

# WITHDRAWN: A new method of bio-catalytic surface modification for microbial desalination cell

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## Research

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## EDITORIAL NOTE:

The full text of this preprint has been withdrawn by the authors while they make corrections to the work. Therefore, the authors do not wish this work to be cited as a reference. Questions should be

directed to the corresponding author.

# Abstract

Microbial desalination cell (MDC) built on surface modification has been studied for seawater desalination. Herein, the bio-catalytic surface modification for maintenance the long-term MDC performance during desalination process has been developed. The goal of this study is to provide and develop a seawater desalination system without requiring energy support by applying a modification of anode as an electron acceptor, and the different potential charges that occur between anode and cathode can play as driving force for electro dialysis of seawater desalination. Yeast has been applied as biocatalyst, meanwhile neutral red has been chosen as redox mediator to facilitate the electron transport from bioactivity of cells. Several types of surface modification have been conducted, *i.e.* biocatalyst-mediator immobilization and electropolymerization of NR at the surface of the anode. The optimization of each device has been characterized by cyclic voltammetry, chronoamperometry, and observed in Microbial fuel cell (MFC) prior functioned in MDC. The concentrations of salt ion migration have been determined by Ion Exchange Chromatography. MFC results reported that the best configuration of surface modification was obtained from CF/PNR then applied in MDC. CF/PNR delivered the highly significant performance by having the maximum value of all tested parameters, *i.e.* 42.2% of current efficiency; 27.11% of bio-devices efficiency; 92.5 mA m<sup>-2</sup> of current density and also 61% of NaCl transport. The profiles of surface devices have been detected by Scanning electron microscope (SEM) and Energy Dispersive X-ray spectroscopy (EDX). A several spherical shapes around 4 nm within alginate layer have been detected from SEM images and it was confirmed as yeast, meanwhile 5.04% of N has been found from EDX spectrum and was indicated from PNR. The results show that surface modification could be a promising method for bioelectricity generation which simultaneously produces electricity and seawater desalination and provides a green chemistry technology.

## Introduction

As a newly-developed technology, MDC is an electrical energy production system and assimilated with MFC and electro dialysis process. Recently, owing to the environmental approachable and free energy requirement create MDC received extensive attention for wastewater treatment and desalination. In the continuation of their performance, MDC could be used as a stand-alone process or can be shared with other desalination processes such as electro dialysis or reverse osmosis (RO) [1]. As mention previously, that MDC technology is an extension of MFC was shown in Fig. 1a, the MFC unit is consists of an anode, cathode, and each chamber was separated with the cation-selective membrane, and also the external wire. Meanwhile, the MDC unit (Fig. 1b) has adapted with MFC as well, the presence of an anode and cathode chamber is require and there is the addition of a desalination chamber as known as dilute and concentrate chamber, respectively. The MDC configuration, the desalination chamber put in the middle designed by inserting the cation-exchange membrane (CEM) and anion-exchange membrane (AEM) on either side [2-5]. The aerobic and anaerobic conditions have been conserved, in anode and cathode chamber, respectively. In our last work, MFC based *Saccharomyces cerevisiae* as known as bakery's yeast has been delivered and the electron transfer has facilitated by the presence of a mediator as seen in Fig.

1a. Neutral red (NR) was appropriated as a redox mediator for the migration of electron to the anode surface [6, 7]. However, some MFCs operate with or without a mediator, the activity of microbes was oxidizing of organic matter realizing protons and electrons [8, 9].

In direct electron transfer, the available bacteria are proliferated and produce a thick cell aggregate in anode surface which is called biofilm [8-11]. As mentioned, in MDC construction, the anode plays and responsible for the organic degradation route and delivers an electricity generation, cathode chamber finalizes the electrical loop, meanwhile, the salt removal from seawater has been held liable by the middle chamber [12].

A simple desalination process in MDC occurs and initiation as follows: the organic mechanism has been done in the anode chamber as a product of the bacteria activity oxidize the organic matter.  $\text{CO}_2$  and proton loosed into anolyte, then the electron streams into the cathode through an external circuit, and current across the cell is recognized. Meanwhile, in the cathode chamber, the external electron acceptor and oxygen in the catholyte consume these electrons to the reduction process and produce water [13, 14]. This situation causes a potential gradient transversely the anode and cathode chamber and in direction to preserve electro-neutrality. In the meantime, the anion such as chloride ion migrate from the dilute chamber contain seawater across the AEM into the concentrate chamber and sodium ion flow across CEM to the cathode chamber. This route is known as desalination and is able to eliminate more than 99% of the salt from saline water and at an equal time harvest more energy and does not requiring an external energy supply because they can operate the system use their own energy [4, 15, 16].

During the performance, the desalination rate (DR) is one of the most essential parameters of the MDC action, and significantly dependent on the salt concentration of the seawater. Normally, MDC is well considered to be proper for desalinating highly concentrated salt water. The higher salt concentration would cause a reduction of the ohmic resistance and resulting in a high current density across the circuit and upgrade the DR value [17]. Besides that, the salt concentration in the dilute chamber ideally should be higher than the electrolyte in the concentrate chamber is due to the lower concentration could affect to the decreasing of DR value as dialysis happened by the reverse concentration gradient between the concentrate and dilute chamber which contains an electrolyte solution [17, 18].

However, there also some great challenges that must be pointed out for further expansion, despite the abundant interest and development in MDC technology. The possibility enhancement of MDC performance should be done and exploit more. First, compared with conventional desalination technology the low rate of desalination process of MDC should be maintained. This condition has been confirmed that related to the limitation of current density delivered from bio-anode or desalinating process has been occurred in low-salinity water [14]. Second, the cost operational of MDC manufacturing is still high and is related to the material cost such as an electrode, catalyst, or membrane. The wastewater treatment and desalination application generated from MDC should be well addressed. As mentioned, the wastewater treatment and desalination is the main point and also give a benefit for MDC technology. With the appropriate assessment of MDC, both wastewater treatment and saline water

desalination could be delivered from MDC. In fact, currently, the scaling-up of MDC has been demonstrated and resulted in a good application [19]. However, the construction and operation associated with the bio-anode performance are required to investigate more.

Recently, MDC has been advanced as a low-energy desalination technology. In the past century, the technology of MDC has been developed significantly is due to its capability to provide the sustainability of freshwater through saltwater desalination. A new desalination technology as known as MDC has successfully demonstrated that saline water could be desalinated without the presence of an energy supply. Moreover, this process could also simultaneously integrated with wastewater treatment and energy production [3, 20, 21]. During the desalination process, ion salt will have removed from saline water through a conductive solution in the concentrate chamber and this situation will cause the salinity increases in the concentrate and cathode chambers, respectively. While this addition of ion is generally acceptable for wastewater treatment and supports with the conductivity conditioning [22].

