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A Novel Technology for Treatment of Oil Field Produced Water of Upper Assam basin

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Abstract: **-- Produced water (PW) is a complex mixture of organic and inorganic compounds and the largest volume of by-product generated during crude oil recovery operations. It contains substantial quantity of contaminants and other suspended particles and so, it cannot be disposed directly or cannot be injected to the sub-surface for secondary recovery purposes keeping in view of the environmental concerns. Therefore, evaluation of PW characteristics is important and essential for both environment and reservoir management. This study deals with quantification and qualification of physical and chemical parameters of PW collected from different depths and horizons of Upper Assam oil fields and treat it by a self-designed novel technology. The characterization of PW is analyzed and compared with the World Health Organization (WHO) specification to meet the minimum discharge regulations of waste water for a greener ecosystem. The novel technology is the design of the treatment technology by intervention of different membrane technologies. Hollow fibre set-up was used for the treatment of PW by incorporating filter membranes of the order of micro, ultra and nano sizes. The fouling effect of the membranes was found to be minimized. All the membranes showed optimum efficiency with respect to their treatment performances.**

Keywords: **Evaluation, Characterization, Environment, Produced water.**

I. INTRODUCTION

Currently, it has been well known that the oil industry has to handle more PW than oil which makes the oil industry looks more like a "water industry" [1]. In the United States, oil wells produce about 7 to 10 barrels of water for each barrel of oil [2]. It was estimated that, about 210 million bbl of water was produced each day in 1999 worldwide and is an integral and unavoidable part of oil and gas recovery processes [1, 3, 4]. This PW includes the formation water and water resulting from drilling, production and work over activities [5, 6]. Out of various options for management of PW, mostly adopted options by the hydrocarbon exploration industries are underground injection for increasing oil recovery in the deep reservoir zone and the injection to non-pay zones in the porous rocks for mere disposal purpose [7, 8]. PW is sometimes discharged to the surrounding environment or may be used for water flooding or reservoir pressure maintenance [2, 5]. The quality of PW vary considerably depending on the geographic location of the reservoir oilfield, the geochemistry of the producing formation, the type of hydrocarbon product being produced and the characteristics and type of the producing well [10,11,15].

The North-East India PWs are the by-products generated during various operations in the hydrocarbon exploration industries are major sources of pollution in the area. These pollutants find their way and traverse to various environmental receptors causing potential danger of polluting the same. The water bodies, both surface and underground are more susceptible to such pollution in oil fields. Management of PW is a key issue for the oil and gas producers because of its large volume of generation and high handling cost. The aging oilfields of Upper Assam basin belonging to Oil India Limited, Duliajan and Oil and Natural Gas Limited, Nazira, produces crude oil with very high water cuts of more than 90%. Production of PW from these aging oilfields is also in increasing trend. This PW is highly saline, very rich in dissolved minerals and has a high temperature than the normal atmospheric water temperature. The salinities of the PWs from these oil fields range from 1000 - 3000 mg/l [11, 15] i.e., 1000 – 3000 ppm. The oil field in the study area has disposed in an average 3000 m3 of PW on a daily basis from its various oil fields which are an environmental concern since the injected PW has a potential to migrate and contaminate the ground water of the area. A membrane is a barrier that separates the two phases and controls the transmission of different chemical components in a certain approach. There are generally two phases in a membrane process that are physically separated from each other by the third phase (membrane). The phases are composed of components that one of the mixture components is transferred more than the others. In other

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words, the membrane has selectivity to one of the components. Hence, the transition of that component from one phase into another will be carried out by the membrane. Thus, one phase is enriched of that component and the other is depleted from it. Such a functioning can be seen in Figure 1 [12].

