Treatment of landfill leachate waste using sono (US) and photo (UV) based advanced oxidation processes: Studies on various operating parameters

P. Asaithambi[a,b,*], Dejene Beyene[a] Esayas Alemayehu[a,*]

[a]*Faculty of Civil and Environmental Engineering, Jimma Institute of Technology, Jimma University, Jimma, Po Box – 378, Ethiopia,
Tel. +251 472115547, Fax +251 471111450, email: drasaithambi2014@gmail.com (P. Asaithambi),
dejenebeyeneaau@yahoo.com (D. Beyene), esayas16@yahoo.com (E. Alemayehu)*
[b]*Department of Chemical Engineering, Faculty of Engineering, University of Malaya, Malaysia – 50603*

ABSTRACT

In this study, the treatment of landfill leachate by sono (US) and photo (UV) based advanced oxidation processes (AOPs) was investigated in terms of % color and COD removal, together with electrical energy per order. Experimental results showed that, the hybrid sono–photo–Fenton (US/UV/Fe^{2+}/H$_2$O$_2$) process has shown that higher removal of color (100%) and COD (96%) with required of low electrical energy per order (0.71 kWh/m^3) than the other processes. The influence of various experimental parameters such as H$_2$O$_2$ and Fe^{2+} concentration, COD concentration, solution pH, sonication (US) and photo (UV) power on the % color and COD removal with electrical energy per order has been studied to find out the optimum conditions leading to maximum % removal efficiency of hybrid US/UV/Fe^{2+}/H$_2$O$_2$ process. The best results of US/UV/Fe^{2+}/H$_2$O$_2$ process of landfill leachate have been obtained using 80 mM of H$_2$O$_2$, 40 mM of Fe^{2+}, pH of 3, COD concentration of 2,000 ppm, sonication power of 100 W and UV power of 32 W and after 3 h of reaction time. The synergy index between sonication (US) and photo–Fenton (UV/Fe^{2+}/H$_2$O$_2$) process has been studied and critically reported. Therefore, the combination of US and UV based AOPs has been proved to be efficient treatment techniques for removal of pollutant from industrial effluent and wastewater.

Keywords: US/UV/Fe^{2+}/H$_2$O$_2$, Landfill leachate, Color and COD removal, Electrical energy per order, Synergy index

1. Introduction

Landfill leachate generation is a major problem for municipal solid waste landfills and causes significant threat to surface water, groundwater and environmental pollution [1], so the untreated landfill leachate is a hazard to the environment, if it is allowed to enter a body of water and environment [2]. Different methods have been used for treating the landfill leachate waste including coagulation–flocculate, chemical oxidation [3], granular activated carbon adsorption [4], chemical precipitation [5,6], reverse osmosis [7], biological treatment [8], electrochemical [6,9–11], nano filtration [12] and ion exchange [13] process.

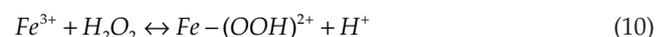In recent years, sono (US) and photo (UV) based advanced oxidation processes (AOPs) has received consid-erable attention as alternative treatment methods for the removal of pollutant from landfill leachate waste [14–17]. The US and UV based AOPs, which is mainly involve the generation of strongly oxidizing species like free hydroxyl radicals (•OH) for the treatment of organic and inorganic pollutants [18–22]. AOPs has been developed that can be operate at or near room temperature and pressure and are based on the promotion of highly reactive species, free hydroxyl radicals (•OH, E° = 2.8 V vs. *SHE*) [23]. The hydroxyl radicals produced by AOPs do not selectively attack organic compounds. One of the most important AOPs used for the treatment of industrial effluents is the sono– photo–Fenton process (US/UV/Fe^{2+}/H$_2$O$_2$), in which the pollutant is treated by a combination of US and UV with H$_2$O$_2$ and Fe^{2+} reagents. This process has been shown to be the most promising method for removal of pollutant from various types of wastewater [24,25].

─────────────
*Corresponding author.

The combined treatment techniques using ultrasound (US) and ultraviolet (UV) along with Fenton reagent (Fe^{2+}/H_2O_2) is known as $US/UV/Fe^{2+}/H_2O_2$ process, which is enhanced the production of OH radicals in an aqueous system significantly. Sonolysis of water produces OH radicals and hydrogen atoms. However, significant loss of $^\bullet H$ and $^\bullet OH$ species occurs due to the recombination [26].

$$H_2O+))) \rightarrow HO^\bullet + H^\bullet \tag{1}$$

$$HO^\bullet + H^\bullet \rightarrow H_2O \tag{2}$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \tag{3}$$

$$2HO^\bullet \rightarrow H_2O_2 \tag{4}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{5}$$

$$H^\bullet + H_2O_2 \rightarrow HO^\bullet + H_2O \tag{6}$$

On the other hand, the application of photo (UV) light, converted the H_2O_2 produced by recombination of OH radicals, and in turns increased the amount OH radicals. The intermediate complex formed due to the reaction of Fe^{3+} with H_2O_2 during the Fe^{2+}/H_2O_2 reaction could be reduced to Fe^{2+} by US and UV process. Hybrid $US/UV/Fe^{2+}/H_2O_2$ process produces extra $^\bullet OH$ radicals, regenerates Fe^{2+} and to significantly increase the rate of removal of pollutants from wastewater according to the following reactions [27].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \tag{7}$$

$$HO^\bullet + HO_2^\bullet \rightarrow H_2O + O_2 \tag{8}$$

$$\left[Fe(OH)\right]^{2+} + hv \rightarrow Fe^{2+} + HO^\bullet \tag{9}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-(OOH)^{2+} + H^+ \tag{10}$$

$$Fe-(OOH)^{2+} +))) \rightarrow Fe^{2+} + HO_2^\bullet \tag{11}$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \tag{12}$$

