Chemical, Petroleum and Environmental Engineering

Removal of Cadmium from Simulated Wastewaters Using a Fixed Bed Bio-electrochemical Reactor

Duaa R. Saad
MSc. Student
Biochemical Engineering Department, Al-Khwarizmi College of Engineering, University of Baghdad, Iraq
duaarsaad9287@yahoo.com

Ziad T. Alismaeel
Lecturer
Biochemical Engineering Department, Al-Khwarizmi College of Engineering, University of Baghdad, Iraq
ziadalismaeel@yahoo.com

Ali H. Abbar
Assistant Professor
Chemical Engineering Department, University of Al-Qadisiyah, Iraq
ali.abbar@qu.edu.iq

ABSTRACT

In this research, the removal of cadmium (Cd) from simulated wastewater was investigated by using a fixed bed bio-electrochemical reactor. The effects of the main controlling factors on the performance of the removal process such as applied cell voltage, initial Cd concentration, pH of the catholyte, and the mesh number of the cathode were investigated. The results showed that the applied cell voltage had the main impact on the removal efficiency of cadmium where increasing the applied voltage led to higher removal efficiency. Meanwhile, increasing the applied voltage was found to be given lower current efficiency and higher energy consumption. No significant effect of initial Cd concentration on the removal efficiency of cadmium but increasing the initial concentration would be given higher current efficiency and lower energy consumption. The results established that using a pH value lower than three results in a sharp decrease in the removal efficiency as well as using a pH value higher than seven results in decreasing the removal efficiency. Using a mesh number higher than 30 gave a lower removal efficiency. The best operating conditions were found to be an applied potential of 1.8 V, an initial Cd concentration of 125 ppm, and a pH of 7. Under these operating conditions with the using a stack of stainless with mesh number 30 as a packed bed cathode, a complete removal efficiency of Cd(100%) was obtained at a current efficiency of 83.57% and energy consumption of 0.57 kWh/kg Cd.

Keywords: Fixed bed electrode, Cadmium removal, Microbial electrolysis cell, Porous graphite, Wastewater treatment.

*Corresponding author
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الخلاصة

تم في هذا البحث إزالة الكادميوم من المخلفات الصناعية من خلال استخدام مفاعل بايوكهروكيميائي مؤلف من كاتد ذو حشوة ثابته. حيث تم دراسة أهم العوامل المسيطرة على كفاءة عملية الازالة مثل الجهد المسلط على الخليه,التركيز البدائي للكادميوم، الداله الحامضية لمحلول الكاثولايت وحجم الثقوب في المشبك الكاثودي. اظهرت النتائج أن الجهد المسلط هو العامل الأساسي المؤثر على كفاءة الازالة للكادميوم حيث أن زيادة الجهد تؤدي إلى زيادة كفاءة الازالة وكذالك زيادة تدفق الاملاح تؤدي إلى انخفاض كفاءة الازالة. والاضارب الطاقه الكهربائية المصروفة لكل كيلوغرام من الكادميوم أظهرت النتائج عدم تأثير التركز البدائي على كفاءة الازالة ولكنه يؤثر على كفاءة التيار والطلقة المستثناة حيث يعني زيادة تدفق الاملاح عند استخدام داله حامضية أقل من (3) يؤدي إلى انخفاض كفاءة الازالة وانخفاض كفاءة الازالة عند استخدام داله حامضية أكبر من (3) يؤدي أيضا إلى انخفاض كفاءة الازالة. استخدام حجم ثقوب المشبك الكاثودي أكثر من (30) يؤدي أيضا إلى انخفاض كفاءة الازالة.

بالإضافة إلى ذلك، اظهرت النتائج أن أفضل الظروف التشغيلية هو استخدام恢طيل (1.8 V) وتركيز كادميوم بمقدار (125 ppm) وداله حامضية بمعامل (7) واستخدام مشبك كاثودي ذات حجم ثقوب بكفاءة (30) حيث تم الحصول على كفاءة الازالة تامة للكادميوم في ظل هذه الظروف بكفاءة تيار (83.57%) وطاقه مستهلكه بكفاءة (0.57 kWh/kg Cd).

الكلمات الرئيسية: Qطب ذو حشوة ثابته,ازلة الكادميوم,الخليه البايوكهروكيميائيه,الكريفات المسبحة,معالجة المياه.

1. INTRODUCTION

Pollution of the environment by heavy metals such as cadmium, lead, cobalt, nickel, zinc, and copper is a serious environmental and health hazard since these metals are toxic and non-biodegradable. They have the affinity to bio-accumulate through the food chain even at low concentrations leading to many diseases and disorders (Amarasinghe and Williams, 2007; Choi, et al., 2014). Among these heavy metals, cadmium (Cd) is highly toxic to humans and has an extremely long biological half-life (greater than 20 years). The harmful effects of cadmium involve acute and chronic metabolic disorders, such as emphysema, renal damage, hypertension, and testicular atrophy (Choi, et al., 2014).

