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Exploiting carbon and nitrogen compounds for enhanced energy and resource recovery

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Introduction

Energy Concerns

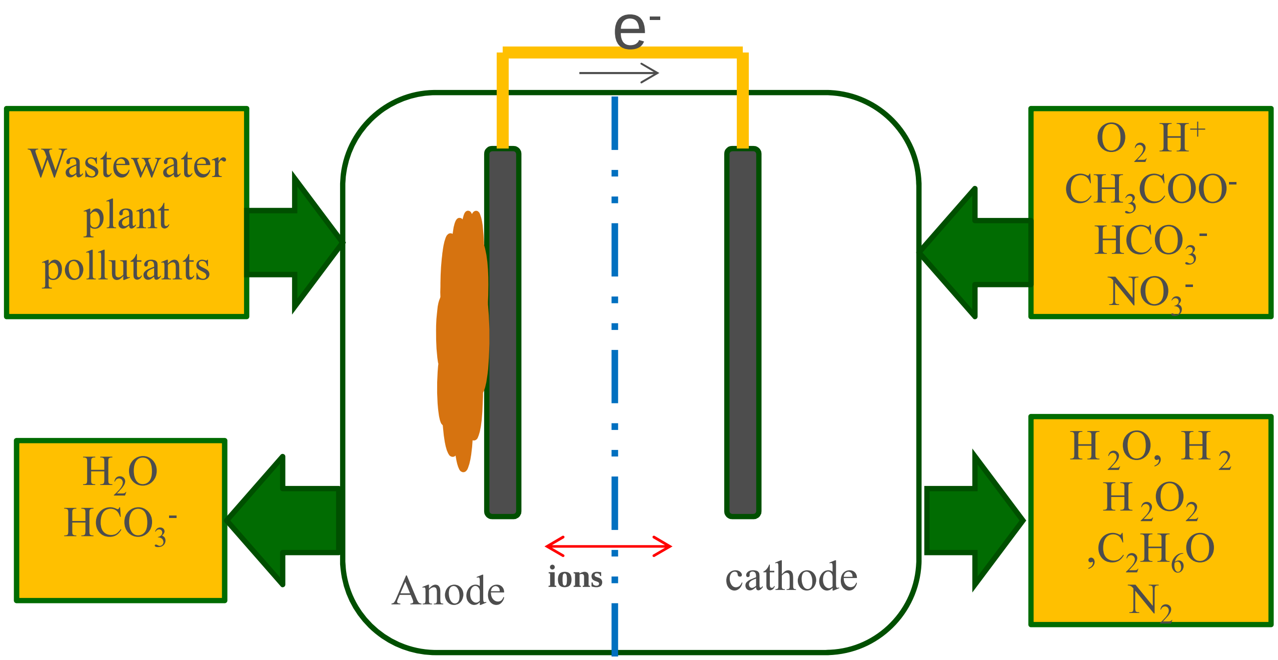
- **Over 95% of the world's energy requirement is currently met by fossil fuels, coal, oil, and natural gas.**

- **Provision of clean water and wastewater treatment requires about 4 Kwh m-3 .**

- **Needs for alternative non-fossil, non-nuclear, environmental friendly and renewable energy producing technologies.**

Introduction

Bioelectrochemical Systems(BES)



Introduction

Reactions with Standard potential (E^0),ad actual potential (E)

		E^0 (V vs NHE)	E (V vs NHE)
Anodic oxidation reaction			
Acetate	$C_2H_3O_2^- + 4\ H_2O \rightarrow 2\ HCO_3^- + 9\ H^+ + 8\ e^-$	0.187	−0.289
Glucose	$C_6H_{12}O_6 + 12\ H_2O \rightarrow 6\ HCO_3^- + 30\ H^+ + 24\ e^-$	0.104	−0.429
Glycerol	$C_3H_8O_3 + 6\ H_2O \rightarrow 3\ HCO_3^- + 17\ H^+ + 14\ e^-$	0.118	−0.396
Malate	$C_4H_5O_5^- + 7\ H_2O \rightarrow 4\ H_2CO_3 + 11\ H^+ + 12\ e^-$	0.01	−0.274
Citrate	$C_6H_5O_7^{3-} + 11\ H_2O \rightarrow 6\ H_2CO_3 + 15\ H^+ + 18\ e^-$	0.022	−0.242
Glycine	$C_2H_5NO_2 + 4\ H_2O \rightarrow 2\ HCO_3^- + 7\ H^+ + 1\ NH_4^+ + 6\ e^-$	0.131	−0.24
Serine	$C_3H_7NO_3 + 6\ H_2O \rightarrow 3\ HCO_3^- + 12\ H^+ + 1\ NH_4^+ + 10\ e^-$	0.105	−0.273
Sulfur	$HS^- \rightarrow S^0 + H^+ + 2e^-$	−0.062	−0.23
Cathodic reduction reaction			
Oxygen to water	$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$	1.229	0.805
Oxygen to hydrogen peroxide	$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$	0.694	0.269
Protons to hydrogen	$2\ H^+ + 2\ e^- \rightarrow H_2$	0	−0.414
Bicarbonate to methane	$HCO_3^- + 9\ H^+ + 8\ e^- \rightarrow CH_4 + 3\ H_2O$	0.227	−0.248
Acetate to ethanol	$C_2H_3O_2^- + 5\ H^+ + 4\ e^- \rightarrow C_2H_6O + H_2O$	0.128	−0.408
Nitrate to nitrogen gas	$2\ NO_3^- + 12\ H^+ + 10\ e^- \rightarrow N_2 + 6\ H_2O$	1.246	0.734

(Hamelers et al. 2010)

Introduction

Photosyntheitc Microbial Desalination Cell

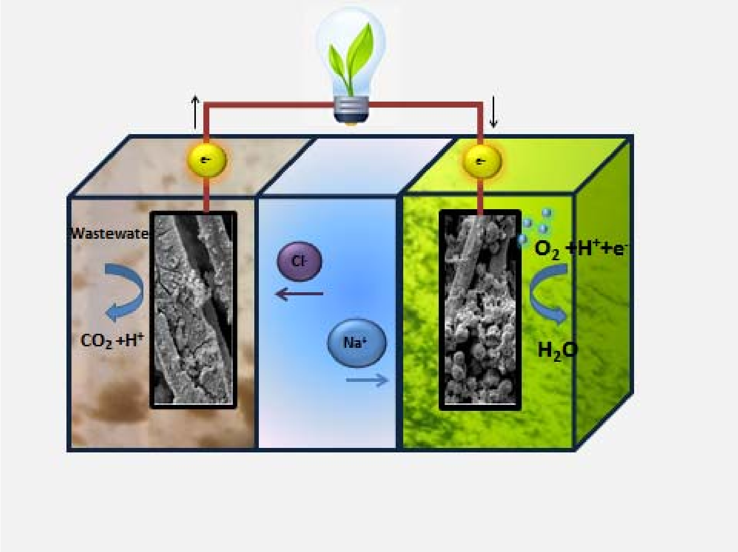
Anodic Reaction

$$C_6H_{12}O_6 + 12\ H_2O \xrightarrow{\text{Anodiphilc Bacteria}} 6HCO_3^- + 30H^+ + 24e \quad E=-0.429$$

Cathodic Reaction

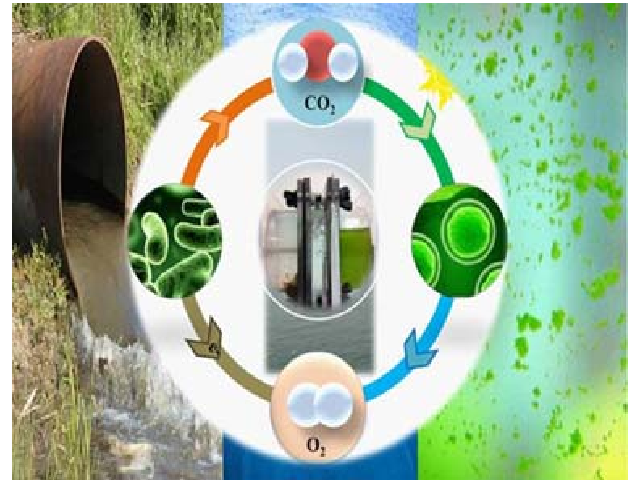
$$O_2 + 4H^+ + 4e \xrightarrow{\text{Algae}} H_2O \quad E=0.805$$

- Self sustainable system
- O_2 production/utilization
- Electricity production
- Desalination of sea water
- Wastewater treatment



Introduction

Why Algae?



