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Electrochemical oxidation of activated sludge by using direct and indirect anodic oxidation

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ABSTRACT

The electrochemical oxidation of activated sludge (EOAS) was studied by direct anodic oxidation on the surfaces of stainless steel and graphite electrodes as well as by indirect anodic oxidation on Pb/PbO_2 surface. The effects of several operating parameters such as current density, charge passed, initial pH, mixing speed, and configuration, and position of electrodes on the removal rate of chemical oxygen demand (COD), total and fecal coliform were investigated. The experimental data indicated that COD removal rates were, respectively, 66.9 and 77.5% in direct and indirect methods. The results also showed that the Pb/PbO_2 electrode through indirect electrooxidation mediated based on the electrogeneration of physisorbed hydroxyl radical and other oxidants like active chlorine has higher mineralization rates and consumes the least energy. Over 99% of total and fecal coliform was removed, which is mainly attributed to electrogeneration of hypochlorite and chloride ions in the aqueous solution. Kinetic trend of COD and total and fecal coliform removal for Pb/PbO_2 electrode were obtained. In order to better function of EOAS, selection of suitable mixing speed and configuration and position of electrodes are essential.

Keywords: Activated sludge; Electrochemical treatment; Direct and indirect anodic oxidation

1. Introduction

Over the past few decades, huge amounts of sludge have been produced from various wastewater treatment plants owing to sharp development and industrialization and urbanization, and it is expected that it will be generated much more in the future. Sludge is yielded from different types of wastewater and requires to be processed enough to meet environmental discharge standards; of course, its later reuse and disposal are very crucial. Sludge processing costs 60% of the whole capital cost of plants [1,2]. Moreover, sludge management is troublesome and difficult work, particularly in industrialized societies. Due to strict

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[1] The first and the second authors have the same contribution.

laws for sludge disposal and environmental issues, its treatment is very important [2,3].

In spite of advantages of biological aerobic and anaerobic methods (decreasing the volume, removing the smell and pathogens, low energy need, and recycling methane), such ways need high detention time. Furthermore, particularly, intracellular biopolymers solubilization and conversion to the lower molecular weight compositions of solid degradable organics like sludge by hydrolysis is a rate restricting phase [2,4,5]. Earthworm micro-organism interaction which is another biological method for sludge stabilization needs a high detention time of about 160 day [1]. Other physical, mechanical, and chemical ways to enhance sludge reduction and stabilization, for example, thermal and ozone pretreatment [6], ultrasonic [2], calcined aluminum salts [7], and fly ash [8] are not economical [9].

To our knowledge, the application of electrochemical oxidation of activated sludge (EOAS) has not been seen before. Anodic oxidation as one of the advance oxidation processes also so-called "electrochemical incineration processes" [10] has widely been used to treat different kinds of organic matters in wastewaters. A few applications of which, that have had good results, are as follows: electrochemical treatment of organic matters and colloids in municipal wastewater [11], small organic molecules [12], organic polymers [13], pharmaceutical wastewater [14], landfill leachate [15], ethanol and methanol [16], petroleum refinery wastewater [17], herbicides [18], azo dyes [19], and non-biodegradable organic contaminants [20].

EOAS may be attributed to: (i) direct anodic oxidation on anode surface (Eq. (1)) (Biomass (BM) as indicator of activated sludge), (ii) indirect anodic oxidation (Eqs. (2) and (3)), (iii) indirect electrochemical oxidation mediated based on the electrogeneration of physisorbed HO° at the anode surfaces (Eqs. (4) and (5)) [10,19,21], and (iv) indirect electrochemical oxidation is mediated by electrogenerated oxidants such as peroxydisulfates (in the presence of SO_4^{2-}) and active chlorine (in the presence of Cl^- (Eqs. (6)–(10)) [21–23].

$$BM_{red} \longrightarrow BM_{ox} + ne^- \tag{1}$$

At the surface of electrode:

$$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 4H^+ + 2e^- \tag{2}$$

In the solution:

$$PbO_2 + BM_{red} \longrightarrow Pb^{2+} + BM_{ox} \tag{3}$$

$$PbO_2 + H_2O \longrightarrow PbO_2(HO^{\circ}) + H^+ + e^- \tag{4}$$

$$PbO_2(HO^{\circ}) + BM_{red} \longrightarrow PbO_2 + BM_{ox} \tag{5}$$

$$PbO_2(HO^{\circ}) + Cl^- \longrightarrow PbO_2(^{\circ}OCl) + H^+ + 2e^- \tag{6}$$

$$PbO_2(^{\circ}OCl) + Cl^- \longrightarrow PbO_2 + 1/2O_2 + Cl_2 + e^- \tag{7}$$

$$Cl_2 + H_2O \longrightarrow H^+ + Cl^- + HOCl \tag{8}$$

$$HOCl \longleftrightarrow H^+ + OCl^- \tag{9}$$

$$BM_{red} + OCl^- \longrightarrow Cl^- + BM_{ox} \tag{10}$$

This paper gives a detailed description of EOAS using graphite and stainless steel anodes for direct anodic oxidation and Pb/PbO_2 anode for indirect anodic oxidation. The Pb/PbO_2 electrode was used because it is an inexpensive material, commercially available, and prepared easily and rapidly as well as it has low resistivity, good chemical stability, and a high surface area [10,19,21]. Actual activated sludge was applied in this research and electrochemical treatment was done in a batch reactor to evaluate the effects of the key variables, i.e. initial pH, charge passed, current density (CD), and cell parameters (mixing speed and cell design) on the amount of chemical oxygen demand (COD) removal (values have been related to the total concentration of organic matter in the solution) [24], total coliform (TC), and fecal coliform (FC) removal. Energy consumption and mineralization current efficiency were determined and briefly discussed in terms of environmental, economical, and technical features.