In our configuration study, yeast has been worked as a biocatalyst to provide the presence of electron from its activities in organic degradation. This work has been motivated that some microorganisms *i.e* direct electron transfer has been observed, however, the possibility of such a new method using yeast as biocatalyst for MDC application has never been demonstrated. A glucose solution has been added during MDC performance. Meanwhile, in the cathode solution, ferricyanide has been selected as catholyte as observed in a previous study [7]. The most usually selected as catholyte next to oxygen is ferricyanide or hexacyanoferrate (III) which value of standard potential is 0.361 V / NHE. The advantages of using them are they have greatly soluble in water and do not need a costly metal on cathode like Pt. Results confirmed that the test with ferricyanide delivered greater power generation than applying with oxygen. A little polarization of the cathode has been responsible for this reason so that cathode potential reached is relatively close to that calculated for the standard condition [23, 24]. Beside anode, cathode plays an important element also in MDC. The cathode has a prodigious influence on the electricity typical generation. Some studies have been focused on the nature and type of the electrode and the catalyst on the electrode [25, 26]. The designated cathode material is one of the critical factors for biofuel cells includes MDC. The oxygen reduction process normally needs a four-electron transfer, but this situation may not be reached. It was also probable that another molecule could be conducted as hydrogen peroxide production and this reaction only require a two-electron transfer reaction. The presence of H<sub>2</sub>O<sub>2</sub> is unexpected and causes a problem, is due to their strong oxidizer characterization. They could damage the surface of the membrane or cathode itself. However, they could also act as disinfectants for maintenance of the cathode surface or to prevent biofilm formation.

As mention above, the application of MDC as a new approach for desalination has been conducted both in reactor designs or operational conditions. Several patterns of MDC, from two-chamber up-flow tubular to three-chamber or multi-chamber, have been investigated and included the system performance [14, 20, 27, 28]. The MDC performance can also be enhanced using multiple pairs of ion-exchange membranes (IEMs), placed in between the anode and cathode chambers. This condition has been done on the grounds that the charge transfer efficiency would improve and may impact to significantly enlargement

the quantity of salt ion removal from saline water [29]. On the other hand, the utilization of some microorganisms in MDC has been observed [30]. In previous work, the use of yeast as biocatalyst has been studied and results confirmed that it could affect to MFC performs [31-33], but the wider application for MDC is required to be observed more.

With this perspective in mind in order to improve the electricity generation during the MDC process, we propose a surface modification. Bio-catalytic surface modification has been done by biocatalyst-mediator immobilization and electropolymerization of NR at the surface of the anode [6, 7]. A previous study of biocatalyst immobilization reported that as a promising method and new strategy for enhancement longer working lifetime than free cell [34]. Moreover, this situation can be adapted in MDC operation. Cell immobilization can be categorized refers to the technique delivered, such as physical entrapment within a porous matrix, encapsulation, or chemical-cross linking attachment [35]. The principle of immobilization entrapped method is based on the cell localization within a polymer matrix or membrane and this method is common and preferable used in cell immobilization. Several advantages have been obtained from this method such as easy to operate, has a great loading capacity, and decreased cell leakage [36]. In addition, this method could be applied in a wide variety of polymer material including synthetic and natural polymers. In our work, a natural polymer *i.e* calcium alginate has been chosen is due to the mostly used for cell immobilization and has good stability [37–39].

One of the successful factor of immobilization is the polymer support must be conductive to allow the viability of the cell as well as has a good permeability to permit oxygen transport, the supply of nutrient, and sufficient diffusion. Nevertheless, by applying physicochemical immobilization between mediator and cell as simultaneously is suitable to overcome a problem, because the presence of a mediator in the solution can create an environmental problem if processed without proper treatment. Besides for sustainable green energy production, the enlargement of system operational with electron carrier powerfully immobilized at bio-device is being desirable. Mediator immobilization has been conducted using several procedures, such as direct covalent attachment through the formation of the film deposited electrochemically on the surface of the electrode [40], mediator electropolymerization of the electrode surface [41, 42] or just only adding and mixing into carbon pasta. The advantages of this technique are to have a large catalytic response and long-term performance stability [42].

Meanwhile, PNR has been synthesized and characterized electrochemically as redox polymer to provide electron transfer in biosensor [6, 43–45]. The formation of PNR has been carried out from the electropolymerization procedure by allowing the monomer to be oxidizing for 20-30 cycles of polymerization on the electrode material. The resulting film (PNR) plays as an electrons carrier during MDC performance. Challenges for designing cost-efficient MDC systems can be adopted from MFC experience-based anode modification. Nowadays, the enlargement of MDC concept based desalination has resulted but deployed yeast as biocatalyst concurrently with surface modification is a new application. The yeast fuel cell has an attractive potential as a low-cost desalination process with significant environmental profit. Therefore, the challenge to employ yeast and anode modification should be investigated more to enhance the desalination performance and resulting in a significant number of

ion salt migration. Surface modification has been focused on the development of anode modification. Herein, we have been demonstrated the potency of yeast and the effect of bio-catalytic surface modification for the practical application of seawater desalination as a sustainable method for desalination.

## Materials And Methods

### *2.1 Cell preparation*

A slurry of yeast have been prepared refers to previously reported [32] and should be cultivated in 30 °C for 24 h. It was composed of 2 g of dried yeast mixed with 1.8 g peptone; 1.5 g dextrose; 1 g malt extract where all the chemicals were obtained from Sigma-Aldrich, France, then dissolved in 50 mL of phosphate buffer (PB) pH 7. The cells were centrifugated at 5000 rpm for 5 min, harvested then washed twice in PB pH 7. Re-suspended cells have been conducted in PB pH 7. Prior to use, the cells have been activated at 40 °C for 5 min and stored at 4 °C as a storage temperature.

### *2.2 Bio-catalytic devices modification*

Carbon felt (CF) (Alfa-Caesar, United Kingdom ) with dimension 7 x 1.5 x 0.5 cm and nickel size 7 x 1.5 cm, have been selected as anode and cathode then connected externally by a copper wire. The electrodes were cleaned from trash material successively using 1 M HCl for 48 h, rinsed with ultra-pure water. A mixture of 1:1 of the ethanol-water solution has been used to soak the electrodes for a few minutes then followed by sonication in ultrapure water subsequently dried in the oven at 100 °C for 15 min [32]. Meanwhile NR has been selected as a redox mediator to facilitate the electron transport to the anode.