- ❖ **Photoautotrophic microorganisms**

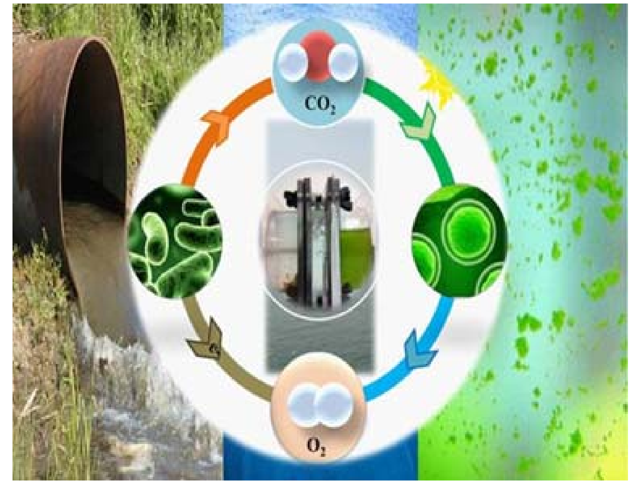
provide oxygen as an electron acceptor to the cathode reaction.

$$nCO_2 + nH_2O \xrightarrow{algae, hv} (CH_2O)_n + nO_2$$

- ❖ **Biocatalystic role of Algae increases the sustainability of MDCs and makes them more environmental friendly by replacing the toxic, unsustainable chemical cathodes.**

- ❖ **Algae function as or provide a substrate for supplying electrons**

Introduction



Why Algae?

- ❖ **Energy Resource, Algal Biofuel**
  - **Biodegradable**
  - **Harmless to the Environment**
  - **Only release CO_2**

- ❖ **Ease of growth**
  - **They provide many vitamins including: A, B1, B2, B6 and C, and are rich in iodine, potassium, iron, magnesium and Calcium**

- ❖ **Nutrition**

- ❖ **Nutrient Removal (Nitrogenous and Phosphorus compounds)**

- ❖ **CO_2 Fixation and Sequestration**

$$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 78\ H_20 \longrightarrow C_{106}H_{175}O_{42}N_{16}P + 150\ O_2$$

Objectives

- To investigate the effect of light/dark cycles on the Current generation
- To Study the effect of wastewater organic concentration on PMDC performance
- To elucidate the role of microalgae in the biocathode of microbial desalination cells
- To detect microbial communities responsible for electricity generation

Material and methods

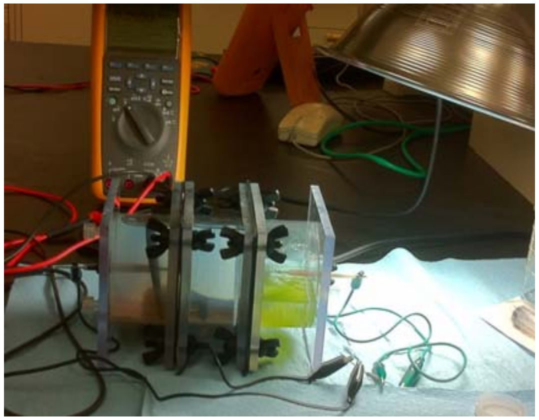
- **Anode:**
- Microbial consortium from wastewater treatment plant in Starkville
- medium used in anode chamber was a synthetic waste water containing: Glucose 468.7 mg/l, KH_2PO_4(4.4 g/l), K_2HPO_4(3.4 g/l), NH_4Cl(1.5 g/l), $MgCl_2$ (0.1 g/l), $CaCl_2$ (0.1 g/l), KCl(0.1 g/l), $MnCl_2 4.H_2O$(0.005 g/l), and $NaMo.O_4.2H_2O$(0.001 g/l)

- **Cathode:**
- The micro algae-Chlorella vulgaris-
- $CaCl_2$ (25 mg/l), NaCl (25 mg/l), $NaNO_3$ (250 mg/l), $MgSO_4$ (75 mg/l), KH_2PO_4 (105 mg/l), K_2HPO_4 (75 mg/l) , and 3 ml of trace metal solution with the following concentration was added to the 1000 ml of the above solution: $FeCl_3$ (0.194 g/l), $MnCl_2$ (0.082 g/l), $CoCl_2$ (0.16 g/l), $Na_2Mo.O4.2H_2O$ (0.008 g/l), and $ZnCl_2$ (0.005 g/l).

Material and methods

MDC Reactors

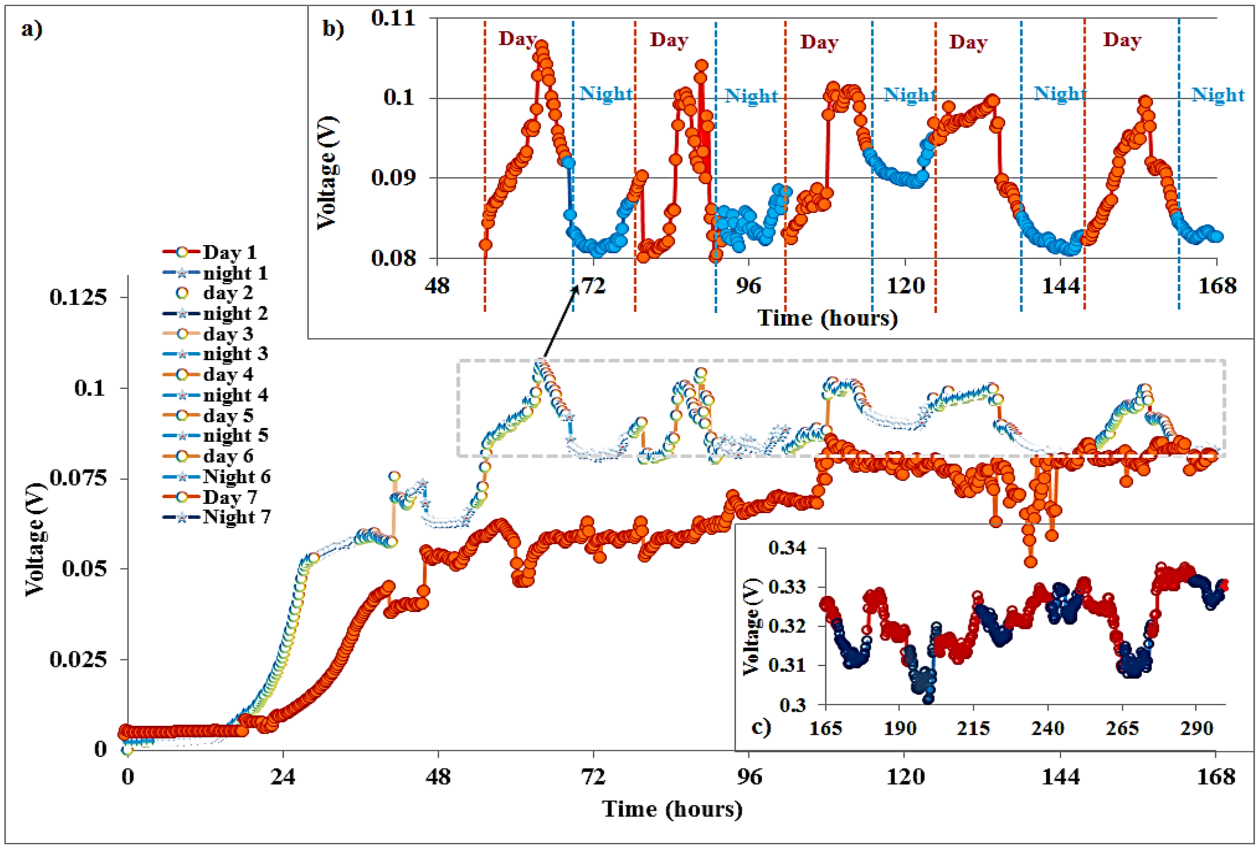
- 2 plexiglass cylindrical-shaped with 7.2 cm diameter, V=180 ml
- Graphite papers as electrodes
- Cation exchange membrane (CEM, CMI 7000, Membranes international,)
- Anion exchange membrane(AEM, AMI 7001, Membranes international)
- Volume of desalination chamber=200 ml
- Initial NaCl=10 g/l
- Initial COD= 500 mg/l



