MINISTRY OF EDUCATION AND SCIENCE OF KAZAKHSTAN REPUBLIC

Kazakh National Research Technical University named after K.I. Satpayev

Institute of Geology, Oil and Mining named after K. Turusov

Department of Petroleum engineering

Karastekov Aslan Erlanovich

Improving methods of preparing water for maintaining reservoir pressure in oil fields

MASTER'S DISSERTATION

Specialty 7M07202 – Petroleum engineering

Almaty 2021

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Karastekov Aslan Erlanovich

MASTER'S DISSERTATION

For the application of academic master's degree

The name of the dissertation Improving methods of preparing water for maintaining reservoir pressure in oil fields

Direction of the study 7M07202 – Petroleum engineering

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Almaty 2021

MINISTRY OF EDUCATION AND SCIENCE OF KAZAKHSTAN REPUBLIC

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THE TASK
to complete for master's dissertation

For undergraduate Karastekov Aslan Erlanovich
(*Full name)*

Тема: Improving methods of preparing water for maintaining reservoir pressure in oil fields
(the name of master's dissertation)

Approved *by the order of the University Rector № 330 – M from " 11 " of November 2019 y.*
The deadline of completed dissertation "___"____________*20 y.*
Initial data for the master's dissertation: ____
The list of questions to be considered in the master's dissertation:
a) To review current state of the problem
b) To review existing methods for produced water treatment
c) To analyze the ways to improve the produced water treatment process
d) To conduct an appropriate literature review of the investigated methodology
e) Based on the studied data to develop an improved means of the produced water treatment

Recommended literature:

1 Maurice Stewart, Ken Arnold., Produced Water Treatment Field Manual // Gulf Professional Publishing, 2011. – 244 p.

2 Gyan Singh., Industrial Water Treatment // Scitus Academics LLC, 2016. – 279 p.

SCHEDULE

Preparation of the master's dissertation

Name of sections, list of questions being considered	**Terms of submission to the scientific director**	**Notes**
Literature review on water treatment and technologies in general	21.05.2020	-
Theoretical basis of the dissertation	07.01.2021	-
Full report on the work done with a conclusion	30.05.2021	-

Signatures

of consultants and norm controller for the completed master's dissertation with an indication of the related sections of the dissertation

The name of sections	**Consultants full name (science degree, rank)**	**The date of signatures**	**Signature**
Produced water and the characteristics of it with specification of major constituents	Kudaikulov A.A., PhD, assistant-professor	25.06.2021	
Algae-based treatment		25.06.2021	
Algae combined with fungi treatment method		25.06.2021	
Cost-effectiveness of the technology		25.06.2021	
Application of microalgae-based system in the treatment plant of PW		25.06.2021	
The main drawbacks in application of algae-based treatment for oil-field PW, challenges, and possible solutions		25.06.2021	
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Date 25.06.2021y.

MINISTRY OF EDUCATION AND SCIENCE OF KAZAKHSTAN REPUBLIC

KAZAKH NATIONAL RESEARCH TECHNICAL UNIVERSITY named after K.I. SATPAEV

FEEDBACK

FROM SCIENTIFIC DIRECTOR

For master's dissertation of

Karastekov Aslan Erlanovich

Specialty 7M07202 – «Petroleum engineering»

On the topic: «Improving methods of preparing water for maintaining reservoir pressure in oil fields»

The task of the work is by reviewing current state of the problem and existing methods to analyse the ways to improve the produced water treatment process and by conducting appropriate literature to develop an improved means of the produced water treatment process. The topic of the master's thesis fully matches the specialty 7M07202 – «Petroleum Engineering» and accords with the content of the work.

Karastekov Aslan Erlanovich fully completed the tasks assigned to him. Received considerable knowledge and orientation in the chosen direction, based on which could gain practical capability of proposing certain techniques and methods in oil-field produced water treatment area. Could successfully show actuality of the problem and demonstrate the application potential of proposed methods

Karastekov Aslan during his education in the master's demonstrated independence and responsibility and has grown as a specialist in the oil and gas field industry, acquired the necessary research skills, which in the future will contribute to become a good specialist and to able to independently set and decide scientific and practical tasks. The work indicates the focus of the student to solve actual problem, the demand for which enhances with progressive environmental concerns and following tight ecological restrictions for the produced water disposal. In general, the work was performed at a sufficient level and satisfy all the requirements, in this regard it definitely deserves a positive assessment, and its author Karastekov A.E is worthy of being awarded a master's degree in the specialty 7M07202 - Petroleum Engineering.

Scientific director

Assistant-professor, PhD **Kudaikulov A.A.**

25.06.2021y.

F. KazNTU 706-23. Feedback

MINISTRY OF EDUCATION AND SCIENCE OF KAZAKHSTAN REPUBLIC

KAZAKH NATIONAL RESEARCH TECHNICAL UNIVERSITY named after K.I. SATPAEV

REVIEW

For master's dissertation of

Karastekov Aslan Erlanovich

Specialty 7M07202 – «Petroleum engineering»

For the master's dissertation of Aslan Yerlanovich Karastekov, specialty 7M07202 – «Petroleum Engineering» on the topic "Improving methods of preparing water for maintaining reservoir pressure in oil fields". Reviewed work is presented on 44 pages.

The work reviewed is devoted to improving the methods of produced water treatment, which used to maintain reservoir pressure in oil fields. The work consists of 6 chapters.

With the goal to advance the methods of purification of the extracted water, the author proposed the following solutions:

- application of microalgae based biological treatment of produced water, instead of typical bacteria;

- in order to engraft the resistance to the environment, as well as to the outflow of cells, an immobilization technique was proposed;

To justify the recommended solutions, the application and research experience for the other types of wastewater treatment was taken as a basis. A variety of capabilities have been shown to effectively clean up groups of pollutants that are present in oil-field produced water and the disadvantages and potential difficulties of implementing such a technology for oil-field produced water were rationally taken into consideration. In general, the work is interesting, and its author was able to show the actuality of the problem and the potential of using the proposed technology for oil-field produced water.

The comment include the lack of a slightly more detailed description of the economic feasibility of this technology.

In general, the work was performed at a sufficient level, meets all the requirements and is complete, in this regard it deserves a positive assessment, and its author Karastekov A.E is worthy of being awarded a master's degree in the specialty 7M07202 - Petroleum Engineering.

Reviewer ____________ Asilbekov B.K

Position: Head of research laboratory, PhD

24.06.2021y.

F. KazNTU 706-52-08. Review

Протокол анализа Отчета подобия

заведующего кафедрой / начальника структурного подразделения

Заведующий кафедрой / начальник структурного подразделения заявляет, что ознакомился(-ась) с Полным отчетом подобия, который был сгенерирован Системой выявления и предотвращения плагиата в отношении работы:

Автор: Карастеков Аслан Ерланович

Название: Improving methods of preparing water for maintaining reservoir pressure in oil fields **Координатор:** Азиз Кудайкулов

Коэффициент подобия 1:6.8

Коэффициент подобия 2:3.5

Замена букв:0

Интервалы:0

Микропробелы:11

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Протокол анализа Отчета подобия Научным руководителем

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Название: Improving methods of preparing water for maintaining reservoir pressure in oil fields

Координатор:Азиз Кудайкулов

Коэффициент подобия 1:6.8

Коэффициент подобия 2:3.5

Замена букв:0

Интервалы:0

Микропробелы:11

Белые знаки: 0

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Обоснование:

обнаруженные в работе заимствования являются добросовестными и не обладают признаками плагиата. В связи с чем, признаю работу самостоятельной и допускаю ее к защите

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………25.06.2021 у……………… ………______……………………………

Дата *Подпись Научного руководителя*

АҢДАТПА

Мұндай зерттеулерге деген қызығушылық өндірілген суды қайтадан айдаудың ұлғайып бара жатқан сұранысына байланысты. Суды қабатқа қайтадан айдау процессі, қоршаған ортаға саналы әрі еріксіз күтім және тұщы судың шектеулілігіне байланысты мемлекеттік экологиялық нормалар күйінде салаларға енгілізген шаралар арқылы осындай сұранысқа ие болып жатыр. Сондықтан, экологиялық нормалардың қатаң аясында максималды пайдаға бағытталған мұнай компаниялары, өндірілген суды тазарту сияқты үлкен әрі үздіксіз процесте өздерінің қатысуын әрдайым жетілдіргісі болып келетін. Осы магистрлік жұмыста мұнай кен орындарынан өндірілген суды тазарту процесін жақсарту амалдары зерттелді. Қарастыру үшін жетілдірілген технологиялардың түрлерін іздеу орнатылды, бұл соңғы жылдары ағынды сулардың басқа түрлерінде танымал бола бастаған биологиялық тазартудың жаңа тармағын табу арқылы жүзеге асырылды. Жалпы қызығушылық; оның ортадан ластаушы заттардың көптеген түрлерін тиімді тазарту қабілетіне, сондай-ақ тазартудың химиялық түрімен салыстырғанда қосымша ластанусыз жұмыс істеудің қарапайымдылығына және тазартудың тәсілінің экологиялық тазалығына байланысты болып келеді.

АННОТАЦИЯ

Интерес к подобным исследованиям заключается в растущем спросе на повторное использование пластовой воды, вызванной сознательной и неизбежной заботе об окружающей среде и ограниченностью пресной воды, навязанной отрасли путем государственных экологических норм. Следовательно, в жестких рамках экологических норм, настроенные на получение максимальной прибыли нефтяные компании, хотели бы совершенствовать свое присутствие в таком крупном и непрерывном процессе, как очистка пластовой воды. В данной магистерской работе были исследованы способы улучшения процесса очистки пластовой воды нефтяных месторождений. Был определен поиск на более продвинутые технологий для рассмотрения, что было осуществлено путем нахождения нового ответвления биологической очистки, которое в последние годы приобретает обоснованную популярность для других типов сточных вод. Общий интерес обусловлен его эффективной способностью обрабатывать многочисленные типы загрязняющих веществ из среды, а также простотой эксплуатации без дополнительного загрязнения по сравнению с химическим типом очистки и экологичностью очистки.

ANNOTATION

The interest in such investigations consists in an increasing demand for produced water reuse, caused by conscious and inevitable environmental and fresh water scarcity concerns obliged to the industry by state ecological regulations. Consequently, in tight framework of ecological regulations, oil companies that tuned to make maximum profit would want to perfect its presence in such large and continuous process as treatment of produced water. In this master’s thesis it has been investigated the means of improving oil field produced water treatment process. It was determined to find more advanced technologies to be considered, which was performed by discovering new offshoot of biological treatment that is gaining reasonable popularity in recent years for other types of wastewater. The overall interest comes from its effective capability to treat numerous types of contaminants from the medium, along with its easiness of operation, with no additional pollution compared to chemical type of treatment and its environmental friendliness.