A protocol of anode modification has been adopted based on our previous studies where the immobilization of yeast-mediator [7] and PNR [6]. Na-Alginate (Sigma-Aldrich, France) has been applied as a polymer matrix in the immobilization method. As seen in Fig. 2a, three-kind of bio-catalytic surface modifications have been deployed as anode and successfully showed an excellent electrocatalytic activity and current generation. They were CF/Immobilized yeast-NR (yeast-NR entrapped in Na-alginate immobilized on CF); CF/PNR (PNR polymerized on CF); CF/PNR-Immobilized Y (PNR layer covered by yeast entrapped in Na-alginate immobilized on CF), respectively. The third surface is a combination of the first and the second of the modification method.

The electrochemical characterization has been controlled by chronoamperometric and tested in 0.1 M glucose (Sigma-Aldrich, France) using 0.3 V / SCE as potential applied where CF modified as working electrode (WE), SCE as a reference electrode (RE), and platinum as a counter electrode (CE). The observations of the anode surface have been performed by SEM and EDX from Hitachi S-4800 and Hitachi S-4500, respectively.

### *2.3 biofuel cell construction and process.*

An MFC and MDC chamber have been designed as presented in Fig 1a and 1b. MFC compartment consists of anode and cathode chambers, meanwhile the MDC compartment compose of the anode, concentrate, dilute, and cathode chambers, with CEM, placed next to the anode, followed by AEM separating the concentrate and dilute chamber and CEM located close to the cathode chamber. Each chamber has a volume capacity of 80 mL. As a membrane, CEM and AEM have been prepared using CMX (CMI-7000) and AMX-SB (AMI-7001) (Tokuyama Soda- Japan) and the diameter size of the membrane was 3 cm. 0.1 M glucose in PB pH 7 has been made as to the carbon source in the anode chamber, meanwhile 0.5 M  $\text{KNO}_3$  (Sigma-Aldrich, France) has been placed in the concentrate chamber, and the dilute chamber has been filled with seawater. 0.02 M  $\text{K}_3\text{Fe}(\text{CN})_6$  (PF) (Sigma Aldrich France) has been acting as an electron acceptor in the cathode chamber, this solution has been diluted in PB pH 7. Prior used, all membranes have treated by soaked in 0.1 M  $\text{HNO}_3$  for 1 h then washed with ultrapure water. All the bio-catalytic surface modifications have been applied as an anode, meanwhile, the nickel plate plays as a cathode.

Fig. 2b explained the scheme design of MDC modification, this section aims to observe the best configuration for MDC design. As preliminary, the MDC experimental has been set up refers to model 1, but herein the arrangement of the concentrate and dilute chamber location has been changed and called model 2. The composition of the solutions used consists of 0.1 M  $\text{KNO}_3$  and 0.1 M  $\text{NaCl}$  in the concentrate and dilute chamber, respectively.

All desalination performs have been operated at ambient temperature ( $25 \pm 1^\circ\text{C}$ ). Digital multimeter Volcraft (model VC 850) was employed to investigate the potential (E) generated and the current was calculated according to the equation  $I = E/R$  with an external resistance fixed at 1 k $\Omega$ . The monitoring of salt ion removal from dilute and concentrate chambers have been measured by ion-exchange chromatography (DIONEX ICS 900 for cation and DIONEX ICS 1000 for anion). Meanwhile, the percentage of ion salt removal was calculated using Eq. 1.

**See formula 1 in the supplementary files section.**

C and  $C_0$  is concentration in  $\text{mg L}^{-1}$ , where C is ion concentration at time measurement and  $C_0$  is initial concentration.

## Results And Discussion

### *3.1 The bio-catalytic devices modification characterization and its electrocatalytic activities.*

The surface images of anode modification by immobilization of yeast within the alginate polymer and PNR layer on the anode surface have been observed by SEM and EDX as displayed in Fig. 3.

Images found that there are several spherical shapes around 4 nm, spread homogenously within the alginate polymer film and it was confirmed as yeast cells. The thickness of alginate polymer film was varied from 4 to 16 nm and has a good roughness is due to the presence of yeast inside and ready to be

used for the electro-catalytic process. Fig. 3c and 3d show the morphology of the PNR film deposited on the CF support refers to the EDX spectrum. Results found that 5.04% of N has been contained in CF modified and it was confirmed that the PNR has been presented at the CF surface. The presence of C and N atoms was completed expected since they come from NR and CF, meanwhile, potassium and oxygen atoms from the  $\text{KNO}_3$  solution which used as the supported electrolyte solution during the synthesis of polymer and sodium could be delivered from the phosphate buffer as supporting pH solution.

The observation of current density delivered from bio-devices modification has been recorded and All the experiments result as seen in Fig 4.

The chronoamperometry observation has been performed, electrodes were polarized at 0.3 V / SCE to ensure glucose oxidation. All surface modifications have been tested as working electrode and Pt as a counter electrode. Results reported that CF/PNR has the highest current density delivered compared with others. Meanwhile, CF without modification has been examined also using 2 % of yeast and 10 mM NR in PB pH 6 solution. Fig. 4a reports that compared with the conventional method, employing surface modification through the formation of the PNR layer gives the best performance delivered 64% of current density value against CF/Y-NR in solution. While CF/Immobilized Y-NR and CF/PNR-Immobilized have been resulted in enhancement 43% and 35% of current density value compared with the conventional method *i.e* anode without modification. Besides that, CF/Immobilized-Y without involving NR has been acting as a baseline of measurement. All the current density values generated have been monitored for 2 h after 30 min of stabilization time.

The next electro-catalytic observation was continued through MFC and dual-chambers of MFC have been prepared. All the surface modification electrodes have been applied as an anode, there were CF/Immobilized Y-NR; CF/PNR; CF/PNR-Immobilized Y. However, a conventional MFC has been carried out also using yeast and NR in a solution where CF without modification has been played as an anode. Results confirmed that the utilization of PNR as a surface modification method provides good effectiveness of the MFC process during 10 days of observation as displayed in Fig. 4b.

According to the results, PNR leads to a higher power density followed by CF/Immobilized Y-NR then CF/PNR-Immobilized Y. In our case, after 10 days of experimental observation, the maximum power density delivered from CF/PNR was  $5.02 \pm 0,25 \text{ W m}^{-2}$ . It is difficult to compare this value with previous research that has been studied because MFC operates under a large variety of conditions such as temperature, pH, availability of mediator, material electrode, size of the reactor, and time of operation. However, the maintenance of pH is important to provide the optimum operating conditions. In this present study, the measurement has been done at pH 7 as a good alternative to get high performance of MFC [32].