Results

Light/dark effect

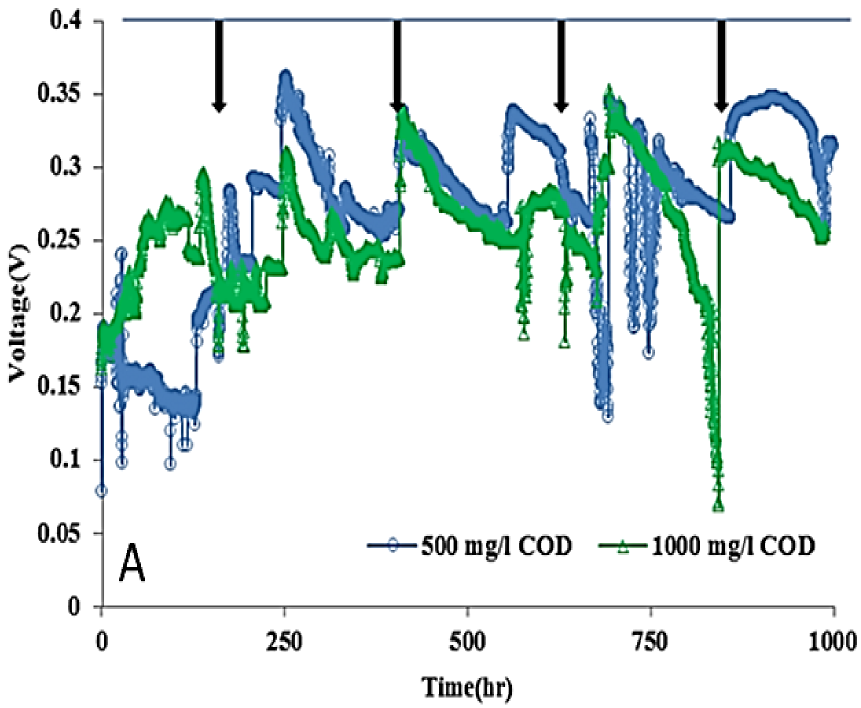
	Anode chamber		Desalination Chamber	Cathode Chamber	
	COD(mg/L)	pH	NaCl(g/L)	pH	DO (mg/L)
influent	1039.4	6.5	9.9	7.9	7.78
Effluent	366.3	5.7	6.9	10.7	5.56



Results

Effect of organic carbon Concentration

Voltage generation

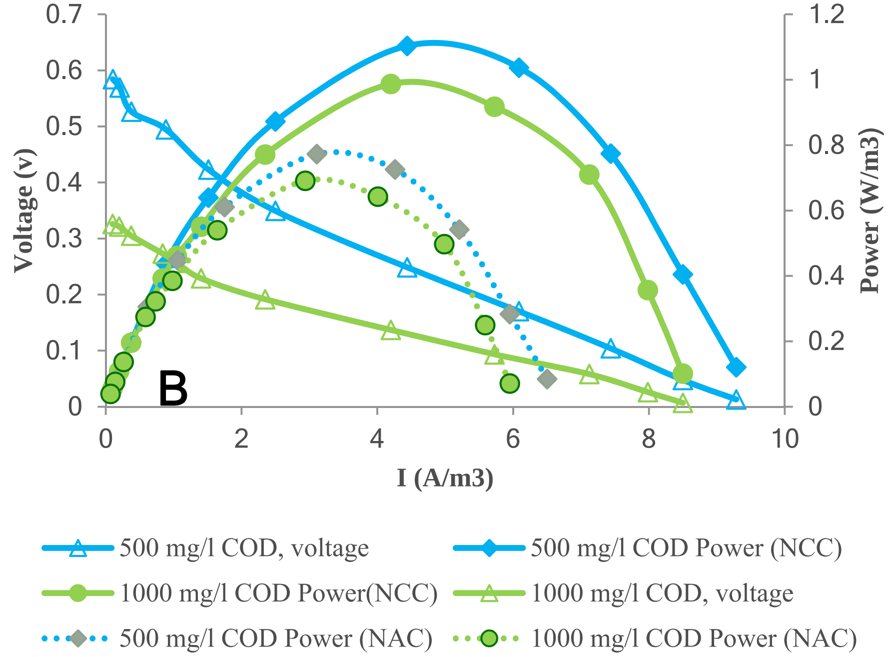


	COD	pH	DO_{ave}	$DO_{St. Dev}$
Cycle 1				
initial		8.1	7.5	0.172
final	500	11.3	6.6	0.030
	1000	11.4	5.9	0.036
Cycle 2				
initial		8.2	7.8	0.026
final	500	11.4	5.3	0.151
	1000	11.6	5.7	0.415
Cycle 3				
initial		8	8.3	0.115
final	500	11.7	5.5	0.515
	1000	11.4	5.9	0.300
Cycle 4				
initial		8.2	9.6	0.206
final	500	12	4.3	0.212
	1000	11.7	4.5	0.175

