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Application of the eco-friendly bio-anode for ammonium removal and power generation from wastewater in bio-electrochemical systems

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ABSTRACT

In this new insight, the potential application of the eco-friendly bioanode material was investigated with the aim of ammonium removal and its recovery, alongside power generation from wastewater in bio-electrochemical systems (BES_s). In this procedure, biodegradation of ammonia was directly accrued via bioanode compartment driven by in-situ generated bioelectricity. To this end, this protocol was implemented with the anaerobic microbial as a biocatalyst in an anode chamber, as well as aerobic cathode chamber and a Nafion117 membrane as a separator with attractive results for the BES. The findings of the study suggested that BES, at the optimum operational conditions, can be an effective process for removing the high concentrations of organic materials and ammonium from industrial wastewater. The maximum BES efficiency was obtained 94% for the ammonium removal with a chemical oxygen demand (COD) concentration of 10,000 mg/L and a maximum organic removal rate of 78% with a substrate concentration of 2000 mg/L. The maximum voltage, power and current density of the BES was 481 mV, 62.7 mW/m^2, 570 mA/m^2, respectively. Further, an increase in NH_4Cl concentration improved the maximum current density (808 mA/m^2). The results demonstrated that the bio-electrochemical system could be utilized to treat industrial wastewater, containing high amounts of ammonium and organic materials, by adjusting the organic matter to ammonium (COD/NH_4^+) ratio while simultaneously generating electricity. Generally, the application of this eco-design, and sustainable bioanode material can be a good foundation and new perspective for practical application with regards to green and sustainable chemistry.

1. Introduction

Implementation of the eco-friendly and sustainable procedures for power generation caused by wastewater treatment, along with the removal of pollutants is considered as one of the appealing aspects of bio-electrochemistry (Palanisamy et al., 2019). Bio-electrochemical systems (BES_S) are one of the reproducible energy supplies in which bacteria play as active biocatalysts in oxidation reaction of a substrate like organic materials. In addition, BESs transform chemical bond energy of organic wastewater to electricity without passing through extra intermediate stages (Chatterjee et al., 2019). In these systems, there is a bio-electrochemical cycle in which microbial and chemical processes occur. Bacteria consume a substrate anaerobically which results in producing electrons and protons. Electrons through anode and external circuit reach cathode surface on which a chemical reaction starts in presence of protons and oxygen. Therefore, in a BES system, one of the main components is the bioanode (Rossi et al., 2018). A dense anodic biofilm results in a good behavior of BES. By an excellent exoelectrogenic biofilm on anode electricity

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production will be increased. It is more economical to apply mixed culture biocatalyst. However, mixed cultures from various sites are different from each other by exoelectrogens percent. It counts a concern but the researchers have shown that the performance of mixed culture can even be better than pure case in long-term run of BES for electricity generation. Hence, due to the key role of bacteria in BES, electricity produced by this device is called bioelectricity (Li et al., 2018).

As mentioned, microorganisms consume organic materials as substrate. From simple sugar like glucose to complex ones such as cellulose, starch all can be utilized as substrates in BESs. Up to now, acetate and glucose have been known as the most useable and productive organic materials in BESs. In the case of glucose being used as fuel for the BES, the anodic and catholic reactions have been presented in equations (1) and (2) (Rahimnejad et al., 2015).

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

$$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O \quad (2)$$

Fig. 1 (A). Shows the needful components of a BES, consisting mainly of an anode and a cathode. In BES, electrogenic microorganisms attach to the anode electrode and degrade the organic material and substrate into protons, electrons, and carbon dioxide. Fig. 2 (B) is a schematic diagram of different electron transfer mechanisms in a bioanode: (I) direct electron transfer; (II)) electron transfer through microbial nanowires; (III) electron transfer through electron shuttle (mediators); (IV) direct electron transfer via outer surface Redox-active protein (Li et al., 2018).

The present study aimed to use bioanode in bio-electrochemical systems for organic material and ammonium removal in addition to electricity generation. To the best of our knowledge, this is the first study that separately evaluated the effect of the high initial concentration of ammonium and COD on the rate of ammonium biodegradation and the amount of ammonium transfer from the cation exchange membrane (CEM). In this regard, ammonium removal and its recovery is a critical issue in modern wastewater treatment systems which can lead to electricity generation (Daverey et al., 2019). Previous literature review shows considerable scientific efforts for ammonium removal that can be generally categorized as biological and abiotic procedures (Ye et al., 2018). Electroadsorption, reverse osmosis, Nano filtration, and ion exchange are among some of the abiotic approaches that are widely employed for removing ammonium ion from the wastewater. From the environmental view, these procedures still suffer from several disadvantages including the production of brine and other by-

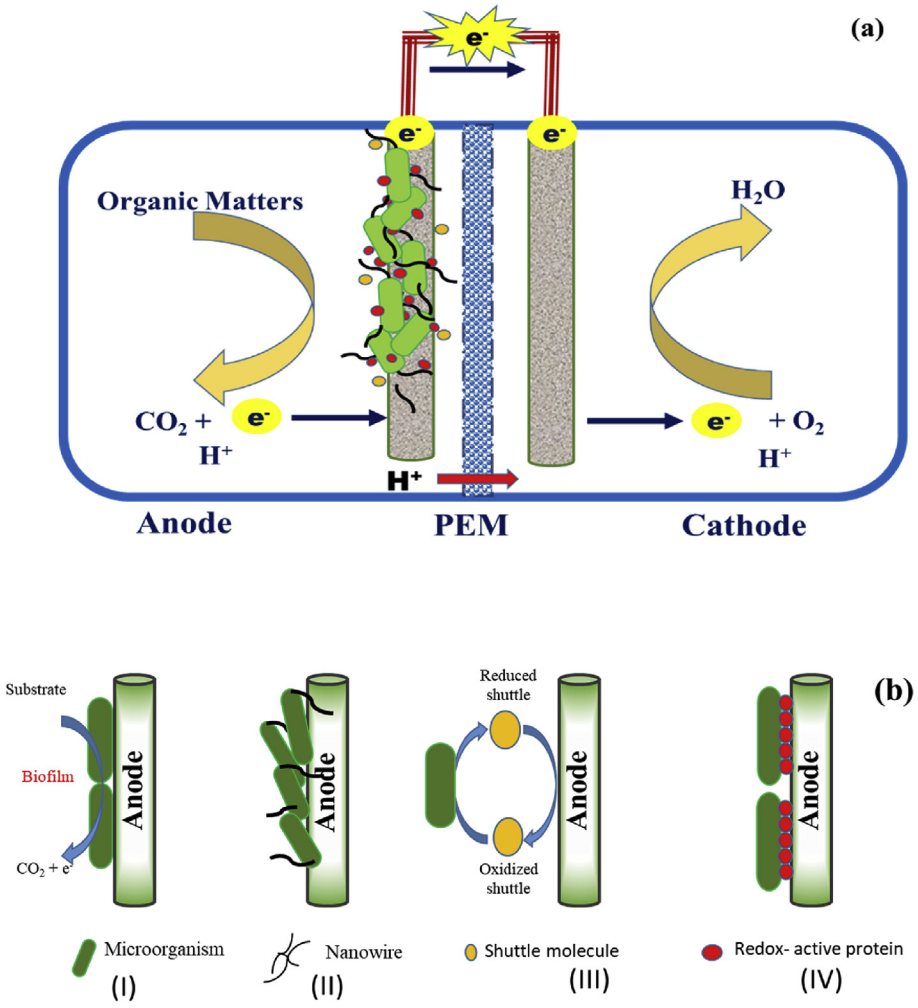
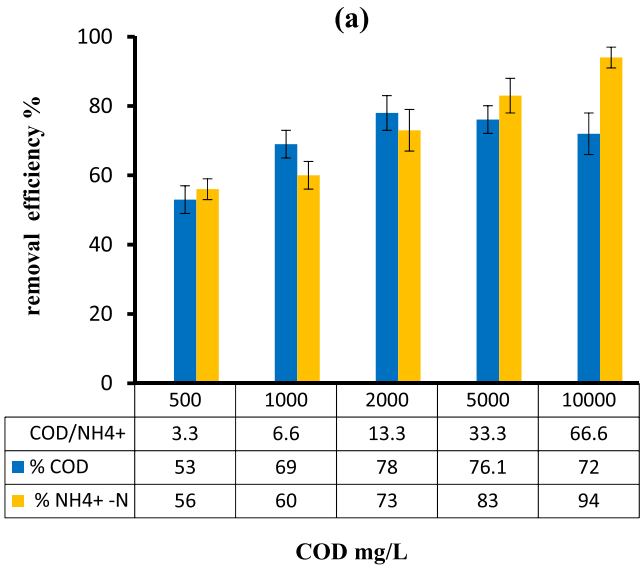