Meanwhile, the scheme of electron transfers from glucose to the electrode has been explained in Fig. 4c. MFC working with surface modification shows a good stability of current especially stable by using NR as a mediator entrapped within the surface of the anode. During perform as an anode in MFC, the biological activity of yeast within glucose oxidation has been facilitated by PNR. The PNR oxidized form captures

electrons generated and PNR reduced form will directly transfer an electron to the anode. The recycling of NADH to NAD<sup>+</sup> is important to keep the sustainability of the glycolysis process in fermentation pathways. The use of redox mediators, substituting between oxidized state (PNRox) and reduced state (PNRred) is obligatory to touch the electron transfer chain which is found at the mitochondria within the cytoplasm [46].

### *3.2 Microbial desalination cell Characterization.*

As preliminary work, the determination of the best configuration has been done using surface non-modification. The composition of each chamber on the MDC consists of 2% yeast in 0.1 M glucose; 0.1 M KNO<sub>3</sub>; 0.1 M NaCl and 0.02 M PF as a solution at the anode, concentrate, dilute, and cathode, respectively. The observation of current density has been recorded for 10 days delivered from each variation of MDC design and results can be seen in Fig 5a.

Fig 5a illustrates that from model 2, the % transport of salt ion was lower than model 1. Refers to model 1, 31% of salt ion has successfully migrated from dilute to concentrate chamber, meanwhile, 20% of NaCl has been removed from the initial concentration. Cl<sup>-</sup> has migrated from dilute to the anode and passing AEM, in contrast, Na<sup>+</sup> has moved to the concentrate chamber after passing through CEM. Moreover, the measurement of pH on anolyte has been investigated also, the results were obtained the fact that the pH anolyte has decreased from 6.88 as initially to 4.78. It was assumed that protons could not pass through the AEM membrane, so they remain on the anode chamber. At the same time, the presence of Cl<sup>-</sup> ion will react with proton and produced HCl. The evolution of pH value on anolyte could affect the stability of biocatalyst performance. Based on this situation, model 2 is no longer recommended for used the next MDC demonstration.

In addition, Fig 5b describes the diffusion process during MDC where the concentration gradient across to ion exchange membrane (IEM) can also induce the ion diffusion processes. In our study, this phenomenon has been monitored using model 1 of MDC for 14 days of operation and without the presence of yeast in the anode. Results confirm that 9.3% of Cl<sup>-</sup> ion concentration has been decreased from the dilute compartment. This can be interpreted that diffusion can contribute to the MDC process. Meanwhile, Fig 5c presents the conductivity from the dilute and concentrate chamber has been observed and the conductivity values of the concentrate chamber have been increasing up to 9% from the initial 50.8 mS s<sup>-1</sup> into 55.2 mS s<sup>-1</sup>. The concentration gradient across to IEM also induce osmotic water transport. It was suggested that the transport of osmotic water has been delivered from the cathode and compartment chamber to the dilute chamber. During the diffusion process, 8.4 mL of water has been moved into the dilute chamber for 14 days of MDC perform and results up to 9.3% of reduction of salinity (initially 3.5 g L<sup>-1</sup> NaCl).

In the meantime, the electro dialysis process has been monitored using chronopotentiometry by the current employing of 50 μA, which refers to the average value of the current generated from model 1. Fig 5d. reports that Cl<sup>-</sup> ions have been migrated from dilute to concentrate chamber during electro dialysis and

produced 16% of ion transport for 14 days of the electrodialysis process. However, it should be noted that the most important as driving force in MDC is the electric current generated by exoelectrogenic microbes.

### *3.3 Microbial desalination cell using bio-devices modification.*

The first MDC observation has been made by employing surface non-modification, 43% of NaCl transport and 73.3 mA m<sup>-2</sup> of maximum current density have been obtained from 30 days of running. The observation of salt ion concentration has been measured from the dilute chamber. The maintenance of all MDCs perform has been conducted by the addition of 1 g glucose in anolyte and refreshing of 0.02 M PF in catholyte every 13th day of performing. As described in Fig 6d. Initially, the currents generated were an increase then gradually decreased until 13th days, but after refreshment of the anolyte and catholyte solution, the improvement of the current value does not appear until at the end of the perform. It can be assumed that the lifetime of yeast has been reached.

Hereinafter, studies were performed by varying the bio-catalytic surface modification as the anode to understand the effect of modification and its MDC behavior on the desalination process during 30 days perform. CF/Immobilized Y-NR has been tested in MDC and resulted in the 83 mA m<sup>-2</sup> of maximum current density and 55% of NaCl transport. Fig 6a describes, on the 11th day the current begin reduce slightly and start from the 20th day, there has been declined until the end of the process.

The second modification is CF/PNR-Immobilized Y and the bio-catalytic activity as anode has been recorded in MDC as displayed in Fig 6b. The maximum current density and percentage of NaCl transport created were 80.2 mA m<sup>-2</sup> and 51.53%. After the 11th day, although glucose and PF have been added, it seems there was no significant effect on the signal produced. According to the surface modification by the formation cell-mediator within alginate layer, whether produced by CF/Immobilized Y-NR and CF/PNR-Immobilized Y, the thickness of the layer should be considered. It was assumed that the existence of the alginate layer could inhibits glucose to penetrate into the layer and this condition causes the slightly decrease current generated until MDC accomplishment, although this reason is very necessary for further exploration. Hence, the thickness of the alginate layer can also be one of the obstacles in the process of entry of glucose into the surface of the layer, where the electricity generated mostly dependent on glucose oxidation.

Refers to MFC based immobilization anode within alginate layer as described in our previous work [7], result reported that normally the electrochemical signal will increase in line with the glucose addition and PF replacement in anode and cathode chamber. This situation can affect to uptime of biofuel perform. However, the life time of yeast is also limited and generally it was proven when there is no significant effect although the system has been maintained.

The last modification is the formation of CF/PNR and the electro-signal behavior has been investigated and delivered 92.5 of max current density; 61 % of NaCl transport as illustrated in Fig 6c. Compared with others, this value is highest both for current density and % of NaCl transport. The reduction of the electrochemical signal has been occurred on the 12th day and slightly becomes drop from the 19th day

until completed the process. It was suggested that the presence of the PNR layer has been successful plays as a redox mediator at the surface of the anode and provides the effectiveness of the electron transport process. All the MDC experiments resulted from the effect of surface modification can be seen in Fig 6d.