Results

Effect of organic carbon Concentration

Cyclic Voltammetry test

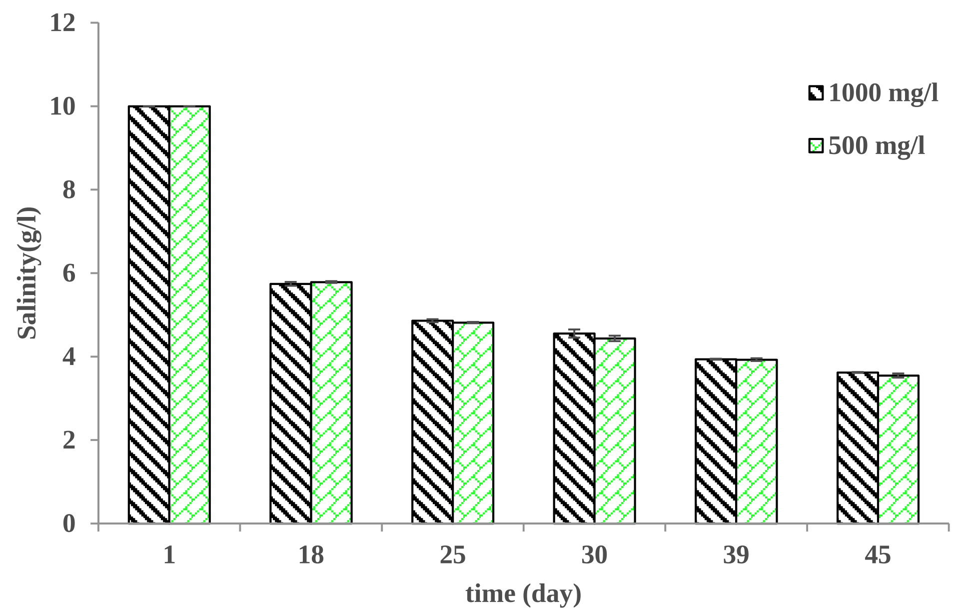


Wastewater	CE%
500 mg/l	64.21%
1000 mg/l	63.47%

Results

Effect of organic carbon Concentration

Salinity test



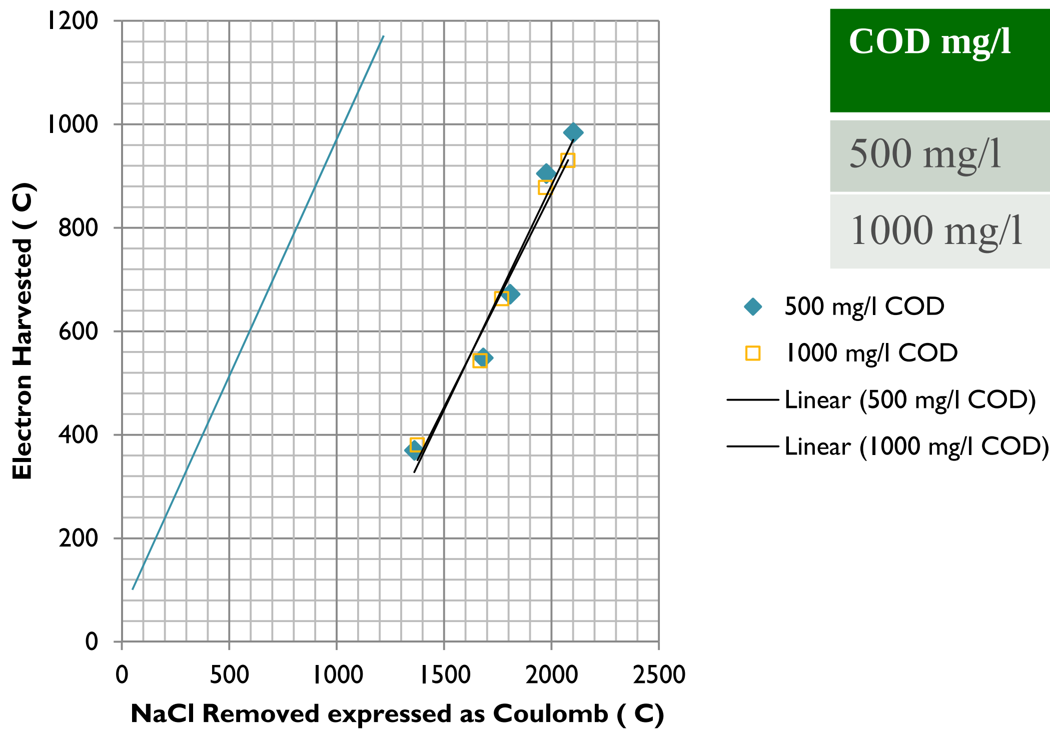
Results

Effect of organic carbon Concentration

Current Efficiency

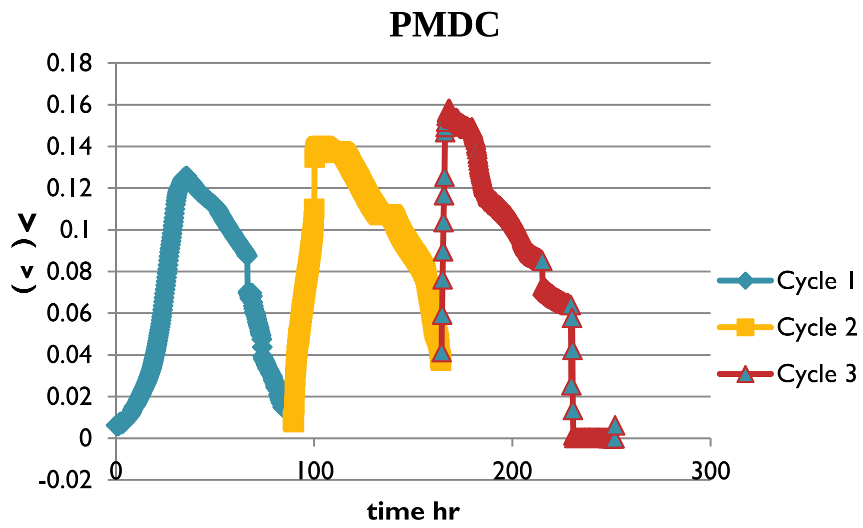
$$\eta = \frac{F * (C_{in} - C_f) * V_D}{\sum I(A) * t(s)}$$

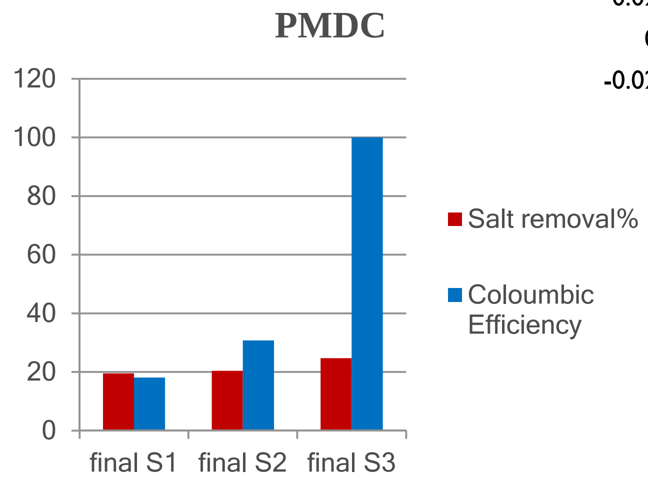
COD mg/l	Current Efficiency
500 mg/l	216%
1000 mg/l	226%



