were applied to ‘polish’ the biodegraded effluent from the Zahn-Wellens test (Figure 5).

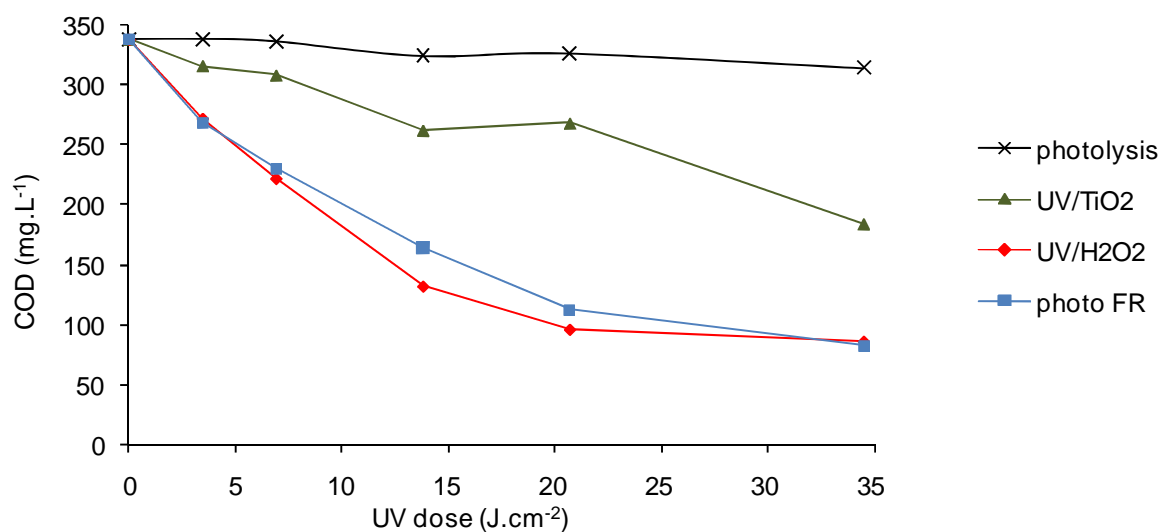


Figure 5. The removal of bio-recalcitrant COD by an AOP: UV/H₂O₂ (4 g.L⁻¹, pH 9), UV/TiO₂ (10 g.L⁻¹, pH 9) and photo-Fenton (0.165 g.L⁻¹ Fe, 4 g.L⁻¹ H₂O₂ and pH 3) using the CB apparatus.

Direct photolysis was unable to treat the bio-recalcitrant COD and showed only marginal COD or TOC removal, 7% and 6% respectively. During the UV/TiO₂ treatment, the residual COD decreased by 46% at the higher UV dose applied with the TOC removal only 25%. Photo-Fenton and UV/H₂O₂ proved to be equally effective to treat the biodegraded effluent. Both processes reduced the COD from 338 mg.L⁻¹ by approximately 70% at a UV dose of 20 J.cm⁻². However, there was still ~1 g.L⁻¹ of H₂O₂ remaining at this stage but no further improvement in removal was observed when a higher UV dose was applied. At 34.5 J.cm⁻² the COD removals were 75% for UV/H₂O₂ and 76% for photo-Fenton with equivalent TOC removals of 68% and 66% respectively. This indicates that the remaining ~100 mg.L⁻¹ of COD was highly recalcitrant. The photo-Fenton and TiO₂ exhibited lower initial rate constants for the biodegraded effluent (0.36 h⁻¹ and 29.0 mg.l⁻¹.h⁻¹ respectively), whereas the rate constant of UV/H₂O₂ (0.43 h⁻¹) increased when compared to the constants obtained for the non-treated wastewater. However the UV dose

required for removing 72% of the recalcitrant COD was still very high (20.7 J.cm^{-2}) rendering this approach very expensive.

4. Technology comparison

The presented treatability results highlighted the capability of utilising $\cdot\text{OH}$ for the treatment of MWF either as the main treatment process or as a polishing process post pre-treatment in a biological reactor. The common feature across all the options is the use of UV lamps to generate the $\cdot\text{OH}$ radicals and so further comparison was undertaken in terms of energy utilisation and costs associated with the different options based on the optimum conditions established in the treatability tests (Table 1).

