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A Novel Bio-electrochemical Cell with Rotating Cylinder Cathode for Cadmium Removal from Simulated Wastewater

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Abstract

A Novel microbial electrolysis cell (MEC) with a packed bed rotating cathode was utilized to evaluate the removal of cadmium (Cd) from a simulated wastewater. Effects of operating factors that govern the cathodic deposition of cadmium, such as the applied voltage across the cell, the initial concentration of cadmium, the initial pH of the catholyte, and the cathode rotation speed were studied. It was found that the applied cell voltage plays the main role that effect on the cadmium removal efficiency where higher removal efficiency of Cd could be obtained as the applied voltage increases, while the increase in the initial concentration of Cd has the opposite effect. The increase in pH up to 6 improves the removal efficiency as well as the increase in rotation speed up to 500 rpm gives higher removal efficiency. The optimal working parameters were an applied voltage of 1.5 V, initial Cd concentration of 150 ppm, initial pH of 6, and rotation speed of 300 rpm, which resulted in Cd removal efficiency of 99.13% and specific energy consumption of 0.918 KWh/kg Cd after 4h of electrolysis, that is significantly less than the energy required for cadmium removal using the traditional electrolysis approach. These findings showed that MEC with the new design could be a cost-effective and efficient way to remove Cd from wastewaters.

Keywords: Cadmium, Cathodic deposition, Microbial electrolysis cell, Rotating packed bed electrode, Wastewaters.

1.   Introduction

Heavy metal contamination considers one of the most significant environmental impacts due to the toxicity of heavy metals, the non-biodegradability, and the bioaccumulation which causes hazardous impact on the environment and public health [1]. Cadmium, zinc, copper, nickel, mercury, and chromium are frequently found in the industrial wastewaters [2]. Heavy metal toxicity can cause many impacts such as mental and neurotoxicity damage, lowering levels of energy and damage to the blood, lungs, liver, kidneys, and other important organs. Cadmium, in particular, is one of the most hazardous heavy metals for human health which has been blacklisted in the European community and classified by the U.S. Environmental Protection Agency as a probable human carcinogen [3]. Cadmium exposes human health to severe risks, for example, kidney dysfunction, anemia, renal. damage, and osseous disease with effects similar to osteoporosis, and Itai-Itai disease [4]

Many sources of cadmium enter aquatic environments such as industry, smouldering units, PVC plastic, mining, electroplating, pigments, ceramic, batteries, and paper industries in addition to much other manufacturing and processing industrial plants [5]. Through using various intra- and extracellular mechanisms, Cd (II) can be removed via application of bioaccumulation, biosorption, bio-mineralization, enzymatic reduction or oxidation [6]. In addition to other tradition methods such as Ion-exchange [7], precipitation using chemicals [8], electrodialysis, reverse osmosis [9], and Coagulation – Flocculation [10]. Conventional biological processes could be considered as another strategy to physical-chemical processes for remediation of Cd (II)-contaminated sites [6]. On the other hand, the majority of these processes have negative economic and environmental repercussions, such as the production of contaminated sludge and expensive capital and operating cost [11].

Electrochemical cleaning technique via cathodic deposition is particularly useful to control pollution by removing transition and heavy metals through redox processes [12].The treatment of concentrated effluents as well as the diluted effluents that contained Cu, Zn, Ni, and Cd from mining wastes, wastewater, plating, and recycling operations has been effectively achieved by utilizing rotating cylinder electrode reactors (RCE) [13,14]. The RCE consists of an inner cylinder (cathode) that deposits metal and provided with turbulence promotions to improve mass transfer (high mass-transfer coefficient), as well as a single cylinder anode or several anodes that are concentrically bonded to the reactor walls and interconnected. To get satisfactory current and potential distributions for selective recovering, this type of cell provides a uniform concentration profile in the inter-electrode gap [15].

Electrochemical treatment of diluted solutions requires the use of an electrochemical reactor having a high specific surface area of the electrode as well as a high mass-transfer coefficient to increase the space-time yield. This goal can be achieved by using a packed bed rotating cylinder electrode, which was described as a successful electrochemical reactor for the removal of heavy metals [16]. Wastewater treatment by cathodic deposition has gotten additional importance in the early two decades when metallic screens were used as a three-dimensional electrode in the formation of the cathode [16, 17]. Abbar et al., 2018 studied the mass transfer characterization of a spiral-wound woven wire mesh rotating cylinder electrode. This electrode was made up of a central core or axis (typically used as a current feeder) that is wrapped in continuous mesh layers [17]. They found that this packed bed electrode has high turbulence promotion and high mass transfer coefficient due to its large surface area per unit volume [17].

Bioelectrochemical systems (BESs) involving microbial electrolysis cells (MECs) and microbial fuel cells (MFCs) have been known to be a talented technology for removing heavy metals from wastewaters [18,19]with generating energy such as electricity or hydrogen gas simultaneously[20]. MECs were used to recover heavy metals such as zinc, cadmium, lead, and cobalt by applying an external voltage. In these MECs, the organic materials are oxidized by exoelectrogenic bacteria that existing at the cell's bioanode, while at the cathode surface two reduction reactions occurred, the first is the hydrogen gas generation due to the water reduction and the second is the deposition of heavy metals due to the reduction of their ions. As a result, treatment of wastewater is happened with the recovery of energy in the form of hydrogen gas. In MECs, specifically at the anode chamber, organic compounds such as acetates are oxidized by the bacteria (forming bio-layer on the anode surface) and converted to CO_2 and H_2O with generating electrons [21].

Multiple reactors of bioelectrochemical systems have been employed for cadmium recovery where one reactor (MFC) used to power the other (MEC) for the reduction of Cd (II) to Cd. [22]. Chen et al., 2016 used biocathode for enhancing Cd removal with hydrogen production [23]. Saad et al., 2020 used fixed bed cathode for removal of cadmium from a simulated wastewater using soil as a source of bacteria [24]. However, the majority of previous works employed stationary cathodes. As a result, the goal of this research is to see how well MEC with a spiral-wound woven wire mesh rotating cylinder cathode can be used to remove cadmium from simulated wastewater. To the best of the authors' knowledge, no such research has been conducted. The impacts of operating parameters like the applied voltage, pH, initial concentration of Cd, and rotation speed on the cadmium removal efficiency were investigated.

