

Activated sludge treatment by electro-Fenton process: Parameter optimization and degradation mechanism

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Abstract—This study was conducted to evaluate the mineralization of activated sludge (MAS) by a facile and environmentally friendly electro-Fenton process (EFP). The effects of initial H₂O₂ concentration, pH value, applied current density and operating time on MAS through determining the removal rate of chemical oxygen demand (COD) and total coliform (TC) were studied. 72% of COD was removed by indirect oxidation double-mediated based on the electro-generation of hydroxyl radical and active chlorine, under the following optimum conditions: 127 mmol L⁻¹ of hydrogen peroxide, pH=3.0, 10 mA cm⁻² of DC current, 120 min of operating time, and 0.22 mol L⁻¹ of NaCl as the supporting electrolyte. Only in 10 min and pH 3.0 approximately 100% of TC was removed. The findings indicated that EFP can be applied efficiently for MAS by selecting appropriate operating conditions. The bottom line is that the process is entirely effective owing to the application of green oxidants (hydroxyl radical and active chlorine) and lack of being influenced by environmental situations, which can be introduced as an alternative to current conventional methods.

Keywords: Activated Sludge, Mineralization, Electro-Fenton, COD, Total Coliform

INTRODUCTION

Activated sludge consists of high rates of organic, chemical and microbial pollutants. If they are not stabilized completely and discharged safely, they may become a potential pollution source, threatening soil and water bodies. Therefore, activated sludge management is identified as an important issue in wastewater management. The cost of sludge treatment makes up 30-60% of the operational cost of a sewage plant [1]. Biological treatment systems, especially aerobic and anaerobic systems, are the most common methods, being frequently used to treat activated sludge. Despite the advantages of these systems, anaerobic methods require high retention times (approximately 20 days) [2,3] and a rate-limiting phase, particularly intracellular biopolymers solubilization and conversion to the lower molecular weight compounds of solid degradable organics like sludge by means of hydrolysis. However, high-energy cost, and lower pathogen inactivation can be main disadvantages of aerobic digestion [2].

A disadvantage of wet oxidation is that some of the organic matter is solubilized over the process and the liquors have a high chemical oxygen demand (COD) and biological oxygen demand (BOD) increase; unless they are separately treated, they lead to a significant organic load to the wastewater treatment plants effluents [4]. Although chemical methods such as ozonation and chlorination

have advantages in terms of economic features and efficiency, these systems raise the issue of chlorinated by-products (THMs), and chlorine gas itself imposes risks to the activated sludge system and, more importantly, weak sludge settleability and significant increased soluble chemical oxygen demand (SCOD) in the effluent [1,5]. The use of ultrasonic as pretreatment is limited to disintegrating and liquefying sludge to enhance digestion of sludge by other treatment methods like biodegradation [1]. It is clear that incineration and sludge melting need a high amount of energy [4].

In recent years, the electro-Fenton process (EFP), as one of the advanced oxidation processes (AOPs), has applied to treat different kinds of water and wastewater [6-11], landfill leachate [12], special compounds such as 4-nitrophenol degradation [13], phenol [14], dyes and synthetic dyes [15-18], acetaminophen [19], acid fuchsine [20], picloram [21], flumequine [22], COD from propham [23] and so on as well as to enhance biodegradability of wastewater [11]. EFP is indirect electrolysis of pollutants through generating chemical oxidizing agents, especially hydroxyl radical. Hydroxyl radical, known as the strongest oxidizing species after fluorine, is electrochemically produced by the reaction of H₂O₂ and Fe²⁺ ion (reaction 1) [11]. The produced radical attaches non-selectively to organic compounds and breaks them down into often more biodegradable intermediates, and thus reduces their concentration (reaction 3). H₂O₂, as a clean reagent, is an ecofriendly chemical that leaves no hazardous residuals in solution [18]. Fe²⁺ ions are regenerated mainly from the reduction of Fe³⁺ ions at the cathode (reaction 2).



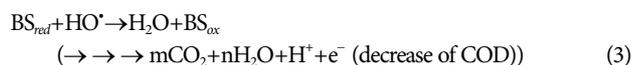
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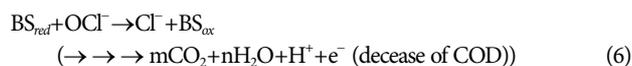
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Generally, the electrochemical oxidation of activated sludge (bio-solid) takes place by the hydroxyl radical attack (reaction 3).



As a whole, there are four categories of the EFP measures: (i) ferrous ion and H_2O_2 are electro-generated through sacrificial anode and an oxygen sparging cathode, respectively; (ii) H_2O_2 is externally injected while a sacrificial iron anode is applied as a ferrous ion source; (iii) ferrous ion is externally injected and H_2O_2 is generated using an oxygen sparging cathode; and, (iv) Fenton's reagent is applied to generate hydroxyl radicals in an electrolytic cell and ferrous ions are reproduced by the reduction of ferric ions on the cathode [14]. When NaCl is used as the supporting electrolyte, conductivity of wastewater is better and the active chlorine species are generated by reactions 4 and 5. Reaction 6 shows how active chlorine oxidizes activated sludge via indirect electro-oxidation.



