THE EFFECT OF FENTON´S REAGENT IN COMBINATION WITH OZONE TO THE BIODEGRADABILITY OF METALWORKING FLUIDS WASTEWATERS

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ABSTRACT

The investigation reported refers to the application of different advanced oxidation processes to metalworking fluids wastewaters as pretreatment technologies. Their effect on the biodegradability of metalworking fluids is studied. The main goal is to study the effect of the ozone molecule, that of the Fenton's reagent and the synergistic effect of both on the biological oxidation taking place. 80 % decrease of the organic load is achieved through the combined process (in presence of ozone and the Fenton's reagent), while only 10 % decrease is obtained in case of a sole application of ozone to waste waters treatment within 60 min. A biodegradability level increase of 20 % is achieved with the application of the combined process when compared to that of the non-treated sample. The application of ozone only leads to 30 % decrease.

Keywords: Fenton chemistry, biodegradability, ozone, metalworking fluids, wastewater.

INTRODUCTION

Metal working fluids (MWF) are widely used as industrial lubricants and refrigerants to extend the life of tools, prevent corrosion, and improve productivity [1]. The systems of treating exhausted MWFs dispose oil or water-based fluids. There are several options for the minimization of the total volume of MWFs at the end of their lifetime. They refer to evaporation, ultrafiltration, reverse osmosis or a chemical waste treatment. Even the minimizing techniques produce waste that needs to be disposed, while incineration and landfilling are no longer available according to EU legislation. The water-based fluids primarily undergo treatments where the oil portion is separated from the water phase after which each component is treated independently. The produced waste waters still contain an organic load and toxic substances, while some of these may be toxic even when present at very low concentrations.

Nowadays, the biological methods are well recognized for being the most cost-effective option for organic matter removal. Therefore, they are used for MWFs treatment [2]. In certain cases, the biological processes are not effective due to the recalcitrant nature of the contaminants present. Therefore, oxidation processes are preferred to degrade such organics present [3]. The advanced oxidation processes are recognized tools destroying recalcitrant compounds or, at least, transforming them into biodegradable species [4]. They can be used as a pre- and/or a post-treatment of the biological systems. In the former case, AOPs aim to improve the biological treatability of the wastewaters [5]. The advanced oxidation processes may be treated as methods which provide the creation of free hydroxyl radicals at ambient pressure and temperature. The generation of these reactive agents can be achieved by, for example, sonolysis, ozone-based interactions, Fenton-based reactions, a heterogeneous photocatalysis. Each of these has a specific way of production of free radicals [5]. Combinations of different oxidation processes have been extensively investigated aiming to increase the oxidation efficiency [6]. Several combinations such as the Fenton's reagent (H_2O_2/Fe^{2+}) application, the photo-Fenton ($H_2O_2/UV/Fe^{2+}$) reagent application, peroxidation combined with Ultraviolet light (H_2O_2/UV), Peroxone (O_3/H_2O_2), Peroxone combined with Ultraviolet light ($O_3/H_2O_2/UV$), O_3/UV system, $O_3/TiO_2/H_2O_2$ and O_3/TiO_2/Electron beam irradiation, etc. are used [7]. The hydroxyl radicals are extremely unstable and reactive because of their high oxidation potential. The reactions with their participation are extremely fast and nonspecific [8].

Fenton process

The oxidation system based on the Fenton reagent has been used for the treatment of both organic and inorganic substances under laboratory conditions as well as of real effluents from different resources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning, etc. [9]. In Fenton like chemistry H_2O_2 reacts with Fe^{2+} in water under acidic conditions forming hydroxyl radicals. The rate constant of the reaction of the ferrous ion with hydrogen peroxide is high - Fe^{2+} oxidize to Fe^{3+} in a few seconds to minutes in a presence of an excess amounts of hydrogen peroxide, which decomposes by Fe^{3+} and generates hydroxyl radicals [5]. The factors affected the Fenton chemistry are well described [3, 9]. The major of them refer to the pH of the solution, the amount of the ferrous ions, the concentration of H_2O_2, the initial concentration of the contaminants and the presence of other ions. The Fenton reagent action can be significantly improved under the effect of UV radiation [5].