2. Experimental work

2.1. Materials and system

The bio-electrochemical system used in the present work for cadmium removal consists of a rotating packed bed bioelectrochemical reactor, a magnetic stirrer hotplate (IKA, Germany), an electrical motor (type, Phoenix-USA), two Avometers (type, Kwun Tong, Kowloon, Hong Kong), and a power supply (model UNI-T: UTP3315TF-L). Figure 1 shows the schematic diagram of the electrochemical system.
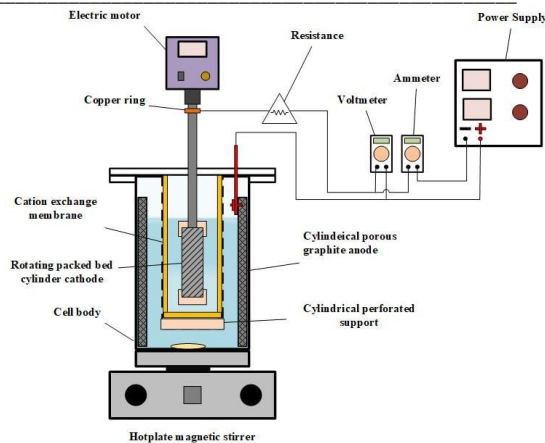
Figure 1 schematic diagram of the electrochemical system

The bioelectrochemical cell is a new design cell composed of a cylindrical cell body having dimensions (14 cm in length x 11 cm in diameter) ended above by a flange with dimensions (15 cm outside diameter with a thickness of 0.5 cm). The cell and its flange were made from Perspex material. Cylindrical porous graphite with dimensions (10 cm in length x 9.8 cm in diameter with 0.5 cm thickness) and having an apparent lateral surface area of 270.176 cm^2 was used as anode. It was purchased from HP Graphite Handan Co., Ltd. The BET surface area of the porous graphite was measured using ISO-9277-2010 method at petroleum R &D center, ministry of oil in Iraq using BET surface area analyzer model-No. Qsurf9600, Thermo Finnegan Co. USA. The cathode was a spiral-wound woven wire mesh rotating cylinder. It was composed of continuous mesh layers of stainless steel wrapped around a central rode having dimensions (15 cm in length x 0.8 cm in diameter) made from the same material. These wrapped mesh layers form a packed bed with an external diameter of 2 cm and a length of 4.8 cm and bounded by two Teflon sleeves which have 2.6 cm external diameter and 2 cm in length. The stainless steel woven screen used in the construction of the cathode has a mesh no. of 30 wires per inch and its specific surface area was 38.06 cm^{-1}. More information about estimating the specific surface area of this screen was described elsewhere [21]. The dimensions of the woven wire sheet used for constructing the packed bed cathode were (48 cm in length and 4 cm in width) and one of its ends was fixed on the central road through a slit (1-mm- wide and 40-mm-long). The sleeves formed a right angle to the cathode and protruded by a small distance from it. In this case any sharp increase in current density that lead to growth a localized dendrite deposition would be prevented [25]. This configuration of the rotating cylinder electrode produces higher turbulence as the rotation speed of the electrode increases. The catholyte chamber is a new design made from Perspex material. It was composed of two main parts: the first is a supporting cylindrical perforated container having

dimensions (11 cm in length x 7 cm in diameter) and perforated with 10 mm holes on its lateral surface. The distance between any two holes was (1.5 cm) and the total numbers of the holes were (40). This supporting container was ended on its top with a flange having dimensions (15 cm in diameter with a thickness of 0.5 cm) and contained four holes with a diameter of 0.4 cm for fixing the cathodic chamber with the cell body via bolts and nets after inserting a gasket between them. The second part is a cylindrical ion exchange membrane chamber. It was constructed from a cation exchange membrane in a cylindrical form with dimensions (11cm in length x 5.6 cm in diameter) and joint at the bottom with a cylindrical Perspex disc with dimensions (5.5 cm in diameter and 0.5 cm in thickness). The cylindrical membrane chamber was made by taking a sheet of the membrane with dimensions (11cm in width and x18 cm in length) then rounded as a cylinder by fixing its lateral edges with an epoxy adhesive (Epoxy Syringe- Seisli, Turkey) and it's bottom on the disc. The cation exchange membrane was (IONIC-64LMR).

The anode was inoculated with activated sludge as a source of bacteria taken from a local biological unit of Al-kargh wastewater treatment–No.2/Baghdad sewage department/Iraq and fed with the nutrient medium as a source of carbon-containing (per liter): Na_2HPO_4 4.58g , $NaH_2PO_4 \cdot H_2O$ 2.45 g, CH_3COONa 1 g, NH_4Cl 0.31 g, KCl 0.13 g, adjusted to pH = 7 [26]. The cathode chamber was provided with a catholyte solution composed of cadmium chloride ($CdCl_2$) at different concentrations based on the conditions of the experiment. A fresh cathodic mesh screen was used in every experiment and it was cleaned by rinsing with nitric acid solution (1M) in an ultrasound cleaner for 10 min then washed thoroughly with double-distilled water before using.

Experiments were conducted by the agitation of anolyte for one hour at a rotation speed of 300 rpm using a magnetic hot plate stirrer without connecting the anode and cathode to the power supply for activation of the bacteria in the activated sludge. After that DC power supply was used to apply the suitable voltage across the cell via joining the negative lead of the power source in series with a 10 Ω resistor and the cathode while the positive lead was connected to the anode. All runs were performed at temperature of 25 ± 2 ℃. During the electrolysis, samples were taken every 10 min at the first hour, then every 30 min at the second hour, followed by every hour until the end of the electrolysis at 4 h Atomic absorption spectroscopy (Varian SpectrAA 200 spectrometer) was used to measure the concentration of cadmium. A new catholyte was used after each experiment at the cathode chamber.

Graphite structure was determined by an X-ray diffractometer (XRD)) using XRD 6000 /Shimadzu/ Japan). The XRD was operated at 40 kV and 30 mA with CuKα radiation as the X-ray source, λ=1.54060 Å. The scan step time was 1.2 sec with a step size of 0.2 degrees and a scan range of 10 – 90 degrees. Graphite SEM image was obtained by Scanning Electron Microscopy (SEM) using TESCAN-VEGA/USA. The measurement parameters were: AV = 15 kV, bias = 0, spot = 3.0 and HV = 2 kV, bias = 1400 V. Stainless steel identification was performed using a scanning electron microscope(FEI_ Company, Netherlands, Model: Inspect S50) provided with Energy Dispersive X-Ray Spectroscopy (EDX) using Bruker Company/ Germany, XFlash_6l10/Model. The strategy adopted in the present work for studying the effect of variables is one factor at a one-time methodology consequently effect of the applied voltage was studied by considering different values in the range of 0.6 to 1.8 volt with fixing all other parameters. After determining the best value of the applied voltage, the effect of the initial concentration of Cd was then studied by changing the concentration between (50-250 ppm) for determining the best value of the initial concentration then pH effect was investigated at a pH range of 3-7 and finally the effect of rotation speed of the cathode was evaluated at values 100-500rpm after determining the best pH value.

