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Heavy metal ions removal from waste-activated sludge by Fered-Fenton electrochemical advanced oxidation process (EAOP) with the aim of agricultural land application

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ABSTRACT

According to the characterisations of the waste-activated sludge, its reuse as fertilizer in farms and agricultural lands is an interesting environmental and economic issue. One of the main hazards associated with waste-activated sludge reuse on agricultural land is the potential long-term accumulation of toxic materials in the crops and soil. Due to the various limitations, the conventional sludge stabilization processes are not able to remove the heavy metals ions from waste activated sludge to make it reliable enough to be utilized as fertilizer in agricultural lands and farms. In this regard, various promising novel technologies and processes have been studied with the aim of its efficient stabilization and reuse in agricultural applications. Fered-Fenton is one of the most promising electrochemical advanced oxidation processes (EAOPs) which has demonstrated significantly reliable performance in waste-activated sludge stabilization. In this regard, this study has been conducted to evaluate the Fered-Fenton process efficiency to remove the frequent heavy metals (chromium, molybdenum, copper, lead, zinc, and mercury) from waste activated sludge at three different operating pH values equal to 3, 5 and 7, and supplying current densities equal to 450, 650 and 850 mA with the aim of agricultural land applications. The results of the experiments demonstrated that this process is highly effective in removing chromium, molybdenum, zinc, copper and lead ions from waste activated sludge to the limits, lower than the specified concentrations by the USEPA regulations. Also, this process has significant ability to reduce the concentration of mercury ions in the waste activated sludge.

Keywords: Waste activated sludge; Heavy metals removal; Electrochemical advanced oxidation process (EAOP); Fered-Fenton; Reuse; Agricultural land application

1. Introduction

Increasing concerns about the environmental impacts of continuously increasing quantities of the waste materials discharge (like sewage sludge) into the environment have prompted endeavors to develop the strategies such as sustainable development, which implies ecological, economic and social responsibilities [1]. In this regard, reuse (as one of the most important strategies of the waste management) has been considered by urban water, wastewater and/or stormwater managers in order to control the impacts on the environment as well as improve the waste materials recycling [2,3]. Therefore, lots of the related researches have been concentrated on removing the toxic materials such as heavy metal ions and complexes from the waste materials before their disposal and/or application for various purposes [4,5]. Conventional activated sludge wastewater treatment methods generate remarkably large amounts of waste activated sludge, daily and this material is considered as one of the main ever increasing waste materials in the world [6,7]. Due to this largely produced volume and its noticeable content of nutrients and biodegradable materials, waste activated sludge is assumed to be utilized as

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fertilizer in agricultural land applications [8,9]. On the other hand, waste activated sludge contains noticeable concentrations of heavy metals, and poorly biodegradable organic compounds as well as pathogens which are capable of creating and spreading serious problems if disposed into the environment without the suitable stabilization [8]. Therefore, considering the remarkable characteristics of the waste activated sludge, attentions have been concentrated on the reuse of this matter [2,10,11] and various studies have been carried out in order to minimize or completely eliminate its potential threats to human health and environment [12,13]. In this regard, various promising novel technologies and processes have been approached with the aim of its efficient stabilization and reuse [14,15]. As mentioned before, according to the fertilizing characterizations of waste activated sludge, its application as fertilizer in farms and agricultural lands is an interesting environmental and economical alternative [16–18]. Obviously, due to the potential content of toxic compounds and ions [19,20] as well as the related probable soil, ground water, and crops contamination [16, 21], there is a great concern about the agricultural land applications of waste activated sludge which has been stabilized by usual stabilization methods. Thus, sludge treatment systems must provide a final product reliable for agricultural land application and fulfilling legislation requirements [22]. Due to the various disadvantages of conventional sludge stabilization processes [23–25], it is going to be increasingly apparent that novel efficient technologies are necessary for preventing serious problems during the eco-biological cycle and as a result, convenient reuse of the stabilized sludge in the agricultural applications [26].