2. Methods

2.1. Experimental unit

A schematic representation of the reactor used in this study is shown in Fig. 1. EOAS was carried out in a 600 mL glass reactor with 450 mL of effective volume. When the plate electrodes were used, three and four monopolar electrodes were placed in the cathode and anode, respectively, with dimensions of 12 × 5 × 0.2 and 12 × 5 × 0.4 cm in the middle of the cell (Fig. 1(a)). In the case of rod electrode, six electrodes were placed per cathode and anode with dimensions of 1 × 12 cm for all types of electrodes in around of the cell (Fig. 1(b)). The distance among electrodes (1 cm) and effective electrode area (195 cm^2) was fixed in all experiments. The electrodes were connected to the

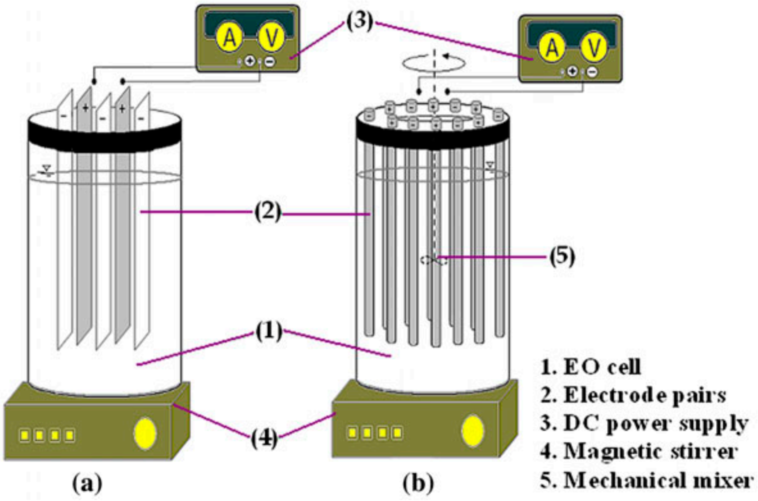

Fig. 1. Cell design for EOAS reactors. (a) monopolar plate electrodes and (b) rod electrodes.

terminals of a DC power supply (Aram Tronik CO. Iran) characterized by the ranges 0–6 A for current and 0–40 V for voltage. All experiments were conducted under mixing to ensure good dispersion of the activated sludge and effective contact with electrodes' surfaces by means of a magnetic stirrer and a mechanical mixer.

2.2. Chemicals and activated sludge

The samples ($N = 20$) were taken from disposed activated sludge of the secondary sedimentation tank in the poultry slaughterhouse wastewater treatment plant of Goshtavaran Company, Hamadan, Iran. Measured properties of raw activated sludge samples are shown below: COD = 7,090 ± 550 mg/L, FC = $93 \times 10^5 \pm 1 \times 10^4$ MPN/100 mL, TC = $23 \times 10^6 \pm 1 \times 10^5$ MPN/100 mL, total solids = 6,440 ± 810 mg/L, total suspended solids = 5,725 ± 675 mg/L, total dissolved solid (TDS) = 695 ± 150 mg/L, electroconductivity (EC) = 1,480 ± 290 µS/cm, Cl^- = 604 ± 95 mg/L, total Kjeldahl nitrogen = 998 ± 110, temperature = 21 ± 3˚C, and pH 7.2 ± 0.3. The obtained samples were transported to the laboratory at 4˚C, and then were rapidly examined. It was tried to acquire fresh samples from the wastewater treatment plant to repeat the experiments.

Sulfuric acid and sodium hydroxide were used to adjust the pH of solutions. All products were provided from Merck Company with purities more than 99.5%. Prior every run, the electrodes were cleaned with HCl solution (15% Wt.) and then washed with distilled water. All the samples were tested in duplicate to ensure data reproducibility, and an additional measurement was carried out, if necessary.

2.3. Methodology

Conductivity and TDS were measured by using conductimetry (HACH Conductivity/TDS meter; model No. 44600) and pH was determined by a lab pH meter (Model EC20, HACH Co., USA). In order to investigate the pH variable during the EOAS process, pH values of 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0 were used. COD, TC, and FC were measured in accordance with the Standard Methods [25]. The sludge digests prior to COD determination. All experiments were performed at room temperature (25˚C). In order to provide the Pb/PbO_2 electrode, it was put in sulfuric acid (10%) in the CD of 10 mA/cm^2 at 25˚C for 90 min (Eqs. (11) and (12)) [26]:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- \tag{11}$$

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \tag{12}$$

In order to optimize the variables in this study, first, three variables: initial pH, CD, and charge passed were optimized by keeping two parameters fixed and changing the third one to optimize it through investigating the amount of COD, TC, and FC removal. In this case, fixed figures—charge passed = 7.11–56.84 C/cm^2 and CD = 2.56–12.82 mA/cm^2, and changing amounts of pH values between 2 and 9 were used; next, after optimizing these three variables, the optimized amounts were applied to optimize mixing speed ranging from 100 to 400 rpm. Moreover, the best state of cell design was achieved in this research. Finally, all optimized data were used to calculate the consumed energy.