2.2 Analysis and calculations

Equation 1was adopted to calculate Cadmium removal efficiency (RE %) [21]:

$$RE(\%) = \frac{c_i - c_f}{c_i} \times 100 \qquad (1)$$

where C_i and C_f represent the initial and final concentrations of Cd in ppm respectively during an electrolysis period (Δt).

cathodic current efficiency (CE%) as an important measurement which defined as a ratio of electrical current used specifically for metal ion reduction to the total current used for electrolysis process. Therefore, its value represents the amount of cadmium deposited on the surface of cathode during the electrolysis operation only, as shown in Equation 2 [21]:

$$CE\% = \frac{n_{Cd} \cdot z_{Cd} \cdot F}{\int_0^t I \cdot dt} \times 100 \qquad (2)$$

Where I denotes to current used in mA, t represents electrolysis time in second,n_{Cd} is amount of Cd deposited in mmol, z_{Cd} denotes to the required number of electrons for reducing cadmium ions(2 mol(e-)mol^{-1} Cd),and finally (F) known as Faraday's constant (96485. C mo^{-1} (e-)).

Eq. 3 can be used to find the specific energy consumption (SEC) which represents the required energy for deposition of cadmium only (kWh kg^{-1} Cd)[21]:

$$EC = \frac{E \int_0^t I \cdot dt}{n_{Cd} \cdot MW_{Cd} \cdot 3600} \qquad (3)$$

Where *MW* is the molecular weight of Cd (112.414 g mol^{-1}) and *E* is the voltage applied across the cell (V).

3. Results and discussion

3.1 Characterization of the electrodes
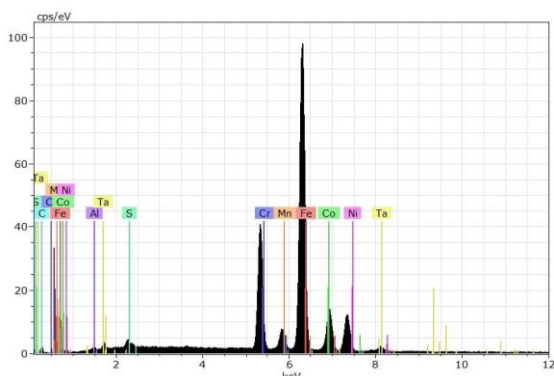
a) Cathode

EDX results of the stainless steel screen with mesh no. 30 are shown in figure 2 and Table 1. The EDS

analysis (Table 1) demonstrates the stainless steel mesh composed of Fe, Co, Cr, Ni, Mn, and Ta element. The existence of tantalum (Ta)indicates that the type of stainless steel could be stabilized as AISI347 austenitic stainless steel [25]. This type of stainless steel has been used in both conventional and nuclear power plants due to its excellent corrosion resistance properties at elevated temperatures [27].

b) Porous graphite anode

Figure 4 shows the XRD of the porous graphite anode. XRD results of the graphite display a sharp diffraction peak at $2\theta = 27.122°$ with C (002) and d-spacing of 3.28514 Å. It corresponds to the standard structure of graphite based on the reference code (96-901-2231)[28].

Figure 5 illustrates an SEM image of the porous graphite anode at a magnification of 500x. Results showed that graphite has a porous structure with organized structure containing large pores. The BET analysis showed that porous graphite has specific surface area 0.89 m^2/g. This porous structure could be enhanced the stability of biofilm formation on the anode


**Figure2** Analysis of EDS for stainless-steel cathode

Figure 3 shows an SEM image of the stainless steel screen where it was observed that the woven type of screen is a plain square with a wire diameter of 0.247mm.

Table1. Analysis of EDS for stainless-steel cathode
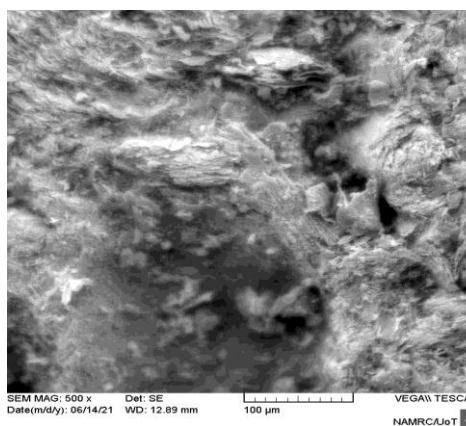
El	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Fe	26	K-series	47.12	35.86
Co	27	K-series	14.56	10.5
Cr	24	K-series	13.93	11.38
C	6	K-series	8.99	31.82
Ni	28	K-series	6.29	4.55
Ta	73	K-series	4.64	1.09
Mn	25	K-series	2.38	1.84
S	16	K-series	1.34	1.78
Al	13	K-series	0.74	1.17
Total:			100	100
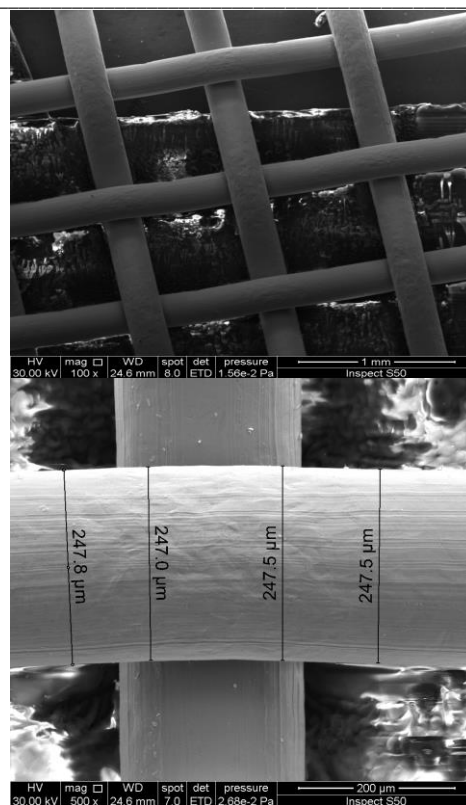
Figure 3 SEM images of stainlesssteel screen cathode
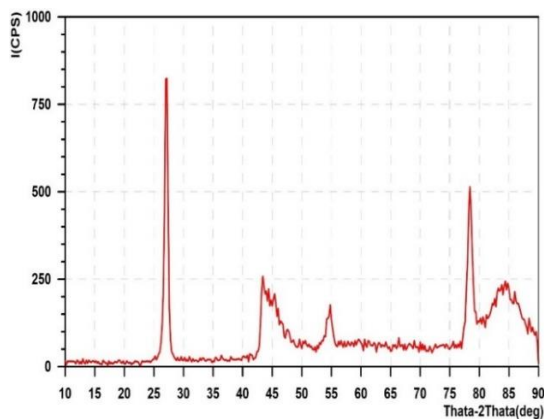

