QATAR UNIVERSITY

COLLEGE OF ARTS AND SCIENCES

THE IMPACT OF USING PRODUCED WATER FOR PLANT IRRIGATION AND ITS EFFECTS ON PLANTS AND SOIL CHARACTERISTICS

BY

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ABSTRACT

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Title: The Impact of Using Produced Water for Plant Irrigation and its Effect on Plants and Soil Characteristics

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In this study, locally produced water was physically and chemically characterized. The results showed high concentration of total dissolved solids (TDS), chloride, sodium, boron ions and sodium adsorption ratio as 300, 122, 61, 0.038 g/L and 139.9 meq/L respectively. The generated water was used after different dilution:0, 10, 20, 30, 40 and 50% for plant irrigation in greenhouse for *Medicago sativa*, *Zea mays*, *Helianthus annus*, *Sorghum bicolor*, *Phramites australis* and *Salsola baryosma* using a complete randomized design with three replications. The results showed that all plants could not survive except *Medicago sativa* which tolerated up to 10% produced water with a decrease in intensity, length and biomass. *Salsola baryosma* tolerated up to20% produced water without any significance differences on the morphological characteristics. The FTIR results for *Salsola* tissues showed that cellulose structure has the great role in metals adsorption and transportation inside the plant tissue through the shifting or disappearance in transmission bands at 1028, 1334, 2852 and 2921 cm^{-1}. The soil used in this study was sandy loam which showed a huge accumulation of sodium ions with increase in salinity and sodium adsorption ratio (SAR). The organic contents of produced water were below detection limits of gas chromatography (GC) and ultra-performance liquid chromatography (UPLC) instruments after dilutions at different levels. The results of polycyclic aromatic hydrocarbons (PAHs) extraction showed accumulation of less polar PAHs in 30% irrigated soil.

DEDICATION

I dedicate this work for my parent, who spent their life just for supporting me.

Also, I dedicate this work for my family who are suffering and tolerate a lot during my studies.

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Chapter 1: Introduction

The State of Qatar has one of the highest per capita in water consumption rates in the world. The country is still working on a National Water Act to be achieved in 2023 with a complete national strategy for using water and regulation (Saleh, 2013).

Qatar is considered one of the lowest amounts of annual rainfall in the world;the average rainfall is significant, 100 mm (3.9 in) per year. The three main sources of the state's water are sea water desalination, groundwater, and recycled water. Seawater is the most important source of water for Qatar residents, secretarial for about half of the water used. Seawater is desalinated through a high cost and energy-high consumption thermal process.

Simultaneously, increase population and industrial activities add more challenges for water resources and energy consumption, so water security and energy are identified as major grand challenges, now State of Qatar uses the more advanced technologies for wastewater treatment, however the treated wastewater is not considered as viable water to use in agriculture and landscaping demands (Basem et al., 2014). Also State of Qatar is one of the biggest gas production countries so it is facing another problem of huge amounts of by-product, which is water coming with exploration of gas and oil which is called produced water (PW).

Sustainable management of water resources is a very challenging concern. In the Gulf council counties (GCC), this concern is particularly complex owing to the harsh-arid environment and increasing anthropogenic input of pollutants from different sectors. The development of countries rich in oil and gas, such as State of Qatar, but poor in water resources requires new, dynamic, and sustainable water resource schemes in times of extreme growth. The increasing population growth in the State of Qatar's coupled with remarkable development and industrialization add more stress to the existing renewable water resources.

Qatar is considered as one of the highest water consuming countries in the world, and the desalinated water feeds 99% of the country's municipal demand and the annual growth in demand is about 10%. Municipal water consumption reached 675 liters of water per capita per day (Qatar General Secretariat for Development Planning, 2011). Nearly twice the average consumption in the EU. Presently, Qatar uses the best innovative technologies for treating wastewater; nevertheless, the treated wastewater is not considered a sustainable water resource and is not used in agriculture and landscaping (Saleh, 2013).

The development of Gulf societies over the last two decades was mostly enabled; thanks to the advances in desalination technologies powered by cheap fossil fuels. Those specific conditions make the water cycle in Gulf countries almost unique. There is, however, an obvious need to have smart water technologies and a management plan to meet the local water demand according to Qatar's development (Qatar General Secretariat for Development Planning, 2011).

Water production, storage, re-use and management is considered one of the priority themes in the national priorities research program (NPRP 10). Concurrently, population growth and industrial development have substantially increased Qatar's energy, water and other resources needs. That threatens Qatar's environmental sustainability beyond international standards, which is why energy and water security were identified as major Grand Challenges.

Opportunities for sustainable water resources gains flourishing, cutting across sector boundaries. Through confronting incompetency in technology, infrastructure, and processes, Qatar can make a robust impact in enhancing the use of water resources over time. Qatar's National Development Strategy 2011–2016 pinpointed a variety of initiatives to confront the technical in competencies in the production, distribution, implementation, and use of water in order to improve environment management and contribute to sustainable development. These initiatives are: altering water consumption patterns in agriculture; continuing substantial investments in educating and training of Qataris; achieving a fully integrated approach to water management and a rethinking of regulatory approaches.

However, the ministry of development planning and statistics (MDPS), has started mobilizing national efforts to prepare the second national development strategy (NDS2) (2017-2022). “Environment sustainability, natural resources and built environment” sector is expected to be included into the NDS2. Pertaining to "environment sustainability", it has been confirmed that NDS 2011-2016 was able to achieve most of what this goal is intended for.

There is also a vital need to establish standard treatment procedures of produced water. Produced water is a potentially valuable source of water and could prove highly useful for Qatar’s bid to improve its long-term water security, as per the National Vision 2030. The economic argument for reusing, or recycling produced water can be justified if low cost treatment plants and technologies are applied to the process (Saleh, 2013).

Produced water is known as the water that present in subsurface creations and is gotten to the surface during oil and gas production industries (Neff, 2002 & Veil et al., 2004). Water is produced from conventional gas and oil production, as well as the production of unconventional sources such as tight sands, coal bed methane and gas shale. The concentration of components and the quantity of produced water differ dramatically depending on the location and type of the petroleum compounds (Bader, 2007). Produced water accounts for the highest waste stream quantity connected with oil and gas production, global ratio of water to oil is 3:1 that means water cut is 70% (Fakhru’l-Razi et at., 2009) while in Qatar can be reach 4:1 in some oil production fields (Jumana, 2014).Raising the extraction of offshore oil and gas industries and development in harsh/Arctic environments needs more active and intelligent offshore produced water management, as these environmental areas are much more critical to changes in water quality than more temperate climates. However, the number and scope of studies of offshore produced water management in harsh/Arctic environments are limited.

Quality of produced water differs expressively according to geographical location, type of hydrocarbon manufactured, and the geochemistry of the producing formation. In general, the total dissolved solids (TDS) concentration are ranging from 100 to over 400,000 mg/L. Sludge, sodium, particulates, bicarbonate, and chloride ions are the most commonly occurring inorganic constituents in produced water. Benzene, toluene, ethylbenzene, and xylene (BTEX) mixtures are the most commonly occurring organic pollutants in produced water. The types of pollutants present in produced water and their concentrations have a large impact on the most appropriate type of beneficial use and the degree and cost of treatment required (Ray & Engelhardt, 1993).

Various treatment processes could be used for produced water treatment; many treatment processes can be used together in the same case of treatment according to initial composition of produced water and the final target proposes. After the treatment processes the quality of the end product defined the purpose of use; irrigation, industries uses, stream flow and livestock watering. Most of the treatment processes such as filtration, chemical processes and reverse osmosis are highly expensive that mean more budget spending to get the final result treated water not for drinking proposal but for plant irrigation or livestock use (Salem and Abdul Wahab, 2014).

Around the world, there is increasing trend to apply innovative technology for produced water remediation, using phytoremediation or plant remediation (Hazrat et al., 2013). Phytoremediation is a developing biotechnology highly suggested for the following reasons; (i) Low cost and solar driven remediation technology, (ii) Effective in superficial position with low contaminant level, (iii) Efficient in remediation of wide range of environmental pollutants, (iv) Useful in place of mechanical cleanup method, and (v) Environmentally friendly treatment (Dhir, 2013).

Therefore, the main research plane of this environmental study includes characterizationof one of a local produced water in Qatar and apply it to irrigate four crop plant species; ***Helianthus annuus*** **(**sunflower), ***Zea mays*** (maize), ***Sorghum bicolor*** (grain sorghum) and ***Medicago sativa*** (alfalfa)in addition to Qatari native desert plants that are known to be salt tolerant and survive under contaminated soils such as ***Salsola baryosma***(gaghraf)and***Phragmites australis***(ghab). All plant species selected are not for human or animal consumption, but only for increase green cover and finding valuable use in industries.

Objective of this research are summarized as following:

1. Investigate different Qatari plants species which are able to remediate the pollutants from produced water.
2. Carry out comprehensive physical and chemical characterizations of the local produced water using different and highly advanced analytical techniques.
3. Carry out comprehensivephysical and chemical characterizations of the soils used as model soils for growing the selected plants.
4. Studythe effects of produced water on the plant survival and plant growth parameters as well as accumulation of produced water pollutants in plants.
5. Study the adsorption mechanisms of various pollutants onto root. This is possible using common Fourier transform infrared (FTIR) technique.
6. Perform statistical analysis for better peresentation of collected data.

Chapter 2: Literature Review

Produced water

Water generated during oil and gas production from both onshore and offshore wells known as produced water (Collins, 1975), it has two types of origin; (i) Formation water: is water that trapped with oil and gas in a geological reservoir in sedimentary rocks since millions of years and (ii) Injection water: including seawater, freshwater and/or production chemicals which are injected to the well to enhance the rate of recovery and for safety purposes (Neff, 2002 & Veil et al., 2004).

Produced water is the large waste by-product generated in industries of oil and gas production and it is composed of a mixture of organic and inorganic constituents dissolved and suspended in a huge water amount (Jumana, 2014).

The amounts of salts dissolved in produced water are 5 – 6 times higher than in sea water (Hayes & Aurther, 2004).Katie Guerra et al., 2011 defined produced water as the water that present in subsurface formation, then it is brought up to the surface during oil and gas exploration.

Produced water quantity

As presented in Fig. 1, the quantity of the produced water differs according to geological location of extraction and the life time of production. In 2003 the estimated amount of produced water discharged to the ocean from offshore production around the world was 800 million m^3(Jerry et al., 2011). The average daily estimation of produced water production around the world is 250 million barrels in front of only 80 million barrels of oil production giving ratio of production water to oil around 3:1 that is to say water cut is 70%(Fakhru'l-Razi et al., 2009).Annual amount production of oil and gas produced water is 14 billion barrels approximately (Arthur et al., 2005). In state of Qatar, in some of oil production fieldsthis ratio varies from 2:1 to 4:1 which means that the produced water production would reach to around 177 million barrels/ year (483736 barrels/day)(Jumana, 2014).The amount of discharged produced water is increasing within time due to the growing up in energy requirement around the world. Figure 2, illustrates the dramatic increase of produced water for last decades.

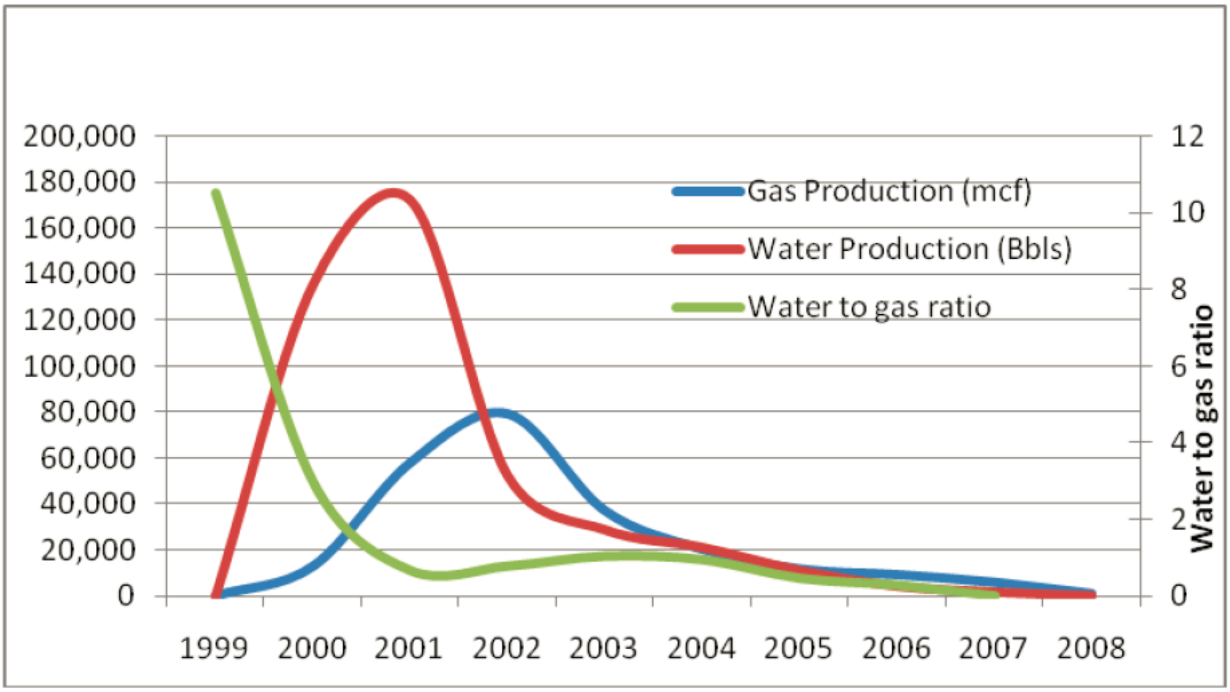


Figure 1: Typical water and gas production for Coal bed methane source (Katie et al., 2011)

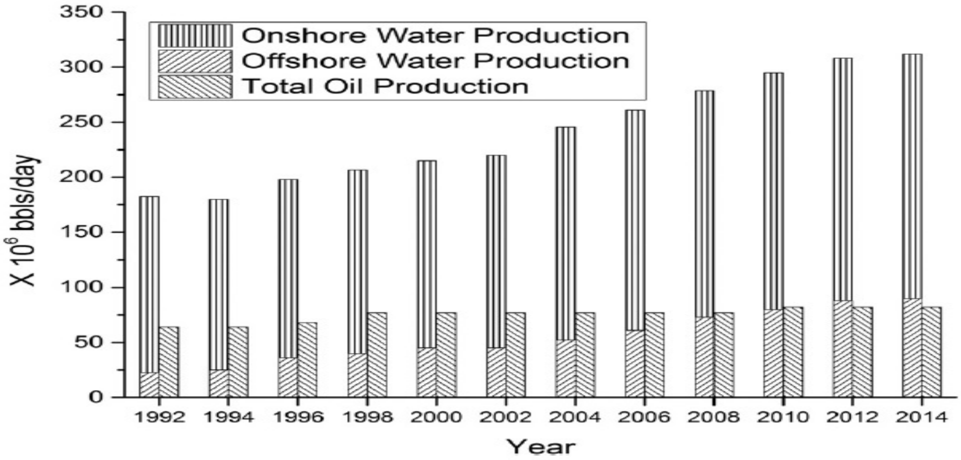


Figure 2: Amount of produced water last decades (Ferro and Smith, 2009).

Produced water compositionand its analysis techniques

The chemical, physical and biological characteristics of produced water vary depending on two factors; (i) The geographical location and (ii) Geological formation of the reservoir which stated the qualitative and quantitative prosperities of inorganic (salts, silt and metals), organic (BTEX, PAHs and light or heavy oils) and microbial (anaerobic bacteria, algae and fungi) contents which co-existed in produced water (Bader, 2007). In addition to the additive chemicals such as corrosion inhibitors, scale inhibitors, emulsion breakers, dissolvers and biocides, which add more complications for treatment management.

Electrical conductivity (EC)

According to ASTM D1125, EC measure the conductivity (ability to carry up electric current) of water sample which is the reverse value of electric resistance. EC value is related to the ionic contents of dissolved salts in water. Also it is very critical to determine if this water applicable for irrigation directly or need dilution before use. Also it determines the plant species can be irrigated with. It indicates the salinity of water sample with the total dissolved salts. In the literatures, great variation in the EC value could be presented. This is due to type of produced water, if it is injected water or it is formation water and the type of reservoir rocks. The EC value changes from 0.838, 18.77, 20.8, 23.8, 24.4, 47.6, 107.28 and 109 mS/cm (Alley et at., 2011; Gen& Kenneth, 2016; Jumana, 2014and Mehmet et al., 2008)

Total suspended solids (TSS)

Total suspended solids (TSS) indicate the particulates which are not dissolved in water coming from even particles of reservoir rocks (clay or/and quarts) under effect of water pressure or chemical precipitations due to chemicals injections such as iron sulfide, the particle size may change from 1 mm to 0.1 µm according to type of particles, and this could be due to the suspended solids are more denser than water and it can be separated easily by gravity precipitation, unless it cause problems in pipe lines or vessels, so in this case the protective action is needed (Blumer, 2007).

Total dissolved solids (TDS)

Major dissolved solids in produced water are salts of sodium, calcium, potassium and magnesium as cations and chlorides, bicarbonates, sulfates as anions. Range of TDS differs according to geological properties of reservoir and type of wells production. 70% of produced water have TDS more than 100,000 mg/L which known as brine (Blumer, 2007) while the TDS of sea water in extreme conditions is about 40,000 mg/L.In some cases concentration of TDS reaches to 300,000 mg/L due to the high evaporation rate (Fakhrul-Raziet at., 2009).

Major anions and cations in produced water

Produced water has almost the same salts content as the sea water; in which sodium and chloride are the most abundant ions then coming calcium, magnesium, potassium, sulfate, bromide, bicarbonate, iodide and boron. But produced water differs than sea water in the total salinity (Collins, 1975).As it in sea water ranges from 32 to 36% while in produced water varies from few parts of thousand % to saturated brine ~ 300% (Jerry et al., 2011). Table1, shows the concentration of major ions in produced water compared to sea water

Table1: Compare between major ions concentrations in sea water with different published produced water.

Element/ion (mg/L)	**Sea water (Collins 1975)**	**Produced water (Collins 1975)**	**(Gen & Kenneth, 2016)**	**(Alley et al., 2011)**	**(FkhrulRazi et al., 2009)**	**Two fields in Qatar (Jumana, 2014)**	**(Mehmet et al., 2008)**	**(Yeung et al., 2011)**
Salinity	35000	5000 – 300 x10^6	25,638 – 17,365	24,400	1,200 – 10,000	154,000- 328,000	35,800	32,000
Na^+	10,700	23,000 – 57,300	5,553 – 4,384	405 – 126,755	132 – 97,000	479 – 1,860	3,165 – 14,322	2,910
Cl^-	19,353	46,100 – 141,000	7072 – 8,458	36 – 238,534	80 – 200,000	73,330 – 229,360	3,199 – 16,745	n/a
Ca^{+2}	416.00	2,530 – 25,800	104 – 269	4 – 52,920	13- 25,800	n/a	n/a	1,220
Mg^{+2}	1,294	530 – 4,300	15 – 37	2 –5,096	8 – 6,000	23 – 56.8	n/a	8,512
K^+	387.00	130 – 3,100	n/a	1.6 – 42.6	24 – 4,300	16 -62	n/a	45.8
SO_4^{-2}	2,712	210 – 1,170	29 – 368	8 – 13,686	5 – 1,560	15 - 49	355-1,700	0.33
Br^-	87.00	46 – 1,200	n/a	n/a	n/a	n/a	n/a	n/a
Sr^{+2}	0.008	7 – 1000	16.5 – 32	0.5-2.2	0.02 – 1,000	3,623- 6,535	n/a	102
NH_4^+	-	23 – 300	n/a	n/a	n/a	3	n/a	n/a
HCO_3^-	142.00	77 – 560	955 – 1,190	n/a	n/a	n/a	n/a	
I^-	167.00	3 – 210	n/a	n/a	n/a	n/a	n/a	
Boron	4.45	8 – 40	n/a	n/a	5 – 95	0.379 – 1,023	n/a	2.2

n/a: not analyzed

Alley et al., 2011 conducted a comparison studies for different numbers of produced water from five sources;541 wells of Shale Gas (SGPW), 4000 wells of conventional natural gas (NGPW), 165 wells of conventional oil (OPW), 377 wells of coal-bed methane (CBMPW) and 137 wells tight gas sand (TGPW), the authors concluded that the majority of SGPW, NGPW, OPW and TGPW had chloride ion concentrations range from saline 30,000 mg/L to hyper saline 40,000 mg/L while CBMPW had chloride less than 5000 mg/L. Also one of the interested conclusions in their study was the significance difference between constituents of SGPW and CBMPW due to distinct source rocks and water flow pattern.

Sodium adsorption ratio (SAR) (equation. 1) and electric conductivity (EC) of the produced water are very critical for the probability of suitability to use water in irrigation or not. Also concentration of boron must be considerable for the healthy life of plants (Ayers and Westcot, 1994)

$$SAR = \frac{[Na]}{\sqrt{0.5([Ca]+[Mg])}} \qquad \text{…………equation 1}$$

Where the concentration in meq/L, if value of SAR is more than 3 it means that high salt accumulation in soil, so more water quantity is needed to wash soil sodicity accumulation (Ayers and Westcot, 1994).

Chemical oxygen demand (COD)

COD is defined as the amount of oxygen molecules in milligrams needed to chemically oxidize all chemicals per liter of water sample, which give fast indication about how much that water sample contaminated with toxic compounds as waste (APHA, 1980).Different standard methods are available to measure COD and all of them are depending on strong digestion of the sample in presence of strong oxidizing agent such as chromate ion with carry on blank test in order to determine total chromate with the remaining in sample test. The amount of COD can be determined usingAPHA5220D (1980). According to the literature the

COD vary from 1220, 16000 and 24000 mg/L (Fakhrul-Razi et al., 2009;Jumana, 2014 and Mehmet et al., 2008) respectively.

Determination of COD value in wastewater gives indication about how this water contaminated with organic compound and how much oxygen molecules will be consumed to oxidize these organics. It also decreases the dissolved oxygen amount of the water body, which will have a negative impact on the living organisms. Also, when it compared with BOD_5 give indication about how much the bioremediation will be successful in remediation processes.

Biochemical oxygen demand (BOD)

Biochemical oxygen demand or biological oxygen demand refers to the amount of milligram oxygen consumed by microorganisms to digest organic materials present in waste water during specific time period under certain temperature (US EPA 5210B). It gives indication about the amount of waste contaminants which can biologically degraded. It was 595 mg/L in (Veil et al., 2004), 2800 and 4800 mg/L in (Jumana, 2014) and 7000 mg/L in (Mehmet et al., 2008).

Different standard methods were used to determine BOD; dilution method following (US EPA 5210B) which depends on measuring dissolved oxygen before and after incubation period, Manometric method depends on measuring the difference in pressure during incubation in closed pressure sensor bottles and biosensor which depends on enzymatic biosensors measurement.

Benzene, Toluene, Ethylbenzene and Xylene (BTEX)

The most soluble volatile compounds in water are BTEX with solubility product values of 1790, 526, 169 and 178 mg/L of benzene, toluene, ethyl benzene and xylene, respectively (Frintrop et al., 2011).It is important to measure them in produced water. Maryam, 2016 investigated the concentration of benzene, toluene, ethylbenzene and xylene in gas produced water and the results were 11170, 278.1, 4648.6 and 1156.8 µg/L, respectively. Neff, 2002also investigated three offshore productions and the BTEX results were 84 to 2300 µg/L Benzene, 89 to 800 µg/L toluene, 26 to 110 µg/L ethyl benzene and 13 to 480 µg/L xylene. Dorea et al., 2007conducted a study on Permian basin oil field, and the results of BTEX were as following: 1500 to 778510 µg/L Benzene, 100 µg/L toluene, 2010 to 399840 µg/L ethylbenzene and 10 to 460 µg/L xylene. Jumana, 2014 showed that the total BTEX was ranged from 4500 to 6740 µg/L.