$$Fe^{3+} + H^\bullet \rightarrow Fe^{2+} + H^+ \tag{13}$$

$$H_2O_2 + hv \rightarrow 2HO^\bullet \tag{14}$$

Few literature studies and reported that US and UV based AOPs for removal of pollutant from various types of wastewater [24,25,28–32]. Segura et al., investigated the application of sono–photo–Fenton process for degradation of phenol using Fe_2O_3/SBA-15 as a heterogeneous catalyst. TOC degradation of 45% was observed with the sono–photo–Fenton process where as 30% and 40% TOC degradation was observed with the sono–Fenton and photo–Fenton processes, respectively [28]. Mendez-Arriaga et al., examined the degradation of recalcitrant pharmaceutical micro–pollutant ibuprofen using sono–photo–Fenton, sono–photo–catalysis and $TiO_2/Fe^{2+}/$sonolysis processes. The results showed that, the hybrid system is a promising method for complete elimination/mineralization of the recalcitrant micro–contaminant ibuprofen [24]. Vaishnave et al. conducted a study on the degradation of azure-B by sono–photo–Fenton and photo–Fenton processes and they found that, the dye was completely oxidized and degraded into carbon dioxide (CO_2) and water (H_2O) [25]. Babu-ponnusami and Muthukumar studied the performance of Fenton, sono–Fenton and sono–photo–Fenton processes for oxidation of phenol and they found that hybrid sono–photo–Fenton technique showed that better performance than other process [29]. Verma et al. investigated and reported for the degradation of dyes and they found that varied in the following order; sono–photo–Fenton > photo-Fenton > UV to US process > US to UV process > sono–Fenton > Fenton [30]. Chitra et al. studied and reported that, the sono-photo-Fenton process was effectively degrades the ethylenediaminetetraacetic acid (EDTA) [31]. Zhong et al. reported that coupled heterogeneous sono–photo–Fenton system appears as a promising process for dye wastewater treatment [32]. These studies have shown that the ultrasonic (US) and/or photo irradiation (UV) alone is ineffective for the removal of pollutant, but quite effective when combined with other advanced oxidation processes.

Most of the previous literature works carried out for the removal of pollutant using synthetic solution and only few works has been studied for the removal of pollutant using real industrial effluent. The most of the research work has focus on treatment efficiency based on the removal of color, TOC, dye and phenol. In US and UV based AOPs, the electrical energy per order having important parameter due to operating costs and economical point of view of the hybrid process. So, in this research work, we are focus on the removal of pollutant in terms of % color and % COD removal and also determination of electrical energy per order using various sono and photo based AOPs from landfill leachate waste.

The goal of this research work is (i) Comparison of various sono and photo based AOPs in terms of % color, % COD removal and electrical energy per order and to select the better one. (ii) To study the effect of operating parameters such as H_2O_2 concentration (20–120 mM), Fe^{2+} concentration (10–60 mM), solution pH (2 to 7), COD concentration (1,000–5,000 ppm), US power (20–100 W) and UV power (8–32 W) on the removal of % color, % COD and determine the electrical energy per order using $US/UV/Fe^{2+}/H_2O_2$ from landfill leachate. (iii) Synergy index between the sonication (US), photo–Fenton ($UV/Fe^{2+}/H_2O_2$) process has been studied. (iv) The best of our knowledge, this is the first report on the removal of % color and % COD with electri-

cal energy per order from landfill leachate using ultrasound and photo based AOPs.

2. Material and methods

2.1. Characterization

A real landfill leachate was collected from a municipal solid waste sanitary landfill located nearby Kuala lumpur, Malaysia and it was transferred into clean plastic sample bottles which were immediately transported to the laboratory to be properly stored for the future use. The characteristics of landfill leachate are presented in Table 1. $FeSO_4 \cdot 7H_2O$, H_2O_2 (50 wt%), $Na_2S_2O_3$, H_2SO_4 and NaOH were obtained from YEW SII SIE lab analytics supplies (Malaysia). All the chemicals were of analytical grade, commercially available and used without further purification.

2.2. Methods

The experimental setup of hybrid $US/UV/Fe^{2+}/H_2O_2$ process is schematically shown in Fig. 1. The experimental set up consists of photochemical reactor and ultrasonic water bath (US). The cylindrical type of photochemical reactor made up of glass with the net capacity of 1000 mL (YEW SII SIE lab analytics). The top of the photochemical

Table 1
Characteristics of landfill leachate

Parameters	Range
pH	8.6–18.8
COD (mg/L)	4,850–5,150
Color	Brownish
Turbidity (FAU)	280–310
TSS (mg/L)	145–160
Temperature (°C)	27–31

Fig. 1. Schematic diagram of $US/UV/Fe^{2+}/H_2O_2$ process.

reactor having two port for the purpose of feeding the catalyst and withdraw the sample. The volume of solution was used 750 mL and pH of the solution was measured and adjusted using a pH meter (Elico: Model LI120) with NaOH and H_2SO_4. The source of UV irradiation was a 32 W low-pressure mercury vapor lamp with maximum emission at 254 nm placed in a quartz tube and the UV lamp was immersed in the solution. The ultrasonic water bath (Model: D-7822 K, Elma Ultrasonics) was filled with distilled water up to an optimum level and also to maintain a constant temperature (30 ± 1°C) using a cooling water system. The temperature of the distilled water was monitored using a thermocouple immersed in the water. After our required experimental condition, the photochemical reactor was placed inside the ultrasonic water bath. During the $US/UV/Fe^{2+}/H_2O_2$ process, the different time intervals of samples were collected from sampling port and quenched with Na_2SO_3 to arrest the solution, then filtrate using a filter paper and then immediately to find out the removal efficiency in terms of color (Spectroquant Pharo®300) and COD (Spectroquant® TR320) removal.

2.3. Analysis

The efficiency of color and COD removal was calculated using the following equation is given below (15) and (16).

Color removal, (%)

$$\text{Color removal, (\%)} = \frac{Abs_i - Abs_t}{Abs_i} \times 100 \qquad (15)$$

where Abs_i and Abs_t are the absorbance of initial and at any time t samples for corresponding wavelength λ_{max}.

COD removal, (%)

$$\text{COD removal, (\%)} = \frac{COD_i - COD_t}{COD_i} \times 100 \qquad (16)$$

where COD_i and COD_t (in ppm) are chemical oxygen demand of initial and at reaction time t, respectively.

2.4. Evaluation of electrical energy per order

Electrical energy per order is a convenient tool for comparing the process performance and energy efficiency of the various AOPs. The US and UV based AOPs of organic and/or inorganic pollutant is an electrical energy driven processes and electrical energy per order typically represents a major fraction of operating cost. Therefore, the calculations based on the electrical energy per order can be very informative and useful [33]. The "electrical energy per order of removal" figure-of-merit is basically defined as the electrical energy (in kWh) required to reducing the concentration of a pollutant by one order of magnitude in 1 m³ of wastewater [33]. The electrical energy per order for removal of COD and color from landfill leachate using the US and UV based AOPs was calculated using Eq. (17):

Electrical energy per order =

$$\frac{P_{el} \times t \times 1000}{V \times 60 \times log\left(\dfrac{COD_i}{COD_t}\right)}, \text{(kWhr/m}^3\text{order}^1) \quad (17)$$

where P_{el} is the rated power in kW (0.008, 0.016 and 0.032 kW for photo (UV) process and 0.02, 0.04, 0.06, 0.08 and 0.100 kW for sonication (US) process), t is the reaction time (in h), V stands for the reactor volume (L).

