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COLLEGE OF ARTS AND SCIENCES

ENHANCING PRODUCED WATER QUALITY USING MODIFIED ACTIVATED  
CARBON

BY

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## Abstract

The formation produced water from natural gas production process in the North field offshore considered largest volume of waste water in Qatar, which could be considered a potential benefits source for the industry as well as for other domestic uses if it was treated properly, taking in to consideration economical cost and conditions aspects. This project aims to study the physical and chemical characterizations of the produced water associated with natural gas from the North field, in the same time examine the removal of major inorganic and organic pollutants and heavy metals from the produced water by using different treatment method such as the use of sand filtration, activated carbon filtration and modified activated carbon filtration.

Samples of produced water were collected from the North field offshore gas production platforms and analyzed to examine the physical and chemical characterizations of the produced water, the result were compared with the chemical composition of other field produced water, the concentration were within the range among other field except for sulfide and treatment chemical production (additive chemicals) concentrations.

The average results briefly showing that, pH , COD, TOC, BOD, conductivity, sulfide, oil and grease (HEM) and total nitrogen parameters as follows: 4.43 , 10496.6 mg/l , 2405 mg/l , 1034 mg/l 7035  $\mu\text{s}/\text{cm}$  ,326.3 mg/l ,40.5 mg/l, 47.4 mg/l respectively. Also the study includes other characterizations such as organic acids, phenolic, B.T.E.X, production Chemicals (Additive Chemicals), inorganic anions, metals and cations and the average values of the B.T.E.X (Benzene, Toluene, Ethyl Benzene and Xylene) were found as the following 11170 ppb, 278.1 ppb, 4648.6 ppb and 1156.8 ppb respectively.

After the sand filtration (SF) the removal efficiency of the TSS , COD, acetate, propionate, corrosion inhibitor and TN (total nitrogen) parameters were the following 77.5% ,10.1%, 7.82 %, 4.5%, 94.1% and 63.7 % respectively. Meanwhile, the removal efficiency of the B.T.E.X (Benzene, Ethyl Benzene and Xylene) found as the follows: 93.14%, 99.8% and 96.7% except for Toluene was 27.6%. The highest removal efficiency for the metals and cations was for iron, chromium and manganese were as the follows 99.5%, 97.5% and 95.8% respectively.

Activated carbon filtration was found to be more efficient to remove COD and TOC with 23.7% and 30.7% respectively among the three media. Regarding the removal efficiency of the Activated Carbon for the organic acid was the highest for the acetate and propionate with 83.6% and 88.7% respectively and for the inorganic ions- phosphate the removal efficiency was 94.9%. Also the AC showed removal for some metals such as zinc, copper, boron, nickel, iron and chromium and highest removal efficiency more than 97% for the all B.T.E.X compound except for the Ethyl benzene was 76.9%.

Modified Activated Carbon was found to be more efficient to reduce the TOC with 31.1% whereas the COD concentration increased by 12.6%. MAC showed also removal efficiency for the inorganic ions phosphate and sulphate with 94.9 and 48.4% respectively. For the metals, MAC was more efficient than the AC to reduce the zinc, molybdenum and boron concentration and less efficient than AC to reduce copper and acetate (Organic acid), Regarding the B.T.E.X removal efficiency is similar to AC more than 98% except for the Ethyl benzene which was 92.3% higher than AC 76.9%.

Keywords: Produced water, Sand filtration, Activated carbon, Modified activated carbon.

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## List of Acronyms

<b>AC</b>	activated carbon
<b>AGR</b>	acid gas removal unit
<b>bpd</b>	barrel per day
<b>BOD</b>	biological oxygen demand
<b>BTEX</b>	benzene, toluene, ethylbenzene, and xylene
<b>COD</b>	chemical oxygen demand
<b>CTAB</b>	cetyltrimethyl ammonium bromide
<b>DC</b>	deposited carbon
<b>m<sup>2</sup>/g</b>	square meters per gram
<b>MCF</b>	million cubic feet
<b>MF</b>	microfiltration
<b>Mg/L</b>	milligrams per liter
<b>MTA</b>	million ton annum
<b>ORS</b>	organosulphur
<b>PAC</b>	powdered activated carbon
<b>ppm</b>	parts per million
<b>S/cm</b>	Siemens per centimeter
<b>scf</b>	standard cubic feet
<b>SDS</b>	sodium dodecyl sulphate
<b>SRU</b>	sulphur recovery unit
<b>TDS</b>	total dissolved solids
<b>TOC</b>	total organic carbon

<b>TPH</b>	total petroleum hydrocarbons
<b>tscf</b>	trillion standard cubic feet
<b>TSS</b>	total suspended solids
<b>UF</b>	ultrafiltration
<b>VOC</b>	volatile organic chemicals
<b>MAC</b>	Modified Activated Carbon
<b>µg/L</b>	microgram per liter
<b>µm</b>	micrometers
<b>Tcf</b>	trillion cubic feet

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*To my Father soul*

*To the one who is the role module teacher in my life who inspires me and promotes the  
energy and power in mine to learn & develop*

*May ALLAH blessed his soul and settle with merciful*

*NO words deliver my thanks & appreciation to you Dad*

*As I do a promise to you*

*I will continue to learn & strive to Excel*

*You're Daughter Maraym Ali Al Kaabi*

## **1. Introduction**

Natural gas is growing to be one of the main fossil fuel resources for energy production due to its clean burning emissions compared to other fossil fuels and abundant resources (Martínez et al., 2007). One of the main challenges associated with-natural gas-industry is the high quantity of waste water produced along with the gas (Stephenson,1992; Havard Devold, 2013).

The State of Qatar is the third country in the world with the largest reservoirs of Natural Gas after Russia and Iran, which means it own 14% of the total gas reserves of the world (BP Statistical Review of World Energy, 2015). In spring 2011 Qatar became the highest exporter of liquefied natural gas (LNG) in the world with LNG export capacity of 77 million tons per year (International Gas Union-World LNG Report – 2013).

The natural gas of the State of Qatar is extracted from the enormous offshore North Field, the natural gas production comes associated with the condensate and produced water which is considered the highest produced water stream source in Qatar; In the Process of LNG production the gas phase separate from the liquid phase “condensate” and the produced water on the offshore or in shore facilities after that the produced water is separated from the condensate on onshore facilities, finally the produced water is injected in inshore injection wells (Natural Gas operation at Qatar petroleum, 2014).

Produced water is the "brine", or "formation water. Trapped since millions of years with oil and gas in geological reservoirs and becomes produced water when the reservoir is produced from the oil or gas production wells (Collins, 1975).

The global estimation of the produced water production is about two hundred fifty (250) million barrels in a day in comparison with approximately eighty (80) million barrels in a day of oil. Based on this estimation , the ratio of water to oil, is around 3:1 which means 70% waste water has to be cutout (Ahmadun et al., 2009).On other hand, the average water : gas ratio for natural gas production in the Qatari North field is 1.20 and the average produced water production in the year 2014 was 23,554 BBLS/D (Natural Gas operation at Qatar petroleum, 2014).

This produced water is generally acidic and has high content of (HEM) oil and grease, phenols, B.T.E.X (Benzene, Toluene, Ethyl Benzene and Xylene), (TSS) total suspended solids,(CN)cyanide,(S) sulfide, total nitrogen compounds and heavy metals such as (Fe)-iron, (Cd) cadmium, (Ni) nickel, (Cr) chromium, (Cu) copper, (Mo) molybdenum, (Se) selenium, (V) vanadium and (Zn) zinc (Collins, 1975; Stephenson, 1992; Fillo & Evan, 1995; Lee & Neff, 2011; Li & Harold, 2013)

The risks of produced water contamination for people's health and the surrounding environment is caused mainly by the volatile organic compounds which are highly toxic , for example, phenol and BTEX compounds which are present in effluents come from oil and gas wells (Ahmadun et al., 2009).

Many countries with oil and gas fields, which also are suffering from low fresh water resources, have been working on increasing the efficiency and finding alternative low-cost ways to purify the pollutants and toxic impurities to enhance the available & limited fresh water. The impact of reinjection of produced water on the environment has recently become an important matter of environmental concern (Ahmadun et al., 2009). The available published information about the characterization and composition of the North Field



produced water is limited, and this project; therefore illustrates the different treatment methods of formation-produced water. However, finding a suitable, low cost and environmentally friendly treatment is considered challenging for one of the biggest waste streams generated in Qatar.

Applying different treatment techniques are necessary to evaluate the adversely environmental effects and to meet the standards required for reuse, reinjection and discharge of the produced water (Miller, 2006). This could promote safe discharge and reinjection or reuse such as using the treated produced water in plant irrigation which will contribute in the sustainability of Qatar environment.

Chemical and physical parameters of produced formation water could different from one location to another and it depends primarily on the geographical location of the natural gas field as well as on the injected additives chemicals which are used for production process activities (Lee &Neff, 2011). Therefore, it is essential to study the chemical and physical characterization of produced water in a certain field to further propose treatment techniques viable for water reuse. Involving the naturally occurring and environmental friendly materials, which could significantly reduce the cost of treatment for produced water and the treated water, will reduce the usage of the very expensive desalination of sea water. There are many types of techniques conducted on produced water treatment in the past, such as chemical and physical treatment by using different types of filtration such as sand filters, synthetic polymers, activated carbons and others. This research examines three types of filtration by using sand filtration, activated carbon filtration and finally modified activated carbon filtration. Sand filtration treatment is a simple and cheap technique which uses the

sand as media and can remove many pollutants such as fine solids and could remove more than 90% of iron (Adewumi et al., 1992)

Activated carbon is the most common media used in filtration systems in commercial and industrial sectors as the activated carbon is consisting of treated carbon to obtain low-volume which will increase adsorption on surface area (Marsh & Rodríguez, 2006). Activated carbon can remove for example, BTEX and free hydrocarbons that contribute in (TPH) total petroleum hydrocarbons in produced water effluent (Ahmadun et al., 2009).

The combination of water, the hydrocarbons and amphiphilic complexes (small chain alkanols (named surfactants) is comprised a system called Microemulsion forming the thermodynamically steady, transparent thinning out of two immiscible liquids, stabilized by an interfacial film of surfactants, homogeneous and optically isotropic solutions (Paul & Moulik, 1997; Abe, et al., 1986; Khraisheh and Al-Ghouti, 2005; Vandamme, 2002).