The formation of PNR has given the best results compared to monomer of NR entrapped within alginate immobilization, although CF/PNR has been tested in yeast without involved in immobilization but the bio-catalytic activities resulting the best performance. The similar results were obtained from MFC using CF/PNR as anode and giving the best performance compared with other modifications as illustrated in Fig 4b.

One of the factors that support the assumed above was current efficiency value. The current efficiency from this experiment has been measured refers to Eq. 2 [48].

**See formula 2 in the supplementary files.**

The current efficiency ( $\eta_i$ ) is the amount of ion divided by the number of electrons transferred at the bio-devices modification. Where  $\Delta c$  is the reduction of saltwater concentration,  $V$  is the volume desalinated,  $N_{cp}$  is the number of cell pairs and  $i$  is the current. All the current efficiency values are explained in Table 1. However, the current efficiency is also dependent on the existence of a mediator in anolyte, because electron transport has been facilitated by the mediator. Table 1 also describes the efficiency of bio-devices modification expressed per availability mass of mediators from each bio-devices.

Table 1 shows that the highest efficiency value was obtained from CF/PNR followed by CF/Immobilized Y-NR and CF/PNR-Immobilized Y. It was assumed that the manifestation of the PNR layer at the anode surface is more effective than the monomer (NR) entrapped in the yeast immobilization layer.

We can estimate the amount of PNR deposited on surface refers to Eq. 3:

**See formula 3 in the supplementary files.**

where  $b$  is the number of electrons exchanged per mole involved in the redox couple of PNR ( $b=2$ );  $w$  (g) is the weight of PNR;  $F$  is Faraday constant (96.500 C);  $M$  is NR molecular weight; and  $v$  represents the scan rate. According to eq. 3, the amount of PNR is  $14.2 \mu\text{g cm}^{-2}$  from  $10.2 \text{ cm}^2$  of surface area.

Meanwhile, prior used, the composition of seawater has been determined and the large concentration was coming from sodium and chloride (*i.e.*  $12.14 \text{ g L}^{-1}$  and  $22.85 \text{ g L}^{-1}$ ). While the other ions such as nitrate ( $1.35 \text{ g L}^{-1}$ ); nitrite ( $0.99 \text{ g L}^{-1}$ ); sulfate ( $6.30 \text{ g L}^{-1}$ ) potassium ( $2.05 \text{ g L}^{-1}$ ); calcium ( $3.05 \text{ g L}^{-1}$ ); magnesium ( $2.05 \text{ g L}^{-1}$ ) and phosphate ( $0.98 \text{ g L}^{-1}$ ). During the MDC process, the electrical potential gradient was created by the electrode reactions, and commonly responsible for the salt ion migration. Besides that, the IEM junction potential and water transport could affect also to the desalination rate. In a four-chamber MDC, these factors work can play also as additional driving forces for desalination.

## Conclusion

Many challenges for designing the cost-efficient of MDC systems have been demonstrated by employing bio-catalytic surface modification as an anode in MDC, and that is just beginning to be developed. We have presented a simple method of bio-catalytic surface modification to be applied in MDC with a simple design of construction. Results founded that CF/PNR generated the highly significant performance shown by the maximum of current efficiency, bio-devices efficiency, current density, and also the value of percentage of NaCl transport. However, the findings demonstrated in this present study are greatly substantial to be exploited more and for future challenges in industry application. However, MDC will have unique challenges for development compared to other systems and the integration of MFC based yeast into MDC has delivered a great opportunity for wider application.

## Declarations

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### Authors' contributions

Ummy Mardiana planned and conducted the experiment, while Christophe Innocent, Marc Cretin and Buchari have supervised the project.

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### Availability of data and materials

The data used to support this works are available from author and some materials are provided by supervisor of the project.

### Competing Interest

The author declares that they have no competing interests.

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## Table

Table 1 Current efficiency, bio-devices efficiency and flux delivered from MDC

No	Bio-devices modification	Current efficiency ( $\eta_i$ )	Amount of mediator ( $\mu\text{g}$ )	Bio-devices efficiency ( $\eta_i$ )/g
1	CF/PNR	42.2 %	14.2 $\mu\text{g}$	27.11
2	CF/Immobil Y-NR	38.5 %	0.029 g	22.84
3	CF/PNR-Immobil Y	36.1%	15.8 $\mu\text{g}$	15.55
4	CF non modified	29.3 %	1.599 g	0.18

## Figures

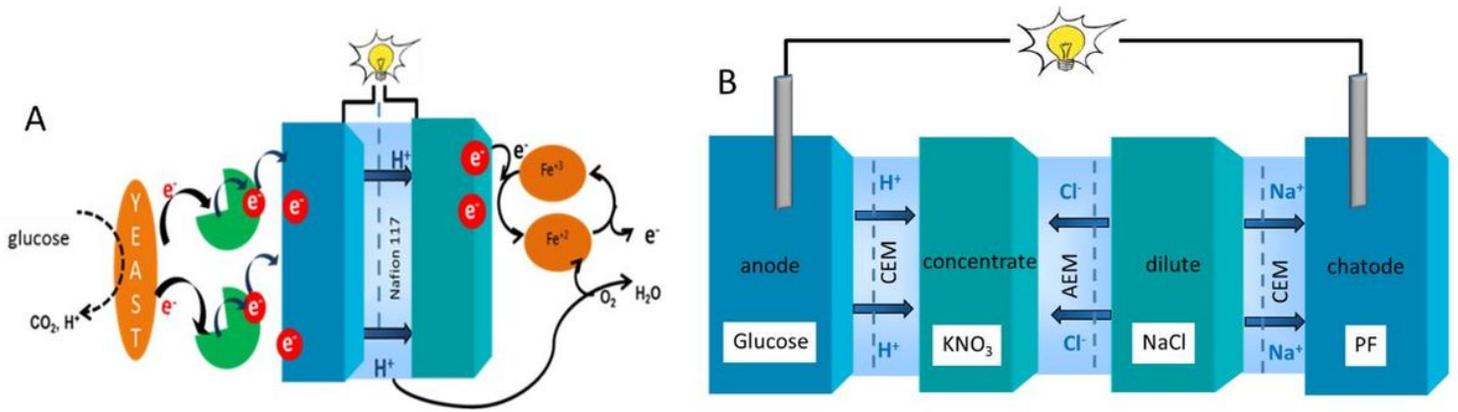


Figure 1

Configuration design of: (A) MFC; (B) MDC.