Various industrial processes, such as smelting and refining of nonferrous metals, battery manufacturing, electroplating, and inorganic pigment industry, result in cadmium contamination in wastewater streams (Kurniawan, et al., 2006). Hence, the development of effective methods for removing of cadmium from wastewaters is an essential task with regards to the protection of public health and environment.

Traditional methods for cadmium removing involve physical, chemical, biological and electrochemical methods (Soares and Soares, 2011; Malaviya and Singh, 2011). The physical and chemical methods, such as adsorption, chemical precipitation, reverse osmosis, ion exchange, and membrane filtration, can be unsuccessful or may be very expensive, especially if the concentration of cadmium is below 100 mg/L (Ahluwalia and Goyal, 2007). For example, ion exchange needs a large quantity of chemicals for the regeneration of resin, while membrane processes are susceptible to fouling, causing high operation costs (Kurniawan, et al., 2006). Traditional biological processes are considered as an alternative strategy to physical-chemical processes for cadmium removing via different mechanisms such as bio-sorption, enzymatic reduction, bio-mineralization, and precipitation (Bai, et al., 2008; Pagnanelli, et al., 2010).
However, these traditional biological processes suffer from subsequent more sludge generation, and more organic carbon consumption (Pagnanelli, et al. 2010).

Electrochemical processes can be removed Cd efficiently with no organic carbon consumption and no sludge production, but these methods required using intensive energy with high capital cost and relatively low efficiency at dilute concentration (Khairy, et al., 2014). Hence, providing environmentally friendly and cost-effective method for cadmium removing with less sludge generation and lower energy demands still remain a challenge.

Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are considered as promising technologies to accomplish sustainable wastewater treatment with simultaneous value-added products and clear energy generation (Zhang, et al., 2015). MFCs have been used for recovery of various metals including chromium (Li, et al., 2008), copper (Heijne, et al., 2010), iron (Lefebvre, et al., 2013), vanadium (Zhang, et al., 2009), and selenium (Catal, et al., 2009) by using a two-chamber design where these metals are removed in the anaerobic cathode chamber through cathodic metal reduction. In contrast, organics in the anodic chamber were used as carbon sources and electron donors (Abourached, et al., 2014).

By applying an external voltage, MECs have been used to recovery heavy metals such as lead, cadmium, cobalt, and zinc (Jiang, et al., 2014). In these MECs, exoelectrogenic bacteria oxidize organic substances at the bio anode of the cell while water is simultaneously reduced to hydrogen gas at the cathode in combination with the reduction of heavy metal ions into metallic solids (Logan, et al., 2008). Thus, wastewater can be treated while energy is recovered in the form of hydrogen gas.

In the MECs, bacteria cultivate as a bio-layer on the surface of the anode then perform an oxidation process for the organic substances existing in the anode chamber such as acetates converting them to CO$_2$ and H$_2$O, with generating of electrons at the same time upon the surface of the anode. Therefore, the success of MEC is influenced by the enrichment of bacteria on the surface of anode. The source of bacteria used in MECs may be coming from sewage sludge, wastewater, and soils (Lee, et al., 2003; Logan, et al., 2005; Schampheiraire, et al., 2008; Schampheiraire, et al., 2010). Based on investigations done by Bond et al. 2002 and Holmes et al., 2004, the main bacteria in the soil are Deltaproteobacteria (average 75%), with about 60% in the Geobacteraceae family. However, different electricity generating abilities can be obtained from different sources of soils that contain different microbial communities. Hence, the efficiency of MEC depends on the type of soil that has been used in the anodic chamber (Schampheiraire, et al., 2010).

During the last two decades, the application of the electrochemical technology in wastewater treatment has been increased due to the development of a three-dimensional electrode (Ismail, et al., 2013). The main benefit of this electrode was the high mass transfer rate as well as the high specific surface area. Removal of heavy metals by three-dimensional electrodes was achieved using different configurations such as those based on carbon or metal particles (Bennion and Newman, 1972; Fletcher and Walsh, 1990 ), felts, metallic or metal-plated foams (Tentorio and Casolo-Ginelli, 1978; Montillet, et al., 1993), reticulated vitreous carbon (Wang, 1981), expanded metals and screens (Grau and Bisang, 2003; Mohammed, et al., 2015; Sulaymon, et al., 2017; Abbar, et al., 2019). Using screens in fabricating of three-dimensional electrodes gave a better performance than other types of electrodes because of their availability at low cost, high porosity, high specific surface area, high promotion ability for turbulence, and ease of coating with a catalyst (Ferreira, 2008; Abbar, et al., 2018).

Recovery of cadmium has been demonstrated using multiple reactors of bioelectrochemical systems where one reactor is used to power the other reactor for the reduction of Cd$^{2+}$to Cd (Choi, et al., 2014; Zhang, et al., 2015). Few studies have been performed on the removal or recovery
of cadmium from wastewater using MECs (Choi, et al., 2014; Zhang, et al., 2015; Abourached, et al., 2014; Modin, et al., 2012; Colantonio and Kim, 2016; Chen, et al., 2016). Most of them have been used a flat cathode with no attempt to utilize three-dimensional electrodes as a cathode material.