Table 1: The options for treatment of metalworking wastewater ranked based on the treatment efficiency and energy and chemical costs (biological treatment and sludge disposal were not included). The AOPs considered were at the following conditions: UV/ H_2O_2 (4 g.L^{-1} , pH9), UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (0.165 g.L^{-1} , 4 g.L^{-1} , pH 3), UV/ TiO_2 (10 g.L^{-1} pH9).

Process	Irradiation time (h)	Half Life* (h)	Max. Removal (%)	E_{EO} (kWh/m^3)	Electricity cost (£/m^3)	Chemical cost (£/m^3)	Total cost (£/m^3)
1. UV/ TiO_2 (reactor)	0.33	0.14	82	1500	60	0	60
2. UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$	3	1.1	85	1814	73	3.2	76
3. UV/ H_2O_2	5	2.1	89	2612	104	3.1	107
4. Bio + UV/ H_2O_2	3	1.6	91	2634	105	3.1	108
5. Bio + UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$	3	1.9	92	3002	120	3.2	123
6. Bio + UV/ TiO_2	5	5.7	90	9088	364	0	364

*relates to COD

Combined electricity and chemical costs of the different options ranged from $\text{£}60.\text{m}^{-3}$ to $\text{£}364.\text{m}^{-3}$ with the chemical costs making up a maximum of 4.7% of the combined costs. Photocatalysis clearly seems to be the best option under the conditions studied here (10 g.L^{-1} TiO_2 , pH 9). Comparison to the current disposal cost of $\text{£}20\text{-}40.\text{m}^{-3}$ (DTI, 2004) indicates that these processes are likely to become economically suitable only once the disposal cost raise as is expected with predicted levels estimated to potentially be as high as $\text{£}100.\text{m}^{-3}$ within the next 10-15 years. Overall, direct treatment with AOPs appears more

economically effective than utilising them as a polishing stage as equivalent UV doses achieve similar levels of treatment indicating that the utilisation of the $\cdot\text{OH}$ radical is less effective when used in a polishing process. The electrical energy per order, defined as the kWh of electrical energy required to reduce the concentration of a pollutant by 1 order of magnitude (90%) in 1 m^3 of contaminated water, is the most common method used to compare electricity use of AOPs. As mentioned in Section 2.5, modified E_{EO} was used where $< 90\%$ were achieved. Across the trials the E_{EO} ranged from $1500\text{ kWh}\cdot\text{m}^{-3}$ for the photocatalysis to $2612\text{ kWh}\cdot\text{m}^{-3}$ for UV/ H_2O_2 which compares to values between 344-2000 $\text{kWh}\cdot\text{m}^{-3}$ when treating $5\times 10^{-4}\text{ mol}\cdot\text{L}^{-1}$ of reactive azo dyes using the same three treatments [29]. Both studies identified the photocatalysis as the most energy efficient and the UV/ H_2O_2 as the least efficient reflecting differences in light adsorption between TiO_2 and H_2O_2 at the operating wavelengths of the UV lamps [29].

Previous scale up of UV systems has indicated a substantial economic saving through improved efficiency such that likely electricity costs associated with the UV will decrease by a factor of ten when applied at full scale. Whilst this makes the economics of the UV seem more favourable the total cost of using such systems would then need to include peripheral equipment such as membranes in the photocatalysis and sludge management and chemical handling in the cases of UV/ H_2O_2 and photo-Fentons. Overall, estimated operating costs are likely to be a factor of 2-4 times lower and when coupled to the general benefits of compact footprint and rapid start up without performance deterioration then AOPs appear to be a viable option of small scale decentralised treatment of industrial wastewaters such as spent MWFs.

Conclusions

The semi-synthetic spent MWF studied here was found to be biodegradable during Zahn-Wellens test. Further, the wastewater was found to be treatable by $\cdot\text{OH}$ radicals and high removals were achieved in UV/ TiO_2 reactor and by UV/ H_2O_2 and photo-Fenton processes. The UV/ TiO_2 reactor was also found to be the cheapest option and could offer a viable alternative especially for smaller businesses. Photo-

Fenton was also found to improve the biodegradability of spent MWFs and all AOPs were found to degrade the recalcitrant COD. However to apply the combined treatment would not be economical. Where biological treatment is not an option, optimised UV/TiO₂ would be the best alternative. Future challenges for its implementation include a development of better systems with significantly lower energy requirements through better understanding of the mechanisms involved in the UV/TiO₂ process and the use of alternative UV sources such LEDs or solar.

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