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INTRODUCTION

Actuality

Water flooding is an extensively used method for oil exploration. It implemented by injecting water through injection wells with the target of displacing the oil located in the pores of the reservoir rocks, enhancing the production. [1]. A huge quantity of produced water are generated during the oil or gas exploitation, and the volume rises drastically in the late stage [2]. In oil exploration activities, a substantial amount of freshwater is injected to maintain petroleum recovery. After injection, this water gets back to the surface loaded with salts, hydrocarbons, and other pollutants usually known as "produced water". This water represents one of the biggest streams of process wastewater created in the industry. Produced water comprises a mix of dissolved and particulate organic and inorganic chemicals, and its characteristics variate over time. The amount produced, changes greatly depending on where the petroleum reservoir is located and how old it is. In general, it is approximately 7−8 times bigger in volume than the extracted oil. However, as wells age, the production rate of oil goes down. Therefore, it is predicted that the volume ratio between oil production to produced water may globally ramp up to 12 by 2025 [3]. *Hence, the development of produced water treatment technologies is vital for oil industry*.

The main problem and goal of the investigation

Oil-field produced water is the biggest by-product, which is inevitably produced during oil and gas extraction operations. Generally, about 250 million barrels of this water is generated each day all around the world, (40 percent of which is discharged to the environment) whereas the corresponding produced oil is 80 million barrels. Oil-field produced water comprises various organic and inorganic materials including dissolved oil, heavy metals, salt, dispersed oil, dissolved gases, different solids and treating chemicals. The geological field layers and the kind of produced hydrocarbons affect the concentration of these compounds in the produced water together with its chemical and physical characteristics. Disposal of this water to the environment brings many dangerous environmental consequences. Thus, stringent limiting standards have been accepted for the disposal of this produced water to the environment that lead to a major challenge for oil and gas industry worldwide. Moreover, the necessary immense quantities of water for oil production aggravates the scarcity of water in different countries. Therefore, the strict standards for the oil field produced water before its disposal or reuse together with the necessity for clean water in various regions with scarce fresh water resources led to the application of required extensive water treatments [4]. Beneficial reuse of PW directly reduce the withdrawal of potable water, vital commodity in many areas of the world.

Year after year, impacts of produced water disposal on environment have obliged authorities to set progressively more stringent standards [5]. Hence, proper management and treatment of produced water has become *a big problem for oil and gas industry* [6]. Increasingly stringent environmental standards and economic constraints are forcing the investigation of *more advanced treatment methods. Finding and demonstrating application potential of which - is the main goal of this work.*

Novelty of the work

Advances always come with big or little findings and novelties. Novelty of this work lies in the application of previously known or used technologies from other spheres to a new object of research. Namely, the consideration of the microalgae-based technology and immobilization technique application for the new medium called oil field produced water.

The overall tasks of the research

Biological treatment proved to be an effective method, which is one the advanced methods that are widely being used for produced water treatment in oil industry due to natural consumption of dissolved organic pollutants by microorganisms, such as bacteria. However, that is not the only option to choose for bioremediation of water. Recently, utilization of other versatile and highly beneficial microorganisms called microalgae is gaining popularity for other types of wastewater such as sewage wastewater and which is catching our attention as well. Nevertheless, many factors should be concerned for considering the application of this type of biological treatment for produced water from oil fields, as characteristics of wastewaters are not the same, as well as additional challenges that it may pose. However, by investigating the main pollutants of PW and the abilities of microalgae to treat them, together with how and where to use them in water treatment plant, as well as reviewing the additional means to improve them and by facing the challenges we will able to see the potential of this technology for PW.

1 Produced water and the characteristics of it with specification of major constituents

Generally, in order to advance towards improving treatment processes it is necessary to know the composition of PW. Produced water from oil field is not a single product, it has a simple to compound composition, which is variable, and it is recognized as a mix of particulate and dissolved organic and inorganic chemicals. Physical and chemical characteristics of produced water vary significantly that depends on multiple factors including, depth and age of the geological formation, geographic location of the field, extraction method, hydrocarbon-carrying formation geochemistry, kind of the produced hydrocarbon, along with its chemical composition in the reservoir. Specific researches for each region ought to be done as its properties varies from region to region and such researches will also assist in investigating the environmental risks of its disposal.

The main constituents observed in produced water are categorized and summarized in Table 1 as well as their concentrations from the source. In general, the main composites of oil-field produced water are: total dissolved solids (TDS) or electrical conductivity, salt content (salinity), polyaromatic hydrocarbons (PAHs), oil and grease (O&G), benzene, toluene, ethylbenzene, and xylenes (BTEX), organic acids, phenols, natural organic and inorganic compositions that brings to scaling and hardness (e.g., magnesium, calcium, sulfates and barium), and chemical additives such as biocides and anti-corrosion inhibitors, which are utilized during fracturing, drilling and operating of the well [7].

Conductivity, salinity and total dissolved solids

The salinity of produced water varries from few parts per thousand (‰) to ~300‰ (saturated brine) that is much higher than the salt concentration of seawater which is in the range of 32–36‰ and due to this fact produced water is commonly denser than seawater. Higher salinity is the consequence of dissolved chloride and sodium presence mainly as the concentrations of magnesium, potassium and calcium are usually lower. According to a research done by Guerra et al. [8], TDS was in the range of 370–1940 mg/l due to the enhanced concentrations of both bicarbonate and sodium.

TDS concentration over period for produced water was investigated [9]. Results demonstrated the changes of produced water quality over time, which affects the reuse and management of produced water. Variations in the concentration of TDS happens due to multiple reasons that contain the location of the well in the field, geological variations between basins and the resource of the produced water. Moreover, the concentration of TDS ranges between the conventional and unconventional wells since it was investigated that the concentration of TDS was<50,000 mg/l in CBM wells whereas in the conventional wells it was as high as 400,000 mg/l as shown in table 1 [8, 7].

Inorganic Ions

Sodium and chloride are considered as the most prevalent salt ions found in produced water, whilst phosphate has the lowest concentration. In produced water from both conventional and unconventional wells; sodium is known as the predominant cation with 81 percent in conventional wells and more that 90 percent in unconventional wells. Nevertheless, the amount of anions in conventional and unconventional wells is not exactly similar. The conventional wells are almost entirely chloride anions representing 97 percent of the total anions, while 32 and 66 percent of the unconventional wells comprise chloride and bicarbonate anions respectively. Moreover, magnesium, sodium, chloride, sulfate, bromide, iodide, potassium and bicarbonate are detected abundantly in produced water with high salinity, which is shown in Table 1. The presence of sulphide and sulfate ions in produced water can leads to sulfide and insoluble sulfate at high concentrations in produced water. Furthermore, the presence of bacteria in the anoxic oil-field produced water, cause the decrease of sulfate and in turn leads to the presence of sulfides (hydrogen sulfide and polysulfide) in the produced water. However, the concentration of these cations and anions varies from location and their ranges are demonstrated in Table 1 [7].

Metals

Produced water may comprise certain metals like Al, Cd, Pb, Fe, Cu, Cr, Ni, Ba, Zn and others [10, 7]. Their concentration may reach 10^2 to 10^5 times the one found on seawater [10]. Nevertheless, differences in the concentration, kind and chemical content of the metals are affected by the geological age and properties, chemical composition and injected water volume. Generally, mercury, barium, zinc, iron and manganese are in produced water at higher concentration than the seawater concentration. For example, Hibernia produced water have high concentrations of iron, manganese and barium as compared to seawater. Additionally, it was also reported that the sodium, barium, iron, potassium, strontium and magnesium in natural gas field produced water are present at higher concentrations [7].

Table 1 - Main components and their concentration found in produced water [7]

Parameter	Concentration (mg/l)	Parameter	Concentration (mg/l)
Major parameters		Metals	
COD	1220–2600	Na	0–150,000
TSS	1.2–1000	Sr	0–6250
TOC	0–1500	Zn	0.01–35
TDS	100–400,000	Li	0.038–64
Total organic acids	0.001–10000	Al	0.4–410
Production treatment chemicals		As	0.002–11
Glycol	7.7–2000	Ba	0–850
Corrosion inhibitor	0.3–10	Cr	0.002–1.1
Scale inhibitor	0.2–30	Fe	0.1–1100
BTEX		Mn	0.004–175
Benzene	0.032–778.51	K	24–4300
Ethylbenzene	0.026–399.84	Pd	0.008–0.88
Toluene	0.058–5.86	Ti	0.01–0.7
Xylene	0.01–1.29	Other ions	
Total BTEX	0.73–24.1	B	5–95
Other pollutants		Ca^{2+}	0–74,000
Saturated hydrocarbons	17–30	SO_4^{2-}	0–15,000
Total oil and grease	2–560	Mg^{2+}	0.9–6000
Phenol	0.001–10,000	HCO_3^-	0.15,000
		Cl^-	0–270,000

TSS, TOC and TN

TSS in produced water may comprise the drifting or floating materials found in the water such as sediment, silt, algae, plankton and sand. It has been reported that TSS concentration in produced water varies between 14–800 mg/l and 8–5484 mg/l. Furthermore, for produced water from oilfield found that the TSS concentration was in the range of 1.2–1000 mg/l as presented in Table 1 [7]. Moreover, Rosenblum et al. [9], investigated the time variation of TSS concentrations in produced water and found that there was up to 59 percent decrease in the concentration of TSS within first 4 days with no more further considerable changes noted for next few days. Nevertheless, followed 40 percent reduction was noticed in the concentration of TSS in the period of 55th day of observation until 80th day. The range of TOC in oil-field produced water is from 0 to 1500 (mg/l) (Table 1). Different naturally occurring water possess TOC concentration between less than 0.1 mg/l and to greater than 11,000 mg/l. The average concentration value of TOC noted in produced water from Hibernia platforms is 300 mg/l. Similarly, the concentration of TOC in the range of 0–1500 mg/l has been noted for produced water samples gathered from different sources [7].

Produced water samples which were gathered during a 200-day time period from two wells and utilized TOC concentration as a macro-indicator for the quality of the produced water and noted that the concentration value of TOC from both wells before 30 days was changing considerably, but after this timespan it was stabilized at 2000 mg/l [7]. Total nitrogen is the cumulative amount of all the nitrogen composites in the water, including nitrate-nitrogen (NO3 minus N), ammonia-nitrogen (NH3 minus N), organically bonded nitrogen and nitrite-nitrogen (NO2 minus N) [8]. According to UNITAR [8], total nitrogen by **TKN** is the total organic nitrogen composites and ammonia with excluding nitrite-nitrogen and nitrate-nitrogen. The presence of nitrogen and other nutrients brings to the formation of hypoxic zones.