In the present work, we investigated the removal of cadmium using a new design of MEC composed of a fixed bed of parallel stainless steel screens as a cathode and porous graphite as an anode with the using locally soil material as a source of bacteria. The effects of operating parameters, such as applied cell voltage, initial Cd concentration, pH of the catholyte, and mesh size of the screen on the performance of the MEC were investigated. To the best of author knowledge, no such bio-electrochemical system has been used for the removal of cadmium. The choice of stainless steel screens as cathode material is based on the observations of previous works which confirmed that this material gives a higher performance in the production of hydrogen by MEC systems at lower cost (Zhang, et al., 2010)

2. Materials and methods
2.1 Characterization of soil and electrodes

A sampling of soil was performed at an area located near al-Ghwarizm College at the University of Baghdad, Al-Jadriya, Iraq. Samples of soil were taken at 0.1 m deep from the surface of the soil. The samples were subjected to screening using a sieve of 2 mm in diameter then stored at 4 °C for two weeks before using. Analyzing the samples of soil for determining their physiochemical properties was performed via routine methods (Page, et al., 1982). Briefly, the maximum water holding capacity (MWHC) of the soil was calculated by considering the difference in weights between dry and soaked soil samples. The pH of the soil was measured by taking a ratio (1:2.5) of soil to water, while the electrical conductivity of the soil was determined by taking a ratio (1:5) of soil to water.

Diagnose the types of bacteria in the soil was performed using VITEK 2 compact system (bioMérieux, France) by following the procedure provided by this system. In this procedure, three to five well-isolated colonies were transferred to a glass tube inclosing 3 ml distilled water, then adjusting the turbidity to represent a bacterial cell count per 1 ml equal to 0.5 OD by DensiCHEK Plus. Samples were then put into the VITEK 2 compact system machine to transfer the bacterial suspension to a cassette by negative pressure, and the cassettes were incubated to complete a biochemical reaction within 12 h. the software of the VITEK 2 compact system was used to interpret the results.

The X-ray diffractometer (XRD) technique (Philips Analytical X-Ray B.V. with PC-APD, diffraction software, Philips expert, Holland) was used to determine the soil structure. XRD system was operated at 40 kV and 30 mA with CuKα radiation as the X-ray source, λ=1.54056 Å. The scan step time was 0.5 s with a step size of 0.02° and a scan range 10°–99.99°.

Stainless steel 316-AISI screens were used as cathode materials having different mesh sizes 30, 40, and 60 in⁻¹. The porosity of screens and their specific surface area were determined using Eqs. 1 and 2, respectively (Sioda, 1976):

\[ \varepsilon = 1 - \frac{m_s}{\rho_s l a_s} \]  \hspace{1cm} (1)

\[ s = (1 - \varepsilon)r \]  \hspace{1cm} (2)
where \((\varepsilon)\) is the porosity, \((m_s/a_s)\) is the weight/area density (g/cm\(^2\)), \((\rho_s)\) is the density of stainless steel 316-AISI (8.027 g/cm\(^3\)) (Green and Perry, 2008), \((l)\) is the thickness of the screen (cm), \(l=2d\), \((r)\) is the ratio of surface to volume of the wire forming the screen (cm\(^{-1}\)), \(r=4/d\), and \((s)\) is the specific surface area (cm\(^{-1}\)). The type of screen woven was recognized by an Olympus BX51M with DP70 digital camera system while the diameter of the wire \((d)\) was determined using a digital calliper.

The anode material was rectangular porous graphite \((59 \times 59 \times 15 \text{ mm})\) with 20–26% porosity supplied by Tokai Carbon Co., Ltd. The same X-ray diffractometer (XRD) mentioned previously was used to determine the structure of porous graphite. Scanning electron microscopy (SEM) (Tescan Mira3 FESEM, France) was used to identify the topography of the graphite surface. The SEM system was operated at \(AV = 15 \text{ kV}, \text{bias} = 0\), spot = 3.0 and \(HV = 2 \text{ kV}, \text{bias} = 1400 \text{ V}\).

BET method using BET Tavana, Iran which based on the software of micrometrics (MicroActive for TriStar II plus 2.03) was used to determine the specific surface area of the graphite.

### 2.2 Bio-electrochemical system

The fixed bed bio-electrochemical system adopted in the present work comprises from a fixed bed electrochemical cell, two reservoirs for the anolyte and catholyte solutions (each one is 1 L conical Pyrex flask), two dosing recirculation pumps (IML, HC-100, Italy) having a flow rate range 5–8 l/h, and two calibrated flowmeters at a flow rate range 0–0.25 l/min. Fig.1-a shows a schematic diagram of the system, while Fig.1-b displays the picture of the system. This configuration is known as a batch recycle mode which permits the recirculation of the anolyte and catholyte in two separate loops through the reactor.