Figure 4. XRD pattern of graphite


Figure 5. SEM images of porous graphite

3.2 Effect of using activated sludge

To see the effect of using activated sludge as a source of electrooxygenated bacteria for electrons generating in the present work with the case of no using it, different runs were performed using different volume ratios of activated sludge to a fixed volume of the catholyte (160ml). Figures (6. a,b) in combination with Table 2 show the comparison of the using different volume ratios of activated sludge. Figure 6.a shows current profile with time at various activated sludge volume ratios, where greater current peaks were recorded at the start of operation when activated sludge was used in comparison with no sludge. This recognizes the role of bacteria in the sludge in creating electrons via the oxidation process, resulting in additional current being generated in addition to the current provided by the power source for cadmium reduction on the cathode surface. Figure 6. b demonstrates the Cd concentration profile over the time. It can be seen that employing activated sludge with a volume ratio of (50ml/160ml) results in a larger decrease in the concentration of cadmium. The concentration decay seems to be an exponential decay confirming the electrochemical deposition of cadmium is under mass transfer control and this behavior is well-matched with most previous studies since the concentration of metal is very low [29]. Employing activated sludge with a volume ratio (50ml/160ml of catholyte) provided higher removal efficiency approaching 97.67% with a final concentration of cadmium ions lower than 3.5 ppm as shown in Table 2. For further investigation of the effect of other variables, this ratio was adopted. Without sludge, the removal efficiency was 90% with 15ppm as Cd final concentration.

Table 2 further stated that the specific energy consumption are approximately closer in their values for all cases, hence using activated sludge results in increasing the removal efficiencies at the same energy consumption
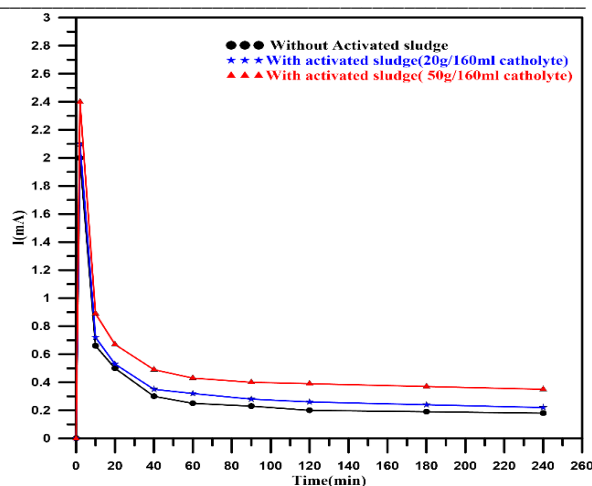
(a)
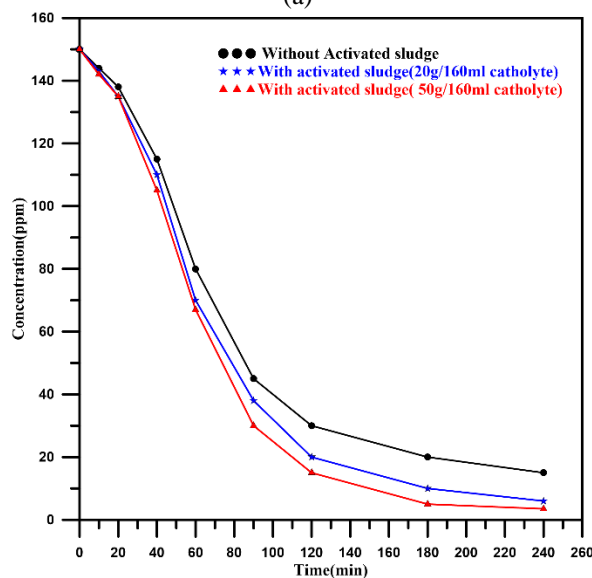
(b)

Figure 6. Effect of activated sludge on the efficiency of cadmium removal. a) Current profile with time, b) Concentration profile with time: E=0.6V, [Cd]=150ppm, pH=5, 300rpm.

Table 2 Effect of activated sludge on the efficiency of cadmium removal E=0.6V,[Cd]=150ppm,pH=5,300rpm

| Anolyte	Final Conc. (ppm)	pH		RE%	SCE (KWh/kg)
		initial	final		
Without activated sludge	15	5	9.5	90	0.0335
With activated sludge (20g/160mlcatholyte)	6	5	9.5	96	0.0377
With activated sludge (50g/160ml catholyte)	3.5	5	9.6	97.67	0.0532

3.3   Effect of Applied voltage

Figures (7-a,7-b) illustrate the current profile and concentration profile at different applied voltage respectively while Table 3 demonstrates the impact of applied voltage on the Cd removal efficiency. As illustrated in Fig.7.a, higher applied voltage results in a higher current peak and higher current end value. Furthermore, as seen in Table 3, utilizing a higher voltage resulted in increasing the removal efficiency and lowering the final cadmium concentration as evidenced by Fig.7.b. Similar results were observed by previous works [24, 30]. Results showed that

increasing applied voltage lead to increasing of the specific energy consumption and decreasing current efficiency. Current efficiency greater than 100% was observed and similar behaviour was observed by Weng-Fang Cai et al., 2010. [31]. It's worth noting that the current efficiency and energy consumption were calculated using Eqs.1 and 2, which based on current coming from power supply only. As a result, current efficiency higher than 100% indicates that the cadmium was removed via a technique other than by direct current reduction on the cathode from the power source.
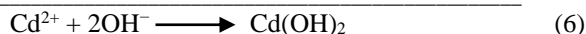
Cadmium is known to be removed from MECs using cathodic reduction or electrodeposition:

$$Cd^{2+} + 2e^- \longrightarrow Cd \quad E^0 = -0.40V vs. SHE \quad (4)$$
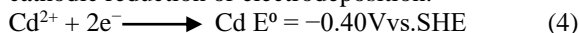
The local pH at the cathode rises due to the hydrogen evolution reaction by reduction of water