3. Results and discussion

3.1. Effect of anode material

To remove organic matters, glassy carbon, carbon, gold, steel, dimensionally stable anodes (DSA) such as TiO_2 nanotubes/Sb-doped SnO_2, RuO_2, IrO_2, PbO_2, and BDD, and so forth have vastly been used in literature studies [20,27,28]. Based on Fig. 2, graphite and stainless steel electrodes were applied for direct EOAS, based on Eq. (1) and Pb/PbO_2 for indirect EOAS, according to Eqs. (2)–(5).

Fig. 3 shows the effect of anode type on EOAS with $CD = 8.97\,mA/cm^2$ (in 75 min); the results illustrated that the percentages of COD removal by Pb/PbO_2, graphite, and stainless steel were 75.9, 67.7, and 36.6%, respectively. TC and FC were removed over 98%; stainless steel had low efficiency in EOAS, but it was very effective in TC and FC removal. Compared with stainless steel, graphite had better efficiency of EOAS, but use of which at high CDs can lead to mechanical ruin of the anode, which raised the turbidity of the oxidized activated sludge. PbO_2 is an electrical conductor cover that prevents the surface against both dissolution (in pure lead) and chloride formation ($PbCl_2$). Thus, PbO_2 was prepared in accordance with Eqs. (11) and (12). In comparison with stainless steel and graphite (as active electrodes), Pb/PbO_2—as an inactive DSA—was very effective in EOAS. A series of reactions are effective in the degradation of organic matters in sludge. However, in view of the fact that the major mechanism of sludge mineralization by using the Pb/PbO_2 electrode takes place by physisorbed HO°, better efficiency of this electrode compared to two other ones is attributed to week reaction HO° and the surface of the electrode and, in turn, hydroxyl radicals react easily with organic matters. On the other hand, since there is a strong reaction between hydroxyl radicals and the electrodes of stainless steel and graphite, these radicals cannot easily destroy organic matters.

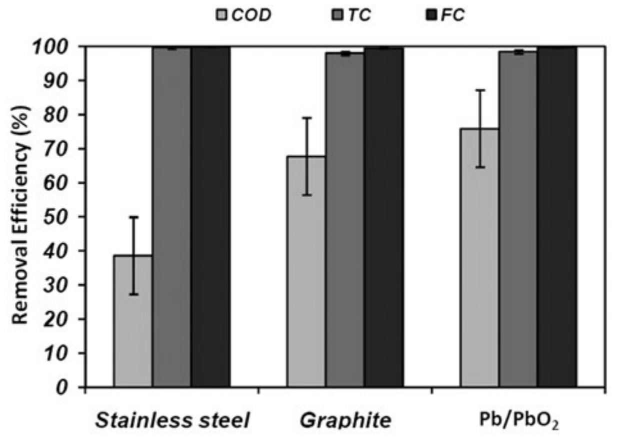

Fig. 3. The effect of anode type on COD, TC, and FC removal (%); $CD = 8.97\,mA/cm^2$ and $t = 75$ min.

In the course of time, calcium and magnesium sediments (Ca^{+2}, Mg^{+2}) along with harmful anions: SO_4^{2-}, HCO_3^- appeared on electrodes' surface raising ohmic resistance of the electrochemical cell and consequently

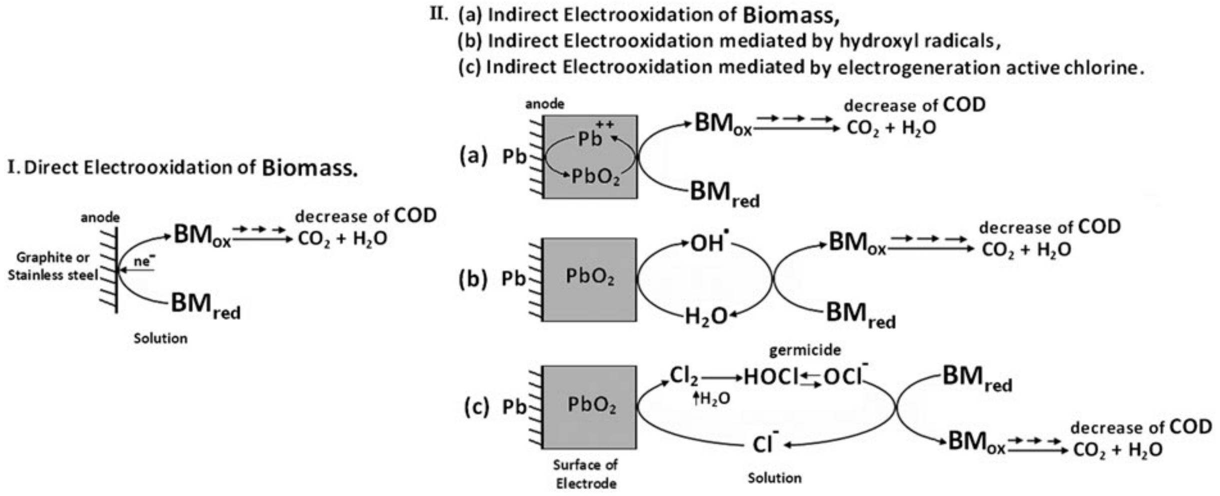

Fig. 2. Direct and indirect electrooxidation of activated sludge using stainless steel and graphite electrodes and Pb/PbO_2.

energy consumption went up [24]. Handy and periodic cleaning of electrodes and increasing ionic power i.e. soluble electrical conductivity can prevent ohmic resistance [29]. In the presence of Cl^- as the amount of electrical conductivity and consequently the efficiency of CD increased, the consumed energy and the effects of these anions decreased. Besides, chloride ion was used to raise the formation of strong oxidants for removing FC and TC. However, based on Eqs. (6)–(10), it has an important role in indirect EOAS.