Ozone is a very powerful oxidizing agent ($E° = 2.07$ V) that can react at high rates with most species containing multiple bonds (such as C=C, C=N, N=N, etc.), but not with singly bonded functionalities such as C–C, C–O, O–H [9]. The oxidation of the organic species may occur due to a combination of reactions with molecular ozone and those with $OH^{\bullet}$ radicals [4, 10 - 11]. The rate of the attack by $OH^{\bullet}$ radicals is typically 10^6 to 10^9 times faster than the reaction rate of reactions with the participation of molecular ozone [10]. Ozone and/or hydroxyl radicals generated by the decomposition of ozone degrade recalcitrant organic compounds to smaller molecules, which are more hydrophilic and biodegradable [12]. Ozone alone promotes the partial oxidation of pollutants, while it can increase the effluent biodegradability [4]. Anyway, the reaction products from the reaction of ozone with organic compounds in aqueous solutions are often difficult to predict and establish [11]. The ozonation can produce toxic oxidation by-products; it should be investigated whether the toxicity increases after ozonation and if a subsequent treatment is sufficient to remove these toxic species [13].

Only a little is known and published about the technologies for treating the exhausted MWFs wastewaters, where a combination of advanced oxidation processes pre-treatment step and a biological post-treatment step is applied. Anyway, few examples are discussed below.

A pre-treatment by ozonation is effective in transforming otherwise recalcitrant and toxic MWF components into biologically degradable intermediates [14]. The results demonstrate 70 % decrease of the chemical oxygen demand (COD) after the combined ozone-biological oxidation by an acclimatized bacterial consortium from an initial value of 3100 mg L^{-1}, of which 45 % is attributed to a second-stage biological oxidation. 78 % decrease of COD by nZVI oxidation at pH 3.0 and 67% decrease at neutral pH (7.5) is confirmed with 85 % concurrent reduction of toxicity. This makes the nZVI treated effluent more amenable for a second stage biological oxidation step [15]. An overall COD reduction of 95.5% is 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.

The interactions of both the chemical (UV/H_2O_2, photo-Fenton and UV/TiO_2) and biological treatments is studied [16]. The photo-Fenton process is found efficient in terms of a degradation rate leading to 84 % COD removal (1M Fe^{2+}, 40M H_2O_2, 20.7 J cm^{-2}, pH 3) as well as improving the wastewater's biodegradability. Although this increase is significant, it comes at a very high price as the energy required to achieve it is also substantial [16].

The feasibility of employing a sequential Fenton-biological oxidation for the treatment of recalcitrant components of MWF wastewater is investigated [17]. The results demonstrate that the Fenton pre-treatment of the MWF effluent greatly improves the biodegradability index (BOD_5/COD increases from 0.160 to 0.538) with a synchronous decrease of the toxicity of the wastewater, making the recalcitrant component more amenable to subsequent biological treatment. An overall decrease of

92 % and 86 % in chemical oxygen demand (COD) and total organic carbon (TOC), respectively, is achieved by the two-step treatment method developed by the authors [18].

The aim of this study is to determine the effect of the ozone molecule, that of the Fenton reagent as well as that of the ozone and the Fenton reagent combination on selected metalworking fluids followed by a biological oxidation.

EXPERIMENTAL

All chemicals were of an analytical grade and were used without any further purification. The volume of the treating samples varied in the different experiments. The preliminary study of the Fenton reagent ability to oxidize the organic load was carried out in 1L batch reactors containing 500 mL of a waste water sample, while the experiments of ozonation and those referring to the combined process of ozonation and the Fenton reagent participation were carried out in 3L glass reactor of a total volume of the sample of 1.5 L. The samples preparation for the final test of the biodegradability was realized in 1.5 L batch reactors containing 1 L of treated wastewater sample.

