

VARIATION IN CHARACTERISTICS OF PRODUCED WATER TREATED BY BIOELECTROCHEMICAL MICROBIAL FUEL CELLS

Namita Das*

Department of General Education, City University College Ajman, Ajman, United Arab Emirates

Received: 09-Aug-2022, Manuscript No. ICP-22-71569; **Editor assigned:** 12-Aug-2022, PreQC No. ICP-22-71569 (PQ); **Reviewed:** 26-Aug-2022, QC No. ICP-22-71569; **Revised:** 01-Sep-2022, Manuscript No. ICP-22-71569 (A); **Published:** 09-Sep-2022, DOI: 10.4172/0970-2083.002

Key words: Produced water, Microbial fuel cells, Wastewater, Micro-organisms, Gas production.

ABSTRACT

Produced water is the wastewater released from the oil fields while oil is being extracted out. The huge amount of contaminated water released require immediate response as this can prove detrimental for the environment. During the past decade Bioelectrochemical system has rapidly advanced as a sustainable technology for dual purpose of energy production and wastewater treatment. These systems are adept at converting chemical energy into electrical energy with the help of microbes as catalyst. The success of the electrochemical reactions depends on the functional activity of the micro-organisms.

INTRODUCTION

Human civilization has come a long way in terms of development. Discovery of oil as a fossil fuel was a turning point in the development industries. This production of oil and gas led to the formation of wastewater called produced water (Nallakukkala, et al., 2021). A common name in the oil and gas industry is produced water which is the wastewater released during the extraction (Al-Ghouti, et al., 2019). It is one of the largest streams of wastewater produced in these industries, with global production estimated to be >70 billion barrels per year in 2009, with the United States alone producing 21 billion barrels. Average production of produced water from a shale gas is around 2-4 million gallons. (Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions, Environmental Science & Technology n.d.). Thus the organic waste like low grade wastewater and biomass were converted into electricity using Microbial Fuel Cells (MFC). In Microbial Electrolysis Cell (MEC) this electricity is used to produce hydrogen. Water management has emerged as the most difficult problem, as it requires massive quantities of freshwater and produces large volumes of complex liquid wastes polluted by a variety of potentially toxic elements at different rates. Produced water is the water that is

coming from two sources, primarily the water that is present with the oil and secondly the water that is injected into the well to release the oil. Produced water makes up most of the waste stream in offshore oil and gas operations, accounting for 80% of residuals and wastes produced during natural gas production. Furthermore, as the well gets older and oil and gas output declines, the amount of produced water produced rises (Kusworo, et al., 2018). Furthermore, according to the International Association of Oil and Gas Producers (IOGP), in 2014, 0.6 tons of produced water was discharged and 1.2 tons of hydrocarbon produced was reinjected, with offshore activities accounting for 92 percent of the produced water. The amount of produced water from a given reservoir does not stay constant over time (Al-Ghouti, et al., 2019). Water output is initially low, but it gradually increases.

Produced water is not a single product; it is a mixture of dissolved and particulate organic and inorganic chemicals with a basic to complex composition that varies. Geographical location, age and depth of the field, hydrocarbon-bearing formation geochemistry, extraction method, type of the produced hydrocarbon, as well as its chemical composition play an important role in determining the physical and chemical properties of PW.

*Corresponding author's email: namitaprabhan@gmail.com

CHARACTERISTICS OF PRODUCED WATER

PW contains a complex mixture of dissolved organic and inorganic chemicals. Geographical location, age depth of geological formation, hydrocarbon forming geochemistry, extraction, geographical location play an important role in determining the physical and chemical properties. The main components found in produced water are salt content, Benzene, Toluene, Ethyl benzene and Xylene (BTEX), oil and grease, Polyaromatic Hydrocarbons (PAH), phenols, organic acids, calcium, magnesium, and barium (D. Arther, 2011).

The level of salinity can range between few parts per million to 300‰ which is more than the salt concentration in sea water. Therefore, the produced water is denser than sea water. The reason for high salinity is the presence of dissolved sodium and chloride which less concentration of calcium, magnesium, and potassium. Guerra et al. suggested the high TDS is due to higher concentration of sodium and bicarbonate (Rosenblum, et al., 2017).