To our best knowledge, no studies have been conducted on mineralization of activated sludge (MAS) using EFP. In this study, we investigated MAS through EFP by double-mediated based on electro-generation of hydroxyl radical and active chlorine due to high mineralization effectiveness, no harmful chemicals addition, environmental compatibility and high efficiency in the electrochemical production of hydroxyl radical [7]. Using a simple reactor without using other extra processes is the upside of this research. Organic matters in sludge are mineralized and finally converted to CO_2 and H_2O without creating by-products. In view of lack of comprehensive studies in this field, we optimized the operating parameters and also the mechanisms of sludge destruction were investigated. H_2O_2 was injected manually, and Fe^{2+} was provided from disposal cast iron anodes. Then, the feasibility of EFP was investigated in detail for MAS and optimum operation conditions of initial pH, initial H_2O_2 and NaCl concentrations, applied current density (CD), and operating time were determined. Treatment efficiency of the process was evaluated by means of COD and total coliform (TC) removals. In addition, electrochemical energy consumption (EEC) and current efficiency were calculated.

MATERIALS AND METHODS

1. Chemicals and Activated Sludge

The sludge used in this study was actual and taken from a poultry slaughterhouse wastewater treatment plant which its wastewater stems from different processes (poultry slaughter, preparation, conversion wastes unit and so on) and was taken from disposed sludge of the secondary sedimentation tank from the Goshtavar wastewater treatment plant in Hamadan, Iran, with polyethylene bottles. The samples were kept in a refrigerator at 4°C and

Table 1. Physicochemical characteristics of the activated sludge

Parameter	Value
pH	6.4-7.6
COD/(mg L ⁻¹)	6400-7900
Conductivity/($\mu\text{S cm}^{-1}$)	1400-1600
Total dissolved solid/(mg L ⁻¹)	580-850
Total suspended solid/(mg L ⁻¹)	5050-6400
Total solid/(mg L ⁻¹)	5630-7250
Color/(TCU)	61-206
Fical coliform/(MPN 100 mL ⁻¹)	90×10^5
Total coliform/(MPN 100 mL ⁻¹)	20×10^6

then were immediately examined. Physicochemical characteristics of the activated sludge are given in Table 1. Sulfuric acid and sodium hydroxide were used to adjust the pH of the solutions, and sodium chloride was used to improve ionic conductivity and to support electrolyte with purities of more than 99.5%. H_2O_2 (30% w/w) and all other chemicals were purchased from MERCK CO, Germany. All solutions were prepared with distilled water as explained in the Standard Methods [24].

2. Electrolytic Systems

The experimental apparatus used in this study was a batch mode containing four main compartments (Fig. 1): an electro-Fenton cell (made of Pyrex glass, with an effective volume of 450 mL), a DC power supply with the range of 0-5 A for current and 0-40 V for voltage (Adak, ps_405, Hamadan Kit CO, Iran), the iron electrodes had a length×width×thickness dimension of 1 cm×12 cm×0.1 cm and a magnetic stirrer. The gap between the electrodes was fixed at 1 cm. The electrodes were connected to specified poles (anode and cathode) of a direct current power supplier.

3. Analytical Methods and Procedure

COD (open reflex) and TC (the 15-tube method) of the sam-

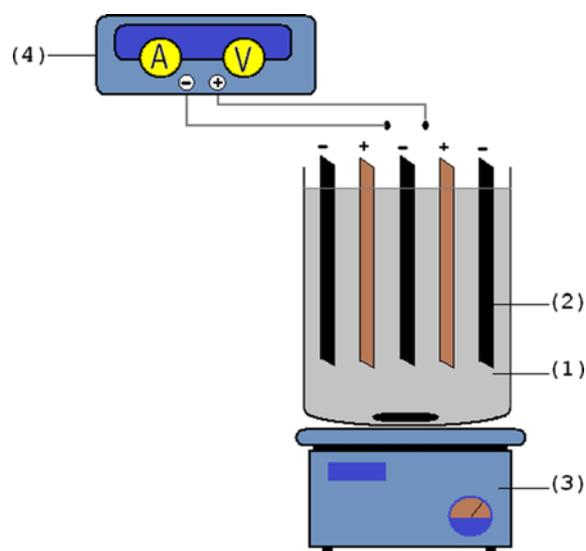


Fig. 1. A schematic diagram of activated sludge treatment by EFP.
 (1) Electrochemical cell (3) Magnetic stirrer
 (2) Pair electrodes (4) DC power supply

ples were measured based on the procedure detailed in Standard Methods [24]. Total dissolved solid (TDS) were measured by a lab HACH-type conduct meter. Electrical conductivity (EC) was measured by a WTW LF 330 conductivity meter and pH value was measured by Orion 250A pH meter. The procedure used included operating the system with different run times ($t=5-130$ min), different initial pH values (2-9), different CD ($i=0-14$ mA cm^{-2}), different NaCl concentrations ($0.1-0.3$ mol L^{-1}) and different H_2O_2 concentrations ($51-177$ mmol L^{-1}). Removal of COD and TC were investigated to determine the effectiveness of EFP. To adjust pH at 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 during EFP, buffer pH volumes were used to protect variations of pH volumes. For pH values of 2, 3, 6 and 7 phosphate buffer was used and for pH values of 4 and 5 acetate buffer was used. They (phosphate and acetate buffers) do not interfere directly in electrochemical process. The removal efficiency (RE) (in%) of TC and COD after EFP was determined using Eq. (7):

$$\text{RE}(\%) = \frac{C_i - C_t}{C_i} \times 100 \quad (7)$$

Where C_i and C_t denoted the measured parameters, COD (mg L^{-1}) and TC (MPN 100 mL^{-1}) in the feed solution and in the EF treated solution, respectively.