It is more complicated to remove the non-biodegradable component of the organic nitrogen than the biodegradable component that is easier to treat and less detrimental for the environment. Moreover, separation of macro particle is easier than the soluble part. Thus, the separation of TKN before the injection of the water back to the environment or reuse is crucial. The presence of NH3, NO3 minus, NH4, NO2 minus in produced water from fifty platforms of either oil, gas or mixed production wells, noted that the highest average concentration of NO3 minus (2.71 mg/l) was found in produced water from mostly gas wells, while the highest concentration of NH3 and NH4 was found in produced water mainly from oil wells (92 mg/l). On the other hand, similar concentration of 0.05 mg/l was determined for $NO2^{-}$ in produced water from all tested wells [7].

COD and BOD

The evaluated COD concentration in produced water was in the range of 2600 mg/l and 120,000 mg/l. A study conducted in East China, where onshore produced water samples were gathered from treatment plant at different sampling locations, demonstrated that the concentration of COD (mg/l) at each sampling location was: 285.5 plus or minus 76.1 for the point 1, 108.9 plus or minus 29.2 for the point 2, 195.2 plus or minus 32.9 for effluent of oil separation tank, 109.5 plus or minus 58.4 for effluent of bio-contact oxidation tank and 190.7 plus or minus 53.8 for effluent of flotation tank. Consequently, it was noted that these concentrations are higher than the admissible limit set by the Environmental protection agency of China, i.e. less than 150 mg/l. The concentration of COD was 280 mg/l for oil-field produced water in Canada. Similarly, COD level of produced water derived from gas stream in an Iranian gas refinery was 270 mg/l. On the contrary, water samples gathered from oil fields in USA had high range of COD from 27,000 to 35,000 mg/l [7]. Another study in which the physicochemical properties of produced water gathered from two oil facilities in Nigeria were tested, found that the COD does not differ much among the two locations as it was noted to be 3.91 plus or minus 1.32 mg/l for both points, which was less than the admissible limit of 125.0 mg/l. . Decreased inorganic components such as Mn and Fe, utilized fluids for well drilling, and additive chemicals may consequent to higher BOD concentrations in produced water gathered right from the well. High volumes of organic compounds in drilling fluids may result to the high BOD values in produced water. Moreover, dissolved oxygen can harshly deplete in water bodies getting produced water with high BOD content, hence, significant oxidation of this water ought to be provided to prevent the disposal of wastewater with high BOD levels into natural waters [7].

Dissolved gases

The main dissolved gases in produced water are oxygen, hydrogen sulphide and carbon dioxide. [77].

Organic acids

The major organic acids that are noted in produced water from oil-field are monocarboxylic acid and dicarboxylic acid (COOH) of both aromatic hydrocarbons and aliphatic possessing low molecular weight, such as hexanoic acid, formic acid, propanoic acid, pentanoic acid, butanoic acid and acetic acid. Nevertheless, the most prevalent organic acids in oil-field produced water are acetic acid and formatic acid. Earlier, it has been noted that the concentration value of formic acid was from not detectable values to 68 mg/l, propionic acid up to 4400 mg/l in produced water and acetic acid from 8 up to 5735 mg/l [7].

Dissolved oil

It contains water-soluble organic compounds: phenols, BTEX, low molecular weight aromatic compounds, aliphatic hydrocarbons and carboxylic acid. The water-soluble organic constituents in PW are commonly polar compounds with a low values of carbons, like organic acids such as propionic and formic. Temperature, pressure and pH (in the reservoir or during extraction process) enhance soluble organics in PW. Salinity levels does not substantially affect the dissolved organics. Consequently, the quantities of soluble oil in PW depend on volume of water production, type of oil, age of production and artificial technique [10].

BTEX

BTEX are volatile aromatic constituents, which are naturally occur in oil and gas products including diesel fuel, natural gas and gasoline, hence, during the water treatment process they easily fly away to the atmosphere. Benzene is prevalently noted in produced water, nevertheless, enhancing the alkylation result to the reduction of benzene concentration. Moreover, the BTEX concentration present in produced water gathered from oil field in Gulf of Mexico, the benzene concentration was found to be highest (0.44–2.80 mg/l), followed by toluene, xylene, and ethyl benzene [7]. These results together with the results of Neff [11], in which benzene was at highest concentration values (0.084–2.30 mg/l), followed by toluene, ethyl benzene and xylene. Similarly, the properties of Permian basin produced water and the highest concentration values was for benzene (1.5–778.51 mg/l), followed by ethyl benzene, xylenes, and toluene [7].

Phenols

Phenolics or phenols are part of aromatic organic constituents that include 1 or more hydroxyl group bound to an aromatic hydrocarbon group. Different levels of phenols are present in oil and gas field produced water, nevertheless, gas condensate production was noted to possess the highest concentration values of phenols. The comparison of the concentration values of phenol in oil and gas field produced water indicate that gas field produced water possess higher concentration values of phenol than oil field-produced water concentration. The concentration of phenol in produced water gathered from the Louisiana Gulf Coast and Norwegian Region of the North Sea noted that the concentration of phenols in produced water varies between 2.1–4.5 mg/l and 0.36–16.8 mg/l, respectively [7].

Production chemicals (treating chemicals)

Treating chemicals are commonly added to the oil and gas field for the management of the operational issues such as to facilitate gas, oil and water separation process, methane hydrate formation in the gas production system and prevention of pipeline corrosion. The required chemicals for the production process are unique and vary along with the various production systems. Common treating chemicals are biocides, inhibitors, anti-foams, water treating chemicals like flocculants, reverse emulsion breakers, emulsion breakers and coagulants, which are used in hydrocarbons' pumping and recovery. These chemicals are soluble in oil, avoiding the necessity for the mechanism of disposal. The chemicals such as biocides and corrosion inhibitor are detrimentally affecting the environment and their overall utilization in the industry has been decreased [7].

2 Algae based treatment

2.1 Why microalgae?

Microalgae are microorganisms or plants living in fresh water, marine and soil environments. Phylogenetically, microalgae is different compared to terrestrial plants. Less than half of the 72.500 identified algal species have been investigated. The possibilities of algal technologies for a wide range of utilization is indisputable. Algae sequester carbon (C), produce oxygen (O2), remove nutrients such as phosphorous (P) and nitrogen, and absorb numerous contaminants during their photosynthetic growth in WW. Due to these capabilities, microalgae are excellent for wastewater treatment applications [12].

Biological treatment methods are an effective and economical technique that can absorb contaminants and harmful chemicals from the environment [13]. Biological processes perform well compared to the chemical and physical processes, which are generally costly to be utilized in most places. [14].

Microalgae enhance the elimination of heavy metals, inorganic nutrients and organic pollutants from different types of wastewater. Regarding nitrogen, the ammonia present in wastewaters can be reduced due to ammonia volatilization and cell assimilation [15].

Nowadays, eco-technology is a new approach that has been represented for the treatment processes of produced water where sustainable solution and greater removal rates of contaminants from produced water can be reached [16]. Consequently, the use of microalgae-based treatment for the treatment of PW is determined by these Eco-technology approaches. Generally, biological treatment of oil-field produced water using the microalgae can be more beneficial comparing with other types of wastewater due to their capability using certain pollutants present in PW abundantly as nutrient sources [17]. BTEX can be used as a sole carbon source by certain microalgal species such as *Parachlorella Kessler* [18]. Also, water soluble fraction gasoline was utilized to study its toxicity and it provides a valuable foundation for the effect of BTEX on the enlargement of microalgae. However, 50 percent growth reduction on cultures of microalgae is affected by increasing the BTEX concentration with more contact time. Heavier hydrocarbons provide higher toxicity on microalgae growth. Moreover, produced water generally comprises enough concentration of nitrogen and phosphorus, which act as growth factors for microalgae. Moreover, there are different elements other than phosphorus and nitrogen that are important for microalgal growth, which present in produced water as well. Thus, growing microalgae in produced water has the potential to be implemented as efficient treatment process where the microalgae biomass production is enhanced during treatment process. The microalgae strains utilized in various water treatments for contaminants bioremediation includes *Monoraphidium sp., Scenedesmus sp , Chlorella vulgaris* as shown in Figure 1.2. [19, 7].

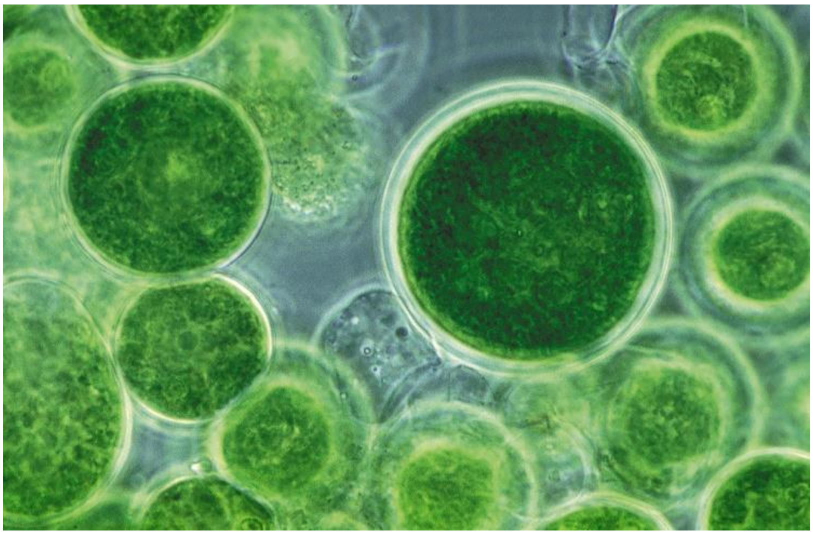

Fig 1.1 - Microscopic view of microalgae [20]

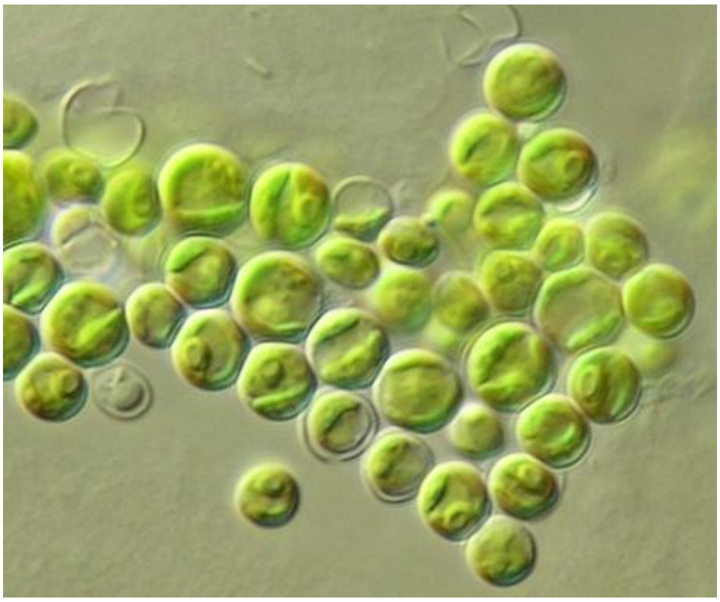

Fig 1.2 - *Chlorella vulgaris* [21]

Generally, algae remove toxic compounds by mechanisms such as **biosorption** and **bioaccumulation** [13].