Results

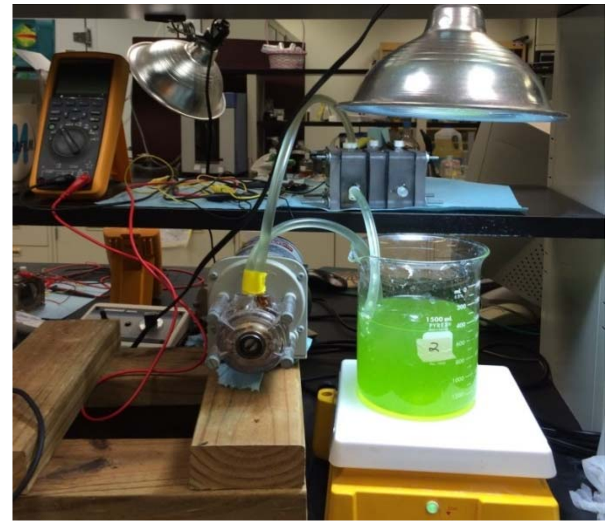
Effect of batch test



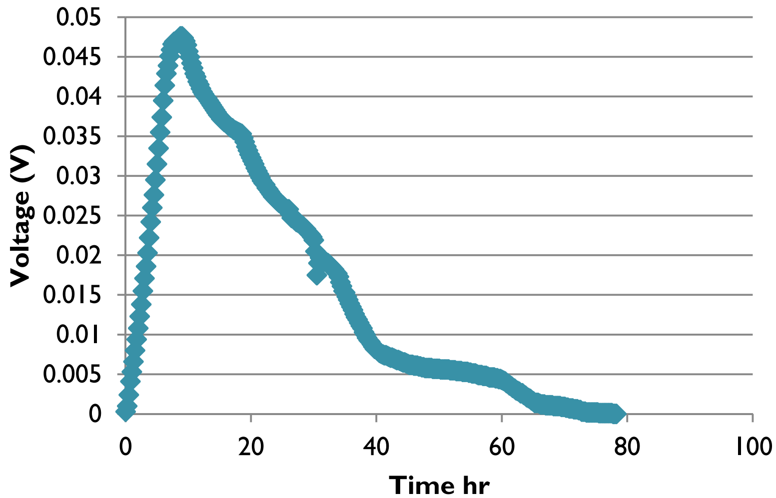


Results

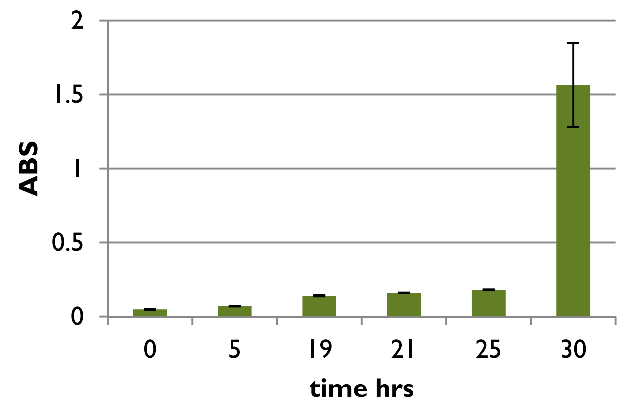
Continuous PMDC



Voltage Generation in Continuous Flow Mode



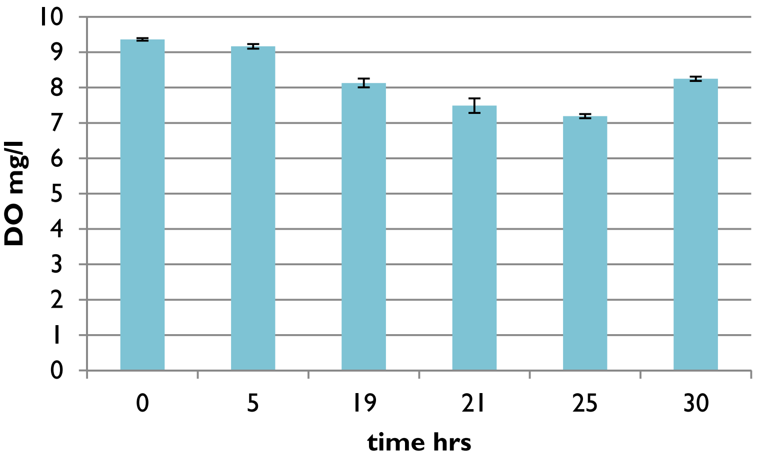
Algae OD



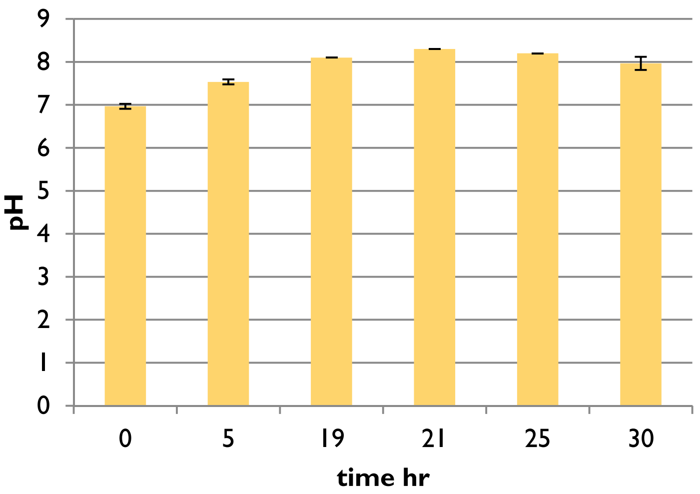
Results

Continuous PMDC

Cathode DO



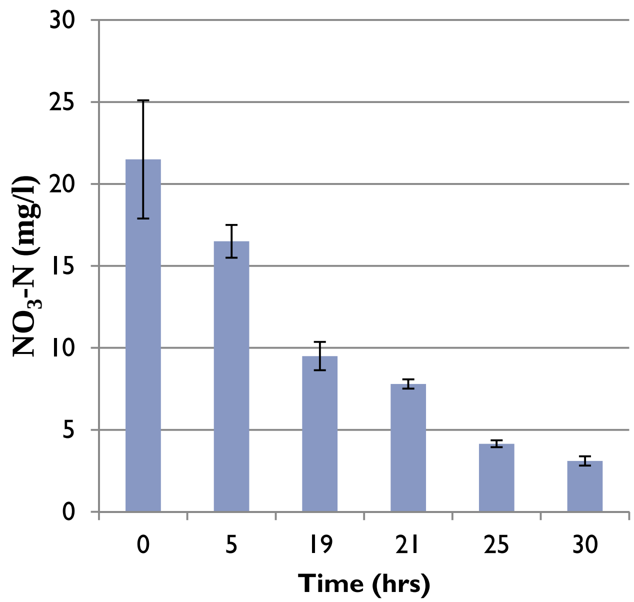
Cathode pH



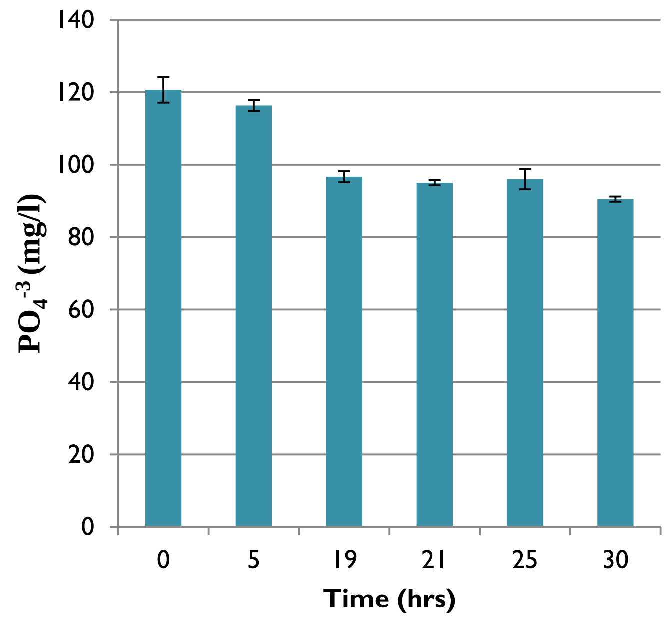
Results

Continuous PMDC

NO_3-N



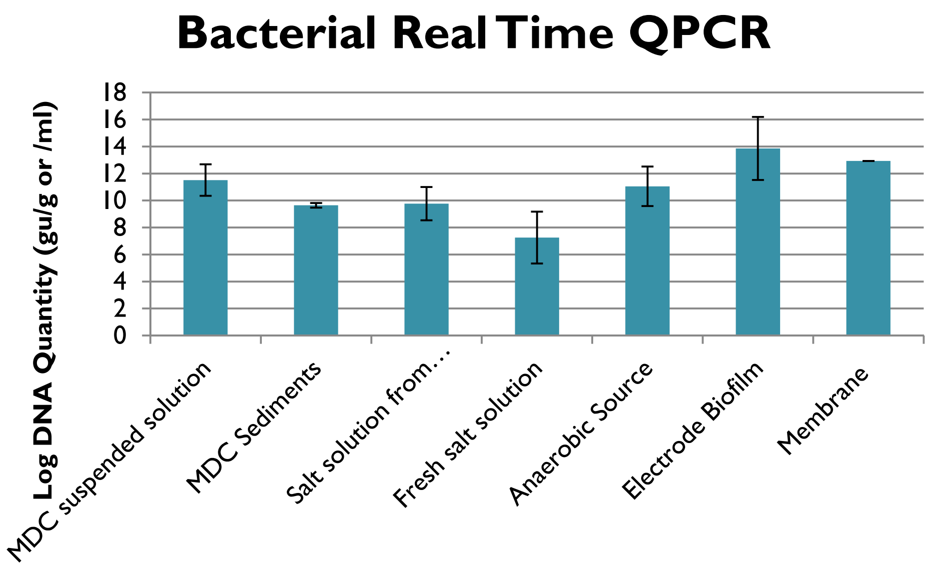
PO_4^{-3}



Results

Microbial Analysis

Real Time QPCR



Results

Microbial Community Result

- **Anode suspension solution**

Bacteroides graminisolvens

Paludibacter sp.(Bacteriodes)

- **Electrode Biofilm**

Toluene-degrading methanogenic consortium

Proteobacterium **(Reported as Exoelectrogenic bacteria)**

- **Anode Sediment**

Klebsiella pneumoniae (Gammaproteobacteria class, **Reported as Exoelectrogenic bacteria***)*

alpha proteobacterium **(Reported as Exoelectrogenic bacteria)**

- **Salt solution**

Klebsiella pneumoniae (Gammaproteobacteria class, **Reported as Exoelectrogenic bacteria***)*