3.2. Effect of pH

pH had a little effect on EOAS and COD reduction. Acidic pH was slightly more effective than both neutral and alkaline pHs. Therefore, acidic pH was used for further experiments. Meanwhile, under acidic pHs hydroxyl radical had better oxidation property, which improved organic matters destruction. Moreover, because of the presence of Cl^- ion in the solution, Cl_2 is created electrochemically (Eqs. (6) and (7)) thereby producing HOCl (Eq. (8)) in water [23]. Furthermore, due to the fact that the germicidal effect of HOCl, as the strongest disinfectant of chlorine in acid pH, is 80% more than those of neutral and alkaline pHs and also the fact that this disinfectant is produced as the result of competing with OCI in low pHs [30], the acidic pH was selected for more production of HOCl and more significant removal of FC and TC. The optimum pHs for removal of COD, TC, and FC for the electrodes of stainless steel, graphite, and Pb/PbO_2 were 2, 2, and 4, respectively. These values were separately applied for each electrode in next steps. The obtained results in the experimental conditions showed the best value of pH. However, EOAS performance was good in all pH values; operators, under real circumstances and practical works, can apply neutral pHs (7.2 ± 0.3). In this case, COD removal efficiencies were 70.5, 64.3, and 31.5% for Pb/PbO_2, graphite, and stainless steel, respectively. It must be pointed that in this study buffer pHs were used to optimize pH value, thereby controlling the pH changes to 0.1; otherwise, it would not be controllable and its amount would increase by between 0.8 and 2; in these conditions, the solution was not acidic.

3.3. Effect of CD and evaluation of mineralization current efficiency

CD is a very important variable particularly in terms of controlling electrochemical reaction rates. The electrode efficiency is also dependent on applied CD [31]. Fig. 4(a) and (b) present CD effect on COD, TC, and FC removal; at fixed conditions (surface and gap distance between the electrodes, charged passed temperature, and pH), as CD increased, the amounts of EOAS, FC, and TC removal rose for all electrodes. When CD increases, direct EOAS on the surface of electrodes and indirect EOAS by formation of greater quantities of hydroxyl and hypochlorite radicals increase and organics are more quickly oxidized [20]. In the constant charge passed of 18.94 C/cm^2, the optimum amounts of CD for stainless steel, graphite, and Pb/PbO_2 were, respectively, 7.69, 8.97, and 8.97 mA/cm^2. The amounts of COD, TC, and FC were, respectively, 42, 99.9, and 9.99% for stainless steel, 63.5, 98.8, and 99.7% for graphite, and 77.6, 99, and 99.6% for Pb/PbO_2.

A rise in CD results in more electrical energy consumption and this increase more than the optimum content wastes more energy in the form of heat and raises solution temperature. Although temperature increase by using high CDs leads to a rise in electrochemical reaction rates and as well as germicide amounts, these CDs are not economical [32,33]. Moreover, the application of CDs more than the optimum

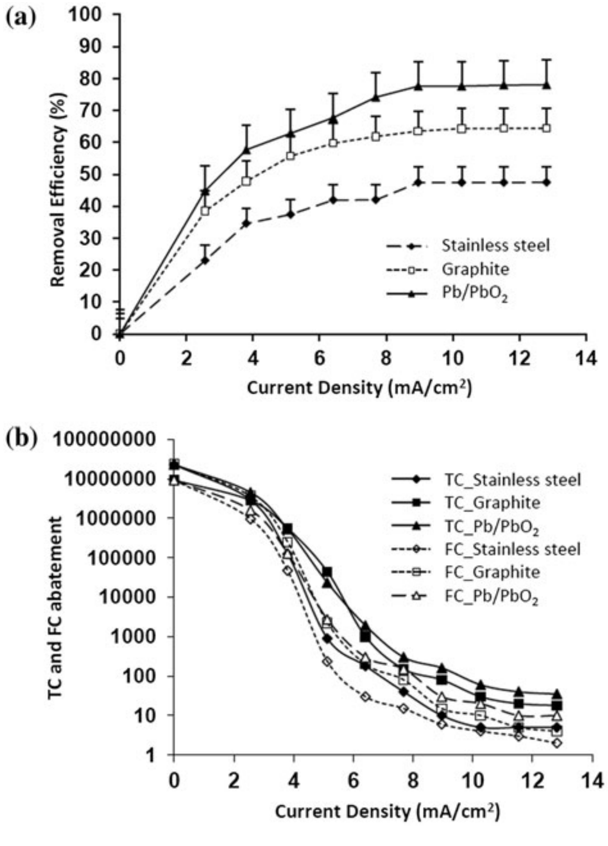

Fig. 4. The effect of CD on (a) COD removal (%), (b) TC and FC removal (%); charge passed = 18.94 C/cm^2.

content leads to H_2O electrolyze and oxygen creation instead of hydroxyl radicals, which is not suitable. Consequently, in the case of high CDs, there is no increase in the efficiency and even at very high CDs there is reverse result.