The interest in micro-algal cultures comes from the valuable advantages that offer this technology over other conventional treatments:

Easy to operate, less human footprint;

No chemical additives, that often lead to secondary pollution;

Rare case of possible utilization of certain pollutants that present in PW - as nutrient sources;

Ability to treat decent variety of pollutants simultaneously;

Cost-effective and environmentally friendly system;

Versatility of microalgae strains, which allow these photosynthetic organisms to grow in a broad spectrum of wastewaters;

Little nutritional input or in most cases absence of them, due to rich characteristics of PW;

Amongst beneficial characteristics they produce oxygen, have a disinfecting effect due to increase in pH during photosynthesis;

Additional production of valuable biofuels that can potentially be utilized for marginal purposes;

2.2 Treatment capabilities of major pollutants that present in PW by microalgae

By observing the application of microalgae-based biological treatment for other types of wastewater, we will able to see the treatment efficiency of such technology for major pollutants that present in PW.

2.2.1 TN and TP removal by microalgae

Microalgae are able to use N from a variety of organic and inorganic sources [22]. Common forms in which they occur in wastewater are nitrite, nitrate and ammonia [14]. Several findings were reported that the interaction between different nitrogen sources would cause interference in N uptake. Although not completely inhibited, nitrate uptake can be partially reduced by the ambient concentration of ammonium and the effects vary depending on the algal cultures. Light is an important environmental variable that light-limited conditions enhance the inhibition of nitrate uptake by ammonia compared with under saturating and moderate irradiation. In addition to light, the repression in nitrate uptake by decreases with the decrease in temperature [23]. Once moved across the membrane, ammonium can accurately be incorporated into amino acids required for growth and other metabolic purposes [24].

The removal capability of *Chlorella vulgarisin* was at 86 percent of efficiency for inorganic N and nitrogen removal of 50.2 percent in industrial wastewater [14].

The removal rate for nitrate N in 7 days were 99.7 and 98.2 percent for *Scenedesmus sp.* and *Chlorella sp.*, respectively [25]

Phosphorus is fundamental and a critical macronutrient to microalgae. With P, algae synthesize nucleic acids (e.g. RNA and DNA) to express their genetic information, ATP for energy requirement in different metabolisms, and phospholipids as the main membrane component [23]

C*hlorella vulgarisin* was able to remove phosphorus at 85.7 percent in industrial wastewater treatment [14].

It is widely accepted that inorganic phosphate (P, including PO43 minus, hydrogen phosphate and H2PO minus) is the most preferred P form for algal uptake. For many years, they were even thought to be the only inorganic P form for microalgae. However, polyphosphate and phosphite are also biologically available for microalgae [23].

In microalgae, P is a significant element involved in countless metabolic pathways [26]. When P is limited, NO3 minus grown cells show higher photosynthesis efficiency compared to ammonium grown cells. Therefore, it is indicated that C, N, and P metabolisms should be linked and affect each other [23] Moreover, in P-rich environments, microalgae is able to store P in excess of their metabolic necessities and accumulate it [24].

A microalgae culture demonstrated a substantial reduction in the above nutrient. Phoshate ions was removed up to 80.5 and 70 percent [25].

The nutrient removal capability of *chlorella vulgarisin* was at efficiency of 78 percent for inorganic P and phosphorus at 97.8 percent in domestic wastewater [14]

2.2.2 The significance of carbon for microalgae and reduction of COD

In **photoautotrophic process**, microalgae is able to utilise inorganic carbon, predominantly carbon dioxide, as their primary source of carbon [24]. While microalgae can grow efficiently using light, the additional capability of microalgae to consume inorganic carbons can be vital in natural light absent places for optimal microalgae growth. To rise the accessibility of carbon in a wastewater the form of CO2 is commonly utilized [24]. It makes possible for microalgae to be used in closed systems, along with additional naturally occurred carbon dioxide quantities that present in some type of wastewaters.

With the supply of carbon dioxide in the range of 1 to 6 percent characterised as optimum to enhance nutrient removal and microalgae growth. The tolerance to concentration of CO2 is specie dependent, with certain strains capable of acclimating to carbon dioxide concentrations up to 100 percent [24].

Although, oil-field produced water usually comprises much higher content of organic carbons compared to inorganic ones, it does have inorganic carbons such as carbon dioxide present as dissolved gases in PW. Therefore, it will be fair to say, that PW from oil wells is a natural supplier of inorganic carbons, which were linked to enhancement of microalgae growth and eventually increasing overall performance and cost effectiveness of microalgae-based technologies for PW. In fact, *I. galbana* and *N. oculata* reduced 68 and 66.5 percent of the oil, respectively, at the 50 percent PW loading in 21 days [13].

Besides nutrients, *Scenedesmus sp*. and *Chlorella sp.* was able to reduce up to 95 and 84 percent, respectively on the 7th day (Table 2.1) [25].

Table 2.1 – Percentage removal (maximum) of pollutants by the 7th day of cultivation [7]

Parameters		*Chlorella* sp.		*Scenedesmus* sp.		NEQs limit
Name	Units	Final	% Removal	Final	% Removal	
PO_4^{-3}–P	mg/L	5.3 ± 0.56	70.5	3.5 ± 0.56	80.5	NA
NO_3_N	mg/L	0.165 ± 0.005	98.2	0.024 ± 0.02	99.7	NA
SO_4^{-2}	mg/L	BDL[a]	100	BDL	100	1
COD	mg/L	28 ± 5.6	84.86	8 ± 2.5	95	150
Turbidity	NTU	4 ± 0.5	93.73	3.5 ± 0.8	94.93	NA

[a] *BDL* below detection level

This COD removal was because of the microalgae growth, cells visibly increased, transmuting the wastewater colour from blackish gray to green [25].

2.2.3 Treatment of heavy metals by microalgae

In living microalgae cells nutrient metals (such as Mo, Co, Mg, Ca, Zn, Cu, Pb, Cr and Se) are stored intracellularly by active biological carriage [14].

The natural gas field produced water from Qatar was gathered by the investigation team of Al-Ghouti et al. (unpublished data) and was used to study the removal of heavy metals utilizing microalgae. In order to investigate the growth of different microalgae species, their capabilities of heavy metal removal, the filtered water was utilized. Table 2.2 demonstrates the ability of species to remove different heavy metals from produced water [7]

Table 2.2 – Characteristics of produced water collected from natural gas field in Qatar [7]

Parameters	Characteristics of produced water	
	Raw produced water	Filtered water
Total organic carbon (mg/l)	389.1	317

Continuation of Table 2.2

Total nitrogen (mg/l)	35.77	27.6
Total phosphorus (µg/l)	277.78	180
Benzene (mg/l)	21	16.1
Toluene (mg/l)	3.8	3.21
Ethylbenzene (mg/l)	1.22	1.05
Xylene (mg/l)	3.43	3.11

As shown in Table 2.3, 100 percent removal efficiency of Fe Al and Zn from produced water was obtained by microalgae, while K experienced the lowest removal efficiency of 11.27 percentage. Toxicity level of the PW could increase with the concentration increase of these elements [27]. According to the results received in this research, *Dictyosphaerium sp.* can extract more elements since it grew better than other species. Due to earlier studies, *Dictyosphaerium sp*. is actually able to grow within metal abundant water [7]. Additionally, *Cladophora glomeratain* noted that were great accumulators of zinc [14].

Table 2.3 – Removal of trace metals from produced water using microalgae [7]

Trace metals	Feed water (ppb)	Filtered water (ppb)	Microalgae species	Removal Percentage
K	736.18×10^2	677.40×10^2	*Scenedesmus* sp.	11.27
Mg	417.15×10^2	392.57×10^2	*Dictyosphaerium* sp.	13.9
Sr	111.98×10^2	105.73×10^2	*Dictyosphaerium* sp.	21.23
B	425.9×10^2	374.7×10^2	*Dictyosphaerium* sp.	20.23
Mn	318.56	318.56	*Neochloris* sp.	87.80
Cu	224.97	180.78	*Dictyosphaerium* sp.	91.65
Fe	287.94	100.19	*Neochloris* sp.; *Chlorella* sp.	100
Ba	55.69	43.35	*Monoraphidium* sp.	13.06
Cr	24.09	17.20	*Dictyosphaerium* sp.	19.36
Al	114.41	13.68	*Neochloris* sp.	100
–	–	–	–	–
Ni	7.83	3.71	*Dictyosphaerium*	92.29
V	1.87	1.46	*Scenedesmus*	36.26
Cd	0.09	0.06	*Chlorella*	97.37

Among 14 metals that were noted to be present in the assembled PW, almost half of them are regarded as micronutrients, such as K, which plays a significant role in various enzymatic reactions. *Cladophora glomeratain* noted that were great accumulators of zinc. Together with Cu, K and Fe have vital role in the photosynthetic electron carriage system, while Zn is used by the microalgae through the transcription means of DNA and uptake of P. As microalgae absorb CO2 due to their photosynthetic process and, if the replacement in medium is not done via absorption from atmosphere and bacterial oxidation of organic matter, the pH of the medium starts to increase. Phosphorus can also be eliminated by chemical reactions that happens in cultures. The pH rise (the result of photosynthetic activity of microalgae) leads to phosphorus overthrow by complexation with metal ions (iron, calcium and magnesium) in medium, decreasing the concentration of this nutrient in the solution [15]. On the other hand, some metals such as Cr and Cd could harmfully affect the cell separation and reduce the photosynthetic ability if occur at high concentration [7]. Intensity of *Scenedesmus sp* and *Chlorophyll a.* could substantially decrease if Cr present in concentration higher than 0.75 ppb [28]. Unlike *Scenedesmus sp.*, certain species were noted to tolerate higher concentrations of Cr, as *Dictyosphaerium sp.*, which can tolerate up to 13–17 mg/l, and *Chlorella pyrenoidosa* that able to tolerate up to 2 mg/l. Moreover, high biomass productivity of *Chlorella sp., Scenedesmus sp.* and *Dictyosphaerium sp.,* was investigated in study that can be linked to the low chromium concentration present in the tested produced water. The case study demonstrates that the PW after minimal treatment can be utilized for microalgae production. Although, microalgae able to help to remove several metals from the PW, the effect of different compounds of PW on the growth of microalgae ought to be investigated [7].

Additionally, *Coelastrum proboscideum* removes 100 percent of Pb from 1.0 ppm medium with 20 h and nearly 90 percent after only 1.5 h.[14].