In recent years, electrochemical advanced oxidation processes (EAOPs) have been developed as innovative treatment and stabilization methods for the removal of a broad range of organic contaminants and complicated compounds, as well as pathogens [17,27–29]. These processes demonstrate outstanding advantages such as environmental compatibility, versatility, safety, selectivity, fast treatment rate, convenience and simplicity in wastewater and waste sludge treatment. These methods are assumed to be efficient economical alternative processes for the situations that the conventional treatment methods are not able to work properly in removing contaminants partially or completely from wastewater or sludge [30–32]. The most popular technique among EAOPs is the electro-Fenton (EF) process, in which H_2O_2 is generated at the cathode with oxygen or air feeding while an iron catalyst (Fe^{2+}, Fe^{3+}, or iron oxides) is added to the influent. Combined EF methods have also been reported for wastewater remediation [33]. Various studies have been carried out in order to modify EF process [29,34]. One of the most efficient methods which have been established on EF and has demonstrated more efficiency in waste sludge and wastewater treatment in various cases is the Fered-Fenton process. The Fered-Fenton process consists in the adding of either Fe^{2+} or Fe^{3+} to the initial wastewater along with the continuous injection of H_2O_2 during the treatment into an undivided electrolytic cell. Fe^{3+} is then reduced to Fe^{2+} in the cathode which reacts with the added H_2O_2 to generate ·OH via Fenton's reaction. Water is also reduced to H_2 at the cathode and then oxidized to ·OH at the anode surface. Gentle oxidation of small quantities of Fe^{2+} to Fe^{3+} at the anode is also practicable [34–36]. One of the main hazards associated with waste activated sludge reuse on agricultural land is the potential long-term accumulation of toxic materials [37]. The volatile suspended solids (VSS) removal from the waste activated sludge by the Fered-Fenton process has been reported, recently [27]. The main purpose of this study is investigating the ability of the Fered-Fenton process to remove heavy metal ions (chromium, molybdenum, copper, lead, zinc, and mercury ions) from waste activated sludge with the aim of agricultural land application. In this regard, the removal efficiencies of the process have been evaluated at different pH values and current densities as operational parameters.

2. Material methods

The investigations were conducted in a laboratory scale reactor which has been demonstrated in Fig. 1. The reactor cell was made of plexiglass with a volume equals to 0.9 L and contained four graphite electrodes (i.e. two anodes and two cathodes). The electrodes dimension was 1 mm × 140 mm × 60 mm, placed at a distance of 1.5 cm from each other [38]. The depth of the electrodes placed in the sludge was 100 mm and the contact surface was 100 mm × 60 mm. An electrical mixer (Zheng, zs-ri, 6(V), DC, 3.66 rpm) was utilized accordingly. A digital laboratory model power supply (Mps, DC-3003D, 0–30 (A), 0–30 (V)) has been used for the amperage adjustment.

The chemicals used in this work included $FeSO_4$ and H_2O_2 as Fenton reagent and concentrated sulfuric acid

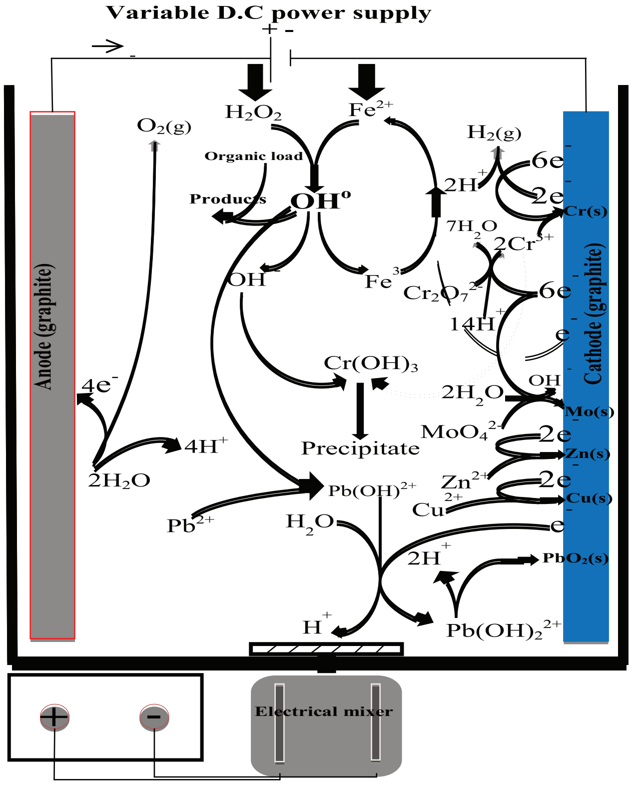

Fig. 1. The schematic of the utilized Fered-Fenton reactor in the laboratory and the related reactions.

(H_2SO_4) and caustic soda (NaOH) for pH adjustment. Thus, $CuSO_4$, $Pb(NO_3)_2$, $HgSO_4$, $K_2Cr_2O_7$, Cl_2Zn and $(NH_4)_6Mo_7O_{24}$ were added to the sludge samples for making alterations to initial heavy metals ion concentrations. All of the utilized chemicals in this study have been provided by Merck® Co. Also, the treated samples were filtered by using Whatman® filter papers (No. 42).