This study aims to study water quality of the produced water from natural gas production in the North Field in Qatar. Some primary chemical and physical tests will be performed to examine the common constituents in the produced water. A thorough review on the history of natural gas production, produced water volume, chemical and physical characterizations and efficient produced water treatment methodologies will be presented in Chapter 2. Chapter 3 gives details on sampling, characterization techniques and a produced water treatment experimental setup. Chapter 4 discusses the spatial distribution of produced water characteristics and the results of the methods of treatment used. Treatment methodologies involved the use of sand filtration, activated carbon filtration and modified activated carbon filtration. The last chapter, Chapter 5, gives a summary of the conclusions and general recommendations related to the entire thesis.

## **Research Objectives**

Produced water from gas extraction comprises the most important part of the “waste” with respect to volume which can be considered a potential benefit stream for the industry as well as for other domestic uses such as irrigation. Treatment methods of this wastewater depend on the quality of the produced water, hence; understanding characteristics and contaminants present in the produced water is essential.

In our study, samples of produced water from gas production process which are located in the Qatar North Field are collected. Characterizations of water quality are conducted and reported. Several treatment processes are studied to find out the effect of the applied treatments on the produced water quality.

The major objectives of this project are:

- 1- Study the physical and chemical characterizations of the produced water associated with natural gas from North Field in State of Qatar.
- 2- Examine the removal of various heavy metals and inorganic pollutants from the produced water by using different treatments techniques such as sand filter, activated carbon and modified activated carbons (Microemulsions techniques).

## **2. Background and Literature Review**

### **2.1 History of Global Natural Gas Production**

Natural gas formed since millions of years and then extracted from underground wells. The first time was discovered and known in America as early as 1626 when French explorers found out that Native Americans used to ignite gases that were seeping around Erie Lake (Speight, 2007). The first well was dug in 1859 by Colonel Edwin Drake with a depth of 69 feet below sea level, which was marked by most historians in the earlier stage of natural gas production in North America. Nevertheless, the first well intended specifically to get natural gas was dug by William Hart in Fredonia, New York in 1821. Hart, therefore, was considered by many to be the “*Father of Natural Gas*”.

During 19<sup>th</sup> century transportation of natural gas by pipelines was not yet developed therefore Natural gas was mainly used as a source of light. Robert Bunsen in 1885 came with the discovery of Bunsen burner that opened up new safe ways for using the natural gas (LPG which is a part of natural gas composition) for cooking and heating. The Bunsen burner is a device that mixes air with natural gas in certain amounts to create a flame. Nevertheless, the domestic use of natural gas for homes, was still not feasible before the construction of the first major pipelines in 1891 (Abu Bakar & Ali, 2010) new applications of natural gas were developed, when the transportation of natural gas was possible. These uses included heating, cooking and industrial and manufacturing purposes (Jacobs, 2011) and natural gas has been discovered in all continents and the largest reserves are located in Russia and secondly, in the Middle East (Abu Bakar & Ali, 2010).

## 2.2 Natural Gas Composition

Natural gas is a mixture of flammable gas that occurs alone or associated with oil (petroleum) in the reservoirs (Speight, 2007). The actual component of natural gas depends mainly on the extracted production field (Ly, 2002). Natural gas is mostly consist of methane, but it can also consist of ethane, propane, butane and pentane and other gases for example oxygen, nitrogen, hydrogen sulfide and other traces of gases as shown in Table1.

**Table1:** Typical composition of natural gas (Abu Bakar & Ali, 2010).

<b>Chemical name</b>	<b>Chemical formula</b>	<b>Percentage (%)</b>
Methane	CH <sub>4</sub>	70–90
Ethane	C <sub>2</sub> H <sub>6</sub>	
Propane	C <sub>3</sub> H <sub>8</sub>	0–20
Butane	C <sub>4</sub> H <sub>10</sub>	
Carbon dioxide	CO <sub>2</sub>	0–8
Oxygen	O <sub>2</sub>	0–0.2
Nitrogen	N <sub>2</sub>	0–5
Hydrogen sulfide	H <sub>2</sub> S	0–5
Rare gases	A, He, Ne, Xe	Trace

Over the last twenty years, in the worldwide energy the share for oil has decreased, while the share of gas has increased (U.S. Energy Information Administration, 2014). The primary reason for this move is mainly due to the less price of natural gas compared to oil on an

energy content (Btu) basis and the comparatively lower costs of new natural gas electric generators (U.S. Energy Information Administration, 2014). The second reason of the growing use of natural gas for power generation is related to the fact that natural gas is the cleanest burning fuel amongst the non-renewable fossil fuels since it produces significantly lower carbon emissions than coal or oil, as well as lower levels of other pollutants (Taghipour et al., 2012). Moreover, the minimized emissions associated with natural gas use are increasingly essential as many countries force tighter emission standards.

## **2.3 Natural Gas Production Technology in Qatar**

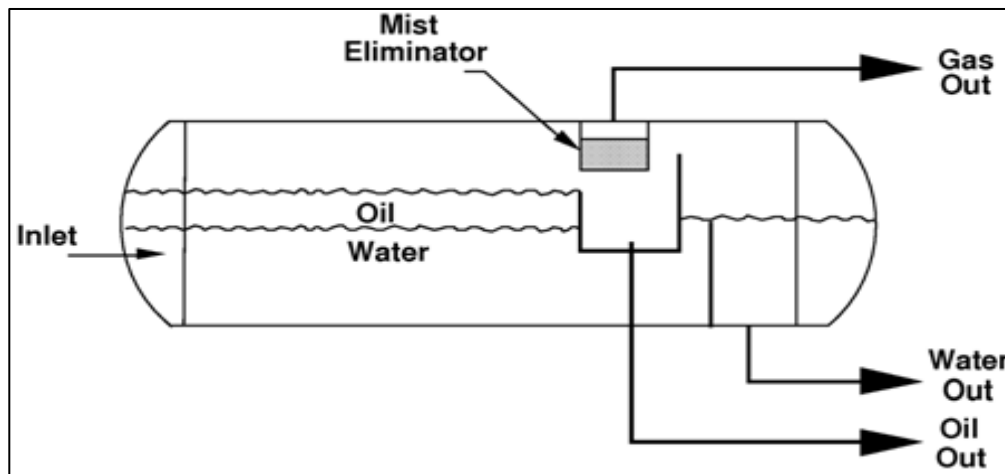
In Qatar, natural gas is explored from the enormous offshore North Field. Fortunately, the nature of the reservoirs does not require unconventional production processes that require water injection to the well. Natural gas production comes associated with the condensate and the formation-produced water, which is considered the largest wastewater stream in Qatar (Natural Gas operation at Qatar petroleum, 2014).

The gas production process first involves separating the gas phase from the liquid phase condensate together with the produced water in the offshore or inshore facilities. Produced water is defined as the "brine", or "formation water" which is the water that has been stuck for millions of years with natural gas and/or oil in a geologic reservoir. When the production process takes place, the separated water is then named as "produced water" (Collins, 1975). After separating the phases from each others, the produced water is separated from the condensate on onshore facilities where it is finally injected in inshore wells (Natural Gas operation at Qatar petroleum, 2014).

### 2.3.1 Natural Gas production Process

The production header directs the well fluid to the main pipeline or intra-field pipeline leaving the wellhead platform while the gas is sent to onshore facility either as dry gas (if water and condensate removed in offshore facility) or as wet gas (if water and condensate was not removed) (Natural Gas operation at Qatar petroleum, 2014).

The gas that has been transported to the onshore facility consists of a mixture of light and heavy hydrocarbons ranging from  $C_1$  to  $C_{5+}$  with produced water, condensate and other impurities like  $H_2S$ ,  $CO_2$  and Mercaptan. This mixture of gases, along with the condensate (heavier hydrocarbons of  $C_{6+}$ ), produced water and small quantities of solid material from the wells is received into the inlet facility where the slug catcher separates the stream into three phases (three streams) ; Gas stream, Condensate stream and Produced water stream. (Natural Gas operation at Qatar petroleum, 2014) as shown in Fig. 1.



**Figure 2:** Slug catcher separating the stream into gas, oil (Condensate) and produced water, Typical Horizontal Skimmer (Bucket and Weir Design) (Stewart & Arnold, 2011).

### **2.3.1.1 Gas stream**

The separated gas stream consists of lighter components of hydrocarbons such as methane, ethane, propane and butane along with inert gases such as nitrogen and helium. The wet Sour Gas stream from the slug catcher is sent for purification using an acid gas removal unit (AGR) to remove the H<sub>2</sub>S and CO<sub>2</sub> in the feed gas. The removed H<sub>2</sub>S and CO<sub>2</sub> is then absorbed by formulated amine solution in the amine absorber by counter current contact and are both sent to sulphur recovery unit (SRU) for recovery of product sulphur from hydrogen sulphide (Natural Gas operation at Qatar petroleum, 2014).

Converted sulphur is condensed and sent to sulphur storage facilities. The sweet gas from the AGR unit is sent to the dehydration unit for the removal of moisture, which is followed by passing it through dryer pre-cooler where about 50% of the moisture is condensed and separated from the feed gas, by cooling. The moisture content is further reduced to < 1ppm by passing through molecular sieve bed operating in adsorption mode where moisture and sulphur compounds are adsorbed. The outlet of the molecular sieve bed is passed through a mercury removal bed where the trace amount of mercury in the feed gas are eliminated by adsorption, and then the gas send to the liquefaction unit, which the gas is precooled or chilled and super cooled to -161°C at which it condenses into a liquid state (Natural Gas operation at Qatar petroleum, 2014).

### **2.3.1.2 Condensate stream**

The condensate stream from the slug catcher is stabilized by stripping in the condensate stripper to separate H<sub>2</sub>S and CO<sub>2</sub>. The stabilized condensate is then cooled and sent to



MeriChem unit for treatment and pumped to storage tanks (Natural Gas operation at Qatar petroleum, 2014).

### **2.3.1.3 Produced water stream**

Produced water stream send to sour gases removal unit by stripping the sour gases (H<sub>2</sub>S & mercaptant compounds then pH adjustment (Caustic solution is injected at feed (produced) water to control pH at 6.0 ~ 7.5. Finally send to filtration unit to reduce TSS before injection in injection wells (Natural Gas operation at Qatar petroleum, 2014).

