ABSTRACT

The treatment of wastewaters from machine works may be difficult because of their variable composition. Moreover they may contain poorly soluble substances. Advanced oxidation processes (AOPs) look very promising in pre-treatment of different kind of wastewaters with high organic load. Hydroxyl radicals produced by the AOPs are non-selective and very effective in the oxidation of many organic substances. It was assessed the effect of the Fenton-like processes to the biodegradability of wastewaters from machine works. It was found that higher amount of organics was oxidized with increased addition of ferrous ions. However, samples treated by Fenton’s reagent reached lower biodegradation level than the non-treated one. All tested samples were identified as readily biodegradable.

Keywords: Fenton chemistry, biodegradability, metalworking fluids, wastewaters.
more readily treated in subsequent biological treatment steps [7]. The combination of the partial oxidation and consequent biological processes belongs to the cheaper processes of the resistant and toxic organic substances treatment.

In recent years, advanced oxidation processes (AOPs) have been studied as a promising kind of organic wastewater treatment based on the in situ generation of hydroxyl radicals (OH•), which have a strong oxidation capacity (standard potential = 2.80 V versus standard hydrogen electrode) [2]. AOPs comprise of techniques that under certain conditions could transform the vast majority of organic contaminants into carbon dioxide, water, and inorganic ions as a result of oxidation reactions [8].

Fenton’s reagent (mixture of hydrogen peroxide and ferrous iron) is one of the most effective methods for the oxidation of organic pollutants. Fenton’s reaction is based on the catalysed decomposition of hydrogen peroxide by Fe2+ to produce very reactive hydroxyl radicals. The hydroxyl radicals which are the second only to fluorine among common oxidants, could react rapidly and non-selectively with nearly all organic pollutants [9]. It has many advantages such as high performance and simplicity (operated at room temperature and atmospheric pressure) for the oxidation of organics and non-toxicity (H2O2 can break down into environmentally safe species like H2O and oxygen) [2]. The efficiency of the Fenton reaction depends mainly on H2O2 concentration, Fe2+/H2O2 ratio, pH and reaction time. The initial concentration of the pollutant and its character as well as temperature, also have a substantial influence on the final efficiency [10]. Recent applications of Fenton’s reagent include the pre-treatment of olive-oil mill, dye, pharmaceuticals, pulp mill effluents, etc. [2, 11 - 13].

Continuous treatment process coupling heterogeneous photo-Fenton oxidation and membrane filtration was studied. Both liquid and solid phases were analyzed with enough precision to determine the fate of the pollutant during the batch oxidation [15, 16]. The effect of some ions and ligands (SO42−, F−, I−, Cl−, Br−, phosphate, carbonate, oxalate, EDTA orthophenantroline) on the degradation of Methyl Red by Fenton’s process have been investigated [17].

The hybrid technologies application to MWFs wastewaters were studied by some authors. The treatability of metalworking fluids wastewaters by the combination of UV/H2O2, photo-Fenton and UV/TiO2, followed by the biodegradation, was studied [11]. It was observed the increase in the biodegradability of the MWF wastewater during the photo-Fenton process with the BOD5/COD ratio increasing by 44 % at 20.7 J cm−2 and by 59 % at 34.5 J cm−2. The feasibility of employing a sequential Fenton-biological oxidation for the treatment of recalcitrant components of MWF wastewater was investigated. An overall decrease of 92 % and 86 % in chemical oxygen demand (COD) and total organic carbon (TOC), respectively, was achieved by a two-step treatment method developed by the authors [7].

EXPERIMENTAL

Materials and Methods

All chemicals were analytical grade and employed without any further purification. Samples of wastewater were obtained from Secop Ltd. Slovakia, which used physico-chemical treatment for their wastes from exhausted metalworking fluids. General physico-chemical parameters were as follows: TOC 637.0 mg L−1, TIC 46.0 mg L−1, TC 683.0 mg L−1, pH 7.8. Carbon analysis was determined by direct injection of the undiluted sample into a Shimadzu TOC-VCPN analyser, calibrated with standard solutions of potassium phthalate and hydrogen carbonate.