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad (5)$$
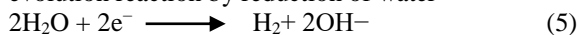
Cadmium can also be removed by precipitation as cadmium hydroxide in addition to cathodic reduction as pH exceeded 8.5 [32]

$$Cd^{2+} + 2OH^- \longrightarrow Cd(OH)_2 \quad (6)$$

The pH values of the cathode effluent increased from 5 to 11 when the applied voltage was raised. A similar remark was made by Colantonio & Kim, 2016 [22]. With a final concentration of 2 ppm, it appears that applying a voltage of 1.5 volts resulted in a removal efficiency of 98.67% with a current efficiency of 80.944% . As a result, it was used in subsequent research to look at the effects of other variables.
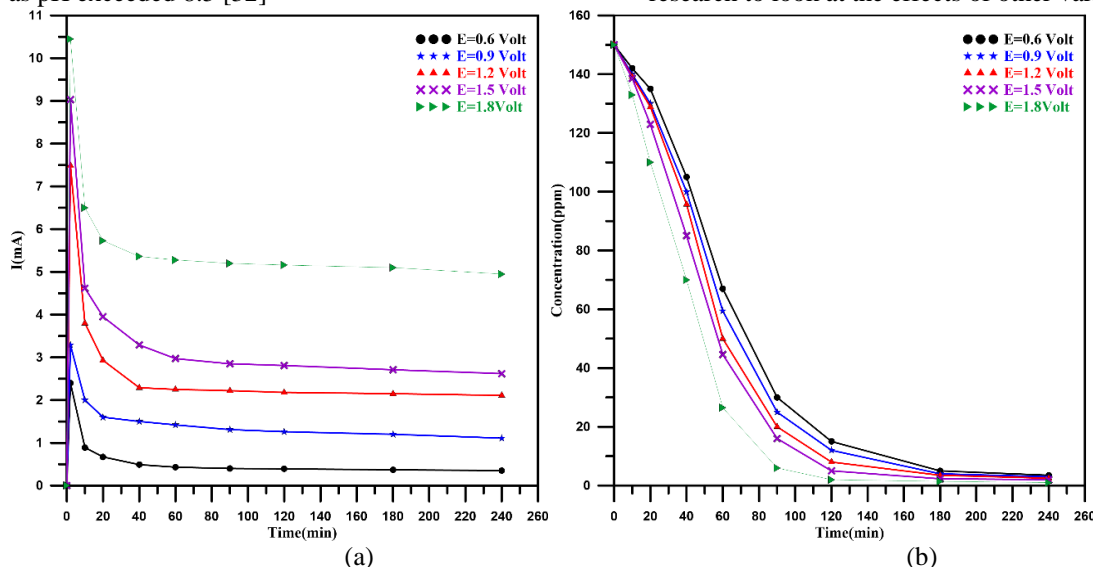
Figure 7. Effect of applied voltage on the efficiency of cadmium removal.a) Current profile with time). Concentration profile with time. [Cd]=150ppm,pH=5,300rpm

Table 3 Effect of applied voltage on the efficiency of cadmium removal. [Cd]=150ppm,pH=5,300rpm

E (Volt)	Final Conc. (ppm)	pH		RE%	CE%	SCE (KWh/kg)
		initial	final			
0.6	3.5	5	9.6	97.67	573.78	0.0532
0.9	3	5	10	98	179.34	0.2393
1.2	2.5	5	10.2	98.33	101.73	0.5624
1.5	2	5	10.4	98.67	80.944	0.8836
1.8	1	5	11.1	99.33	45.25	1.8966

3.4 Effect of initial concentration

Figures (8-a,8-b) illustrate the current profile and concentration profile at different initial concentrations of Cd respectively while Table 4 demonstrates the impact of initial Cd concentration on the removal efficiency of cadmium. As can be seen in Fig.8-a increasing concentration of cadmium results in increasing the current peak value. Increasing the conductivity of the catholyte solution could be the reason in rising current peak and the end current values where increasing of Cd content from 50 to 250ppm leads to rise the catholyte conductivity from 320 to 1400 µS/cm. Higher catholyte conductivities greatly decreased the BES system's internal resistance, resulting in improving the performance of the system[33,21]. As illustrated in Fig.8.b, increasing the initial Cd concentration led to a higher final cadmium concentration. Table 4 shows that the removal effectiveness decreased slightly up to 200ppm, then began to drop as concentration increased. Meanwhile, increasing of Cd concentration gives lower specific

energy consumption and higher current efficiency. At almost all cadmium concentrations, the final pH became approximately 10.4. Previous investigations have shown that the pH around the MEC cathode is high enough to facilitate salt precipitation and that a high local pH was maintained [34].

As indicated in Table 4, a concentration of 150ppm results in a good cadmium removal (98.67%) at a current efficiency of 80.994% with a lower energy consumption than those obtained at concentration of 50ppm, therefore it was chosen for future investigation of the effect of operational parameters.

3.5 Effect of pH

Figures (9-a,9-b) illustrate the current profile and concentration profile at different pH respectively while Table 5 demonstrates the impact of initial pH on the Cd removal efficiency. Figure 9-a. shows that the beak of current rises as pH decreased, whereas their corresponding end values had the opposite impact. The impact of a side reaction is more obvious. The