## **2.4 Produced Water Associated with Natural Gas Production**

The produced/formation water accompanied with natural gas production is the biggest waste effluent stream in the production process and exploration worldwide (Stephenson,1992; Harvard Devold, 2013). Due to the contaminated nature of the produced water, there has been raised environmental concerns drinking well water and surface water contamination from both drilling activities and fluid disposal (Li, 2013). One of the main matters associated with the quality of the produced water is that it contains beside the clays, and the chemical additives, dissolved metal ions and dissolved hydrocarbon , heavy metals, radio nuclides, brines and organics compound that can make the treatment of wastewater complicated and expensive. The formation brines usually include comparatively high concentrations of chloride, sodium, bromide, and other inorganic elements, such as arsenic, barium, other heavy metals, and radionuclides. Meanwhile, formation- produced water from gas production has higher aromatic hydrocarbons compounds of low molecular weight, such B.T.E.X (Benzene, Toluene, Ethyl Benzene and Xylene) and they are more toxic than those

from oil operations as they have higher concentrations (Collins, 1975; Stephenson, 1992; Fillo& Evan, 1995; Lee &Neff, 2011; Li &Harold, 2013).

#### 2.4.1 Produced Water volumes

The volume of formation-produced water from oil or natural gas production is not constant. It depends on the location and technology used for extraction as shown for example in Table 2 shows the formation-produced water volume associated with gas production in some of USA states (Clark & Veil, 2009).

**Table 2:** Produced water volume associated with gas production in some of USA states (Clark & Veil, 2009)

State	Total gas (Mmcf)	Produced water (bbl/year)
Alabama	285,000	119,004,000
Louisiana	1,382,000	1,149,643,000
Michigan	168,000	114,580,000
Texas	6,878,000	7,376,913,000

Global estimation of the produced water production about two hundred fifty (250) million barrels in a day in comparison with approximately eighty (80) million barrels in a day of oil, the ratio of water to oil , is about 3:1. This means 70% of waste water has to be cutout as per the estimation conclusion (Ahmadun et al., 2009). For instance, in 1995 the produced water in the United was about 18 billion barrels for onshore oil and gas operations (Li, 2013). On other hand the average water to gas ratio for natural gas production for Qatari North field is

1.20 and the average produced water production in year 2014 was 23,554 BBL/D as shown in Table 3 (Natural Gas operation at Qatar petroleum, 2014).

**Table 3:** Volumes of produced water in North Field-Qatar in BBL/D between 1998 and 2014 (Natural Gas operation at Qatar petroleum, 2014).

<b>Production Amount in North field</b>	<b>1998</b>	<b>2014</b>
Cumulative water production in BBL/D	415,048.92	50,508,816.54
Average water production in BBL/D	557	23,554
Average water gas ratio in BBL/D/MMSCF	0.36	1.20

## **2.5 Chemicals and Physical Characterization of Produced Water:**

Formation-Produced water is a composite mixture of dissolved and particulate inorganic and organic chemicals (Collins, 1975; Stephenson, 1992; Fillo& Evan, 1995; Lee &Neff, 2011; Li &Harold, 2013). Produced water’s chemical and physical components vary in accordance to the depth, age, and geochemistry of the component that carries the hydrocarbon. The chemical composition also varies depending on the composition of gas and oil in the reservoir, as well as additional chemicals that are added during the production process. Seeing as produced water existed in geological formations for many years before extraction, it contains a wide range of natural compounds that originated from these formations, and from the channels that the water used. Impurities found in produced water include radioisotopes, metals, and wide variety of inorganic and organic compounds and mainly the hydrocarbons (Collins, 1975; Stephenson, 1992; Fillo& Evan, 1995; Lee &Neff, 2011; Li &Harold, 2013).

### 2.5.1 pH

PH is an indicator of acidity & alkalinity of any liquid. A comparison study carried out by shell operated gas and oil production in north sea, study found that the pH level of the produced water from the gas fields is more acidic and ranges between 3.5 – 5.5 compared to produced water from the oil fields is slightly acidic to neutral and the range is between 6- 7.7 (Jacobs et al., 1992). In China, a study done by (Li & Harold. 2013) found that the pH of produced water associated with Coal Bed Methane (CBM) ranges from 8.1 to 9.2. It has a high alkaline content as well as higher bicarbonate content. Table 4 shows the pH values in oil, gas and coalbed methane field.

**Table 4:** Produced water pH characteristics which demonstrate differences between oil, gas fields operated by Shell Expro and NAM (Jacobs et al. 1992) and Coalbed Methane (Li& Harold, 2013).

<b>Produced water</b>	<b>pH parameter</b>
<b>Oil Fields</b>	
Brent	6-7.7
Other northern	6-7.7
Central North Sea	6-7.7.
<b>Gas fields</b>	
UK sector	3.5-5.5
Dutch sector	3.8-5.5
<b>Coalbed Methane (CBM)</b>	8.1-9.2

## 2.5.2 Conductivity and salinity

The ability of a solution to pass electric currents is what is referred to as conductivity. The current in solutions is carried by the cations and anions. For this reason, the conductivity is commonly used to determine the ionic content in solutions in industrial and environmental applications. Ahmadun et al.(2009) conducted compression study for two separate studies for natural gas produced waters by (Fillo & Evans, 1992) and (USEPA, 2000).Summary of the two studies, the conductivity concentration ranged from 4200 to 180,000  $\mu\text{S}/\text{cm}$ , and 136,000 – 586,000  $\mu\text{S}/\text{cm}$ . Table 5 shows the conductivity values for natural gas produced water.

**Table 5:** Conductivity concentration in  $\mu\text{S}/\text{cm}$  in natural gas produced water, A (Fillo & Evans, 1992), B (USEPA, 2000).

<b>Parameter</b>	<b>Minimum value (mg/l)</b>	<b>Maximum value (mg/l)</b>
Conductivity A	4200	180,000
Conductivity B	136,000	586,000

Salinity measures the concentration of salts in a solution. The electrical conductivity (EC) of a liquid can be used to determine the salinity. To convert the conductivity to Salinity we have to convert  $\mu\text{S}/\text{cm}$  (EC) to  $\text{ds}/\text{m}$  by dividing by 1000 and from  $\text{ds}/\text{m}$  to ppm (mg/l) by multiplying by 640 (Gibbs, 2000).The range of the salinity concentration in produced water is very wide. It can range from a very low salt content to the extreme where the salinity is higher than that of seawater. Salts content depending on the formative geological rocks and the formation process, (Collins, 1975). Ayers and Parker, 2001 study showed that the salinity of Hibernia produced water is in the range between 46–195 ‰.

### 2.5.3 Inorganic Anions (Chloride, Sulfate, and Phosphate)

#### 2.5.3.1 Chloride

Produced water contains anions such as chloride  $\text{Cl}^-$ , sulfate  $\text{SO}_4^{2-}$  and phosphate  $\text{PO}_4^{3-}$ . The same review study done by Ahmadun et al. (2009) found variation in chloride concentration. In the first study done by Fillo & Evans (1992), the concentration ranged from 1400 to 190,000 mg/l, while in the second review by USEPA (2000) the range was 81,500 to 167,448 mg/l. In a different study by Tibbetts et al. (1992), the chloride concentration from oilfield produced water ranged from 80-200,000 mg/l as shown in (Table 6).

**Table 6:** Chloride concentration in mg/l in natural gas produced water A (Fillo & Evans, 1992), B (USEPA, 2000) and C (Tibbetts et al. 1992).

Parameter	Minimum value	Maximum value (mg/l)
Chloride A	1400	190,000
Chloride B	81,500	167,448
Chloride C	80	200,000

#### 2.5.3.2 Sulfate

Comparison studies have been performed by Johnson et al. (2008) for Fillo et al. (1992) and Shepherd et al. (1992) the review study found that the sulfate concentration on natural gas produced water ranges from 1.0 to 47 mg/l. In another study for Hibernia produced water that was obtained from the reservoir on the Grand Banks off Newfoundland, Canada was found to have sulfate concentrations of 248–339 mg/L  $\text{SO}_4^{2-}$  (Ayers and Parker 2001). Tibbetts et al. (1992) review paper for oil field produced waters concluded that sulfate

concentrations were ranged from <2 to 1650 mg/L. In other similar studies by McIntosh et al. (2002), and McIntosh and Walter (2005) found that sulfate concentration in produced water from shale gas is range from ND- 3663 mg/l as shown in (Table 7).

**Table 7:** Sulphate concentration in mg/l in natural gas produced water A (Johnson et al. 2008 ; Fillo & Evans, 1992; Shepherd et al. 1992) , B(Ayers and Parker 2001) , C (Tibbetts et al.1992) and D (McIntosh et al. (2002); McIntosh and Walter 2005).

<b>Parameter</b>	<b>Minimum value (mg/l)</b>	<b>Maximum value (mg/l)</b>
Sulphate A	1	47
Sulphate B	248	339
Sulphate C	<2	1650
Sulphate D	ND	3663

### 2.5.3.3 Phosphate

Among the three inorganic anions found in produced water, phosphates have the lowest concentration. For instance, in the Hibernia produced-water, the phosphate content was about 0.35 mg/L as P (Johnsen et al., 2004). Similarly, in the shale gas produced water the concentration of phosphates ranged from ND to 5.3 mg/l (McIntosh et al., 2002 and McIntosh and Walter 2005).

### 2.5.4 Sulfide

Sulfides (Polysulfide's and hydrogen sulfide) found in anoxic produced waters is the product of bacterial reduction of sulfates (Neff, 2002). Sulfide concentrations are higher in formation-produced waters from sour oil and gas rigs. For example Witter and Jones (1999)

found the sulfide concentration in formation water produced from California wells range between 48 and 216 mg/L.

### **2.5.5 Metals and Cations**

Dissolved or micro particles of metals can also be available in formation -produced water. However, the type, concentration, and chemical content of the metals differ depending on the formative geological features, their age, and the amount and chemical composition of the water that injected into the hydrocarbon reservoir (Collins, 1975). The common metals present in formation-produced water include mercury, zinc, barium, manganese, and iron and usually is higher than the sea water concentration (Neff et al., 1987) (Table 8).

For instance, Hibernia produced water were found to be highly concentrated in barium, iron, and manganese as compared to seawater. The concentration of iron (Fe) and manganese (Mn) is usually high in formation water because it is anoxic. When water that is high in these two metals comes to the surface and is exposed to atmosphere, the metals precipitate to form of iron (Fe) and manganese (Mn) oxyhydroxides. Additional metals present in the water could co-precipitate along with iron (Fe) and manganese (Mn) and be absorbed, complexed or dispersed with solid hydrous iron (Fe) and manganese (Mn) oxides (Lee et al. 2005a; Azetsu-Scott et al. 2007). Zinc (Zn) and possibly lead (Pb) in produced water could be resulting from galvanized steel pipelines in contact with the formation water or with other waste water streams that may be exposure during treatment in the water/oil separator system. (Neff, 2002)



Another review Article conducted by Johnson et al. (2008) for two different studies showed that metals found in natural gas produced waters in high concentrations include barium, sodium, iron, magnesium, potassium, and strontium. As shown in (Tables 8 and 9).