Photobacterium damselae subsp.(Gammaproteobacteria class*)*

- **Purple Solids**

Bacteroides graminisolvens

Salmonella enterica (Gammaproteobacteria class*)*

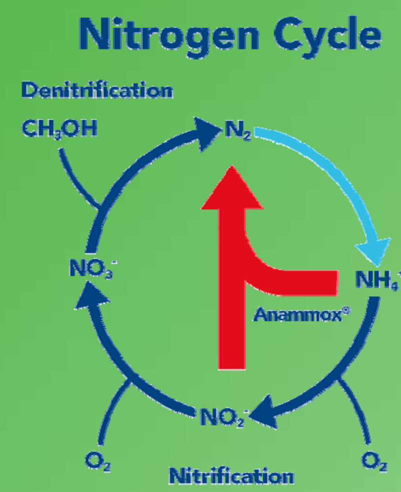
- **Biofilm on Anion exchange membrane**

Klebsiella pneumoniae

Results

- **The algae biocathode performs better under natural light/dark cycles.**
- **Increasing initial concentration of organic compound in PMDC did not have a considerable effect on salinity removal but a slight reduction in maximum power density was observed**
- **Regular renewal of algae medium in the cathode chamber maintains the PMDC performance in long term operating hours**
- **Salt removal in our system mostly occurred due to the osmosis pressure than current transfer. Future Studies should focus on improving current density .**
- **Continues flow mode biocathode PMDC allows for Algae growth, nutrient removal as well as electricity generation and desalination**
- **Microbial Analysis confirmed the growth of electroactive bacteria in our cells.**

Introduction



Anammox biocathode in MDC(ANXMDC)

- **Anammox Reaction**
- **ANaerobic AMMonium Oxidation (1999)**

- **$1.00\ NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02\ N_2 + 0.26NO_3^- + 0.066CH_2O_{0.5}N0_{.15} + 2.03\ H_2O$**

Compared to Conventional nitrification/denitrification

Reduced 58% of the oxygen requirement

100% of the carbon requirement

83% of the biosolids production

By-products do not include greenhouse gases

Introduction

Annamox Microbial Desalination Cell (ANXMDC)

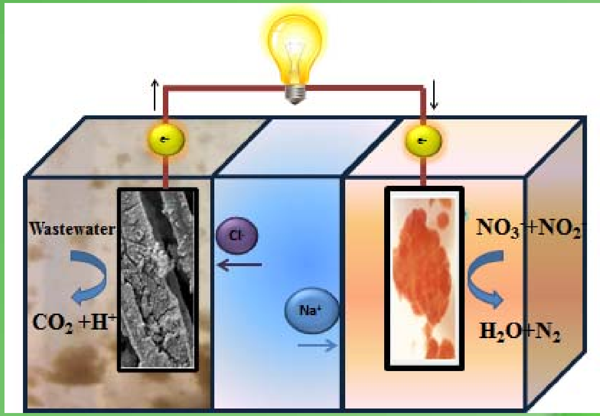
Anodic Reaction :

$C_6H_{12}O_6 + 12\ H_2O \longrightarrow 6HCO_3^- + 30H^+ + 24\bar{e}$ E=-0.3919

Cathodic Reaction :

$HNO_2^- + 3H^+ + 3e \longrightarrow 1/2N_2 + 2\ H_2O$ E=0.98 v

$2NO_3^- + 12H^+ + 10e \longrightarrow N_2 + 6H_2O$ E=0.706 V



- **Electricity production**
- **Desalination of sea water**
- **Wastewater treatment, nutrient Removal**
- **Self Sustainable system, less bioslids production**
- **Less energy consumption**

Objectives

- To Prepare the culture for growing Anammox bacteria in Anaerobic condition
- To test the proof of concept by using Anammox bacteria as biocathode in Microbial Desalination Cell (MDC)
- To evaluate Nitrogenous compounds removal and anammox reaction and the efficiency of Anammox-MDC
- To study the effect of increase in ammounium concentration and adaptation process of anammox bacteria

Material and Methods

Anode

- Microbial consortium from wastewater treatment plant in Starkville
- medium used in anode chamber was a synthetic waste water containing: Glucose 468.7 mg/l, KH_2PO_4(4.4 g/l), K_2HPO_4(3.4 g/l), NH_4Cl(1.5 g/l), $MgCl_2$ (0.1 g/l), $CaCl_2$ (0.1 g/l), KCl(0.1 g/l), $MnCl_2 4.H_2O$(0.005 g/l), and $NaMo.O_4.2H_2O$(0.001 g/l)

Cathode

- Anammox Source from Hampton Roads Sanitation District in Virginia
- Growing at T=35 Cº, 150 rpm
- Anammox media: NH_4Cl(382 mg/l), NaNO2(493 mg/L), $KHCO_3$ (200 mg /L) KH_2PO_4 (27 mg /L), $FeSO_4 \times 7H_2O$ (9.0 mg /L), EDTA (5.0 mg /L), $MgSO_4 \times 7H_2O$,(240 mg /L), $CaCl_2 \times 2H_2O$, 143(mg/L),300 µl of trace metal solution.

Material and Methods

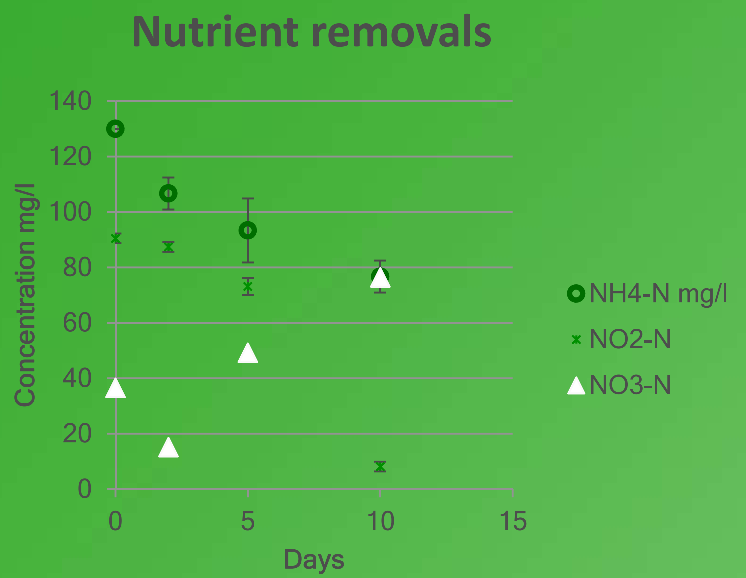
Anammox growth

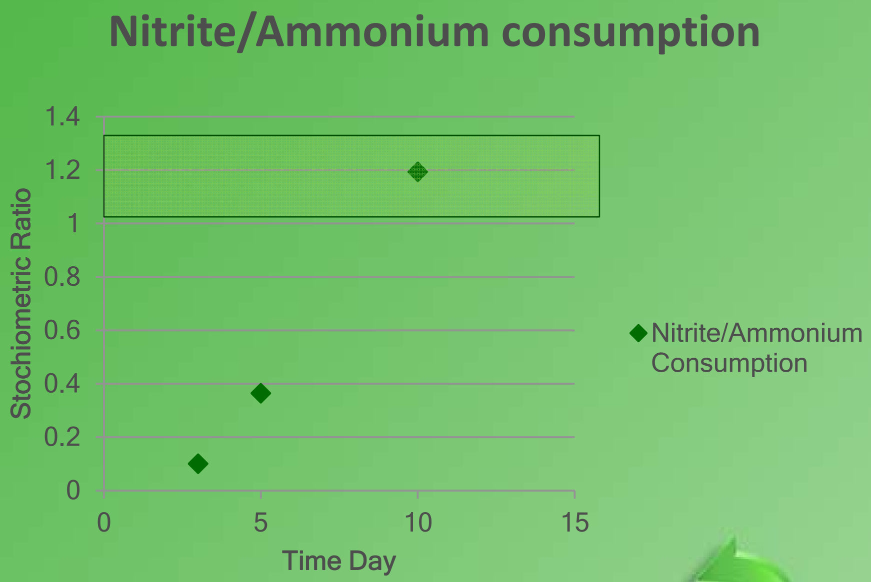
Anammox MDC

- Plexiglass rectangular-shaped, V=70 ml
- Carbon cloth as electrodes
- Cation exchange membrane (CEM, CMI 7000, Membranes international)
- Anion exchange membrane(AEM, AMI 7001, Membranes international)
- Volume of desalination chamber=30 ml
- Initial NaCl=10 g/l