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons or poly nuclear aromatic hydrocarbons which have a great concern last decades due to their carcinogenic effect on human and animals (Manoli& Samara, 1999).This is due to their lipophilic character which they are easily absorbed through skin and distributed to inter organisms (WHO 2004) and due to their hardness to degrade even by simply chemical reactions or by biodegradation for that they have long residence time(Hussein et al., 2016).The average concentration of PAHs in produced water range from 0.04 to 3 mg/L(Jerry et al., 2011).Dorea et al., 2007 investigated concentration of total PAHs in oil field produced water in Brazil, and the results were ranging from 0.003 to 4540 mg L^{-1}.Faksness et al., 2004 in a review study explained that the major PAHs individuals in produced water are 2 or 3 aromatic rings, such as naphthalene and phenanthrene rather than the 4 or 6 aromatic rings which are less water soluble.

Phenols

The concentration of total phenolic compounds are ranged from0.009 to 23 mg/L (Fakhru’l-Razi et al., 2009)**.** The highest concentration of phenols in produced water could be from the chemicals that could be added during production to facilitate the pumping of waxy and viscous oil or the degradation of added surfactants such as PolyPhenol ethoxylate surfactants which contain octylphenols and nonylphenols (Getliff and James, 1996).

Heavy metals

One of the major sources of risk causing pollutants in produced water is heavy metals (Collins, 1975). They cause toxicity for human, animal and plants even with low concentration. Presence of heavy metals in water body can be from natural sources such as rocks minerals erosion or anthropogenic chemicals adding (Olsen et al., 1995). It can be dissolved in water or particulates suspended matter matrix. Their concentration range varies according to metal type and produced water sources from fragmentation of part per billions to hundreds of part of millions. Flame atomic spectrometer (FAS), inductive coupled plasma optical emission spectrometer (ICPOES) and inductive coupled plasma with mass spectrometer (ICPMS) are the main techniques used to analyze heavy metals in produced water after sample preparation as filtration and dilution to be within the calibration curve ranges according to (US EPA 200.8). Fakhru’l-Razi et al., 2009 reviewed the average of heavy metals concentration in different types of produced water as shown in Table 2.

Table2: Heavy metals average concentration by (Fakhrul-Razi et al., 2009)

Metal	Conventional mg/L	Unconventional mg/L
Antimony	n/a	ND – 0.005
Aluminum	< 0.50 – 410	0.005 – 1.52
Arsenic	0.004 – 151	ND – 0.158
Barium	ND – 1740	0.445 – 125
Beryllium	< 0.001 – 0.004	n/a
Bicarbonate	ND – 14,750	4.53 – 49,03
Boron	ND – 95	0.05 – 30.6
Bromide	150 – 1,149	ND – 41.1
Cadmium	< 0.005 – 1.21	ND – 0.076
Calcium	ND – 74,185	ND – 5,530
Chloride	2 – 254,923	ND – 52,364
Chromium	ND – 1.1	ND – 3.71
Cobalt	n/a	ND – 0.010
Copper	< 0.002 – 5	0.001 – 1.448
Fluoride	n/a	0.57 – 20
Iron	ND – 1,100	0.001 – 258
Lead	0.002 – 10.2	ND – 0.098
Lithium	3 – 235	ND – 1.50
Magnesium	ND – 46,656	1.2 – 918.9
Manganese	< 0.004 – 175	ND – 3.11
Mercury	< 0.001 – 0.002	ND – 0.014
Molybdenum	n/a	ND – 0.448
Nickel	< 0.08 – 9.2	ND – 0.082
Selenium	n/a	ND – 1.27
Silver	< 0.001 – 7	ND – 0.14
Sodium	1 – 149,836	97.3 – 32,013
Strontium	0.02 – 6,200	ND – 47.9
Tin	ND – 1.1	n/a
Titanium	< 0.01 – 0.7	n/a
Vanadium	n/a	ND – 0.290
Zinc	0.01 – 35	0.005 – 5.639

Alley et al., 2011 studied the differences in heavy metals concentration between different produced water well types; shale gas (SGPW), tight Gas (TGPW), coalbed methane (CBMPW), natural Gas (NGPW) and oil wells produced water (OPW) as shown inTable3.

Table3: Comparison between different well types produced water in heavy metals content (Alley et al., 2011)

Metal symbol mg/L	Shale Gas produced water (541 samples)	Tight gas produced water (137 samples)	Coalbed methane produced water (377 samples)	Natural gas produced water (4000 samples)	Oil produced water (165 samples)
As	n/a	0.17	0.0001-0.06	0.002 -11	0.17-0.857
B	0.12-24	n/a	0.002-2.4	Nd-58	n/a
Ba	nd-4370	n/a	0.01-190	0.091-17	0.07-7.4
Br	nd – 10600	n/a	0.002-300	0.038-349	n/a
Cd	n/a	0.37	0.0001-0.01	0.02-1.21	0.03-0.2
Cr	n/a	0.265	0.001-0.053	0.002-0.231	0.1-1
Cu	nd – 15	0.539	Nd-0.06	0.02-5	0.33-2.68
Fe	Nd-2838	0.015	0.002-220	Nd-1100	0.1-0.5
Li	Nd-611	n/a	0.0002-6.88	0.038-64	n/a
Mn	Nd-96.5	0.525	0.002-5.4	0.45-6.5	1.4-8.1
Ni	N/a	0.123	0.003-0.2	0.002-0.303	2.7-9.5
Sr	0.03 – 1310	n/a	0.032-565	0.084-917	0.05-2.2
Zn	Nd – 20	0.076	0.00002-0.59	0.02-5	6.3-17.4

Discharging produced water.

Due to that produced water is highest waste byproduct of oil and gas industries, all companies deal with it as waste for disposal, but the most driven force for disposal choices is the economic cost. So oil and gas producers have many choices between land disposal, subsurface reinjection, surface sea water discharge or beneficial using (Katie et al., 2011).

Land disposal or discharge is not expansive method however it is applicable only in case of high quality produced water. Rather than, it will cause huge contamination for soil, water and vegetation of surrounding environment. Reinjection of produced water into the injection well near to production well is the first choice to keep required pressure and water level of that geological area up to required (Veilet al., 2004).However, reinjection in some cases can be imposable; these could be due to geological formation of subsurface that cannot accept the re-injected water.Reinjection can cause contamination for other water aquifer present in this area, or it can be used as injection water for new well production but after certain treatment (Neff, 2002).Clark and Veil, 2011 estimated the average of treatment of injected water costing in range of 1 to 4 US$ per barrel. The produced water can be directly discharge to sea water,especially in offshore production wells which have high negative impact on marine biology (Mount et al., 1997). UK oil and gas Environmental report 2016mentioned that since 2000 the volume of sea discharged produced water in the UK decreased by 37 % and one fifth of the total volume of produced water in 2015 were re-injected.In 2014, the report of the international association of oil & gas producers (IOGP) stated that 0.6 tons of produced water globally were discharged and 1.2 tons were re-injected per ton of hydrocarbon produced. (IOGP, 2014)**.**

Discharge regulation guidelines

Taken in account the technical, environmental and economic issues, many of standards have been set to regulate the discharge of produced water, one of them is European Union standard which set level of hydrocarbons and TDS in discharged produced water must be less than 5mg/L and 10 mg/L respectively (Ashagi et al., 2007). In addition,two discharge limits have been developed by The US Environmental Protection Agency (EPA); one based on technology and another based on water quality. Effluent limit guidelines (ELGs) founded on Best Available Technology Economically Achievable (BATs) focus on oil and grease limits in produced water, and established monthly and daily limits average as 29mg/L and 42 mg/L, respectively based on air flotation technology.Beside the national oil and grease limits, there are other regional limits like flow rate, toxic metals, organics, toxicity and NORM which are varying according to vulnerability of each area (Jisi et al., 2016). In State of Qatar, the Environmental Protection law no 30 for 2002 give regulation roles and standards for all industrial waste discharge and management with guidelines limits in executive list annex 3& 4 of the law as shown in Tables(4 – 5).

Table4:Shows the Guideline limits of waste discharge in seawater according to Qatari Decree Law No.30 for 2002

Parameter	Symbol	Limit	Unit
Total Dissolved Solids	TDS	1500	mg/ L
Total Suspended Solids	TSS	50	mg/ L
pH	pH	6-9	
Ammonia	NH_4^+	3	mg/ L
Chlorine Residual	Cl_2	0.05	mg/ L
Cyanide	CN	0.1	mg/ L
Fluorides		1	mg/ L
Phosphate as P	PO_4^{-3}	2	mg/ L
Sulphate	SO_4^{-2}	0.1	mg/ L
Biochemical Oxygen Demand	BOD5	50	mg/ L
Chemical Oxygen Demand	COD	100	mg/ L
Urea		2	mg/ L
Nitrogen (total)	TKN	100	mg/ L
Aluminium	Al	3	mg/ L
Arsenal	As	0.5	mg/ L
Barium	Ba	2	mg/ L
Boron	B	1.5	mg/ L
Cadmium	Cd	0.05	mg/ L
Chrome (total)	Cr	0.2	mg/ L
Cobalt	Co	2	mg/ L
Copper	Cu	0.5	mg/ L
Iron	Fe	1	mg/ L
Lead	Pb	0.1	mg/ L
Manganese	Mn	0.2	mg/ L
Mercury	Hg	0.001	mg/ L
Nickel	Ni	0.5	mg/ L
Zinc	Zn	2	mg/ L
Silver	Ag	0.005	mg/ L
Oil & Grease	O & G	15	mg/ L
Phenol (total)		0.5	mg/ L
Halogenated Hydro carbonates & pesticides of all types		0.1	mg/ L
Dioxin		1.34×10^{-7}	mg/ L
Tri Halo methane	THM	100	mg/ L

Table5: shows the Guideline limits for treated wastewater using in irrigation proposals according to Qatari Decree Law No.30 For 2002 executive list Annex 3/4

Parameter	Symbol	Limitfor Irrigation	Limit for landscape	Unit
Total Dissolved Solids	TDS	2000	2000	mg/L
Total Suspended Solids	TTS	50		mg/L
pH	pH	6-9	6-9	
Ammonia as N	NH_4^+	15	15	mg/L
Chlorine Residual	Cl_2	0.1	0.1	mg/L
Cyanide (Total)	CN	Nil	0.2	mg/L
Dissolved Oxygen	DO	> 2	> 2	mg/L
Fluoride	F	15	15	mg/L
Phosphate as P	PO_4^{-3}	30	30	mg/L
Sulphate	SO_4^{-2}	400	400	mg/L
Sulfide	S^{-2}	0.1	0.1	mg/L
Biochemical Oxygen Demand	BOD5	10	50	mg/L
Total Kjeldahl Nitrogen as N	TKN	35	35	mg/L
Chemical Oxygen Demand	COD	150	150	mg/L
Aluminum	Al	15	15	mg/L
Arsenic	As	0.1	0.1	mg/L
Barium	Ba	2	2	mg/L
Boron	B	1.5	1.5	mg/L
Cadmium	Cd	0.05	0.05	mg/L
Chromium ,total	Cr	0.01	0.2	mg/L
Cobalt	Co	0.2	0.2	mg/L
Copper	Cu	0.2	0.5	mg/L
Iron	Fe	1	1	mg/L
Lead	Pb	0.1	0.1	mg/L
Manganese	Mn	0.05	0.05	mg/L
Mercury	Hg	0.001	0.001	mg/L
Nickel	Ni	0.2	0.5	mg/L
Zink	Zn	0.5	0.5	mg/L
Sodium Absorption rate	SAR	10	10	mg/L
Oil & Grease		10	10	mg/L
Phenols		0.5	0.5	mg/L
Total Organic Carbon	TOC	75	75	mg/L

While polycyclic aromatic hydrocarbons (PAHs) are considered as none decaying solid and liquid substances, which are completely prohibited to discharge in the water Environment.

Produced water as waste and environmental risk

As already mentioned in the previous sections, it highly recommended not discharging crude produced water without fully treatment processes in order to eliminate or reduce some of risk causing parameters. Also the impact and resulted risks are depending on receiving environment, volume and rate of discharged produced water.

Marine environment

The marine is first environment could be affected by produced water discharge. Dose-related risk and Effect Assessment Model (DREAM) is a numerical three dimensional time-dependent model, that computes transport, exposure, dose, and effects in the marine environment which has developed at SINTEF with cooperation with Total, ENI, ExxonMobile, ConocoPillips, Petrobras, Shell and British Petroleum as decision support tool for operational Marine discharge management (Neff & Kenneth, 2011). Environmental Impact Factor (EIF) would be used as an indicator for the potential impacts from produced water and drilling release into marine environment (Reed 1989; Reed & Hetland, 2002; Johnsen et al., 1998; Rye et al. 1998). Many of studies tried to illustrate the impact of produced water discharge on marine environment such as Mount et al., 1997. They developed a multi regression model by conducting more than thousand acute experiments to describe the toxicity of common salt ions to zooplankton and fathead minnows. They concluded that all major ions have a lethal concentration causing multiple toxicity equal to summation of individual ion toxicity.

Torgeir et al., 2013 summarized the great impacts of produced water discharge of alkylphenols and PAHs contents due to accumulation in cod (*Gadus morhua*) and blue mussel caged causing interruption for reproduction function, and affect several physiological biochemical pathways and genetic expression, and toxicity effect can restrict to about 2 Km distance from the discharge point.

PAHs may cause over oxidation metabolic stress (Sturve et al., 2006), DNA denaturation (Aas et al., 2000), toxic effect for embryos (Carls et al., 2008), forming neoplasia and DNA adducts in liver of some fishes by metabolic intermediates (Myers et al.,

1991) or/ and cardiac function disorder (Incardona et al., 2004). Alkyl phenols (Aps) have great impacts due to their hormone interfering (Arukwe et al., 2000).According to Meier et al., 2011,APs reduce the amount of spermatozoa in male fish and delay the maturation of gonads in females and males at a significant body dose of 20 mg AP/kg.

Other researcher have debated that APs exposure have very low negative effect risk on fish populations (Gray, 2002), Jonny Beyer et al., 2012 studied the major oil producing regions of Tampen, Ekofisk and Sleipner, to perform most risk assessments based on two risk threshold values 40 and 4 ng/L of alkyl phenols (APs) in sea water through two study steps; the first one screening then second step is comparing the results with fish distribution data for three fish species Cod, Saithe and Haddock, they found that none of three species reach the positive risk level.(Eriksen et al., 2006) compered the bioavailability of R^{226} for Juvenile Atlantic Cod in presence and absence of scale inhibitor (SI4470) when found that presence of SI4470 enhance the uptake of Ra^{226} rather than alone bioavailability. Huge amounts leaks cause dramatic effects such as killing fishes; small releases might contribute to aggregate variations in the total salt structure and marine population diversity (Aïda et al., 2014)

Landscape

Discharge of produced water to land space even in constructed impoundments such as artificial reservoirs, associated wetlands or standing bodies of surface waters can be source of groundwater pollution (Romeo, 2014). Deleterious effects from produced water to the soil often have been done (Vance et al., 2008). Andy et al., 2015 used produced water in irrigation proposal and found the sodium adsorption ratio (SAR) increased from 2 to 21meq /L due to sharp increase for sodium ion with huge decrease of calcium and magnesium ions in tested soil. Two main soil parameters: salinity and sodicity are affected by produced water (United States Salinity Laboratory Staff, 1954). Hydrocarbon oil pollution can cause deterioration of soil structure such as loss fertility and organic, minerals contents, nutrient constituents, loss of soil (Palese et al., 2003).

Produced water treatment techniques

The main objective of produced water treatment is to remove all harmful constituents (Ebenezer and George, 2013). Arthur et al., 2005 summarized the objectives of produced water treatment in:

1- De-oiling (remove oil and grease)
2- Remove soluble organics
3- Disinfection
4- Dissolved sold & salts removal
5- Gases removal
6- Softening by remove hardness
7- Miscellaneous; removing NORM

Using only one technology to treat produced water almost is not sufficient to be acceptable in all global environmental standards, so more than two or three technologies are required to be incorporated to give reasonable results that would meet with environmental standards (Ray et al., 1993).Due to the large volume of produced water as waste, so the economic cost of treatment technologies is effective choice in implantation of treatment for the producers (Neff, 2002). Shell Company has established formal water to value program to help the producers to minimize quantity of produced water, minimize the costs of treatment technologies and searching for available facilities to be handled with large volumes of produced water (Khatib and Verbeek 2003).

Physical Treatment

Gravity separation

The simplest oil separation method is the gravity separation tank with different configuration which allows to oil float to the water surface and suspended particulates and solids to still down (Al Malah et al., 2000) but still need more techniques for dissolved parameters.

Adsorption

The adsorption method is applicable to remove Mg, Fe, TOC, BTEX, oil and heavy metals with an efficiency of 80% removal from produced water. Different types of adsorbents as activated carbon, organoclays, activated alumina and zeolites could be used (Spellman, 2003). Carbon after activation by wet air oxidation process can used for adhering organic compounds in produced water (Hansen & Davies, 1994)and enhance its quality by removal of BTEX (Maryam et al., 2016). Also Organo-caly produced by combining sodium montmorillonite clay with a cationic quaternary amine salt is used to remove free insoluble hydrocarbons from produced water (Fakhrul-Razi et al., 2009). Combination between activated carbon and organoclay reduce the hydrocarbon concentration below the water quality standards and to undetectable limits (Doyle et al., 1997 and 2000). Methyl methacrylate based copolymer beads and di-vinyl benzene copolymers reduced oil content by 85% efficiency from produced water (Carvalho et al., 2000). Hydrophobic zeolite pellets in fixed bed or resin packed column were used to remove soluble organic compounds and can be regenerated by acid wash with optimization of factors enhance adsorption capacity such as temperature, pH, salinity, oil contents and column dimensions (Hansen et al.,1994). Janks and Cadena, 1992 succeeded to get efficiency of BTEX removal with 85% by using “tailored” zeolites (made by adsorbing neutralized amines to zeolites) from saline produced water. Combination between Crudersorb and polymeric resins technologies reduce oil and grease in offshore produced water less than 29 ppm (Ali et al., 1998). Sulfonated copolymer of styrene and di-vinyl benzene was successful as acid ion exchange resin in removing calcium and magnesium from oil free produced water in case of TDS less than 50,000 ppm and fall in others due to sodium competition (Jan et al., 1992). Total Oil Remediation and Recovery

(TORR^{TM}) is a technology developed by The EARTH Canada Corporation to remove and recover dispersed oil in water 2µm and more by multi-stages of adsorption and separation systems (Plebon et al., 2005). Generally, adsorption used in multi-steps processes as polishing step since it can be overloaded (saturation) easily by adsorbates and need to be back flashed periodically (Colorado School of Mines, 2009).

Filtration

Filtration technologies used for removing oil, grease, TOC, suspended solids and dissolved salts by passing produced water through porous beads such as sand, gravel, anthracite, walnut, shells, ceramic, metal oxides and others. Efficiency of produced water filtration can be reach 90% or more if enhanced by adding coagulants before filtration process (Colorado School of Mines, 2009).

Sand filter

Heavy metals can be removed by sand filtration after the pH adjustment, aeration and sufficient retention time for settling of solids reaching results more than 90% iron removal (Adewumi et al., 1992).

Membrane filter

Membranes filters are porous films with special pore size, which selectively separate liquid from its contents. Four types of membrane filters were used for waste water treatment; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Xu P & Drewes, 2006), which utilize high pressure to achieve filtration of produced water. With special characteristic for the removed species as molecular weight which has known as Molecular Weight Cutoff (MWCO) as Daltons. Arthur et al., 2005 summarized the different MWCO of membrane filters in Table (6)

Table6: Summarize the different membrane filters comparison according to Arthur et al., 2005

	MF	UF	NF	RO
MWCO (**Arthur et al., 2005**)	>100,000 Daltons 10-0.1 µm	10,000 – 100,000 Daltons 0.05 – 5x10^{-3} µm	1,000 – 10,000 Daltons 5e^{-3} – 5x10^{-4} µm	Salts and smallest MWCO 1 x10^{-4} – 1x10^{-5} µm
Application (**Arthur et al., 2005**)	Bacteria, viruses, suspended solids etc	Protein, starch, viruses, colloid, silica, organics, dyes, fats, paint solid etc	Starch, sugar, pesticides, herbicides, divalent ions, organics, BOD, COD, detergents etc	Metal ions, acids, sugar, aqueous salts, dyes, natural resins, monovalent salts, BOD, COD, ions etc
Energy consumption	Not available	Not available	It uses electrical energy and its energy requirement is less than what is required in RO systems. Approximately NF system requires 0.08 Kwh/bbl to power its high-pressure pumps (*Ventresque et al., 1997*)	RO use electrical energy for its operation. requires 0.46–0.67 KWh/bbl if energy recovery device is integrated 0.02–0.13 KWh/bbl of energy to power the system's pumps (*Xu Pei et al,. 2009)*
Life cycle.	10 years	7 years or more	3–7 years	3–7 years
Overall cost	Not available	capital cost is \$0.02–\$0.05/ bpd. Approximate Operation and Maintenance costs \$0.02–\$0.05/bpd (Colorado School of Mines)	Capital cost range from \$35 to \$170/bpd. Operating cost is _\$0.03/bbl.	Capital costs of from \$35 to \$170/bpd and operating costs are _\$0.03/bbl.

Al zahrani and Mohammad (2014) reviewed the implementation of membrane filters in produced water treatment.They concluded that, the advancement of membrane treatment require; (i) A standard reference for waste water and produced water composition developed by comprehensive characterization, (ii) Investigation of contribution done by chemical additives to the membrane filters, (iii) Integrating membrane technologies with a creative solution for minimizing produced water generation, (iv) Extensive research is necessary to achieve zero liquid discharge by recycling treated produced water within refinery processes that require low water quality levels, such as water for crude washing, quench water, and service water and finally (v) Future research to recover valuable by-products from produced water treatment, such as lithium which is used for power generation.

Hydrocyclones

Hydrocyclone is a physical method used to separate solids from liquids. They are made from separator has cylindrical top and conical base made from metals, plastics or ceramic with no moving parts. Its performance is related to the angle of its conical section (Ebenezerand George, 2013). Hydrocyclones can remove particles in the range of 5–15 mm and have been widely used for the treatment of produced water (Jain Irrigation Systems, 2010). Around 8 million barrel per day of produced water treated with hydrocyclones (Svarovsky, 1992). It is used as a pre-treatment process in combination with other technologies. It has a long lifespan and do not need chemical use or pre-treatment of feed water. The main disadvantage of this technology is large slurry of concentrated solid waste generation (Ebenezer and George, 2013).

Evaporation

Evaporation treatment methods are proposed for treating saline wastewater containing oil components (Bertness et al., 1989). Vertical tube, falling film, and vapor compression evaporation are effective methods for produced water treatment because they:

1. Eliminate physical and chemical treatments; no chemical sludge is therefore, produced, and the costs of waste and life cycle are lowered.
2. Require less materials and labor for maintenance.
3. Reduce the amount of produced water de-oiling equipment.
4. Increase Once Through Steam Generators (OTSG) feed-water quality, and improve OTSG reliability (Heins & Peterson, 2005).

However, due to presence of high impurity levels of solid salts, the reuse of these materials is impossible (Lefebvre& Moletta, 2006). Becher, 2000 proposed wastewater distillation using two proprietary new designed systems (PNDS). The system recovered over

95% of the energy required distilling water as follows; new mechanical vapor recompression (MVR) system recycled the produced water into distilled water.

Ion exchange

Ion exchange is a reversible chemical reaction where positively or negatively charged ions available in water are replaced by which in resin (Arthur et al., 2005).Resins of ion exchange are classified to cation exchangers which exchange positively charges, and anion exchangers which exchange negatively charges such as strong and weak acids for cations and strong and weak base for anion exchangers. The Ion exchange is widely applied technologies in industries operations for wastewater treatment specially removing of monovalent, divalent ions and metals by resins (Clifford, 1999). Also the Ion exchange process has been suggested to remove boron from produced water (Nadav, 1999). However, the process has a lifetime around 8 years and requires pretreatment options for solid removal, and chemicals for regeneration and disinfection of resins (Ebenezerand George, 2013). The process is also used in produced water treatment when the range of TDS about 500 – 7000 mg/L depending on the chemistry of feeding water and quality of resin used (Ebenezer and George, 2013). The major disadvantages of ion exchange are the high operating, chemical cost with high fouling sensitivity.

Gas flotation

The mechanism of gas flotation is governed by the density differences between bubble-particles aggregate and water. Different types of gases can be used in flotation technique; air the most common gas except in specific flotation processes. When air is not preferable due to presence of oxygen which leads to possible metal precipitation and explosion. Methane gas may be used instead of air due to its availability and compatibility with feeding influent water. Carbon dioxide and nitrogen can also be used in some specific gas flotation processes.