highest current (11.24mA) is reached at pH=3, then drops significantly to 8.76 mA at pH=7. The experimental results showed that increasing the initial pH results in increasing the removal efficiency, where it was only 71.65 % at pH=3 then quickly improved to 80.83 % at pH=7. Specific energy consumption dropped as pH decreased, while current efficiency increased.   Ma. de Lourdes Llovera-Hernández,et al.,2015[35] noticed that the efficiency of removing the cadmium increases as the catholyte's starting pH rises in the traditional removal of cadmium by electrolysis. Using soil as a source of bacteria, we found previously that pH had a comparable effect on removal efficiency [21].
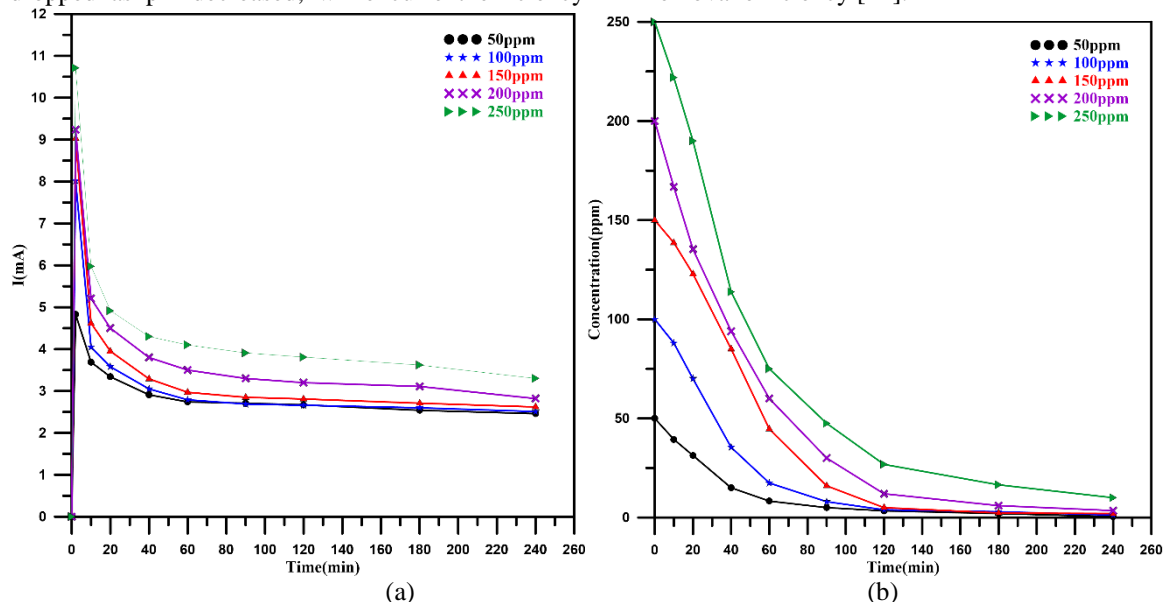
Figure 8. Effect of initial concentration on the efficiency of cadmium removal. a) Current profile with time, b) Concentration profile with time: E=1.5V, pH=5,300rpm

Table 4 Effect of initial concentration on the efficiency of cadmium removal. E=1.5V,pH=5,300rpm

Conc. (ppm)	Final Conc. (ppm)	pH		RE%	CE%	SCE (KWh/kg)
		initial	final			
50	0.5	5	10.4	99.0	29.18	2.45
100	1.3	5	10.6	98.7	56.35	1.269
150	2	5	10.4	98.67	80.944	0.8836
200	4	5	10.4	98.0	93.42	0.765
250	10	5	10.4	96.0	98.102	0.7291
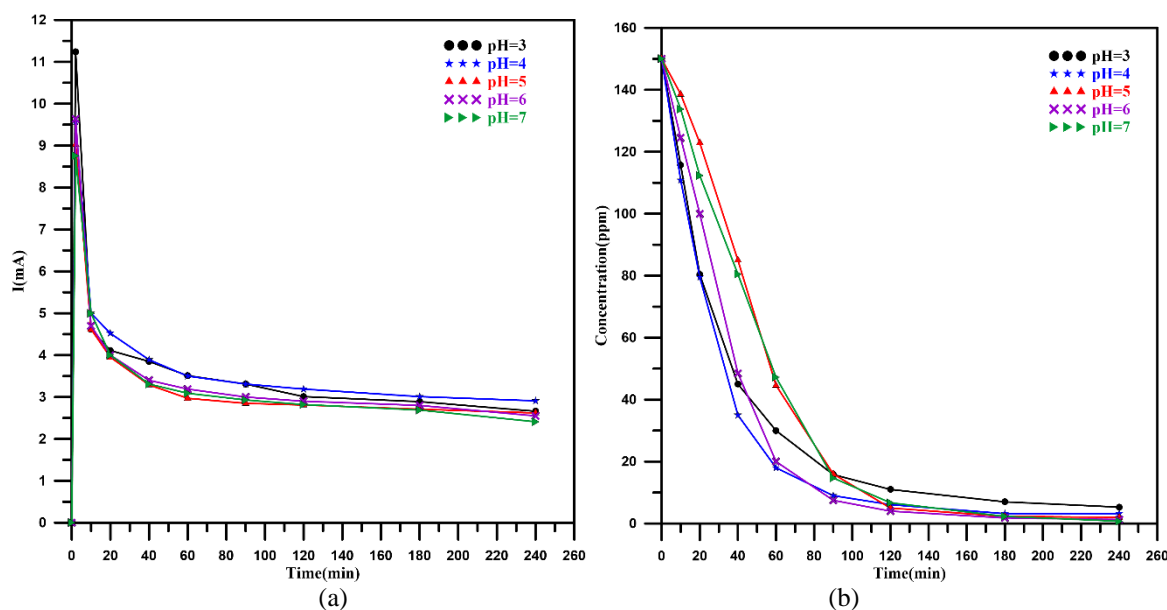
Figure 9. Effect of pH on the efficiency of cadmium removal. a) Current profile with time, b) Concentration profile with time: E=1.5V, [Cd]=150ppm, 300rpm