Mineralization current efficiency (in %) was calculated as follows [30]:

$$\text{Mineralization current efficiency} = \frac{\Delta C V_R \times 10^{-3}}{(16It/2F)} \times 100 \tag{13}$$

where F is the Faraday constant (96,485.3 C/mol), V_R is the solution volume (L), ΔC is the difference in COD in mg/L, I is the applied current (A), and t is the electrolysis time (S).

The mineralization current efficiency values, calculated using Eq. (13) for the trials of Fig. 4(a), are given in Table 1. It was observed that the maximum amount of mineralization current efficiency in the constant charge passed 18.94 C/cm^2 in the operating time of 24 min for stainless steel, graphite, and Pb/PbO_2 were, respectively, 103.9, 138.3, and 165.8%; as operating time increased (up to 120 min), with constant charge passed, such amounts fell by 53.5, 45, and 67.5%. This decline is due to persistent substances and by-products [27] produced over the reactions in this process. That is, at the beginning of the reactions, even with the existence of refractory compounds, more simple and degradable ingredients were quickly decomposed. However, as the reactions continued, even with an increase in operating time and CD, by-products and persistent combinations could not be degraded and mineralization current efficiency noticeably decreased. In different studies, an increase in mineralization current efficiency to over 100% and even 400–500% has been reported [27,30]. Besides, mineralization current efficiency over 100% is related to a series of electrochemical reactions and intervening physical processes which cause decrease in COD. In the present work, this matter expressed that COD is not a chemical composition to follow Faraday's law in a thermodynamic sense. These higher value efficiencies may just denote that there are a large chemical reactions and physical processes like adsorption to help COD reduction. In addition, the formation of vigorous oxidizing agents such as chlorine (Cl_2), hypochlorite (OCl^-), and chlorate (ClO_3^-) may happen and these intermediate products may chemically oxidize pollutants of effluent in a long period of electrolysis [30].

3.4. *Effect of charged passed and evaluation of EC and TDS variations*

With the application of optimized CDs for each electrode, as operating time increased not only EOAS amount increased but also COD, TC, and FC contents decreased (Fig. 5(a) and (b)). When charge passed was 28.42 C/cm^2, the removal amounts of COD, TC, and FC for stainless steel were 39.6, 99.6, and 99.1%, for graphite were 66.1, 96.3, and 98.9%, and for Pb/PbO_2 were 75.7, 96.9, and 99%, respectively. As the amount of charge passed exceeded 28.42 C/cm^2, more removal amount did not achieve.

According to Fig. 5(c), in the case of the Pb/PbO_2 electrode (the best electrode for EOAS), an increase in COD removal results in TDS and EC increase as their previous amounts of EC = 1,515 μS/cm and TDS = 849 mg/L (before electro-oxidation) reached to EC = 7,590 μS/cm and TDS = 3,714 mg/L. As can be seen, a rise in operating time and charge passed as well as a fall in COD concentration led to more mineralization. The reason for such condition is that the enhancement of charge passed increases production of

Table 1
The calculated mineralization current efficiency (%) according to Eq. (13), for stainless steel, graphite, and Pb/PbO_2 for trial of Fig. 4(a)[a]

Tim (min)	Stainless steel (%)	Graphite (%)	Pb/PbO_2 (%)
24	103.9	138.3	165.8
27	102.5	136.6	163.7
30	103.6	138.1	165.3
34	104.7	137.6	149.2
40	91.1	132.9	142.9
48	91.9	128.4	143.7
60	81.9	119.8	130.8
80	76.8	104.0	127.6
120	50.4	93.3	98.3

[a] Charge passed = 18.94 C/cm^2.

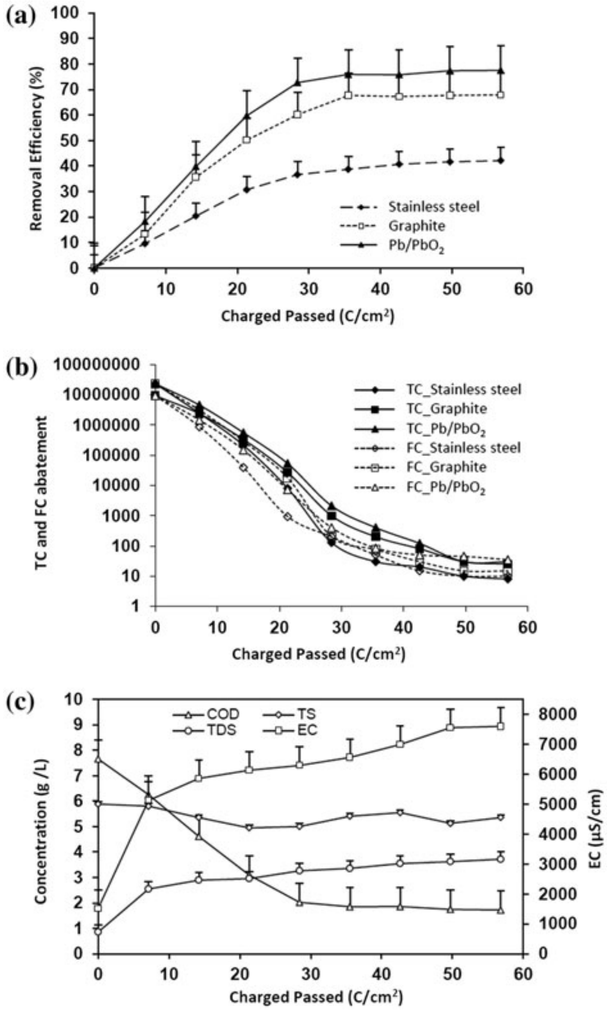

Fig. 5. The effect of charged passed on (a) COD removal (%), (b) TC and FC removal (%), (c) variation of EC and TDS to decrease COD for the trials of (a) for Pb/PbO_2.