The particles such as TSS and oil adhere to gas bubbles forming lighter agglomerates that easily float to the surface then skimmed from the top. (Jayaprakash et al., 2016)

(Wang et al., 2010) summarized the key steps of gas flotation as following:

i. Gas bubbles generation with considering volume and size of bubbles related to oil concentration in produced water to forming a stable bubble-particle aggregate.
ii. Collision between bubbles and oil droplets to promote the bubble –drop
iii. Attachment of gas bubbles to oil droplets creating strong adhesion between them.
iv. Rise and floating of aggregates then skimming them continuously to enhance more floating.

Moreover, Eskin et al., 2015 listed the developments of flotation system as following:

i. Reducing aeration time e.g. pressure accumulator, pressure vessel with porous media and electric discharge, etc.
ii. Uniform distribution of gas bubbles by modification of internal flotation cell structure, using ring aerator and/or parabolic baffles, etc.
iii. Integrated framework as using multi stages dissolved flotation, hybrid combination with cyclone, filtration, etc.

Freeze-thaw/evaporation (FTE)

Freeze thaw evaporation (FTE) process developed in 1992 by Energy & Environmental Research Centre (EERC) and BC Technologies Ltd (BCT). It is a process that used naturally occurring temperature swings to alternately freeze and thaw produced water, concentrating the dissolved solids and creating relatively large volumes of clean water suitable for beneficial uses (Sorensen et al., 2002). Salts and other constituents of produced water lower its freezing point below zero degree so when produced water is cooled below 0^{o}C but not below its freezing point, pure ice crystals and unfrozen solution are formed. The unfrozen solution have high concentration of dissolved contents in produced water and are drained from ice to collect pure ice then melted to obtain clean water (Boysen, 2007). 50% of water can be recovered during winter with low ambient temperature but at other seasons no recovery occurred so FTE works as evaporation pond. FTE applicable for removing TDS, TSS, volatile and semi-volatile organics with a 90% removal efficiency (Boysen et al.,1999).

Chemical treatment

Chemical treatment of produced water is limited to the chemical reactions that lead to precipitation or oxidation by normal chemicals.This would avoid risk of adding new chemicals to the treated water and avoid production of new wastes (Barratt et al., 1997).

Chemical precipitation

Chemical precipitation is the converting of dissolved salts into undissolved forms to be easily removed through different types of chemical reactions such as changing in pH. This would encourage the electron transfer to a participated form (Fe^{2+} to Fe^{3+}) or addition of precipitate chemicals as lime. Produced water with 10,000 ppm TDS and 2000 ppm hardness was successfully transformed into steam generator quality feed water by modified hot lime process (Fakhrul-Razi et al., 2009). Suspended solids and oil can be removed to levels 97% with adding coagulation chemicals such as mixed metals Fe, Mg and Al polynuclear polymers (Zhou et al., 2000).Houcine, 2002 succeeded to remove <95% of heavy metals from the produced water by using spill sorb, calcite and lime.

Oxidation

Chemical oxidation treatment technique depends on oxidation reduction reactions for the pollutants exist in produced water by adding highly active oxidant (Barratt et al., 1997) such as oxygen, ozone, peroxide, permanganate, and chlorine. Recently, many investigations have been focused on advanced oxidation processes (AOP) by using a combination of strong oxidants (Renouet al., 2008) causing breakdown for their toxic form into less toxic or completely oxidation to carbon dioxide and water (Wang et al.2003). It can be used for treat color, odor, COD, BOD, organic and some inorganic pollutants (All consultant handbook, 2003). Its cost during process is relatively high due to the chemicals consumption and the energy usage which is around 18% of the total cost, with a high life time exceed over 10 years (Colorado. 2009). The disadvantages of chemical oxidation are the byproducts which can be created during the process and not easy to be removed. And in some cases, the chemical oxidation process used in other treatment process as pretreatment step to improve the final product, such as in biodegradation (Renou et al., 2008).

Biological treatments

Biological treatment means using living organisms such as bacteria, fungi, algae and plants in removing or reducing the toxicity effect of various pollutants of produced water (Palmer et al., 1981). In most cases, the pollutants used as energy feeding source, and therefore, the right choice of the organism specie, optimization, establishing and maintenance of feeding processes, environmental conditions, additives and consortia are the most critical parameters that used to enhance the treatment efficiency (Lawrence et al., 2008). Biological aerated filter (BAF) is a film of bacterial growth fixed or attached to packed bed media such as rocks, gravel or plastics which are permeable and downstream feeding with wastewater to allow the contact between pollutants in wastewater with bacterial film when biochemical oxidation processes occur (Katie et al., 2011). It is the most effective on feeding waters with chloride concentration less than 6,600 mg/L (Ludzack and Noran, 1965), COD less than 400 mg/L, BOD less than 50 mg/L and oil level below 60 mg/L (Katie et al., 2011). Li et al., 2005 studied the COD removal from produced water starting with 2600 mg/L. They able to achieve more than 90% removal efficiency by using immobilized *Bacillus* sp attached to polyvinyl alcohol (PVA) under aerobic conditions. Ji et al., 2009 achieved 65% removal efficiency under anaerobic condition using microbial community of Clostridia, Rhodopseudomonas and Methanosarcina. Mang et al., 2009 achieved biodegradation efficiency 63.5% of COD, 45% of NH_4, 79.5% for TSS and 68% TPH for three months conducted acidification/bio-oxidation system with hydraulic retention time (HRT) 32 Hours and volumetric load of 0.28 kg COD/m^3/day. Zahra et al., 2015 developed spiral microbial electrochemical cell (SMXC) (Fig. 3) as fuel cell to enhance produced water treatment with power and hydrogen production where achieved 330 mV and H_2 gas 400mL/m^3/day, with 90% in organic removal with starting salinity >200,000 ppm using consortia of halophile and halotolerant anaerobic microbial community which obtained from sludge of sedimentation tank.

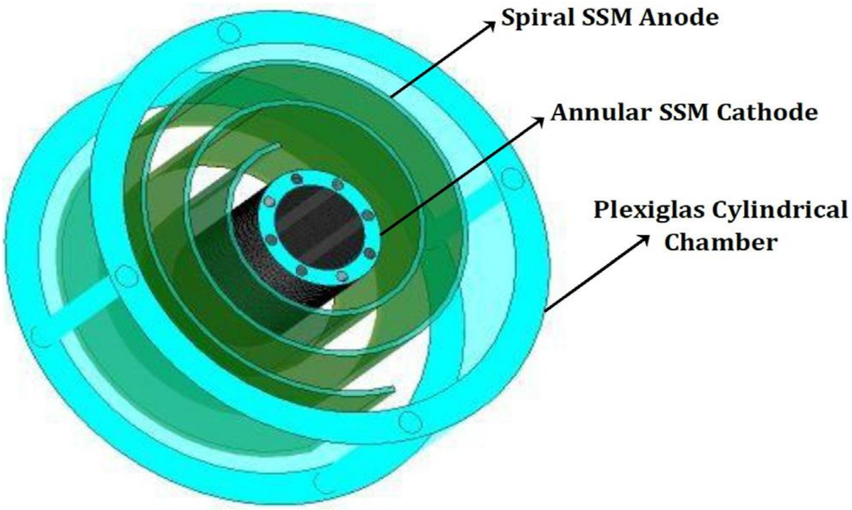


Figure 3: Schematic diagram of spiral microbial electrochemical cell (Zahra et al., 2015)

Zachary et al., 2015 used microbial capacitive desalination cell (MCDC) (Fig.4) for biodegradation of organic compounds in produced water. They succeeded to remove 6.4 mgTOC/hr in biological reactor and 36 mgTDS per gram carbon of electrode per hour with producing electric potential average 0.25 V

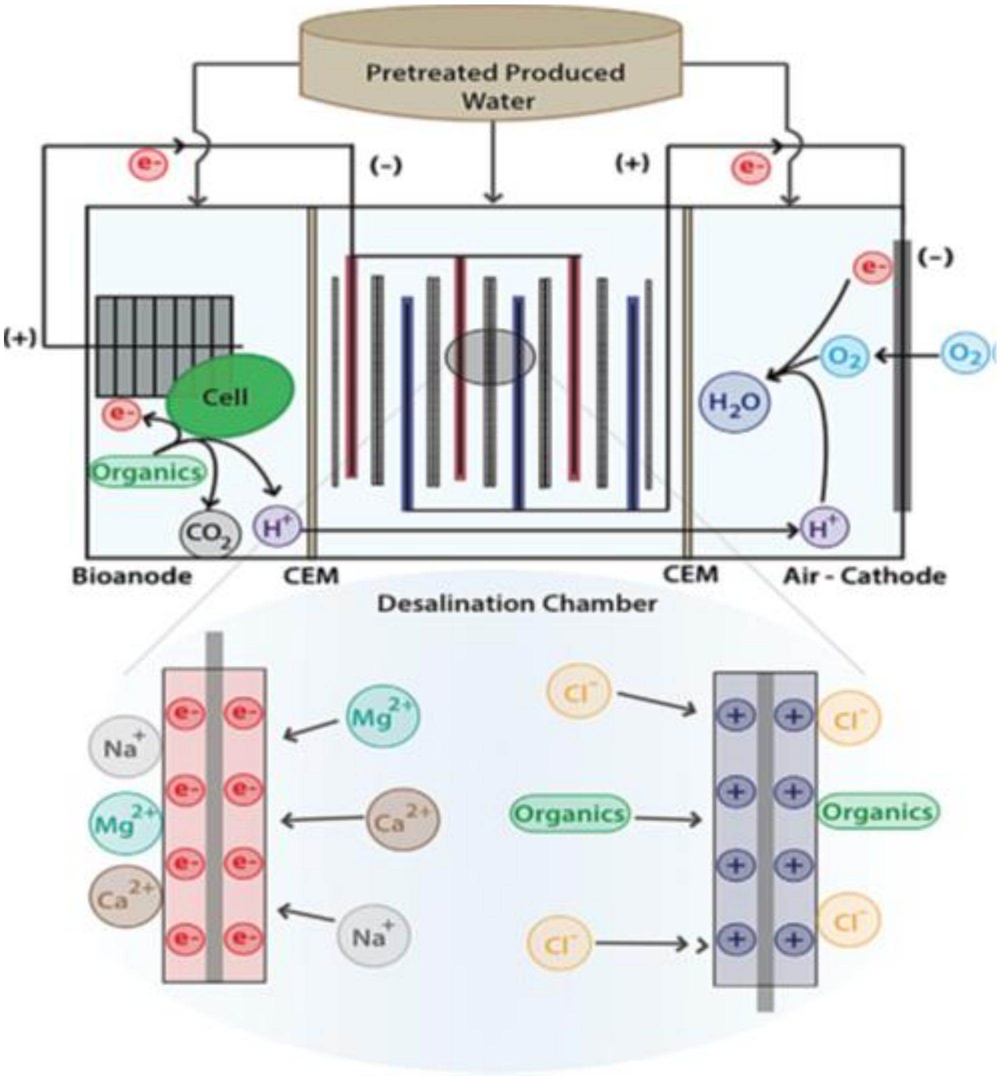


Figure 4: Schematic diagram of MCDC of (Zachary A. et al., 2015)

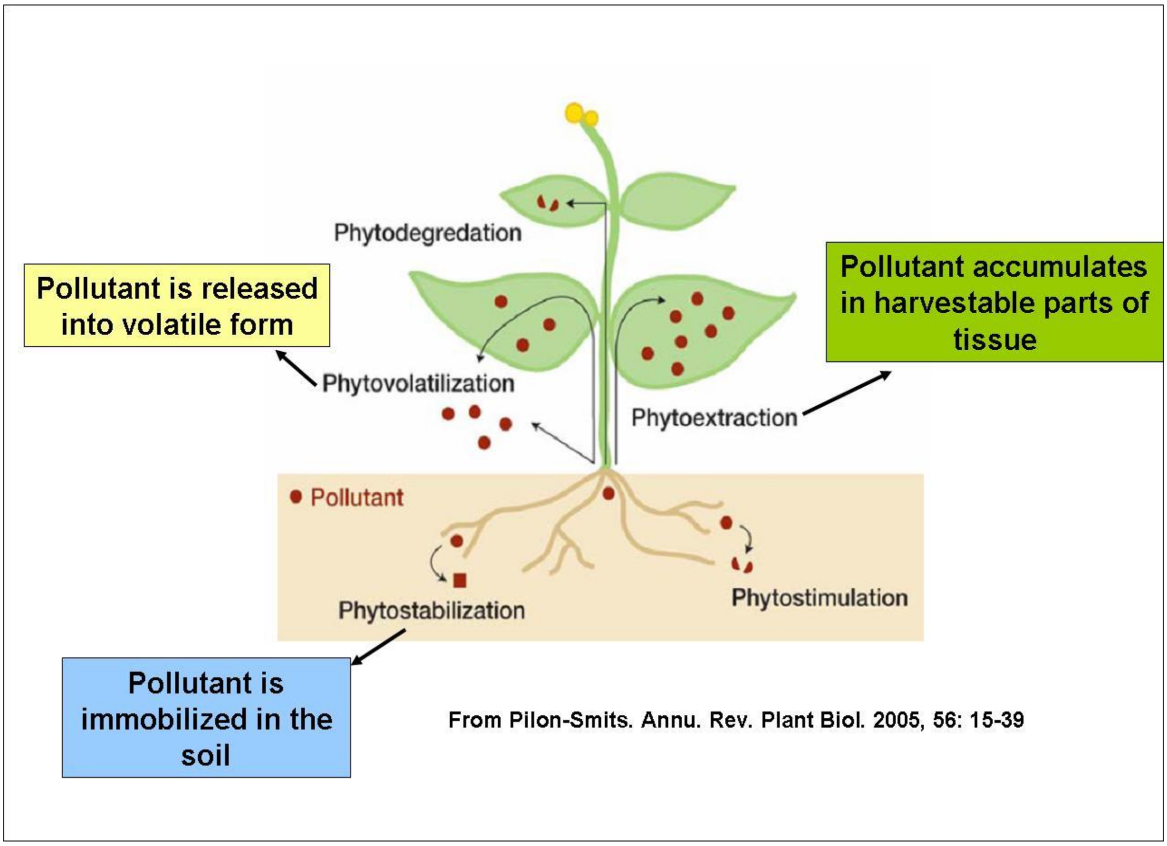
Mahapatra et al., 2014 succeeded to treat wastewater with algal growth with removal efficiencies 86% for TOC, 90% for TN, 89% for NH4, 70% for TP and 76% for OP with algal biomass productivity 122 mg/L/d, which gave heat production 123.4 J/g after decomposition.

Phytoremediation

One of the economic effective and promising biotechnologies for cleaning of polluted water and soil is phytoremediation (Hazrat et al., 2013).Salt et al., 1998 defined phytoremediation as the use of living green plants for in situ degradation, removal and control of contaminants in soil, surface water and ground water. Phytoremediation technologies are highly suggested for many reasons such as low cost as the driven forces is solar energy, effective in superficial position with low contaminants level, efficient in treatment of wide range of environmental pollutants and environmentally friendly technologies(Dhir, 2013). Phytoremediation is divided into different types according to mechanism of remediation as (Fig. 5) (i) Phytoextraction in which the pollutants are absorbed by roots, and they are translocated to above ground parts where it can be harvested; it is applicable for remediation of heavy metals. (ii) Phytostabiliztion where the plants used to inhibit mobility of pollutants in the soil layers by absorption onto root tissues, (iii) Rhizofilteration in which the roots of plants act as filters prevent passing of contaminants with surface water, (iv) Phytovolatilization which is ability of plants to absorb and metabolite the contaminants then emitted them to atmosphere through leaves tissues, (v) Rhizodegradiation; known as the breakdown of pollutants in the soil by the microbial consortia localized in root zone of the plant where the root's execration enhance the microbial activity and (vi) Phytotransformation; which is metabolization and degradation of pollutants within plant physiological processes (Burken et al., 1997; Thompson et al., 1998; Campos et al., 2008 and Dhir, 2013). The plants able to absorb and accumulate more than 100 mgCd/Kg, 1000 mgAs, Cr, Co, Cu, Ni, Pb or Se/Kg or 10,000 mgZn or Mn/Kg are defined as Plant hyper-accumulators (P-H) (Brooks & Schnoor, 1998; Roosens et al., 2003; Vamerali et al., 2010; Ucer et al., 2013and Goolsby et al., 2015).

George et al., 2007 used co-produced water from coalbed natural gas wells which had 1.6 - 4.8 dS/m electric conductivity and 17 – 57 mmol/l SAR for irrigation of grasslands, seeded grass hayfields, and alfalfa hayfields during 2003 to 2004 the results show decreasing in overall species evenness also increase in the soil EC and SAR values to depth 30 cm with reducing in surface infiltration rate.

Different plant species were successfully used in phytoremediation. Some were terrestrial and others were aquatic, while terrestrial species have been found more effective in phytoremediation applications as they have larger root systems which enhance higher contaminations uptake. So trees and grass species were commonly used. (Dhir, 2013). Alfalfa, sunflower, Indian mustard, *Thalspi* sp., maize and sorghum have been explored because their characteristics such as high biomass production, biofuel production and fast growth (Schnoor, 2000).



From Pilon-Smits. Annu. Rev. Plant Biol. 2005, 56: 15-39

Figure 5: Summarizes the phytoremediation mechanisms

Zea mays

Zea mays (maize or corn)is an annual crop plant belong to family Poaceae (grasses) (USDA 2005). It is growing up to 4 m tall and the leaves are broad sheath arranged in two opposing rows along the stem. Zea mays could be used in human feeding, animal feeding, and industries purposes such as paper production and biofuel production.Changjun et al., 2015 suggested that adding surfactant for maize growing in PAH contaminated soil enhancing the phytoremediation and tissue accumulation of PAHs by helping microbial activity in the soil. Bittsanszky et al., 2010 transformed Zea mays with Glutathione S-transferase GSTs which is detoxifying enzyme catalyzes the conjugation of glutathione tripeptide with organic pollutants such as herbicides. Van et al 2013 produced biogas from *Zea mays*that was grown on contaminated soils with cadmium with an average yield 20 x 10^3 mg dry biomass/hectare.Gheju et al., 2013 exposed *Zea mays* to soil contaminated with Zn from concentration range 64 mg/Kg to 1800 mg/Kg and they have gotten success results of phytoextraction by adding trisodium citrate, disodium oxalate or disodium dihydrogen ethylene diamine tetra acetic acid and chelation agents. Meers et al., 2010 proposed using zea mays in moderately contaminated soil with Cd, Zn and Pb with meaning of phyto-attenuation for production of energy reach to 46,000 kWh per hectare per year.

***Sorghum bicolor* (grain sorghum)**

It belongs to family Poaceae. Sorghum is used as a drought tolerant, summer annual rotational cover crop either alone or seeded in a warm season cover crop mixture (Barkworth, 2003). Sorghum would be one of the ideal candidates for phytoremediation of contaminated soil because of its high phytoremediation potential, large biomass production, and utilization in biofuel production (Kokyo et al., 2015).

***Medicago sativa* (Alfalfa)**

Medicago sativa (alfalfa) is a perennial flowering plant belong to family Fabaceae (legumes) with trifoliate leaves. *Medicago sativa*is used mainly for livestock feeding. Gardea-Torresdey et al., 1998 used alfalfa shoots to remove 90% Pb, Cu, Ni and Zn ions from aqueous solution at optimum pH 5 then recovered with 0.1 M HCl, as phytofiltration application. Karina et al., 2016 used plant alfalfa and soybean in DDT contaminated soil. The results showed that no morphological effects, while the main effects were in levels of protein contents; glutathione synthesis transferase activity and antioxidant capacity in stem, leaves and roots. Anna Muratova et al., 2015 used the alfalfa roots exudates to oxidize phenanthrene presence in quartz sand 0.03 g/kg. Alfalfa can tolerate much higher average root zone EC levels up to 8.0 dS/m before significant yield reductions or mortality occurs (Kevin et al., 2005)

***Helianthus annus*(Sunflower)**

Sunflower is fast-growing, annual herb and belongs to family Asteraceae (tournesols). Harry et al., 2008 carried out study on *Helianthus annus* exposed to 30 mg/L of Cd, Cr and Ni for 17 days. The results showedthe highest metal accumulation in roots of plant with over expression of class III chitinase which induced at level of transcription in presence of As. Cafer et al., 2004 used the sunflower in application of phytoremediation for Cd, Cr and Ni from a silty-clay loam soil in presence and absence of chelators as EDTA and Citric acid and the results showed the highest yield obtained in presence of EDTA at concentration of 0.1g/kg.

***Salsolabaryosma*.**

Salsola baryosma is shrubby plant with continuous branches, reddish not jointed stemand fleshy alternate leaves. It belongs to family chenopodiaceae and is known in Qatar as “Gaghraf” (Batanouny, 1981).

Rui et al., 2012 studied the tolerance mechanisms of *Salsolasp*. for stress of different Pb concentrations compared with *Chenopodium* sp. the results indicated that *Salsola* sp. exhibited higher Pb tolerance than *Chenopodium* sp. by two ways to reduce Pb toxicity; cell wall precipitation and state transfer of free Pb. Kilani et al., 2013 studied the Cd accumulation in root and shoot systems of *Salsola* sp in presence or absence of NaCl or EDTA. The highest Cd accumulation was in shoot system in presence of EDTA which increase the bioavailability of Cd, while presence of high concentration of NaCl reduced the root accumulation of Cd.

***Phragmites australis* (Ghab)**

Perennial robust reed with creeping rhizomes and hollow culms, flat leaf-blades. The plant is fairly common in spilling sewage area, and belongs to family Poaceae (gramineae) (Batanouny, 1981). Angelique et al., 2013 obtained log-linear correlation between Phragmites root concentration factor and partition coefficient after 7 days of exposure of phragmites to organochlorines (OCs) such as 1,4-dichlorobenzene, 1,2,4-trichlorobenzene and hexa-chlorocyclohexane where the plant’s bio-concentration factors were highly significant, the study represent that the translocation of organochlorine from roots to shoots increases with solubility and volatility of OCs.

Chapter 3. Experiments and methodology

Soil preparation

The soil was collected from the Mesaieed area in Qatar.It was then mixed with peat moss purchased from the local market.Peat moss composition is shown in Table (7). The plant samples were then planted in 20 cm diameter plastic pots.

Table7: Peat moss composition.

Basic material	Mixture of slightly and fully decomposed raised bog peat (H2-H8)
Density	>200 kg/m^3
Electric conductivity (EC)	< 1.0 mS/cm
Salt contents	< 1.5 g/l
pH	5.5 – 6.5
Nutrients	50 – 300 mg/L Nitrogen (N) 80 – 150 mg/L Phosphorus (P_2O_5) 80 – 400 mg/L Potassium (K_2O)

The collected soil was kept dry in sunlight outside the greenhouse, thenit was passed throw 2mm siever. The soil was then mixed with peat moss by ratio 3:1 (*v*:*v*) using 5kg-pot. 108 pots were used for plantation experiment. 500 g of the mixed soil was packed in a plastic bag and labeled as a control soil before treatment and transferred to laboratoryfor further analysis.

Plantation

The seeds of the crop plant species were purchased from the local market (Sunflower, maize, alfalfa and grain sorghum), while the seedlings of *phragmitis*. sp (Ghab) werecollected from El-Khour area (North of Doha)and *Salsola. sp*. was collected from the biology field of Qatar University campus, at least 20 seedling for each species.

Seeds of crop plants were sown in 18 pots as four seeds in each pot, while the native Qatari plants were transferred directly from natural habitat to the pots in the greenhouse; each pot had one seedling for total 20 pots (18 pots were used in experiments and 2 pots for recovery, if needed). The irrigation was then started with tap water for the first ten days till healthy seedlings were obtained for all species. Then, the pots were randomly divided into six groups, each group contained three pots for each plant species; each group received different treatment as shown in Table8.