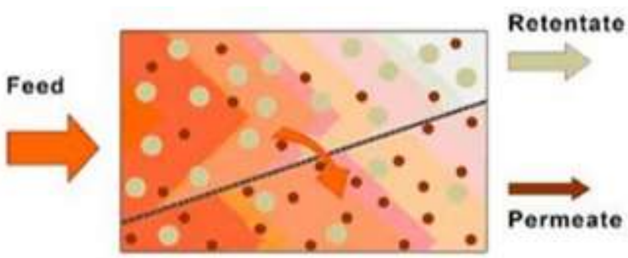

Fig 1: Schematic model of the membrane functioning

Membrane fouling is a process whereby a solution or a particle is deposited on a membrane surface or in membrane pores in a treatment process so that the membrane's performance is degraded. It is a major obstacle to the widespread use of this technology. Membrane fouling can cause severe flux decline and affect the quality of the water produced. Severe fouling may require intense chemical cleaning or membrane replacement. This increases the operating costs of a treatment plant. There are various types of foulants: colloidal (clays, flocs), biological (bacteria, fungi), organic (oils, polyelectrolytes, humics) and scaling (mineral precipitates).

II. EXPERIMENTAL

A. Materials

10 (ten) samples of PWs were collected from oil fields of Upper Assam. Oil samples were collected from well head along with PW.

Table 1: Materials used in the experiments

SN	Materials	Specification	Source
1	PWs samples	Barail Formation	OIL E & P
2	EDTA (Ethylene Diamine Tetra Acetic Acid)	0.01M	
3	Erichrome black indicator	0.5g in 100ml	RFCL Limited
4	Sodium Chloride (NaCl)	M.W. 58.44 g/mol	
5	Hydrochloric Acid (HCl)	M.W. 36.46 g/mol, Sp. Gr. at 250C is about 1.18	
6	Phenolphthalein	pH range 8.2-10 (colourless to pink)	
7	pH buffer	pH 10	WTW
8	Potassium Chloride (KCl)	M.W. 74.56 g/mol	Avantor Performance Materials India Limited
9	Calcium Carbonate ($CaCO_3$)	M.W. 100.09 g/mol	Merck Specialities Pvt. Ltd.
10	Lithium Carbonate (Li_2CO_3)	M.W. 73.89 g/mol	Spectrochem Pt. Ltd. Mumbai (India)
11	Petroleum Ether	Wt. per ml at 200C, 0.630-0.645g	Fisher Scientific
12	Methyl Orange	-	Human Diagnostics & Surgichem

Experimental

a. Physical and chemical characterization of PW

i. Water Analyzer

The physical properties of formation water like pH, Sal, EC, TDS, Turbidity and DO are determined by Water Analyzer.

ii. *Titration methods*

Alkalinity: 50 ml sample water + methyl orange titrated with 0.05 N HCl = T

Bicarbonate, HCO_3 in gm/L = $\dfrac{T \times 0.05 \times 50 \times 1000}{sample}$

Total Alkalinity = $HCO_3 \times 0.82$

Total hardness: 50 ml sample water + buffer solution 10 (3-4 drops) + Erichrome black indicator, then titrated with EDTA 0.01 M or 0.02N. A change to ink color was observed after titration.

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$$\text{Total hardness} = \frac{EDTA \times 1000}{sample} \text{ mg/L}$$

iii. O&G

20 ml sample water +20 ml petroleum ether in separating funnel was mixed and shaken for a half an hour. Appearance of two layers was observed where the lower layer was separated out in the beaker then dried in the oven and weighed = y, x= wt of the empty beaker.

$$O \,\&\, G = \frac{(y-x)\times 10^6}{sample} \text{ mg/l}$$

iv. Flame photometer

Flame Photometer instrument is used to determine Na, K, Li and Ca present in the PW.

Preparation of stock standard solution

Na: A standard solution of 1000 ppm is prepared by dissolving 2.5416g NaCl in one litre of distilled water.

K: A standard solution of 1000 ppm is prepared by dissolving 1.9070 g KCl or 2.5869 g KNO3 in one litre of distilled water.

Ca: A standard solution of 1000 ppm is prepared by dissolving 2.497 g $CaCO_3$ in approx 300 ml glass distilled water and adding 10 ml conc. HCl in one litre of distilled water.

Li: A standard solution of 2000 ppm is prepared by dissolving 4.945 g Li_2CO_3 in approx 300 ml glass distilled water and adding 15 ml conc. HCl in one litre of distilled water.

v. AAS

Determination of Fe, Cu, Mn and Cr in PW was conducted in the instrument Atomic Absorption Spectrophotometer (AAS). Prior to the determination of the amount present, the AAS equipment was calibrated and analyzed using blank solution of 2% Nitric acid (HNO_3) solution and standard solutions of 1ppm, 2ppm, 3ppm and 4ppm of Fe solution for Fe test. Similarly for Cr, Mn and Cu 1ppm, 2ppm, 3ppm and 4ppm of Cr, Mn and Cu standards samples were made respectively. After calibration samples were aspirated, the results were obtained.

b. HFM separation of PW contaminants.