Wastewater characteristics

Samples of wastewater were obtained from Secop Ltd. Slovakia, which treat their wastes from exhausted metalworking fluids by a physico-chemical treatment which was not specified. The general physico-chemical parameters referred to: TOC of 294.7 mg L^{-1}, TIC of 89.3 mg L^{-1}, TC of 384.0 mg L^{-1}, pH of 7.94.

TOC (Total organic carbon), TIC (Total inorganic carbon) and TC measurements (Total carbon) were determined by a direct injection of the undiluted sample into a Shimadzu TOC-V_{CPN} analyzer calibrated with standard solutions of potassium phthalate and hydrogen carbonate.

Fenton´s oxidation chemistry

The pH of the samples of wastewater for treating with the Fenton reagent was at first adjusted to 3.0 with a stock solution of H_2SO_4 (2 mol L^{-1}) under stirring with a magnetic stirrer. After a definite amount of $Fe(SO_4).7H_2O$ was added and completely dissolved, a definite volume of H_2O_2 (30 % w/v) was poured into the mixture (the molar ratio of Fe^{2+}:H_2O_2 was found equal to 1:10). The reaction in the samples taken at defined time intervals was stopped by pH adjusting to 9.0 with a stock solution of NaOH (2 mol L^{-1}). After sedimentation (approximately 2 h) an appropriate volume was taken for TOC analysis. The samples used for the biodegradability evaluation stood for 24 h, while the decantation was realized several times.

Fenton reagent and ozone

In the experiments following the combined oxidation effect of the Fenton reagent and the ozone the pH of the sample was initially adjusted to 3.0, then $Fe(SO_4).7H_2O$ was added and completely dissolved. This was followed by the introduction of a definite volume of H_2O_2 (30 % w/v) to the mixture (the molar ratio of Fe^{2+}:H_2O_2 was found equal to 1:10). After that ozone was bubbled through the mixture. Samples for TOC analysis were collected at definite time intervals from the bottom of the reactor through a sample valve.

Ozone application

Ozone was produced from air using OZONFILT® OZV a type 2 ozone generator (Prominent). It could produce up to 15 g of O_3 per hour. Compressed air was supplied as a feed gas for the production of ozone at a rate of 20 L min^{-1}. The ozone was introduced to the sample by a ceramic diffuser. It was allowed to bubble through the wastewater of an adjusted pH value of 9.0. The oxidation was evaluated on the ground of samples collected from the bottom of the reactor at definite time intervals.

Biodegradability measurements

The principle of the biodegradability measuring corresponds to the test method OECD 301 B with some modification [18]. Four samples treated by the Fenton reagent were prepared for the biodegradability measurement. These samples contained different amounts of ferrous ions (0.25 g L^{-1}, 0.50 g L^{-1}, 0.75 g L^{-1} and 1.00 g L^{-1}) as it was in the preliminary experiments of TOC removal and an appropriate amount of hydrogen peroxide keeping the molar ratio of the ferrous ions and the hydrogen peroxide unchanged (1:10). The treatment time was 30 min. A sample containing the combination of the Fenton reagent and ozone was treated within 60 min with the addition of Fe^{2+} of 1.30 g L^{-1}. Another one containing only ozone was also treated within 60 min. All samples were diluted prior to the test to an identical concentration of TOC (150 mg L^{-1}). The pH value was adjusted to 7.5 to exclude any harmful effect on the inoculum.

RESULTS AND DISCUSSION

Fig. 1 illustrates the kinetics of TOC removal efficiency in case of an application of different AOPs. The greatest decrease of the organic load is observed during first 5 min - 20 min after the hydroxyl radicals' introduction. After that, no significant decrease of TOC is recorded. The highest efficiency in respect to TOC removal (76 %) is achieved after the introduction of ozone (15 g h^{-1}) together with the Fenton reagent (1.3 g L^{-1} of Fe^{2+}). The highest decrease of TOC content in this case is explained by the greater oxidation ability of the hydroxyl radicals provided by the ozone. The presence of ferrous ions is of about 0.3 g greater than that in case of the single Fenton reagent (1.00 g) but the decrease of TOC content remains nearly equal. The lowest efficiency in respect to TOC removal (10 %) is recorded in case of a single ozone participation. The pH value of 9.0 during the ozonation process predicts an increased formation of hydroxyl radicals but the inorganic carbon species present in the sample (89.3 mg L^{-1}) inhibit the ozone decay to hydroxyl radicals as they act as a radical scavengers. The low decrease of the organic load could be explained with the lower oxidizing ability of the ozone direct attack in comparison to that of the hydroxyl radicals which act more indiscriminately providing a much faster attack. Moreover, ozone reacts predominantly with organic compounds containing double bonds.