Table8: The irrigation treatment groups

Group no	Treatment no.	Irrigation with
1	Control	Tap water
2	Treatment 1	10% produced water
3	Treatment 2	20% produced water
4	Treatment 3	30% produced water
5	Treatment 4	40% produced water
6	Treatment 5	50% produced water

Water for irrigation

The produced water sample was provided by Total Company and used at different dilution percentages for irrigation as shown in Table (8). Tap water was used for irrigation in the first ten days of plantation and continued for the control group. Tap water was also used for dilution of produced water to create the percentages used in irrigation of other groups as experimental treatment as illustrated in Table(8).Table(9) shows the water volume used for irrigation throughout the experiments.

Table9: Preparation of water treatment used in irrigation

Treatment	Produced water volume added	Tap water volume added	Total volume	Percentage
Control	0	10 L	10L	0%
Treatment 1	1L	9L	10L	10%
Treatment 2	2L	8L	10L	20%
Treatment 3	3L	7L	10L	30%
Treatment 4	4L	6L	10L	40%
Treatment 5	5L	5L	10L	50%

Each pot was irrigated with 150 mL every three days for each treatment group. Samples of 1.0 L for both produced and tap waterswere collected in separate dark, clean and sterile glass bottles and were transferred to the laboratory for chemical analysis.

Water characterization

Physical characterization (pH, DO, EC, TSS & TDS):

The pH, dissolved oxygen (DO) and electric conductivity (EC) of the samples were measured using multi-probes pH meter from WTW. The calibration procedure was performed using buffer solutions provided with the instrument according to the reference method ASTM E70, D888 and D1125 for pH, DO and EC, respectively.

Total dissolved solids TDS and total suspended solids TSS (ASTM D5907):

The filtered 100 mL of the water samples on the previous weighted 0.45 µm filter paper (F1) were transferred to 250 mL pyrex beaker weighted before as (B1). Then both filter paper and the beaker were completely dried at 105 ^{0}C. After complete dryness they were allowed to cool in the desiccator, then the weights were recorded, the weight of the beaker after (B2) and weight of filter paper after (F2). Then equation 2& equation 3 were applied to calculate TDS and TSS, respectively.

$$\text{TDS (mg/L)} = (B2 - B1) \times 10 \qquad \text{.........equation 2}$$

$$\text{TSS (mg/L)} = (F2 - F1) \times 10 \qquad \text{.........equation 3}$$

Chemical characterization:

Determination of benzene, toluene, ethyl benzene and xylene (BTEX). (USEPA5021a)

In the experiments, headspace auto-samplerTurboMatrix HS-40 was used in order to eliminate the sample introduction and therefore; there is no need for sample preparation.The calibration curve was prepared using the stock standard CLP-BTEX-0.5X 100 µg/mLfor each individual component of BTEX. The standard material and samples were analyzed by Clarus

680 GC from PerkinElmer. Different dilutions of spiked de-ionized water were prepared as shown in Table(10).

Table10: Preparation of standard curve points for BTEX analysis using GC/FID with the head space

No.	Stock standard added	DW added	Final concentration
1	5 µL	4995 µL	0.1 µg/mL
2	50 µL	4950 µL	1 µg/mL
3	250 µL	4750 µL	5 µg/mL
4	500 µL	4500 µL	10 µg/mL

Four dilutions and blank de-ionized water with three repetitions of produced water were prepared, a 5 mL in head space vials and crimped very fast to prevent evaporation process. Then the column optimization was performed under the operating temperature and flow rate parameters as shown in Table (11).

Table11: Gas Chromatography parameters for BTEX analysis.

GasChromatograph	PerkinElmer Clarus 680 GC
Head space connector	Universal connector
Oven program initial Temperature	50 ^{O}C
Hold time1	5 min
Ramp1	8 ^{O}C/min to 280 ^{O}C
Hold time2	6 min
Equilibration time	1 min
Headspace control	On
Column	Elite volatiles- 60m x 320 µm x 1.0 µfilm
Carrier gas	Helium
Flow rate	1.0 mL/min
Detector temperature	250 ^{O}C

Sample Introduction	**PerkinElmer TurboMatrix HS-40 trap**
Needle Temp.	100 ^{O}C
Transfer line Temp.	110 ^{O}C
Oven temp.	80 ^{O}C
Dry Purge (helium)	5 min
Trap hold time	6 min
Thermostating Time	10 min
Pressurization time	1 min
Column pressure	30 psi
Vial pressure	40 psi
Shaker	On

Then, the calibration option of TotalChrom software was used to determine the BTEX content of the produced water.

Determination of dissolved Anions and Cations (EPA300.1 partA and ASTM D6919).

Metrohm ProfAnCat 850 Ion Chromatographywas used. Metrosep A Supp 4 - 250/4.0 column was used for anions separation. Metrosep C4 - 150/4 column was used for cations separation. Sodium carbonate and sodium hydrogen carbonate were purchased from SigmaAldrech and were used to prepare anion' eluent. De-ionized water 18.2MΩ from Millipore was used for dilution.Five digit micro-balance KENAR was used throughout the experiment. Multi-component cation mix 2 CRM for Cations and Multi-component anion mix 2 CRM for anions were purchased from AccuStandard, 0.2 µm syringe filters, accurate micropipette, trace metal HNO_3, dipicolinic acid, magnetic stirrer with magnet bars,50 mL class A measuring flasks and 12mL pointed end PTEF tube with pressured caps were also used in performing the experiments.

A 20 mL produced water sample was filtered through 0.2 µm syringe filter and diluted 100 times by de-ionized water to be within range of linearity of calibration curve.

The setup of the IC instrument was carried out as follows: installation of separation columns in their right positions and direction, followed by preparation of eluent solutions; 3mM $Na_2CO_3$and 1mM $NaHCO_3$ for anions and 1.7mM HNO_3with0.7 mM dipicolinic acid for cations. Calibration curve solutions are prepared by dilution of stock standard solution as shown in Tables (12& 13).

Table12: Preparation of standard curve solutions from stock reference material IC-MAN-2-1 Accustandard.

Curve point	Stock solution added volume (IC-MAN-02-1) (mL)	DW added volume (mL)	Final concentration (mg/L)
Standard 1	0.25	49.75	F 0.5,Cl 1,NO_3 2, Br 2,PO_4 3 and SO_4 2
Standard 2	0.5	4.5	F 1,Cl 2,NO_3 4, Br 4,PO_4 6 and SO_4 4
Standard 3	2.5	47.5	F 5,Cl 10,NO_3 20, Br 20,PO_4 30 and SO_4 20
Standard 4	5	45	F 10,Cl 20,NO_3 40,Br 40,PO_4 60 and SO_4 40
Standard 5	12.5	37.5	F 25,Cl 50,NO_3 100,Br 100,PO_4 150 and SO_4 100

.

Table13: Preparation of standard curve solutions from stock reference material IC-MCA-2-1 Accustandard

Curve points	Stock standard added volume (mL)	D. W. added volume (mL)	Final concentration (mg/L)
Standard 1	0.25	49.75	0.5
Standard 2	1.25	48.75	2.5
Standard 3	2.5	47.5	5
Standard 4	5	45	10
Standard 5	12.5	37.5	25

Determination of trace metals (EPA 200.8)

NexIon 300 PerkinElmer Inductive coupled Plasma- Mass spectroscopy ICPMS was used in determination of the trace metals in produced water samples. ICP-MS calibration std1 for method EPA 200.8 was purchased from AccuStandard, Ultrpure Nitric acid for trace metal analysis and 0.2 µm syringe filters were purchased from local market.

Produced water sample was filtered with a 0.2 µm syringe filter and diluted by 1% Nitric acid up to 50 times, then it was injected on pre-calibrated method of water analysis method using ICPMS. Calibration curve was generated by different dilutionsof the stock standard 10 mg/Lto prepare calibration points from 0.001 to 1 mg/L of different elements available in the standard (Li, Be, Ba, B, Ca, Cu, Cd, Co, Cr, Fe, Pb, Zn, Ag, Au, Sr, Cs, Mg, Na, K, As, V, Ni, Al, Mn, In & Bi).

Chemical oxygen demand COD (colorimetric closed reflux).

Standard solution of KHP 1mg/L equivalent to 1.175 mg/L COD was prepared.Deionized water was used as blank. Several dilution sets of the filtered produced water of range 0.5, 0.1, 0.05 and 0.01 were prepared, then $HgSO_4$ wasadded for the diluted sample in order to eliminate chloride interference by ratio 10:1 (Hg : Cl).Then the sample was filtered again in order to remove excess $HgCl_2$ according to the equation (4).

$$Hg^{2+} + 2Cl^{-} \leftrightarrow HgCI_2 \downarrow \qquad \text{……..equation 4}$$

A volume of 2 mL from each test was added to the kit tube, then the tubes were placed in a hot block at 148°C for 2 hours to complete digestion. After that time, all tubes were kept to cool down in order to precipitate all particles. Then the COD measurements were carried out using HACH 2800 instrument.

Biochemical oxygen demand BOD

A volume of 2mL of the sample was added to the kits test tube and was mixed for 3.0 minutes. Then the BOD measurements were carried out using HACH 2800 spectrometer with following the standard operating procedure.

Determination of polycyclic aromatic hydrocarbons (PAHs) EPA 610:

A 200 mL of filtered produced water mixed with200 mL of dichloromethane UPLC grade in a 1L dry cleaned separating funnel. The sample was, then shake for 5 minutes. The mixture was standing for separation for 10 minutes, then the dichloromethane layer (lower one) was collected in a 500 mL flask. Then the previous step was repeated several times to make sure that all remaining organics were completely extracted. The extraction was re-concentrated under steam of nitrogen in water bath, then it was re-dissolved in acetonitrile for UPLC injection.

UPLC method

The PAH mix standard M-8310-Q-ATI was used to prepare three points of the calibration curve, then inject the extracted sample on the same method using the following UPLC parameter Table(14).

Table14: The UPLC method parameters for PAH determination

Instrument	**WATERS Acquity UPLC**	
Column	Nova Pack C18 4µm 3.9 mm x 150 mm	
Pump method	Mobile phase A: Water, mobile phase B: Acetonitrile	
Gradient	Time (min).	%B
	0	40
	4	40
	23	90
	23.5	90
	24	95
	24.5	100
	25	100
	29	100
	29.5	40
	34	40
Flow rate	1mL/min	
Detector	UV at 230.8 nm, FLD Ex260, Em 420	

Total organic carbon (APHA 5310 B).

Solution of 1M phosphoric acid was fresh prepared and filled in The Skalar TOC instrument bottle. A calibration curve from different concentration of Oxalic acid solutions was prepared. Then the water sample was injected on the same method of TOC.

Soil characterization

Soil granules size determination (FAO, 2006 Guideline for soil description).

A Weigh of 100 g dried soil sample was sieved. Then the ratio for each mesh size weight was calculated to the total weight. By using the soil particle-size classes shape mentioned in FAO 2006 guideline, the soil class was able to be determined.

Determination of accumulated dissolved salts

This test carried out for all soil samples collected from each treatment of *Salsola sp.* from surface to approximately 5 cm depth (root zoon), then well mixed in plastic bag to determine the salts composition and accumulation during experimental period.

A weight of 2 g Soil samples was collected from each treatment pots after the end of the irrigation period. Then it was dried at 80°C overnight. After dryness, a volume of 20 mL de-ionized water was added and was shake well for 30 minutes. The water solution was centrifuged and filtered to be injected on Ion chromatography.

Anions and cations determined using ion chromatography as mentioned before in water analysis, but after getting the concentration of washed soil solution (weight/ volume) we convert the concentration into weight/weight as in equation (5)

Concentration in soil (mg/Kg) = (conc. (mg/L) × 20 mL)/2 gram…..…equation 5

Determination of volatile organic in soil

To determine the volatile organic compounds which are coming from produced water and still accumulated in the soil.

The samples for volatile organic analysis were collected direct from the pots into 20 mL head space vials and closed with crimper directly before transferred to the laboratory, after good closed vials the samples can be preserved in refrigerator at 4^{o}C till suitable time of analysis.

Optimization for head space injection method on GC/FID instrument was done, using calibration standards of diesel range. Volatile hydrocarbons were prepared by addition of stock standard (0, 2, 5 and 10 µl) to 2 gram blank soil into 20 mL vials and crimp them very fast in stable cooled atmosphere away from ventilation or hot temperature in order to eliminate error of volatility. Then the injection sequence was prepared as blank soil, serial standard vials and samples of experimental soil vials (control, 10%, 20%, 30%, 40% and 50% treatments) respectively. Using Total-Chrom software option the results of volatile organic compounds in soil will be calculated.

Determination of Trace metals in soil (USEPA METHOD 3052)

To determine the trace metals accumulated in soil sample and their effect on plant growth and the ratio of transferred metals between soil and plant tissue. Soil sample transfers to laboratory and dried using heating oven at 100^{o}C overnight, mixed very well and grinding using motor grinder, then sieved by 20 mesh size (850 µm), so digestion processes were started using 65% nitric acid of trace metal analysis, 40% hydrofluoric and 30% hydrochloric

From 0.25 to 0.5 grams sieved dried grinded soil sample weighted in complete clean dried PTEF digestor vessel after cancelling the weight of the vessel on five digit balance. In the fume hood area a 9mL of concentrated nitric acid, 3.0 mL of concentrated hydrofluoric acid, 2.0 mL of concentrated hydrochloric acid and 1.0 mL of hydrogen peroxide were added for each vessel. Blank was prepared by adding same quantity of all acids with 0.5 ml de-ionized water in one vessel. All vessels were sealed and placed into the rotor of microwave digestor. After digestion, the digested solutions were transferred to 50.0 mL polypropylene vials, and diluted to 50.0 mL with de-ionized water. Some case centrifugation is needed to precipitate any particulate in solution before injection on ICPMS. NexIon300 ICPMS was calibrated with serial of dilution standards prepared from 10 mg/L stock standard multi-elements ICPMS standard 1, to obtain serial of 0.01, 0.1, 0.5, 1 and 2.5 mg/L standards then the injection and calculation of trace metals in soil samples were carried. Note the gotten results from direct software calculation are in mg/L related to solutions of standard so we converted to mg/Kg by applied equation (6).

$$\text{Final concentration } mg_{metal}/Kg_{\ soil} = (X \times V) / M \text{……….equation 6}$$

Where, X is the concentration from ICPMS in mg/L, V is the volume of final dilution which is 50 mL for all samples, and M is the mass of the soil sample in grams

Determination of polycyclic aromatic Hydrocarbons (PAHs) in soil (US EPA 8310).

a weight of 10 grams of soil sample was weighted and inserted in column of 250 mL soxhelt device, then 100 mL of Dichloromethane add to 250 mL flask, soxhelt closed and installed in mantel heater adjusted at 80^{o}C with connect column to water cooling cycle, system kept 1 hour for complete extraction, after the system cooled, the dichloromethane transferred to clean beaker and kept under ventilation system to re-concentrate by reducing volume to 2 mL, the 2 mL filtered by 0.2 µm syringe filter and injected on UPLC using the same method of PAHs in water analysis.

Final concentration calculated using equation (7)

$$\text{PAHs mg/Kg} = (\text{result mg/L x } 2) / 10 \text{…………….equation 7}$$

Plant characterization

Determination of moisture content ratio

Plant tissues cleaned with deionized water and dried by warping in paper tissues, wet weight (w1) recorded using five digit balance, the weighted parts putted in glass petri dishes and labeled by marker within name of plant species, date and treatment name, then transferred to 100°C heated oven overnight, next day transferred to a desiccator to cool before recording dry weight (w2) with the same balance. Appling equation (8) for moisture content calculation.

Moisture percentage $\% = \frac{W1-W2}{W1} x100$ ……………… equation 8

Determination of trace metals in plant tissues (*Robinson et al. 1986)*

Wet digestion was carried using $HNO_3$and H_2O_2 according to White and Douthit, 1985 as following: The plant' tissues were dried overnight at 100°C, then grinding using mesh size 20. A weight 0.25 to 0.5 g of dry and fine tissue powder was put in PTEF beaker. Then 10.0mL of 70% trace metal grade Nitric acid were added. Then beakers were covered by glass watch and heated at 120°C for 60 minutes on hot plate, after the heating time beakers were allowed to cool. After cooling, 4 mL of 30% $H_2O_2$was added, then heating cycle is repeated for another 30 minutes, and alternative addition of acids and heating till the digestion solution becomes completely clear. After it cooled down the solution was diluted to 50 mL final volume with deionized water.

Using calibrated Optima 7300 ICPOES from PerkinElmer, the digested solution are injected to analyze trace metals in plant tissues.

FTIR scanning for plant parts

Plant tissue parts were dried at 100°C overnight in order to remove free water particles. Then, the dried tissues were mixed and ground to very fine particles. Spectrum 400 FTIR with UATR from PerkinElmer was used in the experiments.

Chapter4. Results and Discussion

Water used in irrigation

The samples of tap water and produced water used in the experiments were physically and chemically analyzed. The results are shown in Tables (15, 16 & 17).

Table15: produced water results (physical and major ions)

Parameter	unit	Produced Water	STD	Uncertainty for PW	Reference method	Equipment used
EC	mS/cm	240	6.81	± 1	ASTM D 1125	WTW multi parameter pH meter
pH		6.54	0.11	±1.55	ASTM E70	
TDS	mg/L	310,000	5571.97	±10	ASTM D5907	Gravimetric
TSS	mg/L	6760	31.58	±10		
F	mg/L	4.0	0.08	±0.5	USEPA 300.1 method A	Metrohm 850 Prof Ion Chromatography
Cl	mg/L	122,000	503.32	±10		
Br	mg/L	710	1.53	±10		
NO_3	mg/L	500	10.00	±5		
PO_4	mg/L	4.0	0.29	±0.5		
SO_4	mg/L	50	5.00	±2		
CO_3	mg/L	134	0.58	±5	ASTM D6919	
Na	mg/L	61,000	543.72	±200		
K	mg/L	1850.0	76.38	±1.8		
Ca	mg/L	10,700.00	50.85	±100		
Mg	mg/L	2,200	11.85	±10		
NH_4	mg/L	126	1.00	±10		
SAR	meq/L	139.94	0.05	±1.25	Calculated by Equation 1	
Ionic strength		3.79	0.00	ND	Calculated by $I = \frac{1}{2} \cdot \sum c_i \cdot Z_i^2$ Where C_i is ion concentration mole/L and Z_i is ion valence	

From Table 15, it can be concluded that the produced water wasa hypersaline according to (Neff & Kenneth, 2011), and the TDS more than 300 g/L, which confirms that the produced water from a conventional oil well.

The results of Cl, Na, Ca, K and Mg were very high concentration 122, 61, 10.7, 1.85 and 2.2 g/L respectively. This level of the highest concentration recorded before in Qatar in the studies of Jumana, 2014 and Maryam et al., 2016. While nitrate and sulfate ions came in lowest concentration 500 and 50 mg/L respectively, comparing to Collins, 1975; Mehmet et al., 2008; Alley et al., 2011& G. Li et al., 2016.

Table16: Produced water heavy metals

Metals	Unit	Result	STD	Uncertainty	Refe. Method	Equipment used
Li	mg/L	4	0.58	±1	EPA 200.8	PerkinElmer NexIon 300 Inductive coupled plasma Mass Spectrometer ICPMS
B	mg/L	38.6	0.5	±2		
Ba	mg/L	5.5	1	±1		
Be	µg/L	0.44	0.01	±0.01		
Bi	µg/L	339	1.5	±5		
Al	µg/L	136	2	±7		
As	µg/L	13.7	0.5	±2.5		
Ag	µg/L	24	0.84	±3		
Cd	µg/L	0.70	0.01	±0.02		
Co	µg/L	0.89	0.01	±0.01		
Cr	µg/L	11.1	0.1	±1.2		
Cs	µg/L	24	0.9	±2		
Cu	µg/L	18.2	0.2	±0.5		
Fe	µg/L	841.4	0.5	±1.5		
Mn	µg/L	276	0.5	±2		
Pb	µg/L	52.5	0.9	±1.5		
Sr	mg/L	750	1.2	±10		
V	µg/L	10.0	0.5	±0.8		
Zn	µg/L	63	1	±2.25		

The results of heavy metals came in moderate range comparing to published results before comparing to Table (2) in literature review chapter1, such as Li was 4 mg/L when it recorded in that Table was 3 - 235 mg/L, B was 38.6 mg/L comparing to 0.158 - 151 mg/L, Be was 0.44 µg/L when it was ranging between < 0.1 to 4 µg/L, Pb was 52.5 µg/L compare to 2 - 10200 µg/L and Zn was 63 µg/L comparing to 5 - 35,000 µg/L (Collins, 1975; Mehmet et al., 2008; Alley et al., 2011, Fakhrul-Razi et al., 2009 & G. Li et al., 2016).

Boron is consider as one of the essential elements cell wall structure and function in plant,(Whittington, 1959) but it is needed in moderately low amounts. If excessive, boron is supplied, then becomes toxic. Toxicity symptoms typically show first on older leaf tips and edges as either a yellowing spotting or drying of leaf tissues (Ayers & Westcot, 1976). The toxicity consequences for growth and yield were less serious for combined B effect and salinity, than what might be expected if impacts of the individual variables were additive (Yermiyahu et al., 2008).

It was noticed also that organic contents of the produced water was almost negligible. This could be due to various reasons namely; delay in delivering the produced water to the university, slow mixing before collecting the samples from 1m^3 tank (fig. 6) and the high temperature during delivery; when it delivered to our University in June; when the average temperature during this period was 35 - 38 ^{0}C. Figures 7 and 8 show the GC chromatograms for the produced water and the BTEX standard respectively. It is clearly shown that all-light hydrocarbons were very small and close to noise area while the heaver hydrocarbons still represented in a high concentration.

Table17: Produced water organic contents

Organic Parameter	Unit	Result	STD	Uncertainty	Ref. method	Equipment Used
Benzene	µg/L	39.5	0.54	±0.5	USEPA 5021a	PerkinElmer Clarus 680 GC with headspace injector and flame ionization detector
Toluene	µg/L	72	0.88	±1		
Ethyle Benzene	µg/L	30	0.3	±1		
Xylene	µg/L	15	0.9	±1		
Total Diesel	µg/L	118	2	±5		
Total PAHs	µg/L	292.5	2.5	±2.5	USEPA 610	WATERS UPLC, PDA & FLD
TOC	mg/L	2430	20	±10	APHA5310B	Skalar
BOD_5	mg/L	10	0.5	±1	APHA 5210 B	HACH 2800
COD	mg/L	8983	15	±20	ASTM D 1252 method B	
Phenols	mg/L	165.5	0.8	±1.5	colorimetric	

Figure 6: 1m3 produced water tank delivered to Qatar University

The BTEX peaks appeared at retention time from 7 to 12 minutes (Fig. 8), while at this time in sample chromatogram (Fig. 7) the areas were very close to noise of base line, which is referred to a low concentration of BTEX. However, the chromatogram showed that the sample was rich in the volatile organics beyond retention time from 20 to 30 minutes; indicating the presence of heavier compounds; which might be diesel range. The BTEX results came incompatible with that illustrated in literature; as the BTEX were the highest organic concentration in produced water (Maryam et al., 2016; Jumana, 2014 and FukhrulRazi et al., 2009). As BTEX had the highest solubility products among the organic contaminations (Frintrop et al., 2011).

Maryam, 2016 investigated the concentration of benzene, toluene, ethylbenzene and xylene in gas produced water and the results were 11170, 278.1, 4648.6 and 1156.8 µg/L, respectively. Neff, 2002 also investigated three offshore productions and the BTEX results were 84 to 2300 µg/L Benzene, 89 to 800 µg/L toluene, 26 to 110 µg/L ethyl benzene and 13 to 480 µg/L xylene. Dorea et al., 2007 conducted a study on Permian basin oil field, and the results of BTEX were as following: 1500 to 778510 µg/L Benzene, 100 µg/L toluene, 2010 to

399840 µg/L ethyl benzene and 10 to 460 µg/L xylene. Jumana, 2014 showed that the total BTEX was ranged from 4500 to 6740 µg/L.