3 Algae combined with fungi treatment method

Fungi-microalgae compound also demonstrates huge potential in wastewater treatment [29]. The application of microalgae together with fungi in wastewater treatment is not a novel concept and has been investigated for a while. Abundant degrading enzyme resources and remarkable surface properties of fungi contribute considerably to the removal of contaminants in the wastewater as organic micropollutants and the biosorption of heavy metal [30, 31, 32].

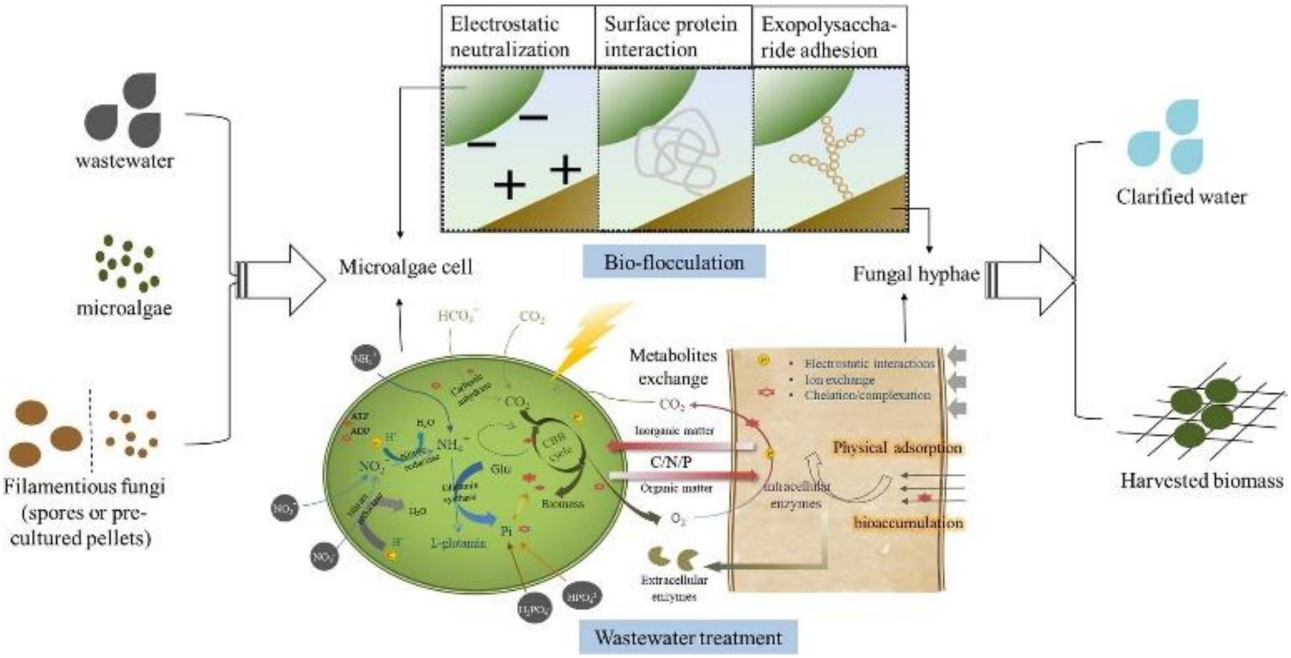

Figure 3.1 – General treatment mechanism of microalgae-fungi technology [32, 33]

Compared with algae or bacteria, fungi-based treatment technique started only recently. Nowadays, there are only a few researches in this field, and they are still in their infancy [32]

Over the last few decades, microalgae presented itself as bio-resource for the elimination of excessive nutrients in wastewater media, such as carbon, nitrogen and phosphorus [34]. Furthermore, current researches consider using microorganisms to remediate polluted water, which contains multiple pharmaceuticals, heavy metals and pesticides. To enhance remediation performances, combined fungi and microalgae noted to be more efficient than the mono-microalgae [35]. Consequently, this part of research summarizes the corresponding efficiency in removing contaminants and the synergistic mechanisms in pollutants elimination by microalgae with fungi in wastewaters are considered as well [33]

3.1 Mechanism of microalgae-fungal treatment system

The mechanisms of fungi-microalgae system contributes to the great performance in the treatment of wastewater. Figure 3.2 illustrates the involved mutual interactions between algae and fungi vividly.

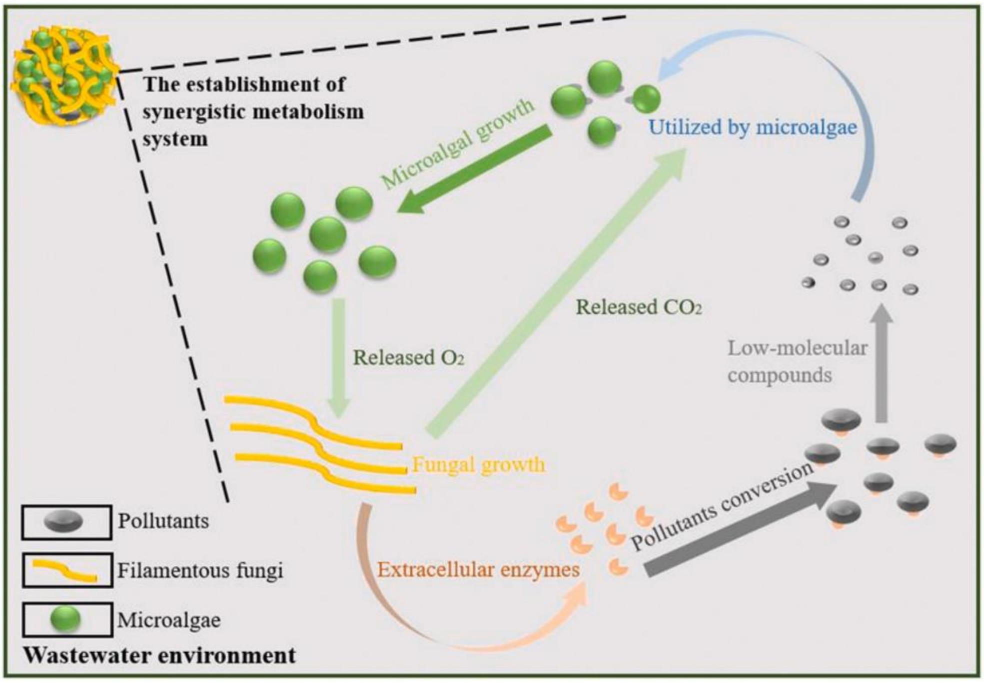

Figure 3.2 - The synergistic metabolism for pollutants removal in fungal-algal system [32, 33]

Some nutrients, specifically carbon and nitrogen appear in suspended solids, which make them challenging for microalgae to be consumed directly. When coupled with co-culture mode, these macromolecular organic elements can be transformed into soluble low-molecular-weight nutrients with the activity of fungal extracellular enzymes. Therefore, it allows microalgae efficiently eliminate more nutrients from wastewater solution due to the assimilation of enzyme-treated soluble compounds [36]. In other words, due to the unique relative reinforcing mechanisms between fungi and microalgae, the co-culture system can be more efficient in the elimination of nutrients (e.g, phosphorus, nitrogen and reducing COD) than a mono-system [33]

Bioremediation of heavy metal-comprising wastewater by the co-culture of microalgae with fungi include two stages. The first stage is described by its fast extracellular passive adsorption (biosorption) that has nothing to do with metabolism of cell [37]. Metal ions may stick to the cell surface by one or more of coordination, surface complexation, ion exchange, micro-precipitation, redox and physical adsorption [38]. Both fungal and microalgal cell walls mainly consists lipids, polysaccharides and proteins that can distribute abundant functional metal-binding groups (hydroxyl, amino, phosphoryl, carboxyl etc.). In addition, the atoms of phosphorus, oxygen, nitrogen and sulphur in functional groups can distribute heavy metal ions with a solitary pair of electrons that are complex and coordinate, so that the heavy metals are densely connected to the cell walls. The storage of heavy metals within the cell is the second stage that is much slower than the first stage, because the process is an energy-controlled metabolism. After the uptake on the surface of cells, heavy metals are dynamically carried into the cytoplasm through the membrane of cell, followed by binding to the internal linking sites of peptides or proteins (phytochelatins, glutathione and metallothionein) and intracellular positive diffusion [39]. Moreover, once within the cells, **organelles** such as **mitochondria**, chloroplasts and **vacuoles** can combine heavy metals with organic compositions (sulphide, sugar, protein) to complex forms, and thus heavy metals are stored in cells in the form of polyphosphates or sulphides [33].

Harvesting can record for up to 50 percent of the total expenses of biodiesel production and is not economically advantageous for big-scale microalgae industry because of the considerable energy requirements and/or the supplement of costly chemicals [35]

Fungi-assisted microalgae cultivation technology does not need the addition of inputs of energy or chemicals, and a number of microalgae species have been proved to be efficient [40]. If this method can be utilized to commercially significant seawater and freshwater algal species, it can bring a solution to one of the main problems related to the costly and the energy-intensive harvesting processes.

Furthermore, granulating of fungal cells during growth in liquid solution makes their harvest much convenient and less expensive than the isolation of the microalgae species [40].

3.2 Microalgae-fungi method reduction of COD

COD is a significant parameter used to describe the degree of organic contamination by wastewater. Biological techniques are widely utilized in the secondary or tertiary of wastewater, and the biosorption of soluble nutrients in wastewater media can be achieved through the metabolism of microorganisms [41]. High COD removal rate is accessible in the microalgae-fungi system due to mixotrophic and heterotrophic growth of fungi and microalgae. As shown in Figure 3.3, free CO2 molecules disperse into microalgae cells and enter the **CBB** cycle with the support of rubisco or other enzymes, providing oxygen and other organic compounds for their metabolisms. CO2 is present in the form of bicarbonate in wastewater and carbonic anhydrase of algae can consume carbonate or transform it into free carbon dioxide directly [42]. Fungal cells utilize the oxygen provided by microalgae for cellular breathing. The gas exchange between the microalgae and fungi promotes each other’s growth and, to some extent, facilitates the implementation of carbon in wastewater [43]. Meanwhile, extracellular enzymes provided by fungi can degrade big suspended solid, leading to the complementary intake of organic compounds by fungi and microalgae [44, 45]. It is also worth mentioning that the microalgae-fungi pellet structure is favourable to the capture of suspended solids. Treated molasses wastewater with fungi-microalgae consortium, microalgae and fungi, and the COD removal efficiencies were 70.68, 25.96, 59.00, percent, respectively [46]. It noted that the co-culture of fungi and algae was superior to mono-culture on the nutrient removal. Co-cultivation systems, for instance, co-culture of microalgae with activated sludge or with fungi, were better than mono-culture to remediate biogas slurry, which is consistent with the outputs of their previous studies [47][32].