Fig. 1. Principles of operation of bio-electrochemical systems (BESs) (a), and schematic diagram of different electron transfer mechanisms in a bioanode (b). (I) direct electron transfer; (II)) electron transfer through microbial nanowires; (III) electron transfer through electron shuttle (mediators); (IV) direct electron transfer via outer surface Redox-active protein.



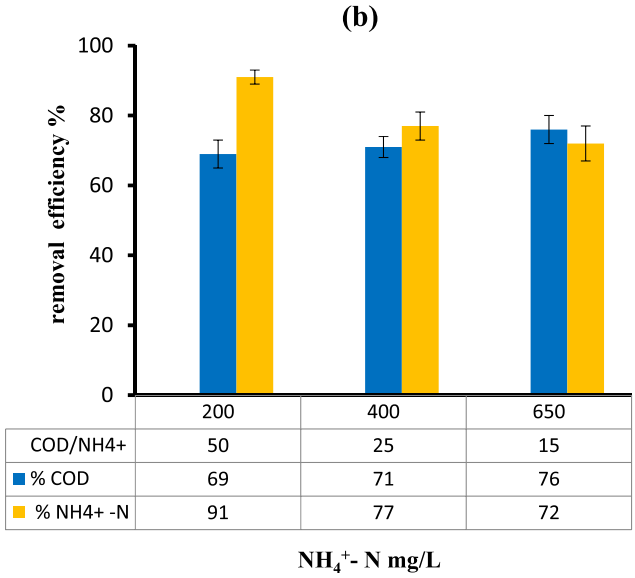


Fig. 2. COD and ammonium removal efficiency (%) in the anodic compartment of BES reactors with different initial COD concentrations, NH_4^+ of 150 mg/L (a), and with different initial NH_4^+ concentration, COD 10,000 mg/L (b).

products (Kim et al., 2014).

From the sustainable chemistry standpoint, energy consumption and current efficiency are procedures neglected as well (Mohamed et al., 2018). On the other hand, BES_S are proposed as an eco-design (Choudhury et al., 2017), powerful, and innovative technology for wastewater treatment and the production of electricity (He et al., 2017). Moreover, numerous studies are conducted to develop BESs for nitrogen removal and its recovery (Sun et al., 2016). In most bio-electrochemical systems, ammonium is removed through nitrification and denitrification processes using bio-cathode materials, along with specific nitrifying and denitrifying bacteria (Gogina and Gulshin, 2016). However, to our knowledge, no study has investigated the biological degradation of ammonium using anaerobic electro-genic bacteria as bioanode material in the BESs. Accordingly, the current study evaluated the amount of removal and the recycling of ammonium ions from wastewater and electricity generation by employing eco-designed bioanode material in a homemade BES.

High concentrations of ammonium are typically found in several major industries such as agro-food industry wastewater (Cecconet et al., 2017), petrochemicals manufacturing (Feng et al., 2015), reject water (Wu and Modin, 2013), coke production (Chan et al., 2009), petroleum refinement (Mohanakrishna et al., 2018), swine wastewater (Kim et al., 2015) and landfill leachate (Hassan et al., 2018). The removal of high concentrations of ammonium is extremely costly and time-consuming by chemical and conventional biological methods, respectively (Huang et al., 2018; Santoro et al., 2017). Accordingly, scholars mainly focused on using simultaneous nitrification and denitrification (SNAD) methods (Ali and Okabe, 2015; Yan Li et al., 2016) or autotrophic denitrification (Nguyen et al., 2015; Pan et al., 2018) in bio-electrochemical systems due to electron (e^-) and hydrogen (H^+) production. Therefore, BES is known as a suitable and highly efficient technology for the removal of high concentration ammonium (Ye et al., 2019), with low oxygen and energy consumption (Do et al., 2018), low sludge production (Keith et al., 2015; Mian et al., 2019), and the lack of any by-products (Mook et al., 2012).

In BES, anaerobic ammonium oxidation processes (e.g., ANAMMOX) were also studied which yielded in suitable results (Zhu et al., 2016). The presence of high ammonium concentration in the anodic chamber is regarded as an important advantage of this perspective that should be highlighted, which is due to the biological growth and activities of bioanode bacteria that can result in improving BES efficiency in removing the organic materials (Qin et al., 2017). Synchronously, the enhancement of BES efficiency leads to a substantial increase in electricity production (Gude, 2016). In addition, high concentrations of ammonium ions in anodic compartment result in adjusting the solution pH as a buffer, which makes a suitable environment for the growth and activity of the bioanode bacteria and improves the performance of the bio-electrochemical system (Zhan et al., 2014b). Similarly, the feasibility of the ammonia recovery of BES is of great importance. The diffusion of NH_4^+-N ions from anodic to the cathodic compartment, which is performed by the membrane for the charge balance during wastewater treatment with a two-chamber BES, provides the possibility of the ammonium recovery (Cheng et al., 2013; Kuntke et al., 2012). Nevertheless, only the anolytes with low strength (i.e., synthetic and real wastewater) is employed in the majority of BESs (Tian et al., 2018; Wu et al., 2017). However, the high concentration of ammonium has an impact on anaerobic digestion by affecting methanogenesis (Yang Li et al., 2016; Liu et al., 2016).

This study further determined that the bio-electrochemical system could be utilized to treat industrial wastewater, containing high amounts of ammonium and organic materials, by adjusting the organic matter to ammonium (COD/NH_4^+) ratio while simultaneously generating electricity. Finally, in the second part, the effect of phosphate buffer concentration on the ammonium transfer and its rate into the cathode chamber, as well as ammonium recycling capacity were investigated under abiotic conditions (without the presence of microorganisms).

2. Materials and methods

2.1. Chemical and materials

Different materials such as glucose ($C_6H_{12}O_6$,H_20), ammonium chloride (NH_4Cl), potassium dihydrogen phosphate (KH_2PO_4), potassium hydrogen phosphate (K_2HPO_4), magnesium sulfate ($MgSO_4$), calcium chloride ($CaCl_2$), potassium chloride (KCl), hydrochloric acid (HCl 37%), sodium chloride (NaCl), sulfuric acid (H_2SO_4 95–97%), hydrogen peroxide (H_2O_2 30%), Nafion117 (Sigma-Aldrich), yeast, peptone were purchased from Merck Company and used without further purification. All aqueous solutions were

prepared daily with distilled water at room temperature and the buffered solutions were prepared based on Kolthoff's tables.