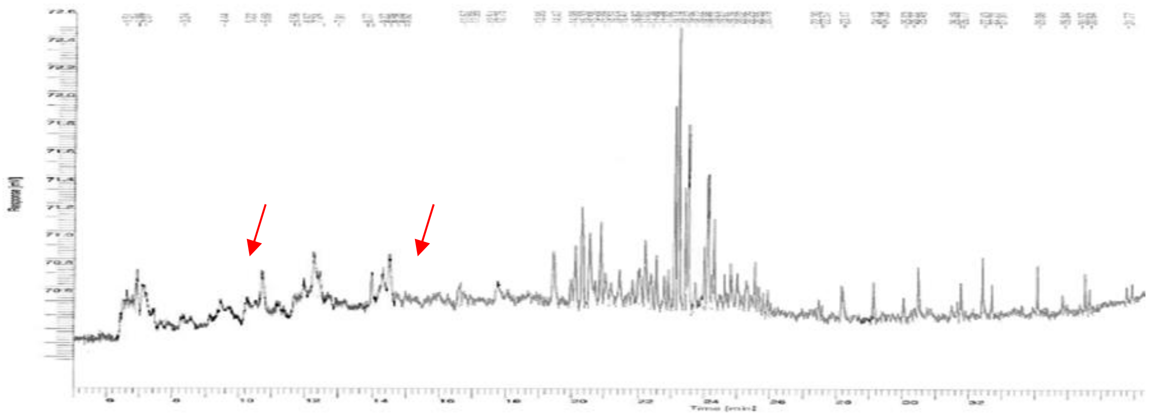


Figure 7 : Gas chromatography of produced water by headspace injector (arrows refere to BTEX retention time)

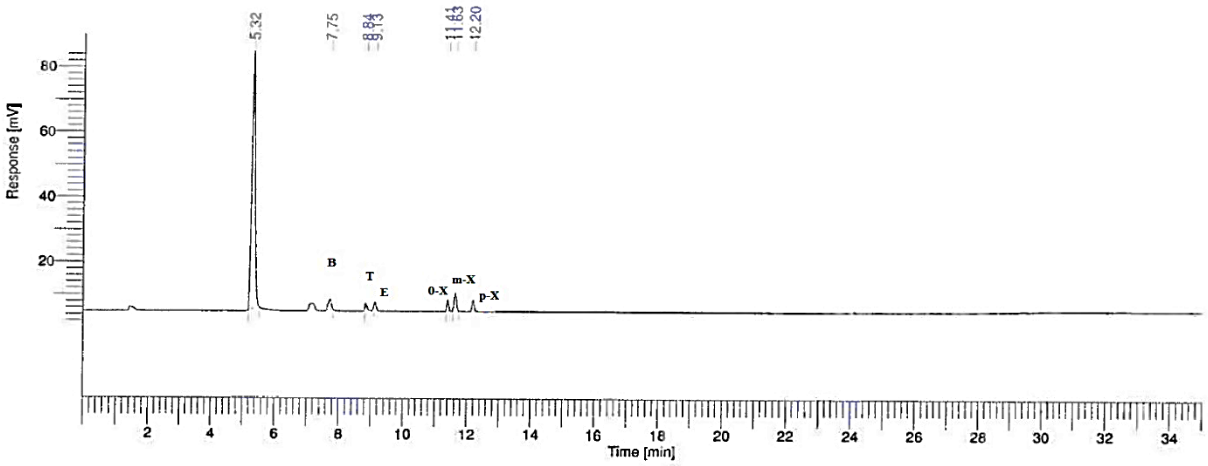


Figure 8: Gas chromatography of BTEX standard (B, T, E, o-X, m-X &p-X are peaks of benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene respectively)

Figures 9 and 10 show the polycyclic aromatic hydrocarbon (PAHs) chromatograms compared to 18 standard result chromatogram. It was shown that PAHs was low at range 0.292 mg/L. Figure 10 represents the PAHs extracted from produced water. The result chromatogram shows very crowded peaks, which are shifted toward the more polar compounds as their peaks started early at 11 minutes and finished at 30 minutes, while in standard chromatogram the peaks started at 17 minute and finished at 37 minutes. According to the C18 column, the more delayed peaks were the more nonpolar compounds. Accordingly, the produced water rich with highly polar PAHs compounds or there were some interferences caused increasing in polarity such as high salinity interference which was observed by Dariush et al., 2009 after their study the interference of salinity on biodegradation of polycyclic aromatic hydrocarbons (PAHs) of heavy crude oil in soil.

The result of 0.292 mg/L PAHs in the produced water was moderate value comparing with 0.04 to 3 mg/L in review study of Jerry et al., 2011 and0.003 to 4540 mg/L for Dorea et al., 2007.

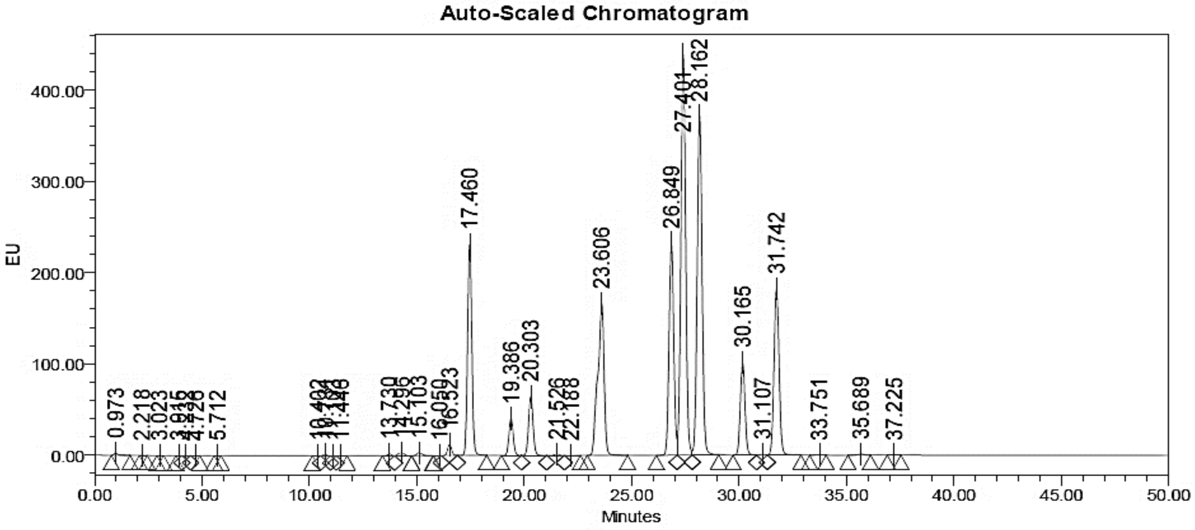


Figure 9: 18 components PAH Standard chromatogram on UPLC-FLD

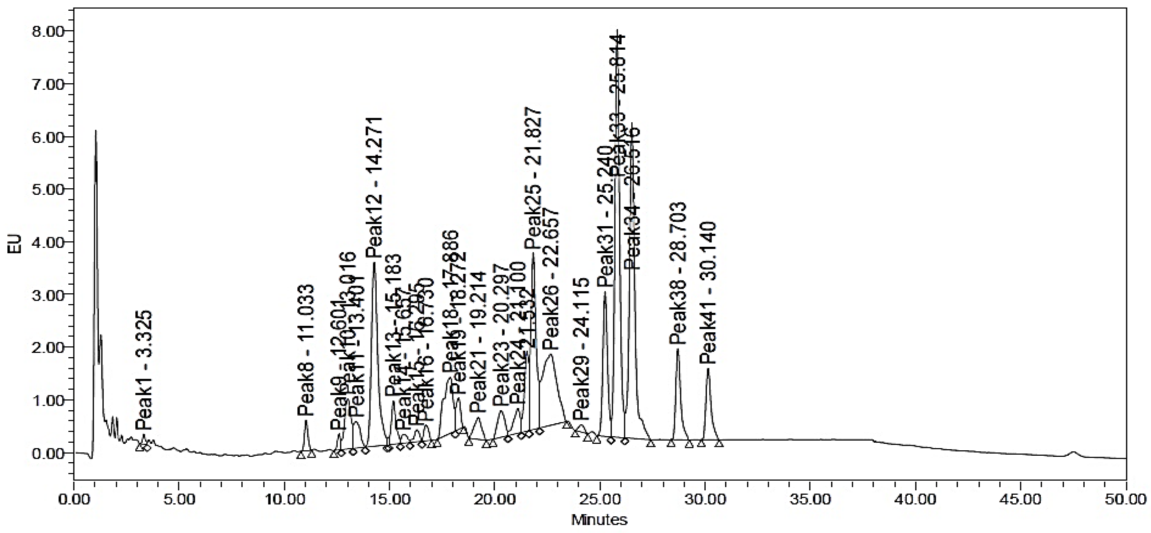


Figure 10: Extracted PW chromatogram on UPLC-FLD

Also it is very clear from the results that COD is much higher than BOD_5which means that, the biodegradable organic contents of the produced water were very small and the largest contents were resistant to biodegradation; BOD_5/COD ratio is very small $1.1x10^{-3}$

Fakhrul-Razi et al., 2009 summarized all the most important parameters from the oil produced water and gas produced water. Our results in this study were compared with the values of Fakhrul-Razi et al., 2009. The comparison results are shown in Table 18.

It was noticed that the produced water after dilution ten times had salinity slightly less than seawater 31,000 and 35,000 mg/L respectively. Where sodium adsorption ratio (SAR) was very high 70, 56, 42, 28 and 13.99 mEq/L for the produced water percentages 50, 40, 30, 20 and 10% respectively. When SAR was 0.13 for tap water.As the guidelines of FAO, 1985 and Ayers& Westcot, 1994for irrigation water, if irrigation water with a high SAR was applied to a soil for a long period, the sodium in the water will displace the calcium and magnesium in the soil. This will cause a decrease in the ability of the soil to form stable aggregates and a loss of soil structure and tilth. This will also lead to a decrease in infiltration and permeability of the soil to water; leading to problems with crop production. According to soil texture the limit of

SAR is differ, such as for sandy soil the impact will be less problematic if SAR was 9, while it will have severe problems if the soil was fine-texture (Ayers and Westcot, 1994).

Table18: produced water comparison with tap water, sea water & literature in physical and major ions

All parameters in mg/L if not mentioned beside it	Results of this study							Collin, 1979	Fakhrul'Razi, 2009	
	100% PW	50%PW	40%PW	30%PW	20%PW	10%PW	tap water	sea water	Oil PW	Gas PW
EC (mS/cm)	240	175.0	116.6	85.1	63.5	33.6	0.1785			4200-180000
TDS	310,000	155,000	124,000	930,93	62,000	31,000		35,000	1,200 – 10,000	2600 – 310,000
TSS	6,760	3,380	2,704	2,030	1,352	676			1.2 - 1000	14 - 800
pH	6.54	6.6	6.7	6.7	6.7	6.7	7.5		4.3 - 10	4.4 - 7
F^-	4	2.0	1.6	1.2	0.8	0.4	ND			
Cl^-	122,000	61000	48800	36636	24400	12200	5.1	19,353	80 – 200,000	1,400 - 190,000
Br^-	710	355.0	284.0	213.2	142.0	71.0	<0.1			150 - 1149
NO_3^-	500	250.0	200.0	150.2	100.0	50.0	ND			
PO_4^{3-}	4	2.0	1.6	1.2	0.8	0.4	ND			
SO_4^{2-}	50	25.0	20.0	15.0	10.0	5.0	1	2,712	2 - 1,600	<0.1 - 47
CO_3^{2-}	134	67.0	53.6	40.2	26.8	13.4	ND	142	77 - 3,990	
Na^+	61,000	30500	24400	18318	12200	6100	3	10,700	132 – 97,000	520 - 120,000
K^+	1850	925.0	740.0	555.6	370.0	185.0	0.15	387	24 – 4,300	149 - 3870
Ca^{2+}	10,700.00	5350.0	4280.0	3213.2	2140.0	1070.0	39.2	416	13-25,800	9,400 - 51,000
Mg^{2+}	2,200	1100.0	880.0	660.7	440.0	220.0	2.5	1,294	8 – 6,000	0.9 - 3,900
NH_4^+	126	63.0	50.4	37.8	25.2	12.6	ND		10 - 300	
SAR (meq/L)	139.94	69.97	55.98	42.03	27.99	13.99	0.13	58.01		
Ionic strength (mol/L)	3.79	1.91	1.50	1.14	0.76	0.31	0.00232	0.695		

ND: Not detected

Table19: heavy metals comparisons of produced water with tap water and literature

Unit mg/L	Results of this Study							Fakhrul-Razi et al., 2009	
	100% PW	50% PW	40% PW	30%PW	20%PW	10%PW	Tap Water	Oil filed PW	Gas PW
Li	4	2.0	1.6	1.2	0.8	0.4	0.011	3 - 50	18.6 - 235
B	38.6	19.3	15.4	11.6	7.7	3.9	ND	5 – 95	ND - 56
Ba	5.5	2.8	2.2	1.7	1.1	0.6	0.013	1.3 - 650	ND - 26
Bi	0.3390	0.1695	0.1356	0.1018	0.0678	0.0339	ND		
Al	0.1360	0.0680	0.0544	0.0408	0.0272	0.0136	ND	310 - 410	0.5 - 83
As	0.0137	0.0069	0.0055	0.0041	0.0027	0.0014	ND	<0.005 - 0.3	0.004 - 151
Ag	0.0240	0.0120	0.0096	0.0072	0.0048	0.0024	ND	<0.001 - 0.15	0.047 - 7
Cd	0.0007	0.0004	0.0003	0.0002	0.0001	0.0001	0.0002	<0.005 - 0.2	<0.02 - 1.21
Co	0.0009	0.0004	0.0004	0.0003	0.0002	0.0001	0.001	ND – 0.010	
Cr	0.0111	0.0056	0.0044	0.0033	0.0022	0.0011	0.001	<0.02 - 1.1	ND - 0.03
Cs	0.0240	0.0120	0.0096	0.0072	0.0048	0.0024	ND		
Cu	0.0182	0.0091	0.0073	0.0055	0.0036	0.0018	ND	<0.002 - 1.5	ND - 5
Fe	0.8414	0.4207	0.3366	0.2527	0.1683	0.0841	ND	<0.01 - 100	ND - 1100
Mn	0.2760	0.1380	0.1104	0.0829	0.0552	0.0276	0.0075	< 0.004 – 175	0.045 - 63
Pb	0.0525	0.0263	0.0210	0.0158	0.0105	0.0053	0.009	0.002 - 8.8	<0.2 - 10.2
Sr	750	375	300	225	150	75	0.021	0.02 - 1000	ND - 6,200
V	0.01	0.005	0.004	0.003	0.002	0.001	ND	ND – 0.290	
Zn	0.063	0.0315	0.0252	0.0189	0.0126	0.0063	0.619	0.01 - 35	0.02 - 5

Table20: organic content of produced water compared with tap water and literature.

Unit mg/L	Results of this study							Fakhrul-Razi et al., 2009	
	100% PW	50% PW	40% PW	30%PW	20%PW	10%PW	Tap Water	Oil filed PW	Gas PW
Benzene	0.0395	0.0198	0.0158	0.0119	0.0079	0.0040	ND	0.39 - 35	0.01 - 10.3
Toluene	0.0720	0.0360	0.0288	0.0216	0.0144	0.0072	ND		0.01 - 18
Ethyl Benzene	0.0300	0.0150	0.0120	0.0090	0.0060	0.0030	ND		
Xylene	0.0150	0.0075	0.0060	0.0045	0.0030	0.0015	ND		
Total Diesel	0.1180	0.0590	0.0472	0.0354	0.0236	0.0118	ND	N/a	
Total PAHs	0.2925	0.1463	0.1170	0.0878	0.0585	0.0293	ND	0.04 to 3 (Jerry et al., 2011)	
TOC	2430	1215.0	972.0	729.7	486.0	243.0	n/a	0 - 1,500	67-38,000
BOD	10	5.0	4.0	3.0	2.0	1.0	n/a		75 - 2,800
COD	8983	4491.5	3593.2	2697.6	1796.6	898.3	n/a	1,220	2,600 - 120,000
Phenols	165.5	82.8	66.2	49.7	33.1	16.6	n/a	0.009 - 23	
CN	0.50	0.25	0.20	0.15	0.10	0.05	n/a		

From the Tables 18, 19 & 20, it is noticed that with diluting produced water ten times most of the above mentioned parameters became non-effective levels except for the: EC, Na, Cl, Ca, Mg, K, B, Sr, SAR, TOC & COD. According to Ayers and Westcot (1994), 10% produced water used for water agriculture came in severe restriction for SAR curve (Fig.11) and tolerance level for boron concentration Table (21). That was noted on the greenhouse results.

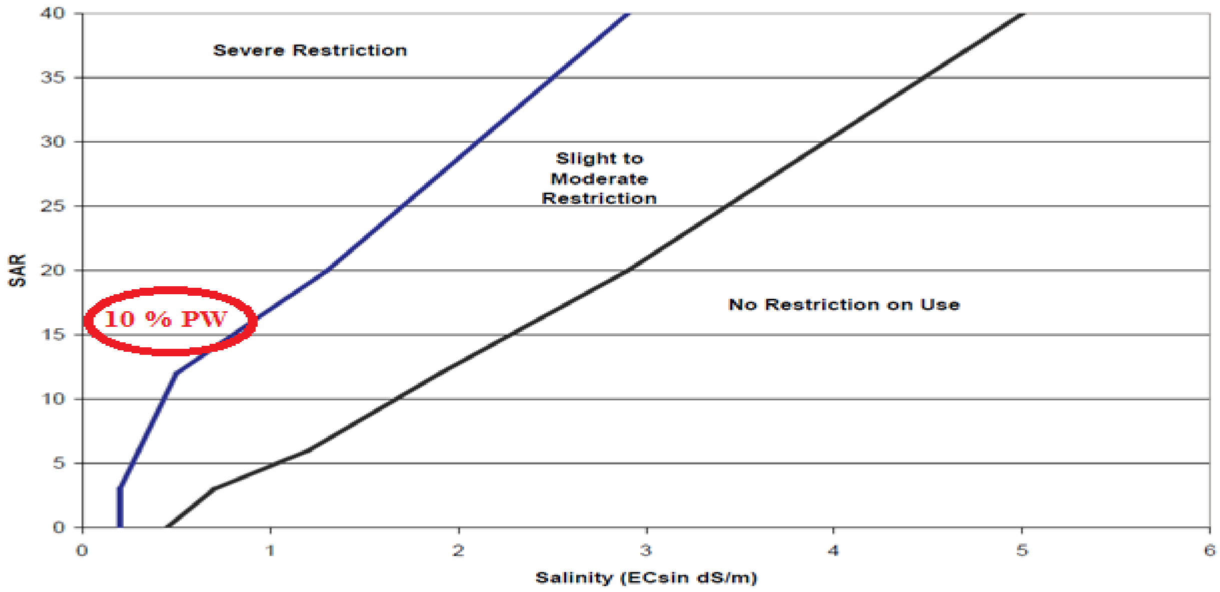
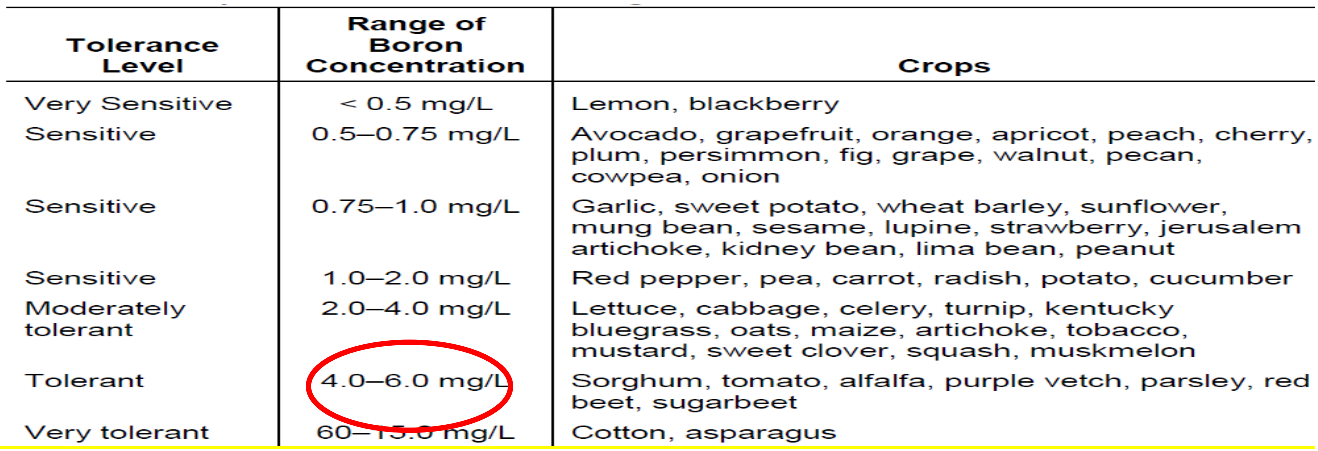


Figure 11: Suitability of water for irrigation (adapted from Ayers and Westcot 1994).

Table21: (Ayers and Westcot 1994). Boron concentration limits & suitable crop



Tolerance Level	Range of Boron Concentration	Crops
Very Sensitive	< 0.5 mg/L	Lemon, blackberry
Sensitive	0.5—0.75 mg/L	Avocado, grapefruit, orange, apricot, peach, cherry, plum, persimmon, fig, grape, walnut, pecan, cowpea, onion
Sensitive	0.75—1.0 mg/L	Garlic, sweet potato, wheat barley, sunflower, mung bean, sesame, lupine, strawberry, jerusalem artichoke, kidney bean, lima bean, peanut
Sensitive	1.0—2.0 mg/L	Red pepper, pea, carrot, radish, potato, cucumber
Moderately tolerant	2.0—4.0 mg/L	Lettuce, cabbage, celery, turnip, kentucky bluegrass, oats, maize, artichoke, tobacco, mustard, sweet clover, squash, muskmelon
Tolerant	4.0—6.0 mg/L	Sorghum, tomato, alfalfa, purple vetch, parsley, red beet, sugarbeet
Very tolerant	60—15.0 mg/L	Cotton, asparagus

So even we diluted produced water ten times still we in restricted area of irrigation due to the original highest of SAR, EC and Boron concentration.

Greenhouse experiment

Most of the plant species didnot tolerate irrigation with the produced water above 10 % for more than 1 week except for *Salsola sp*., whichtolerated well at 30 % for 20 days and at 20% for 35 days same as control, which was irrigated with tap water (Fig.12).

Figure 12: [A] Medicago sp., [B] Salsola sp., [C] Sorghum sp., [D] Helinthus sp., [E] Zea mays [F] Phragmites sp. after 1week irrigation, [G] Medicago after 2 weeks at 10% and [H] Salsola after 20 days irrigation with 20% PW

Figure (12) [A] represents *Medicago sativa* (alfalfa) after one week irrigation with different produced water percentages, [B] *Salsola baryosma* after one week irrigation at same produced water percentages, [C] *Sorghum biocolor* after 1 week, [D] *Helinthus annus* (sunflower) completely dead after 1 week, [E] *Zea mays* (maize) died after 1 week irrigation, [F] *Phragmitesaustralis* (ghap) showed irregular growth, [G] *Medicago sativa* at 10% produced water after 15 days and [H] *Salsola* sp. at 20% produced water irrigation after 20 days irrigation.

The average surviving days under produced water percentages irrigation for different plant species is shown in Table 22. And represented as histogram in figure 13.