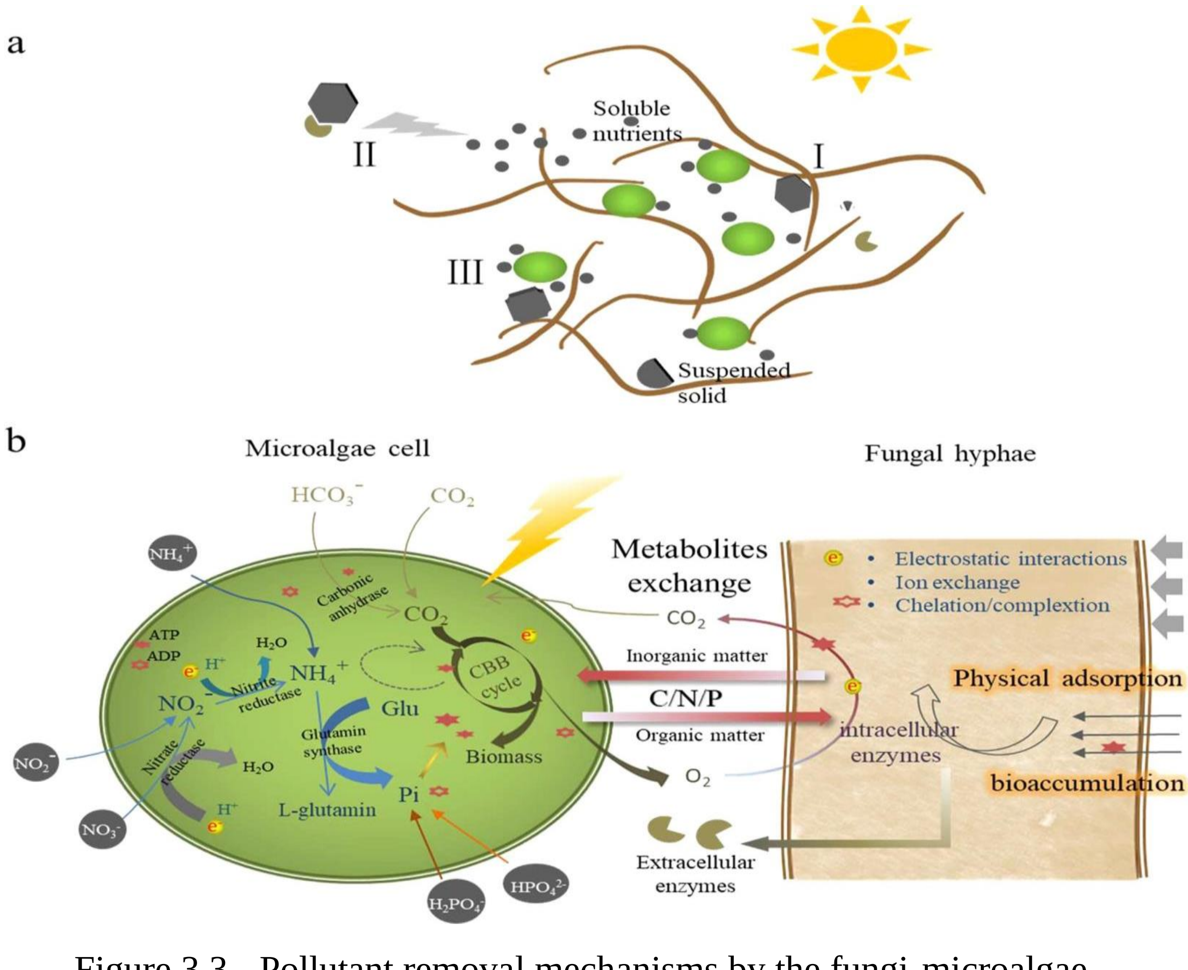

Figure 3.3 - Pollutant removal mechanisms by the fungi-microalgae consortium. a) Fungi and microalgae work together to treat contaminants: I. Adsorption or capture of suspended solids; II. Degradation by extracellular enzymes secreted by fungi; III. Assimilation of soluble nutrients by fungi and microalgae. b) A further depiction of assimilation of soluble nutrients by fungi and microalgae III. CBB cycle; Glu: glucose [32, 33]

The nutrient elemination efficiencies of biogas slurry under the respective optimal conditions utilizing consortium of *C. vulgaris* and *Ganoderma lucidum* and mono-*C. vulgaris* are comparatively summarized in Figure 3.4. Nevertheless, it appears that co-culture had an unremarkable COD elimination efficiency compared with mono-microalgae, even though the elemination efficiency of total nitrogen and total phosphorus by the microalgae-fungi consortium was superb. Various microbial species and wastewater sources, as well as different cultivation environments such as initial COD concentration, illumination conditions, varied biogas slurry compounds and carbon dioxide concentration, may have affected to this distinction. For comparison the nutrient removal efficiency of co-cultivation system and the mono-microalgae system more precisely, more comparative information from the same selection of experiments are necessary [32].

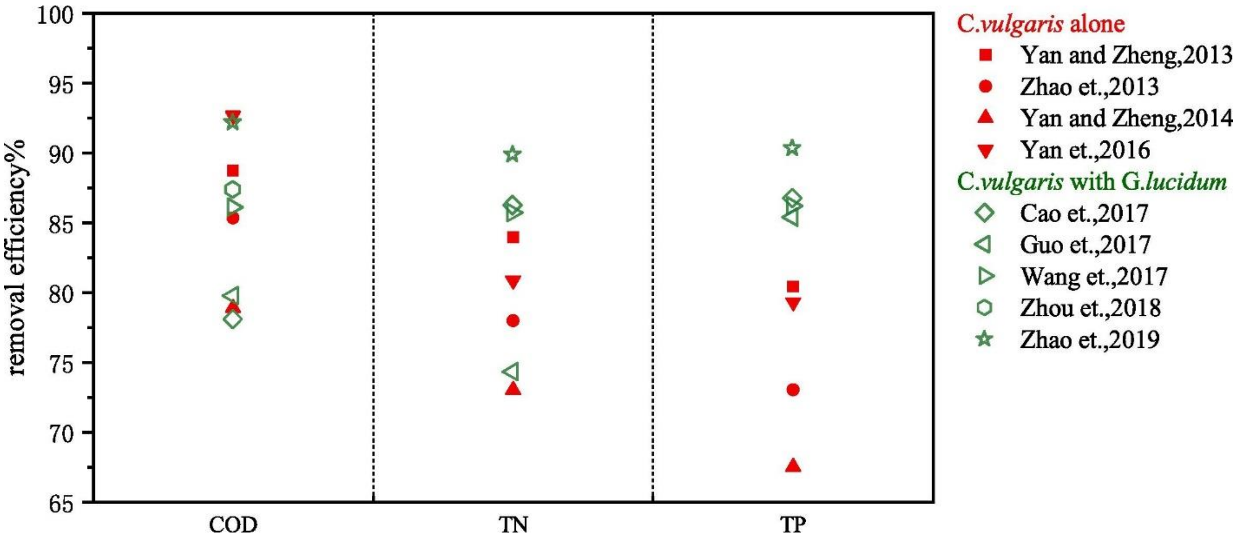

Figure 3.4 - Comparison of nutrient removal efficiency from anaerobic digestion wastewater by *C. vulgaris* alone and *C. vulgaris-G. lucidum* consortium [48, 49, 50, 51, 32]

3.3 Removal of TN by microalgae-fungi consortium

Filamentous fungi are capable of utilizing both inorganic and organic nitrogen but are not as efficient as microalgae. Nevertheless, the co-cultivated system of fungi and microalgae is able to achieve a considerably better removal efficiency. The microalgae and fungi combination in municipal centrate obtained 100 percent removal efficiency of ammonium after one day, far better than other experiments with solitary microalgae [52, 53]. Other experiments also have shown that the elimination efficiency of ammonium by microalgae-fungi pellets reached almost 85 percent [35, 54]. The filamentous fungi implanted into the microalgae system, the elimination rate of ammonium increased remarkably from 19 to 94.72 percent [46].

In addition to further consumption of ammonium N by fungi, it is more likely that the macromolecular nitrogen biodegradation sources such as proteins by fungi promotes the consumption of nitrogen by microalgae. The transfer of nitrogen between microalgae and fungi confirmed by Isotopic labelling experiments [55].

In comparison with ammonium, the elimination of TN by fungi-microalgae consortium, microalgae or fungi was ordinary [56, 52]. Ammonium is the most preferred form of nitrogen for microorganisms because it needs the least energy while accumulation, thus can be quickly integrated into amino acids. Since nitrates more thermodynamically stable than ammonium and it is the most oxidized nitrogen form, this inorganic compound is more common in the oxidized water medium. Nevertheless, the consumption of nitrates does not initiate until ammonium is almost fully absorbed [42]. Even if the total nitrogen efficiency of the microalgae-fungi consortium is lower than that of ammonium, the co-cultivation consortium performance still better than the mono-specie systems as shown in Figure 3.4. [32, 33].

3.4 Microalgae-fungi system elimination of TP

The metabolism and growth of organisms cannot be detached from the phosphorus involvement since many biological macromolecules, such as proteins nucleic acids, phosphates and lipids, comprise phosphorus, and phosphate groups are essential compounds of energy transformation molecules. This element transported into microalgae cells in the forms of dihydrogen phosphate and dihydrogen ortophoshate followed by integration into organic composition through photophosphorylation, substrate-level phosphorylation and oxidative phosphorylation [57]. Fungi are same to microalgae except that the energy from light conversion via photosynthetic process is not available.

The phosphorus elimination efficiency of fungi match to or even better than that of microalgae. The phosphorus consumption of the co-cultivation system performs well even though mono-fungi and mono-microalgae demonstrate relatively low removal efficiency. The treatment technology did not considerably affect TP removal, unlike TN and COD [47]. As illustrated in Figure 3.4., *C. vulgaris-G. lucidum* consortium had visibly higher elimination efficiency for TP in anaerobic liquid medium than *C. vulgaris* alone. For other wastewaters, *C. vulgaris-G. lucidum* consortium also performed with high TP removal efficiency [46, 52].

However, the experimental data demonstrated that the TP elimination efficiency of co-cultivated microalgae and fungi (53 percent) was much lower than that of mono- microalgae (94 percent) or mono-fungi (83 percent), which may be referred to the different cultivation time [29]. The co-cultivated microalgae and fungi performed the highest TP elimination efficiency (87 percent) after 36 h.

Furthermore, a stepwise culture was applied: first culture the microalgae and then the fungi or first cultivate the fungi and then the microalgae. The results indicate that the stepwise cultivation of fungi first had superb nutrient elimination efficiency. Inoculation of the microalgae in wastewater after cultivation the fungi for 48 h, and 95 percent elimination efficiency of TP was obtained 24 h later [29]. Phosphorus elimination is not only dominated by the consumption metabolism of the cell but by external conditions as dissolved oxygen and pH as well. When the pH value rises to 8.0, or the oxygen concentration is high, phoshates will be induced from the medium [42]. According to previous studies done, microalgae autotrophic cultivation usually causes the culture solution to be alkaline, favourable to the precipitation of phosphates. Still, the decrease in pH caused by the co-cultivation of microalgae and fungi hinders this process [22]. Fungi may also produce enzymes that can biodegrade precipitated phosphate ions and facilitate phosphorus consumption by itself and microalgae [58, 32].