The results of the biodegradability testing at 16th day are presented in Fig. 2. The highest biodegradation level (86 %) is achieved after the application of a combined AOP´s (ozone combined with the Fenton reagent). This combination provides 23 % increase of the biodegradability level when compared to that observed in a nontreated sample of metalworking fluids wastewater. In the latter case a value of 63 % is reached. The samples treated by the Fenton reagent are positively affected when the amount of the ferrous ions is greater than 0.5 g. The addition of ferrous ions of 0.50 g, 0.75 g and 1.0 g increases the level of the biological oxidation in the range of 9 % - 11 %. This increase is explained by the destruction of the recalcitrant compounds in the wastewater sample or at least by their transformation to more biodegradable species. The lowest biodegradability level is achieved in case of single ozone application. The biodegradability of 34 % at the end of the test represents 29 % decrease in comparison with that obtained in the nontreated sample. The effect considered is explained with the possible creation of toxic intermediates during the ozonation process which may harmfully affect the utilized inoculum. It is recommended to identify the degradation products or evaluate the possible toxicity increase, e.g. by the OECD 209 test method.

It is recommended to reach 60 % of biodegradability by the control sample at the end of the 10-day window according to the basic rules of OECD 301B. The 10-day window starts to count after the control sample reaches 10 % of the biodegradability level. This basic condition is fulfilled so all results are accepted valid. Fig. 3

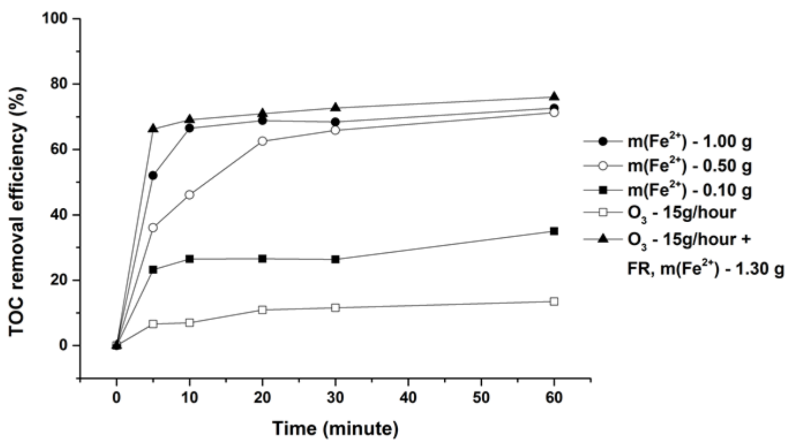

Fig. 1. TOC removal efficiency in case of samples treated by the different AOPs (● – a sample treated with the Fenton reagent (1.00 g of Fe^{2+} added), ○ – a sample treated with the Fenton reagent (0.50 g of Fe^{2+} added), ■ – a sample with the Fenton reagent (0.10 g of Fe^{2+} added), □ – a sample treated with ozone, a dosage of 15 g O_3/h ▲ – a sample treated with ozone and the Fenton reagent, a dosage of 15 g O_3/h and 1.30 g of Fe^{2+} added.