Waste activated sludge was collected from Shahid Mahallati municipal wastewater treatment plant which treats 4,800 m^3 wastewater per day (Tehran, Iran). Table 1 demonstrates the specifications of the characterized municipal raw waste-activated sludge samples used in this study.

The waste activated sludge samples mixed by a relatively low-speed mixer, in order to be homogenous, before being charged into the reactor. The pH values were adjusted by adding an adequate dosage of H_2SO_4 and NaOH. The specified heavy metal ions complexes have been added to the sludge in the Fered-Fenton reactor considering the determined initial concentration for each run. Then, Fenton's reagents ($FeSO_4$ and H_2O_2 were added to the reactor cell and the graphite electrodes were connected to the laboratory model DC power supply system. Stabilized waste activated sludge samples were analyzed by the standard test methods determined by APHA, 1999 [39]. The concentrations of the heavy metals were determined by means of Inductively Coupled Plasma (ICP) Model Varian-710. Concentrations of the other investigated ions were measured by an Ion Chromatography Model Metrohm-IC850. The pH value and the current density were selected the operational parameters that have been investigated in this study. The ranges and the values of these parameters (3, 5, and 7 as pH values and 450, 650 and 850 mA as the supplied current densities) have been selected according to the related literature [27,29,36] which considered the stability of the heavy metal ions species, number of the required experiments and the applicable conditions for stabilization of waste activated sludge in industrial scale. All other operational parameters have been determined according to the results of the recently done related study [27] that reported the optimal conditions of the sludge stabilization by Fered-Fenton process ($[Fe^{2+}]/[H_2O_2] = 0.58$, retention time = 6 (h), $[H_2O_2] = 1568$ (mg/l)). The initial concentration of each heavy metal was considered at the maximum attainable concentration level in the solution and the results have been compared and controlled with the US Environmental Protection Agency Standard (USEPA, 1995) requirements [40].

Table 1
The characteristics of the municipal waste-activated sludge samples

Property	Value
pH	6.5–7.3
Temperature, °C	18.5–23.7
COD, mg/l	5768–10985
SCOD, mg/l	38–67
VSS, mg/l	3136–6682
VS, mg/l	3201–6810
TS, mg/l	4375–8825
TSS, mg/l	4085–8537
VSS/TSS	0.76–0.78

3. Results and discussion

The results of the investigated heavy metals removal from municipal waste activated sludge employing Fered-Fenton process have been presented in this section.

3.1. Chromium ions removal

Fig. 2 demonstrates the results of the experiments for the hexavalent chromium ions removal from waste activated sludge.

As shown in Fig. 2, the efficiency of the Fered-Fenton process for removing chromium ions shows remarkable variations by the change of the pH and the applied current density. Also, according to the results, the effect of pH is noticeably higher than current density. According to the results, the maximum chromium ions removal (i.e. 90%) achieved when the pH value of the reactor content is about 3 and increasing pH reduces the chromium ions noticeably (about 57% at neutral conditions). It seems that the elimination of hexavalent chromium ions from sewage sludge is carried out by electrochemical reduction during the process [41]. The reduction reaction may occur in the cathodic area (near to cathode electrodes) and/or by Fe^{2+} cations which are added to the reactor as Fenton's reagent. In addition, the reduced Cr^{3+} can be electrodeposited on the cathode or remained in the cathodic layer in the form of $Cr(OH)_3$ [42,43]. However, further reactions known as side reactions (i.e. hydrogen evolution) can occur near the cathode resulting in loss of cathodic current efficiency [41–43]. At higher pH values, chromium containing compounds or complexes are there in chromic (Cr^{3+}) form and the reaction between Cr^{3+} and hydroxyl ions generate chromium hydroxide ($Cr(OH)_3$) precipitation [43].

