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Treatment of industrial wastewater contaminated with recalcitrant metal working fluids by the photo-Fenton process as post-treatment for DAF

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ABSTRACT

Post-treatment of the industrial wastewater polluted by metalworking fluids (MWFs) was performed using the photo-Fenton process in following of the chemical addition-dissolved air flotation (CA-DAF) unit. Prior to this study, the CA-DAF was operated as full-scale by trial and error. For the photo-Fenton process as a pilot-scale batch reactor, initial pH value, $FeSO_4$, and H_2O_2 concentrations were considered to study the effect of different operating conditions on chemical oxygen demand (COD) and total petroleum hydrocarbon (TPH) removals. This hybrid approach revealed removal efficiencies of 99.85% and 98.9% for COD and TPH in the optimized photo-Fenton process as pH 3, $FeSO_4$: 100 mg/l, and H_2O_2: 17.8 g/l. The COD degradation results for the photo-Fenton system indicated that it could be well fit using a pseudo first-order kinetic model. By the GC–MS analysis of DAF and applied photo-Fenton effluents, a 73% removal rate of mono(2-ethylhexyl) phthalate was detected. It is likely favorable to increase the biodegradability. The cost analysis of this process for the consumed energy (6 kWh) and chemicals (0.01818 kg $FeSO_4$ and 17.15 kg H_2O_2) was estimated at approximately 26 $ per 1 m^3 of DAF effluent. Generally, these results imply that the CA-DAF unit followed by photo-Fenton is an effective and practical method for treating MWFs wastewater.

Introduction

Metalworking fluids (MWFs) are generally used in manufacturing industries (e.g., tooling industry). These fluids are deliberately added to applied water in metal machining operations to cool and lubricate or inhibit rusting of contact place between machining tools and working fragment. It also has other benefits, such as the removal of small metal scraps by washing, tool protection against corrosion, tool life improvement, friction diminution in fragment and tool interface, and altogether the final quality development of products [1–3]. Despite these advantages, MWFs is known as the main source of oily wastewater in the metal industries sector with high chemical oxygen demand (COD), approximately 10,000–100,000 mg/l [4,5]. MWF formulations are chemically complex and composed of base mineral oil, emulsifiers and surfactants, extreme pressure and anti-weld agents, corrosion inhibitors, biocides (phenolic and aliphatic derivatives), foam inhibitors, friction reduction agents, and alkaline reserve compounds [6–8]. Owing to the presence of all these compounds and microbial agents (bacteria and fungi), which have proven toxic effects, MWFs are non-biodegradable and hazardous and are associated with diseases such as cancer, skin disease, respiratory disease, and other diseases [5,7,9]. It is estimated that more than 2,000,000 m^3 MWF are annually used worldwide and that wastewater volume by dilution of MWFs prior to use could be ten times higher [1,6,10,11]. Because of the complicated chemical contents as trade secrets for MWFs producers, the disposal of related wastewater is progressively difficult [7]. Further, since the MWFs are categorized as

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hazardous wastes along with relative toxicity to aquatic organisms, disposal options for this oily waste is expensive [12].

For the disposal of used MWFs, conventional physical and chemical techniques or minimization approaches are typically used, and generally have single or multiple stages, depending on the stage of treatment needed. In the multiple stage systems, solids and oil phase during the elementary phase is removed, and then the volume and COD loading are reduced by the secondary stage. Finally, for compliance with severe discharge limits, post-treatment is usually appropriate to develop the effluent quality [1]. The toxicity of these fluids is an obstacle because all biological treatment processes need high concentrations of organic compounds with low molecular weight and BOD/COD ratio higher than 0.4 (a desirable value) [4,5,13]. Considering the stable nature of these fluids in high pressures and temperatures, MWF wastewater treatment can be chemically and biologically laborious. Applying the existing approaches or processes requires further refining costs [5]. Evaporation, thermal splitting, and incineration are the most predominant disposal methods, while the latest technique releases a lot of air pollutants (e.g., NO_x, SO_2, HCl) [6–8]. Therefore, we have the risk of untreated wastewater discharge to soil and water resources, such as rivers, lakes, and so on, at any time and any place [5]. Other used treatment options for these recalcitrant wastewaters are chemical stabilization, electrocoagulation, and coagulation along with dissolved air flotation (DAF) [14], microfiltration [15], flow equalization, gravity separation of free oil, chemical emulsion breaking, flocculation (DAF), and clarification/filtration for oil removal [10], coagulation–flocculation [4], advanced oxidation processes, photo-Fenton oxidation system, and Fenton oxidation [16–19]. MWFs treatment problem will not likely be solved with all mentioned approaches (apart from incineration), because of emulsion splits to water and oil phases and thus require additional utilization; further, the defects of these procedures are their inability to completely remove inorganic/organic, volatile/semi volatile compounds, and COD [17,20]. Hence, post-treatment is necessitated for the effluent of each process [17]. Furthermore, applying two or more techniques in combination is more efficient than one [7]. The hybrid technologies were studied by a series of researchers incorporating biodegradation and advanced oxidation process [1], coagulation process combined with mechanically induced air floatation [21], and coupling coagulation and DAF [14], as well as other coupled approaches [5,6,8,22]. In general, the integrated approach is considered as the best option for complex wastewaters [23].