3. Results and discussion

3.1. Various AOPs comparison

The operational parameters such as COD – 2000 ppm, Fe^{2+} – 40 mM, H_2O_2 – 80 mM, pH – 3, UV – 32 W and 254 nm, US – 100 W and 20 kHz, and reaction time – 3 h were applied in of UV, US, UV/H_2O_2, US/H_2O_2, Fe^{2+}/H_2O_2, $UV/Fe^{2+}/H_2O_2$, $US/Fe^{2+}/H_2O_2$ and $UV/US/Fe^{2+}/H_2O_2$ processes in order to compare their efficiency in terms of % color, % COD removal with the associated of electrical energy per order from the landfill leachate and the results are given in Figs. 2a and 2b. It is evident from Fig. 2a the single photo (UV) and sonication (US) processes was not effective for the removal of % color and % COD (less than 20% and 15%).
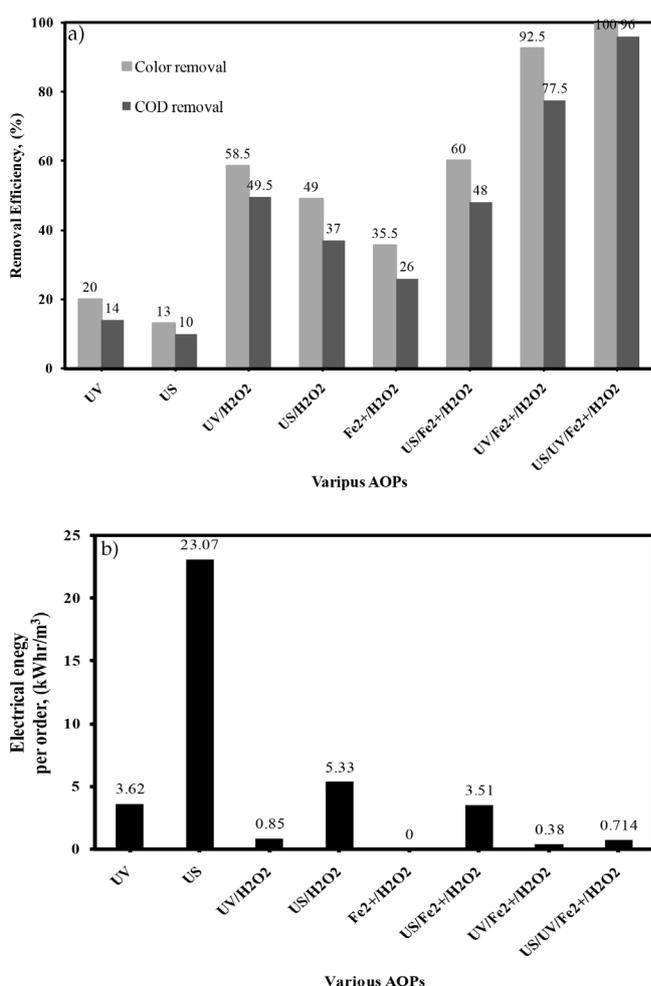

Fig. 2. Comparison of various UV, US, Fe^{2+}/H_2O_2, $UV/Fe^{2+}/H_2O_2$, $US/Fe^{2+}/H_2O_2$ and $US/UV/Fe^{2+}/H_2O_2$ on the (a) % color and COD removal, (b) electrical energy per order (COD: 2000 ppm, Fe^{2+}: 40 mM, H_2O_2: 80 mM, pH: 3, UV: 32 W and 254 nm, US: 100 W and 20 kHz, reaction time: 3 h).

Moderately low % color and % COD removal was observed for the UV/H_2O_2, US/H_2O_2 and Fe^{2+}/H_2O_2, processes as well, less than the 60% and 50%, respectively. The combination UV and US with Fe^{2+}/H_2O_2 process such as $UV/Fe^{2+}/H_2O_2$, $US/Fe^{2+}/H_2O_2$, and $US/UV/Fe^{2+}/H_2O_2$ processes for the removal of % color and % COD were about 60%, 92.50%, 100% and 48%, 77.50%, 96%, respectively. As expected, the hybrid $US/UV/Fe^{2+}/H_2O_2$ process has the best % color and % COD removal efficiency within the investigated UV and US based AOPs. In the hybrid $US/UV/Fe^{2+}/H_2O_2$ process, the $^{\bullet}OH$ radicals are generated in two reactions. The ultrasonic wave can induce the dissociation of H_2O into $^{\bullet}OH$ and $^{\bullet}H$, $^{\bullet}H$ can induce the dissociation of H_2O_2 into $^{\bullet}OH$ and H_2O. Besides, Fe^{2+} is formed by reaction between $^{\bullet}H$ and Fe^{3+} [Eq. (13)]. Each Fe^{2+} ion can produce $HO^{\bullet}$ and Fe^{3+} by Fenton reagent. Ferric ions on exposure to light decomposes water into a proton and $HO^{\bullet}$ radical and Fe^{3+} is reduced to Fe^{2+} [Eq. (9)]. The entire process is a cyclic one. These results were in agreement with those observed for the photo–Fenton assisted sonication of phenol [28,29], of recalcitrant pharmaceutical micro-pollutant ibuprofen [24], of azure-B [25], of dyes [30–32] and of EDTA [31].

Advanced wastewater treatment techniques must have technically and economically feasible. Electrical energy per order is an important economical parameter in AOPs and it is directly proportional to the operating cost [34]. The electrical energy per order was calculated using Eq. (17) for the US and UV based AOPs to treat the landfill leachate and the results are given in Fig. 2b. It is noted from Fig 2b, the electrical energy per order of 0.71 kWh/m³ was required to the 100% of color and 96% of COD removal using the $US/UV/Fe^{2+}/H_2O_2$ process. The other US and UV based AOPs results showed that, having higher electrical energy per order with low % color and % COD removal. The experimental results clearly indicated that superiority of the US and UV with Fe^{2+}/H_2O_2 combination process over other treatment processes studied herein. Further studies were focused on the hybrid $US/UV/Fe^{2+}/H_2O_2$ process for removal of % COD and determination of electrical energy per order from landfill leachate.