First-order kinetic analysis under the optimum operational conditions was obtained from by fitting the time-course performance data for MAS and COD removal:

$$\ln\left(\frac{C_i}{C_t}\right) = K_a t \quad (8)$$

Where C_i and C_t denoted COD (mg L^{-1}) concentrations at the beginning and time t (S) of the reaction and K_a is the apparent degradation reaction (the removal of COD) rate constant in EFP.

All experiments were conducted three times and the errors were between 0.71 and 0.88, being calculated with ICC (Intraclass Correlation Coefficient).

4. Energy Consumption and Instantaneous Current Efficiency

Required electrochemical energy consumed (EEC) to calculate the amount of oxidized organic load in electro-Fenton process is calculated and presented as the amount of the consumed electrochemical energy per each kilogram of COD and TOC [25,26]. Reaction 9 shows COD amounts were used to calculate EEC (in kWh kg^{-1} COD).

$$\text{EEC} = \frac{VIt}{3600 \times 10^3} \times \frac{1}{\Delta C \times V_R \times 10^{-6}} \quad (9)$$

Where V is the average cell voltage (V), I is the applied current (A), t is the electrolysis time (S), ΔC is the difference in COD in mg L^{-1} and V_R is the solution volume (L).

Instantaneous current efficiency (ICE) (in%) values were calculated from Eq. (10).

$$\text{ICE}(\%) = \frac{(\text{COD}_i - \text{COD}_{t+\Delta t}) F V_R}{(8I\Delta t)} \quad (10)$$

Where F is the Faraday constant (96,485.3 C mol^{-1}) and COD (in g O_2 L^{-1}) at times t and $t+\Delta t$.

RESULTS AND DISCUSSION

1. Effect of H_2O_2 and NaCl Concentration

MAS by EFP was carried out under different experimental conditions to investigate the effect of operating parameters on COD and TC removal by one at a time. The performance of sludge stabilization through EFP depends upon H_2O_2 concentration because it plays a major role in production of hydroxyl radical; therefore, the more production of the hydroxyl radical, the more mineralization occurs. The content of H_2O_2 is very important and affects highly operating costs as well as pollutant removal efficiency [9]. In this study, H_2O_2 was injected into the reactor by a syringe pump. Given that the only mineralization mechanism of activated sludge by using H_2O_2 separately (without adding another additional chemical) is indirect oxidation of organics by hydroxyl radical (reaction 3), the optimization of H_2O_2 is necessary and its concentration is an important and limiting parameter in EFP efficiency. However, when NaCl is applied another mechanism, named indirect oxidation, by active chlorine happens (reaction 6); in the case of H_2O_2 and NaCl simultaneously both mechanisms take place. Under constant conditions of $\text{pH}=3.0$; $i=10$ mA cm^{-2} ; $\text{NaCl}=0.22$ mol L^{-1} and $T=25$ °C, as the concentration of H_2O_2 went up (51 to 177 mmol L^{-1}), more reduction was observed in COD amount (Fig. 2). The concentration of 127 mmol L^{-1} was the optimized amount of H_2O_2 for MAS and during a time period of 120 min, COD amount declined from $7,800$ mg L^{-1} to $2,212$ mg L^{-1} . Studies have indicated the concentration of hydroxyl radical is entirely dependent upon two parameters: Fe^{2+} and H_2O_2 concentrations (based on Eq. (11)). Efficiency rose as the H_2O_2 to Fe^{2+} molar ratio went up, but additional increase in the H_2O_2 to Fe^{2+} molar ratio decreased the removal efficiency [13,19].



where k is the second-order rate constant ((mmol L^{-1}) $^{-1}$ min $^{-1}$); λ is the average life of hydroxyl radical (min); $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ are the concentration of ferrous ion (mmol L^{-1}) and H_2O_2 (mmol L^{-1}). Higher concentrations of H_2O_2 (over 177 mmol L^{-1}) had marginal effects on COD removal. At concentrations higher than the optimum value, H_2O_2 self-decomposed on the anode surface based

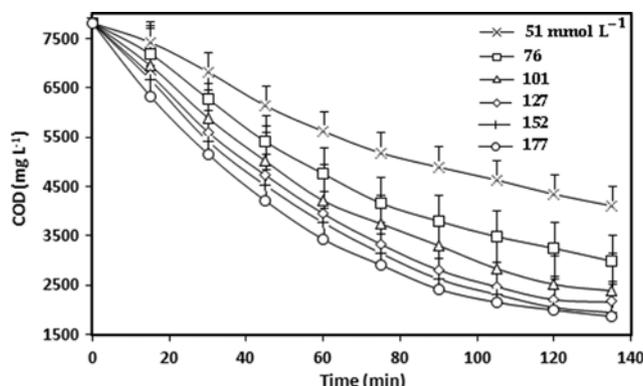


Fig. 2. Effect of H_2O_2 concentration on COD removal during mineralization of activated sludge by electro-Fenton process; operating conditions: $\text{pH}=3$, $i=10$ mA cm^{-2} , $\text{NaCl}=0.22$ mol L^{-1} and $T=25$ °C.

on the reactions 12 and 13. Moreover, reaction 14 indicated that H_2O_2 reacts with hydroxyl radical and generates hydroperoxyl radical (HO_2^\cdot) which has weak oxidation property [7]. Finally, the reduction in COD removal may be due to combination of two hydroxyl radicals to form H_2O_2 (reaction 15). On the other hand, the formation of HOO^\cdot , which has significantly less reactive property than hydroxyl radical, also reduces the reaction rate [14].