2.2. Bio-electrochemical system setup

Biodegradation and ammonia removal were performed in a homemade two-electrode bio-electrochemical system (BES) reactor that was employed in a batch condition at a definite temperature of 30 °C and the ambient barometric pressure (Kim et al., 2015). This reactor encompassed two compartment Plexiglas with a volume of 450 mL, which was divided by a cation exchange membrane (Nafion, 117) with the establishment of two carbon plates (50 mm × 40 mm × 3 mm) as anode and cathode electrodes. An analog-digital data logger and the external resistance of 1000 Ω were connected to the electrodes by the copper wire with 0.5 mm diameter (Rahimnejad et al., 2011). Then, the electricity product was constantly logged every 10 min for 120 h. In order to purify the Nafion, it was first boiled for 1 h in H_2O_2 (30%) solution, then was washed with distilled water and H_2SO_4 (0.5 M) solution, and finally, washed with distilled water once more (Mashkour et al., 2017). Further, the graphite plate electrodes were immersed in acetone for 20 min, boiled in HCl (0.1 M) for 15 min, and finally, washed with deionized water to remove the contaminants from the electrode surfaces (Safari et al., 2014).

2.3. Experimental process

In this study, glucose was used as carbon source and ammonium chloride as nitrogen source. The COD indicator has been used to indicate the amount of organic matter consumed and has been evaluated by estimating the removal rate of COD (Shin et al., 2015). According to the Columbian efficiency calculations given below and from the literature, CE was calculated by determining ΔCOD. The BES containing microorganisms at different concentrations of COD (i.e., 500, 1000, 2000, 5000, and 10,000 mg/L) and at a constant concentration of NH_4^+-N (150 mg/L) was run. The production power and the removal efficiency were investigated for different concentrations of the organic matter, as well. Further, the bio-electrochemical system at a constant COD concentration of 10,000 mg/L and at different concentrations of ammonium (200, 400, and 650 mg/L NH_4^+-N), which resulting in variable COD/NH_4^+-N ratios (Table 1) was assessed. The ratio of carbon to nitrogen (COD/N), as one of the key parameters on the performance and function of biological systems (Liu et al., 2017; Yadu et al., 2018). COD/N ratios was studied in the range of 3.3–66.6, as it was shown in the previous study that biological systems have higher efficiency in the COD/N ratio in the ranges of 15–20 (Khorsandi et al., 2011).

The ammonium recovery efficiency by the migration of the ions through the Nafion117 from the anode to the cathode compartment, and the removal of ammonium ion through biodegradation in the anode chamber were investigated. The ratio of COD/NH_4^+ as one of the key parameters on the performance of biological systems was considered in anode compartment. The cathode chamber was filled with phosphate buffer, then an aerated pump was used to continually supply dissolved oxygen in the cathode chamber as an electron acceptor.

2.4. Anolyte and bioanode preparation

The anodic compartment was equipped with the sludge (i.e., the mixed microorganisms of the anaerobic sludge of the wastewater treatment plant of Hamadan city) and synthetic wastewater as a substrate including (g/L of wastewater) glucose and ammonium (at different concentrations), KH_2PO_4 (0.25), K_2HPO_4 (1.4), KCl, (0.13), $CaCl_2$, (0.1), NaCl (0.1), $MgSO_4$ (0.1), and 0.1 mL of trace mineral solution (Kim et al., 2014). The anolyte was adjusted at the pH of 7.4 by phosphate buffer for microorganism activities in the seed sludge. Furthermore, the anodic compartment was kept under magnetic stirrer and purged by pure nitrogen gas in order to create a suitable anaerobic condition (Kuntke et al., 2011).

Likewise, to prepare anaerobic microorganisms in the anodic compartment, the anaerobic sludge, as an inoculum, was added to the artificial culture medium (including glucose 10 g/L, yeast extract 3 g/L, and peptone 1 g/L) and incubated for 24 h under anaerobic conditions at 30 °C. Moreover, 10% V/V of the prepared inoculum was added to the anode compartment in order to format the electrogenic biofilm layer on the anode surface. Examining the BES performance at different concentrations of the substrate, the concentration of mixed liquid suspended solids (MLSS) in the anode chamber was 2500 ± 500 (mg/L) after inoculation (Birjandi et al., 2016).

2.5. Recording data processing

The power density and polarization curves were recorded by changing the external resistance from 10 to 100,000 Ω at the maximum voltage. Then, power density, normalized based on the employed anodic surface area, was calculated by the strike of voltage and the current normalized based on the employed anodic surface area. The computer linked to the system automatically recorded the voltage, current, and power (Mashkour et al., 2016). The requirements were supplied for the online monitoring of the polarization curve, which reported the alteration of voltage and BES power density according to the current.

2.6. Analytical methods

The chemical oxygen demand (COD) or ammonium removal percentage throughout the process was calculated based on the following equation (Birjandi et al., 2016):

Table 1
Impact of initial substrate concentration in the anode compartment on the electricity production, Columbic efficiency, current density, and ammonia-nitrogen removal efficiency.

COD concentration mg/L	NH_4^+-N Concentration mg/L	COD/NH_4^+	NH_4^+-N removal efficiency %	COD removal efficiency %	voltage mV	Current density mA/m^2	power densities mW/m^2	Columbic efficiency %
500		3.3	56	53	284	300	26.7	12
1000		6.6	60	69	321	365	30.54	13.8
2000	**150**	13.3	73	78	368	400	44.4	14.1
5000		33.3	83	76.1	447	545	52.5	16.6
10,000		66.6	94	72	481	570	62.7	18.6
10,000	**200**	50	91	69	482.6	590	62.37	18.8
	400	25	77	71	528	710	66.5	19.2
	650	15	72	76	558.7	808	84.28	22.3

$$R = \frac{C_i - C_f}{C_i} \times 100\% \quad (3)$$

where, R, C_i, and C_f demonstrate COD or ammonium removal percentage, initial concentration (mg/L), and the final concentration (mg/L), respectively.

The current density (mA/m^2) and power density (mW/m^2) were achieved as follows

$$I = \frac{V}{RA} \quad (4)$$

$$p = \frac{RI^2}{A} \quad (5)$$

where, V is the measured cell voltage and I signifies the produced current. Additionally, R and A represent the electrical resistance and the surface area of the anode, respectively, and P denotes the power density (Kuntke et al., 2011).

Coulombic efficiency (CE_{SYS}), was calculated as the ratio of experimental to theoretical coulombs. For the BES operating in a batch cycle, CE was computed using the following equation:

$$CE_{sys} = \frac{8It}{FV_A \Delta\, COD} \times 100\% \quad (6)$$

where, CE_{SYS} and t are the percentage (%) of coulombic efficiency, and the time (s) and I and F demonstrate the average current density output (A) and the Faraday's constant (96,485 C/mol), respectively. In addition, V_A is the volume anolyte (L) and ΔCOD denotes the organic matter content changes over time (mg/L) (Kim et al., 2015).