Fig. 2 illustrates the design of the bio-electrochemical cell. It is essentially a rectangular Perspex electrolytic cell composed of two chambers. The first is the anodic chamber with dimensions 140 mm length \(\times\) 100 mm width \(\times\) 25 mm thickness while the second is the cathodic chamber having external dimensions 140 mm length \(\times\) 100 mm width \(\times\) 20 mm thickness. Cationic membrane (IONIC-64LMR) supported on both sides by PTFE perforated plates with 2 mm thickness was used to separate the anodic and cathodic chambers from each other. The cathode chamber consists of two cavities: an internal cavity with dimensions \(60 \text{ mm} \times 60 \text{ mm} \times 2 \text{ mm}\) in which a stainless steel plate \((59 \text{ mm} \times 59 \text{ mm} \times 2 \text{ mm})\) was fixed to act as a current feeder, and an external cavity with dimensions \(60 \text{ mm} \times 60 \text{ mm} \times 5 \text{ mm}\) in which stack of seven stainless steel screens (each \(59 \text{ mm} \times 59 \text{ mm}\)) was held to act as a fixed bed cathode. Providing the electrical current to each electrode was made by screw connectors passing through the walls of the cell. The anodic chamber consists of an internal cavity with dimensions \(60 \text{ mm} \times 60 \text{ mm} \times 18 \text{ mm}\) in which a porous graphite block \((59 \text{ mm} \times 59 \text{ mm} \times 15 \text{ mm})\) was fixed and acts as an anode. For increasing the contact surface area of the anode, grooves were made on its surface lengthily.
Figure 1. (a) Schematic diagram of the bio-electrochemical system, (b) Photographic picture of the bio-electrochemical system.
Figure 2. Schematic diagram of the bio-electrochemical cell.

The anolyte used in the experiments consists of (per liter): CH$_3$COONa 1 g, NaH$_2$PO$_4$·H$_2$O 2.45 g, Na$_2$HPO$_4$ 4.58 g, KCl 0.13 g, NH$_4$Cl 0.31 g, adjusted to pH = 7 (Luo, et al., 2014). Catholyte was CdCl$_2$ solution at the required concentration and adjusted to the desired pH via the addition of HCl or NaOH. The cathode was provided with a stack of stainless steel screens at the required mesh size while the anode was provided with 2 g of soil with spreading it on the anode surface. The cell was assembled after inserting a portion of anolyte with closing the inlet and outlet sections of the anode, then brought the cell to a -0.3 bar moisture potential then incubated at room temperature for three days for ensuring biofilm cultivation on the surface of the anode. After this, the bio-electrochemical cell was connected with the flow system. Before starting any run, the anolyte and catholyte were pumped through the cell for one hour with no connecting to power supply for activating of bacteria in the soil; then the required voltage was applied to the circuit using a DC Power Supply (UNI-T: UTP3315TF-L, China) by connecting the negative lead of the power source in series with a 10 Ω resistor to the cathode and the positive lead to the anode. The electrochemical system was run at a temperature of 25 ± 2 ºC.

Samples were taken though each run every 10 min for the first hour, then every 30 min for the second hour, and finally every hour until the end of the electrolysis at 6 hours. The concentration of Cd (II) was measured by atomic absorption spectroscopy (Varian SpectrAA 200 spectrometer). After each experiment, the cathode was replaced with a new stack of screens and the cathodic chamber was provided with a fresh catholyte. The medium in the anodic chamber was changed with a new anolyte medium, and the anode was provided with a new sample of soil. For studying the effect of the applied cell voltage, values of 0.6, 0.9, 1.2, 1.5, and 1.8 V were applied. The impact of the initial concentration was examined at values of 25, 50, 75, 100, and 125 ppm at a constant applied voltage and pH. The impact of pH was studied at values of 1, 3, 5, 7, and 9.

2.3 Analysis and calculations
Cadmium removal efficiency (RE %) was calculated using Equation 3 (Modin, et al., 2017):

\[
RE(\%) = \frac{C_i - C_f}{C_i} \times 100
\]

where \(C_i\) is the initial Cd concentration (ppm) and \(C_f\) is the final Cd concentration (ppm) after a period of electrolysis time (\(\Delta t\)).

Current efficiency (CE%) of the cathodic reactions can be defined as the fraction of electrical current (used for metal ion reduction) to the total current provided during the electrolysis.
Therefore its evaluation is based on the quantity of cadmium deposited during the electrolysis, as shown in Equation 4 (Modin, et al., 2017):

\[
CE\% = \frac{n_{Cd}z_{Cd}F}{\int_{0}^{t}I\,dt} \times 100
\]  

(4)

where \(n_{Cd}\) is the quantity of Cd deposited on the cathodic surface (mmol), and \(z_{Cd}\) is the number of electrons required to reduce Cd\(^{2+}\) \((2 \text{ mol(e}^{-})\text{mol}^{-1}\text{Cd})\). \(I\) is the current (mA), \(t\) is time (s), and \(F\) is Faraday’s constant \((96485.3 \text{ C mol}^{-1}\text{e}^{-})\).