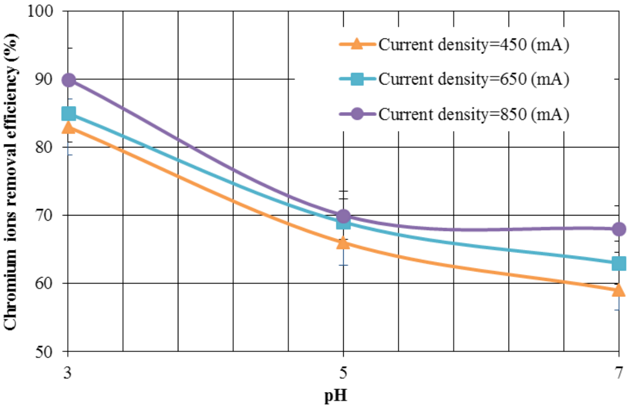

Fig. 2. The effect of the pH value and the current density on the chromium ions removal process efficiency, $[Fe^{2+}]/[H_2O_2] = 0.58$, retention time = 6 h, $[H_2O_2] = 1568$ (mg/L), initial chromium concentration = 1000±80 mg/kg.

3.2. Molybdenum species removal

Fig. 3 shows the effect of pH and current density on the efficiency of the Fered-Fenton process to eliminate molybdenum species from waste activated sludge.

According to Fig. 3, by increasing pH from 3 to 5, the removal efficiency of the process would be increased, but this trend changes by further increase of pH to 7. Also, increasing the current density decreases the ability of the process for elimination of molybdenum ions from waste activated sludge. This decrease is higher when the applied current density increases from 650 to 850 mA. There are various methods for removing molybdenum species from the aqueous solutions. The electro-deposition method is considered as the main effective and economic removal method of molybdenum compounds and ions from the aqueous media such as waste activated sludge, but utilizing this technique is confined due to its dependency on various limiting parameters [44]. The formation of the stable molybdenum compounds (molybdenum oxides or complex polymeric molybdates) is dependent on the various operational parameters especially the pH value of the aqueous medium. It seems that the removal of the molybdenum compounds and ions from waste activated sludge by Fered-Fenton process is occurred by both electrodepositions of Mo on cathode electrode and reduction by Fe^{2+} ions [45,46]. Also, the formation of a thick adherent mixed oxide coating on the electrodes in presence of the Fe^{2+} ions confirms the reduction of $Mo_7O_{24}^{6-}$ species to Mo [44–46]. However, at pH values from 5 to 7, these species convert into predominant MoO_4^{2-} species form. MoO_4^{2-} species would be transformed to Mo due to electrochemical reduction at the electrode surface [45].

3.3. Copper ions removal

Fig. 4 shows the results of the experiment for copper ions removal from waste activated sludge by Fered-Fenton process. As shown in Fig. 4, increasing pH from 3 to 7 as well as decreasing current density reduces the efficiency of the Fered-Fenton process for removal of copper ions from waste activated sludge. The maximum removal efficiency of the process can be achieved when the pH value of the process and the current density are 3 and 850 mA, respectively. The effect of the applied current density is remarkable in the higher pH values. The mechanism of the removing copper ions from the aqueous solution is based on the reduction reaction which results in the deposition of copper species on the cathode electrode surface. The main related reduction reactions with Cu^{2+} ions are the formation of metallic copper and cuprous oxide (Cu_2O) [47]. The significant efficiency of this approach in copper ions removal can be explained on the basis of the high potential of Cu^{2+} reduction [47]. During the Fered-Fenton process, the required electrons for Cu^{2+} ions reduction may be obtained from the applied current density or Fe^{2+} ions.

3.4. Zinc ions removal

Fig. 5 demonstrates the results of the experiments for zinc ions removal from waste activated sludge.

As revealed in Fig. 5, the process efficiency for Zn^{2+} ions removal shows a reduction by increasing the pH value from 3 to 7. Also, the increasing the current density from 450 to 850 mA modifies the efficiency of the Fered-Fenton process for removing zinc ions from waste activated sludge. By applying adequate current density to the sys-

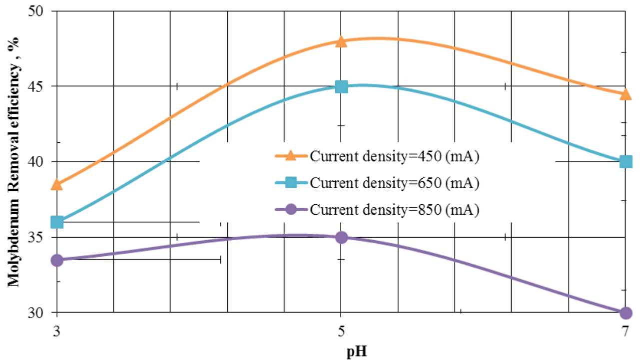

Fig. 3. The effect of pH value and the current density on the molybdenum removal process efficiency, $[Fe^{2+}]/[H_2O_2] = 0.58$, retention time = 6 h, $[H_2O_2] = 1568$ mg/L, initial molybdenum concentration = 75±20 mg/kg.