hydroxyl and hypochlorite radicals. The decomposition of simple compounds in first phases is done quickly but as time passes, even contrary to enhancement of oxidizing factors, the produced by-products and also refractory compounds are slowly oxidized. This result has been proved by Ruiz et al. [27] too. Of course, over the process some reactions occurred that prevent organic matter degradation. This tendency can be stated by higher waste of relative amounts of PbO_2 (HO°) as parasite non-oxidizing reactions like its oxidation to O_2 as well as the formation of O_3, H_2O_2, and by the production of weaker oxidizing species such as $S_2O_8^{2-}$. The reactions as follows [10,27]:

$$2PbO_2(HO^\circ) \longrightarrow 2PbO_2 + O_2 + 2H^+ + 2e^- \quad (14)$$

$$2PbO_2(HO^\circ) \longrightarrow 2PbO_2 + H_2O_2 \quad (15)$$

$$H_2O_2 + PbO_2(HO^\circ) \longrightarrow PbO_2 + HO_2^\circ + H_2O \quad (16)$$

$$3H_2O \longrightarrow O_3 + 6H^+ + 6e^- \quad (17)$$

$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^- \quad (18)$$

As a whole, the findings showed that the exact adjustment of the operating parameters has an important role in mineralization of sludge via the electrochemical method; the use of low CDs and charge passed results in low production of sludge oxidants, particularly hydroxyl radical, which cannot destroy the organic matters entirely. On the other hand, at high CDs and charge passed, adverse reactions occur as well as oxygen is produced instead of hydroxyl radical, which is not suitable. The selection of electrode gender is very important. For example, in this study Pb/PbO_2 had by far better performance in comparison with other electrodes.

3.5. Cell parameters

3.5.1. Mixing speed

In order to destruct organic compounds of activated sludge, suitable mixing for effective contact among organic ingredients, anode surface, and radicals produced during electrochemical reactions is necessary. Proper mixing and increase of effective contact of the activated sludge with electrode surface and oxidizing agents raise both the reaction speed and EOAS rate. The EOAS process was carried out in four different mixing speeds of 100, 200, 300, and 400 rpm (Fig. 6). The findings illustrated that the speed of approximately 300 rpm was enough to be optimal and there was no need for higher speeds. At low mixing speeds, electron transition was not done appropriately and electrochemical reactions continued slowly. When mechanical mixing was near zero level, the solution became stagnant and there was only trivial electrochemical mixing as a result of temperature changes in high CDs. Of course, for an effective mixing, the surface of the oars must be in suitable size that can mix the activated sludge well. A magnetic mixer, even with bigger sizes, cannot adequately mix activated sludge alone.

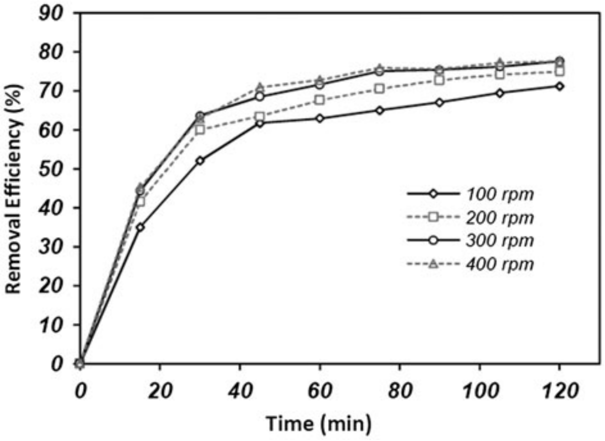

Fig. 6. The effect of mixing speed on EOAS; electrode = Pb/PbO_2 and CD = 8.97 mA/cm^2.

3.5.2. Cell design

In order to investigate this parameter, the electrodes were once put in plate form (at the middle of the cell); next, they were put in rod form with a gap distance of 1.5 cm at the cell environment. In these experiments, it was tried to use the electrodes at two equal manners and levels. Referring to Fig. 7, as the electrodes were placed in the middle of the cell in plate form, and in spite of providing high speeds, the desired mixing did not occur because activated sludge was stranded among the electrodes' sheets. Regarding the fact that the anode surface had a basic influence on EOAS rate, the efficiency dropped noticeably as some part of the anode surface was excluded. But when the rod electrodes were put at the cell environment, the soluble was mixed very well and the whole surface of the electrodes was involved and consequently the efficiency rose.

Previous studies showed that produced micro-bubbles on the surfaces of anode and cathode (respectively, O_2 and H_2), because of being stranded among flocs of activated sludge, made the activated sludge floated and discharged [34,35]. Therefore, when the electrodes were put in the cell environment, in addition to magnetic mixers, a mechanical mixer was applied; a mechanical mixer can evict the gases stranded among the flocs by degassing operation and can prevent the rise of activated sludge. Based on the results, it must be pointed that a suitable cell design and electrode arrangement are required to facilitate an effective contact between electrode surfaces and activated sludge.

Generally, the mineralization of organic matters of sludge is conducted by electrochemical reactions and physisorbed HO˚. However, mass transfer and transmission of organic matters from bulk of the solution to electrode surface should be taken into account. Because of the presence of polymeric substances in activated sludge that floats by creating electrical micro-bubbles during the reactions, enough mixing and proper design of electrochemical cell are completely necessary.