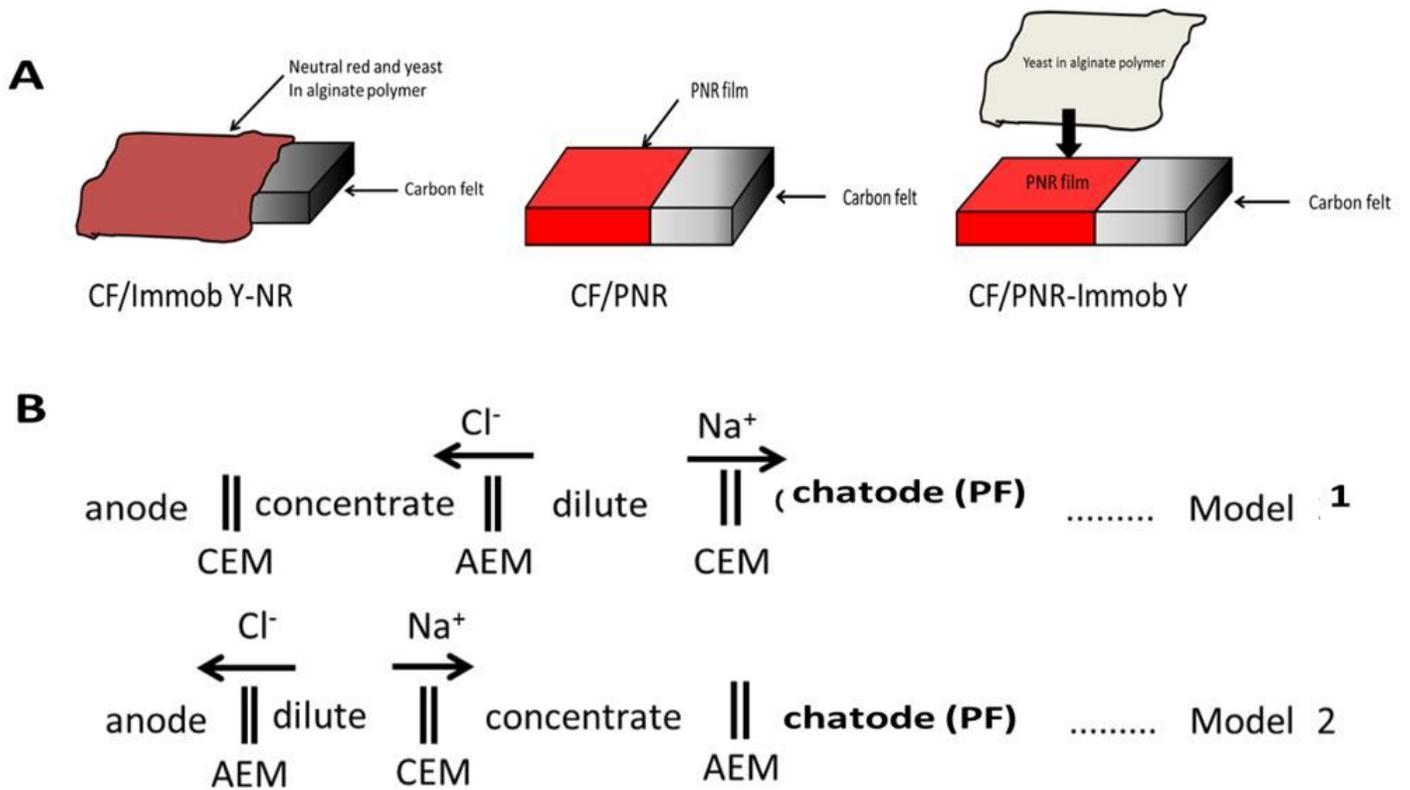
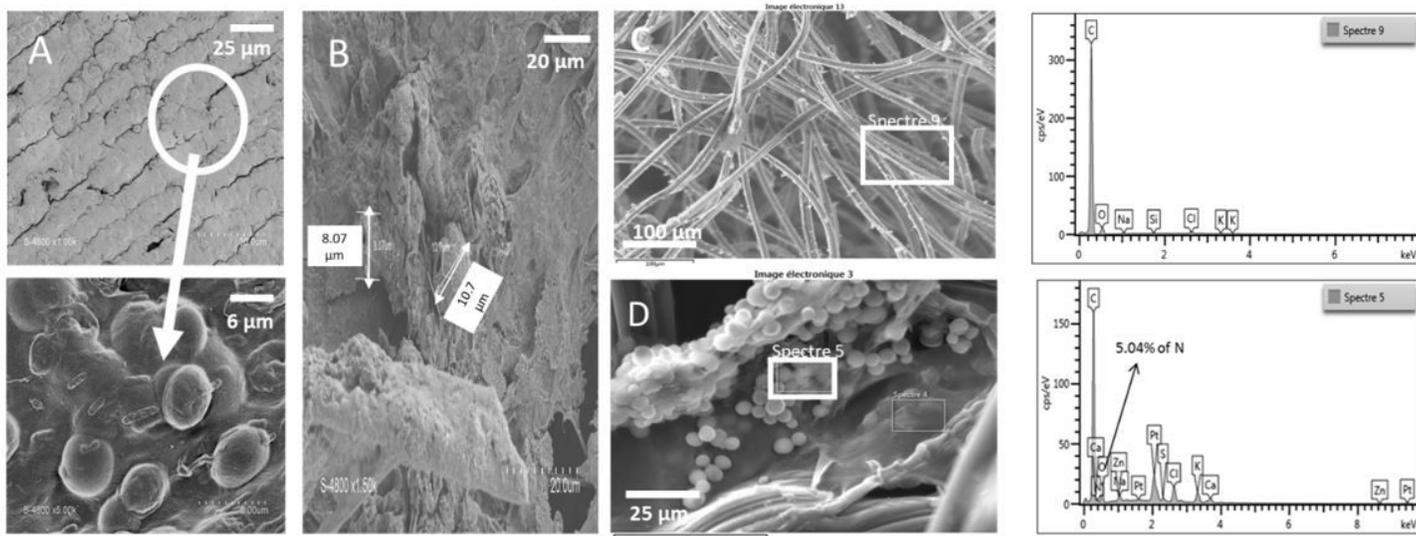