The excess content of H_2O_2 in the solution after the treatment entails a toxicity which may exceed the corresponding limit. Obviously, determination of the optimum amount of Fenton's reagent is difficult as it is highly dependent upon wastewater quality [9].

Hydroxyl radical is also produced without using Fenton. Of course, this produced amount is very little that can be ignored. The iron electrode does not play a role in hydroxyl radical generation. The application of iron without using H_2O_2 in electrochemical cell is accompanied by releasing iron ion from the surface of anode and during its reaction to hydroxyl ions in water, metal hydroxyls are formed which are active in electro-coagulation process. For this

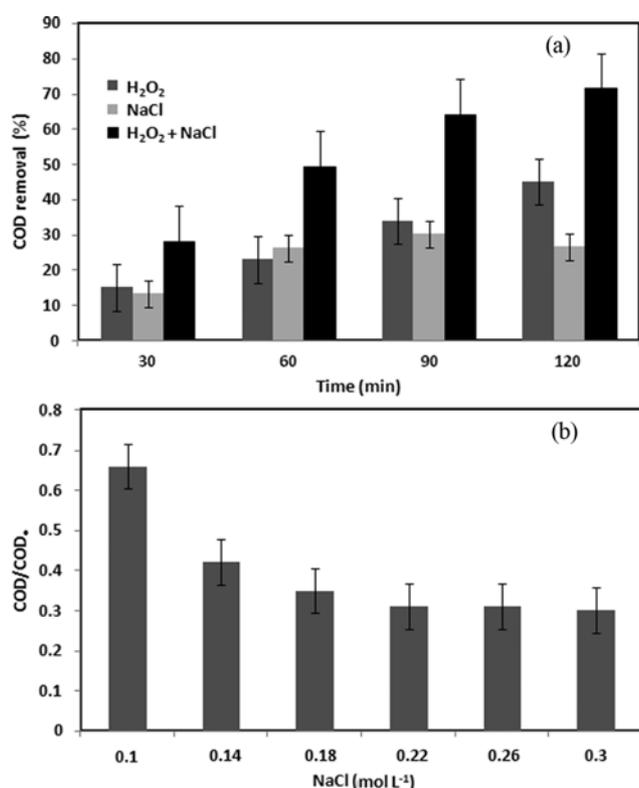


Fig. 3. COD removal by electro-Fenton process. (a) A comparison among H_2O_2 and NaCl separately and H_2O_2 plus NaCl; (b) the optimization of the NaCl concentration on COD removal. Operating conditions: $\text{pH}=3$, $i=10 \text{ mA cm}^{-2}$, $t=120 \text{ min}$, $\text{H}_2\text{O}_2 = 127 \text{ mmol L}^{-1}$, $\text{NaCl}=0.22 \text{ mol L}^{-1}$ and $T=25^\circ\text{C}$.

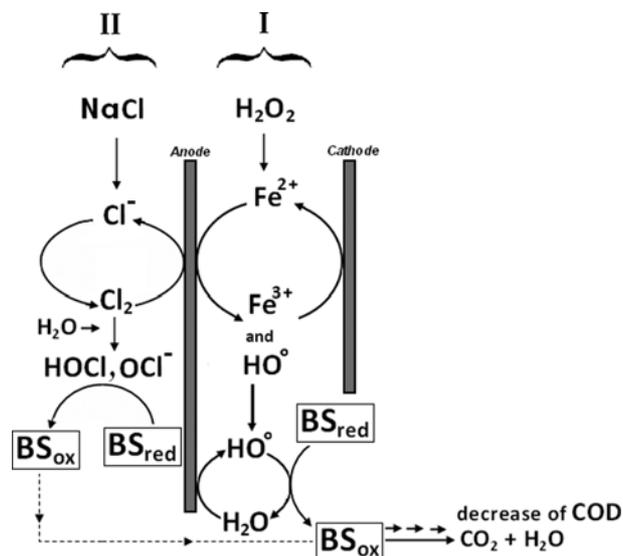


Fig. 4. Schematic diagram of electro-Fenton process for mineralization of activated sludge. (i) mediated based on the electro-generation of HO^\cdot ; (ii) mediated based on the electro-generation of active chlorine; and (i) and (ii) overall indirect oxidation double mediated based on the electro-generation of HO^\cdot and active chlorine.

reason, it can be said that the oxidation of organic matters owing to hydroxyl radical's formation through iron (without using Fenton) is negligible.

Based on the results plotted in Fig. 3(a), when only electro-Fenton was applied, just 47% of COD was reduced; however, while NaCl was applied, as a supporting electrolyte ($0.1\text{--}0.3 \text{ mmol L}^{-1}$), the efficiency went up to 72% by means of indirect oxidation double-mediated based on the electro-generation of hydroxyl radical and active chlorine (see Fig. 4) (There is no possibility to measure active chlorine because it is generated and then used in situ. Thus, its longevity is not enough to be measured directly.). Studies by Zhou et al. [9] and Ahmed Basha et al. [26] indicated that in the presence of chloride active chlorines like hypochlorite, chlorine dioxide and chlorine are generated electrochemically; consequently, indirect oxidation takes place, which could greatly improve the overall electrochemical abatement of organic pollutants.