The specific energy consumption \(EC \text{ (kWh kg}^{-1}\text{Cd})\) was evaluated based on the amount of cadmium deposition (Equation 5) (Modin, et al., 2017):

\[
EC = \frac{E \int_{0}^{t}I\,dt}{n_{Cd}M_{W}Cd \times 3600}
\]  

(5)

where \(E\) is the applied cell voltage (V) and \(M_{W}\) is the molecular weight of Cd \((112.414 \text{ g mol}^{-1})\).

3. Results and discussion

3.1 Characterization of soil and electrodes

3.1.1 Soil

The physiochemical measurements of the soil show that the MWHC was 7.5%, and its pH was 8.1, while its electrical conductivity was 290 \(\mu\text{S cm}^{-1}\). Results of VITEK 2 software system show that the main type of bacteria in the soil were \textit{Pseudomonas aeruginosa}, \textit{Bacillus}, \textit{Klebsiella pneumoniae}, \textit{Kocuria rosea}, \textit{cereus/thuringiensis/mycoides}, \textit{Acinetobacter baumannii}, \textit{Aeromonas hydrophila/caviae}, and \textit{Brevibacillus agri}. These results established the existence of four exoelectrogenic bacteria in the soil: \textit{Klebsiella pneumoniae}, \textit{Pseudomonas aeruginosa}, \textit{Bacillus cereus/thuringiensis/mycoides} and \textit{Aeromonas hydrophila/caviae}. These bacteria have the ability to transfer electrons outside the electrolytic cell via insoluble electron acceptors such as metal oxides or anodes (Raghavulu, et al., 2011; Sharma, et al., 2016). Fig.3 shows the XRD results of the soil which are mainly composed of silicon dioxide and calcium carbonate as showing in Table1.

![Figure 3. XRD pattern of the soil samples.](image-url)
3.1.2 Cathode

Stainless steel 316-AISI screens with the following chemical composition of (in wt %): Cr-16.7, Ni-12.2, Mo-2.1, Mn-1.32, Si-0.56, P-0.03, C-0.022, S-0.012, Cu-0.26, (Fe = balance) was used as a cathode. The properties of these screens are depicted in Table 2 where the specific surface area of these screens is larger than 38 cm$^{-1}$ and their porosities are higher than 0.6. Fig. 4 illustrates the image of three types of screens based on the woven types.

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Score</th>
<th>Compound Name</th>
<th>Scale Factor</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>96-710-3015</td>
<td>67</td>
<td>7103014</td>
<td>0.994</td>
<td>Si3.00 O6.00</td>
</tr>
<tr>
<td>96-702-0140</td>
<td>56</td>
<td>7020139</td>
<td>0.515</td>
<td>Ca6.00 C6.00 O18.00</td>
</tr>
</tbody>
</table>

Table 2. Screen parameters.

<table>
<thead>
<tr>
<th>N (in$^{-1}$)</th>
<th>30</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Woven type</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain square</td>
<td>0.03</td>
<td>0.025</td>
<td>0.02</td>
</tr>
<tr>
<td>d (cm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m/s, (g/cm$^2$)</td>
<td>0.124</td>
<td>0.122</td>
<td>0.129</td>
</tr>
<tr>
<td>s (cm$^{-1}$)</td>
<td>38.06</td>
<td>49.81</td>
<td>73.10</td>
</tr>
</tbody>
</table>

Figure 4. Photographic picture of woven screen mesh: (a) 30 (wire/ in), (b) 40 (wire/ in), (c) 60 (wire/ in).

3.1.3 Anode

Fig. 5 illustrates the XRD results of the porous graphite anode. They are in agreement with the standard graphite structure that has a reference code (96-901-2231) (Li, et al., 2007). Sharp diffraction peak at 20 = 26.6255° with C (002) and d-spacing of 3.34802 Å was observed. A picture of the anode is shown in Fig.6-a, while, the image of SEM related to porous graphite anode is presented in Fig.6-b with a magnification of 7500x. High porosity with large pores formed between interconnected structures was observed, which is entirely differed than the normal, non-porous solid graphite. The BET surface area results confirmed that porous graphite has a value of
a specific surface area equal to 22.75 m²/g, which is higher than those observed in the graphite felt (SGL carbon, GFA6 EA) (2.73 m² g⁻¹) (Jiang, et al., 2019).

Figure 5. XRD pattern of porous graphite.