4 Cost-effectiveness of microalgae-based treatment.

Some microalgae species demonstrates high growth rates (biomass concentration is able to double within hours), which attributes to microalgae an *undeniable economical potential*. Nevertheless, the applications of most is not economically sound, mainly due to the essence of energy, water and nutrients. Furthermore, one of the expensive processes is the microalgae harvesting that comprises about 30 percent of the total costs. Consequently, several researches were done to reduce the overall cost of microalgae production, taking into account its environmental impact as well (water usage and greenhouse gas emissions). *Some types of wastewaters are abundant in nutrients that enhance microalgal growth.* Their utilization as cultivation medium will considerably reduce the requirement of nutrients fresh water. Microalgae consume phosphorus for their growth and they are able to accumulate this element as polyphosphate [15].

Most microalgae species have been adapted to grow efficiently in wastewater. This way, the cost of production may be reduced due to the simultaneous use of wastewater as a water source and nutrient-rich medium for some type of wastewater such as PW, in addition to absence of secondary pollution. [59, 60, 61].

Although PW comprises some toxic compounds that may inhibit algae growth, it comprises some nutrients such as phosphorus and nitrogen, in the form of phosphate and ammonium, respectively that are essential for microalgae cultivation [62]. These vital nutrients are in general available in PW at an adequate level for microalgae growth [62, 63, 13]. *Since the nutrient supplementation represents 50 percent of the cultivation costs, the presence of phosphorus and nitrogen improves the overall economy and return on investment* [13].

In addition, the choice of the cost effective and appropriate systems for microalgae application in PW treatment plant pose good economic benefit, because it may possess certain advantages over other type of systems as better management, hence, representing a lower-cost strategy.

5 Application of microalgae-based system in the treatment plant of PW

5.1 Choosing appropriate system for application of microalgae-based treatment

A microalgae production system is the decision on the kind of system that needs to be constructed that can be either a ***closed*** or an ***open*** system. Open systems, such as lakes, tanks and ponds that demonstrated in Figure 5.1 are the most common and extensively commercialized outdoor systems. These systems are easy to construct, simple to manage and preferred for their low energy consumption. Usually, the water depth in the system is kept between 0.2-0.4 m to enable light to penetrate. Since the open systems are exposed to outdoor environmental conditions, microalgae are prone to contamination and changes in composition of growth medium due to nutrient dilution (because of the rain or precipitation) or concentration (because of evaporation), reducing productivity [64]

Figure 5.1 - Open pond biological treatment [65]

Closed systems, also known as PBRs, are concealed from the external environment, thus avoiding adverse external influences and contamination. Therefore, PBRs often present a higher productivity compared to open systems. Flat-plate or tubular PBRs made of glass or plastic that illustrated in Figure 5.2 are the most common designs used in industry. Air supplemented with gasses, usually CO2, is bubbled via the water column in the PBR [66]. The most significant PBR design features for and low energy consumption and high productivity are culture mixing mechanism and reactor diameter [67]. The major drawbacks of PBRs are limited volume, high energy consumptions and reduced light penetration due to fouling of the reactor walls and difficulty cleaning the system, which results into higher operational costs [66].

Figure 5.2. Closed PBR [68]

Batch, continuous or semi-continuous operational modes are the major strategies utilized for microalgae culture systems [69]. A closed batch system takes less management than a continuous system, hence, represents a lower-cost strategy. The major characteristics of a batch system are as follows: culture medium does not have to be renewed regularly, microalgae continue to grow until all the nutrients are depleted and cell self-shading happens or pH variations and contamination obstruct further growth. In batch systems, interfusion of the culture is critical to ensure nutrient accessibility and gas interchange at the interface between growth medium and cells. Natural or artificial light can be furnished to the cells. In some cases, an additional external CO2 supply is utilized to enrich the air and promote faster cell growth [64].

As microalgae are photosynthetic microorganisms, the metabolic processes related with nutrient consumption are driven by light [70]. Nevertheless, despite that natural or artificial light can be furnished to the cells, many algae strains can grow utilizing organic carbon as an energy source instead of light through mixotrophic or heterotrophic metabolism. This especially helpful for PW from oil wells, that need minimal or in most cases no external carbon supply, because of its composition loaded with various types of carbons (including inorganic, such as CO2 in forms of dissolved gases), making closed batch system for PW more cost and management effective.

5.2 The place of microalgae-based treatment in PW treatment plant.

In order to achieve proper water for reinjection together with the legislator and environmental requirements for reuse, the utilizing of the only one technology for treatment of PW is not sufficient. Thus, there are many various types of technologies involved in PW treatment plant. In accordance with their characteristics, they are gathered accurately for each specific situation. However, they all share general similarity, namely phased treatment of PW, the common scheme of which demonstrated in Figure 5.3.

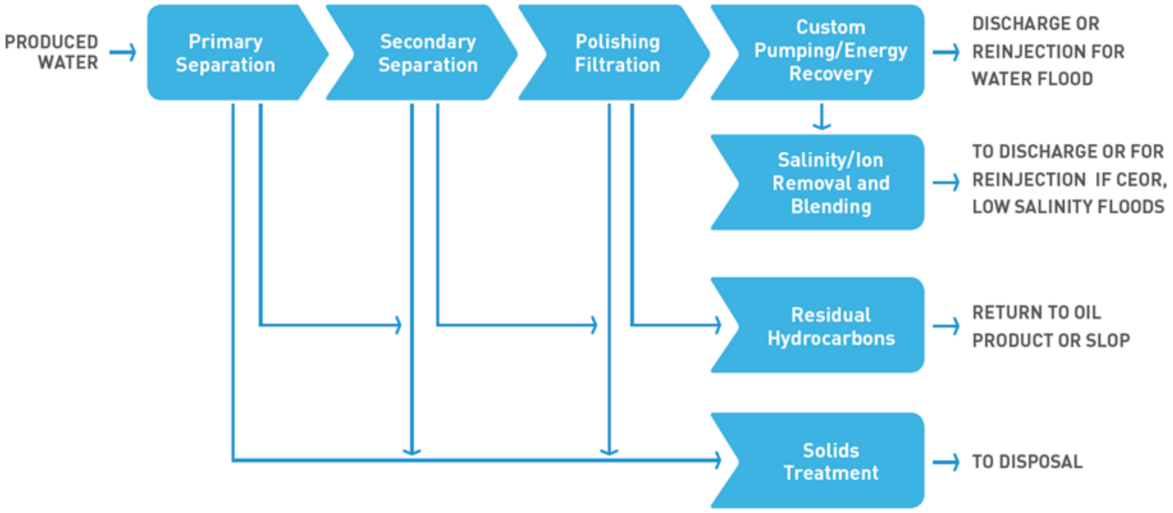

Figure 5.3 - General scheme of PW treatment [71]

Primary treatment is commonly used for physical processes in petroleum produced water treatment plant. The primary treatment step comprises an oil and water separator which can detach solids, water and oil. Gravity separation followed by skimming process is implemented for removal of oil from wastewater [72].

Secondary treatment comprises flocculation, coagulation and further biological treatment to reduce toxicity of petroleum produced water. Flocculation-coagulation is a technique in which chemical additive is supplied to accelerate the precipitation in clarification tank. The coagulants are inorganic and organic components such as aluminum sulfate and aluminum hydroxide chloride or high molecular weight cationic polymer. **Chitosan** for efficient flocculation/coagulation process to treat oil field produced water. [72].

Tertiary treatment utilized to removing trace organics such as PAHs, total suspended solids, suspended and dissolved matter, and reducing COD [72]. Tertiary treatment are also targeted on the salts removal from treated produced water coming from secondary treatment. By utilizing the **reverse osmosis** as tertiary treatment, mostly reducing the levels of phosphates and nitrates. N:P ratio has been reported crucial for treatment of oily wastewater [72].

Keeping in mind that relative expense of treatment doubles for each additional step, biological tertiary treatment seems to perform well compared to the chemical treatments, which often leads to secondary pollution.

As result, microalgae-based technology can be applied in a secondary treatment, considering it as biological treatment. That is prevalent thing to do, due to effective removal of organic compounds and reducing of both chemical and biological oxygen demand. However, it can better be utilized in tertiary treatment as unique way of effectively treating TP and TN, along with heavy metals and BTEX. Moreover, tertiary treatment often viewed as finishing phase, therefore the ability of microalgae to disinfect will be handy for a complementary completion of treatment.

6 The main drawbacks in application of algae-based treatment for oil-field PW, challenges, and possible solutions

The main disadvantages of integration microalgae-based system in PW from oil fields:

Considered as new relatively new technology, thus - the infancy stage of researches made for micro-algae based treatment of PW;

Variety, yet difficulty of microalgae strain choice;

Necessity for additional knowledge in cultivation of cells;

Potential unknown difficulties with an appliance for PW

Numerous factors which may lead to growth inhibition of microorganisms such as excessive amounts of certain compounds;

The main challenges

Challenge: ***Cell outflow.***

One of the major problems in the utilization of microalgae-based treatment is their washout from the treated effluent.

Possible solution:

Among the ways of solving this problem are immobilization techniques.

The activity, viability, and productivity of immobilized cells can be maintained for a long period of time, which facilitates continuous cultivation processes and results in a better operational stability. Cell wash-out is avoided even at the high dilution rates of the continuous operation mode. Immobilized cells can be handled more easily and recovered from the solution without difficulty; and a cell-free product stream simplifies downstream processing. In addition, because immobilization can influence both diffusion properties of molecules through the support and the physiological behavior of the confine cells, noticeable differences of cell growth, metabolism, and physiology are observed upon immobilization. Higher specific rates of product synthesis or substrate consumption for immobilized cells have been successfully demonstrated. Immobilized cells are currently being used industrially for vinegar, organic, and amino acid production, as well as in wastewater treatment [73]. Immobilization can be implemented for cellular organelles, animal, enzymes and plant cells [74]. Immobilized *Scenedesmus* cells were able to consume phosphorus and nitrogen at rates similar to those of free microalgae [14].