Fig. 3(b) shows that the amount of COD removal reaches a peak at the optimized amount of 0.22 mol L^{-1} of NaCl. In addition to indirect MAS by hydroxyl radical, the use of NaCl plays an important role in reducing time of MAS, thereby decreasing dramatically the consumed energy. Furthermore, NaCl prevents sedimentation of Ca^{2+} or Mg^{2+} ions on the electrodes' surfaces (that takes place in the presence of some anions like HCO_3^- and SO_4^{2-}); also, by manual cleaning, ohmic resistance was reduced and then energy efficiency increased [27-29]. Moreover, electrolytes enhanced the conductivity of the solution, thereby improving the electron transfer, which causes an increase in the electro-Fenton reaction [30]. In practice, these are designers and operators to make their decision that is it worth using NaCl in order to improve the efficiency or not; here, the cost-benefit analysis is essential. In this study, we found that the efficiency increased dramatically by using NaCl as a supporting

electrolyte. As regards other electrolytes, in accord with the study of Zhou et al. [7], although ionic capability and conductivity of Na_2SO_4 are higher than those of NaCl and it generates more H_2O_2 as well, NaCl produces different kinds of ions which are effective in pollutant removal and germicide. Moreover, the use of Na_2SO_4 at high concentrations causes the consumption of hydroxyl radical by SO_4^{2-} [16].



2. Effect of pH

pH plays a basic role in EFP and this process is pH-sensitive since pH can affect the iron solubility, complexation, and redox cycling between 2^+ and 3^+ states of iron [31]. Previous studies have shown that the performance of EFP is better under acidic conditions because hydroxyl radical can remove pollutants better; and in the presence of H^+ , H_2O_2 is decomposed more and also hydroxyl radical are produced more [9,14,16,26,32]. To examine the effect of the pH variable in MAS, the optimum figures of $t=120$ min, $i=10$ mA cm^{-2} , $\text{NaCl}=0.22$ mol L^{-1} and $\text{H}_2\text{O}_2=127$ mmol L^{-1} were used (see Fig. 5). A 120 min operating time along with the optimum pH (3.0) led to 71.4% efficiency in COD removal. Some studies have focused on the effect of pH on organic matter mineralization. Their findings have shown that acidic pHs, particularly pHs between 2.0 and 4.0, have the highest efficiency. These studies show that at pH value of 3.0, (as the optimum pH), has extensively been used in different applications of EFP [16,32]. Therefore, in later stages, we used this to optimize other variables. At pH of 6.0 or higher, the efficiency of COD removal declined to less than 50%, confirmed by the results of other studies [7,14,18,32]. This is due to the fall in oxidation potential of hydroxyl radical with a rise in pH. Under acidic conditions, hydroxyl radical is more powerful. As pH was raised over 7, hydroxyl radical was quickly converted to its conjugate base $^\circ\text{O}^-$ and reacted more gradually than did hydroxyl radical. On the other hand, at high pHs, the production of hydroxyl radical declined because of the formation of insoluble ferric hydroxo-complexes. These complexes would form more $[\text{Fe}(\text{OH})_4]^-$ when pH was higher than 9 [14]. A fall in efficiency is not just on account of deactivation of the catalytic action of Fe^{2+} ions from the forma-

tion of ferric hydroxide complexes and then leading to decrease the generation of hydroxyl radical; but also it is by decomposition of H_2O_2 to O_2 and H_2O , leading to lose its oxidation power [16, 19]. At higher pHs, not only pH itself but also aqueous carbonate species (CO_3^{2-} and HCO_3^-) scavenging hydroxyl radical decrease the removal efficiency [9]. Wang et al. [32] indicated that low pH (in particular lower than 2) decreases the efficiency for the following reason: Iron species form stable complexes with H_2O_2 , resulting in deactivation of catalysts. An important point to make here is that in the case of very low pH (<3) H^+ acts as HO^\bullet scavengers. In this situation, the reaction is slowed down because of the creation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, reacting more slowly with H_2O_2 in comparison with that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$. The H_2O_2 becomes solvated in the presence of high content of H^+ ions to form stable oxonium ion $[\text{H}_3\text{O}_2]^+$. An oxonium ion makes peroxide electrophilic to increase its stability and substantially reduces the reactivity with Fe^{2+} ion [14]. The bottom line is that pH adjusting is essential at the beginning of the reactions and it plays a significant role in pollutants destruction [31].

3. Effect of Applied Current Density

The electrical production of Fe^{2+} , and consequently production of hydroxyl radical (reactions 1 and 2) as well as hypochlorite ion in the reactor had a direct relationship with applied CD. The optimization of this variable, in addition to achieving highest efficiency in COD removal and MAS, prevented the application of high CDs, and consequently, the useless increase of consumed energy in MAS. Thus, at the constant charge passed of 7200 colons, CD of 3.75-12.5 mA cm^{-2} was used to optimize this parameter (Fig. 6). At CD of 10 mA cm^{-2} , the highest COD removal, 71%, was acquired, but when CD exceeded this amount, no increase was observed. One of the reasons may be that there are some refractory compounds and final by-products in the sludge, so that increasing the CD up to more than 12.5 mA cm^{-2} could not lead to more COD removal. The higher removal in EFP can be associated with the ferrous catalyst due to a great increment of the hydroxyl radical level in the solution bulk derivable from the catalytic decomposition of H_2O_2 (reactions 2) [31]; hence, the electro-generation of ferrous catalyst to enough concentrations is crucial, which is dependent upon applied