Figure 6. (a) Picture of the anode (porous graphite), (b) SEM images of the porous graphite.
3.2 Effect of applied cell voltage

**Fig.7-a** shows the decay of Cd concentration versus time at different applied cell voltages. The effect of the applied cell voltage was studied at an initial cadmium concentration of 25 ppm, time of electrolysis (6 hr) and pH=7. On the other hand, **Fig.7-b** displays the corresponding current decay with time. It was observed that increasing the applied cell voltage leads to a decrease in the final concentration of Cd starting from 1.2V to 1.8 V where the final Cd concentration became lower than 1 ppm at 1.8V. A similar observation was found by Chen, et al., 2016. However, increasing cell potential from 0.6V to 0.9V; led to increase not decrease the final concentration of cadmium. The interpretation of this behaviour may be the system was under activation control at the applied voltage lower than 9V; hence fluctuation in the concentration of Cd may be happened, besides the hydrogen effect is not significant leading to increase current efficiency to approach 100% (Nancharaiah, et al., 2015). Increasing the applied cell voltage also leads to increase the value of the maximum peak of current and the final value of current (**Fig.7-b**). For the applied cell voltage from 0.6 to 1.8 V, the maximum peak of current increased significantly from 1.4 mA to 7 mA, at the same time, the final Cd concentration decreased from 3.88 ppm to 0.45 ppm. The experimental observation confirmed the undetectable of cadmium in the anodic chamber at the studied applied cell voltages hence eliminating the possibility of cadmium adverse effects on the anodic biofilms (Chen, et al., 2016). With the increasing of the applied potential, the pH values of the cathode effluent increased from an initial 7 to a range of 7.08 to 9.10. The increase in pH results from the reduction of water on the cathode surface leading to evolution of hydrogen as a side reaction and release OH\(^-\) ions in the catholyte (Colantonio and Kim, 2015). Nevertheless, these pH increases could not enhance the Cd (OH)\(_2\) formation in the MEC according to the solubility production of Cd(OH)\(_2\) (\(K_{sp} = 3 \times 10^{-16}\)) (Mortimer, 2008).

![Figure 7](image)

**Figure 7.** (a) Cd Concentration decay versus time at different applied cell voltages, (b) Current decay versus time at different applied cell voltages.
Table 3 shows the removal efficiency, current efficiency based on cadmium reduction, and energy consumption at different applied cell voltages. It is essential to note that values of current efficiency and energy consumption were determined based on Equations (4) and (5), which governed entirely by the current of power supply. It can be seen that increasing cell voltage from 0.6 to 1.8 V leads to increase the removal efficiency from 84.47% to 98.19% respectively. The increase of removal efficiencies was related to the fact that the absolute values of the cathodic potential increased with the applied cell voltage; hence more cadmium deposition is occurred (Nancharaiah, et al., 2015).

Table 3. Cd removal efficiency (RE), current efficiency (CE), and energy consumption (EC) of the microbial electrolysis cell, changing with the applied cell voltage.

<table>
<thead>
<tr>
<th>E(Volt)</th>
<th>RE (%)</th>
<th>CE (%)</th>
<th>EC(kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>84.47</td>
<td>316.96</td>
<td>0.05</td>
</tr>
<tr>
<td>0.9</td>
<td>69.88</td>
<td>117.91</td>
<td>0.34</td>
</tr>
<tr>
<td>1.2</td>
<td>95.5</td>
<td>44.84</td>
<td>0.71</td>
</tr>
<tr>
<td>1.5</td>
<td>97.08</td>
<td>39.56</td>
<td>1.01</td>
</tr>
<tr>
<td>1.8</td>
<td>98.19</td>
<td>24.75</td>
<td>1.94</td>
</tr>
</tbody>
</table>

It is clear that current efficiency decreases with increasing applied cell voltage while energy consumption increases with the increase in cell voltage. Results of current efficiency shows values higher than 100% approve that cadmium deposition is resulted from sharing other sources of current such as current produced by the anodic substrate (bacteria) in addition to that produced by power supply. At lower cell voltage, the contribution of current from the anodic substrate is higher than the current from power supply while at higher value of voltage the contribution of bacteria is decreased. The same behaviour was observed by Sleutels et al., 2011. Results of current efficiency confirmed the activity of Bactria in the soil, releasing more electrons to the anode via the oxidation of organic compounds at the anodic chamber.

Energy consumption was increased with the increase of cell voltage, ranging from 0.05 kWh/kg at 0.6 V to 1.94 kWh/kg at 1.8 V. highlighted the benefits of energy-efficient MEC in the present work over convention electrolysis cell used for cadmium reduction (Sulaymon, et al., 2017). The energy consumption in the present work is also lower than that observed at the previous works (Modin, et al., 2012; Chen, et al., 2016; Wang, et al., 2016). It was cleared that the cell voltage of 0.6Volt gives better current efficiency and lower energy consumption. However, the removal efficiency was very low. To improve the removal efficiency at this value of cell voltage further electrolysis time is needed, which may be resulted in reducing the current efficiency and increasing power consumption. Therefor cell potential 1.8V was adopted for further investigation of the effect of other parameters.