High concentration of sulfates and sulfides are formed in produced water because of the sulfate and sulfide ions. The bacteria also reduce sulfate and results in formation of sulfides and hydrogen sulfide in produced water. Location is an important parameter when deciding about the concentration of anion and cations (Neff, et al., 2011). A variety of chemicals like mercury, zinc, manganese, iron and barium are present on higher quantity in produced water than in seawater. Geological age, chemical composition and injected volume determine the type and concentration of metals. Floating and drifting material like silt, sediment, sand, algae and planktons make up the Total Suspended Solid (TSS) (Tibbetts, et al., 1992). The value of TSS can range between 1-1000 mg/L concentration. The range of TOC values are from 1-1500 mg/L.

worked to find the concentration of NO₃⁻, NO₂⁻, NH₃, NH₄ in produced water. According to the work done by Fillo, et al., and Johnson et al., the level of COD is found to be in the range of 2600-120000 mg/L while BOD is found in the range 75-2870 mg/L (Veil, et al., 2004; Al-Kaaba, et al., 2019; Bierman, et al., 2019). Produced water characteristics, treatment and reuse, membrane filtration. BTEX are aromatic organic compounds that readily get mixed in the atmosphere during the water treatment process. Among the other compound's benzene is present in higher amounts in BTEX. Phenols are also organic compounds that contain a hydroxyl group attached to hydrocarbon group. The concentration of phenol is found to be in higher value (Callaghan, et al., 1990). Phenols are also present in varying concentrations in oil wells produced water (Tab 1).

Tab 1. Range of major and trace inorganic constituent in Produced Water.

Constituents	Min-Max (mg/L)
Calcium	2.5-3002

Magnesium	1.05-8.72
Potassium	1.6-42.6
Sodium	8.8-430
Chloride	5-48
Bicarbonate	433.3-976
Carbonate	14.6
Zinc	17.4
Lithium	3-50
Phenols	0.009-23
Volatile fatty acids	2-4900
Alkalinity	300-380 mg/L CaCO ₃
Conductivity	838-1500 μmhos
Hardness	5-20 mg/L CaCO ₃
pH	7.2-8.5
Total dissolved solids	704-1370 mg/L
Total suspended solids	3.2-26 mg/L
Biological oxygen demand	4.4-9.4 mg/L
Salinity	1000-300,000 mg/l
Chemical oxygen demand	1220-2600 mg/L
Density	1014-1140 Kg/m ³
Volatiles	0.39-35 mg/L

Sources of Produced Water

Studies into the composition and isotopic data presented a different idea about the origin of produced water. Level of salinity, maximum TDS and presence of Chlorine suggested the source of PW as evaporated sea water (Scanlon, et al., 2020). Common shale specific processes like hydrocarbon maturation and water clay interactions control the composition of the PW (Engle, et al., 2016; Nicot, et al., 2018; Phan, et al., 2016; Stewart, et al., 2015). The geological history and depth give information about the source of produced water.

Produced Water Management Methods

The basic purpose of treating the produced water is to remove dispersed oil and grease, salt, dissolved gases, soluble organics and hardness so that it can be used for variety of purpose (Patel, et al., 2005). The treated water can be reused in different sectors provided it meets the quality standards. Any treated water if does not meet the quality standards in released into the ocean. With concerns to the onshore PW any of the following three options can be taken into consideration.

- Considerably reduce the quantity of PW from reaching the surface.

- Try reusing and recycling.
- Dispose off.

Apart from the energy industry, there is a lot of interest in reusing PW because it is thought that PW represents huge quantity of water and that reusing it will bring it back into the hydrologic cycle. However, major amount of PW is generated in semiarid areas, where water shortage is a considerable issue. Taking into consideration, water treatment criteria and recovery factors will reduce PW volumes even more. In the Bakken, PW will account for 2% of irrigation, 5% in the Permian Delaware Basin, and 63% in the Permian Delaware Basin. 77% in the Barnett AOI and 50 percent in the Oklahoma AOI, assuming recovery percentage is 50% for the treatment.

Before releasing produced water to surface water or recharging groundwater, detailed site-specific studies need to be done to remove any hazard. As a result, it appears that produced water reuse would not aggravate water shortage issues in most areas. Reusing the treated produced water within the energy sector will make it convenient to address the issue of water scarcity related to oil and gas production. Apart from the energy sector, not many sectors are supporting the reuse of produced water. Among the other factors that limit the use of produced water in other sectors is the reduced knowledge of produced water chemistry, improper measuring methods, no proper regulation for various sectors (Scanlon, et al., 2020). The awareness about the quality of treated produced water should be properly created to allow other sectors to also benefit from it.

The other factors that limit the application of produced water reuse outside of energy sector: a lack of understanding of produced water chemistry, inability to accurately quantify produced water quality due to high salinity matrix and interference issues, lack of appropriate measuring methods, lack of suitable specifications, and a lack of regulations for different sectors to consider.

Treatment of Produced Water

Treatment of produced water is an important step towards the solving a crucial issue of wastewater. The methods used for treatment of polluted water is a deciding factor as it should be environmentally friendly and cost effective.