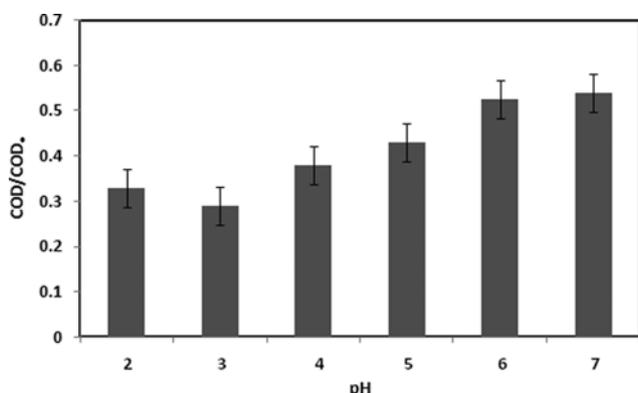


Fig. 5. Effect of pH value on COD removal during mineralization of activated sludge. Operating conditions: $i=10$ mA cm^{-2} , $t=120$ min, $\text{H}_2\text{O}_2=127$ mmol L^{-1} , $\text{NaCl}=0.22$ mol L^{-1} and $T=25$ $^\circ\text{C}$.

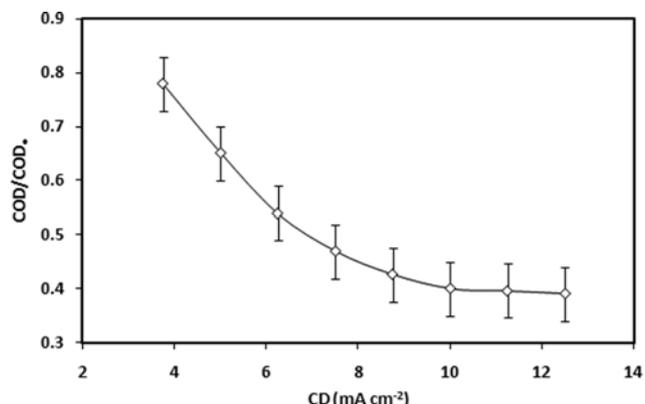
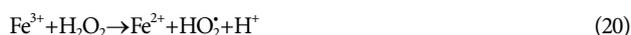


Fig. 6. Effect of applied current density on COD removal during the oxidation of activated sludge. Operating conditions: $\text{pH}=3$, Charged Passed= 36.9 C cm^{-2} , $\text{H}_2\text{O}_2=127$ mmol L^{-1} , $\text{NaCl}=0.22$ mol L^{-1} and $T=25$ $^\circ\text{C}$.

CD; otherwise at low contents of ferrous catalyst, the oxidation of H_2O_2 into O_2 at the anode is remarkable. However, the application of high CDs is not helpful enough in organic matters destruction because H_2O_2 is oxidized first [14,16,31].

The application of high CDs leads to a decrease in efficiency for the following reasons: First, H_2O_2 is oxidized (reactions 17 and 18) [14,16,31]. Second, Fe^{2+} in competitive reactions reacts with hydroxyl radical and forms Fe^{3+} (reaction 19) and according to the Fenton-like reaction, Fe^{3+} reacts with H_2O_2 and produces HO_2^\cdot (reaction 20) [7,13,14,31].



Fe^{3+} precipitates as $\text{Fe}(\text{OH})_3$ at high concentrations and cannot convert to Fe^{2+} again. In this study, we observed that at the CDs of 12.5 mA cm^{-2} and higher, mineralization efficiency was lower than that at CD of 10 mA cm^{-2} . Since Fe^{2+} consumption is quicker than its production through Fe^{3+} reduction, regeneration of Fe^{2+} is considered as a limiting factor because there are several species such as H_2O_2 , HO_2^\cdot , O_2^\cdot , and organic radical (R^\cdot), which can lead to a slow reduction of Fe^{3+} [13]. Even though an increase in CD results in more Fe^{2+} generation, and consequently more hydroxyl radical production, the rise in CD increases the applied potential proportionately. Therefore, it is suggested that the CD is kept limited to prevent adverse effects such as heat generation and higher energy consumption [28]. Thus, increasing CD causes H_2O_2 to be converted to two molecules of water (reaction 21) [32].



In this process, Fe^{2+} was provided electrochemically from the sacrificed anode and hydroxyl radical was generated as a result of reaction between H_2O_2 and Fe^{2+} which this reaction changed Fe^{2+} to Fe^{3+} . On the surface of cathode the produced Fe^{3+} was changed to Fe^{2+} reversibly to be used for creating hydroxyl radical. At the end of the process, the separated iron was disposed from the reactor alongside the treated sludge. Note that the amount of this residual Fe was $20\text{--}40 \text{ mmol L}^{-1}$.

4. Effect of Operating Time

Fig. 7(a) shows that an increase in time results in an increase in the amount of MAS (for all CDs). The highest decline of COD happened at CD of 10 mA cm^{-2} in 120 min. However, after 120 min and at CDs of over 10 mA cm^{-2} no more COD removal was observed. Some organic compounds may be in the sludge that cannot be decomposed even at high CDs and these operating times. Electro-chemical decrease of COD during operating time follows a first-order reaction (corrective coefficient 0.97) for $3.75\text{--}12.5 \text{ mA cm}^{-2}$ and is related to CD, passed charge, concentration of H_2O_2 and the supporting electrolyte, and pH value.