The HFM setup consisting of a booster pump which pumps the PW from the feed tank and feed it into the membrane holder. The permeate is collected and further characterization tests were done. The retentate flows through a rotameter before flowing back into the feed tank.

Three membranes were used for the analysis

- Microfiltration (MF)
- Ultrafiltration (UF)
- Nanofiltration (NF)

C. Fouling effect of the membrane treatment

Membrane fouling is a process whereby a solution or a particle is deposited on a membrane surface or in membrane pores in a process, so that the membrane's performance is degraded. The fouling effect was experimented for all the above samples and also compared with tape water and distilled water.

III. RESULTS AND DISCUSSION

A. Physico-chemical characterization of PW

Table-3: Comparison of formation water quality with WHO specification

Parameters	**WHO specification**	**Present study report**	
		Before treatment	**After treatment**
pH	6.0 to 9.0	7.4-7.99	6.14-7.83
EC (mS)	0.25-0.75	1.43-6.5	0.0402-6.42
TDS (ppt)	24.59	0.8-3.89	0.1-3.39
DO (ppt)	0.007	0.004-0.044	0.0051-0.072
Salinity (ppt)	0.2-0.4	0.8-4.5	0.04-3.28
Turbidity (NTU)	5-10	1.5-5.3	0.09-3.1
Hardness (ppt)	0.3	0.068-0.7	0.03-1.1
O & G (ppt)	0.25	2-3.5	0
Na (ppt)	0.002	0.026-0.6132	0.0167-0.387
Ca (ppt)	0.075	0.021-0.522	0.00365-0.403

Table 3 is the comparison tables of the values obtained from the experimental study to the WHO specification which is a standard for safe disposal of water to the environment. EC, Hardness, O&G, Na showed values much higher than the safer limits for its disposal. Whereas DO value showed lower values than the permissible limits which indicates low level of free, non-compound oxygen present in water [11]. Table 4 shows that the most of the parameters of PW showed values higher than the maximum permissible limits for its disposal. The pHs of the ten samples were almost neutral. The high value of conductivity can be attributed to

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the fact that PW has ions so the conductivity is well above pure water which is 0.55 mS [12]. PW has dissolved and suspended solids which lead to its high value of TDS. DO is the amount of gaseous oxygen (O_2) present in water. The DO values showed much lesser values than the discharge regulation values which is harmful for the aquatic animals. The saline PW must be treated or it affects the agricultural and aquatic habitat. The high values of turbidity are due to the presence of suspended and dissolved solids in PW. It poses several problems for stream systems. Higher turbidity levels are often associated with higher levels of viruses, parasites and some bacteria because they can sometimes attach themselves to the dirt in the water [13]. Hardness, a physico chemical property of water, is generally a measure of calcium and magnesium ions in water [14].The high values of hardness is detrimental for human health. O & G in OFPW is due to the presence of suspended oil particles in the water sample.

B. Treatment of physical and chemical contaminants of PW

The characterization of the PW resulted in values which are much higher than the discharge regulation values according to WHO Standard. So these values much be controlled for its disposal. HFM filtration of PW is performed to reduce its contaminants. Three membranes were used during the process.

- MF (0.1-0.4) µm
- UF (0.001-0.02) µm.
- NF 0.0001 µm.

Table 4: Physico and chemical characterization of PW

Parameters	PW-1	PW-2	PW-3	PW-4	PW-5	PW-6	PW-7	PW-8	PW-9	PW-1
pH	7.7	7.5	7.62	7.77	7.65	7.54	7.68	7.99	7.89	7.56
EC (mS)	3.73	4.45	2.5	2.5	2.02	6.5	1.43	2.04	4.05	3.2
TDS (ppt)	1.55	2.3	1.5	1.32	1.24	3.89	1.4	1.25	2.3	2.2
DO (ppm)	4.4	4.2	4.1	4.4	4.7	4.3	4	4.2	4.2	4.4
Salinity (ppt)	1.89	2.68	1.5	1.8	1.78	4.5	1.9	1.23	2.03	1.89
Turbidity (NTU)	4.5	4.2	1.7	2.99	5.3	3.5	3.2	2.4	1.5	4.5
Hardness (mg/L)	68	70	50	48	40	53	42	58	62	33
O&G (mg/L)	2000	3500	1333.3	1000	2000	1100	1778.9	2360	2778.6	1356.1