Conventional Methods

The conventional methods used for treating produced water range from membrane filtration technology which includes microfiltration, ultrafiltration, polymeric ceramic membrane, reverse osmosis and Nano filtration., thermal technologies include multistage flash, multieffect distillation, vapour compression distillation, multieffect distillation, vapour compression hybrid, biological aerated filters, gas flotation, evaporation, adsorption, media filtration, ion exchange technology, chemical oxidation, electro dialysis and freeze thaw evaporation. Though all the methods have their own positives and negatives but

none of the were successful in removing the contaminants from the produced water (Fig 1).

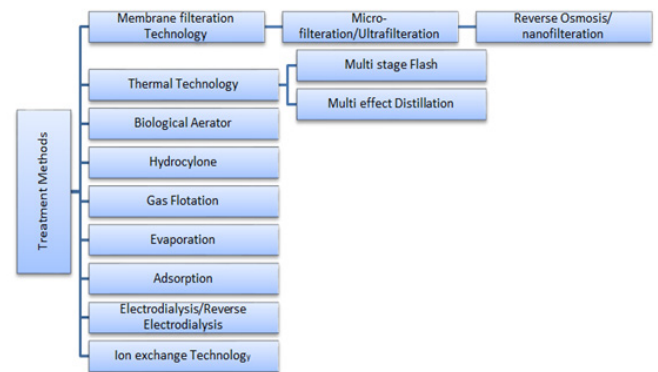


Fig. 1 Different treatment methods being used for removing contaminants in produced water.

Different analytical methods are used to analyse the removal of contaminants in PW. Gas chromatography is used to isolate chemical components, mass spectroscopy to measure materials and high-performance liquid chromatography to identify and purify as well. The organic and inorganic components tend to cover the surface of the porous material. Adsorption is an options that remove copper, lead, iron, manganese BTEX and heavy metals resulting in 100% recovery of water. Activated carbon, activated alumina, and zeolites are the commonly used adsorbents. (Investigations into the Use of Modified Zeolites for Removing Benzene, Toluene, and Xylene from Saline Produced Water).

Types of Bioelectrochemical System

Bioelectrochemical systems are a different type of system which functions by transforming chemical energy into electric energy using microbes and catalysts. Basically BES performs dual function of reducing and treating the waste and generates electricity also (Bajracharya, et al., 2016). BES is a multidisciplinary stream which includes bio electrochemistry, biotechnology, electrochemistry environmental science, microbiology and materials science (Mohanakrishna, et al., 2010a, 2018a; Harnisch and Schröder, 2010; Pant, et al., 2010). A potential difference is created between the oxidation at anode and the reduction at cathode, generating a flow of electrons that create electricity. The movement of electrons through the external circuit is calculated as the electric current (An Overview on Emerging Bioelectrochemical Systems (BESs), Redox, and Electrochemistry). Another advantage with the BES is its ability to combine with other applications as well like microbial desalination cells for removal of salinity from the water, plant microbial fuel cells where the roots of the plant work to treat contaminants with the production of energy(Bajracharya, et al., 2016). BES work efficiently as bioreactors known as microbial electro remediation or Bioelectrochemical Treatment (BET) for remediation of pollutants and toxic wastewater (ElMe-kawy, et al., 2014). Microbial fuel cells are a type of BES

which treats produced water along with the production of electricity (Sheikhyousefi, et al., 2017; Jain, et al., 2017; Mohanakrishna, et al., 2018a, 2018b) (Fig 2).

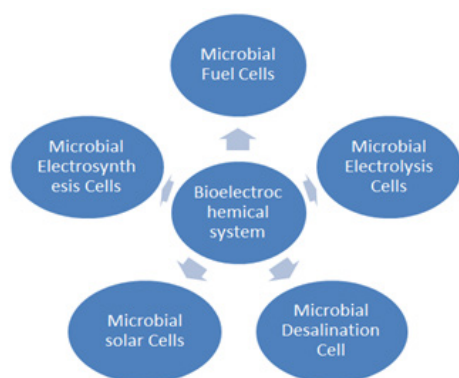


Fig. 2 Showing different types of BES systems.

Attempted to treat produced water using MFC with substrate from Bakken shale (Shrestha, et al., 2018). Petroleum hydrocarbons that are the main contaminants in the petroleum refinery wastewater were also treated using an MFC (Li, et al., 2019; Mohanakrishna, et al., 2018b). The performance of a MFC is dependent on configuration, operating conditions, substrate, anode and cathode material (Li, et al., 2014; Wang, et al., 2015; Khalili, et al., 2017).