Results

Anammox growth in shaker



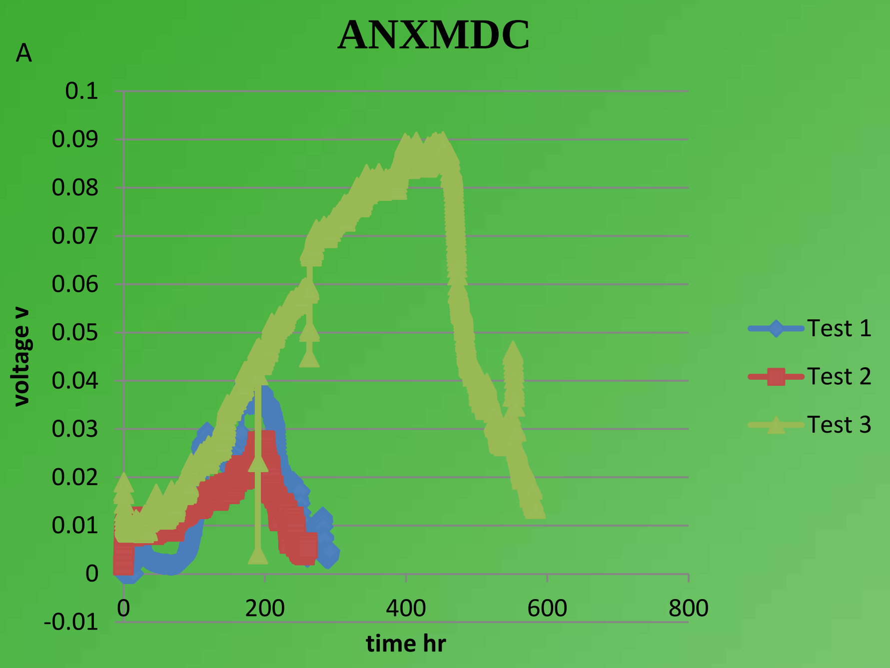


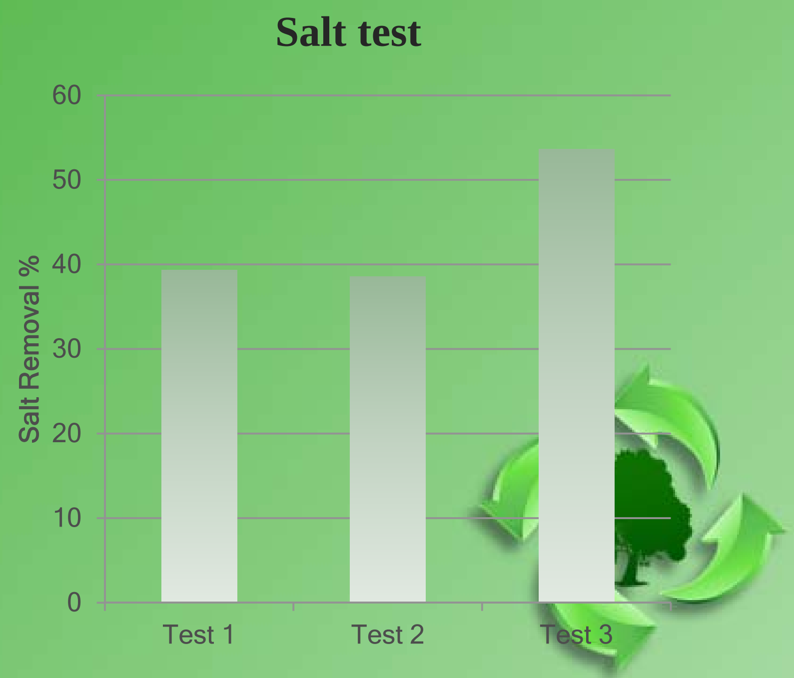
Results

- **ANXMDC**

$$CE = \frac{\sum I(A) * t(s)}{96485\left(\frac{C}{mole\ e^-}\right) * COD_{removed}(mole) * 4\left(\frac{mole\ e^-}{mole\ O_2}\right)}$$

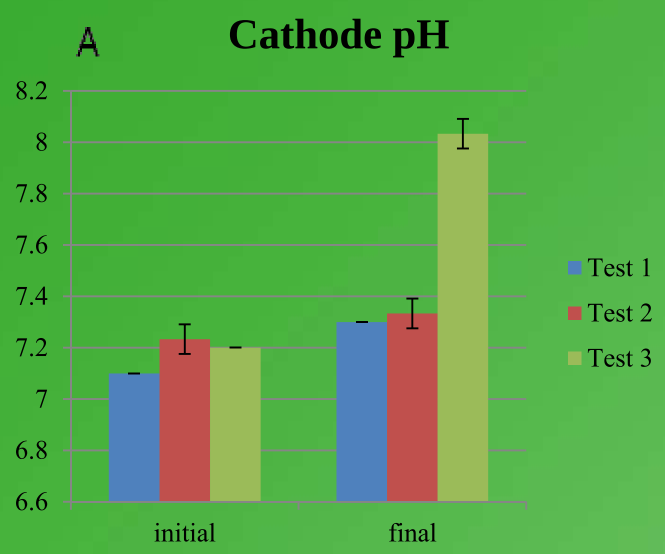
CE Test 1	CE Test 2	CE Test 3
3.4%	6.02%	52.72%