Air flotation, in all its varieties, is an efficient technique to separate light particles and oils from wastewater. DAF not only is more efficient and faster than sedimentation techniques, but also produces minor sludge volumes [24,25]. The organic matter removal by this technique can be higher than 98%, depending on the main operating parameters (e.g., saturation time and separation time and pressure, size and diameter of the gas bubbles, and chemical additive dosage) [14,25,26].

The photo-Fenton can be divided into two phases with regard to hydroxyl radical ($^{\bullet}$OH) formation. First, in Fenton reaction, ferrous iron oxides are oxidized into ferric iron oxides in the presence of hydrogen peroxide (Eq. (1)) [27]. In the next step, ferric oxides generated in the Fenton reaction are photo-catalytically transformed to ferrous ions (Eq. (2)) [16].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad k = (63-76)\ M^{-1}S^{-1} \tag{1}$$

$$[Fe(OH)]^{2+} \xrightarrow{hv} Fe^{2+} + HO^{\bullet} + H^+ \tag{2}$$

In the presence of organic matter, hydroxyl radical reacts with this, increasing the oxidized products (Eq. (3)) [16,28].

$$HO^{\bullet} + RH \xrightarrow{chain\ propagation} R + H_2O \tag{3}$$

The aim of this research was the evaluation of COD, total petroleum hydrocarbon (TPH), and oil removal efficiencies by the photo-Fenton reaction as post-treatment coupled with a full-scale DAF unit. The specific goals of this work, considering COD and TPH as indicators, were to determine: (1) the effect of the reagent concentrations ($FeSO_4$, H_2O_2) and initial pH value in COD and TPH removal, (3) the synergistic effect of $FeSO_4$, H_2O_2, and ultraviolet (UV) radiation in the optimized condition, (4) the organic matters analysis, (5) the removal kinetics of COD, and (6) cost analysis for running of process in optimized condition.

Materials and methods

Reagents and chemicals

Hydroxyl radicals were provided by hydrogen peroxide (H_2O_2; 30%, Catalog Number 1085979025) as oxidant and ferrous sulfate

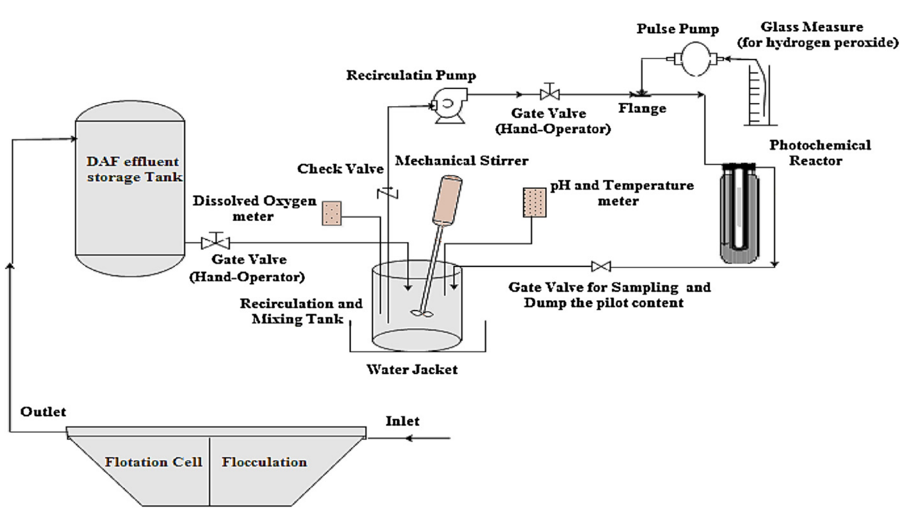

Fig. 1. The pilot-scale photo-Fenton unit coupled with a full-scale Chemical Addition-Dissolved Air Floatation (CA-DAF) system.