**Table 8:** Concentration ranges ( $\mu\text{g/L} = \text{ppb}$ ) of several metals in formation-produced water from the Scotian Shelf and the Grand Banks, Canada, compared to produced water discharged to northwestern Mexico gulf and the Norwegian region of the North Sea (Neff, 2002).

<b>Metal</b>	<b>Seawater</b>	<b>Gulf of Mexico a</b>	<b>North Sea b</b>	<b>Scotian Shelf c</b>
Arsenic	1–3	0.5–31	0.96–1.0	90
Barium	3–34	81,000–342,000	107,000–228,000	13,500
Cadmium	0.001–0.1	<0.05–1.0	0.45–1.0	<10
Copper	0.03–0.35	<0.2	12–60	137
Iron	0.008–2.0	10,000–37,000	4,200–11,300	12,000–28,000
Lead	0.001–0.1	<0.1–28	0.4–10.2	<0.1–45
Manganese	0.03–1.0	1,000–7,000	NA	1,300–2,300
Mercury	0.00007–0.006	<0.01–0.2	0.017–2.74	<10
Molybdenum	8–13	0.3–2.2	NA	NA
Nickel	0.1–1.0	<1.0–7.0	22–176	<0.1–420
Vanadium	1.9	<1.2	NA	NA
Zinc	0.006–0.12	10–3,600	10–340	10–26,000

a. Combined results from seven platforms (Neff, 2002), b. Combined results from 12 platforms (Neff, 2002) and c. SOEP/DFO (SOEP, 1996).

**Table 9:** Constituents of Metals in (mg/l) in produced waters of natural gas (Johnson et al., 2008) .

<b>Parameter</b>	<b>Minimum value</b>	<b>Maximum value</b>
Iron <sup>a</sup>	ND	1100
Iron <sup>b</sup>	39	680
Lead <sup>b</sup>	<0.2	10.2
Magnesium <sup>a</sup>	0.9	4300
Magnesium <sup>b</sup>	1300	3900
Manganese <sup>a</sup>	0.045	6.5
Manganese <sup>b</sup>	3.59	63
Nickel <sup>a</sup>	ND	0.02
Nickel <sup>b</sup>	<0.08	9.2
Potassium <sup>b</sup>	149	3870
Aluminum <sup>a</sup>	ND	0.4
Aluminum <sup>b</sup>	<0.50	83
Arsenic <sup>a</sup>	0.004	1
Arsenic <sup>b</sup>	<0.005	151
Barium <sup>a</sup>	ND	26
Barium <sup>b</sup>	9.65	1740
Boron <sup>a</sup>	ND	56
Cadmium <sup>a</sup>	ND	0.015
Cadmium <sup>b</sup>	<0.02	1.21
Calcium <sup>a</sup>	ND	25,000
Calcium <sup>b</sup>	9400	51,300
Chromium <sup>a</sup>	ND	0.03
Copper <sup>a</sup>	ND	0.02
Copper <sup>b</sup>	<0.02	5
Sodium <sup>a</sup>	520	45,000
Sodium <sup>b</sup>	37,500	120,000
Strontium <sup>a</sup>	–	6200
Zinc <sup>a</sup>	ND	0.022
Zinc <sup>b</sup>	<0.02	5

a (Fillo,& Evans,1990) b (United States Environmental Protection Agency,2000).

### 2.5.6 Total Suspended Solids (TSS)

(TSS)- Total Suspended Solids are the suspended particles in the water and cannot pass through the filter or are those solids particles (minerals and organic material) and stay stuck on a 1.2 µm filter (U.S.EPA, 1998). Ahmadun et al.(2009) conducted compression study for

two separate studies for natural gas produced waters by Fillo & Evans (1992) and USEPA (2000) found that the concentration of TSS ranged between 14-800 mg/l and 8 – 5484 mg/l respectively. Tibbetts (1992) in his study for oilfield produced water found that the TSS was ranged from 1.2-1000 mg/l.

**Table 10:** TSS concentration in mg/l in natural gas produced water A (Fillo & Evans,1992), B (USEPA,2000) and C (Tibbetts ,1992)

<b>Parameter</b>	<b>Minimum value</b>	<b>Maximum value (mg/l)</b>
TSS A	14	800
TSS B	8	5484
TSS C	1.2	1000

### **2.5.7 The Chemical Oxygen Demand (COD)**

The (COD) , Chemical Oxygen Demand is standard method for measurement the amounts of pollutants that cannot be oxidized biologically in water sample and it seeks to identify and determine the amount of both dissolved and suspended contaminants in water (USEPA, 1993). The COD result expresses by indicating the amount of oxygen dissolved in water, which is expressed as milligrams per a liter or parts per million (ppm) of water, which is used up by the pollutants (USEPA, 1993). The compassion study of natural gas produces waters conducted by (Ahmadun et al., 2009) estimated the COD concentration in produced waters to be between 2600 mg/l and 120,000 mg/ (Table 11). Another study ‘summary review for oilfield –produced water’ gave COD mean values was 1220 mg/l (Tibbetts et al.1992).

**Table 11:** COD concentration in mg/l in natural gas produced water (Fillo & Evans, 1992) (Johnson et al.,2008)

<b>Parameter</b>	<b>Minimum value</b>	<b>Maximum value (mg/l)</b>
COD	2600	120,000

### **2.5.8 Biochemical Oxygen Demand (BOD5)**

(BOD5)-Biochemical Oxygen Demand is a bioassay procedure whose purpose is to measure the amount of oxygen consumed in the decomposition process of organic matter by bacteria (Sawyer and McCarty, 1978). The procedure involves the determination of the mass of dissolved oxygen for fixed amount of solution needs for the biochemical oxidation process. It is performed under the following prescribed conditions, total darkness, 20<sup>0</sup>c, and observation is through a five-day period. The results are expressed in mg of oxygen per a liter of the sample of the liquid (USEPA, BOD5, 1999). Produced formation water from most gas platforms contained higher concentrations of BOD (Table 12) than from oil-field produced formation water. In a study of natural gas produced waters for BOD concentration the results ranged between 75 and 2870 mg/l (Fillo & Evan, 1990).

Produced water directly obtained from wells can have high BOD resulting from both reduced inorganic elements, such as iron and manganese, and from fluids used to drill wells and additive chemicals. If drilling fluids contain significant quantities of organic material, such as the guar bean used in some gels, then very high BOD's can result (Ray & Rainer, 1992). High BOD content in produced water can cause water quality problems such as severe dissolved oxygen depletion in receiving water bodies. Therefore, water of this nature must be substantially oxidized to prevent discharge of high BOD materials into receiving streams.

**Table 12:** Mean biological oxygen demand in concentrations (mg/L) of several primary nutrients in formation-produced water from 50 platforms discharging to the Mexico gulf at hypoxic zone off Louisiana coast; mass loadings are concentration  $\times$  discharge volume in kg/day (from Veil et al. 2005; Bierman et al. 2007).

Parameter	Mostly oil	Mostly gas	Oil and gas	Mass
No. platforms	6	20	24	50
BOD	595	1,444	642	16,330

### 2.5.9 Total Organic Carbon (TOC)

Total Organic Carbon (TOC) is a measure of the total amount of organic compounds in the water samples; this is useful in determining the level of pollution that the wastewater would content. Also, it is becoming increasingly essential to have a reliable and rapid technique for determination of TOC in wastewater used for better purification procedures by knowing the amount of Total Organic Carbon in the wastewater (Dolezal et al., 2003).

The concentration of TOC, which is measured in mg/L (parts per million), of several of naturally occurring water vary from  $< 0.1$  up to  $> 11,000$  mg/L (Neff, 2002). The TOC concentration varies significantly from one well to another and Produced water, for example, from Hibernia platforms has a TOC concentration mean value 300 mg/L (Ayers and Parker, 2001). In another study for Louisiana rigs Produced water wells TOC concentration ranges between 67–620 mg/L of (Veil et al., 2005).

Tibbett's et al.(1992) conducted summary of quoted literature values for the TOC concentration which were range from 0-1500 mg/l. Table13 shows comparative of TOC mean concentrations (mg/L) of several produced water samples from different platforms oil,

gas and mix production which were discharged in Mexico gulf (Veil et al. 2005; Bierman et al. 2007).

**Table 13:** Mean TOC concentrations (mg/L) of several primary nutrients in formation-produced water from 50 platforms discharging to the Mexico gulf at hypoxic zone off Louisiana coast; mass loadings are concentration × discharge volume in kg/day (from Veil et al. 2005; Bierman et al. 2007).

Parameter	Mostly oil	Mostly gas	Oil and gas	Mass loading
No. platforms	6	20	24	50
Total organic carbon (TOC)	551	888	297	6,400

### 2.5.10 Oil & grease by Hexane Extractable Material (HEM)

(HEM) Hexane Extractable Material is a procedure which used hexane to extract material preferably (oil and grease) from an aliquot of the sample which has been acidified. The solution with hexane is heated and hexane evaporated at 70 °C. The residue left behind is defined as oil and grease. Oil and grease has two major components, these are petroleum based hydrocarbons (termed as ‘nonpolar materials’) and fatty compounds of animal or vegetable origin (USEPA; 1999; 2010).

In a compression study of natural gas produced waters by Ahmadun et al. (2009), the oil & grease concentration shown in (Table 14) ranged between 6-60 mg/l (Fillo & Evans, 1992) and 2.3 –38.8 mg/l (USEPA, 2000). Another compression study was done for natural gas-produced formation water for Oil and Grease content the range was between 2.3 and 60 mg/l (Shepherd et al., 1992 and Johnson et al., 2008). Another research on formation -produced water in the western United States by (Benko and Drewes, 2008) found the oil and grease concentration ranged between 40 mg/L to 2,000 mg/L.

**Table 14:** Oil & grease concentration in mg/l in natural gas produced water A (Fillo & Evans, 1992), B (USEPA, 2000), C (Shepherd et al., 1992; Johnson et al., 2008) and D (Benko and Drewes, 2008).

<b>Parameter</b>	<b>Minimum value(mg/l)</b>	<b>Maximum value(mg/l)</b>
Oil & grease A	6	60
Oil & grease B	2.3	38.8
Oil & grease C	2.3	60
Oil & grease D	40	2000

### 2.5.11 Organic Acids (Formate, Acetate, and Propionate)

The organic acids that are mainly present in produced water are mono- and di-carboxylic acids (COOH) of saturated (aliphatic) and aromatic hydrocarbons. An abundance of the Total organic compound, TOC, in formation-produced water consists of a combination of carboxylic acids with low molecular weight, such as formic, acetic, propanoic, butanoic, pentanoic, and hexanoic acids (Means and Hubbard, 1987; Barth, 1991; Røe Utvik, 1999). Formic and acetic acids are the most abundant and plentiful organic acids present in formation-produced water. The amount of these acids is indirectly proportional to the molecular weight (typically reductions with increasing molecular weight) (MacGowan and Surdam 1988). Table 15 shows comparison of organic acid concentration between USA offshore and Norwegian North Sea.