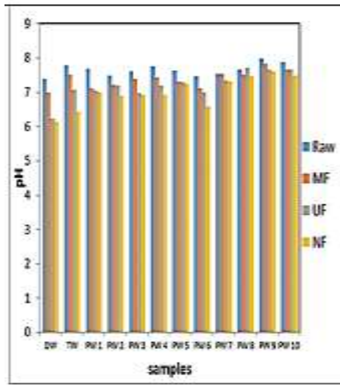

Fig 2: Comparison diagram of pH after treatment

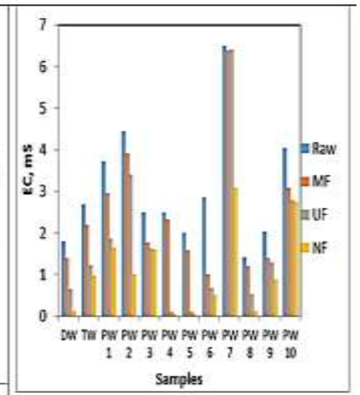

Fig 3: Comparison diagram of conductivity after treatment

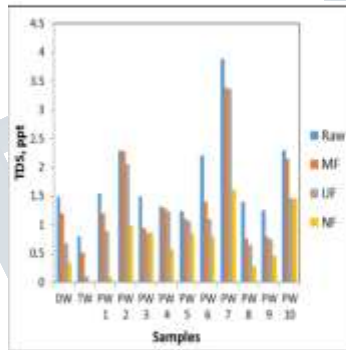

Fig 4: Comparison diagram of TDS after treatment

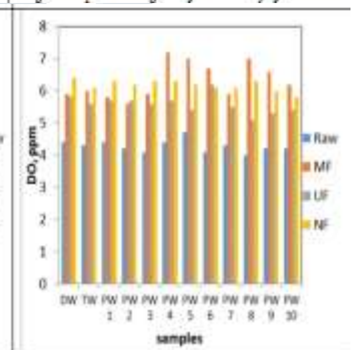

Fig 5: Comparison diagram of DO after treatment

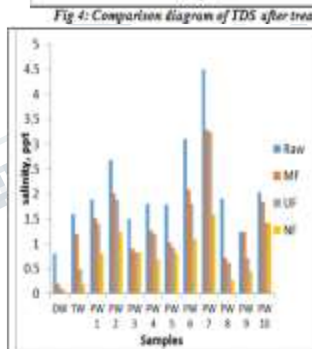

Fig 6: Comparison diagram of salinity after treatment

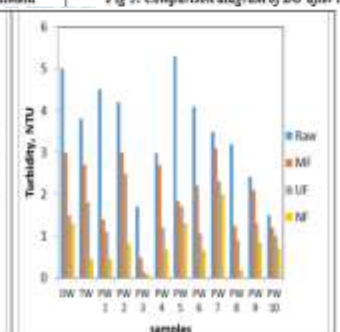

Fig 7: Comparison diagram of turbidity after treatment

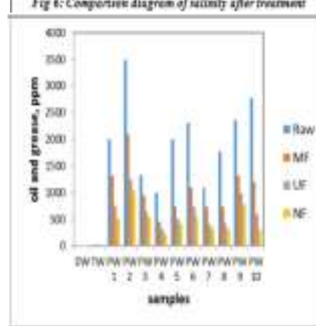

Fig 8: Comparison diagram of oil & grease after treatment

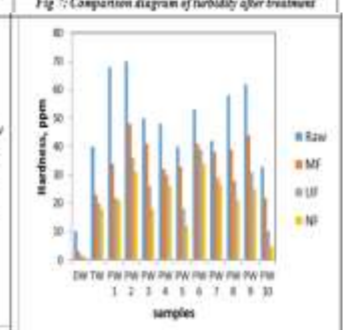

Fig 9: Comparison diagram of hardness after treatment

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From the Figure 2 to 9, values obtained from the parameters determined by water analyser, it can be inferred that that the contaminants of PW of the samples are drastically reduced after the filtration processes. The parameters pH, Salinity, EC, and Turbidity are greatly reduced due to the membrane treatment process. Whereas DO in figure 5 shows good result after microfiltration membrane. Thus, from the above filtration process it is seen that all the parameters of the PW are reduced by filtration process. Thus, their values are reduced and it can be discharge as it is below the permissible limits of disposal. Sample 7 shows high salinity, conductivity and TDS due to the presence of ions in the sample