3.6. Energy consumption and environmental, technical, and economic assessment

Energy consumption (kWh/kg COD) for the trials of Fig. 5(a) was calculated from Eq. (19) [30]:

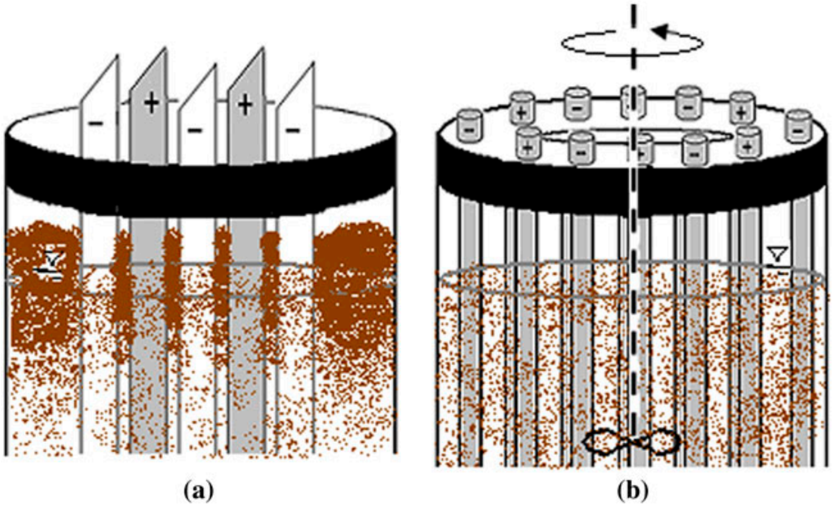

Fig. 7. The configuration and position of electrodes, (a) plate form and (b) rod form (distance = 1 cm).

$$\text{Energy consumption} = \frac{VIt}{3,600 \times 10^3} \times \frac{1}{\Delta C \times V_\mathrm{R} \times 10^{-6}} \tag{19}$$

where V is the average cell voltage (V).

As CD, operating time, and the average of applied cell voltage increased, the amount of consumed electrical energy increased. The amounts of consumed electrical energy for the electrodes of stainless steel, graphite, and Pb/PbO_2 (kWh/kg COD) ranged between 14.1–28.6, 7.4–16.1, and 8.0–12.8, respectively (Fig. 8). As can be seen, for each kg of COD, the consumed electrical energy for Pb/PbO_2 was lower than those of the other electrodes; at the constant charge passed 35.53 C/cm^2 (75 min) and COD removal amounts of 38.7, 67.7, and 75.9%, the amounts of consumed electrical energy for stainless steel, graphite, and Pb/PbO_2 were, respectively, 22.5, 11.1, and 8.6 kWh/kg COD. On the whole in the case of the Pb/PbO_2 electrode, the amount of consumed electrical energy for preparing the electrode, EOAS, and dewatering of the activated sludge was about 65.36 kWh per each m^3 (according to Eq. (20)) [32].

$$E = VIt/V_\mathrm{R} \tag{20}$$

The energy consumption which was required to remove COD was entirely enough to remove both FC and TC. One of the drawbacks in removing TC and FC is that FC and TC are stranded among the flocs and they become out-of-reach oxidizing factors. The management of activated sludge is crucial in terms of both economical and environmental features. Based on previous studies, among conventional methods for activated sludge treatment the anaerobic digestion is the best approach, which is both economical and an eco-friendly [3,36]. However, it is rather sensitive to solids content and pH; moreover, odor and bioaerosols are produced [37]. This method is influenced by environmental factors such as temperature and pH; so to carry out digestion, it requires a very long period of time for micro-organisms to adapt to the system conditions. Owing to this, it needs much area and high investing cost. This method is in conjunction with land-filled drying and incineration processes which have a high contribution to global warming potential [36].

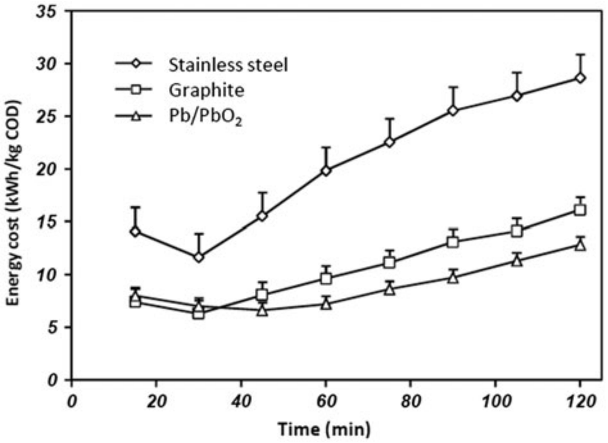

Fig. 8. Energy consumption for the experiments of Fig. 5(a).

The investigations of Mittal [37] revealed that techniques like aerobic, anaerobic digestion, composting (thermophilic), alkaline stabilization, drying (>80°C), and gamma and beta irradiation require certain operational conditions such as time, temperature, and ammonia concentration and, of course, land availability and by-products production are important. The findings of Hong et al. [36], who investigated different conventional ways for managing sewage sludge, showed most of these methods have limitations. Nonetheless, in view of the fact that electrochemical reagents are electrons and hydroxyl radicals they are very environmentally benign. Moreover, the electrochemical method requires low investing cost (particularly with regard to required land) because of being efficient in low time span (maximum of 2 h in this study). Additionally, removal efficiency was easily controllable through CD; it had very good stable efficiency, and it did not need adoption time like biological methods.