3.2. Effect of operating parameters

The $US/UV/Fe^{2+}/H_2O_2$ processes are affected by the operating parameters such as H_2O_2 and Fe^{2+} concentration, solution pH, initial COD concentration, UV and US power was studied in terms % COD removal and electrical energy per order and the results and discussion was given below.

3.2.1. Effect of H_2O_2 concentration

The effects of H_2O_2 and Fe^{2+} concentrations are important key factors in improving the efficiency of $US/UV/Fe^{2+}/H_2O_2$ process [25,29]. However, both H_2O_2 and Fe^{2+} concentration can also react with $^{\bullet}OH$ and can therefore inhibit the oxidation reactions if either of them is not at the optimal concentration. Effect of H_2O_2 concentration on the % COD removal and electrical energy per order of landfill leachate was investigated and the results are shown in Fig. 3a. Fig. 3a illustrates that the % COD removal efficiency was increased from 60.50 to 96% with an increasing of H_2O_2 concentration
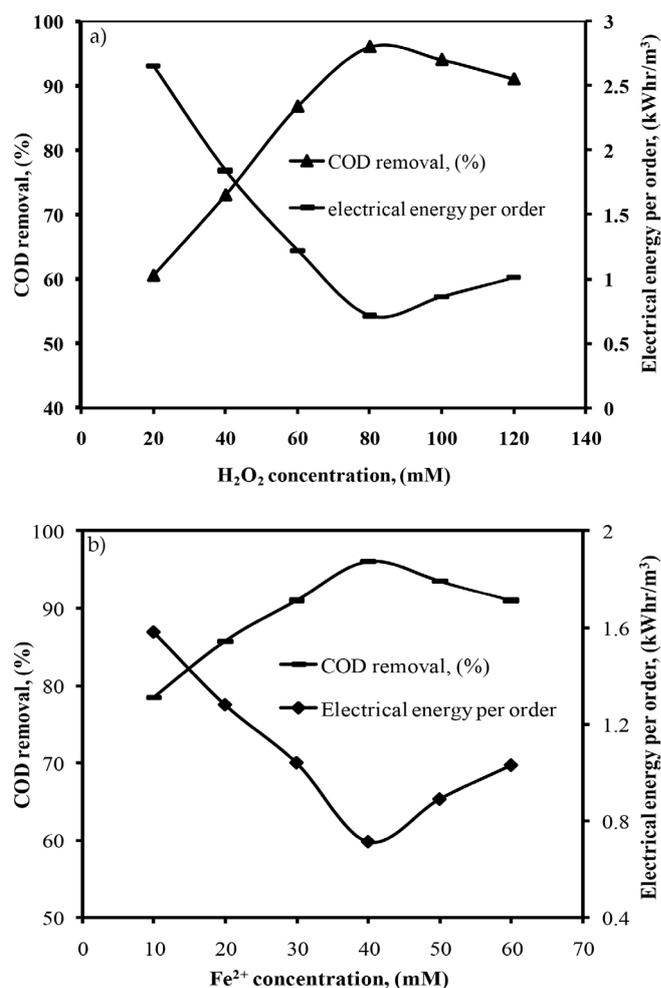
Fig. 3. Effect of (a) H_2O_2 and (b) Fe^{2+} concentration on the % COD removal and electrical energy per order in US/UV/Fe^{2+}/H_2O_2 process (COD: 2000 ppm, Fe^{2+}: 40 mM, H_2O_2: 80 mM, pH: 3, UV: 32 W and 254 nm, US: 100 W and 20 kHz, reaction time: 3 h).

of up to 80 mM. Afterwards, the removal of % COD was not improved significantly. It could be noticed that H_2O_2 is a source of •OH in the US/UV/Fe^{2+}/H_2O_2 system and increase of H_2O_2 concentration would lead to more •OH produced, this is indicating that the generated •OH were sufficient enough to achieve the almost complete removal of COD [27]. However, when H_2O_2 concentration further increasing from 80 to 120 mM, the % COD removal was dropped slightly. Excess amount of H_2O_2 concentration may result in a self-consumption and the scavenging effect of •OH can be described through Eqns. (18), (19), thus not only decreasing the rate of reaction but also leading to wastage of H_2O_2 [32].

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{18}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow O_2 + H_2O \tag{19}$$

Fig. 3a reports that the effect of H_2O_2 concentration on electrical energy per order after 3 h of reaction time using US/UV/Fe^{2+}/H_2O_2 process. It can be ascertained from Fig.

3a that the electrical energy per order decreased from 2.65 to 0.71 kWh/m^3 with increasing H_2O_2 concentration from 20 to 80 mM. However, further increasing of H_2O_2 concentration from 80 to 120 mM, the electrical energy per order was increased from 0.71 to 1.01 kWh/m^3, this is may be due to that, the coincident of •OH consumption at high concentration of H_2O_2 according to reactions (18) and (19) [35]. In order to achieve a higher removal of % COD with the low electrical energy per order, the concentration of H_2O_2 should be optimum and was fixed at 80 mM.

3.2.2. Effect of Fe^{2+} concentration

The effects of Fe^{2+} concentration on the removal of % COD and electrical energy per order was employed using US/UV/Fe^{2+}/H_2O_2 process and the results are given in Fig. 3b. As shown in Fig. 3b, the % COD removal efficiency was increased from 78.50 to 96% with increasing Fe^{2+} concentration from 10 to 40 mM. Further increasing Fe^{2+} concentration from 40 to 60 mM, the % COD removal rate was decreased slightly. This effect can be explained by the fact that the excess of Fe^{2+} may scavenge the formed •OH, which would decrease COD removal efficiency [36]. In additionally, a higher addition of iron salt resulted in brown turbidity that hindered the absorption of UV light required for photolysis and caused the recombination of •OH radicals. In this case, Fe^{2+} reacted with •OH radicals as a scavenger according to reaction (20) [37].

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^- \tag{20}$$

Fig. 3b shows that electrical energy per order variation with Fe^{2+} initial concentration by US/UV/Fe^{2+}/H_2O_2 process. It can be seen from Fig. 3b that the electrical energy per order was decreased from 1.58 to 0.71 kWh/m^3 with increasing Fe^{2+} initial concentration from 10 to 40 mM, as a result of enhancement in % COD removal due to higher available HO• radicals; however, electrical energy per order tends to increased slightly with initial concentrations of Fe^{2+} more than 80 mM. The results indicating that the optimum conditions concentrations of Fe^{2+} and H_2O_2 with US and UV process to produce more HO• with comparing other experimental conditions [35].