3.3 Effect of initial concentration

Fig.8-a illustrates the cadmium concentrations profiles with time at different initial Cd concentrations for operation at an applied voltage of 1.8V, time of electrolysis of 6hr, and pH=7. It can be seen that increasing of initial cadmium concentration from 25 ppm to 125 ppm results in obtaining the same final value of Cd concentration, which is lower than 1ppm. A similar observation was found by Chen, et al .2016. Choi, et al., 2014 found that cadmium removal efficiency was 93.43 ± 0.17%, 93.30 ± 0.74%, for 50 ppm, 100 ppm after 60 h at an applied voltage 1.57 V in their work for cadmium recovery by coupling double microbial fuel cells. This is an
indication that the system within this range of concentrations is operated at electrode potential higher (more negative) than standard potential of cadmium reduction (-0.40 V vs. SHE) (Colantonio and Kim, 2016); hence most of cadmium was removed. However, current efficiency would be lower at low concentration of cadmium due to compete of hydrogen evolution. Fig.8-b shows the corresponding current decay with time where the maximum current peak increased from 7 mA to 10 mA when the concentration increased from 25ppm to 125ppm. Such an increase of current with the initial concentrations might be related to the increase of catholyte conductivities. The increase of catholyte conductivities effectively reduced the internal resistance of BES system, thus improved the system performance (Jiang, et al., 2014).

**Figure 8.** (a) Cd concentration decay versus time at different initial Cd concentrations, (b) Current decay with time at different initial Cd concentrations

Table 4 represents the removal efficiency, current efficiency, and energy consumption at different initial Cd concentrations. It was observed that increasing of initial concentration leads to higher current efficiency and lower energy consumption. As shown in Table 4 concentration of 125ppm gives a complete removal efficiency of cadmium (100%) at 83.57% current efficiency and lower energy consumption in comparison with 25ppm therefore, concentration of 125ppm was chosen for further study of the effect of operation parameters. The energy consumption in this case is lower than previous works (Modin, et al., 2012; Wang, et al., 2016).

**Table 4.** Cadmium removal efficiency (RE), current efficiency (CE), and energy consumption (EC) of the microbial electrolysis cell, changing with initial Cd concentration.

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>RE (%)</th>
<th>CE (%)</th>
<th>EC(kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>98.2</td>
<td>24.32</td>
<td>1.97</td>
</tr>
<tr>
<td>50</td>
<td>97.12</td>
<td>43.66</td>
<td>1.10</td>
</tr>
<tr>
<td>75</td>
<td>98.95</td>
<td>58.60</td>
<td>0.82</td>
</tr>
<tr>
<td>100</td>
<td>99</td>
<td>68.52</td>
<td>0.70</td>
</tr>
<tr>
<td>125</td>
<td>100</td>
<td>83.57</td>
<td>0.57</td>
</tr>
</tbody>
</table>
3.4 Effect of initial pH

Fig. 9-a displays the Cd concentration decay with time at different initial pH of the catholyte and the corresponding current decay is shown in Fig. 9-b for operation at an applied cell voltage of 1.8V, initial Cd concentration of 125ppm, and time of electrolysis of 6hr. The results confirmed that the performance of the system completely differs at pH=1 than other pH values where the effect of side reaction is more noticeable. At pH=1, the peak of current is maximum (19mA), then decreased sharply to 6.89 mA at pH=9.

Figure 9. (a) Concentration decay versus time at different initial pH values, (b) Current decay versus time at different initial pH values.

Table 5 shows the effect of pH on the removal efficiency, current efficiency, and energy consumption. Results show clearly how the initial pH effect significantly on the removal efficiency where it was no more than 8.22% at pH=1 then increased rapidly to 80.64% at pH=3 and to 100% at pH=7 then decreased to 96.94% at pH=5 and 94.85% at pH=9. It was observed that pH =9 gives higher current efficiency and lower energy consumption but the removal efficiency not exceeded 94.85%, besides the final concentration of cadmium (6.44ppm) is greater than 1ppm (allowable limit); therefore, it is preferred to select pH =7 for further study since it gave complete removal efficiency of Cd and its related energy consumption is lower than previous works (Modin, et al., 2012; Chen, et al., 2016; Wang, et al., 2016).
Table 5. Cd removal efficiency (RE), current efficiency (CE), and energy consumption (EC) of the microbial electrolysis cell, changing with the initial pH.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>RE(%)</th>
<th>CE(%)</th>
<th>EC(kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.22</td>
<td>3.06</td>
<td>15.65</td>
</tr>
<tr>
<td>3</td>
<td>80.64</td>
<td>116.81</td>
<td>0.41</td>
</tr>
<tr>
<td>5</td>
<td>96.94</td>
<td>113.26</td>
<td>0.42</td>
</tr>
<tr>
<td>7</td>
<td>100.00</td>
<td>83.57</td>
<td>0.57</td>
</tr>
<tr>
<td>9</td>
<td>94.85</td>
<td>139.55</td>
<td>0.34</td>
</tr>
</tbody>
</table>