C. Characterisation of inorganics present in PW

Table 5: Inorganics determined by AAS and FP

SN	Parameters (ppm)	PW-1	PW-2	PW-3	PW-4	PW-5	PW-6	PW-7	PW-8	PW-9	PW-10
1.	Fe	2.47	1.011	0.024	0.337	0	0.312	1.236	2.13	0.216	0.056
2.	Cu	0	0	0	0	0	0	0	0	0	0
3.	Cr	0	0	0	0	0	0	0	0	0	0
4.	Mn	0.057	0.057	0.046	0.031	0.075	0.072	0.052	0.048	0.047	0.039
5.	Na	437.8	613.2	400.1	323	396.6	422.3	515.3	368.9	392.4	435.6
6.	K	26.3	44.2	19.46	8.74	14	32.5	10.2	7.1	22	9.2
7.	Ca	982	379	56.6	446.9	513.4	522	98	21	141.9	135.6
8.	Li	4.4	5.3	3.2	2.99	2.4	2.2	4.8	4.6	4.7	4.2

Table 5 shows the presence of inorganics in PW samples. The values are higher than the minimum discharge values of the WHO Standard and so it must be treated for its disposal.

D. Treatment of inorganics present in PW

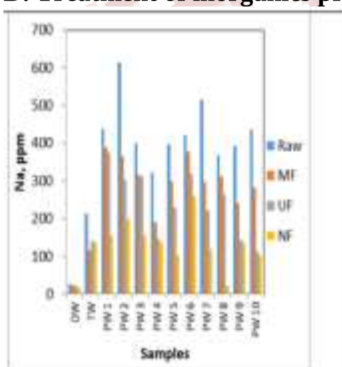

Fig 10: Comparison diagram of Na after treatment

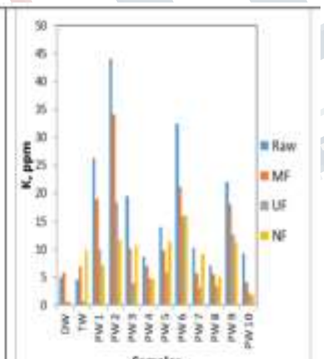

Fig 11: Comparison diagram of K after treatment

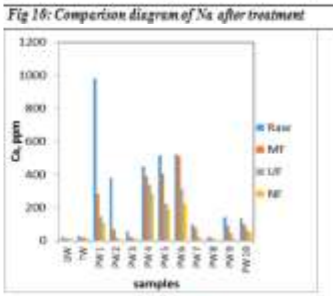

Fig 12: Comparison diagram of Ca after treatment

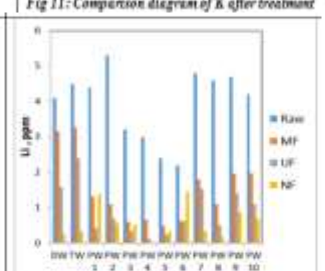

Fig 13: Comparison diagram of Li after treatment

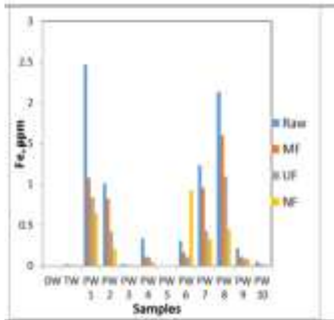

Fig 14: Comparison diagram of Fe after treatment

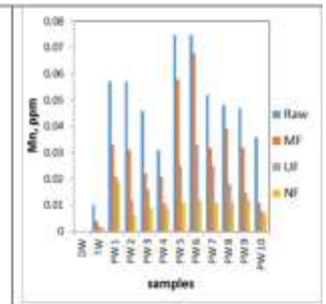

Fig 15: Comparison diagram of Mn after treatment

The inorganic parameters obtained from the treated PW analysed in a FP and AAS are found to be drastically reduced in comparison to that of the raw samples. From the figure 10 to 15, it can be seen that NF process gives better result than other membrane treatment processes.