3.2.3. Effect of pH

The effect of solution pH plays an important role in the US/UV/Fe^{2+}/H_2O_2 process and in generation of hydroxyl radicals (HO•) [25,27,29,38]. Experiments under various pH were conducted and the results are shown in Fig. 4a. It can be seen from Fig. 4a that the % COD removal efficiency was increased appreciably with initial pH decreasing from 7 to 3, but further decrease of initial pH from 3 to 2 led to an unpronounced decrease of COD removal rate. Generally, the optimal solution pH of the Fe^{2+}/H_2O_2 and UV/Fe^{2+}/H_2O_2 process is around 3 [39,40] because the main species at pH 2–3, Fe(OH)$^{2+}$, Fe(OH)$_2^+$ is the one with the largest light absorption coefficient and quantum yield for •OH radical production, along with Fe^{2+} regeneration [38]. Decreasing the % COD removal at pH of the solution above 3 is due to the coagulation of hydroxo complex of Fe^{3+} formed during the
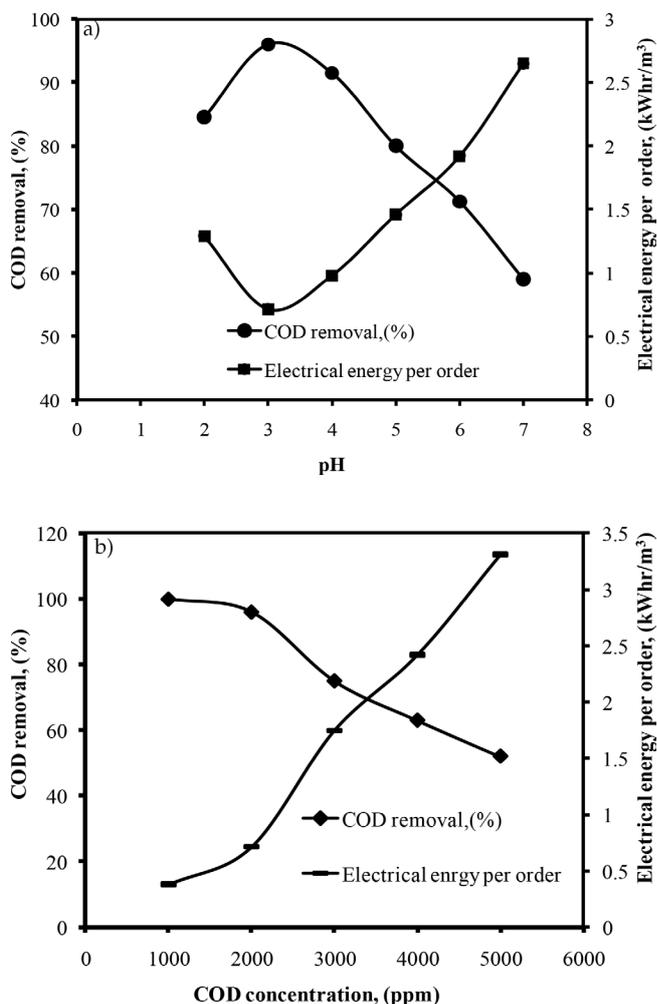
Fig. 4. Effect of (a) pH and (b) COD concentration on the % COD removal and electrical energy per order in $US/UV/H_2O_2/Fe^{2+}$ process (COD: 2000 ppm, pH: 3, Fe^{2+}: 40 mM, H_2O_2: 80 mM, UV: 32 W and 254 nm, US: 100 W and 20 kHz, reaction time: 3 h).

reaction [41]. The low % COD removal at solution pH of 2 is also due to the $^\bullet OH$ scavenging of H^+ ions equations [36,42].

$$HO^\bullet + H^+ + e^- \rightarrow H_2O \qquad (21)$$

The effect of pH on the electrical energy per order was determined for the removal of % COD from landfill leachate using $US/UV/Fe^{2+}/H_2O_2$ process and the results are presented in Fig. 4a. It can be seen from Fig. 4a that the electrical energy per order was decreased from 1.29 to 0.71 kWh/m^3 with increasing solution pH from 2 to 3, but further increasing solution pH from 3 to 7, the electrical energy per order was increased from 0.71 to 2.65 kWh/m^3. The results indicating that, at solution pH of 3, in this condition produce more oxidizing species compared with other conditions.

3.2.4. Effect of COD concentration

Initial COD concentration has a significant effect on the rate of hybrid $US/UV/Fe^{2+}/H_2O_2$ process and this was

studied by varying the COD concentration from 1,000 to 5,000 ppm, at a constant Fe^{2+} loading of 40 mM, pH of 3, with 80 mM of H_2O_2 on the removal of % COD and determination of electrical energy per order and the results are given in Fig. 4b. The results from Fig. 4b reveal a decrease in the % COD removal from 100 to 52% with an increasing in the COD concentration from 1,000 to 5,000 ppm, respectively. This might be explained by the fact that there was limited production of the $^\bullet OH$ in the solution while the COD concentration of waste water was increasing, causing a reduction in the rate of reaction [36,40]. Another reason might be explained by the Beer–Lambert law, according to which as the initial COD concentration increased, the path length of photons entering the solution was decreased, thus resulting in a decreased in the COD removal efficiency with increasing initial COD concentration. Effect of initial COD concentration on the electrical energy per order was investigated by $US/UV/Fe^{2+}/H_2O_2$ process and the results are shown in Fig. 4b. Fig. 4b shows that the electrical energy per order was increased from 0.38 to 3.31 kWh/m^3 with an increasing initial COD concentration from 1,000 to 5,000 ppm. This might be that, the remaining experimental conditions were constant, so the production of $^\bullet OH$ was same with increasing initial COD concentration, causes the electrical energy per order was increased with increasing initial COD concentration.

3.2.5. Effect of US power

The effect of sonication power on the removal of pollutant is a vital role in US based AOPs due to operating cost and achieving complete removal of pollutant [43]. The experiments were employed under varying the sonication powers in the range of 20–100 W with the conditions of $H_2O_2 - 80$ mM, $Fe^{2+} - 40$ mM, pH – 3, COD – 2,000 ppm and UV–32 W using $US/UV/Fe^{2+}/H_2O_2$ process and the results are presented in Fig.5a. It is noted from Fig. 5a that the % COD removal was increased from 60 to 96% and the electrical energy per order was decreased slightly from 1.04 to 0.71 kWh/m^3, with increasing sonication power from 20 to 100 W, respectively. The reason for the observed increasing of % COD removal and decreasing electrical energy per order with increasing sonication power may be due to that the increased number of active cavitation bubbles and hence the generation of more $^\bullet OH$ as well as H_2O_2 produced [42]. Consequently, the removal of % COD was increased and electrical energy per order was decreased.