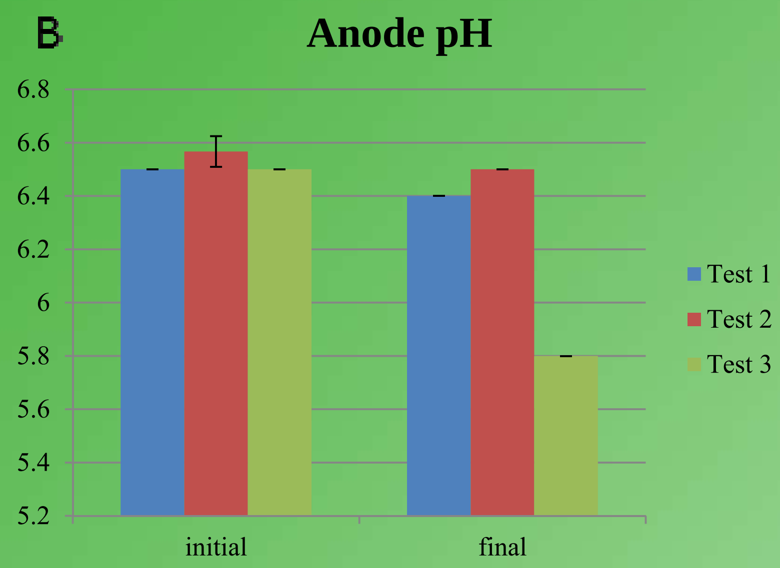




Results

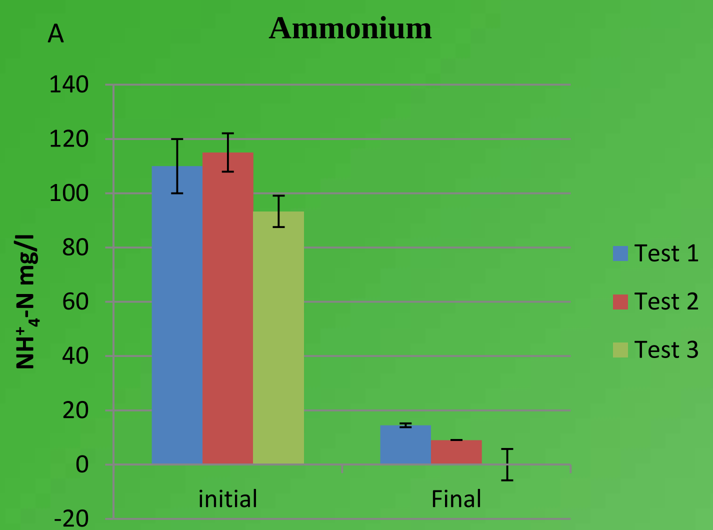
- **ANXMDC**

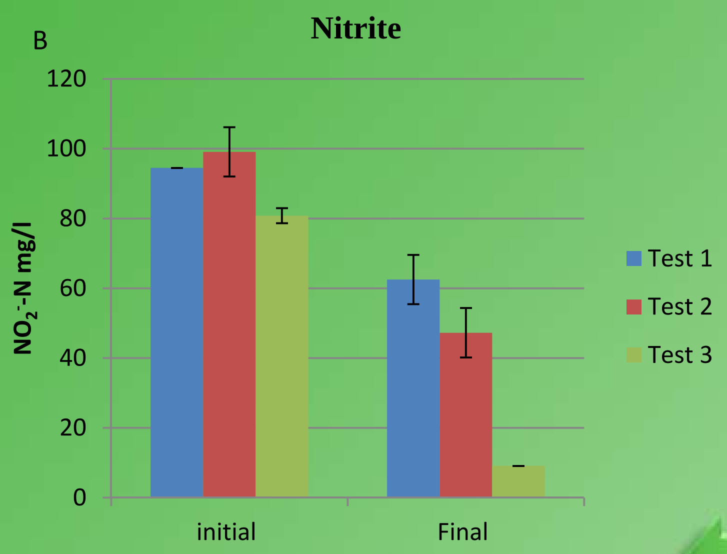




Results

- **Ammonium and Nitrite removal in cathode chamber of ANXMDC.**

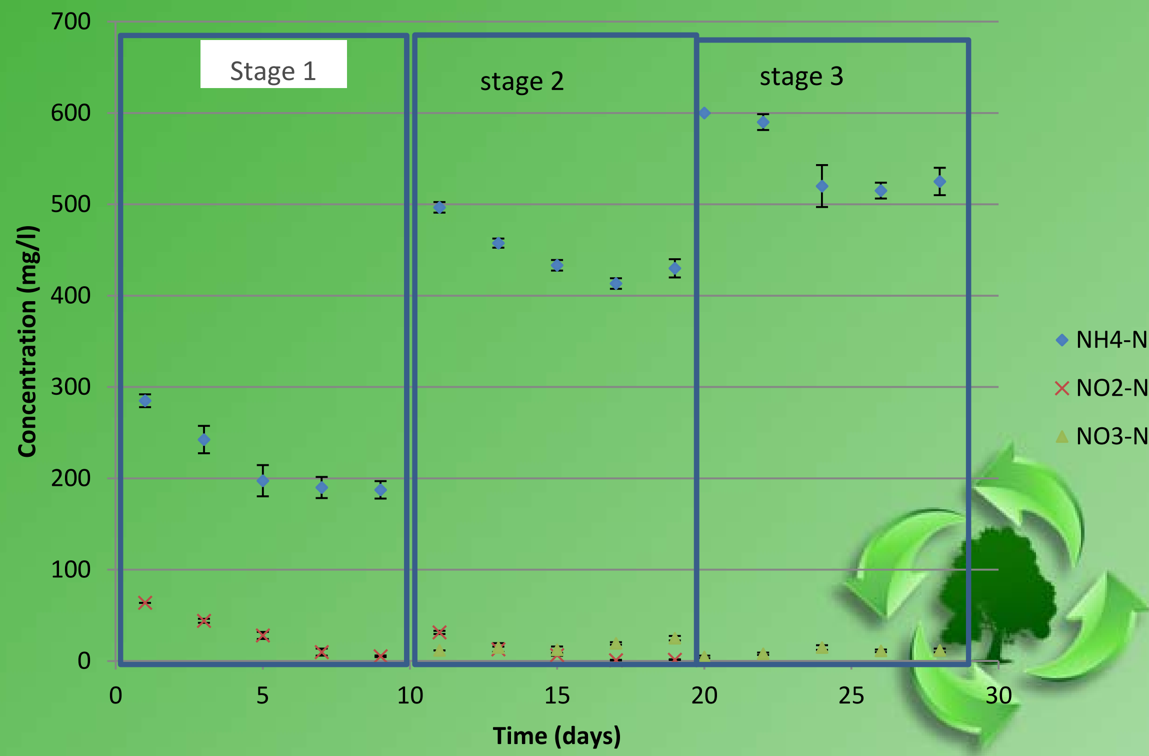




Results

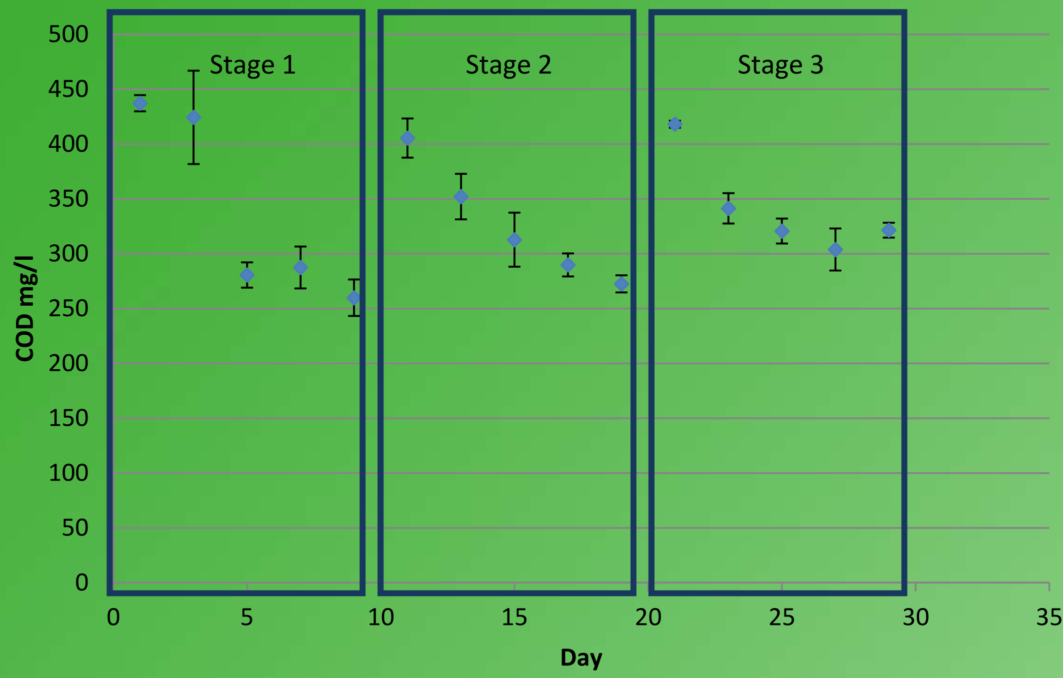
Effect of Ammonium increase and Nitrite decrease on Annamox

- **DO=2 mg/l, 7<pH<7.8**
- **Ammonium (300, 500, 600 mg/l)**
- **Nitrite (60, 30, 0 mg/l)**



Results

- **Effect of Organic carbon on Anammox**



Conclusion

- Anammox bacteria can act as a novel anaerobic biocathode in MDCs with simultaneously contributing to Energy production, Salt removal, organic carbon removal and nitrogenous Compound removal.
- The Anaerobic condition in the biocathode allows for efficient performance of MDC for long operating time.
- Series of batch experiments will improve the formation of biofilm on the electrodes that will result in better performance of the ANXMDC.
- Gradual increase of ammonium and decrease of nitrite at low DO and pH less than 8 allow for growth of Ammonium oxidizing bacteria to remove ammonium by anammox bacteria

Future Work

- Direct transfer of treated wastewater from anode chamber of a ANXMDC to cathode chamber for advanced treatment of Ammonium and to be used as catholyte of the cathode chamber.
- Microbial analysis of samples during ammonium adaptation and ANXMDC process
- Conducting continues flow ANXMDC whereas wastewater in the anode and then cathode chamber will be continuously fed.
- Larger scale application with new configuration

Acknowledgement

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