The chemical flux through the Nafion 117 can be calculated in terms of the mass transfer coefficient (K_{Cm}). The calculation was slightly different for the chemicals that could not be kept at a constant concentration in one of the compartments. K_{Cm} is given using (Kim et al., 2014):

$$K_{cm} = \frac{V}{2A_m t} \ln[c^*] \quad (7)$$

$$C^* = \frac{\left(c_{An,0} - C_{Cat,\ (t)}\right)}{C_{An,0}} \quad (8)$$

where A_m, V, and $C_{An,0}$ are considered as the membrane cross-sectional area, the volume of the fluid substance in the anode compartment, and the initial NH_4^+ content in the anode compartment, respectively. Further, $C_{Cat,(t)}$ is identified as the NH_4^+ content in the cathode compartment at time t. As the slope was attained from the association between t and ln C*, K_{Cm} was estimated using the following equation (see Fig. S1)(Kim et al., 2014):

$$lnC^* = -\frac{-2A_m K_{Cm}}{V}\ t \quad (9)$$

The chemical diffusion throughout the membrane (D_{Cm}) was estimated from the membrane thickness (δ_m) as represented in the following equation:

$$D_{Cm} = K_{Cm} \cdot \delta_m \quad (10)$$

2.7. Instruments

The characterization of the bioanode film was managed by the FEI (NanoSEM 450 apparatus) for recording FE-SEM.[1] Furthermore, the samples were pretreated during the night with glutaraldehyde 2% (V/V) in order to place the bacteria on the graphite surface (with a pH of 7.5 at 4 °C). Consequently, the added water and alcohol solution (30–70%, V/V) led to dehydration. A HACH (Sension™1) pH meter was employed for measuring the pH of the wastewaters. Eventually, the COD of wastewater was measured with closed reflux by a calorimetric method (the Palin test system, photometer 6000, HACH) at 600 nm. The concentration of NH_4^+ –N was tested through the spectrophotometric (DR 6000, Nessler Method, Ammonia, 380N HACH).

3. Results and discussion

3.1. Ammonium and COD removal through anodic bio-oxidation in BES reactor

The efficiency of bioanode material in a bio-electrochemical system (BES) was investigated for synthetic wastewater treatment according to COD and NH_4^+ removal performance. In this regard, the batch experiments were conducted to optimize efficient factors including the amount of COD and ammonium in the anode compartment in order to obtain the maximum wastewater treatment. Moreover, different COD concentrations were applied to evaluate the performance of the BES in batch experiments. In this study, the bioanode systems were first assessed to remove carbon and ammonium, as well as the power production at a constant concentration of 150 mg/L of ammonium at variable COD concentrations.

The results showed that COD removal efficiency increased with increasing COD concentration up to 2000 mg/L, but COD removal efficiency decreases with increasing COD to 10,000 mg/L. This is due to the accumulation of waste materials and the creation of acidic and inappropriate conditions that make the conditions unfavorable for microorganisms. The highest efficiency of removal of organic matter and favorable activity of microorganisms is in the COD/N ratio of 13.3 which is consistent with the results of previous studies. Ammonium removal increases with the increasing of COD/N ratio, that is because of the increased activity of microorganisms and the greater need for nitrogen for cell growth and proliferation (Zhan et al., 2014a).

3.1.1. Effect of different initial COD concentrations on the system performance

To investigate the effect of organic matter concentration on the efficiency of bioelectrochemical system (BES) and electricity generation, ammonium concentration was constant in the anode chamber (150 mg/L NH_4^+-N) while organic matter concentration was different (e.g., 500, 1000, 2000, 5000, and 10,000 mg/L). As shown in Fig. 2 (a), initial COD concentration increased from 500 to 10,000 mg/L, the COD removal efficiency firstly increased at COD of 500–2000 mg/L and lately decreased with COD of 2000–10000 mg/L, whereas ammonium removal efficiency continued increased with the increased initial COD concentration. According to previous studies conducted regarding the effect of substrate concentration on the performance of bio-electrochemical systems, it is shown that electricity generation increases with an increase in the rate of the organic matter, but the efficiency of the system regarding COD removal fails to follow the same rule. Various

[1] Field-emission scanning electron microscopy images.

reasons can be presented for the efficiency reduction by increasing the initial concentration of COD. By such an increase, the environmental conditions become inappropriate for the growth of microorganisms due to the density and mass of external production resulted from the decomposition of organic materials (i.e., organic materials and acids from incomplete degradation)(Liu et al., 2017). Moreover, the organic acids produced by glucose decomposition are revealed as the COD while these materials are no more considered as substrates. Additionally, in the first stage of the experiment, the initial ammonium concentration (150 mg/L NH_4^+-N) was constant by changing the initial COD concentration. Therefore, COD/NH_4^+ is in an appropriate range 15–20 at the initial COD concentration of 2000 mg/L, which is regarded as another reason for better performance of the microorganisms and the best efficiency in COD removal at a concentration of 2000 mg/L (Zhang et al., 2018). However, an increase in the efficiency of ammonium removal by rising the initial COD concentration is the result of the increased activity of microbial population due to the high amount of substrate and the need for nitrogen for cell growth and proliferation. Therefore, a high percentage of ammonium is removed through biological degradation and is used for cell activity and growth (Kim et al., 2015). The ratio of COD/NH_4^+ altered by changing COD concentration in the anode chamber. In addition, this ratio was equal to 66.6 (150/10,000) in evaluating the rate of organic matter at the COD concentration of 10,000 mg/L. In this condition, organic matter concentration is extremely high compared to the ammonium concentration, therefore, a large part of the ammonium is promptly removed by the biodegradation of bio-anode microorganisms (Kim et al., 2015).

The results indicate that a significant percentage of ammonium is used for microorganisms if the ammonium concentration is lower compared to the organic material in the environment. However, when COD/NH_4^+ concentration is in the range of 10–20, COD removal efficiency of the system enhances, but the percentage of ammonium biological removal reduces by 40.5%. Further, 32.5% of ammonium migrates to the cathode chamber through the Nafion membrane whereas 27% of ammonium remains in the anode chamber. Considering industrial wastewater treatment containing high amounts of organic matter and ammonium, the findings of the present study help us control the rate of biological treatment or ammonium recycling by adjusting COD/NH_4^+ ratio (Yadu et al., 2018).

3.1.2. Effect of different initial ammonium concentrations on the system performance

In Fig. 2 (b), COD concentration is constant at 10,000 mg/L, while ammonium is present at different concentrations (200, 400, and 650 mg/L NH_4^+-N), resulting in variable COD/NH_4^+-N ratios. With initial ammonium concentration increased from 200 to 650 mg/L, COD removal efficiency gradually increased (from 69% to 76%), but ammonium removal efficiency decreased continuously from 91% to 72%. As indicated above, the COD/NH_4^+ ratio is effective in optimizing bioanode microorganism activities and BES efficiency. The results further represent that the BES performance enhances in organic material removal and electricity generation by increasing the concentration of ammonium in the anode chamber, in which the COD/NH_4+ratio reaches the range of 15. Therefore, the bioanode efficiency was 76% and 808 mA/m^2 in COD removal and current density, respectively, which as at the maximum level at this phase.

By increasing the initial amount of ammonium, the rate of nitrogen increases in bioanode microorganisms thus ammonium removal efficiency decreases through biological degradation although a percent of ammonium migrates to the cathode chamber through the Nafion membrane. Previous studies demonstrated that even excessive concentration of ammonium in the anode compartment can be toxic for bio-anode and thus reduces microorganism activities. The results of the present study are in line with those of other studies (e.g., Liu et al., 2017; Yadu et al., 2018). Similarly, increasing the initial concentration of ammonium leads to an increase in the current density and power generation. Further current density is probably due to: a) the improvement in bioanode microbial activity, which is due to the presence of COD/N in the range of 15; and b) the buffering properties of ammonium in the anode compartment since, like H^+, it can pass through a cation exchange membrane, leading to an increase in the current density.

3.1.3. Effect of COD/NH_4^+ ratio on ammonium biodegradation

Similarly, ammonium concentration changes in both anode and cathode compartments were measured every 12 h in order to evaluate the system performance during the activity. The percentage of ammonium ions removed by biodegradation in the bioanode, the amount of ammonium ions migrated to the cathode compartment, as well as the percentage of ammonium ion remained in the anode chamber at different concentrations of COD (Fig. 3) and the ammonium ion (Fig. 3 (b)) were separately estimated as well. The results further revealed that the maximum removal of ammonium ion by the biodegradation of bioanode material reached 91–92% at high C/N ratios (Fig. 3(a) and (b)). Additionally, a small percentage (5–6.5%) of ammonium ions remained in the anode chamber without any degradation while 2.73% of these ions could be migrated to the cathode chamber through the Nafion membrane.