**Table 15:** Concentrations (mg/L = ppm) of low molecular weight organic acids in formation-produced water from four production facilities on the Norwegian continental shelf (Røe Utvik 1999), in Mexico gulf off the Texas and Louisiana coast, and in the Santa Maria Basin off the California coast (MacGowan and Surdam 1988).

Organic acid	Formula	Offshore USA	Norwegian North Sea
Formic acid	CHOOH	ND-68	26-584
Acetic acid	CH <sub>3</sub> COOH	8-5,735	ND
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> COOH	ND-4,400	36-98

NA: not analyzed. ND: not detected.

### 2.5.12 Benzene, Toluene, Ethyl Benzene, and Xylene (B.T.E.X)

B.T.E.X is the term which used for volatile aromatic compounds Benzene, toluene, ethyl benzene, and xylene which naturally found in oil and gas products, such as natural gas, gasoline and diesel fuel. (USEPA, 2010). BTEX are extremely volatile and thus they are lost quickly during produced water treatment by air stripping and during the early mixing of the produced water spiral in the sea (Terrens and Tait, 1996). Of all BTEX components, Benzene is the most abundant but its concentration decreases with increases in alkylation (Dórea et al. 2007; Chapters 3 and 24). Concentration of BTEX in oil field produced water collected from the Gulf of Mexico showed that the Benzene is the most abundant with concentration range of between 0.44-2.80 ppm. Toluene came second while xylenes and ethyl benzene came third and fourth respectively. Similarly, BTEX tests done on Indonesia produced water showed that benzene is the most abundant with a concentration range of 0.084 to 2.30 ppm, toluene, ethyl benzene, and xylenes came second, third and fourth respectively (Neff,2002).

In another similar study done (Dórea et al. 2007) on produced water obtained from the Permian basin, the results found the benzene had the highest concentration at 1.5-778.51



ppm, followed by ethyl benzene, xylenes, and finally toluene respectively. The concentrations of the BTEX in oil field produced formation water collected from the Bonsucesso plant effluent, State of Sergipe in Brazil confirmed that benzene is the most concentrated with a range of 1.291 to 1.511 ppm (Khan et al. 2016) as shown in Table 16 and 17.

**Table 16:** Concentrations (mg/L) of BTEX in formation-produced water from four platforms in the US Gulf of Mexico and from three offshore production facilities in Indonesia (Neff, 2002), Oil Field - Permian Basin Produced water (Dórea et al, 2007), Oil Field – Bonsucesso produced water effluent Barzil (Khan et al, 2016).

Compound	Molecular formula	7 Gulf of Mexico produced waters ppm	3 Indonesian produced waters ppm	Oil Field - Permian Basin Produced water Ppm	Oil Field – Bonsucesso produced water effluent Barzil ppm
Benzene	C <sub>6</sub> H <sub>6</sub>	0.44–2.80	0.084–2.30	1.50-778.51	1.291-1.511
Toluene	C <sub>7</sub> H <sub>8</sub>	0.34–1.70	0.089–0.80	0.1-0	1.167-1.357
ethyl benzene	C <sub>8</sub> H <sub>10</sub>	0.026–0.11	0.026–0.056	2.01-399.84	0.136-0.158
Xylenes (3 isomers)	C <sub>8</sub> H <sub>10</sub>	0.16–0.72	0.013–0.48	0.01-0.46	0.283-0.345

**Table 17:** BTEX in produced water from platforms of the oil production Oseberg F., Oseberg C., and Brage (Utvik, 1999).

Component	Units	Brage	Oseberg F	Oseberg C
Benzene	mg/L	4.5	4.6	3.7
Toluene	mg/L	3.5	2.7	1.5
ethyl Benzene	mg/L	0.3	0.6	0.3
Xylene	mg/L	0.7	0.4	0.2

Sum BTEX	mg/L	9.0	8.3	5.8
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### 2.5.13 Phenols

Phenols, also known as phenolics, are considered as a part of the aromatic organic group of compounds having one or more hydroxyl groups that is attached to an aromatic hydrocarbon group. Produced water from oils & gas production has been found varying in the amount of phenolics concentration. However, the highest concentrations of phenols are found in produced water from gas condensate production and have the same aromatic compounds that have low molecular weight (Callaghan, 1990).

In most produced waters, the concentration of phenols is usually less than 20 mg/l. (Neff, 2002) asserts that the global content of phenols in formation-produced water ranges is from 0.4 to 23mg/l. An example that sought to determine the phenol concentration in produced water from Gulf coast of Louisiana and the Norwegian Region of the North Sea established that the concentrations of phenols are range from 2.1-4.5 mg/L and 0.36-16.8 mg/L, respectively as shown in table 18 (Neff, 2002 and Johnsen et al., 2004 and Johnsen et al., 2004). Table18 shows the comparison of the phenols concentration between oil and gas field which show that produce water from gas field have higher phenols concentration.

**Table 18:** Average concentrations of phenols data in produced waters discharged by Shell Expro and NAM collected in 1989 from their 12 oil and 15 gas platforms in mg/L (Neff, 2002).

Produced water	Phenols
<b>Oil Fields</b>	
Brent	1.6
Other northern	1.4
Central North Sea	5
<b>Gas fields</b>	
UK sector	0.6
Dutch sector	6.4

### 2.5.14 Total Nitrogen (TN)

Total nitrogen is the cumulative sum of all the nitrogen compounds in the water. It includes ammonia-nitrogen (NH<sub>3</sub>-N), nitrate-nitrogen (NO<sub>3</sub>-N), nitrite-nitrogen (NO<sub>2</sub>-N) and organically bonded nitrogen (UNITAR, 2016). Whereas total nitrogen by total kjeldahl nitrogen refers to the sum of organic nitrogen compounds and ammonia but excludes nitrate-nitrogen and nitrite-nitrogen. Total nitrogen is some time is regulated for municipal and industrial water treatment plants (UNITAR, 2016).

Produced water from fifty platforms was tested for nitrate, nitrite, and ammonia concentrations. It was found that the nitrate concentration had mean value 2.71 mg/L higher than that of oil or mixed production. The mean value of Nitrite concentration was 0.05 mg/l for the oil and mixed productions. Finally, the ammonia and ammonium concentrations in mostly gas production mean is 57 mg/l. as shown in Table 19.

**Table 19:** Mean concentrations of Nitrate, Nitrite & ammonia (mg/L) of several produced water samples from 50 platforms discharging to Mexico gulf at hypoxic region off Louisiana coast ; mass loadings are concentration × discharge volume in kg/day (Veil et al., 2005; Bierman et al., 2007).

Parameter	Mostly oil	Mostly gas	Oil and gas	Mass loading
<b>No. platforms</b>	<b>6</b>	<b>20</b>	<b>24</b>	<b>50</b>
Nitrate (NO <sub>3</sub> <sup>-</sup> )	1.14	2.71	1.94	31.0
Nitrite (NO <sub>2</sub> <sup>-</sup> )	0.05	0.05	0.05	1.40
Ammonia & Ammonium (NH <sub>3</sub> , NH <sub>4</sub> <sup>+</sup> )	92	57	85	2,160

### **2.5.15 Production Chemicals (Treating Chemicals)**

The production process of produced water in oil or gas field requires addition of certain chemicals in addition to the naturally occurring ones (Karman et al., 1996 ; Johnsen et al., 2004). These chemicals are mainly used to manage operational problems. They have functions such as facilitating the separation of oil, gas, and water, preventing corrosion of the pipeline, and preventing the formation of methane hydrate (ice) in the gas production system. The chemical requirements for the production process vary and unique across different production systems (Karman et al., 1996 ; Johnsen et al., 2004).

Chemicals used in the production process can be put into three broad categories namely gas processing chemicals, production treating chemicals, stimulation and work over chemicals. Production treating chemicals are the chemicals which are added during the production process. They include scales inhibitors; corrosion inhibitors; hydration inhibitor; biocides; water treating chemicals; emulsion breakers; flocculants and anti-foams; reverse emulsion breakers and coagulants, which are used in the recovery and pumping of hydrocarbons (Karman et al., 1996 ; Johnsen et al., 2004). Since these chemicals are used in large amounts, it is a good thing that most of them are soluble in oil thus they eliminate the need for disposal mechanisms. Some are also soluble in water and are disposed with the formation-produced water. Treatment chemicals are used to correct specific issues, for this reason, they are not added to the system unless necessary. Their use is kept to a bare required minimum because they present negative environmental problems if overused particularly harmful chemicals such as biocide and corrosion inhibitor (Karman et al., 1996 ; Johnsen et al., 2004).

However, the amount of chemicals in treated produced water is very low. The use of corrosion inhibitors, scale inhibitors, and gas treatment chemicals (glycol and methanol) is directly proportional to the same extent of the problems that in a production system experiences and consequently the concentration in produced water (Karman et al., 1996; Johnsen et al., 2004). Table 20 & 21 show the different types of production chemicals and their concentrations.

**Table 20:** Production treating chemicals used on North Sea platforms of gas and oil production and the estimated quantities in produced water discharged to the ocean (Johnsen et al. 2004).

Chemical	Typical use concentration (ppm, v/v)	Amount discharged to North Sea (t/y)
Scale inhibitor	3–10	1,143
Corrosion	25–100	216

**Table 21:** Concentrations (mg/L) of several production treatment chemicals in formation-produced water discharged in the Gullfaks and Staffjord fields in the North Sea with trade names of commercial formulations included (Karman et al. 1996).

Chemical	Concentration(mg/l)
Well treatment scale inhibitor (S432)	6.8
Glycol	7.7
Corrosion inhibitor (PK 6050)	1.5
Corrosion inhibitor (VN 6000 K)	0.3
Process scale inhibitor (SP 250)	2.1
Process scale inhibitor (SP 2945)	0.2

## **2.6 Produced Water Treatment**

One of the simple methods of treating water is through filtration. This is the process that separates water from suspended micro particulate and colloidal impurities by passing the water through a filter media, which is porous to allow the water but not the impurities to pass through. This process changes the chemical composition of the water since there are some components that have been removed.

There is a wide range of material that could be used as a filter media, as long as it is porous. These include sand, crushed stone, and activated carbon. However, sand is most widely used because it is relatively easy to obtain, cheap and a relatively good filter (Scholz, 2016).