Table21: Average surviving days for plant species at different produced water percentages irrigation

Average survival days

Plant Sp.	0% PW as Control	10%PW	20%PW	30%PW	40%PW	50%PW
Alfalfa	35	30	5	2	2	2
Sorghum	35	20	2	2	2	2
zea mays	35	2	2	2	2	2
sunflower	35	2	2	2	2	2
phragmitis	35	2	2	2	2	2
Salsola	35^{a}	35^{a}	35^{a}	20^{b}	13^{b}	7^{b}

(a,b litter give the significant differences according to Tukey test of means comparison)

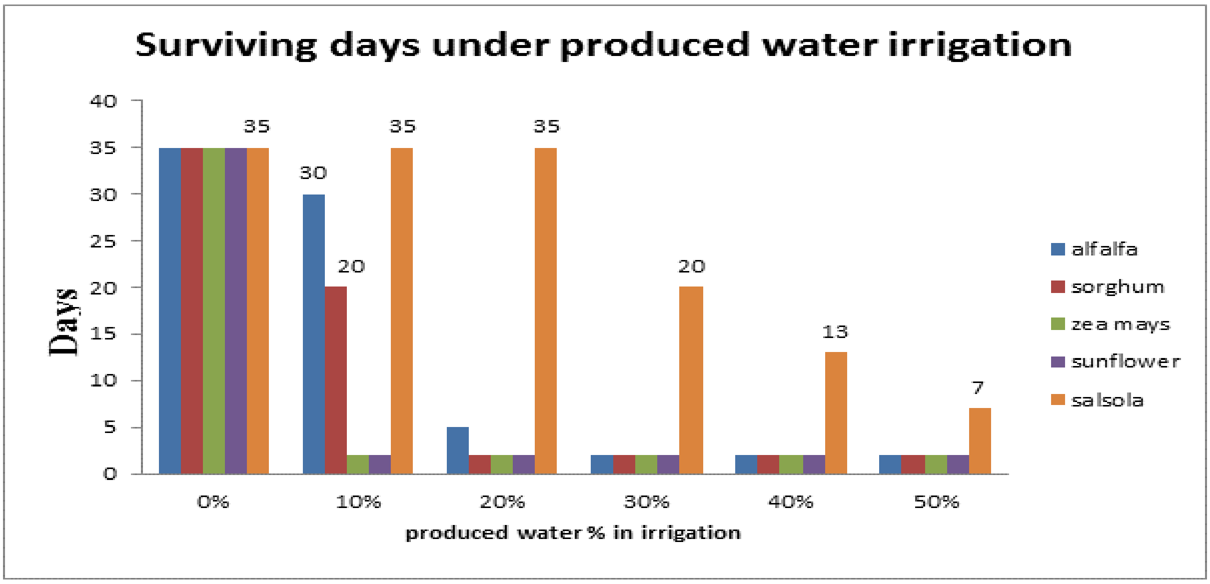


Figure13: The diagram of surviving plant irrigated with different percentages of produced water.

From the above results, it could be concluded that the main challenge of using produced water in irrigation wasthe produced water's salinity; even at 20% irrigation. this was clearly appear on the dead plant as they showed complete dehydration with weakness even they were still green(Fig. 14); which is known as osmotic shock due to increase of ionic strength in irrigated solution more than in plant tissue and the differences between them cannot be tolerated by cell walls in most plant species except *salsola.*(Ashraf et al., 2010)

Figure 13: Shows the plant species are start welting and dehydrated with using produced water in irrigation.

Figure 15, shows the moisture loss percentage for each plant species. Salsola sp. takes regular behavior in moisture loss throughout increase of produced water percentages, from control to 10% the specie loss about 24.7 % of its weight as moisture, from 10% PW to 20% PW the plant loss about 30% of its weight as moisture, while from 20 to 30% PW loss percentage was 15% weight, then this loss percentage starts to reduce with increasing the PW percentage up to only 8% from 40 to 50% PW. The main conclusion could be that Salsola sp. had a regular mechanism for moisture loss with produced water irrigation and these mechanisms start to be corrupt after 20% PW, while other plant species were completely irregular in their behavior mechanisms for moisture loss. Which was explained by Jelte and Henk, 2013, for differences in behaviors between halophytes and glycophytes under salinity conditions.

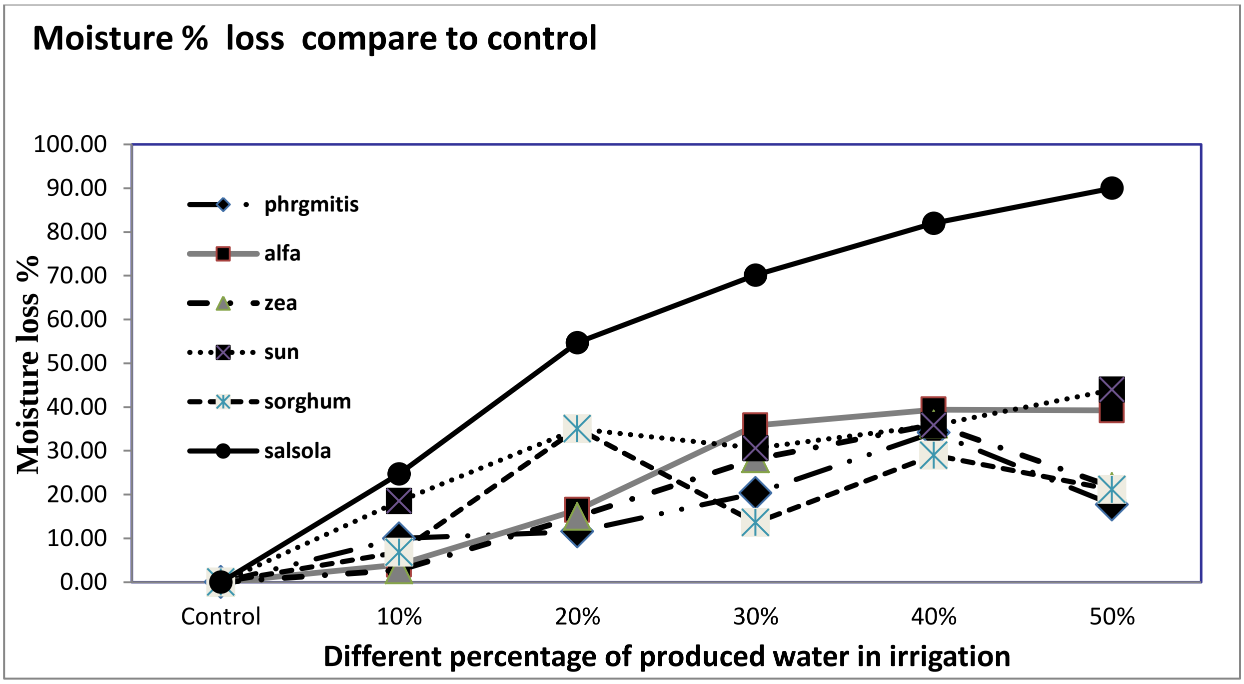


Figure 14: The moisture loss behavior of different plant species with increase PW%

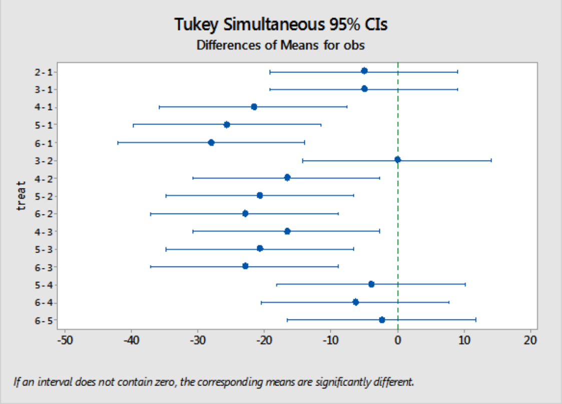
Salsola as halophyte tolerates drought and soil salinity with succulent leaves (Ashraf et al., 2010), which means that the plant contains more stored water contents. So under effect of the produced water irrigation, the moisture lost percentages from *Salsola* sp. were higher than other species and in negative linear correlation with produced water percentages.

Statistical analysis for *Salsola. Sp* showed no significance difference between the control experiment and the 10% and 20% PW irrigation, while there were significance differences between the control and other experimental treatment irrigated with produced water more than 20 %, as it appear by applying Tukey comparison, Table (23).

Table22: Tukey test comparison of Salsola sp. at diff PW% irrigation

Grouping Information Using the Tukey Method and 95% Confidence

Treatment	N	Mean (surviving days)	Grouping
Control (0% PW)	3	35	A
treat1 (10%PW)	3	30	A
treat2 (20%PW)	3	26	A
treat3 (30%PW)	3	13	B
treat4 (40%PW)	3	9	B
treat5 (50%PW)	3	7	B



In contrast, after irrigation of the *Salsola* sp. with 20% produced water, the morphological shape did not change and had a very close shape to that one in natural hebetate rather than irrigated with tap water in greenhouse (Fig.16). The leaves shape, hardness and aggregation and hardness of stem were completely different in tap water irrigation. This may be due to the effect of salinity. That agreed with study of Gabriel et al., 2011, on the anatomical and morphological alterations produced by excess salts.

The *salsola* plant may use salts in saline water to support its tissue structure and hardness or the tolerance modifications could be occurred by the plant in the presence of stress conditions, which were similar in the natural habitats with 20% PW irrigation, while these stress conditions are completely disappeared with tap water irrigation (Neumann, 1995; Gabriel et al., 2011 and Ashraf et al., 2010).

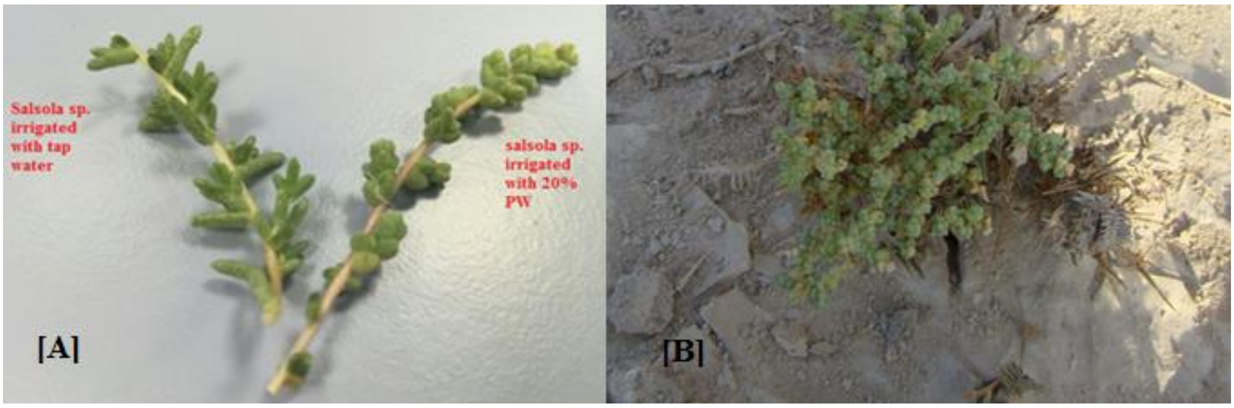


Figure 15: The morphological shape change in shoot system of Salsola sp. [a] in greenhouse and [b] in the nature

Heavy metal analysis

The heavy metals results for the whole plant tissue of *Salsola* sp. are shown in Table (24).The heavy metals were divided into two groups in regard to their behavior. The first group is Al, Ba, Co, Cr, Cs, Cu, Fe, Li, Mn, Pb, V and Zn Figure (17). Their concentrations in the plant were decreased with the 20% produced water irrigation. This could be explained to the fact that the feeding concentration was very small or the ions exchange mechanism was involved to give the plant chance to accumulate and tolerate the highest ions concentration. Similar conclusions were illustrated by Datta et al., 2000; Yadav et al., 2002 and Rattan eta l., 2005 for some sewage-irrigated soils; most concentration of metals in all the crops grown on sewage effluent irrigated soils were below the background levels.

The second group is Na, K, Ca, Mg, B and NH_4 Figure (18).Their concentrations were highly increased with 20% PW irrigation more than the control; as type of accumulation in response to produced water irrigation.

Table23: Level of heavy metals in Salsola plant

	mg/kg		
	Salsola 0%	Salsola 20%	Salsola 30%
Al $\times 10^3$	1.49	1.16	0.85
As	1.90	0.00	0.00
Ba	27.34	8.28	7.58
Cd	0.63	0.72	0.31
Co	1.99	0.58	0.57
Cr	7.79	2.34	2.09
Cs $\times 10^3$	1.72	1.07	1.01
Cu ×10	1.8	0.66	0.60
Fe $\times 10^3$	1.44	0.53	0.44
Li	10.38	8.96	8.53
Mn ×10	8.21	7.18	4.02
Pb	2.16	1.17	0.30
U	22.49	5.06	5.69
V ×10	2.68	1.22	1.15
Zn ×10	7.95	5.35	1.42
Na $\times 10^4$	6.19	12.63	12.34
Ni	10.38	3.90	2.84
K$\times 10^4$	2.09	2.15	2.43
Ca$\times 10^4$	2.62	2.90	2.07
Mg$\times 10^3$	5.70	11.00	11.75
B×10	3.25	4.88	4.74
$NH_4 \times 10^2$	4.22	6.42	18.77

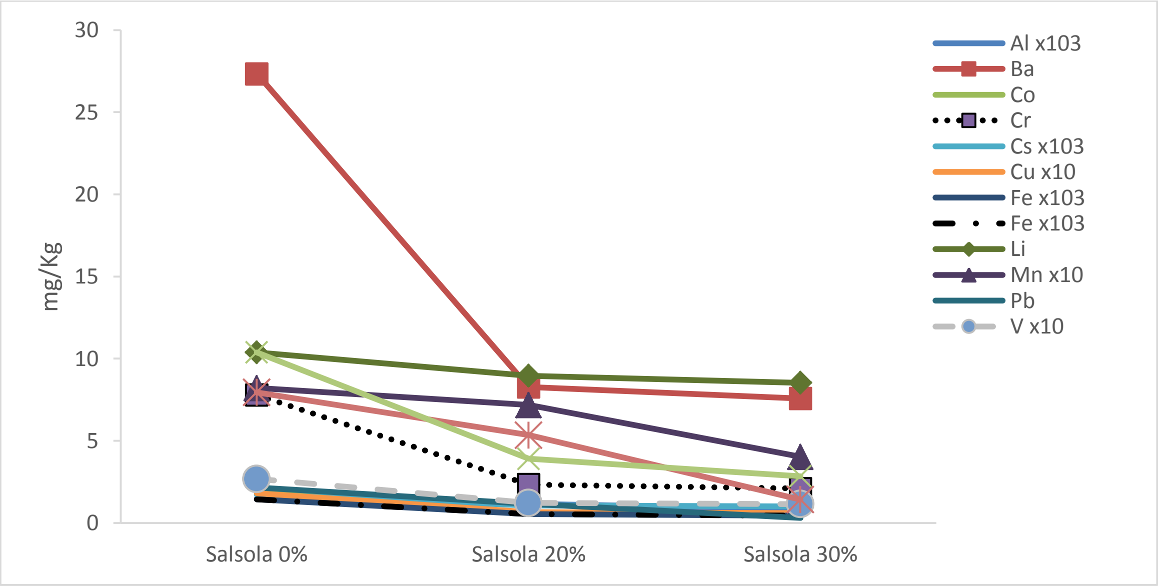


Figure 16: Metals decrease within produced water irrigation in Salsola tissues.

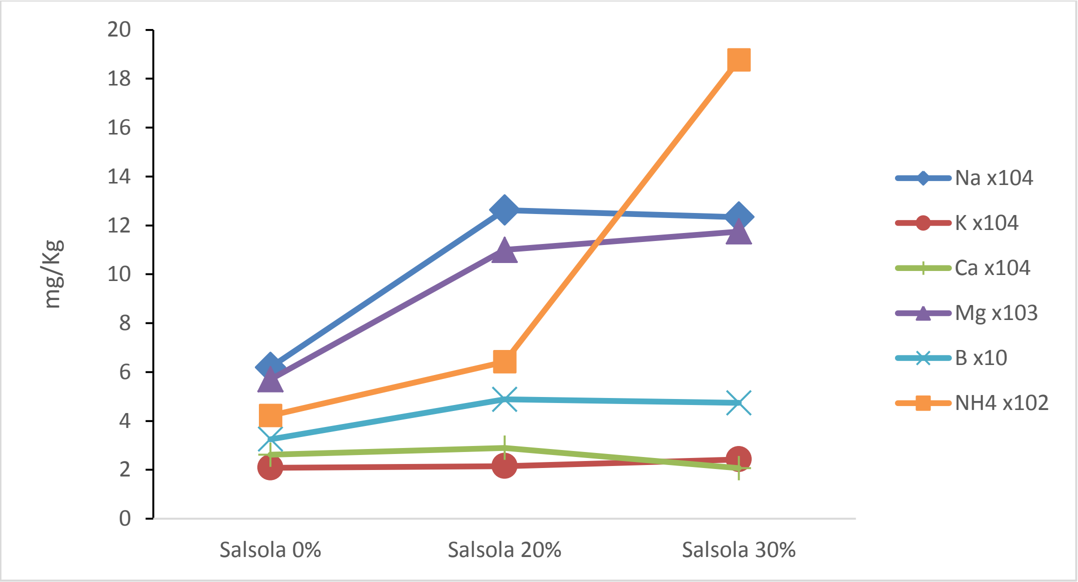


Figure 17: Metals increase within produced water irrigation in Salsola tissues.

C, H & N percentages

The great impact was seen on the C% which was decreased from 35.9% to 16.13 % with irrigation with the produced water. This gave indication for biomass decreasing as impact for PW irrigation. But this decreasing in C% became stable between the different PW percentages 20, 30 and 40% at about 16%.

The change in nitrogen %was slightly small between control and 20% as it was 2.45% and 2.21% respectively. While this change increased after 20% to 30% of PW from 2.21 to 1.6% which gives indication that 20%PW consider as critical tolerance point for *Salsola* sp. in Pw irrigation Figure (19). Which was correlated with all data results before.

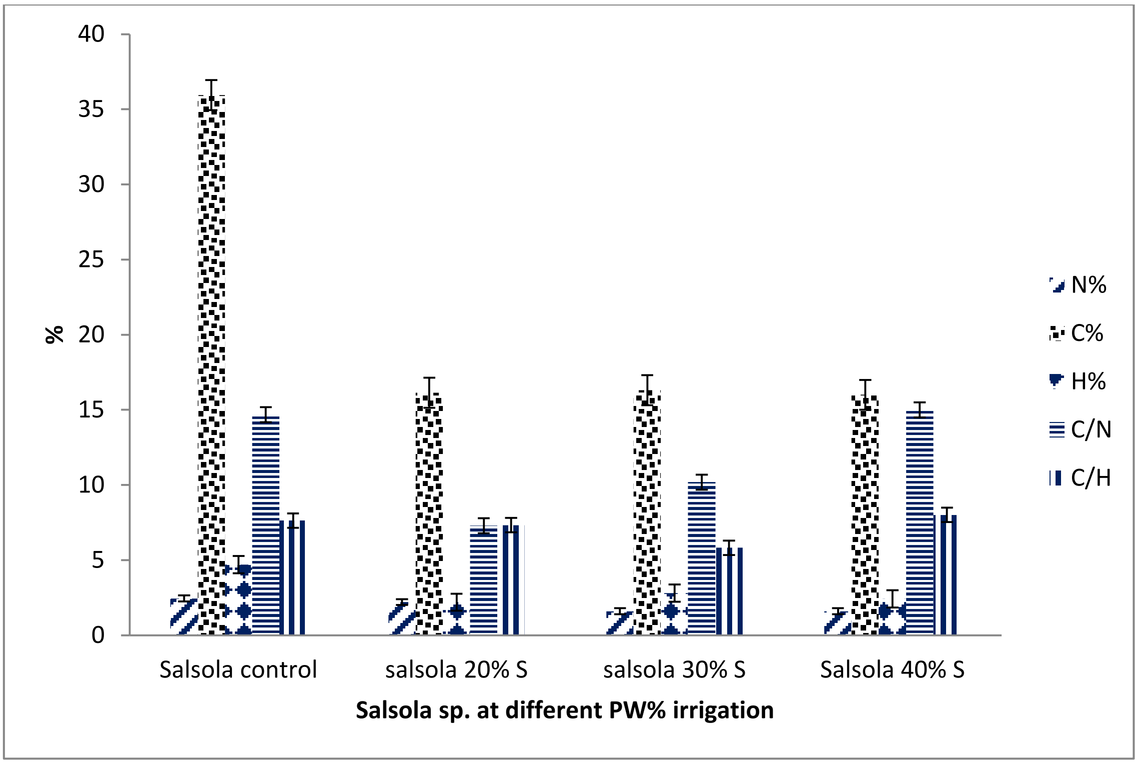


Figure 18: Carbon, Nitrogen & Hydrogen % variation in Salsola sp with different PW% irrigation.

Carbon % was highly affected comparing to nitrogen %; this might be due to C% represent the biomass structure of storing materials inside the plant tissues while N% represent the critical compounds such as proteins and amino acids (James et al., 2003).

FTIR spectrum

The FTIR spectra were acquired using UATR (ZnSe-Diamond crystal) with no special sample preparation. The changes in the FTIR spectra were used to illustrate the changes in plant tissues structure with produced water irrigation.

It was noticed from the FTIR figures that, the most effective component structure could be cellulose (Fig. 21). Which is represent the highest percentages of plant tissue structure. Here, the main functional groups OH, C-O & CH_2-OH were shifted and/or disappeared under the adsorption of various metals. This conclusion agreed with study of Rajesh et al., 2017 on cellulose as bio-sorbents.

Table 24: Interpretation on FTIR spectrum of Salsola Shoot system.

Peak wave number (cm^{-1})	Effect	Related group	References
3305	Shift right	Amid N-H stretching Amide A band	*Mizi et al., 2012;Yang et al., 2005 & Eckel et al., 2001.*
2922	Shift right and disappear	C-H stretching	*Wu et al., 2001 & Zanyar et al., 2008*
1735	Shift left and disappear	C=O stretching in polysaccharides & hemicellulose	*Ruiz et al., 2004 & Zanyar et al., 2008*
1621	Shift left and disappear	Carbonyl group stretching and ring breathing mode	*Fabian et al., 1995 & Chiriboga et al., 1998*
1372	Shift left and disappear	C-N stretching cytosine, guanine deformation N-H, C-H	*Dovbeshko et al., 1997; Dovbeshko et al., 2002 & Zanyar et al., 2008*
1244	Disappear	PO2 asymmetric stretching Phosphodiester group Phospholipid	*Zanyar et al., 2008* *Mizi et al., 2012*

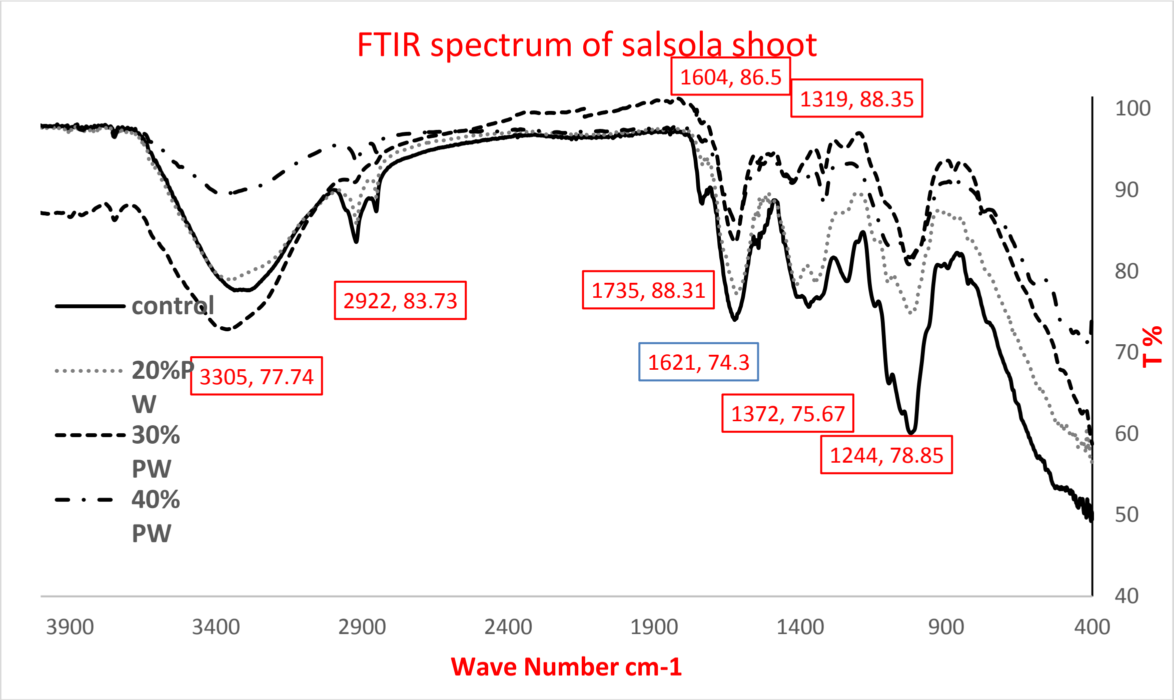


Figure 19: FTIR spectrums of Salsola shoot system at different produced water irrigation

Table25: Interpretation on FTIR spectrum of Salsola root system.