According to Chu et al. [13], mineralization current efficiency is a key parameter for evaluating the effectiveness of electrochemical methods. Therefore, ICE (based on Eq. (10)) for CDs of 7.5, 8.75, 10, and 11.25 mA cm^{-2} was calculated (Fig. 7(b)). As can be clearly

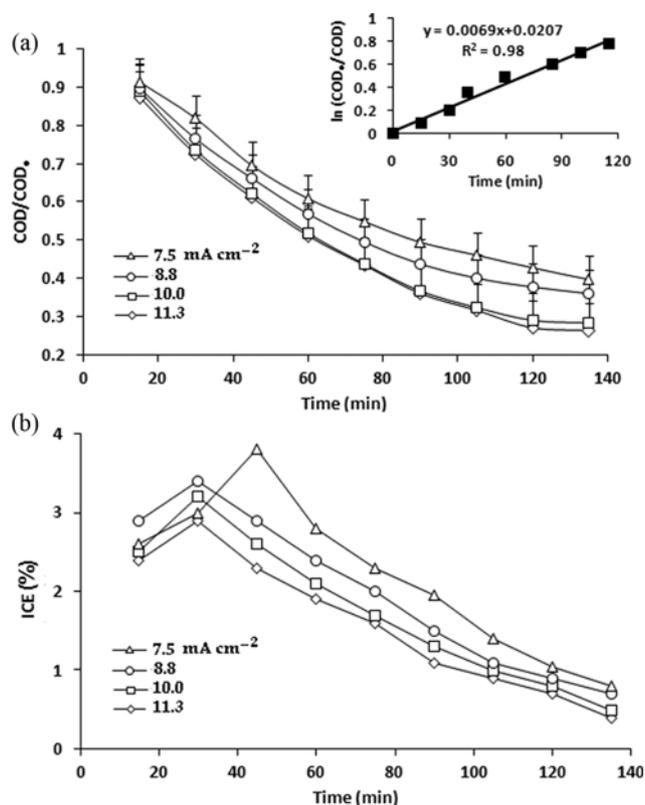


Fig. 7. (a) Effect of operating time on COD removal; (b) evolution of Instantaneous current efficiency (%) from Eq. (10) during the mineralization of activated sludge by electro-Fenton process; operating conditions: $\text{pH}=3$, $\text{H}_2\text{O}_2=127 \text{ mmol L}^{-1}$, $\text{NaCl}=0.22 \text{ mol L}^{-1}$ and $T=25^\circ\text{C}$.

seen, ICE amounts rose to 30–40 min, but, then, declined to 125 min. This is due to quick decomposition of simple organic compounds by produced radicals at the beginning of the reaction because of the high availability of the organic compounds. As time passed, bio-refractory organic compounds were decomposed slowly by EFP, or even they were not decomposed which remain in the solution. Previous studies have reported higher mineralization current efficiency values at the early stages of the electrolysis, which shows a fast conversion of organics into CO_2 , followed by a deceleration at long electrolysis times as a consequence of the loss of organic matter and the formation of more difficultly oxidizable organic intermediates [13,31]. The ICE marginally declines, suggesting that the byproducts formed over that period are more easily oxidized by hydroxyl radical than by the intermediates formed over that time. However, higher volumes of ICE at the beginning of the reaction are attributed to the high concentrations of activated sludge. At higher concentrations of organic compounds, higher mineralization current efficiency was observed [31].

Since the sludge used in this study was taken from slaughterhouse effluent, TC index was used to test the amount of microbial reduction index. The effect of EFP on TC reduction was investigated and the results are given in Fig. 8. Since the pH of 3 had been selected as the optimum figure for sludge mineralization, its effect on TC reduction was investigated. A 99.0% decrease of TC was observed in the first 10 min, and it reached to 100% in 30 min, while

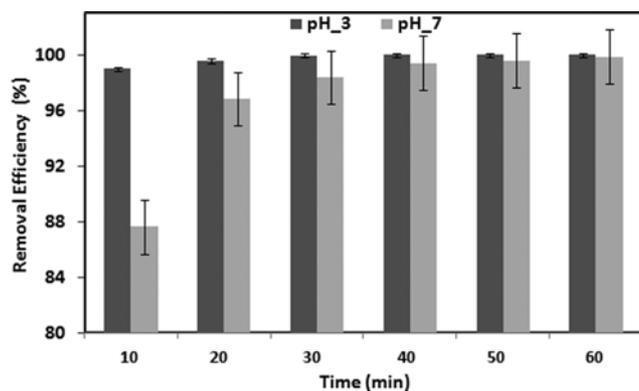


Fig. 8. TC removal during the oxidation of activated sludge. Operating conditions: $i=10 \text{ mA cm}^{-2}$, $\text{H}_2\text{O}_2=127 \text{ mmol L}^{-1}$, $\text{NaCl}=0.22 \text{ mol L}^{-1}$ and $T=25^\circ\text{C}$.

in the case of pH of 7, the amounts of TC removal at the time periods of 10, 30 and 60 min were, respectively, 87.6%, 98.4%, and 99.9%. Previous studies have shown the percentage of the initial concentration of bacteria destruction is attributed to both treatment time and the square of CD obeying the kinetic model $\alpha=ki^2t$ [33]. Barrera-Díaz et al. [34] showed that electro-coagulation at pH of 4.0 removed approximately 93.0% of TC. The mechanisms of TC removal through electro-coagulation are attributed to the following ways: adsorption of TC on the surface of metal colloids, the destruction of cell membrane of the bacteria by means of potential difference produced by the applied CD as well as its removal from the wastewater [35]. Another study also showed that electrochemically oxidation induced by in situ generation of Fenton's reactive has a better efficiency in TC removal (99.9%) compared to electro-coagulation [36]. EFP can remove TC in higher rates than other techniques on account of four main parameters affecting TC removal: (i) the decrease in sludge's pH so as to mineralize the sludge by electro-Fenton (pH=3.0); (ii) the presence of hydroxyl radical; (iii) the presence of active chlorines generated over the process. In addition to indirect oxidation of existing organic materials in the sludge, they play a role in removing microbial agents (based on the reactions 4-6); and, (iv) the electric field produced between two electrodes may damage cell membrane. The stranded bacteria among the sludge's flock are among those limiting factors that affect bacteria's destruction by the produced radicals.