### **2.6.1 Sand filtration:**

#### **2.6.1.1 Slow Sand Filtration treatment system**

The slow sand filter is made up of a sand layer through which the pretreatment water passes downwards. It is also made with special features that control the flow of water and allows for the removal of filtered water from the system. The slow sand filter is somewhat similar to the treatment processes in constructed wetlands. The rate of filtration of the water (in  $\text{m}^3/\text{m}^2/\text{h}$ ) is between 0.1 and 0.4 (Scholz, 2016).

Fine grains of sand are the main component of the filter bed, which have a diameter ranging from 0.15 and 0.35 millimeters and a depth summation of about 1 m before the process of filtration begins. As the filtration goes on, the colloidal and suspended material comes from the untreated water and remains at the high part of the treatment system. When

these particles build up, they clog the system thus reducing its efficiency. Therefore, it is important to remove the clogging material. This is done by scraping off the top layer of the sand that is full of the impurities. The amount of sand to be taken off during the unclogging process should be around one to few centimeters (Scholz, 2016).

#### **2.6.1.1.1 Slow Sand Filter Mechanisms**

The process of filtration in its entirety is the combination of several different processes. These are mechanical straining, chemical and biological activity, adsorption and sedimentation for overall removed the impurities (Scholz, 2016).

Mechanical straining is the simplest part of the process. The large suspended matters particles that cannot go through the gaps between the sand grains are removed. Since the particles are too large to pass through, mechanical straining is done on the filter surface as soon as the water goes through the sand bed and it is not depend on the filtration rate. For the grain size of 0.15 mm, the diameter of the smallest pores are still a little over 20  $\mu\text{m}$  and are therefore incapable to keep hold of the colloidal matter or bacteria with size (0.001-1  $\mu\text{m}$ , and  $\leq 15$  mm) respectively.

In the same process, coarser suspended solids (SS) that are trapped at or near the bed surface are collected forming a very fine porous layer. This new porous layer, which gets thicker with subsequent filtrations, increases the straining effectiveness and consequently decreases effluent turbidity. In addition, straining effectiveness is improved more and more after every subsequent filtration due to the deposition on the grains in the filter bed, which compress the pore openings (Huisman & Wood, 1974; Bourke, 1995; Scholz, 2016).

Sedimentation aims to remove particles that are smaller than the pores of the sand and can thus pass through. It does so by precipitating the impurities to the edges of the sand grains. The ordinary filter bed (grain size of 0.25 mm and porosity of approximately 38%) has sedimentation gross area about  $15,000 \text{ m}^2/\text{m}^3$  of filtering substance. The area for deposition of the sediments can go above  $1000 \text{ m}^2/\text{m}^3$  filter volume easily, even if only a portion of this area is effective. The surface is deemed effective if it is facing upwards, it contactless with other sand grains, and it is exposed to low-scour velocities. The loading of the surface and the deposition area will become very small, with a rate of filtration of  $0.2 \text{ m/h}$  and  $\leq 2 \times 10^{-4} \text{ m/h}$  (Huisman & Wood, 1974; Bourke, 1995; Scholz, 2016).

Collision of suspended impurity particles in the water with the grains sand after the particles have departed from a flow line by centrifugal force is referred to as adsorption. During this process, the impurities stick to gelatinous coating surfaces of the sand grains that are a coat formed by bacteria and colloidal matter deposits. Adsorption is promoted by van der Waals forces of attraction, by physical attraction between particles to another particle. Coulombic forces further enhance it. This is the electrostatic attraction between opposite electrical charges (Huisman & Wood, 1974; Bourke, 1995; Scholz, 2016).

Mass attraction is a phenomenon that occurs almost everywhere. Its magnitude, however, the sixth power of the space between particles leads to decline. From the earlier example mentioned,  $1 \text{ m}^3$  of sand filter has a total area of  $1500 \text{ m}^2$ . With 38% porosity and thus contains  $0.38 \text{ m}^3$  of water, which relates to a thickness of a water film around the grains of 25 mm, when spread over the surface area. These spaces are too big to effectively hold in the sides of the grains the colloidal and molecular dissolved impurities. They would fall off. In this case, purification of the water is only made possible by another force, the centrifugal



force. This force forces the impurity particles to come into direct contact with the absorption surface. Inversely proportional to the second power of the distance, and therefore its influence, reaches deeper into the body of liquid passing. The crystal structure nature on it attracts positive particles in water since the clean quartz sand is a negatively charge (Huisman & Wood, 1974; Bourke, 1995; Scholz, 2016).

The colloidal matter that is attracted to the sand particles includes for example, carbonates, aluminum hydroxide, iron hydroxide and cations such as iron (Fe), manganese (Mn), and aluminum (Al). Organic colloidal matters such as bacteria are negatively charged. Consequently the organic colloids are not attracted, and when new clean sand is taken first into the service of filter, these impurities are not eliminated.

During the process when positive charges particles are adsorbed, a maturing period is needed for the slow sand filter. Oversaturation may occur when positive charges accumulate on some of the filter grains, when this happens the coated particles charge changes from negative to positive (Huisman & Wood, 1974; Bourke, 1995; Scholz, 2016).

The negative charges particles, organic source, colloidal matter of animal and the dissolved impurities such as anions, including  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  are eliminated by the secondary adsorption after the initial adsorption during the breaking-in period. When over saturation occurs by secondary adsorption, the overall charge changes to negative, thus positively charged matter is adsorbed. This cycle repeats itself over and over. Also, sand grains ions may be removed by the flowing fluid; this also reverses the electric charge (Scholz, 2016).

Tyagi et al., (2009) applied slow sand filtration techniques as a pre-treatment step for the up-flow anaerobic sludge blanket (UASB) reactor effluent. A filter column on a laboratory scale with 0.54 m sand media depth and 10 cm diameter was used to study the performance

of the process. It was shown that slow sand filtration with 0.43 mm sand size is the most effective with a filtration rate 0.14 m/h. This sand filtration can remove (COD) chemical oxygen demand, (BOD) bio-chemical oxygen demand (BOD), suspended solids (SS), turbidity, fecal streptococci (FS) and total and fecal coliforms (TC and FC) by (70, 89.1, 91.6, 99.99, and 99.95 % respectively .

Ariyawathie & Suzuki, (1987) studied the removal of several impurities from water. They reported that all the effluent water from sand filtration were free from ammonia at the early stage of the experiment. They also asserted sand filtration is effective because the percentage of nitrogen, phosphorus and chemical oxygen demand (COD) that are removed are high, 100% of phosphorus is removed during the process.

Cha et. al. (2010) engineered a new sand filtration combined with ozonation technique for treatment of produced water (Fig. 2). The technique involves rapid and consecutive cycles of compression and decompression through ozonation. The use of sand filtration with 10 pressure cycles of Ozonation repeated for 20 cycles resulted in oil removal to 20 ppm, and COD from 320 mg/l to 102 mg/l with removal efficiency of 68%.



**Figure 3:** Produced water before and after treatment with pressure-assisted ozonation and sand filtration (Cha et al., 2010).

### **2.6.1.2 High Hydraulic Loadings Sand Filtration Treatment System (HLR)**

Lahbib et al. (2016) conducted a combined treatment using a multi-soil-layering system with sand filters (MSL–SF). The experimental sand filter included three similar sand columns placed parallel to each other. Each column was filled with 10 cm of gravel at the top and the bottom of the filter and 80 cm of fine sand. The three sand columns HLRs (100, 200 and 400 L m<sup>-2</sup> day<sup>-1</sup>) were compared. The got results showed that the conceptual model based on the combination of the MSL method and sand filter (MSL–SF) showed very high efficiency in the elimination of bacteria, organic matter, nutrients, and the reduction of parasites. For the low HLR high performances were noted. The main removal percentage of SS, BOD5, COD, TN and TP were respectively 99.73, 97.78, 98.40, 92.93 and 96.21% for the HLR-100.

A similar research sought to examine the feasibility and possible efficiency of coarse / fine sand filtration in the removable of organic substances from turkey processing effluent. Sand filtration was experienced with hydraulic loadings and three organic. Column operated at low and medium hydraulic loading rates (6132L/m<sup>2</sup>/day) for 80 days. The elimination of TOC and BOD5 was higher than >94%. The elimination at the highest hydraulic loading rate (264L/m<sup>2</sup>/day) dropped after the presence of a black zone in the top layer of fine sand on the 30<sup>th</sup> day for one reactor and the 50<sup>th</sup> day for the other (Young et al., 2007).

Welz et al., (2012) conducted a study on winery wastewater to evaluate the phenolic components removal by using three types of filtration, first sand columns, second biological sand filter column, and third sand microcosm's column. The study established that at low in effluent phenolic concentrations, all the organic material was removed from the water, however at high concentrations; the substrate removal was incomplete and potentially toxic metabolites accumulated. For the treatment of phenolics waste, the sand provided a suitable

substrate, and both biotic and abiotic (52% and 48% respectively) elimination mechanisms effected the elimination of model phenolic. Abiotic elimination is linked to the physical structure and the chemical composition of the substrate with clay, metals and organic carbon being powerfully associated with phenolic binding and/or chemical transformation reactions. The biodegradation rate of phenolic acids significantly enhanced by adaptation of previous microbial communities.

Sand filtration is also able to remove the oil & grease. A study was applied on produced water, the primary oil and grease O&G was 264 mg/l and final oil and grease O&G was 13.3 mg/l with O&G removal recorded at 95.8% (Multon and Viraraghavan, 2006).

#### **2.6.1.3 Intermittent sand filtration treatment system**

Intermittent sand filter are based on the principle of intermitted water flows and levels. Intermittent influent applications placed on the sand bed. Filtration Intermittent sand filter systems (ISF) purification is conducted by biological, physical and chemical mechanisms that can be employed to consistently achieve a significant reduction of total suspended solids (TSS) and chemical oxygen demand (COD) (Darby et al., 1996).

#### **2.6.1.4 Sand /Activated carbon filtration treatment:**

Previous studies came up with a water treatment system that used sand for filtration and carbon for treatment. The treatment system was able to filter out organochlorine, organophosphate and pyrethroid pesticide residues to their detection limit (James et al., 1985).