3.2.6. Effect of UV power

In order to investigate the effect of UV power on the % COD removal and electrical energy per order was investigated using $US/UV/Fe^{2+}/H_2O_2$ process and the results are presented in Fig. 5b. It is observed from Fig. 5b that UV power from 8 to 32 W of a 254 nm UV light was used in the removal % COD from landfill leachate, finding a significant increased of the COD removal from 69 to 96%. When the power of UV light was increased from 8 to 32 W, a faster photo-reduction of Fe^{3+} to Fe^{2+} was obtained, and as a consequence, the regeneration rate of Fe^{2+} increases. Accordingly, the number of $HO^\bullet$ radicals formed increases substantially, also giving rise to a higher COD removal rate [40]. Electri-
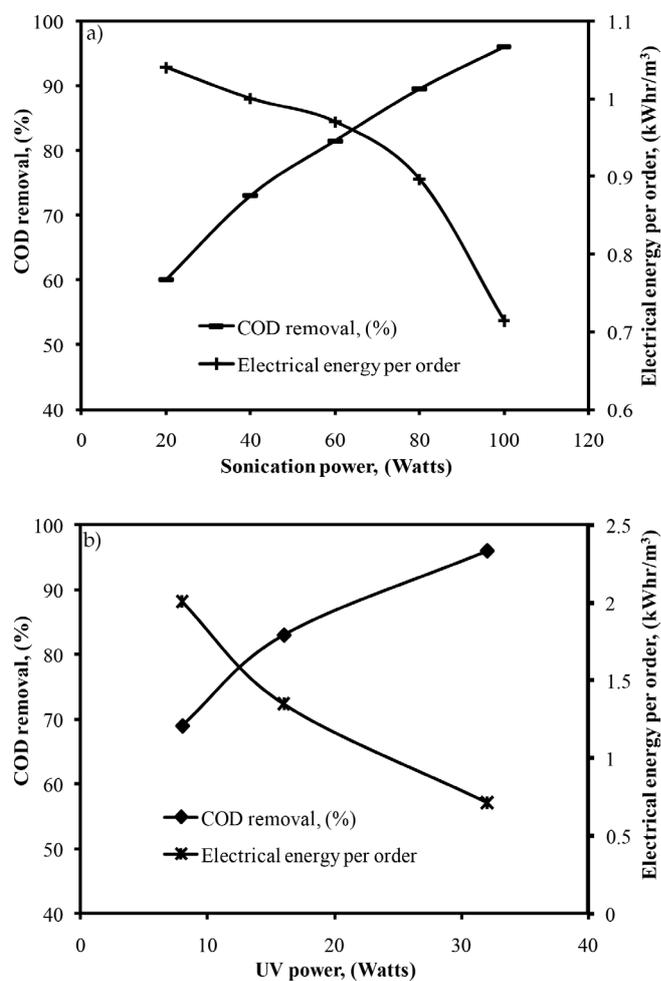
Fig. 5. Effect of (a) US and (b) UV power on % COD removal and electrical energy per order in US/UV/Fe²⁺/H₂O₂ process (COD: 2000 ppm, Fe²⁺: 40 mM, H₂O₂: 80 mM, pH: 3, UV: 32 W, US: 100 W and 20 kHz and reaction time: 3 h).

cal energy per order also calculated for effect of UV power for the system of US/UV/Fe²⁺/H₂O₂. The electrical energy per order was decreased from 2.01 to 0.71 kWh/m³ with increasing UV power from 8 to 32 W, this is may be due to that, the UV power was directly proportional to the $^{\bullet}$OH production, so the % COD removal was increased and electrical energy per order was decreased with increasing UV power.

3.2.7. Study of synergy index

The sono (US) and photo–Fenton (UV/Fe²⁺/H₂O₂) process were performed under optimal selected conditions to determine the synergy index of each process for the removal % color and % COD from landfill leachate. The experimental results showed that there is a synergy index between the US and UV/Fe²⁺/H₂O₂ process for the removal of COD from landfill leachate. Thus the US/UV/Fe²⁺/H₂O₂ process significantly increases COD removal when compared with each individual process (US and UV/Fe²⁺/H₂O₂). The synergy index of the US and UV/Fe²⁺/H₂O₂ processes were cal-

culated using the first order rate constants for the removal of COD according to the Eq. (22) [44].

$$Synergy\ index = \frac{k_{US/UV/Fe^{2+}/H_2O_2}}{k_{US} + k_{UV/Fe^{2+}/H_2O_2}} = 20\% \qquad (22)$$

In Eq. (22) $k_{US/UV/Fe^{2+}/H_2O_2}$ represents the reaction rate constant recorded when the US/UV/Fe²⁺/H₂O₂ process was used, whereas k_{US} and $k_{UV/Fe^{2+}/H_2O_2}$ represents the rate constants when US and UV/Fe²⁺/H₂O₂ process were respectively applied for the removal of COD from the landfill leachate. The synergy index calculated was 20% indicating that the % COD removal was higher when both processes (US and UV/Fe²⁺/H₂O₂) were simultaneously used compared to the removal of COD using the sum of US and UV/Fe²⁺/H₂O₂ processes (US and UV/Fe²⁺/H₂O₂ individually and successively applied). The synergy index observed has been credited to the fact that the combination of US and UV/Fe²⁺/H₂O₂ process generates higher concentration of $^{\bullet}$OH as compared to US and UV/Fe²⁺/H₂O₂ processes. The increased concentration of $^{\bullet}$OH along with their effective utilization due to higher intensity of turbulence created by US significantly accelerates the rate of % color and % COD removal of landfill leachate. Thus, the combined use of US and UV/Fe²⁺/H₂O₂ process provides an alternative and innovative waste water treatment method.