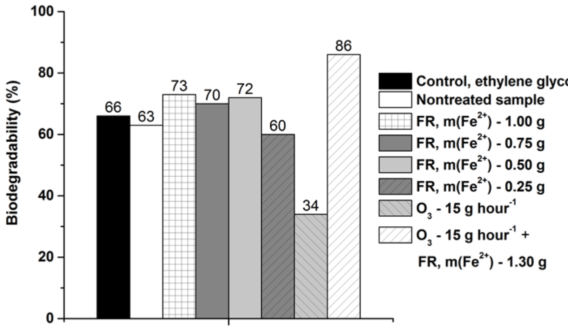

Fig. 2. The biodegradability level at the end of the test a control sample (ethylene glycol), a nontreated sample, a sample treated with the Fenton reagent (1.00 g Fe^{2+} added), , a sample treated with the Fenton reagent (0.75 g Fe^{2+} added), a sample treated with the Fenton reagent (0.50 g Fe^{2+} added), a sample treated with the Fenton reagent (0.25 g Fe^{2+} added) , sample treated using ozone, a dosage of 15 g O_3/h, sample treated using ozone and the Fenton reagent, a dosage of 15 g O_3/h and 1.30 g Fe^{2+} added.

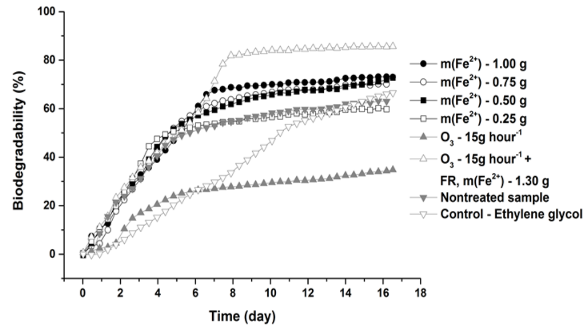

Fig. 3. Biodegradability curves of samples treated by the different AOPs (● – a sample treated with the Fenton reagent (1.00 g Fe^{2+} added), ○ – a sample treated with the Fenton reagent (0.75 g Fe^{2+} added), ■ – a sample treated with the Fenton reagent (0.50 g Fe^{2+} added), □ – a sample treated with the Fenton reagent (0.25 g Fe^{2+} added), ▲ a sample treated with ozone, a dosage of 15 g O_3/h, ▲ a sample treated with ozone and the Fenton reagent, a dosage a 15 gO_3/h with 1.30 g Fe^{2+} added, ▼- a nontreated sample, ▼ - a control sample (ethylene glycol).

depicts the biodegradability curves of all samples. Only two samples contain the Lag phase, which indicates an acclimatization of the utilized bacterial inoculum to the organic load present. This refers to the standard solution of ethylene glycol and the sample treated by ozone only. All other samples contain more biodegradable compounds, while the biodegradation phase starts without an acclimatization of the inoculum. These results clearly demonstrate that the pre-treatment with the Fenton reagent and ozone results in a decreased toxicity of the MWF wastewater enhancing its biodegradability. The destabilization of MWF might be critical in case of ozone utilization for MWF sanitization because the fluid is not able to fulfil its optimal properties during machining after the oil separation from the micro emulsion system. This in turn results in a shorter total lifetime and worse quality characteristics of the machined surface.

CONCLUSIONS

The effect of different advanced oxidative processes on the biological oxidation of waste waters from the metalworking fluids applied after the physico-chemical treatment is studied. The novelty of this study in respect to refs. [14, 17] is that the samples are diluted after the pre-treatment to the same starting concentration of TOC prior to the biodegradability testing. The Fenton reagent increases the biodegradability in the range of 9 % - 11 % in comparison with the nontreated sample. The application of ozone only causes 29 % decrease of the biological oxidation. The best results are achieved in case of the synergic effect of the Fenton reagent and ozone (23 % increase). It is recommended to study the total TOC decrease for all tested AOP´s and if ozone is applied, then an increase of the toxicity should be evaluated. The results of the study clearly demonstrate that the pre-treatment of MWF wastewaters by the Fenton reagent, resp. ozonation, provides the organic content decrease partly through the removal of the anti-microbial compounds, partly by the enhancement of the biodegradability of the wastewater. This novel system of AOP treatment of MWF can decrease TOC concentrations, which is of importance from an economic and a practical point of view.

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