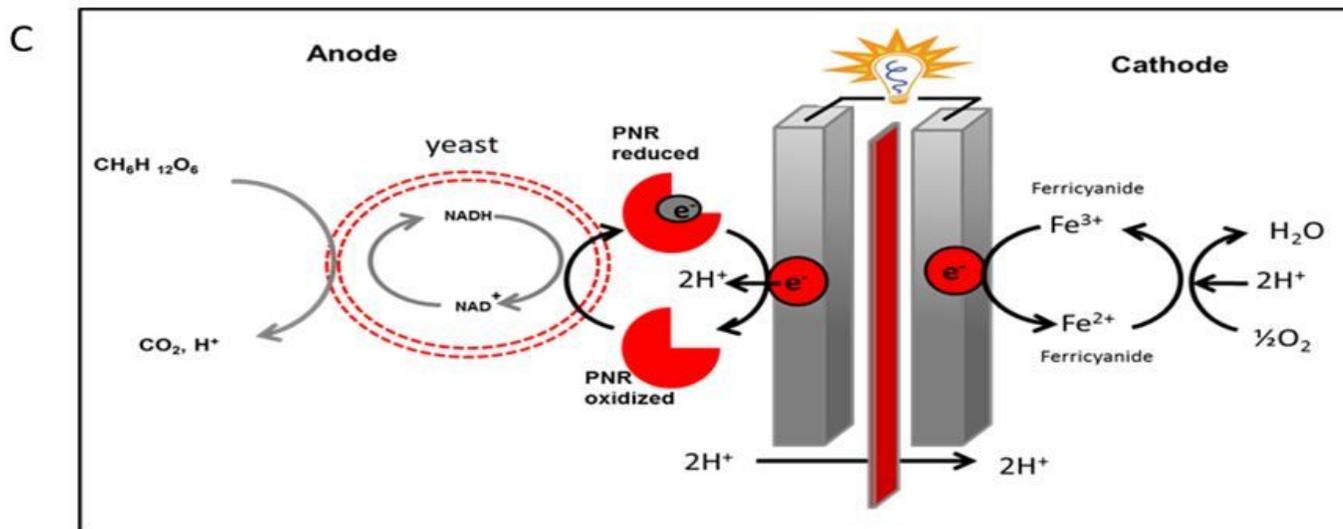
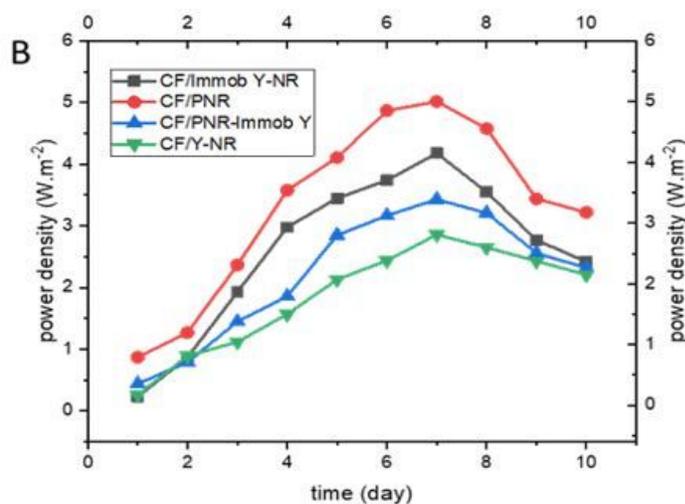
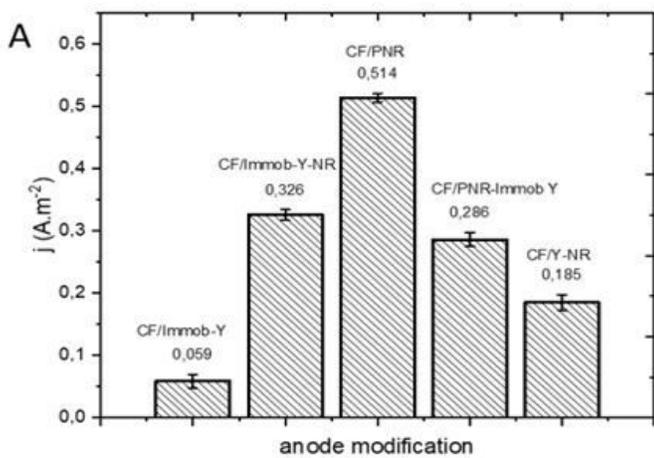
Figure 2

The material and configuration modification: (A). Three-kind of bio-catalytic devices modifications; (B) Scheme configuration modification design of MDC