E. Membrane Fouling

a. Microfiltration membrane

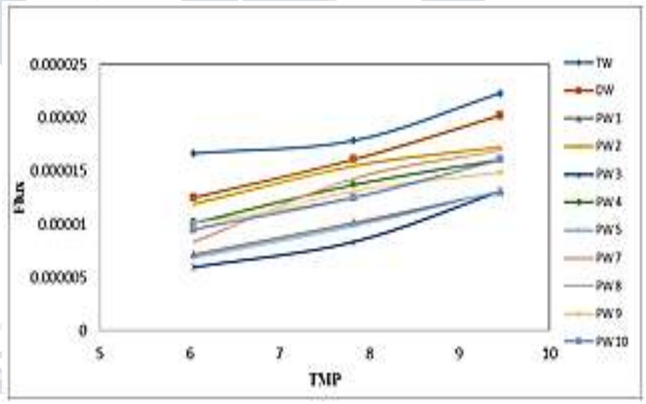

Fig 16: Membrane fouling effect in micro-filtration process

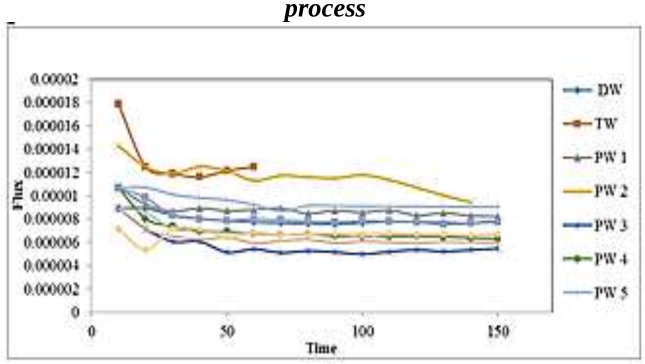

Fig 17: Flux vs Time graph in microfiltration process

Usually with an increase of pressure the flux must increase. From fig 16, it can be inferred that tape water and distilled water is showing the regular trend of increase in flux with

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increase of Transmembrane Pressure (TMP). The PW curves it can be seen that even after a certain TMP, the rate of increase of flux is decreasing very slowly with TMP it means membrane fouling is not yet developed. The pressure must be increased in order to obtain the same amount of flux. This point of decrease of the rate of flux is known as the point of membrane fouling. Membrane fouling results in a decrease in performance of a membrane, caused by the deposition of suspended or dissolved solids on the external membrane surface, on the membrane pores, or within the membrane pores. From figure 17, it is also clearly observed that volume collected after passing through the membrane was not decreasing with the increasing of time that means membrane fouling was not developed during the treatment process.

b. Ultrafiltration membrane

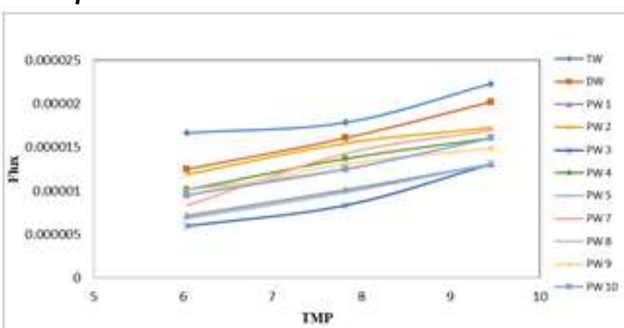

Fig 18: Membrane fouling effect in ultra-filtration process

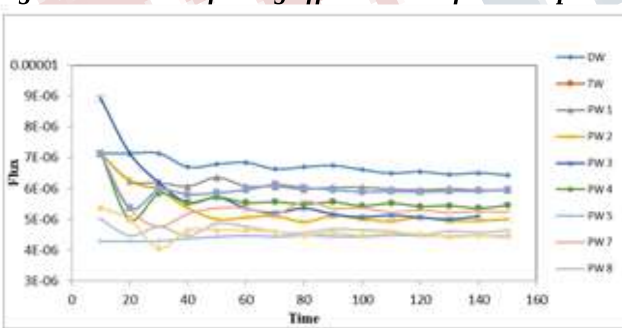

Fig 19: Flux vs Time graph in ultrafiltration process

In case of UF process, the volume thus collected is less than that of MF process due to which flux get reduced for the same TMP and thus fouling effect occurs earlier in case of UF process. From the fig 18 & fig 19 it is clearly observed that there is no occurrence of membrane fouling in UF process as flux is increasing with the increase of TMP.