It can be seen from Fig. 3 (a) that the efficiency of ammonium removal enhanced through biodegradation by an increase in the initial COD concentration since higher amounts of the organic

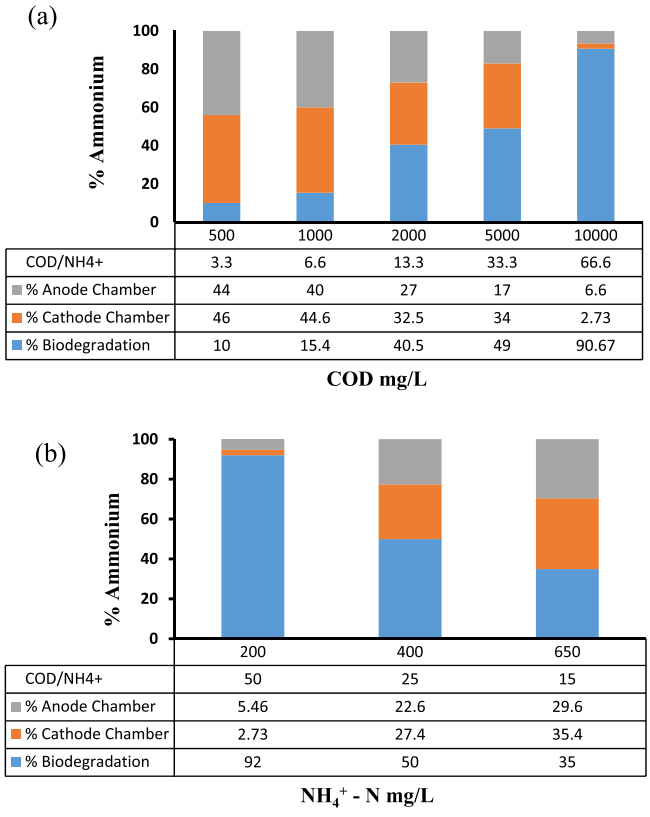


Fig. 3. Amounts of ammonium presence in the anode and cathode and biodegradation loss (%) in the anode of BES reactors with different initial COD concentrations, NH_4^+ of 150 mg/L (a), and with different initial NH_4^+ concentrations, COD 10,000 mg/L (b).

matter lead to further microbial population and activity and thus more ammonium consumption. Accordingly, the contribution of biodegradation to ammonium loss extremely increased as well. The remaining ammonium in the anode compartment was able to pass through the Nafion membrane due to hydrogen ion flux in two compartments. Such contribution was approximately the same and low owing to pH balance in two anode and cathode compartments.

The concentration of initial ammonium in the anode compartment increased from 200 to 650 while the initial COD concentration in the anode was constant, therefore, COD/NH_4^+ reduced from 50 to 15. By increasing the initial concentration of ammonium, the amount of ammonium deposited in the microbial population increased, followed by the biodegradation of ammonium based on the need for cell activity and proliferation. This led to a reduction in such contribution due to a decline in COD/NH_4^+ (Yadu et al., 2018). In addition, the residual ammonium passed through the cationic membrane, taking into account hydrogen ion flux in anode and cathode compartments. Considering the application of phosphate buffer and pH balance, the contribution of the transferred ammonium to the cathode compartment was equal to that of the residual ammonium in the anode compartment (Fig. 3 (b)). The achieved results showed that utilizing of anaerobic bacteria as a microbial source and organic matter in the wastewater as a fuel can be suitable choices for our aim with the enhanced efficiency (Birjandi et al., 2016).

3.2. Electricity production

Initial experiments performed by the proposed BES utilizing the synthetic wastewater demonstrated the production of electricity. Fig. 4 depicts the comparison between the voltage output and power density curves at different amounts of COD for the coupled system. The current in BES was automatically calculated and logged, which separated the attained voltage by definite resistance. Subsequently, the power afforded by the system was calculated by the strike of voltage and the current. At 10,000 mg/L COD, P_{max} and I_{max} were obtained 62.7 mW/m^2 and 570 mA/m^2, respectively. Moreover, the power densities were 26.7 mW/m^2, 30.54 mW/m^2, 44.4 mW/m^2, and 52.5 mW/m^2 at the COD of 500, 1000, 2000, and 5000 mg/L, respectively (Fig. 4 (a)). In other words, power density increased with an increase in COD concentration while it decreased at lower and higher current densities and its maximum amount led to higher current densities by increasing the COD.

Considering the results of previous studies, COD concentration is regarded as a critical parameter for power production. The results of our experiments showed an inverse relationship between the voltage and current density at all CODs. Fig. 4 (b) shows the maximum voltage for the highest COD at the minimum current density, which decreased with an increase in the current density and lower CODs. The initial voltages were low based on the discrepancy of the electric potential between the compartments. However, owing to biological activity, the cell voltage slowly increased and then maintained in a stable state with the maximum amount (i.e., the optimum condition: 481 mV in COD 10,000 mg/L) after 30 h (Fig. 4 (c)). Therefore, a steady microbial population settled in the anode compartment. On the other hand, the increased COD in anode compartment exerted a positive impact on power generation. Particularly, a considerable bioelectricity generation occurred for a long period with the functioning system at higher COD. In addition, our investigation revealed that the concentration of organic matter and the microorganism community growing during the adoption can have a positive effect on microbial activities and thus obtaining the maximum power density from the wastewater.

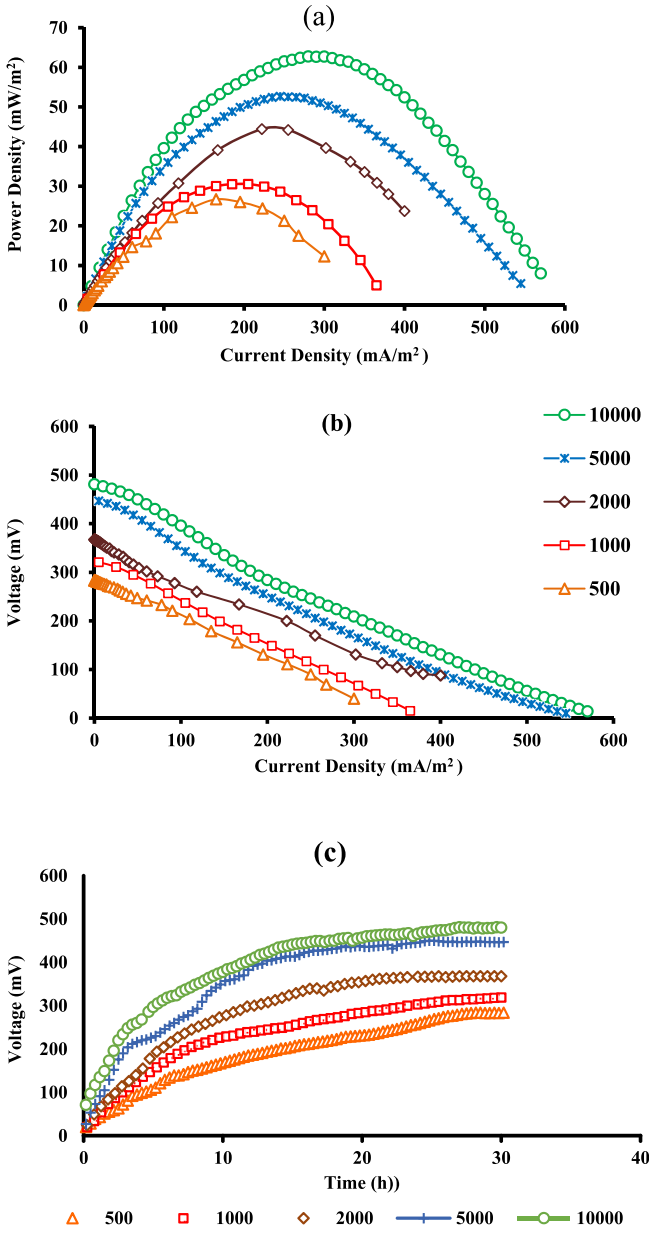


Fig. 4. Power density (a), polarization curves (b) and formed OCV (c) of BES systems in different concentrations of COD in the anode compartment, NH_4^+ of 150 mg/L.