Peak wave number (cm^{-1})	**Effect**	**Group**	**References**
3745	Appear	O-H & N-H stretching Vibration O-H & N-H in hydrogen bonding network	*Wu et al., 2001& Zanyar et al., 2008*
2921	Shift disappear	C-H stretching Asymmetric stretching	*Fabian et al., 1991; Wu et al., 2001& Zanyar et al., 2008.*
2852	Shift& disappear	Vibration CH_2 Stretching of CH_2	*Fung et al., 1996; Zanyar et al., 2008 & Mizi et al., 2012.*
1334	Shift disappear	δ (CH) ring Polysaccharides Cellulose CH2 wagging	*Yang et al., 2005; Shetty et al., 2006 & Zanyar et al., 2008*
1028	shift	C-O & C-C stretching C-O-H deformation motion Carbohydrate peak vibration frequency CH_2-OH	*Huleihel et al., 2002; Dukor et al., 2002; Andrus et al., 1998 & Mordechai et al., 2001.*

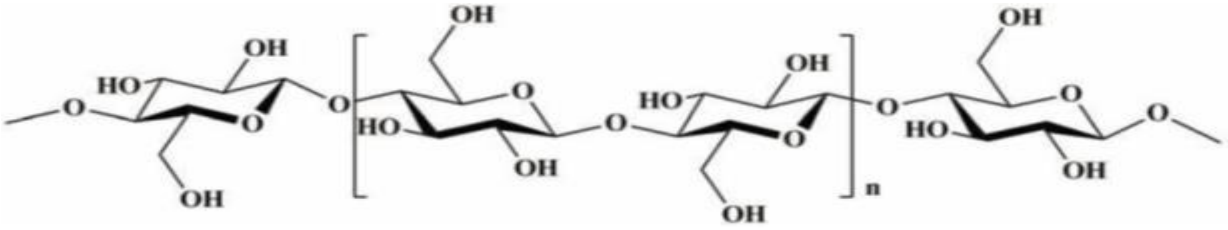


Figure 20: Cellulose Structure.

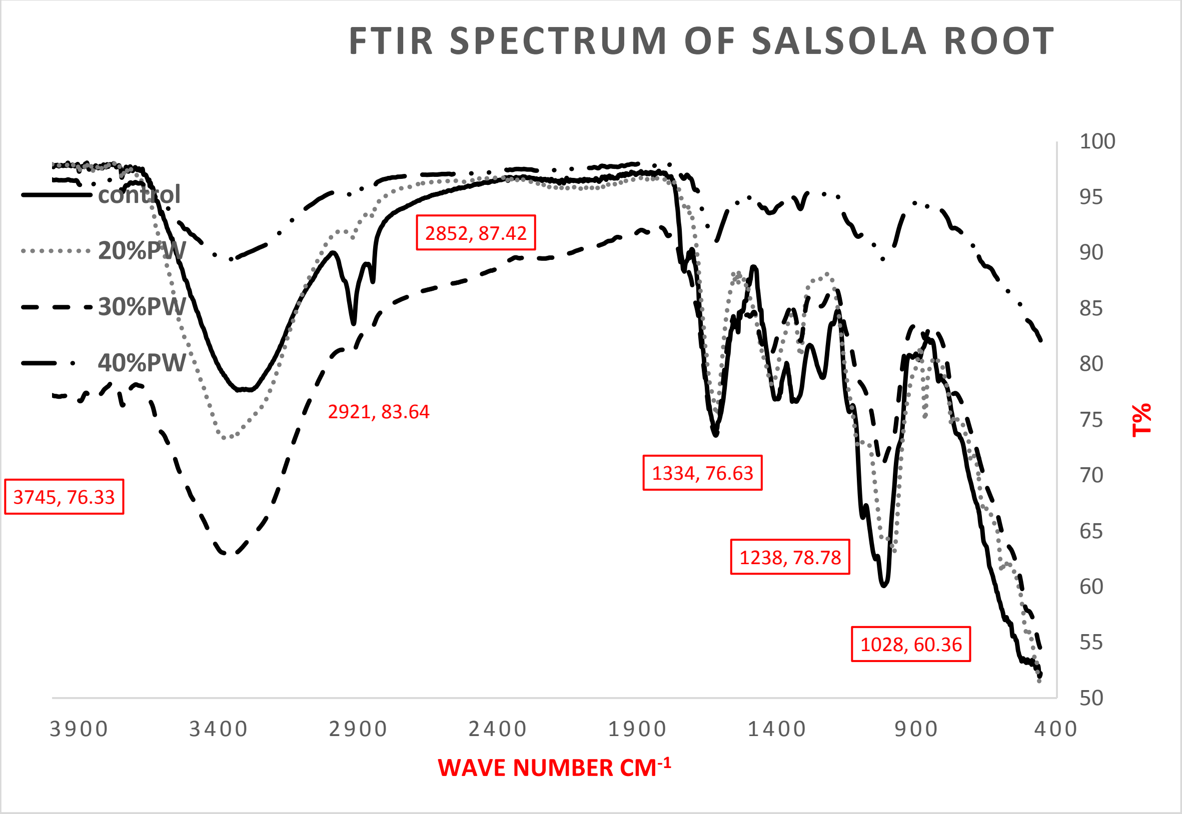


Figure 21: FTIR spectrum of Salsola. sp root at different PW% irrigation

At 30% produced water all plant species were dead except *Salsola*. Sp., after 10 days of irrigation. This because *Salsola* as halophyte has two types of resistance mechanisms; (i) The first is the woody roots which have reduced cortex and endodermis and exodermis act as barriers for variable resistance of water flow (Fig. 23), (ii) The second is the succulent complex leaves (Ashraf et al., 2010).

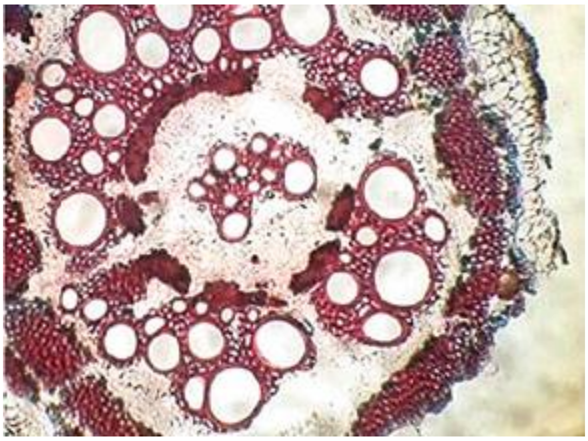


Figure 22: Salsola baryosma root Ashraf et al., 2010

Several morphological and anatomical structures met with halophyte plants give them the tolerance adaptation mechanisms such as salt-secretary trichomes, salt glands and salt accumulation (with specific salt/storage cells). (Ashraf et al., 2010). *Salsola* sp. able to partition toxic salts into vacuoles or to exclude salt at the root zone so it does not affect cell metabolism and division (Butnik et al.,2001 & P'yankov et al., 2001)

Medicago sativa **(Alfalfa)**

In case of *Medicago sativa* (Alfalfa) all experimental treatments have significant differences than control experiment which were confirmed by applying Dunnett test of means comparison.

Table26: Dunnett test of means comparison for Alfalfa

Experimental treatment	Mean of surviving days	Control mean – treatment mean
Control	35	
Treat 1 at 10% PW	30	5 *
Treat 2 at 20%PW	5	30**
Treat 3 at 30%PW	2	33**
Treat 4 at 40%PW	2	33**
Treat 5 at 50%PW	2	33**
Dunnett test	D= $t_{d.f}$ (2MSE/r)^0.5	1.035

Means comparison of all experimental treatments with control experiment in case of alfalfa, using Dunnett test * is significant and ** highly significant.

Medicago sativa (Alfalfa) survived at 10 % produced water but with intensity reduction up to 33% (Fig. 12 G)of total number of individuals per pot also reduction in shoot system length with an increase in root/shoot ratio which give indication that plant try to reach more deeper soil layers to collect more suitable water with shortness in overall growth (Fig.24)

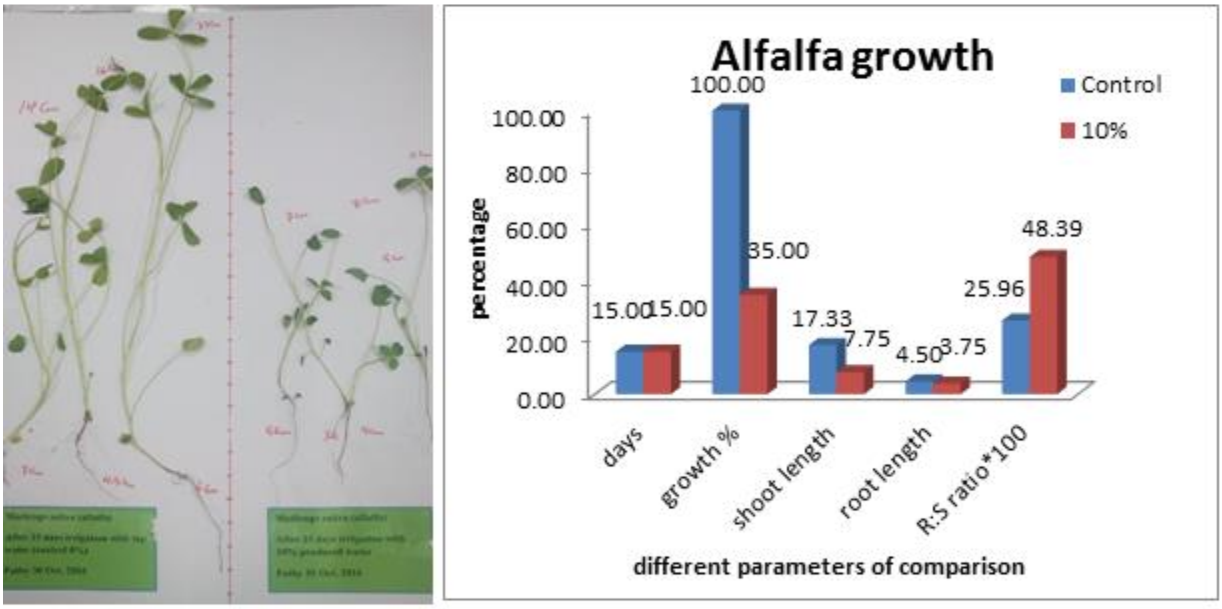
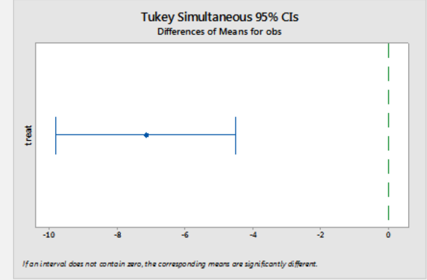
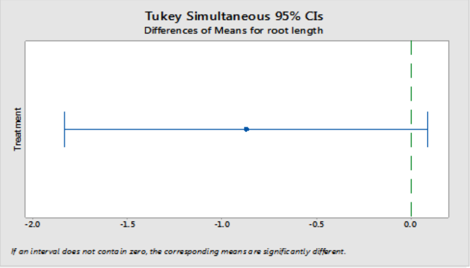


Figure 23: Alfalfa irrigated with tap water and 10% produced water after 15 days

Table (28) compares between the growth of shoot and root of alfalfa at 10% PW irrigation with that one irrigated with tap water. The means comparison gives no significance differences in root growth, while the shoot growth has significance difference, which gives indication that produced water affects the up ground parts of the plant, without effect on below ground parts. Those differences between the plant parts behavior might be as plant tolerance mechanisms in order to overcome the produced water pollutants effect. The shortage in shoot system agreed with the results was obtained by Demetrio et al., 2012, after they recorded a lower growth as -7.2% in height and -5.9% in stem diameter of *Arundo* sp. After wastewater irrigation.

Table 27: Statistical analysis of Alfalfa growth.

Source of variation	**MS**	
	Shoot length	Root Length
Between groups	308.166 *	4.59^{ns}
Within groups	9.803	1.28
Tukey comparison for means	Significant differences	Not significant differences
		

Heavy Metals

Alfalfa survived with 10% PW irrigation in greenhouse and also, was able to accumulate the highest concentration of B, Na, Li, Pb and Zn in its tissues. These results are compatible with Torresdey et al., 1998. But it is not consider as hyper-accumulator according to definition illustrated by Brooks, 1998; Roosens et al., 2003; Vamerali et al., 2010; Ucer et al., 2013and Goolsby et al., 2015.

Figures (25&26) divide the heavy metals into two groups; the first group in which the heavy metals concentrations decreased with irrigation such as Al, Ba, Co, Cr, Cs, Fe, Mn, V, Ca, Ni and K. that decreasing might be due to ions exchange with the second group where the ions and metals concentrations were very high in produced water, such as Na, B, Pb and Zn.

Table28: Content heavy metals of Alfalfa

element	mg/Kg	
	Alfalfa 0%	Alfalfa 10%
Al x10^3	19.72	4.91
Ba x10	4.7	1.5
Co	1.92	0.98
Cr	12.96	3.01
Cs x10^3	1.67	0.93
Cu	8.93	17.06
Fe x10^3	2.69	0.92
Li	5.28	9.86
Mn x10	7.2	6.2
Pb	1.34	4.01
U x10	2.3	1.3
V x10	2.4	1.2
Zn x10^2	1.05	1.32
Na x 10^3	8.20	78.02
Ni	8.64	4.52
K x10^3	29.99	20.57
Ca x10^3	49.42	38.38
Mg x10^3	6.33	6.32
B x10	3.16	4.82
NH4	N/A	N/A

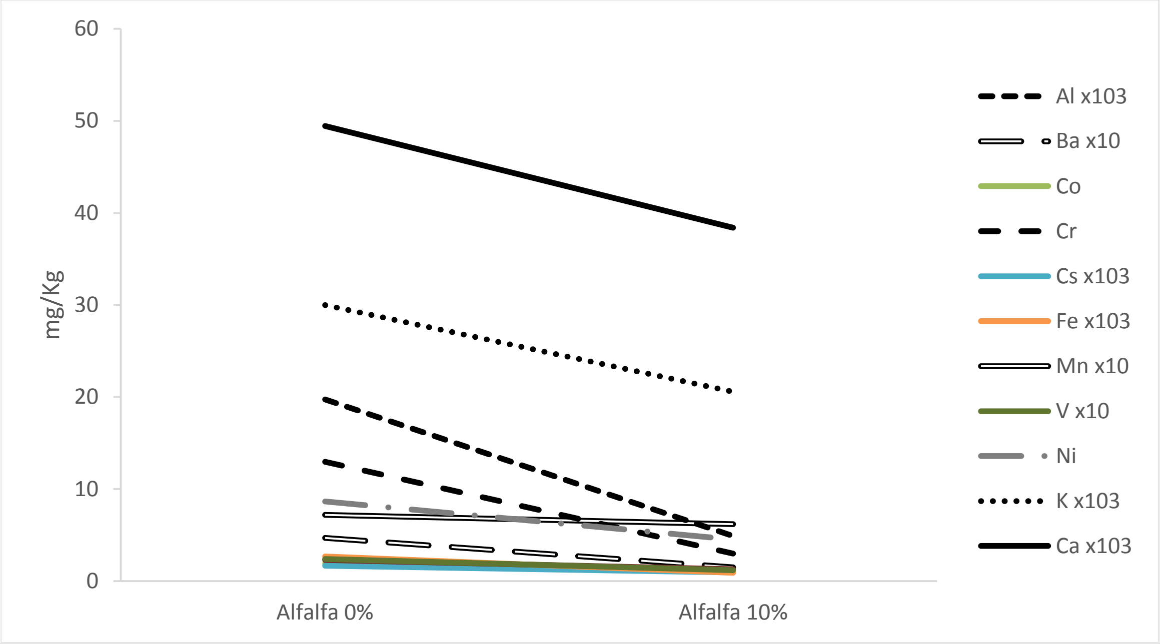


Figure 24: Metals decrease with produced water irrigation for Alfalfa

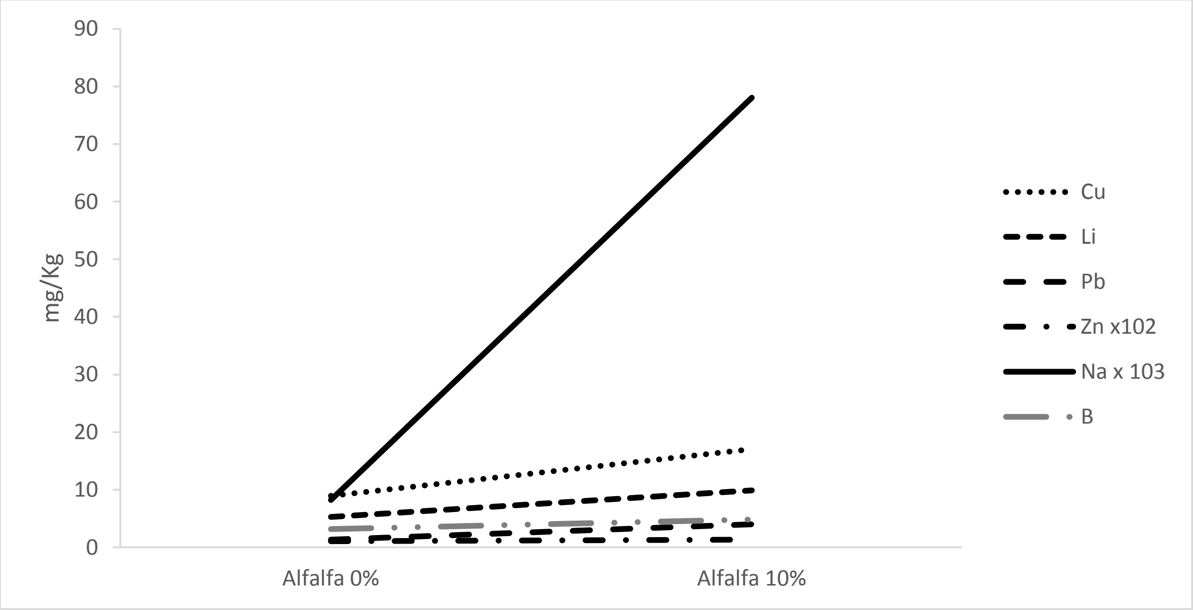


Figure 25: Metals increase with produced water irrigation for alfalfa.

Phragmites

While *phragmites* sp., failed to grow due to its growth depend on what is known as running rhizomes so planting it in greenhouse pots limits its growth, even in case of control; normal growth was limited and not stable (Fig.27).

Figure 26: Phragmites sp not have regular growth in greenhouse pots

Germination test results

15 seedes of *Sorghum biocolor* and *Medicago sativa* were plated on filter paper in Petri dish and watered with produced water at different percentages 0, 1, 2.5, 5 and 10% for four days under lighted conditions. The effect of produced water on germination of root and shoot systems were examined. The results of mean germination comparisons are shown in Table (30).

Table29: Tukey test for means comparison of root & shoot germination.

Treatment	Shoot System length		Root System length	
	Sorghum Mean	Alfalfa Mean	Sorghum Mean	Alfalfa Mean
Control	1.706 ^{A}	2.69 ^{A}	3.87 ^{A}	2.015 ^{A}
At 1% PW	1.58 ^{A}	2.54 ^{A}	2.75 ^{B}	1.695 ^{A}
At 2.5% PW	1.52 ^{A}	2.01 ^{B}	2.58 ^{B}	1.275 ^{B}
At 5% PW	0.4 ^{B}	0.55 ^{C}	1.68 ^{C}	0.795 ^{C}
At 10% PW	0.12 ^{C}	0 ^{C}	0.57 ^{D}	0 ^{D}

A, B, C & D are the grouping letters. If are the same per column it means no significance difference, but if they are differ per column that means significance differences.

From the Table (30), it can be concluded that growth of shoot system in case of sorghum did not show significant differences at 1 and 2.5% of produced water comparing to control, while in case of *Medicago* sp. only 1% had no significances. But the grwoth of root system was only succeeded in case of 1% PW on Medicago sp. Figures (28&29). That means, the root systems of Medicago sp. was more tolerate to produced water which was compatible with the greenhouse results.

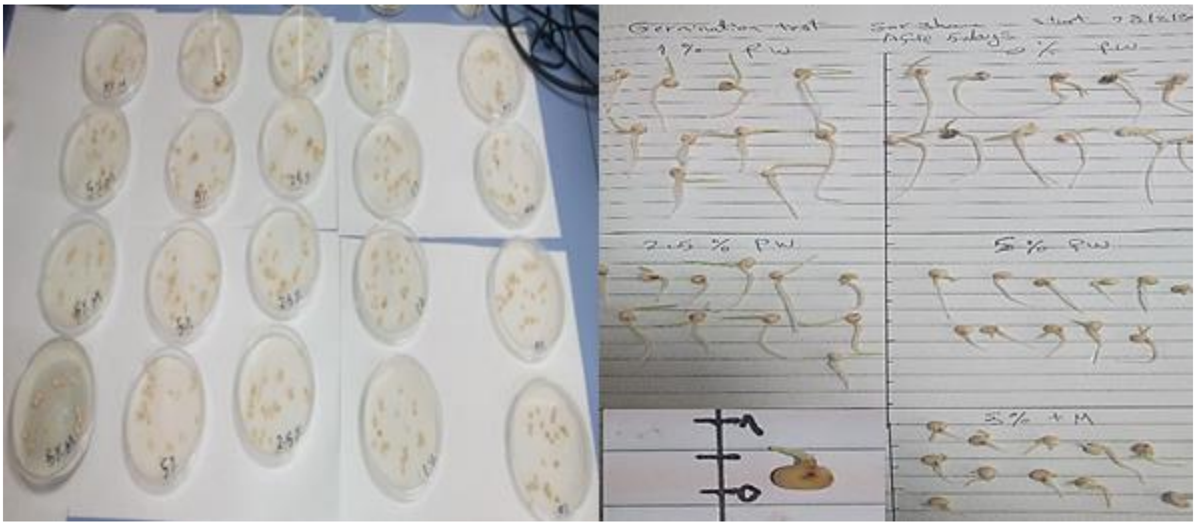


Figure 27: Sorghum bicolor germination.

Figure 28: Alfalfa germination test.

So at only 1% of produced water there is no significant difference with tap water in length of shoot and root while at 2.5, 5 and 10 % of produced water there are huge significant differences.

Germination percentage, seedling growth, shoot length and root length were inhibited in 5% and 10% of produced water while they were decreased in 2.5% PW. However at 1% PW there were no differences. It might be due to osmotic pressure caused due to higher salinity and toxicity (Dhanam, 2009). Osmotic pressure of the produced water at higher concentrations of total salts making inhibition agreed with study of Augusthy et al., 2001. Indicated that length of root system and shoot system in Alfalfa and Sorghum were increased by lowest concentrations of produced water. Similar conclusion had been reported by. Bera and Kanta, 1999 and Rana et al., 2013, after they studied the effect of waste effluents on seed germination.

Soil results

The soils have a ‘sandy loam’ texture according to the USDA triangle (Clay 12.7%, Silt 4.46% and Sand 83%).

Dissolved ions

The dissolved salts in soil were increased exponentially with produced water irrigation with displacement of major anions and cations as illustrate in Table (31). The control soil was showed decreasing in most salt ions after tap water irrigation. That might be due to plant utilization and washing by irrigation (Jie Peng et al., 2016)

Table30: Dissolved major ions in Soil after irrigation

Results in mg/Kg in different soils after irrigation periods in brackets as days (*Salsola* pots)

Dissolved ions	control before (0)	control after (30)	10% (30)	20% (30)	30% (30)
Na	500	340	6170	9600	17600
K	175	102	306	307	450
Ca	1750	1020	3060	3070	4500
Mg	210	160	440	590	—
Cl	810	450	13100	19817	33910
NO_3	81.6	28	128	_	139
SO_4	8280	5020	7580	9870	5200
SAR	0.75	0.5	9.6	9.8	29

The main notice from above results that the soil characterization changed in two ways; first, the ions abundance was completely changed from calcium to sodium as cation and from sulfate to chloride as anions. Second change was the regular and exponential increase of Na & Cl ions with the increase of produced water concentration while in case Ca, Mg & SO_4 ions the increasing was irregular, these might be a result ofthe differences in plant consumption and utilization as illustrated in Fig. (30).