The components present in an MFC include an anode placed in an anaerobic chamber and a cathode placed in aerobic chamber. The two chambers may or may be not separated by a membrane. The membrane helps to regulate the flow of electrons from anode to cathode chamber. Both the electrodes are joined together with an external circuit (Kondaveeti, et al., 2014). Substrate is added in the anode chamber as a fuel for the micro-organisms. The organic compound is broken down by the bacteria and the electrons generated during the process are passed to the cathode via a mediator through an external circuit. This movement of electrons under external load gives

electricity (Lin, et al., 2014). At the same time protons released from the substrate in the anode pass through the proton exchange membrane to cathode chamber where they react with electron acceptors like oxygen, potassium dichromate, ferric chloride, potassium ferricyanide to release water (Kumar, et al., 2017). Micro organic load present microbial fuel cells can easily use the microbial metabolic activity for catalytic decomposition of organic load present in the wastewater by converting 80% of potential energy to bioenergy (Rajeswari, et al., 2016). Microbial fuel cells can remove COD and BOD to 90% and sludge is reduced to around 50-90%, thus reducing the cost for sludge clearance (Du, et al., 2007). The microbial fuel cells work well in dilute solutions also with the same efficiency. In microbial fuel cells the volatile fatty acids do not affect the unit negatively as it can utilize the fatty acids like acetate and butyrate as feedstock (Chang, et al., 2020).

Produced Water Quality

Statistical data about produced water was taken from USGS produced water database, which focuses on conventional oil and gas reservoirs (Blondes, et al., 2017). Total dissolved solids were the primary criteria for deciding the treatment options and method. Additional data were obtained from the literature based on field studies of sampling in selected UOG plays. Most focus was placed on Total Dissolved Solids (TDS) to evaluate water treatment options and treatment goals; But TDS values are not sufficient for evaluating the quality of PW in other sectors. Data was collected for major and trace elements and analysed for the permissible limits of produced water for other sectors. Another sector that requires attention is the maintenance of concentration that requires additional costs.

The below table shows various power densities reported in treating produced water using different Bioelectrochemical systems specially microbial fuel cells (Mohanakrishna, et al., 2015) (Tab 2).

Tab 2. List of power densities reported in PW using different Bioelectrochemical systems using PW.

BES Design	Anode	Cathode	Power Density	References
MFC	Graphite brush	Carbon cloth Pt Coated	721 mW/m ²	Mohanakrishna et. al.,
MFC	Non-catalyzed graphite plates	Non-catalyzed graphite plates	12.02 mw/m ²	K. Chandrasekhar et al.,
Soil MFC	carbon fiber brush	Carbon cloth	132 mW/m ²	Gunda Mohanakrishna et. al.,
DC-MFC	Carbon felt	Carbon felt	850 mW m ⁻²	Sumaya Sarmin et. al.,
Soil MFC	Graphite granules	Graphite rods	850 mW m ⁻²	Lu Lua et. al.,
SMEC	graphite-varnished stainless steel	graphite-varnished stainless steel	0.65 mW/m ²	Zahra Ghasemi Naraghi et. Al.,
Soil MFC	Plain graphite plates	Plain graphite plates	957 mW/m ²	Gunda Mohanakrishna
Soil MFC	Bio anodes	Bio cathodes	725 mW/m ²	Gunda Mohanakrishna et al.,

Abbreviations: MFC: Microbial Fuel Cell; SMEC: Spiral Microbial Electrochemical Cell; DC-MFC: Dual Chamber Microbial Fuel Cell

DISCUSSION

Reuse of Produced Water

Recycled wastewater has been used in a variety of fields like domestic, industrial and agricultural. In industries it is used for injection underground to enhance the oil production, make up water in boilers, controlling dust in coal mines and to control fire (Veil, et al., 2004). Agriculturally it is used for watering wildlife and for habitat. Oil and salt content of the produced water is treated using methods like physical, chemical, and biological treatment methods. The treatment technology to be used in case of produced water depends on two factors: amount of salinity, organic and inorganic constituents and relative quality of the water according to the requirement. Combining two Bes methods can be beneficial in removing salinity and other organic compounds simultaneously (Kaur, et al., 2009).

CONCLUSION

Oil as a fossil fuel has played a very crucial role in the development of industries. Petroleum consumptions around the world is expected to increase from 85 million barrels in 2006 to 106.6 million barrels by 2030 Comparing the overall advantages of petroleum, the wastewater produce water accounts for around 80 percentage of waste liquid that is produced. Treating this wastewater and reusing it will reduce the pressure on requirement of water. Studies have proved the once treated; most of the contaminants can be successfully removed. Bioelectrochemical systems are a unique method that can easily remove the containments with minimum damage to the environment.

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