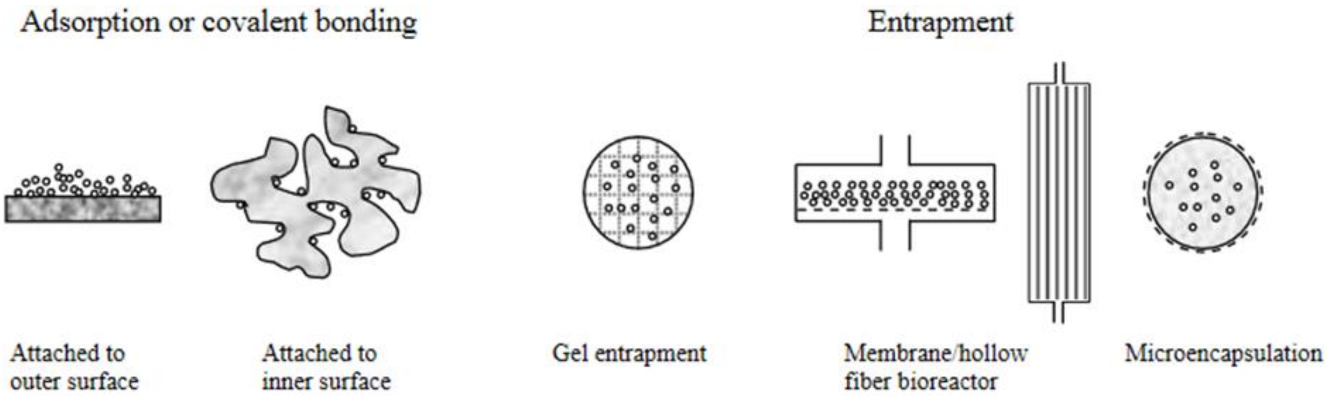

Figure – 6. Immobilization techniques.

Challenge: ***Salinity of PW***

Another challenge culturing microalgae is in salinity of PW. In most cases, the salinity of PW is even higher than seawater, which can potentially supress the growth of microalgae in PW, with the following inhibition of treatment abilities.

Possible solution:

Some freshwater microalgae can tolerate only moderate salinity. Alternatively, marine algal strains can sustain even higher salinity. *Nannochloropsis sp.* has a peak salinity value of around 40 g TDS L minus. Other marine algae *Dunaliella sp*. is noted to withstand salinity between 5 to 359 g L minus 1 [75]. *Dunaliella tertiolecta*, another marine species, in PW with a wide range of salinities 30–210 g TDS L mi1 while salinity growth inhibition occurred at around 180 g TDS L minus 1 [76, 13].

In addition, desalination before biological treatment might be an option, as well.

Challenge: ***The rise of pH levels***.

The levels of pH rise during photosynthesis of microalgae. On the one hand, the rise of pH has disinfecting effect. On the other hand, an increase in pH and dissolved O2 concentration investigated in microalgae cultures can cause a detrimental effect on bacterial activity. Under these conditions, the benefit provided by facultative and aerobic bacteria in PW may be reduced as their function and growth becomes impaired [24].

Possible solution: Although immobilization technique is an excellent solution for cell outflow, its benefits can also be useful to such problem as rise of pH.

Cell immobilization is defined as the physical confinement or localization of intact cells to a certain defined region of space with the preservation of some desired activity [73]. An immobilized molecule is one whose motion in space has been restricted either to a small limited region or completely by attachment to a solid structure [74].

Cell immobilization allows for more efficient operation by reducing the non-productive growth phase. It is well recognized that the high cell density of immobilized cells improves the product yield and the volumetric productivity of bioreactors. Immobilization protects the cells from shear forces and imparts a special stability to the microorganism against environmental stresses (**pH**, temperature, organic solvents, salts, inhibiting substrates and products, poisons, self-destruction). Table 6 shows the comparison between free cell and immobilized cell. Due to these important advantages of cell immobilization, a variety of immobilized cell bioreactors have been developed to optimize processes [73].

Table 6 - Comparison between free cell and immobilized cell.

	Immobilized cells	Free cells
Production	High cell productivity Improved resistance of cells to inhibitory substrates or products	Low cell productivity
Process operation	No cell wash-out in continuous fermentation even at high dilution rate Difficult to perform continuous process due to cell wash-out Reuse of cells for prolonged period of time due to cell regeneration Long-term operational stability and constant product quality Reduced risk for microbial contamination Protection against shear forces ***A special stability provided against environmental stresses: pH***, temperature, organic solvents, salts, poisons, heavy metals. [73]	Difficult to perform continuous process due to cell wash-out Effective separation and concentration steps are necessary in downstream processing Cells cannot be reused Product quality varies lot by lot More prone to contamination Exposure to external damages [73]

As we can see, by selecting ***immobilization technique*** for cell recovery of microalgae, we not only preventing cell outflow from treated PW, but also engrafting high resistance to **pH**, as well as to toxic chemicals, temperature, solvents, heavy metals and salinity, which is especially important for potential appliance of microalgae-based treatment for **PW**.

CONCLUSION

The sustainable development of a produced water treatment system needs to be technologically feasible, environmentally friendly and economically viable. The current evidence is that microalgae as an alternative biological wastewater treatment option is technologically and environmentally feasible.

Despite the fact that the physical and chemical characteristics of produced water vary significantly that depends on multiple factors including, depth and age of the geological formation, geographic location of the field, extraction method, hydrocarbon-carrying formation geochemistry, kind of the produced hydrocarbon, along with its chemical composition in the reservoir, it has the major constituents that are common for almost any produced water from oil fields. Moreover, by reviewing those major constituents and detailed efficient treatment abilities of microalgae we were able to see the explicit accordance that impossible to ignore.

By observing the successful application of this technology for other types of wastewater, we can conclude that it has wide range treatment of pollutants that present in PW, as it is capable of efficiently reduce the amount of such detrimental contaminants as TP, TN, BTEX as well as heavy metals and reducing both biological and chemical oxygen demand. By combining microalgae and fungi we could observe further improvements in decreasing the TP and TN, which indicated to be an important pollutants to treat for oily wastewater.

It is true that, high saline environment could cause microorganisms such as algae and fungi to stop their grow and thereof treatment abilities, however implementation of their marine cultures such as *Dunaliella* which could tolerate salt concentrations up to 359,000 mg L^{-1} can actually let them to be utilized in high saline environments.

Operational costs, micro-algae systems incur little or no operational costs, which altogether makes the technology more sustainable. One of the costly processes of using microalgae is harvesting, which represents about 30 percent of the total costs. Some wastewaters are rich in nutrients, which enhance microalgae enlargement their addition represents around 50 percent of the cultivation costs, thus the presence of them in PW plays a significant role in cost-effectiveness of the technology. Additionally using closed batch system for microalgae application in PW treatment plant pose good economic benefit, because it takes less management and is not exposed to outdoor environmental conditions that lead to additional contamination compared to other system, hence, represents a lower-cost strategy.

In addition, by selecting immobilization technique for cell recovery of microalgae, we not only preventing cell outflow from treated PW, but also engrafting high resistance to pH, as well as to toxic chemicals, temperature, solvents, heavy metals and salinity, which is especially important for potential appliance of microalgae-based treatment for PW.

Although, the application of microalgae-based technology for PW have numerous factors to be concerned about as well as potential uncertainties, overall, the biological treatment methods using microalgae are an economical, effective and considered environmentally friendly technology that can remove harmful chemicals and pollutants from the water. By scaling their advantages, disadvantages and many other factors that described in this work, we can eventually see the undeniable potential of this technology for PW treatment,

ABBREVIATIONS

In this master's thesis, the following abbreviations and terms are used:

PW = Produced Water

WW = Waste Water

CBM = Coal bed methane

BOD = Biological Oxygen Demand

COD = Chemical Oxygen Demand

PAHs = Polycyclic Aromatic Hydrocarbons

TOC = Total Organic Carbon

BTEX = Benzene, toluene, ethyl benzene, and xylene

TDS = Total Dissolve oil and grease

O&G = Oil and Grease

TP = Total phosphorus

TN= Total nitrogen

TKN = Total Kjeldahl Nitrogen

ADP = Adenosine Diphosphate

ATP = Adenosine Triphosphate

BD = Biodegradation

PBRs = Photobioreactors

CBB = Calvin-Benson-Bassham

TERMS

Biological treatment – wastewater treatment method, which treats medium by utilizing natural consumption of dissolved organic pollutants by microorganisms.

Total Kjeldahl Nitrogen – is the total concentration of organic nitrogen and ammonia. The original TKN method was developed by the Danish chemist Johan Kjeldahl in 1883. Today, TKN is a required parameter for regulatory reporting at many plants but is also used to provide a means of monitoring plant operations.

Chemical oxygen demand – is the amount of oxygen consumed to chemically oxidize and decompose organic water contaminants.

Biological oxygen demand – is the amount of oxygen consumed by microorganisms in breaking down organic water contaminants.

Chlorophyll – is the substance that gives plants their green color. It helps plants absorb energy and get their nutrients from sunlight during the biological process known as photosynthesis.

Biosorption – can be defined as the passive uptake of pollutants by dead or inactive biological materials through different physico-chemical mechanisms.

Bioaccumulation – is the gradual accumulation of substances, such as pesticides or other chemicals, in an organism.

Homeostasis – refers to the capacity of the body to maintain the stability of diverse internal variables, such as temperature, acidity, and water level, in the face of constant environmental disturbance.

Symporter channel – is an integral membrane protein that is involved in the transport of two different molecules across the cell membrane in the same direction.

Phosphorylation – allows cells to accumulate sugars because the phosphate group prevents the molecules from diffusing back across their transporter.

Adenosine triphosphate – is an organic compound and hydrotrope that provides energy to drive many processes in living cells, such as muscle contraction, nerve impulse propagation, condensate dissolution, and chemical synthesis.

Adenosine diphosphate – is an important organic compound in metabolism and is essential to the flow of energy in living cells.

Endergonic reaction – is a chemical reaction in which the standard change in free energy is positive, and an additional driving force is needed to perform this reaction.

Photoautotrophic process – is when organisms make their own energy using light and carbon dioxide via the process of photosynthesis.

Xenobiotics – is a chemical substance found within an organism that is not naturally produced or expected to be present within the organism.

Organelles – in cell biology, an organelle is a specialized subunit, usually within a cell, that has a specific function.

Vacuoles - are essentially enclosed compartments, which are filled with water containing inorganic, and organic molecules including enzymes in solution, though in certain cases they may contain solids, which have been engulfed.

Mitochodria – organelle found in most eukaryotic cells, the primary function of which is to generate energy in the form of adenosine triphosphate

Chitosan – commercial chitosan is derived from the shells of shrimp and other sea crustaceans. Chitosan causes the fine sediment particles to bind together, and is subsequently removed with the sediment during filtration. It also removes heavy minerals, dyes, and oils from the water.

Calvin-Benson-Bassham cycle – the chemical reactions that convert carbon dioxide and other compounds into glucose.

Reverse osmosis – is a technology that is used to remove a large majority of contaminants from water by pushing the water under pressure through a semi-permeable membrane.

Immobilization technique – is a process to achieve motion restriction of the body in space either to a small limited region or completely by attachment to a structure.

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