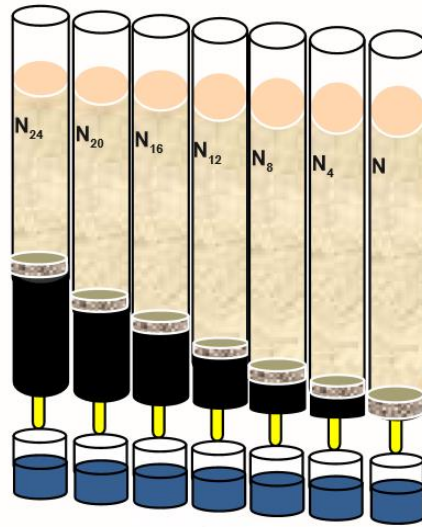
Gherairi et al., (2013) conducted a study for treatment of domestic wastewater. In their experiment, they used a bi-layer filtration system made of sand from a sand dune and activated carbons.

The comparison of COD and BOD results to those obtained from filtration using a bed of sand dune only showed a clear enhancement of the efficiency. Efficiency was improved by between 80% and 95% for COD and 78% and 94% for BOD5. The study was comprised of seven filtration pilots that were made of PVC columns each with a diameter of 80 mm and a height of 700 mm (Raafat, 2012).

The filtration system used in the study was made of a bilayer of sand in contact with activated carbon at various heights (Table 22). Each filter was equipped with a drainage system as demonstrated in (Fig.3) (Gherairi et al., 2013).

**Table 22:** Pilot's dimensions (Gherairi et al., 2013).

<b>pilot</b>	<b>H sand (cm)</b>	<b>H carbon (cm)</b>
N	60	0
N4	56	04
N8	52	08
N12	48	12
N16	44	16
N20	40	20
N24	36	24



**Figure 4:** Filtering pilots (Gherairi et al., 2013)

A mean of 72%, with a range of 4%-99%, of the impurities were successfully removed by the filtering system. This was done by continuously filtering the suspended particles and chemicals. Continuous filtration allows the impurities maximum exposure to the filtration system thus ensuring that most of them are removed. Following the sand filtration, the clean water then passes through the granular carbon where removal of organic impurities is done. The efficiency of the system in removing organics was approximately 91%, with a range of 24% to 99%.

The pH results of filtered water are always greater than those of the raw water. This might be attributed to the presence of alkaline salts in the former (Gherairi et al., 2013). The conductivity of the filtered water usually high differed significantly and depending on the time of collection. The first few droplets collected had high conductivity due to the existence of a high content of salts. Concentration of salts was high in the first waters because it was

the beginning point of leaching of the soluble salts. It is worth mentioning that the conductivity is directly linked to the initial salinity of the sand. From the 3<sup>rd</sup> to the 14<sup>th</sup> day, the conductivity of the water was stable at (3.5 mS/cm) with small variations between filters were observed. However, from the 14<sup>th</sup> to the 42<sup>nd</sup> day, the conductivity of the water reduced to 1.2 mS/cm (Gherairi et al., 2013).

At the beginning of the experiment the filtering efficiencies were about 80.5 % for the COD. An increase of the COD yields for all filters was also observed. The filtering yield of sand only (pilot N) range between 79.1 and 95.3 % while the filtering yield result of sand and carbon (pilot N4) were quite good, range between 82.94 to 94.6 % (Gherairi et al., 2013). These variation can be explained by the adsorption of the organic matter on the (AC) activated carbon (Rani & Dahiya, 2008).

At the beginning of the study the yields result of pilots N8 and N12 range between 82.9 % and 95.3%. After the second week an intermediate best value of 94.6 % was registered. The results remained nearly constant at 82.94% from the second week onwards. The same results have been observed for pilot N20 (85.27 and 96.1 %); while the greater yields were realized with pilot N24 (89.10 % – 97.7 %) (Gherairi et al., 2013).

The efficiency of filtering of the different pilots increased directly with an increase in the quantity of (AC) activated carbon (Dinesh et al, 2008; Ramesh et al, 2007; Muhammad, 2011). The BOD5 yields range between 94% and 99%. During the first days, the DOB5 values were at a mean of 96.7% (Gherairi et al., 2013).

Similarly, another study aimed to determine the effectiveness of using both slow sand and slow slate waste filtration systems which were followed by granular activated carbon filters for treatment greywater (Zipf et al., 2016). The experiment was monitored over a

period of 28 weeks. Monitoring and recording the following parameters include pH, turbidity, apparent color, (BOD) biochemical oxygen demand, chemical oxygen demand, surfactants, total coliforms, and thermo-tolerant coliforms. The system was run at two different filtration rates: 6 and 2 m<sup>3</sup>/m<sup>2</sup>/ day. The average impurities removal efficiencies with regard to the turbidity, apparent color, COD and BOD were 61, 54, 56, and 56%, respectively, for the sand filter, and 66, 61, 60, and 51%, respectively, for the slate waste filter. Both systems sand filter and slate waste showed good efficiencies in removing surfactants, around 70%, while the pH result became around 7.80. The removal efficiencies of the total and thermos tolerant coliforms were of 61 and 90% in average, respectively, for the sand filter and 67 and 80%, respectively, for the slate waste filter (Zipf et al., 2016).

The removal efficiency of sulfide, TDS, TSS, EC and salinity at optimized conditions were 99%, 81%, 96%, 86% and 87%, respectively for liming waste water which was treated batch-wise by H<sub>2</sub>O<sub>2</sub> oxidation, followed by coagulation with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Abul Hashem et al., 2016).

#### **2.6.1.5 Clay**

Clay is also an important component of soil. Clay has chemical and mechanical steadiness, high specific surface area, high cation exchange capacity and layered structure. These qualities give it its importance for cation exchange capacity (CEC) (Tanabe, 1981). As the water flows over soil or percolates into the ground, clay traps the metals in the water. The fact that clay is able to trap metal particles from water makes it useful for removing pollutants from water.



For instance, china clay which is used to eliminate cadmium metals from hazardous waste (Sarma et al., 1991). In another study, zinc removed from aqueous solution by using natural bentonite (Mellah and Chegrouche, 1997). Raw kaolin is used for adsorption of copper Cu(II) , Cobalt Co(II) , Manganese Mn (II), and Nickel Ni(II) from aqueous solutions, (Yavuz et al., 2003). Several other studies, including Lin and Juang, (2002) and Alvarez-Ayuso and Garcia-Sanchez, (2003) have demonstrated the use of modified clays to adsorb heavy metals from water.

Nano clay is the best at controlling filtration. At a concentration of 6%, the nano clay was able to minimize the filtration rate by about 5%. This is better performance than common industrial additives designed to do the same job (Jaber, et al, 2016). Minerals of neat clay are not very effective in eliminating micro-particle contaminants from waste water when compared with other adsorbent such as zeolites and activated carbon. This may be because it has a low comparative surface area. Neat clay is also not desirable because of the difficulties that it presents in recovering clay particles from solutions. This aspect makes them even less attractive compared to adsorbents used for industrial water treatment. This ultimately makes regeneration of these colloidal particles quite difficult (Unuabonah et al., 2008b). In addition, clay minerals are not very effective in trapping organic substances because they have highly hydrated surfaces. The hydrated surfaces reduce the accessibility of the interlayer spaces to aromatic molecules (Borisover et al., 2008).

## **2.6.2 Activated carbon and Modified Activated Carbon**

### **2.6.2.1 Activated carbon**

The utilization of activated carbon in waste water treatment and ecological remediation in altered bed columns has ended up typical. Activated carbon is especially efficient at eliminating a big range of organic compounds from waste water. The activated carbon, in any case, after saturation, must be generated and it is likewise manageable to regeneration the activated for reusing compare with other absorbents (Marsh & Rodríguez, 2006).

It is however important to note that activated carbon is very weak for getting rid of big molecules, for example, humic acid and waste waters that contain emulsified grease as well as oil. This is because of the way that these large compounds plug the macro porous space on the activated carbon external surface along these lines making the micro porous space less effective. It is easy to come across industrial process as well as wastewater streams which have emulsified grease that may make activated carbon insufficient (Speed et al., 1987).

Activated carbon has various of unique characterization, for example, high grade of surface reactivity , high adsorption ability, extended surface area, microporous structure, (Bhatnagar et al., 2013) capability for comprehensive range pollutants removal , thermo-stability, and low acid/base reactivity makes activated carbon one of the highest filtration media in the world (Foo and Hameed, 2010). Produced water organic compounds and part of heavy metals absorbs to the activated carbon porous media of carbon surfaces (Hansen et al, 1994).

They represent flexible adsorbents for industrial processes and are extensively used in many

applications, mainly for the elimination of undesired types from gases or liquids streams.

The functional groups in activated carbons surface are accountable for the diversity of physiochemical and catalytic characteristic considered (Shen & Yihong, 2008).

Okiel & El-sayed (2011) carried out a research to remove oil from petroleum waste water using bentonite, deposited carbon (DP), as well as powdered activated carbon (PAC) (Table 23). The outcomes showed that oil removal percentages increased with increasing the weight and contact time of adsorbents, and reduced with increasing the concentration of adsorbate.

**Table 23:** Oil elimination effectiveness from the oil/water mixtures samples by using adsorption on bentonite, powdered activated carbon, and deposited carbon (Okiel & El-sayed, 2011).

Adsorbent	Weightg/200 ml oil-water emulsion	Time of stirring (h) 400 rpm	Initial oil concentration (mg/L)	Final oil concentration (mg/L)	Oil removal (%)
Bentonite	0.5	0.5	1012	395	60.97
	0.1	1.0	836	647	22.61
	0.5	1.0	836	215	74.28
	0.5	2.0	1012	81	91.5
	1.0	2.0	1012	53	97.0
	0.5	4.0	1012	56	94.5
	1.0	4.0	1012	17	98.32
PAC	0.1	0.5	600	480	20.0
	0.5	0.5	600	160	61.0
	0.5	2.0	836	144	82.78
	1.0	4.0	836	54	93.54
DC	0.1	0.5	1012	698	31.0
	0.5	2.0	1012	96.8	92.0
	1.0	2.0	1012	30.3	97.5
	0.1	4.0	1012	465	54.1

Al-Ghouti et al., (2010) reported research on the reduction of organosulphur compounds (ORS) utilizing activated carbon. Excellent adsorption capabilities of granular bead form activated carbon (NORIT PK 1-3, Holland) of organosulphur compounds (ORS) from diesel-non-aqueous medium. The research exposed that ORS elimination efficiency

was affected by the particle size of the AC, which showed that adsorption primarily happens on the external surface area.

Activated carbon can eliminate BTEX and free hydrocarbons which that participate to TPH (total petroleum hydrocarbons), the activated carbon can be renewed after few runs by running wet air oxidation process. The effectiveness of absorbers is influenced by a few parameters, for example, the temperature, pH, salinity and concentration of low heavy metals and dissolved organic chemicals (Hansen et al, 1994).