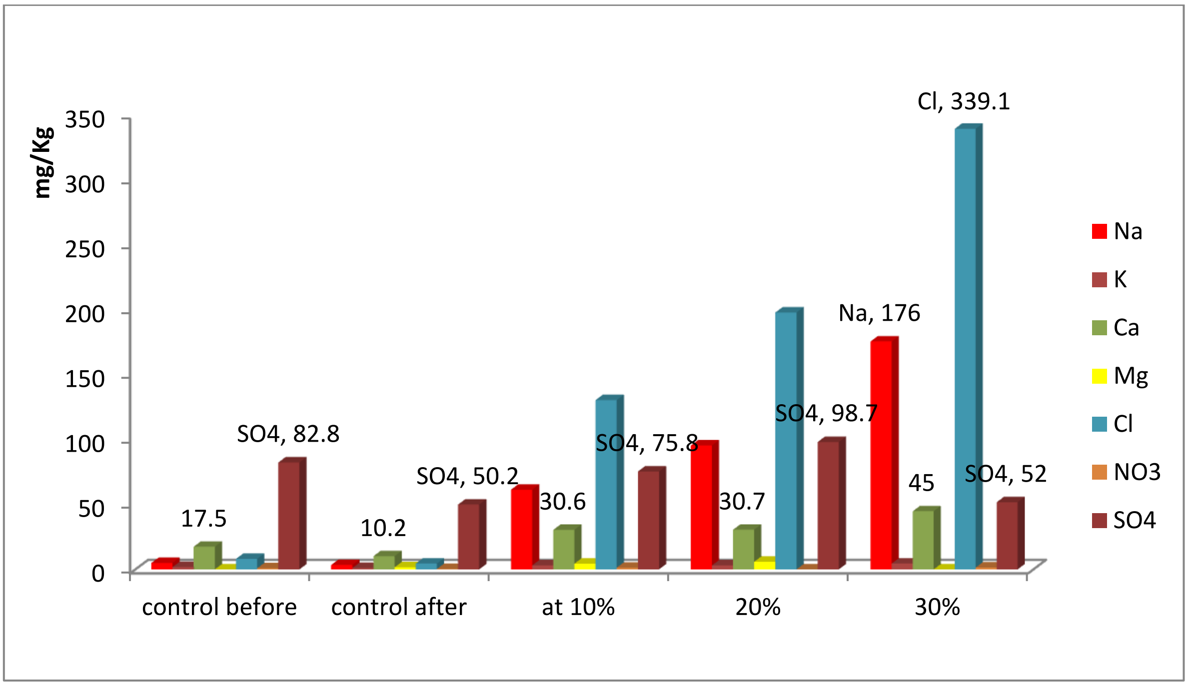


Figure 29: Major dissolved ions in soil after PW irrigation

The Figure (31) gives the changes in SAR value in soil before the irrigation with produced water and after irrigation with different percentages of produced water. From the graph there is very small difference between control soils before irrigation with tap water and after that difference may be due to irrigation creates washing for soil and plant consumption for salts ions (Na, Ca & Mg) are the same. While with produced water irrigation the SAR value increased from 0.7 at control to 9.8 mEq/l in 20% PW. It jumped from normal value to restricted value, but no differences between 10% and 20% as the plant consumption factor still interfere in salts accumulation and distribution between plant tissues and soils. But in case of 30% the SAR value jumped to severe restricted when it was 29 mEq/l due to absence of plant accumulation and all salts accumulated only in soil. Accumulation of salts in soil not only increase the sodicity and salinity but also has second impacts on the physical properties of soil such as permeability.

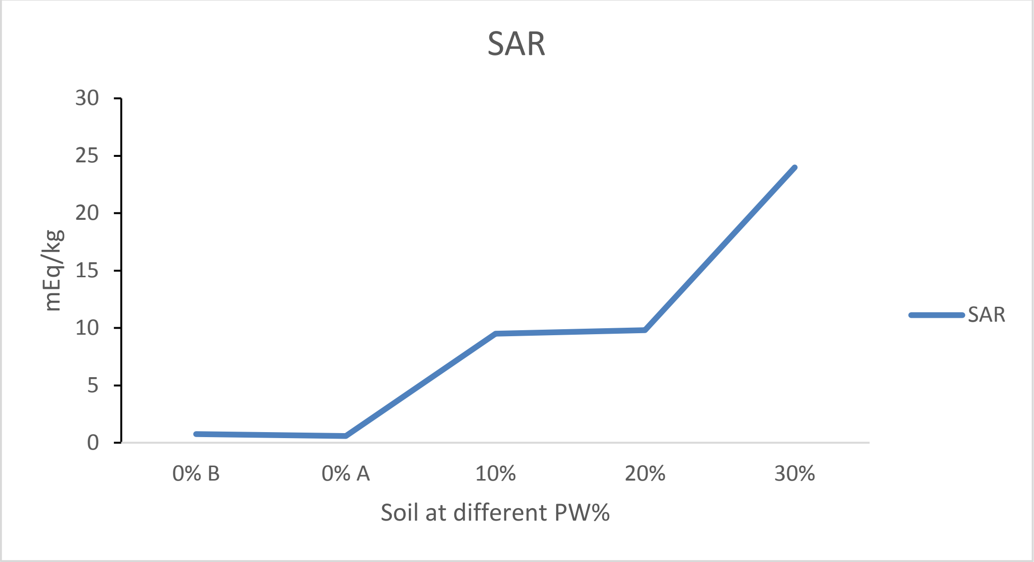


Figure 30: Shows the change in SAR value with produced water irrigation

As the SAR increases to severe effect, the permeability of soil to water infiltration is decreased to cause more difficult to supply the crop with water and may greatly add to cropping difficulties through crusting of seed beds, waterlogging of surface soil and accompanying disease. If too much quantities of soluble salts accumulate in the rhizosphere, the cropshavemore difficulties in uptake enough water from the salty soil solution (Yadav et al., 2002; Kevin & Brown, 2005; Katie et al., 2011 and Khajanchi et al., 2015). This decreased water extraction by the plant can result in slow or poor growth and may also be shown by symptoms similar in appearance to those of drought such as early wilting (Fig.14).

Metals after digestion by acids

The metals in soil were divided into three groups according to the behavior changes. First group of metals toke the same behavior were As, Ba, Co, Cr, Cs, Cu, Fe, Li, Mn, Pb and V (Fig. 32) which slightly variation or little increased with increase the percentage of produced water in irrigation. Second group contained Al, Na, K and B (Fig. 33) were sharply increased with Produced water percentage increasing. While the third group contained Ca, Mg & Zn (Fig. 34). Which were decreased with Produced water percentage increase. All these differences in behavior would be coming from the concentration of metals in feeding irrigation water, as shown in Table (18) of heavy metals contents of produced water used in irrigation were very small, while Na, K, B, Ca, Mg and Zn were very high concentration. But with the differences of their plant utilization, so Na, K and B were increased and accumulated in soil while Ca, Mg and Zn were consumed and their concentration reduced throughout control, 10% and 20% irrigation. But at 30% irrigation the plant utilization is lost so the concentration increased again (Fig. 34).

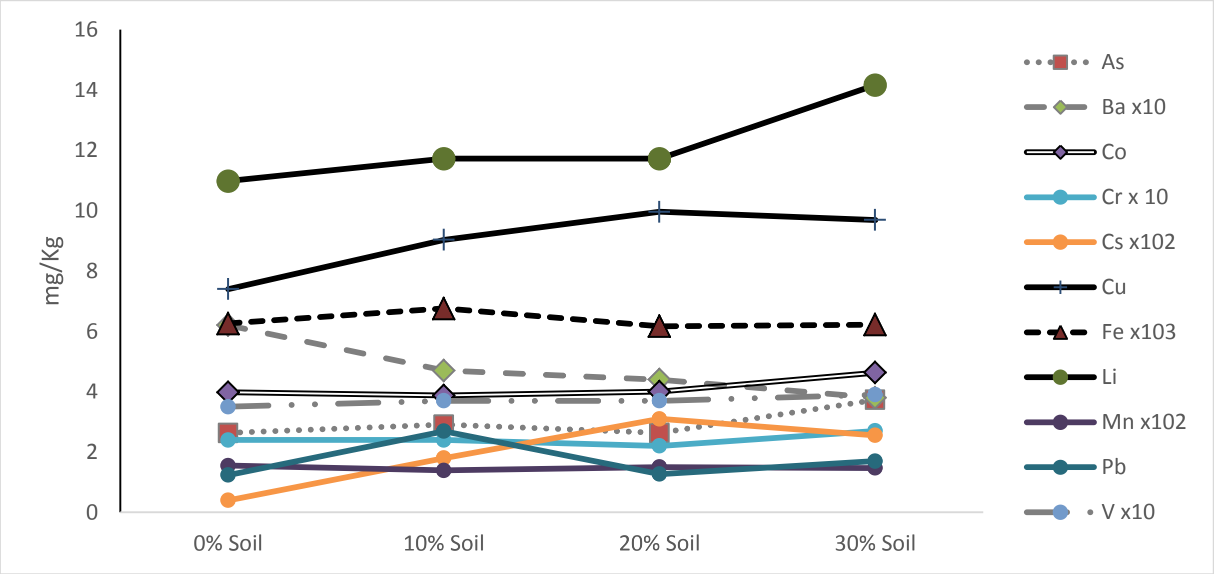


Figure 31: Heavy metals group1 in digested soil

Table31: Heavy metals of digested soil after irrigation

element	Concentration of digested elements in mg/Kg			
	0% Soil	10% Soil	20% Soil	30% Soil
Al x10^3	2.975	9.415	9.629	11.229
As	2.63	2.91	2.63	3.73
Ba x10	6.2	4.7	5.4	3.8
Co	3.98	3.87	4.00	4.63
Cr x 10	2.4	2.4	2.2	2.7
Cs x10	4.0	18.0	31.1	25.5
Cu	7.40	9.03	9.96	9.69
Fe x10^3	6.26	6.758	6.168	6.221
Li	10.98	11.72	11.72	14.16
Mn x10^2	1.55	1.39	1.50	1.47
Pb	1.24	2.69	1.27	1.70
V x10	3.5	3.7	3.7	3.9
Zn x10^2	5.2	2.5	1.9	3.1
Na x10^3	4.8	9.01	21.16	24.518
Ni	20.45	20.18	19.08	22.03
K x10^3	2.752	3.382	3.815	3.363
Ca x 10^4	9.675	9.292	4.087	5.162
Mg x10^3	3.237	3.314	1.062	2.927
B x10	1.1	1.441	2.5	2.1

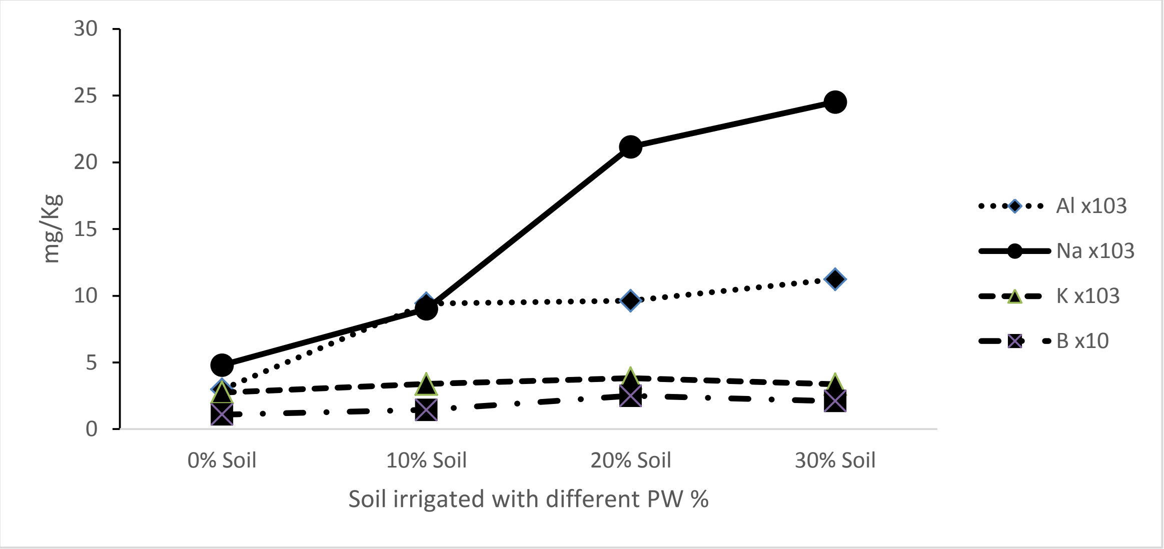


Figure 32: Metals group2 in digested soil

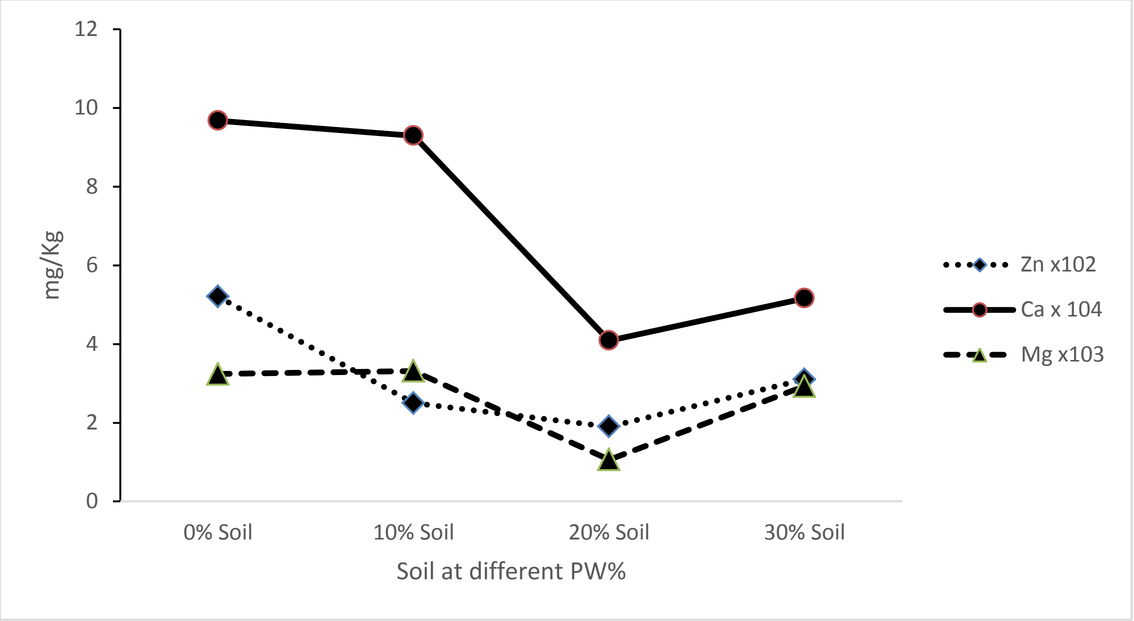


Figure 33: Metals group 3 in digested soil

One of the major constraints for produced water irrigation include sits negative impacts on soil quality in terms of accumulation of heavy metal ions and the contamination of ground water on long term usage. However, the produced water dilutions utilized for this experiment had value of heavy metals below the permissible limits. The changes in soil properties agreed with Yadav et al., 2002; Kevin & Brown, 2005; Katie et al., 2011 and Khajanchi et al., 2015

Carbon and Nitrogen accumulation in soil.

It is appear that the accumulation of Carbon compounds have the same behavior of nitrogen compounds these may be due to both present in the same structure or both are related with the same bioavailability hardness. Carbon accumulation percentage is correlated with organic accumulation in coming title. It is clear that from control to 10 & 20% PW accumulation is smooth and gradually increases while it has sharpness at 30% PW Fig. (35&36).

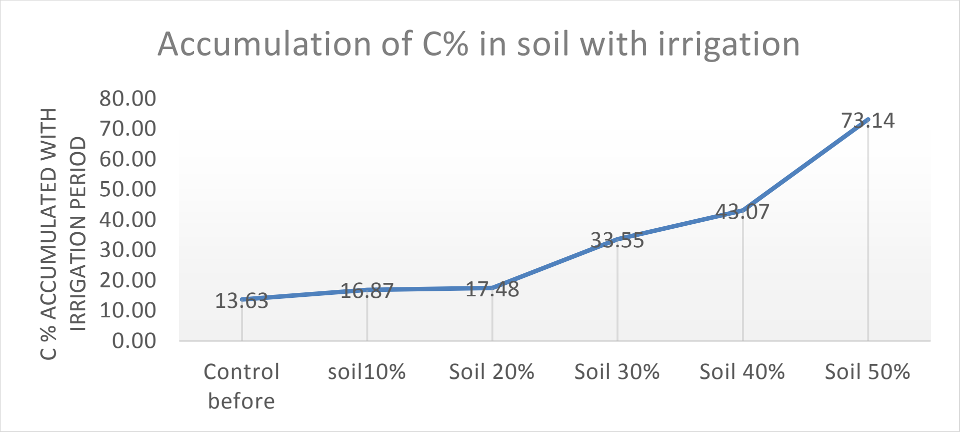


Figure 34: C% accumulated in soil after irrigation period

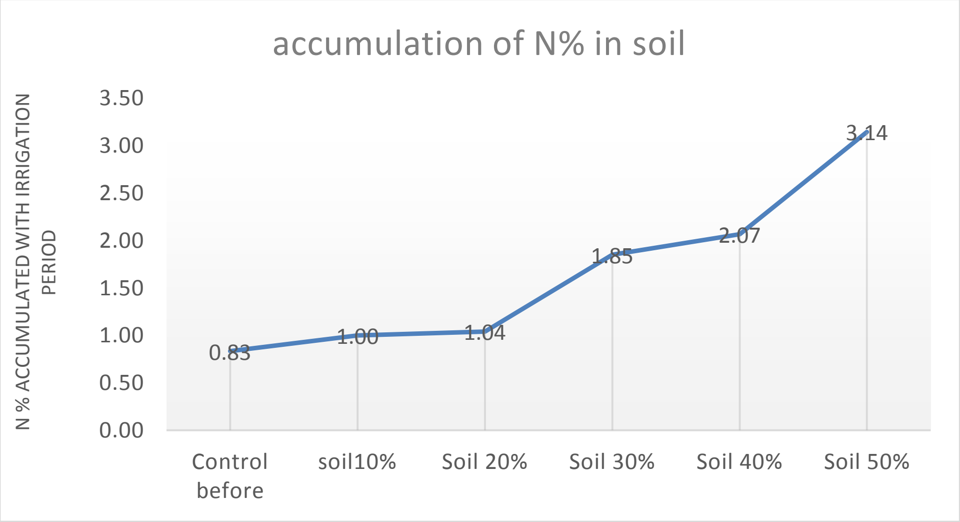


Figure 35: N% accumulated in soil after irrigation period

Organic accumulation in soil

The organic accumulation was below detection limits of UPLC and GC in most irrigated soil samples, after one month irrigation with 10 and 20% of produced water, while it started to detected at 30% produced water irrigation at the same period of irrigation on both types PAHs (fig 37&38) and diesel range with slightly differences in concentration and individuals

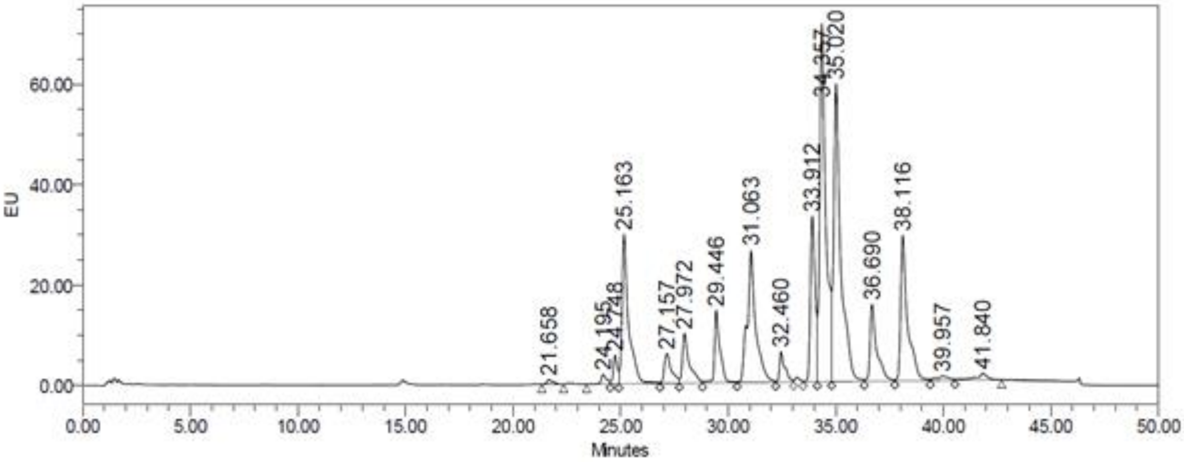


Figure37: The UPLC/FLD chromatogram of extracted soil at 30% PW

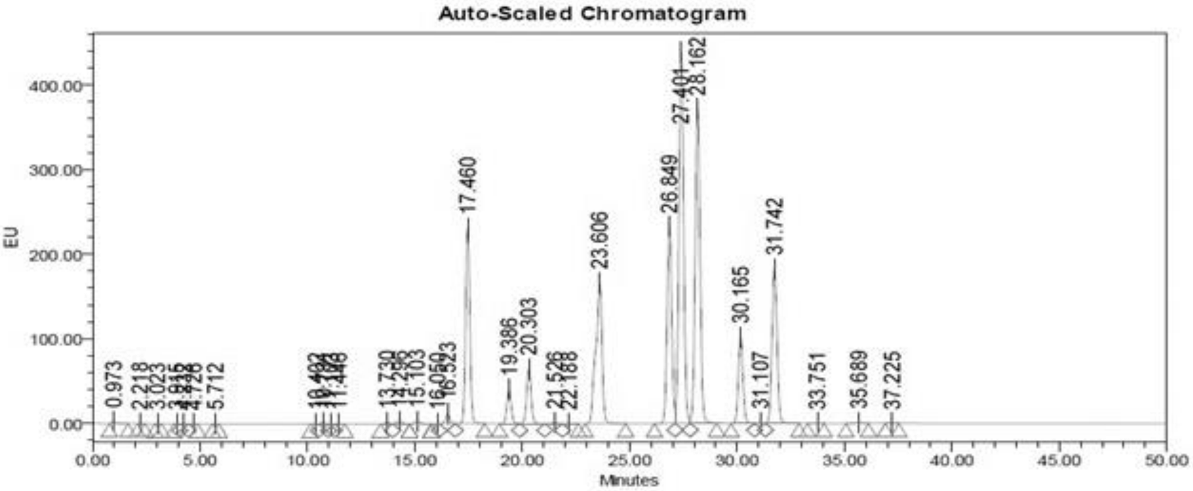


Figure 36: The UPLC/FLD chromatogram of 18 components PAHs standard.

The main notification is that organics accumulated in soil were the less polar or completely non polar compounds as they shifted to more retention time up to 41 minutes more than the standard of PAHs used which end at 37 minutes, also completely differed than PAHs were extracted for produced water itself Fig. (10), which ends at 30 minutes. These give indication that the original PAHs from produced water were divided into two groups; first which is more polar start disappear from rhizosphere soil might be throw plant degradation or migrate more deeper in soil layers with water and second group which was less polar or non-polar which accumulated in rhizosphere zone.

Chapter 5: Conclusion and Recommendation

In this study, the used produced water showed a great impact on both plant and soil even after dilution ten times with tap water. On plant growth level, most the used crop species completely died except the halophyte specie *Salsola baryosma* which tolerated irrigation of produced water at level of 20%. After that level, the morphological growth and heavy metals accumulation start completely disturbed. Also *Medicago sativa* tolerated 10% produced water irrigation with reduction in total growth intensity and length up to 33% of initial growth. On soil level, the main noted impactswere the huge increase in the sodicity and SAR levels which interfere the soil physical characteristics as permeability and water flow. So even after success in using diluted produced water in irrigation of tolerated species, the used soil must be treated after a period of plantation to eliminate the accumulated salts and make some balance between Na, Ca &Mg to reduce the resulted SAR by adding the gypsum salts.

For using produced water in irrigation, its salinity, SAR, boron and heavy metals must be diluted to be in tolerated levels of selected plant species as illustrated by (Ayers and Westcot, 1994). Also the dilution factor up to ten times was not effective to use produced water in irrigation, so some pretreatment technologies for desalinization are required.

Obtained results in this study need further investigation at their individual level to have complete view even on plant tolerance metabolism and effect of different heavy metals on different plant species.

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