3.2.8. UV-vis spectra

The UV-visible (Spectroquant Pharo® 300) absorption spectra of a treated solution of landfill leachate withdrawn from the US/UV/Fe²⁺/H₂O₂ process using COD–2,000 ppm, Fe²⁺–40 mM, H₂O₂–80 mM, pH–3, UV–32 W and 254 nm, US–100 W and 20kHz with different reaction time were recorded and depicted is shown in Fig. 6. As it can be seen from Fig. 6 that with increasing reaction time intervals, considerable decrease in the absorbance of peaks occurred. It might be attributed that, the % color and % COD removal of landfill leachate with increasing of US/UV/Fe²⁺/H₂O₂ process reaction time.
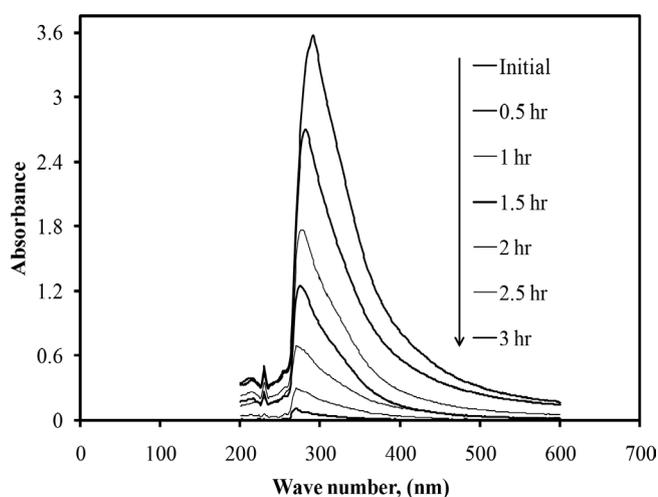

Fig. 6. UV/vis characteristics (COD: 2000 ppm, Fe²⁺: 40 mM, H₂O₂: 80 mM, pH: 3, UV: 32 W and 254 nm, US: 100 W and 20 kHz, and reaction time: 3 h).

4. Conclusion

The scope of this study was to evaluate the application of sono (US) and photo (UV) chemical AOPs such as UV, US, UV/H_2O_2, US/H_2O_2, Fe^{2+}/H_2O_2, $UV/Fe^{2+}/H_2O_2$, $US/Fe^{2+}/H_2O_2$ and $UV/US/Fe^{2+}/H_2O_2$ process on the removal of % color, % COD and determination of electrical energy per order from landfill leachate. The hybrid $US/UV/Fe^{2+}/H_2O_2$ process significantly increased the % color and % COD removal (100% and 96%, respectively) when compared with each individual process. Operating parameters such as H_2O_2 concentration, Fe^{2+} concentration, solution pH, initial COD concentration, UV power and sonication power were studied and reported to obtain the process performance. The synergy index was calculated between the US and $UV/Fe^{2+}/H_2O_2$ process was quantified in 20%. The results of hybrid $US/UV/Fe^{2+}/H_2O_2$ process showed that it could be used as efficient and environmental friendly technique for the complete removal of pollutant from waste water and industrial effluents.

References

[1] Y. Ogata, T. Ishigaki, Y. Ebie, N. Sutthasil, C. Chiemchaisri, M. Yamada, Water reduction by constructed wetlands treating waste landfill leachate in a tropical region, Waste. Manage., 44 (2015) 164–171.

[2] M. Qin, H. Molitor, B. Brazil, J.T. Novak, Z. He, Recovery of nitrogen and water from landfill leachate by a microbial electrolysis cell–forward osmosis system, Biores. Technol., 200 (2016) 485–492.

[3] F.J. Rivas, F. Beltran, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachates: sequential coagulation–flocculation + chemical oxidation process, J. Hazard. Mater., 116 (2004) 95–102.

[4] H.J. Horan, H. Gohar, B. Hill, Application of a granular activated carbon biological fluidised bed for the treatment of landfill leachates containing high concentrations of ammonia, Water Sci. Technol., 36 (1997) 369–375.

[5] J.M. Hur, S.H. Kim, Combined adsorption and chemical precipitation process for pretreatment or post–treatment of landfill leachate, Korean J. Chem. Eng., 17(4) (2000) 433–437.

[6] N. Meunier, P. Drogui, C. Montane, R. Hausler, G. Mercier, J.F. Blais, Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate, J. Hazard. Mater., 137 (2006) 581–590.

[7] A. Chianese, R. Ranauro, N. Verdone, Treatment of landfill leachate by reverse osmosis, Water Res., 33 (1999) 647–652.

[8] C.D. Iaconi, R. Ramadori, A. Lopez, Combined biological and chemical degradation for treating amature municipal landfill leachate, Biochem. Eng. J., 31 (2006) 18–124.

[9] M.J.K. Bashir, M.H. Isa, S.R.M. Kutty, Z.B. Awang, H.A. Aziz, S. Mohajeri, I.H. Farooqi, Landfill leachate treatment by electrochemical oxidation, Waste. Manage., 29 (2009) 2534–2541.

[10] A. Cabeza, A.M. Urtiaga, I. Ortiz, Electrochemical treatment of landfill leachates using a boron-doped diamond anode, Ind. Eng. Chem. Res., 46 (2007) 1439–1446.

[11] M. Panizza, M. Delucchi, I. Sire, Electrochemical process for the treatment of landfill leachate, J. Appl. Electrochem., 40(10) (2010) 1721–1727.

[12] K. Kosutic, D. Dolar, T. Strmeck, Treatment of landfill leachate by membrane processes of nanofiltration and reverse osmosis, Desalin. Water Treat., 55(10) (2015) 2680–2689.

[13] S.K. Fiskum, D.L. Blanchard, S.T. Arm, R.A. Peterson, Cesium removal from simulated and actual hanford tank waste using ion exchange, Sep. Sci. Technol., 40 (2005) 51–67.

[14] D. Hermosilla, M. Cortijo, C.P. Huang, Optimizing the treatment of landfill leachate by conventional Fenton and photo–Fenton processes, Sci. Total Environ., 407 (2009) 3473–3481.

[15] C. Amor, E.D. Torres-Socias, J.A. Peres, M.I. Maldonado, I. Oller, S. Malato, M.S. Lucas, Mature landfill leachate treatment by coagulation/flocculation combined with Fenton and solar photo–Fenton processes, J. Hazard. Mater., 286 (2015) 261–268.

[16] T.F.C.V. Silva, A. Fonseca, I. Saraiva, R.A.R. Boaventura, V.J.P. Vilar, Scale-up and cost analysis of a photo–Fenton system for sanitary landfill leachate treatment, Chem. Eng. J., 283 (2016) 76–88.

[17] Q. Yang, Y. Zhong, H. Zhong, X. Li, W. Du, X. Li, R. Chen, G. Zeng, A novel pretreatment process of mature landfill leachate with ultrasonic activated persulfate: Optimization using integrated Taguchi method and response surface methodology, Process Saf. Environ. Prot., 98 (2015) 268–275.