In the second step, BES at the constant COD concentration of 10,000 mg/L and different concentrations of ammonium (i.e., 200, 400, and 650 mg/L) was run to evaluate the effect of ammonium concentration on energy generation and system performance. The maximum produced power, current, and the voltage were determined in term of different amounts of COD/N ratios (i.e., 15, 25, and 50). The results indicated that power production increases with a reduction in the COD/N ratio while increasing ammonium concentration in the wastewater. The values of 84.28 mW/m^2 and 880 mA/m^2 were obtained for P_{max} and I_{max} with COD/N = 15, respectively (Fig. 5 (a)) and an inverse relationship was observed between voltage and current density at all COD/N ratios (Fig. 5 (b)). In other words, the maximum voltage for the lowest COD/N ratio (i.e., the highest ammonium concentration) decreases by increasing the current density.

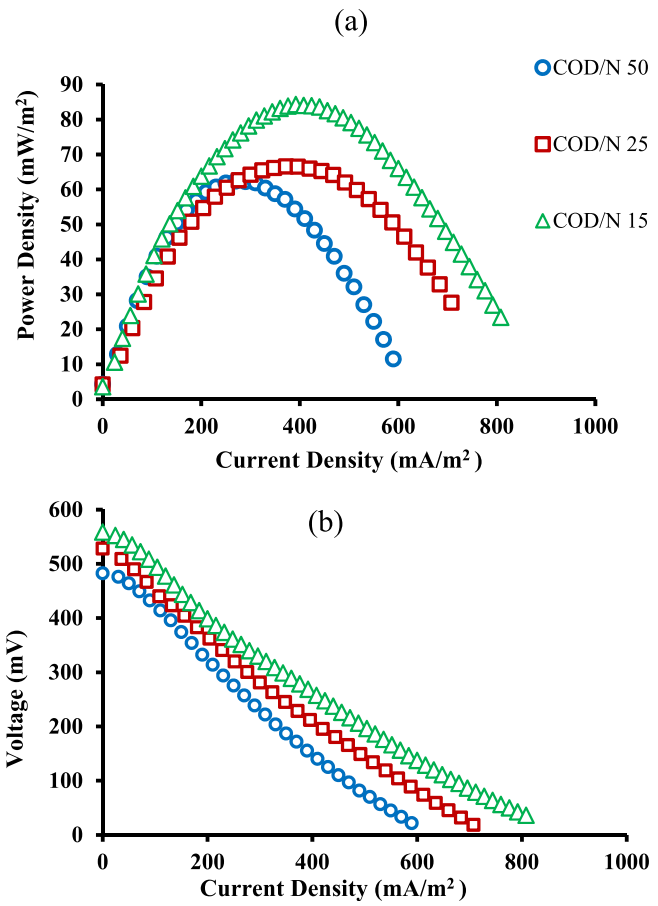


Fig. 5. Power density (a), polarization curves (b), and formed OCV (c) of BES systems in different concentrations of NH_4^+-N in the anode compartment, COD 10,000 mg/L.

3.3. Energy recovery and coulombic efficiency

The created electrons in the BES system and BES were involved in power production, bio-electrochemical reaction, and combination with the other electron acceptors. It should be highlighted that the coulombic efficiency (*CE*) increased, along with an increase in the ammonium concentration and a reduction in COD/N. According to the results, *CE* increase by increasing the COD amount in wastewater. The CE_{SYS} at 500 mg/L COD was 12%, which could rise up to 18.6% with COD 10,000 mg/L. In addition, the *CE* of the system increased to 22.3% at the ammonium concentration of 650 mg/L with a COD concentration of 10,000 mg/L and COD/N = 15. However, Rahimnejad et al. (2011) demonstrated 13% CE_{SYS} by employing glucose as the organic materials. The BES that the biodegradation of sugars by bacterial lead to the formation of some intermediates, which reduce CE_{SYS} values (Xu et al., 2017). The enhanced *CE* of our system can be due to the suitable conditions of microorganism, high-efficiency biodegradation of the organic matter, and more production of electricity. Further, the CE_{SYS} of BES in the presence of substrates such as glucose and acetate could be improved compared to the real industrial wastewater treatment (Birjandi et al., 2016). Therefore, the obtained data indicate that this power, generated in BES by the clean-up of synthetic wastewater, can concurrently be applied in wastewater treatment plans. It has been shown that bacteria growing on the bioanode are able to use most of the NH_4^+-N available for the power generation (Zhan et al., 2014a).

3.4. Investigation of the permeability of ammonium ion from the Nafion117

The evaluation of ammonium mass transfer from the anode to the cathode through Nafion 117 is considered as one of the necessary diagnostic tests for validating BES performance, while removing ammonium from the solution. To this end, the BES reactor was run at open circuit system under abiotic conditions without any seed sludge and at the presence of 150 mg/L NH_4^+-N (anolyte) and Phosphate buffered saline (PBS) at variable concentrations of 10 and 100 mM, along with distilled water. Fig. 6(a)–(f) indicate the amount of migrated and remained ammonium in different conditions and at the concentrations of phosphate buffer. Table 2 summarizes the average ammonium removal/formation behavior in the anode and cathode compartments and ammonium transfer coefficient. Ammonium formation rate was measured in the cathode compartment and ammonium removal rate was measured in the anode compartment (Kim et al., 2015).

Under condition A, where the concentration of phosphate buffer in both compartments was equal to 100 mM, 43% of the ammonium was penetrated by the separation membrane. Meanwhile, fewer ammonium ions were passed (40%) under condition B where the concentration of phosphate buffer in both compartments was equal to 10 mM. Accordingly, the removal and production rates of ammonium ion were equal in these cases. Contrarily, under condition C, where the concentration of phosphate buffer in the anode and cathode compartment was equal to 10 and 100 mM, respectively, the migration rate of ammonium was higher compared to the other conditions (76%). As regards using distilled water in both compartments, the amount of ion penetration reached its lowest rate (19%, 0.33 mg/L/h) and thus a large quantity of ammonium was lost (24%), which was due to pH variation and the conversion of ammonium ions in ammonia. Therefore, the presence of phosphate buffer and its concentration are influential factors in the rate of ammonium ion transfer through Nafion 117 membrane due to pH changes and the ionic strength of the solvent on both sides of the membrane. It was shown that cations (NH_4^+,K^+, Na^+, Ca^{2+} and Mg^{2+}) are even transported versus a concentration gradient via the PEM into the cathode compartment and will lead to an increase of the cathode pH (Rozendal et al., 2006). In this study, the effect of an increased NH_4^+ concentration on potential and current density of an MFC was investigated. Moreover, the transport of ammonium to the cathodes was measured to designate the possibility of NH_4^+ recovery using MFCs. The results showed ammonium recovery can be obtained by migrational ion flux through the CEM to the cathode chamber, driven by the electron production from biodegradation of organic substrate. The charge transport was proportionate to the concentration of ions. Furthermore, a charge exchange process can influence the recovery of specific ions and the charge transport (Kuntke et al., 2011).