When starting at a pH of 6 or 7, an approximately similar response was observed. In spite of operating at a pH of 7 resulted in a decrease in the energy consumption, however the final pH value was increased to be more alkaline. It was preferable to use pH=6 for further exploration of the rotation speed effect.
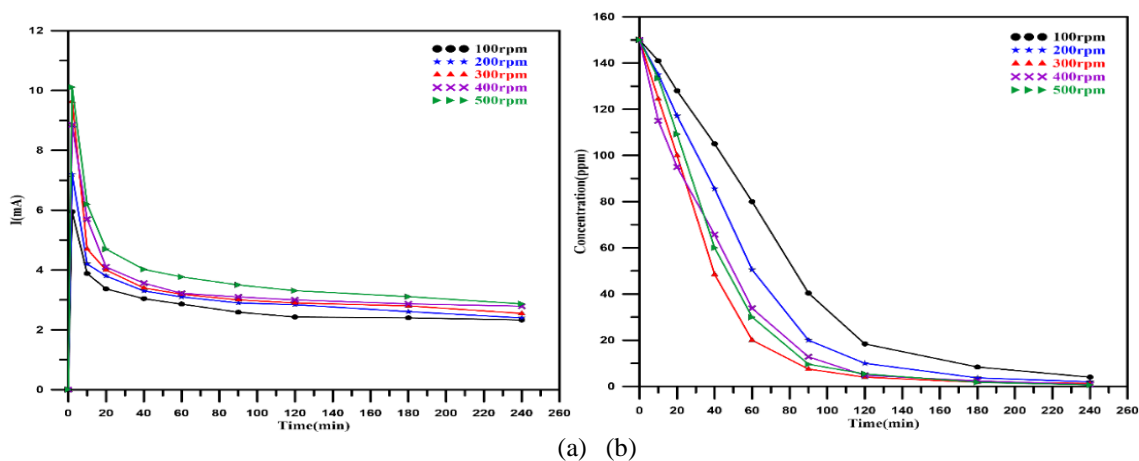
3.6 Effect of rotation speed

Figures (10-a,10-b) illustrate the current profile and concentration profile at different rotation speed respectively while Table 6 demonstrates the impact of rotation speed on the Cd removal efficiency.

The findings showed that rotation speed is the most important element. Because of the strong impact of rotation speed, the present type of rotating cylinder electrode is more susceptible to the experiment's hydrodynamic conditions due to the mass transfer restrictions.[17]. The findings of removal efficiency, current efficiency, and specific energy consumption were given in Table 6. As illustrated in Fig.10.a, the highest peak of current was noticed at 500rpm, whereas the maximum end value of current was reached at 300rpm. Based on Fig.10.b, the lower final concentration of Cd after 4 h operation was identified at rotation rates of 400 and 500rpm.

Table 5 Effect of pH on the efficiency of cadmium removal. E=1.5V,[Cd]=150ppm,300rpm

pH	Final Conc. (ppm)	pH		RE%	CE%	SCE (KWh/kg)
		initial	final			
7	0.76	7	11.3	99.49	80.83	0.884
6	1.3	6	10.5	99.13	78	0.918
5	2	5	10.5	98.67	80.944	0.8836
4	3.2	4	10	97.87	69.79	1.024
3	5.3	3	9.5	96.47	71.65	0.9982

(a)   (b)

Figure 10 Effect of rotation speed on the efficiency of cadmium removal ;a)Current profile with time ,b) Concentration profile with time: E=1.5V,[Cd]=150ppm, pH=6

Table 6 Effect of rotation speed on the efficiency of cadmium removal. E=1.5V,[Cd]=150ppm, pH=6

Rotation speed (rpm)	Final Conc. (ppm	pH		RE%	CE%	SCE (KWh/kg)
		initial	final			
100	4	6	10.7	97.33	88.55	0.8077
200	2.5	6	10.7	98.33	81.85	0.8738
300	1.3	6	10.7	99.13	78	0.918
400	0.8	6	10.6	99.47	74.6	0.958
500	0.65	6	10.5	99.57	76.3	0.937

The removal efficiency increases from 97.33 to 99.57 percent when the rotation speed is increased from 100 to 500 rpm. Chemical precipitation was confirmed by the final pH values, which were roughly within 10.4. The removal efficiency dropped lower than 99% as the rotation speed being below 300rpm. As a result, the optimum value in this work is to use a rotation speed of 300 rpm.

4. Conclusions

The new design of microbial electolyisis cell (MEC) has the ability to remove all cadmium from simulated wastewater using rotating packed bed cathode. The performance of the new design of electrochemical reactor is influenced by several variables, including the applied cell voltage, initial Cd concentration, pH, and rotation speed. As the applied voltage increased, the removal efficiency grew significantly, besides, raising the starting cadmium concentration resulted in a decrease in removal efficiency. A pH of less than (3) results in poorer Cd removal efficiency since most of the current goes to hydrogen generation therefore it is not

advised to operate at pH below 3. To provide efficient turbulence improvement and high mass transfer with acceptable current efficiency and energy consumption, a rotation speed of 300rpm is required. The best operating conditions were determined to be 1.5V cell voltage, 150ppm starting Cd concentration, pH=6, rotation speed of 300 rpm , and 4 h electrolysis time. These conditions result in Cd removal efficiency 99.13% and current efficiency of 78 % requiring energy consumption of 0.918 kWh/kg Cd. Another advantage of the current system is that it can use the created hydrogen gas as a renewable energy source by changing the design of the cathodic chamber to collect and store H_2 for later use. With decreased operational costs, the method used in this study can be used to extract or recover cadmium from real electroplating effluent. As a result, MEC might be adopted as a promising technology for removing cadmium from wastewaters.

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References

1. Abourached, C., Catal, T., and Liu, H., Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production. *Water Research*, **51**, 228–233(2014).

2. Torab-Mostaedi, M., Ghassabzadeh, H., Ghannadi-Maragheh, M., Ahmadi, S. J.and Taheri, H., Removal of cadmium and nickel from aqueous solution using expanded perlite. *Brazilian Journal of Chemical Engineering,* **27**(2), 299–308(2010).

3. Steiner, T. J., Birbeck, G. L., Jensen, R., Katsarava, Z., Martelletti, P. and Stovner, L. J., The Global Campaign, World Health Organization and Lifting the Burden: Collaboration in action. *In Journal of Headache and Pain,* **12**(3), 273–274(2011).

4. Amarasinghe, B. M. W. P. K. and Williams, R. A., Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, **132**(1–3), 299–309(2007).

5. Yaqub, S. and Javed, M., Acute toxicity of water-borne and dietary cadmium and cobalt for fish. *In International Journal of Agriculture and Biology*, **14**(2), 276–280(2012).

6. Kurniawan, T.A., Chan, G.Y.S., Lo, Wai-hung and Babel, S., Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Sci. Total Environ*, **366**, 409–426(2006).

7. Corte´s-Martinez, R., Martinez-Miranda, V., Solache-Rıos, M. and Garcıa-Sosa I., Evaluation of natural and surfactant-modified zeolites in the removal of cadmium from aqueous solutions. *Sep. Sci. Technol.*, **39** (11), 2711–2730(2004).

8. Bhattacharya, D., Shin, J.H., Sun, G.H. and Craig Jr. A.B., Application of sulfide precipitation for the removal of heavy metals from industrial wastewaters, *in: Proc. 2nd World Congress of Chem. Eng*., **I**, 548–552(1981).