c. Nanofiltration membrane

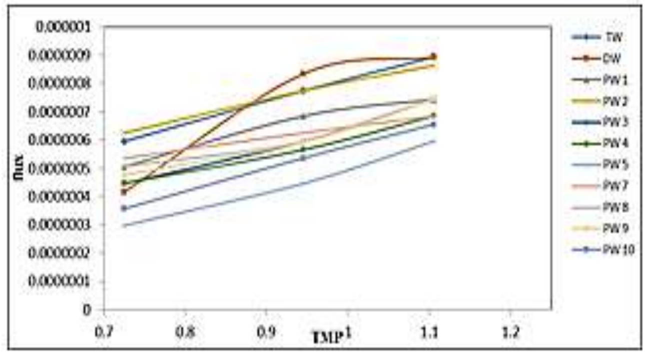

Fig 20: Membrane fouling effect in nano-filtration process

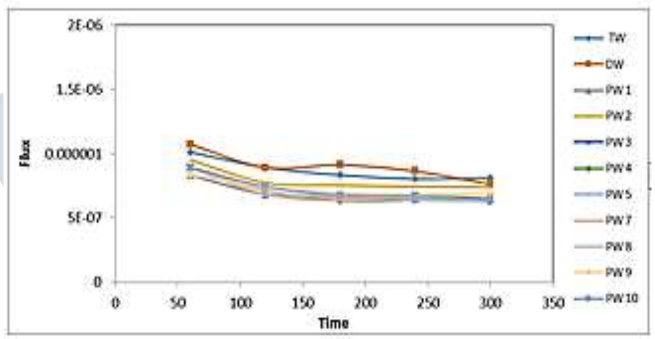

Fig 21: Flux vs Time graph in nano-filtration process

The volume collected in NF membrane is less in comparison to MF or UF membrane. The pore sizes are small in NF membrane and so it is highly inclined to membrane fouling. In our study, we can infer from the graph that there is no substantial fouling effect.

IV. CONCLUSION

The PWs collected from the Upper Assam Basin are treated by using HFM treatment processes. This report examines the physio-chemical and inorganic characterizations of the PW and the comparison is done between untreated water and treated water and their values are compared with the WHO specification for the disposal of water into the environment. It is inferred that some of its parameters have higher values than the safe limits which can be adversely affect the environment. EC, Turbidity, Hardness, Na and Ca showed values much higher than the safer limits for its disposal whereas pH, salinity, DO and TDS gives satisfactory results. This experiment proves that Sample 1 & 8 showing high salinity, EC and TDS due to the presence of Na ion. The collected samples are also treated with HFM using M. All the membranes showed optimum efficiency regarding their filtration processes with respect to their pore sizes. Some of the parameters showed drastic decrease in their values whereas some showed gradual. UF gives better result than the other two membranes. Due to the dilution of the samples to increase the quantity of the PW samples, there are less contaminants and a low amount of film of suspended or dissolved solids deposited on the membrane surface or on the membrane pores does not affect the performance of the membrane. Therefore there was no fouling of the membrane.

V. ACKNOWLEDGEMENT

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4. Dibrugarh University for the laboratory facilities

NOMENCLATURE

AAS Atomic Absorption Spectrophotometer
BOD Biochemical Oxygen Demand
Ca Calcium
CaCO3 Calcium Carbonate
CFC Cross Flow Cell
Cr Chromium
Cu Copper
DO Dissolved Oxygen
EC Electrical Conductivity
EDTA Ethylene Di-Amine Tetraacetic acid
Fe Iron
HCO3 Bicarbonate
HCl Hydrochloric Acid
HFM Hollow fibre membrane
KCl Potassium Chloride
K Potassium
KOH Potassium Hydroxide
Li Lithium
Li2CO3 Lithium Carbonate
MF Microfiltration
Mn Manganese
Na Sodium
NaCl
NF Sodium Chloride
Nanofiltration
O&G Oil and Grease
PW Produced water
TDS Total Dissolved Solids
TMP Transmembrane Pressure
UF Ultrafiltration
WHO World Health Organization

REFERENCES

[1] Y. Du, L. Guan, and H. Liang, "Advances of produced water management," Canadian International Petroleum Conference, 7-9 June, Calgary, Alberta, 2005.