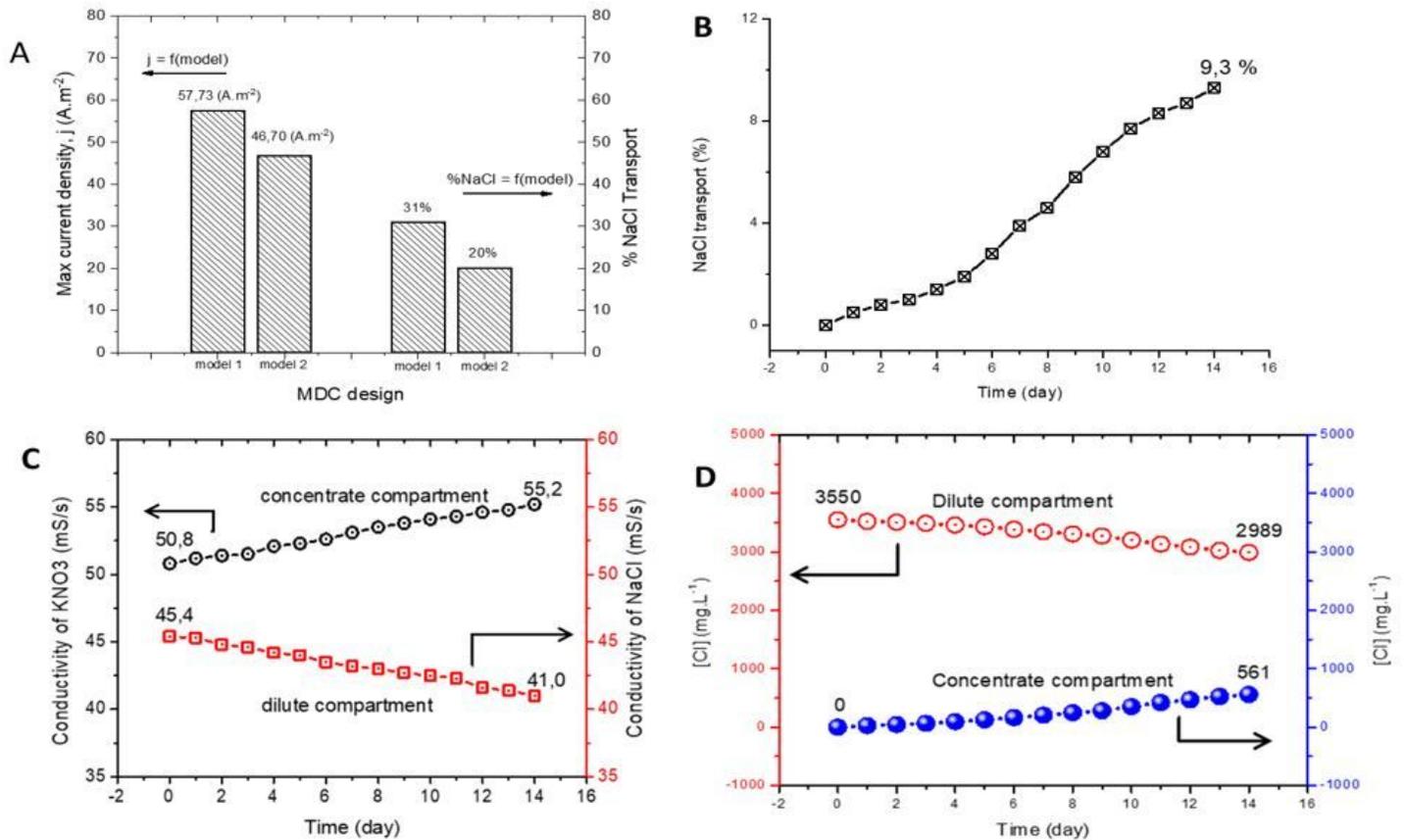
**Figure 3**

Surface images of anode surface: SEM images of : (A) CF/Immobilized yeast-NR; (B) CF/PNR-Immobilized Yeast; EDX spectrum of CF: (C) before modified; (D) after modified by PNR, yeast was identified as cylindrical form meanwhile PNR was identified as layer.



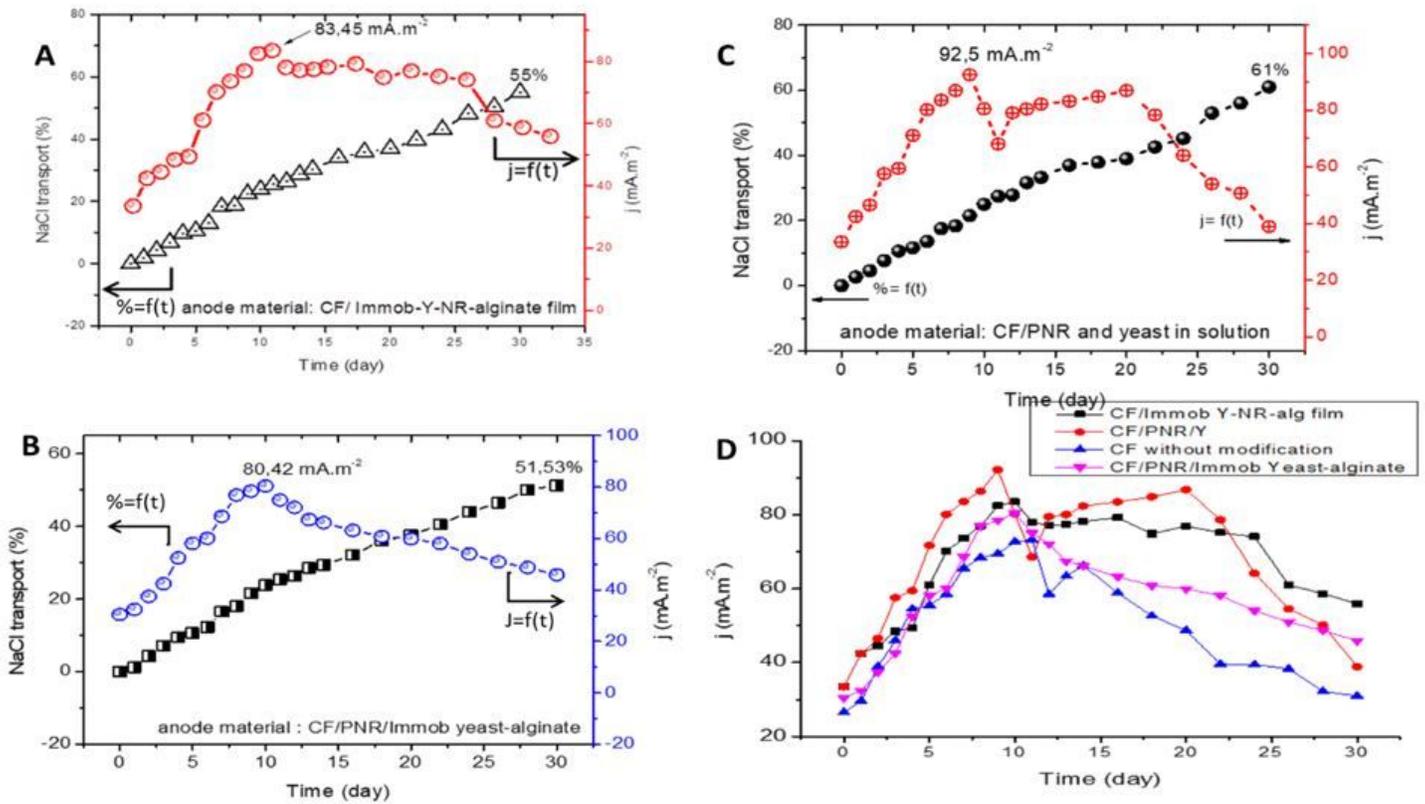
**Figure 4**

(A) Current density generated from all electrodes modification in 0.1 M glucose solution observed by Chronoamperometry; (B) Power density produced from MFC using anode modification for 10 days observation; (C) The scheme of electron transfer facilitated by PNR in MFC during anaerobic fermentation pathway of yeast.



**Figure 5**

The observation of MDC performs: (A) Current density and % NaCl Transport produced from variation of MDC design; (B) % NaCl transport generated from diffusion process; (C) Conductivity value of dilute and concentrate chambers generated from diffusion process; (D) the concentration of Cl<sup>-</sup> ion delivered from electrodiagnosis process.



**Figure 6**

The evolution of current density and % Transport of NaCl generated from MDC using bio-devices modification: (A) CF/Immobilized Y-NR; (B) CF/PNR-Immobilized Y; (C) CF/PNR; (D) summarize of all MDCs experiment part.