The E and F conditions were designed to investigate the adsorption of ammonium ions on the carbon plate and the effect of aeration on permeability rate. The amount of ammonium adsorption by carbon electrode surface was estimated at 6% and the speed of ammonium ion transfer partly increased by utilizing the aeration process. In other words, the removal speed in the anode compartment and the ammonium production speed were 0.82 and 0.76 mg/L/h, respectively. Additionally, the loss of ammonium ions was achieved 0.15 mg/L/h, which could be due to the adsorption of the ions to the surfaces of electrodes and the air stones in addition to the conversion of ions to ammonia gas. In F conditions without the aeration process, the only difference between A and F conditions was the presence of graphite electrodes in the BES. Furthermore, the ammonium ion production rate in the cathode compartment was the same as in A conditions, but the removal rate

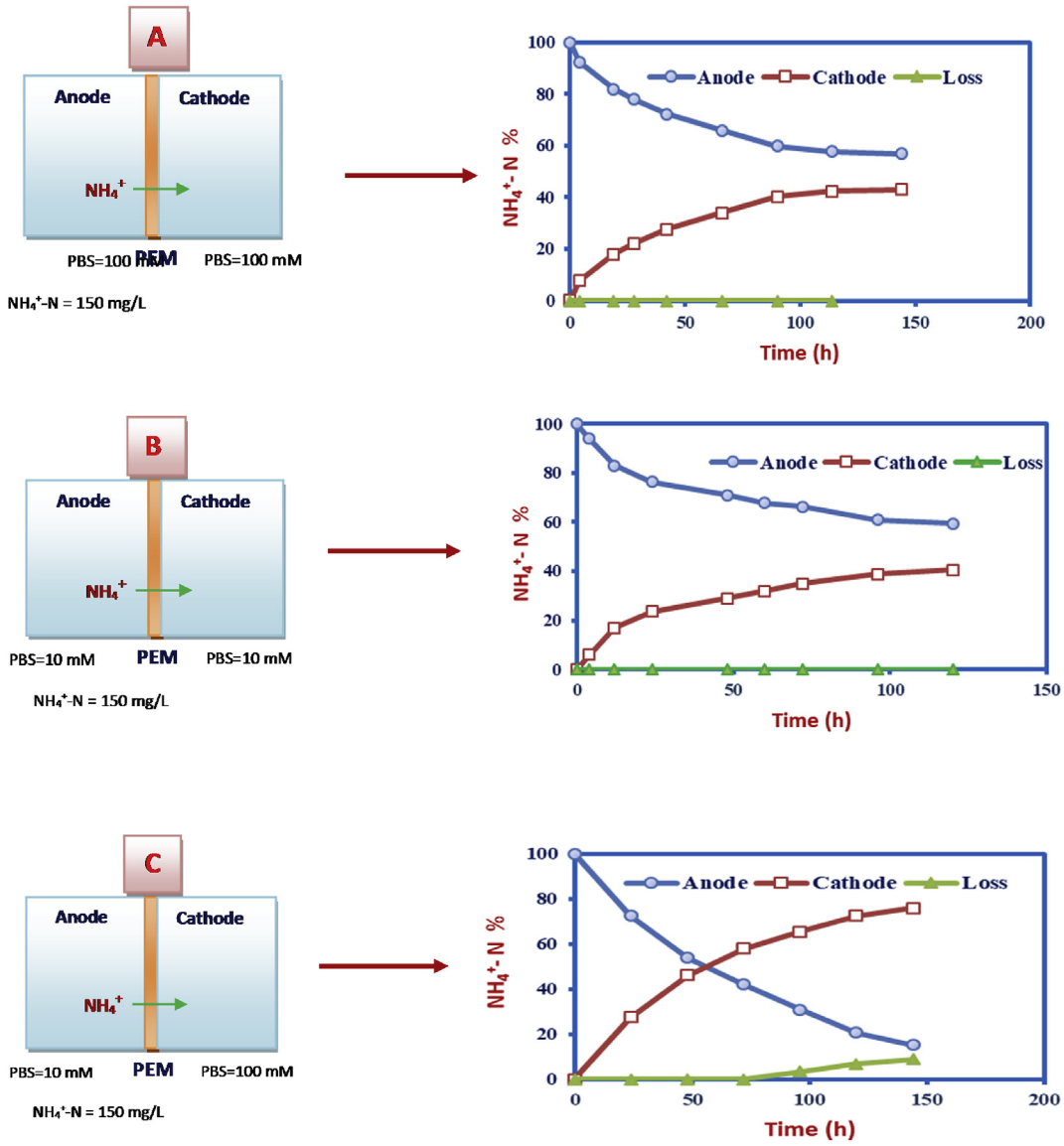


Fig. 6. NH_4^+-N removal rate in the anode compartment, NH_4^+-N production rate in the cathode compartment, and loss of NH_4^+ −N rate, with the circuit cut off. Ammonium concentration of 150 mg/L with different concentrations of phosphate buffer in the cathode and anode compartment and creating different conditions
A: Bio-electrochemical system containing phosphate buffer of 100 mM in both cathode and anode compartments
B Bio-electrochemical system containing phosphate buffer of 10 mM in both cathode and anode compartments
C: Bio-electrochemical system containing phosphate buffer of 100 mM in the cathode compartment and phosphate buffer of 10 mM in the anode compartment
D: Bio-electrochemical system containing distilled water in both cathode and anode compartments
E: Bio-electrochemical system containing phosphate buffer of 100 mM in both compartments with the electrode, air stones, and aeration.
F: Bio-electrochemical system containing phosphate buffer of 100 mM in both compartments with the electrode and without aeration.

of the anode compartment was greater compared to F conditions, since 6% of the ammonium ions was adsorbed onto the electrodes and the rate of loss of ammonium ions from the anode compartment was 0.6 mg/L/h Table 2.

The scheme of ln C* vs. time (t) formed a slope of 0.0046 h^{-1} (Fig. S1). Further, K_{Cm} and D_{Cm} within the membrane were 1.27×10^{-5} cm^2/s and 2.4×10^{-7} cm^2/s, respectively. In the anode compartment, in which the circuit was disconnected, the NH_4^+ removal speed was 0.53 mg/L/h. Consequently, owing to the content gradient between the anode and cathode compartments, the mass transfer of the ammonium arose, therefore, it was likely to transfer nitrogen and the organic materials in the anolyte to the cathode compartment (Kim et al., 2014).

3.5. Mixed culture cells behaviors on the surface of bioanode

The morphology of bio-anode was determined and the growth of microorganisms on the anode electrode surface was proofed by the scanning electron microscopy. Fig. 7 illustrates the close and large view SEM micrographs of the bioanode surface before and after application in the BES. The harvested images represented the complete coverage of both sides of the carbon plate surface by the cluster and growth of the microorganism. To remove organic matter and ammonia simultaneously, a mixture of all types of electrochemical bacteria was required that were provided with anaerobic sludge. The prevailing bacteria on the bioanode appeared bacilli - shaped cell with about 1 μm long, which have