[2] K. Guerra, K. Dahm, and S. Dundorf, "Oil and gas produced water management and beneficial use in the Western United States," U.S. Department of the Interior Bureau of Reclamation, Science and Technology Program Report No. 157, Technical Service Center. Sep. 2011.

[3] Z. Khatib, and P. Verbeek, "Water to Value – Produced Water Management for Sustainable Field Development of Mature and Green Fields," J. of Petroleum Technology, pp. 26-28, Jan., 2003.

[4] S.B. Gogoi, and A.S. Tamuli, " Recent Advances in Treating Oil Field Produced Water: A Review," J. of Petroleum Engineering & Technology, vol. 4, no. 2, pp. 366-370, 2014.

[5] J.A. Veil, M.G. Pruder, D. Elcock, and R.J. Redweik, "A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane prepared by Argonne National Laboratory for U.S. Department of Energy," National Energy Technology Laboratory, Jan., 2004.

[6] A.A. Al-Haleem, H.H. Abdulah, and E.A. Saeed, J, "Components and treatments of oilfield produced water," Al-Khwarizmi Engineering Journal, vol. 6, no. 1, pp. 24 – 30, 2010.

[7] H. Patel, D. Borgohain, and S. Jena, “Hydro geochemistry of Upper Assam Oil field,” J. of Petroleum Technology, vol. 2, pp. 11 – 14, 2003.

[8] B. Stone, “Management of Produced water,” Oxford publications, Washington, 37-41, 2003.

[9] O.F. Joel, C.A. Amajuoyi, and C.U. Nwokoye, “Characterization of formation water constituents and the effect of fresh water dilution from land rig location of the Niger Delta, Nigeria,” J. Applied Sci. Environ. Management, vol.14, no. 2, pp. 37 – 41, 2010.

[10] R.P.W.M. Jacobs, E. Grant, J. Kwant, J. M. Marqueine and E. Mentzer, “ The composition of produced water from shell operated oil and gas production in the North Sea,” In: J.P. Ray and F.R. Englehart, Eds., Produced Water, Technological /Environmental Issues and Solutions, Plenum Press, New York, pp. 13-21, 1992.

[11] Konwar D., Gogoi SB, Barman J, Gogoi MP, “Correlation Analysis of Formation Water of Upper AssamBasin for a Greener Ecosystem” International Journal of Engineering Technology Science and Research (IJETSR), ISSN 2394 – 3386, Volume 4, Issue 8, August 2017

[12] S.B. Gogoi, R.K. Sen, A. Rajbongshi, K. Hazarika, “Characterization of Oil field Produced waters of Upper Assam Basin, India,”International Journal of New Technologies In Science And EngineeringVol. 2, Issue. 1, 2015, Issn 2349-0780.

[13] Vijay S. Kale,“Consequence of Temperature, pH, Turbidity and Dissolved Oxygen Water Quality Parameters”, , International Advanced Research Journal in Science, Engineering and Technology ISO 3297:2007 Certified Vol. 3, Issue 8, August 2016

[14] P.Ramya, A.JagadeeshBabu, E.Tirupathi Reddy and L.Venkateswara Rao,“A Study On The Estimation Of Hardness In Ground Water Samples By EdtaTritrimetric Method”, International Journal of Recent Scientific Research, Vol. 6, Issue, 6, pp.4505-4507, June, 2015

[15] Joyshree Barman, Subrata Borgohain Gogoi, Shilpi Sarmah, “Characterization of Oil Field Formation Water and its Effect on Tap Water Dilution for Eco-Friendly Environment”, International Journal of Engineering Technology Science and Research, ISSN 2394 – 3386, Volume 4, Issue 8, August 2017