[18] P.J.D. Ranjit, K. Palanivelu, C.S. Le, Degradation of 2,4-dichlorophenol in aqueous solution by sono–Fenton method, Korean J. Chem. Eng., 25(1) (2008) 112–117.

[19] A. Naldoni, A. Schiboula, C.L. Bianchi, D.H. Bremne, Mineralisation of surfactants using ultrasound and the advanced Fenton process, Water Air Soil Pollut., 215 (2011) 487–495.

[20] S. Kalal, N.P.S. Chauhan, N. Ameta, R. Ameta, S. Kumar, P.B. Punjabi, Role of copper pyrovanadate as heterogeneous photo–Fenton like catalyst for the degradation of neutral red and azure-B: An eco-friendly approach, Korean J. Chem. Eng., 31(12) (2014) 2183–2191.

[21] J.H. Park, I.H Cho, S.W. Chang, Comparison of fenton and photo-Fenton processes for livestock wastewater treatment, J. Environ. Sci. Health., Part B. 41(2) (2006) 109–120.

[22] M. Sekine, Z. Salehi, M. Tokumura, Y. Kawase, Solar photo-Fenton process for the treatment of colored soft drink wastewater: Decolorization, mineralization and COD removal of oolong tea effluent, J. Environ. Sci. Health., Part A. 47(14) (2012) 2181–2189.

[23] B. Ahmed, E. Limem, A. Abdel-Wahab, B. Nasr, Photo-Fenton treatment of actual agro-industrial wastewaters, Ind. Eng. Chem. Res., 50 (2011) 6673–6680.

[24] F. Mendez-Arriaga, R.A. Torres-Palma, C. Petrier, S. Esplugas, J. Gimenez, C. Pulgarin, Mineralization enhancement of a recalcitrant pharmaceutical pollutant in water by advanced oxidation hybrid processes, Water Res., 43 (2009) 3984–3991.

[25] P. Vaishnave, A. Kumar, R. Ameta, P.B. Punjabi, S.C. Ameta, Photo oxidative degradation of azure-B by sono–photo–Fenton and photo–Fenton reagents, Arabian J. Chem., 7 (2014) 981–985.

[26] C.H. Weng, V. Huang, Application of Fe° aggregate in ultrasound enhanced advanced Fenton process for decolorization of methylene blue, Ind. Eng. Chem. Res., 28 (2015) 153–160.

[27] J.M. Monteagudo, A. Duran, I. San Martin, S. Garcia, Ultrasound-assisted homogeneous photocatalytic degradation of Reactive Blue 4 in aqueous solution, Appl. Catal., B. 152–153 (2014) 59–67.

[28] Y. Segura, R. Molina, F. Martinez, J.A. Melero, Integrated heterogeneous sono-photo- Fenton processes for the degradation of phenolic aqueous solution, Ultrason. Sonochem., 16 (2009) 417–424.

[29] A. Babuponnusami, K. Muthukumar, Degradation of phenol in aqueous solution by Fenton, sono–Fenton and sono–photo–Fenton methods, Clean – Soil, Air, Water., 39(2) (2011) 142–147.

[30] A. Verma, A.K. Hura, D. Dixit, Sequential photo-Fenton and sono-photo-Fenton degradation studies of Reactive Black 5, Desal. Water Treat., 56(3) (2015) 677–683.

[31] S. Chitra, K. Paramasivan, P.K. Sinha, Sono–photo Fenton treatment of liquid waste containing ethylenediaminetetraacetic acid (EDTA), Int. J. Nonferr. Metall., 2 (2013) 89–94.

[32] X. Zhong, S. Royer, H. Zhang, Q. Huang, L. Xiang, S. Valange, J. Barrault, Mesoporous silica iron-doped as stable and efficient heterogeneous catalyst for the degradation of C.I. Acid Orange 7 using sono–photo–Fenton process, Sep. Purif. Technol., 80 (2011) 163–171.

[33] A.R. Khataee, H.R. Khataee, Photooxidative removal of the herbicide Acid Blue 9 in the presence of hydrogen peroxide: modeling of the reaction for evaluation of electrical energy per order (EEO), J. Environ. Sci. Health., Part B. 43(7) (2008) 562–568.

[34] A. Karci, I. Arslan-Alaton, M. Bekbolet, G. Ozhan, B. Alper-tung, H_2O_2/UV-C and Photo-Fenton treatment of a nonyl-phenol polyethoxylate in synthetic freshwater: Follow-up of degradation products, acute toxicity and genotoxicity, Chem. Eng. J., 241 (2014) 43–51.

[35] J. Saien, V. Moradi, A.R. Soleymani, Investigation of a jet mix-ing photo-reactor device for rapid dye discoloration and aro-matic degradation via UV/H_2O_2 process. Chem. Eng. J., 183 (2012) 135–140.

[36] M.S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigm., 71 (2006) 236–244.

[37] L.J. Xua, W. Chu, N. Grahamm, Degradation of di-n-butyl phthalate by a homogeneous sono–photo–Fenton process with in situ generated hydrogen peroxide, Chem. Eng. J., 240 (2014) 541–547.

[38] H. Katsumata, T. Kobayashi, S. Kaneco, T. Suzuki, K. Ohta, Degradation of linuron by ultrasound combined with photo–Fenton treatment, Chem. Eng. J., 166 (2011) 468–473.

[39] M.A. Behnajady, N. Modirshahla, F. Ghanbary, A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process, J. Hazard. Mater., 148 (2007) 98–102.

[40] N. Modirshahla, M.A. Behnajady, F. Ghanbary, Decolorization and mineralization of C.I. Acid Yellow 23 by Fenton and pho-to-Fenton processes, Dyes Pigm., 73 (2007) 305–310.

[41] M. Tokumura, M. Sekine, M. Yoshinari, H.T. Znad, Y. Kawase, Photo-Fenton process for excess sludge disintegration, Process Biochem., 42 (2007) 627–633.

[42] M. Siddique, R. Farooq, G.J. Price, Synergistic effects of com-bining ultrasound with the Fenton process in the degradation of Reactive Blue 19, Ultrason. Sonochem., 21 (2014) 1206–1212.

[43] F. Ahmedchekkat, M.S. Medjram, M. Chiha, A.M.A. Al-bsould, Sonophotocatalytic degradation of Rhodamine B using a novel reactor geometry: Effect of operating conditions, Chem. Eng. J., 178 (2011) 244–251.

[44] J. Madhavan, F. Grieser, M. Ashokkumar, Degradation of orange-G by advanced oxidation processes, Ultrason. Sonochem., 17 (2010) 338–343.