9. Abu Qdaisa, H. and Moussa, H. Removal of heavy metals from wastewater by membrane processes: a comparative study, Desalination, **164** (2004) 105–110.

10. Yongpeng Xu, Leisan Yang and Jingkun Yang, Removal of cadmium (II) from aqueous solutions by two kinds of manganese coagulants. *Int. J. Eng. Sci. Technol.*, **2** (7), 1–8(2010).

11. Ziyath, A. M., Mahbub, P., Goonetilleke, A., Adebajo, M. O., Kokot, S. and Oloyede, A., Influence of Physical and Chemical Parameters on the Treatment of Heavy Metals in Polluted Stormwater Using Zeolite—A Review. *Journal of Water Resource and Protection*, **03**(10), 758–767(2011).

12. Juttner, K., Galla, U. and Schmieder, H., Electrochemical approaches to environmental problems in the process industry. *Electrochim. Acta.* **45**, 2575–2594(2000).

13. Gabe, D.R., The rotating cylinder electrode. J. Appl. Electrochem., **4**, 91–108(1974).

14. Low, C.T.J., De Leon, C.P. and Walsh, F.C., The rotating cylinder electrode (RCE) and its application to the electrodeposition of metals, *Aust. J. Chem.,* **58** , 246–262(2005).

15. Hernández-Tapia, J. R., Vazquez-Arenas, J. and González, I., Electrochemical reactor with rotating cylinder electrode for optimum electrochemical recovery of nickel from plating rinsing effluents. *Journal of Hazardous Materials*, **262**, 709–716(2013).

16. Abbar, A. H., Salman, R. H., and Abbas, A. S., Cadmium removal using a spiral-wound woven wire meshes packed bed rotating cylinder electrode. *Environmental Technology and Innovation,* **13**, 233–243(2019).

17. Abbar, A. H., Salman, R. H. and Abbas, A. S., Studies of mass transfer at a spiral-wound woven wire mesh rotating cylinder electrode. *Chem. Eng. Process. - Process Intensif.*,**127**, 10–16(2018).

18. Nancharaiah, Y. V., Mohan S. V. and Lens, P. N. L., Metals removal and recovery in bioelectrochemical systems: A review. *Bioresour. Technol.,* **195**, 102–114(2015).

19. Wang, H. and Ren, Z. J., Bioelectrochemical metal recovery from wastewater: A review. *Water Research,* **66**, 219–232(2014).

20. Wang, Y., Wang, B., Liu, Y. and Chen, Q., Electricity and hydrogen co-production from a bio-electrochemical cell with acetate substrate. *Int. J. Hydrogen Energy*, **38**, 6600–6606(2013).

21. Saad, D. R., Alismaeel, Z. T. and Abbar, A. H. Cobalt Removal from Simulated Wastewaters Using a Novel Flow-by Fixed Bed Bio-electrochemical Reactor. *Chemical Engineering*

and Processing - Process Intensification, **156**(12), 108097(2020).

22. Colantonio, N. and Kim, Y. Cadmium (II) removal mechanisms in microbial electrolysis cells. *Journal of Hazardous Materials*, **311**, 134–141(2016).

23. Chen, Y., Shen, J., Huang, L., Pan, Y. and Quan, X., Enhanced Cd(II) removal with simultaneous hydrogen production in biocathode microbial electrolysis cells in the presence of acetate or NaHCO3. *International Journal of Hydrogen Energy*, **41**(31), 13368–13379(2016).

24. Saad, D. R., Alismaeel, Z. T. and Abbar, A. H., Removal of Cadmium from Simulated Wastewaters Using a Fixed Bed Bio-electrochemical Reactor. *Journal of Engineering*, **26**(12), pp. 110–130(2020) .

25. J.M. Grau and J.M. Bisang, Electrochemical removal of cadmium using a batch undivided reactor with a rotating cylinder electrode. *J. Chem. Technol. Biotechnol.*, **76**, 161–168(2001).

26. Luo, H., Liu, G., Zhang, R., Bai, Y., Fu, S. and Hou, Y., Heavy metal recovery combined with H2 production from artificial acid mine drainage using the microbial electrolysis cell. *Journal of Hazardous Materials*, **270,**153–159(2014).

27. Yin, Y., Structural Alloys for Power Plants ‖ Austenitic steels and alloys for power plants. 105–152. (2014). doi:10.1533/9780857097552.2.105

28. Li, Z.Q., Lu, C.J., Xia, Z.P., Zhou, Y. and Luo, Z., X-ray diffraction patterns of graphite and turbostratic carbon. *Carbon,* **45**, 1686–1695(2007).

29. Ruotolo, L.A.M. and Gubulin, J.C. Electrodeposition of copper ions on fixed bed electrodes: Kinetics and hydrodynamic study. *Brazilian Journal of Chemical Engineering*,**19**(1),105-118(2002).

30. Choi, C., Hu, N. and Lim, B., Cadmium recovery by coupling double microbial fuel cells. *Bioresource Technology*, **170**, 361–369(2014).

31. Cai, Wen-Fang, Geng, De-Li and Wang, Yun-Hai, Assessment of cathode materials for Ni (II)) reduction in microbial electrolysis cells. *RSC Adv.,* **6**(38), 31732–31738(2016).

32. Purkayastha, D., Mishra, U. and Biswas, S., A comprehensive review on Cd(II)removal from aqueous solution. *J. Water Process Eng.,* **2**, 105–128(2014).

33. Zhang, Y., Yu, L., Wu, D., Huang, L., Zhou, P., Quan, X. and Chen, G., Dependency of simultaneous Cr(VI), Cu(II) and Cd(II) reduction on the cathodes of microbial electrolysis cells self-driven by microbial fuel cells. *Journal of Power Sources*, **273**, 1103–1113(2015).

34. Colantonio, N., Guo, H. and Kim, Y., Effect of Low Cadmium Concentration on the Removal Efficiency and Mechanisms in Microbial Electrolysis Cells. *Chemistry Select*, **1**(21), 6920–6924(2016).

35. Ma. de Lourdes Llovera-Hernández, Álvarez-Gallegos, A., Hernández, J.A. and Silva-Martínez, S. Cadmium removal from dilute aqueous solutions under galvanostatic mode in a flow-through cell, *Desalination and Water Treatment*, **57**(48-49), 22809-22817 (2015).