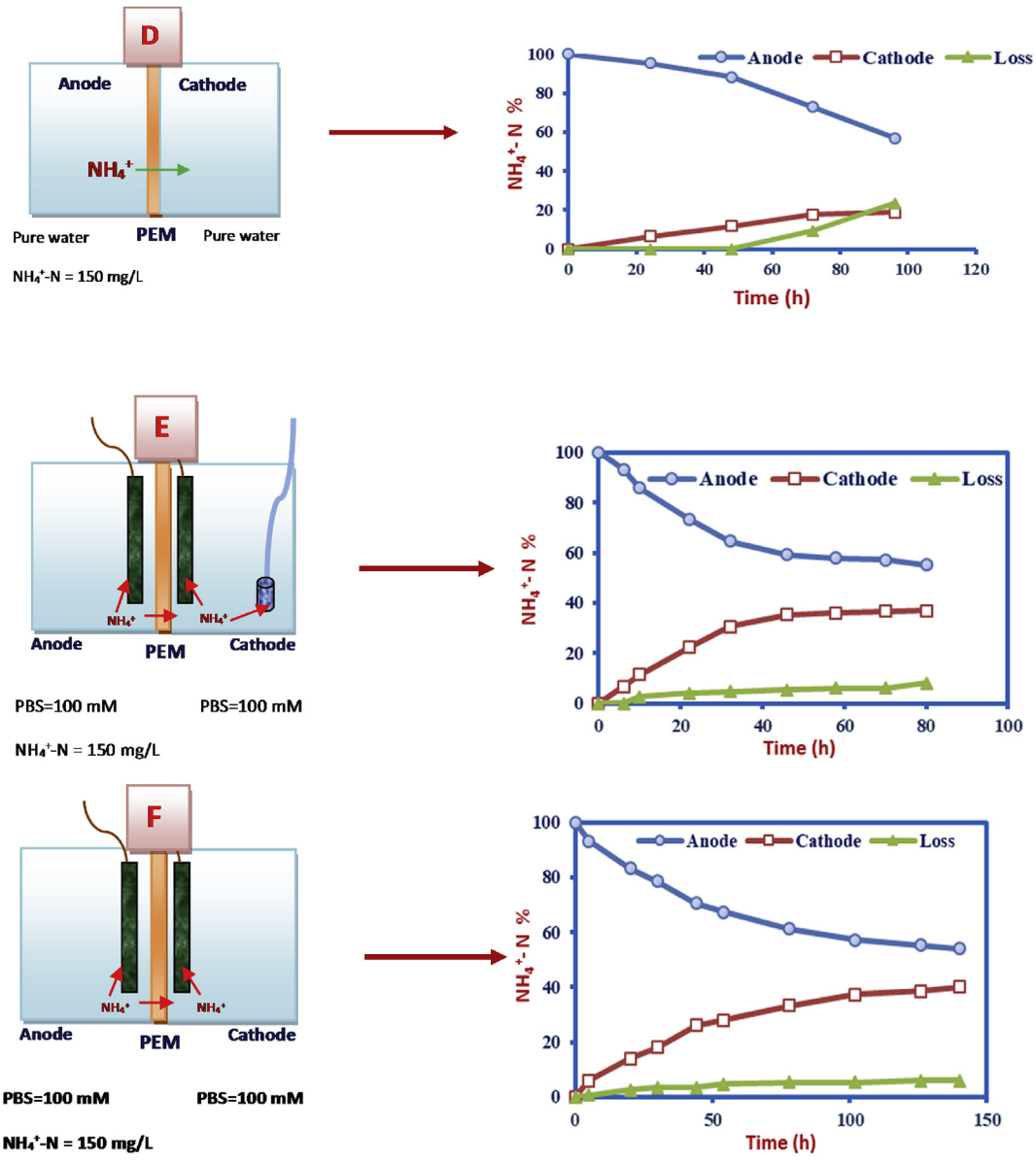


Fig. 6. (*continued*).

morphologies similar to those of exoelectrogenic bacteria such as *Shewanella* and *Geobacter* spp. (Li et al., 2014).

4. Conclusion

Based on the results of the study, the performance of bioanode material for the biodegradation of ammonium ion without needing the ex-situ power source relying on eco-friendly in-situ bioenergy in the bio-electrochemical system (BES). The anode chamber in BES functioned as a suspended growth anaerobic reactor, which was an indicator potential for replacing the BES systems with biological treatment processes. Accordingly, the maximum ammonium removal has been increased up to 94% in the anode compartment with 10,000 mg/L COD. Industrial wastewater, which simultaneously has high rates of organic matter and ammonium content, can be treated to produce clean energy by adjusting the COD/NH_4^+ ratio. The use of the BES for the simultaneous removal of ammonium and organic materials, which are regarded as bio-environmental priorities, along with clean energy production can be a promising technology for the development of cleaner production. The results of the present work are in line with those of other studies. Similarly, increasing the initial concentration of ammonium leads to an increase in the current density and power generation. The study further evaluated the permeability coefficient of ammonium ion through Nafion at the presence and absence of biofilm, the concentration of phosphate buffer is the most essential impact on the amount of ammonium ion that is transferred through the Nafion membrane. In these experiments, a novel NH_4^+-N removal process in bioanode without anammox bacteria were observed, which provided a novel intuition into the pathway of ammonium biodegradation, also a new method for NH_4^+-N removal from industrial wastewater. More research is needed to assess microbial diversity and ammonium removal mechanisms in anaerobic bioanode in the future.

Table 2
Summary of the average ammonium removal/formation behavior in the anode and cathode compartments and ammonium transfer coefficient. Ammonium formation rate was measured in the cathode compartment and ammonium removal rate was measured in the anode compartment.

BES	Ammonium removal rate (mg/L h)	Ammonium formation rate (mg/L h)	slope	K_{Cm} (cm/s)
A	0.53 ± 0.031	0.53 ± 0.026	0.0046	$1.27 \times 10^{-5} \pm 0.25 \times 10^{-5}$
B	0.44 ± 0.027	0.44 ± 0.024	0.0042	$1.16 \times 10^{-5} \pm 0.33 \times 10^{-5}$
C	0.85 ± 0.033	0.76 ± 0.03	0.0099	$2.75 \times 10^{-5} \pm 0.5 \times 10^{-5}$
D	0.76 ± 0.038	0.33 ± 0.04	0.0023	$0.64 \times 10^{-5} \pm 0.41 \times 10^{-5}$
E	0.82 ± 0.041	0.67 ± 0.35	0.0068	$1.88 \times 10^{-5} \pm 0.29 \times 10^{-5}$
F	0.6 ± 0.036	0.53 ± 0.029	0.0042	$1.16 \times 10^{-5} \pm 0.3 \times 10^{-5}$

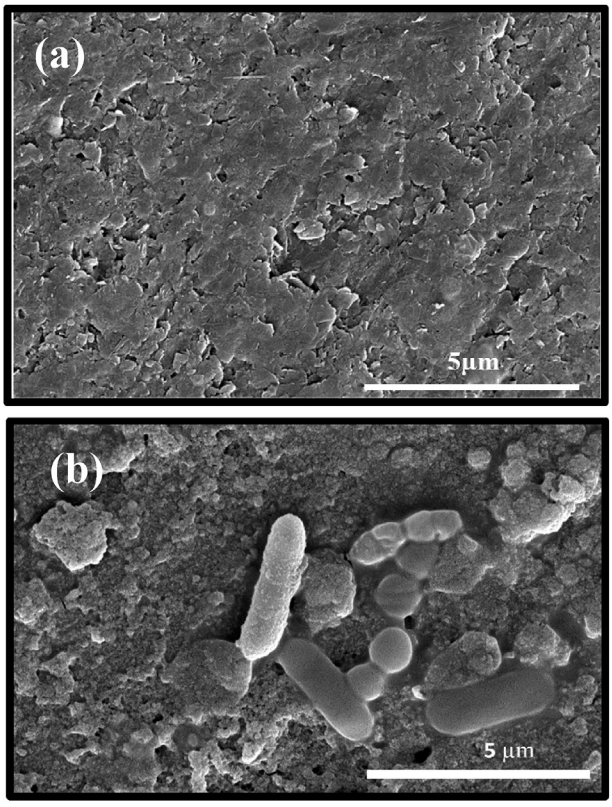


Fig. 7. SEM micrographs of the bio-anode surface before (a), and after (b) employing in the BES.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.118589.

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