3.5 Effect of mesh size

**Fig.10-a** displays Cd concentration decay with time for the two cases the first is without using screens (flat cathode), while the second is with using screens at different mesh numbers for operating at an applied voltage of 1.8V, initial Cd concentration of 125ppm, time of electrolysis of 6hr, and pH=7. The corresponding current decay is shown in **Fig.10-b**. Table 6 illustrates the removal efficiency, current efficiency, and energy consumption in the case of using meshes and flat plate alone. It is clear that a major enhancement of removal efficiency was observed when using screens as a packed bed where the removal efficiency increased from 70% to 100% when using screens with mesh no. 30 in comparison with flat plate. This is an indication of the higher surface area of screens, which leads to more reduction of cadmium. The results showed that using screens with mesh number greater than 30 results in reducing in removal efficiency. The lowering of removal efficiency of screens with mesh numbers 40 and 60 may be resulted from the lower turbulence promoter hence lower mass transfer occurred (Sulaymon, et al., 2017). The current efficiency is higher with a flat plate, besides energy consumption is the lower indicating the feasibility of using flat plate but at lower removal efficiency with a final cadmium concentration (37.5ppm) which is higher than the allowable limit. Therefore it is recommended to use screens with mesh number of 30 for removing of cadmium.

![Graph](image)

**Figure 10.** (a) Cd concentration decay versus time for Cd removal without and with screens at different mesh sizes, (b) Current decay versus time for Cd removal without and with screens at different mesh sizes.
Table 6. Cd removal efficiency (RE), current efficiency (CE), and energy consumption (EC) of the microbial electrolysis cell, changing with screen mesh number.

<table>
<thead>
<tr>
<th>Mesh no.</th>
<th>RE(%)</th>
<th>CE(%)</th>
<th>EC(kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without mesh</td>
<td>70</td>
<td>267.81</td>
<td>0.18</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>83.57</td>
<td>0.57</td>
</tr>
<tr>
<td>40</td>
<td>92.72</td>
<td>135.34</td>
<td>0.53</td>
</tr>
<tr>
<td>60</td>
<td>82.07</td>
<td>127.93</td>
<td>0.37</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS
The results of the present work confirmed the possibility of the complete cadmium removal from simulated wastewater using a fixed bed bio-electrochemical reactor. The performance of this type of electrochemical reactor depends on various operating factors such as an applied cell voltage, initial Cd concentration, and initial pH. The applied cell voltage is the most significant factor in the removal of cadmium where applying cell voltage of 1.8 V could reduce the final concentration of cadmium to lower than 1ppm at the initial concentration of cadmium of 25ppm. The value of pH close to (1) is not recommended since most of the current goes for hydrogen evolution resulting in lower Cd removal efficiency. The present design of the cell can remove Cd with initial concentration ranging from 25-125ppm. Using the fixed bed reactor gave better results than a flat plate because of the higher surface area of the bed. These results suggest that a Fixed Bed bio-electrochemical reactor is a promising reactor design for the effective removal of heavy metals from wastewater. The optimum operating conditions were found to be a cell voltage of 1.8V, an initial Cd concentration of 125ppm, pH=7, and time of electrolysis equal to 6hr. Where a complete removal efficiency of cadmium (100%) was obtained at a current efficiency of 83.57% with an energy consumption of 0.57 kWh/kg Cd.

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REFERENCES


### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta t$</td>
<td>Electrolysis time, s</td>
<td></td>
<td>$m/a$</td>
<td>Weight/area density, g/cm$^2$</td>
<td></td>
</tr>
<tr>
<td>CE</td>
<td>Current efficiency, %</td>
<td></td>
<td>$MW$</td>
<td>Molecular weight of Cd, 112.414 g mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$C_f$</td>
<td>Final concentration, mg/L</td>
<td></td>
<td>$n_{Cd}$</td>
<td>Number of moles of Cd, mmol</td>
<td></td>
</tr>
<tr>
<td>$C_i$</td>
<td>Initial concentration, mg/L</td>
<td></td>
<td>$r$</td>
<td>The ratio of surface to volume of the wire forming the screen, cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter of the wire, cm</td>
<td></td>
<td>RE</td>
<td>Removal efficiency, %</td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>Energy consumption, kWh kg$^{-1}$Cd</td>
<td></td>
<td>$s$</td>
<td>Specific surface area (cm$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>Cell voltage, V</td>
<td></td>
<td>$t$</td>
<td>Time, s</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant, 96485.3 C mol$^{-1}$ (e$^{-}$)</td>
<td></td>
<td>$z_{Cd}$</td>
<td>The number of electron, mol(e$^{-}$)mol$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>Current, mA</td>
<td></td>
<td>$\rho_o$</td>
<td>Density of stainless steel, g/cm$^3$</td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>Thickness of the screen, cm</td>
<td></td>
<td>$\varepsilon$</td>
<td>Porosity, dimensionless</td>
<td></td>
</tr>
</tbody>
</table>