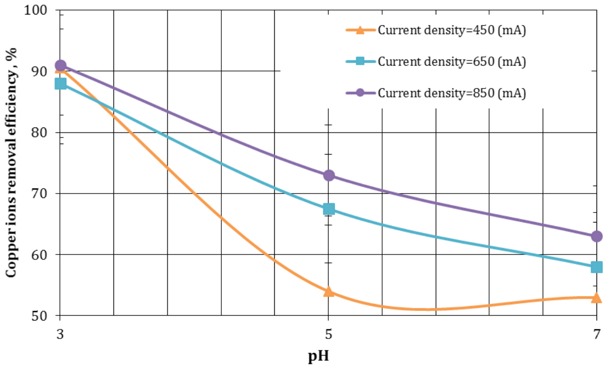

Fig. 4. The effect of the pH value and the current density on the copper ions removal efficiency of the Fered-Fenton process, $[Fe^{2+}]/[H_2O_2] = 0.58$, retention time = 6 h, $[H_2O_2] = 1568$ (mg/l), initial copper concentration = 7600±100 mg/kg.

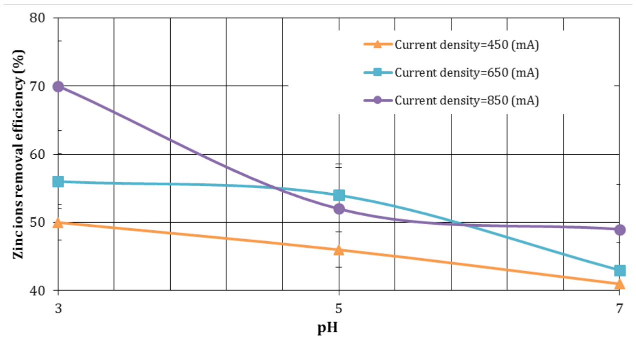

Fig. 5. The effect of the pH value and the current density on copper ions removal efficiency of the Fered-Fenton process, $[Fe^{2+}]/[H_2O_2] = 0.58$, retention time = 6 h, $[H_2O_2] = 1568$ mg/L, initial zinc concentration = 13000 ± 200 mg/kg.

tem, the Zn^{2+} and H^+ ions reduction occur in the cathode proximity and this reduction leads to the removal of zinc ions from the sludge. Therefore, electro-deposition of the zinc on the cathode surface and the simultaneous evolution of H_2 gas were observed [48]. The maximum zinc removal (i.e. 70%) occurs at pH value equals to 3 and current density equals to 850 mA.

3.5. Lead ions removal

Fig. 6 shows the effect of pH and the current density on the lead ions removal efficiency of the Fered-Fenton process.

As shown in Fig. 6, by increasing pH value of the waste activated sludge from 3 to 5, the efficiency of Fered-Fenton for removing lead ions decreases, but this trend changes by further increase of pH value to 7. Also, increasing the current density from 450 to 850 mA increases the lead ions removal in lower pH values, significantly. But this increase has not remarkable effect in higher pH values. According to the results, the maximum lead removal efficiency (i.e. 80%) has been observed at pH value equals to 3 and the current density equal to 850 mA. The mechanism of removing lead ions from the waste activated sludge contains various steps. The hydroxyl ions and/or radicals which have been formed during Fered-Fenton process can be reacted with the lead ions on the electrode surface and produce $Pb(OH)^{2+}$ which are consecutively converted to lead-dioxide (PbO_2) in presence of H^+ ions within several electrochemical reactions. PbO_2 is insoluble in aqueous solutions and therefore, precipitated on the electrode surface [49].

3.6. Mercury removal efficiency

Fig. 7 shows the results of the experiments on removing mercury species from waste activated sludge by Fered-Fenton process.

According to Fig. 7, the efficiency of the Fered-Fenton process decreases by increasing pH values from 3 to 7. Also, increasing current density from 450 to 650 mA increases the removal efficiency of the process, but the further increase from 650 to 850 mA does not have a noticeable effect on the results. It seems that increasing pH value (from 3 to 7) leads to the stabilization of mercury ions in the form of $Hg(SO_3)^{22-}$ in the presence of sulfate anions, and $Hg(OH)^+$ as well as $Hg(OH)_2$ [50,51]. As shown in Fig. 7, the maximum observed value for mercury removal efficiency of the process (i.e about 62%) has been achieved at pH values equal to 3 and the current density equal to 850 mA.