5. Energy Cost

The amount of consumed energy was calculated by Eq. (9) for amounts of Fig. 7. Results are given in Fig. 9. As can be seen, an increase in consumed energy has a direct relationship with the input CD and the average of applied cell voltage. Anotai et al. [37] concluded that CD increase promote both the amount of efficiency and rate of the Fenton reactions. For the applied CD of 10 mA cm^{-2} (the optimum content) with different operating times (15-135 min), these amounts range between $19.5\text{-}32.1 \text{ kWh kg}^{-1} \text{ COD}$. In the optimized reaction time of 120 min, the amount of consumed energy for oxidation of activated sludge of poultry slaughterhouse wastewaters was $28.7 \text{ kWh kg}^{-1} \text{ COD}$. The application of CDs higher than 11.25 mA cm^{-2} consumes more energy as well as decreases efficiency. For optimum conditions of CD (10 mA cm^{-2}) and operating

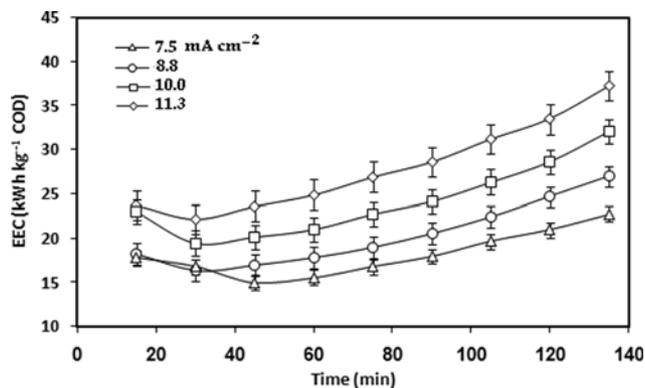


Fig. 9. Electrochemical energy consumption for the experiments of Fig. 7(a); operating conditions: pH=3, $\text{H}_2\text{O}_2=127 \text{ mmol L}^{-1}$, $\text{NaCl}=0.22 \text{ mol L}^{-1}$ and $T=25^\circ\text{C}$.

time (120 min), EEC of achieved sludge was calculated at $88.8 \text{ kWh ton}^{-1}$.

Appropriate mixing, arrangement and position of the electrodes are very important in this method, because these factors highly affect the efficiency and energy consumption. Otherwise, biosolids are carried to the surface of the liquid in inappropriate mixture, that is, out of reach of electrodes and as a result oxidants (OCI^- and HO^\bullet). Consequently, the efficiency of mineralization and microbial removal seriously fall and energy consumption rises. This is because sludge flotation is caused by electro-generation of microbubbles of O_2 and H_2 [29]. Therefore, this problem should be solved by a suitable cell arrangement and adequate mixing. In this study, we used, in addition to a magnetic mixer, a mechanical mixer with sufficient blade with the size of up to 300 r/min for sludge mixing, and the electrodes were bar-shaped and appropriately arranged in the cell environment. To create an appropriate mixture, the mechanical mixer should be placed in the center of the cell; in this case, first, it prevents sludge flotation, and second, it increases the effective contact surface between the sludge and electrode. All this improved the efficiency and saved energy as well. Despite the fact that EFP requires electricity, it has many upsides, introducing the process as a proper option for sludge mineralization. Some of advantages are as follows: Unlike biological systems, it does not need a period time of adoption, as total operating time (maximum 2.5 hours) is rather shorter compared to other methods. Moreover, investment costs are low. In the case of complete mineralization, final products are CO_2 and H_2O , which are eco-friendly. It is not affected by environmental conditions as temperature changes [29]. All stabilization and disposal systems of activated sludge require a significant amount of energy; incineration and drying, to name but a few. Electrochemical ways, particularly EFP, have appropriate energy efficiency. Previous studies have shown that the upside of using electrochemical techniques in environmental applications includes environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost-effectiveness [26,38].

CONCLUSION

Mineralization of activated sludge by means of the EFP process

through double-mediated based on HO[•] electro-generation and active chlorine was studied experimentally to reach suitable COD and TC removal efficiency. EFP- mediated based on the electro-generation of hydroxyl radical does not have a high removal rate (maximum 47.0% COD reduction). However, by using the appropriate electrolyte support, NaCl in this study, in addition to an increase in conductivity, different kinds of active chlorines are generated with an important role in mineralization (up to 72%). It is very crucial to measure the optimum points of CD, H₂O₂ and NaCl concentrations and pH values. Obviously, in the case of high concentrations of H₂O₂ (over 127 mmol L⁻¹), CDs (over 10 mA cm⁻²), pH values above 4 and under 2 removal efficiency decreased due to some harmful reactions which hydroxyl radical is scavenged or produced less. By large, the simplicity of the reactor, enough efficiency, low investment costs, avoiding using chemicals, and short operating time are among the plus factors of this measure.

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