In view of the fact that during electrochemical reactions, hydrogen and oxygen gases are repeatedly produced, after EOAS was accomplished and when the activated sludge production has reduced, the solid materials quickly floated and electrooxidation and dewatered operations in a cell were performed by alternate setting of mixing speed (first by creating suitable mixing for accomplishing EOAS and then by creating suitable environment for floatation of the oxidized activated sludge alongside produced microbubbles). The study of Rahmani et al. [34] revealed that by such action the activated sludge is condensable up to 89%.

One of the main concerns of wastewater treatment plants is sludge (originated from biological processes) whose organic matter concentration and volume must be reduced. This study showed that the electrochemical method can remove a considerable amount of organic matters in a short time and lessen the volume.

This technique is slightly influenced by environmental variables (temperature, pH changes, and so on). It does not require adding extra chemical materials and hence harmful products are not produced; in the case of perfect decomposition, the ultimate products are CO_2 and H_2O. The best electrode of this research was found to be Pb/PbO_2, which is cheap and easily available and its preparation is simple. When compared to expensive electrodes (titanium and diamond), Pb/PbO_2 electrode has a good efficiency, that is approximately 76% of COD removal.

Of course, a very important point to make here is energy issue. Obviously, all existing ways even anaerobic digestion need energy. According to the study of Hong et al. [36] even though energy is produced as biogas, massive amount of energy is required for dewatering and stabilization stages; it can be far worse for incineration and drying through heat. The electrochemical method, which is known as a multiple contaminants removal process [33], consumes by far the least energy. Advantages of using electrochemical techniques in environmental applications include: environmental compatibility, versatility, energy efficiency, safety, selectivity, amenability to automation, and cost effectiveness [20,34]. However separate and precise studies are conducted to compare this method with other conventional ones. By and large, it seems that the electrochemical method is rather better and also has more social acceptability than other processes. Finally, it is really difficult to select the best method in terms of environmental, economical, and technical aspects, because such selection must be based on different situations.

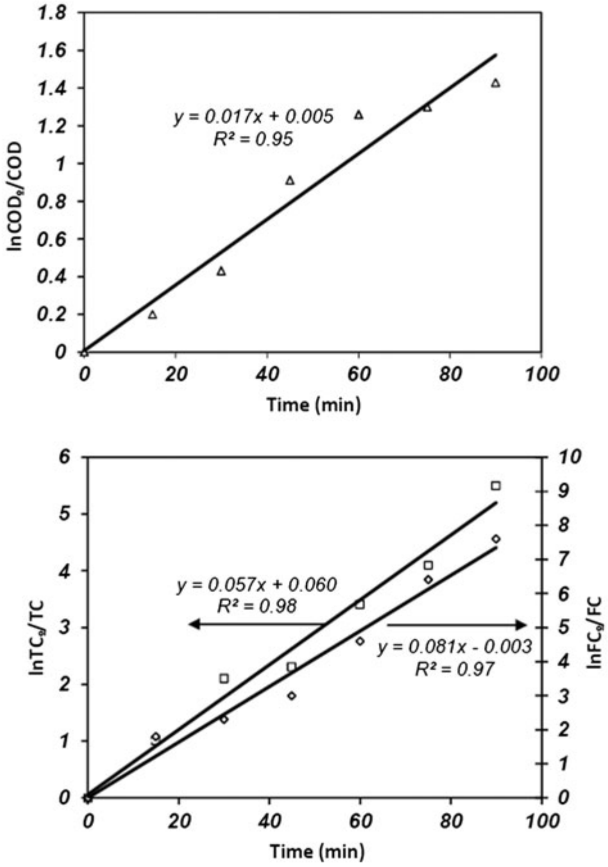

Fig. 9. First-order kinetic analysis for (a) COD and (b) TC and FC removal; $CD = 8.97\ mA/cm^2$ and Pb/PbO_2 anode.

3.7. Kinetic investigations

The obtained results in the optimum conditions for COD, TC, and FC reduction as a function of electrooxidation time were used. COD, TC, and FC abatement could be fitted to first-order kinetic equations with correlation coefficients of 0.95, 0.98, and 0.97 (Fig. 9(a) and (b)). The rates of COD, TC, and FC reduction depend upon CD, charge passed, electrode type, and arrangement, and mixing conditions. Furthermore, if the ions of OCl^- and $HOCl^-$ are created, more reduction will take place and, in turn, this results in more efficiency.

4. Conclusions

The present investigation illustrated the following results for EOAS: (i) The Pb/PbO_2 electrode is preferred because indirect anodic oxidation had a better operation in COD removal than other electrodes. (ii) The most suitable conditions were as follows: pH 4, $CD = 7.69\ mA/cm^2$ and charge passed $= 35.53\ C/cm^2$. (iii) An appropriate cell design (shape and the condition of electrodes) and creation of the suitable mixing condition for effective contact between the activated sludge and electrode surface are very helpful. (iv) for each kg of COD, the consumed electrical energy for Pb/PbO_2 was lower than those of other electrodes (approximately 8.6 kWh/kg COD at the optimum condition). (v) All three anodes could remove TC and FC noticeably; of course, stainless steel was found to be the best anode. (vi) COD, TC, and FC abatement trend can be fitted to first-order kinetic equation. (vii) EOAS treatment (in terms of environmental, economical, and technical aspects) is promising with respect to activated sludge treatment.

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