3.7. The comparison of the results with the related standards for agricultural land applications of waste activated sludge

Table 2 shows the comparison of the optimum operational conditions of the heavy metals removal from waste activated sludge by Fered-Fenton process as well as the maximum allowed concentration limits for each heavy metal, according to the related regulations of the USEPA for waste materials like waste activated sludge applications in agricultural lands. According to Table 2, the Fered-Fenton process is capable enough to remove all of the heavy metals ions except than mercury from the waste activated sludge. In other words, the concentrations of chromium, molybdenum, copper, zinc, and lead ions in the waste activated sludge in noticeably lower than the specified limit by the USEPA standard. It should be noted that, even though the final concentration of the mercury is higher than the specified maximum level of the standard, its concentration has been reduced more than 62% of its initial concentration.

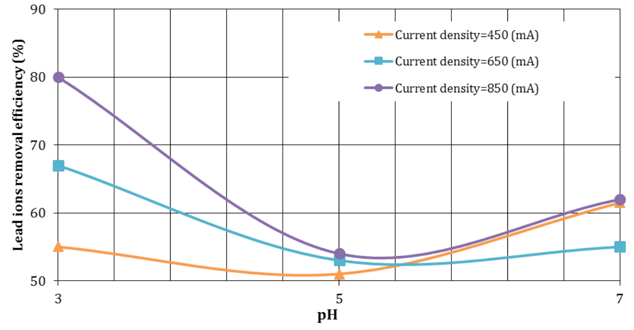

Fig. 6. The effect of the pH value and the current density on the lead ions removal efficiency of the Fered-Fenton process, $[Fe^{2+}]/[H_2O_2] = 0.58$, retention time = 6 h, $[H_2O_2] = 1568$ mg/L, initial lead concentration = 3400±50 mg/kg.

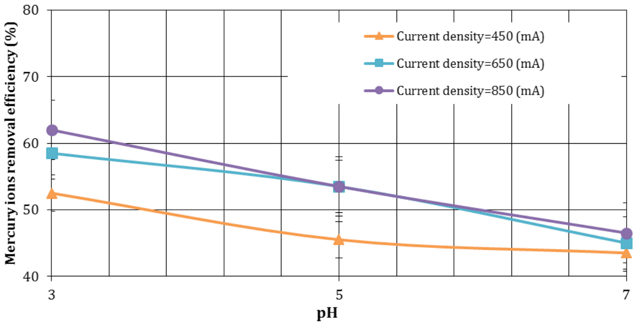

Fig. 7. The effect of the pH value and the current density on the mercury ions removal efficiency of Fered-Fenton process, $[Fe^{2+}]/[H_2O_2] = 0.58$, retention time = 6 h, $[H_2O_2] = 1568$ mg/L, mercury initial concentration = 500±40 mg/kg.

4. Conclusions

In this study, the removal efficiency of the Fered-Fenton process (as an electrochemical advanced oxidation (EAOP)) has been investigated for heavy metals removal from the waste activated sludge with the aim of its reuse in the agricultural land application. The results of the experiments showed that this process is highly effective in removing chromium, molybdenum, zinc, copper and lead ions from waste activated sludge to the, lower than the specified concentrations by the USEPA regulations. Also, this process has significant ability to reduce the concentration of mercury ions in the waste activated sludge. The operational conditions of the process for removing the maximum heavy metals ions of the waste activated sludge have been determined

Table 2
Optimum operating conditions for heavy metals removal from waste-activated sludge employing Fered-Fenton process

Heavy metal ions	Optimum operational condition	Initial concentration (mg/kg)[1]	Effluent concentration (mg/kg)	Maximum concentration limits (mg/kg)[2]	Clarification
Chromium	pH = 3, current density = 850 mA	1000±80	100±10	3000	Lower than the limit
Molybdenum	pH = 5, current density = 450 mA	75±20	39±5	75	Lower than the limit
Copper	pH = 3current density =850 mA	7600±100	684±50	4300	Lower than the limit
Zinc	pH= 3, current density = 850 mA	13000±200	3900±200	7500	Lower than the limit
Lead	pH = 3, current density = 850 mA	3400±50	680±50	840	Lower than the limit
Mercury	pH = 3, current density = 850 mA	500±40	190±20	57	Out of the range

[1,2] [40]

for each heavy metal species (90%, 48%, 91%, 70%, 80% and 62% removal efficiency for chromium, molybdenum, copper, zinc, lead and mercury ions, respectively), too.

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