Fenton´s oxidation chemistry

The volume of treated samples was 1000 mL. The pH of the samples of wastewater for treating with Fenton reagent was at first adjusted to 3.0 with a stock solution of H2SO4 (2 mol L−1) at magnetic stirring. After an addition of defined amount of Fe(SO4)3·7H2O and its completely dissolution, a defined volume of H2O2 (30 % w/v) was poured into the mixture (molar ratio of Fe2+:H2O2 was determined to 1:10). The reaction in samples was stopped after 60 minutes by pH adjusting to 9.0 with stock solution of NaOH (2 mol L−1). After sedimentation (approximately 2 hours) an appropriate volume was taken for carbon analysis. The samples for biodegradability evaluation were allowed to stand for 24 hours while the decantation was realized several times.

Biodegradability measurements

The principle of the biodegradability measuring reflects the test method OECD 301 B with some modification [14]. The biodegradability was measured according to evolved carbon dioxide produced by the inoculum.
The aerobic degradation was carried out in a closed apparatus consisting of two vessels where the air part was pumped by the peristaltic pump from culture bottle to absorption bottle for better reaction of evolved CO$_2$ by the absorption solution. 10 apparatus were prepared for the blank, control and tested substances. In culture vessel, there was 750 mL of culture medium with 0.1 g L$^{-1}$ of SS prepared from activated sludge in the same day as the test began. During the biodegradability test in the cultivation bottle, pH was set up to 7.5. Aeration intensity was 50 - 60 mL min$^{-1}$ and the air:liquid volume was settled to 1:1. The amount of carbon dioxide produced by the microbial inoculum during the degradation was measured by the change of the conductivity in absorption bottle containing 1L of 0.0175 mol L$^{-1}$ Ba(OH)$_2$, by calibrated conductivity probe continuously during the whole test. When the conductivity has decreased below 1.5 mS cm$^{-1}$, the absorption solution was replaced by a fresh one. While the apparatus was opened, the system was filled with fresh air. The performance of the test is more similar to OECD 302 B in the parameters such as the amount of inoculum and concentration of the test substance, but it resembles to OECD 301 B by the degradability measured parameter - CO$_2$. It eliminates misinterpretation in the degradability evaluation when absorption occurred in poorly soluble substances and where the COD or TOC from water phase is used for calculation. The amount of microorganisms used was 3-times higher and concentration of tested substance was 6-times higher than in OECD 301 B. Before the test all samples were diluted to the same concentration of TOC (150 mg L$^{-1}$) and the pH was adjusted to 7.5 to avoid the harmful effect on the inoculum. Test was running for 20 days.

**RESULTS AND DISCUSSION**

Fig. 1 shows the values of the parameter TOC during the application of different amount of ferrous ions to the sample after 60 minutes treatment with the Fenton’s reagent. The increased addition of ferrous ions caused the higher amount of organic load to be oxidized by the created hydroxyl radicals. The addition of ferrous ions higher than 2.0 g did not caused significant decrease. 23.2 % of TOC was removed after addition of 0.50 g ferrous ions. However, when 4 times greater amount of ferrous ions was added, only 60.8 % decrease was recorded. Addition of 3.5 g of ferrous ions achieved 70.6 % removal of TOC.

Biodegradability curves are displayed in Fig. 2. Lag phase was recorded only in the case of the control sample - ethylene glycol. In all treated samples including the non-treated one, the biological oxidation started immediately after the test has begun, so no adaptation of the bacterial inoculum occurred in the samples. After the 10-day window, all samples achieved 60 % of the biodegradations level, so all samples can be signed as readily biodegradable.

The biodegradability results, reached at the end of the test, are shown in Fig. 3.
It is interesting that the highest level of the biodegradability was recorded in the non-treated sample (95%). All treated samples reached biodegradability that is slightly lower than the non-treated sample. The lowest biodegradability in treated samples was observed in the case of the lowest quantity of ferrous ions added (0.50 g). The biodegradability level increased with the increased addition of Fe²⁺ up to 3.0 g.

**CONCLUSIONS**

Fenton’s reagent used for the pre-treatment step before the biological oxidation decreased the biological level. This experiment does not confirmed expectations on possible increase in the biodegradability even when the AOP pre-treatment eliminates high organic load in tested samples of wastewater. It is strongly recommended to test change in toxicity after AOP pre-treatment step of wastewaters.
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REFERENCES