Doyle et al. (Doyle et al., 1997) tried a combination of a modified polymer, bentonite or organocly and bed column packed with activated carbon. The researchers reported that their system could eliminate hydrocarbons steadily and effectively resulting in reduced total petroleum hydrocarbons and B.T.E.X (benzene, ethylbenzene, toluene and xylene ) which is considered as soluble hydrocarbons to non-detectable limits (below the detection limit). However, the principle disadvantage of this system is that it needs repeated renewal of the absorbent substances.

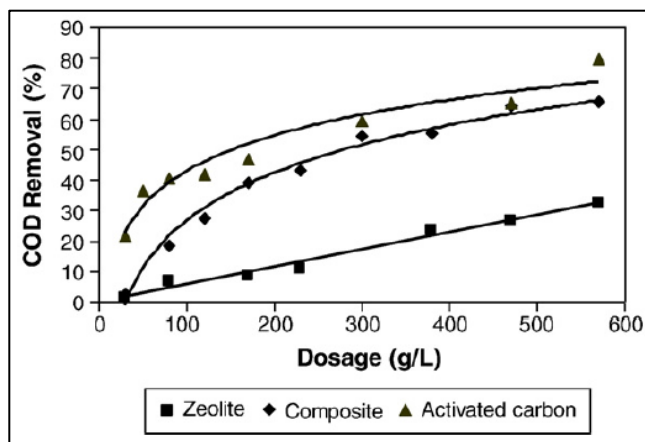
A research carried out by Aleghafouri et al., (2015) to look at the B.T.E.X adsorption from diethanolamine (DEA) solution by using three types of commercially granular activated carbons (AC). The adsorption of BTEX from Diethanolamine (DEA) solution were carried out to eliminate benzene, toluene, ethylbenzene and metaxylene (BTEX) from Diethanolamine solvents and the equilibrium batch adsorption studies for BTEX removal were fitted into Langmuir, Freundlich and Sips model isotherms to obtain the best fitted model.

Research carried out by Luukkonen et al (2014) to examine the elimination of TOC (total organic carbon) remains from make-up water of power plant by using activated carbon. The experimental part was carried out using continuous flow bench scale AC filters at a steam

boiler desalination plant. Four commercial ACs were tested and all demonstrated similarly efficient removing around 42-45% of total and 58–68% of dissolved organic carbon after 30 days of operation. TOC removal efficiencies studied throughout the pilot scale experiment were range from 41.7% to 44.8% for all ACs at the end of test run. Remaining TOC after AC filters varied from 126 to 260 ppb. It can be assumed that the TOC removal is primarily due to adsorption since the nutrient content of deionized water is possibly too low to allow the development of biological activity.

Water characteristics study for one year from (2000–2001) conducted to measure the Rusko waste Water treatment factory. The result showed that the treatment process removed 53% of TOC, starting with TOC average 5.5 mg/l for the raw water and after treatment the TOC became on average of 2.6 mg/l (Myllykangas et al., 2002).

A comparison study by Azhar et al., (2010) demonstrated that the adsorption ability of activated carbon towards COD removal was greater than Composite and zeolite adsorbent. The results for chemical oxygen demand (COD) were different, AC showed the highest adsorption capacity with 37.88 mg/g, then by composite media 22.99 mg/g and finally zeolite with 2.35 mg/g. AC fit well with the pseudo first order model ( $R^2=0.97$ ) and ( $R^2=9317$ ) for and intra particle model and exhibitions a poor correlation ( $R^2=0.5071$ ) for the pseudo second-order model and regarding the COD adsorption fit will with the pseudo second-order kinetic model ( Azhar et al., 2010).

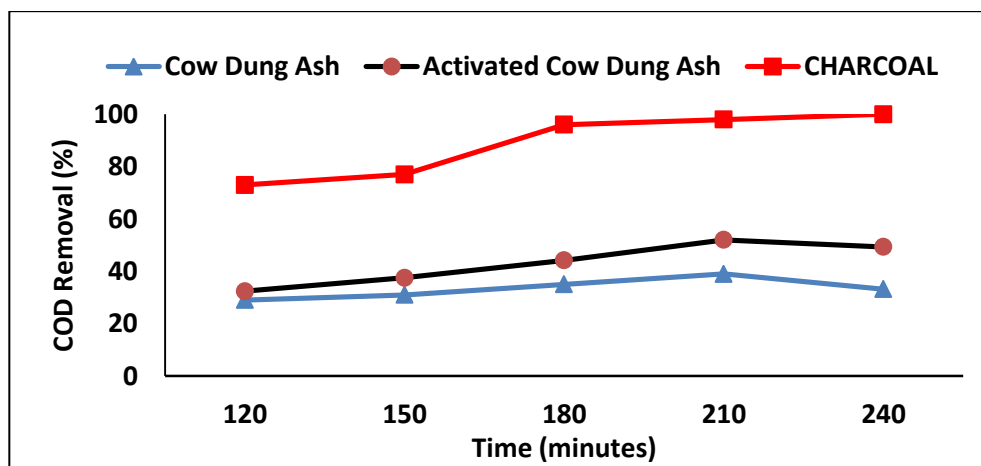


**Figure 5:** COD elimination using three types of adsorbent zeolite, composite media, and activated carbon (Azhar et al., 2010).

Nurshazwani (2015) demonstrated trials of activated carbon prepared from sugarcane bagasse (SCAC) by chemical- physical activation technique for elimination of  $\text{NH}_3\text{-N}$  (Ammonia), color and chemical oxygen demand (COD) from leachate of Landfill located at Sahom, Perak, Malaysia. Sugarcane bagasse was utilized as forerunner to prepare activated carbon with high surface area, sufficient yield of carbon and high pollutant elimination efficiency. Higher pollutant elimination percentage for COD (77.8%) , color (87.3%) and  $\text{NH}_3\text{-N}$  (41.05%). The error percentage between predicted and experimental result of color, COD (chemical oxygen demand), and  $\text{NH}_3\text{-N}$  (Ammonia) was 1.57, 3.67 and 2.63 % respectively.

The use of (CDA) cow dung ash was evaluated for the elimination of organic pollution from the leachate (waste liquid) of the landfill using of identified Chemical Oxygen Demand content. The impact of several factors like adsorbents amount, pH, temperature and time, was studied. Results show that up to 79 % elimination of COD could be accomplished by using (ACA) activated cow dung ash at optimal temperature of 30 °C and pH 6.0 using 20 g/L amount in 120 minutes , whereas 66% removal of COD had been showed by using cow dung

ash (CA) at pH 8.0 using 20 g/L amount, also in 120 minutes, the isotherms of Freundlich and Langmuir adsorption were similarly in 120 demonstrated and the experimental data shows good correlations (0.921 and 0.976). Experimentations were moreover conducted by using (CHAR) commercially charcoal to compare the effectiveness of the three adsorbents. 94% of COD after 180 minutes were removed by using the CHAR at the amount of 2 g/L of leachate. Comparative study of COD elimination effectiveness for the three types at fixed amount 10 g/L which shows that CHAR, ACA performed a good adsorption for the COD elimination and the charcoal is the highest as shown in Fig.5. Alteration in COD elimination effectiveness for the three types could be referred to the alteration in the quantity of presented carbonaceous locations (Kamalpreet et al., 2016).



**Figure 6:** COD removal by three different adsorbents at fixed dose (Kamalpreet et al., 2016).

Removal of contaminants from the waste waters depends on the adsorbent amount and the interaction time which are playing an important role in the removal efficiency of the contaminations. The highest COD elimination from leachate was accomplished by using 20 g/L

amount of Cow ash and activated cow ash in three hours and the COD removal efficiency were 61% and 73% respectively (Devi & Kumar, 2008).

Another research demonstrated matching with the research above where complex of rice hull/Mn Fe<sub>2</sub>O<sub>4</sub> adsorbent was applied. Initial concentration of the waste water was 2088 mg/L and the elimination efficiency of COD was 73% (APHA, 2005). Lv et al. (2009) used bamboo ash activated carbon to reduce the COD concentration from cotton fabric manufacturing wastes water and the elimination efficiency of COD was 72%.

**Table 24:** Comparative overview of different adsorbents employed for COD from the wastewaters/leachate. (Kamalpreet et. al, 2016).

<b>Type of Activated carbon</b>	<b>Type of wastewaters / leachate</b>	<b>COD elimination (%)</b>	<b>References</b>
(ACA) Activated cow dung ash	Leachate	79% at 30 °C	( Kamalpreet et al. ,2016)
(CA) Cow dung ash	Leachate	68% at 30 °C	( Kamalpreet et al. ,2016)
Charcoal	Leachate	89.9% at 30 °C	( Kamalpreet et al. ,2016)
(BFA) Bagasse fly ash	Sugar manufacturing waste water	27%	Lakdawala & Patel,2012)
(CSC) Coconut shell carbon	waste water from Industry	47%–72%	(Mohan et al. ,2008)
(ARH) Activated rice husk	waste water from Industry	45%–73%	(Mohan et al. ,2008)
(AAP) Activated Avocado Peel	Effluent from coffee processing factory	98.2%	(Devi et al. ,2008)
(ADC) Activated date nut carbon	Sugar manufacturing waste water	73%	(Parande et al. ,2009)
Tamarind nut carbon	Sugar manufacturing waste water	74%	(Parande et al. ,2009)



Anirudhan & Sreekumari (2011) examine the adsorptive elimination of heavy metal from industrial waste water using coconut buttons waste activated carbon. The activated carbon manufactured and activated by steam of the coconut buttons which considered as low cost sorbent to eliminate metals such as lead, mercury and copper ions from industrial waste waters. The research showed that the proportions of metals adsorption were dependent on metal connection time, ionic strength, pH, concentration of metals, and carbon amount used in the experiment. The extreme elimination of the metal ions is witnessed at the pH 6.0 for lead and copper, and at pH 7.0 was observed for mercury ions. The equilibrium data fit well with the Freundlich model and the adsorption fit with pseudo second order kinetics.

Wahi et al. (2009) inspected the capability of empty fruit bunches (EFB) activated carbon from palm oil to eliminate the following metals copper, lead and mercury from prepared aqueous solutions was studied. The adsorption ability was defined as a function of adsorbent amounts and adsorbate initial concentration. Adsorption often fits well with isotherm models of Langmuir and Freundlich. The efficiency removal of EFB (activated carbon) found outstanding in eliminating lead and mercury with 100% elimination efficiency percentage even for small EFB dosage. Compare, only 25% elimination of copper by activated carbon of the Empty Fruit Bunches was detected. The research also indicated that the adsorption of lead, copper and mercury is dependent on the initial metals concentration and amount of

adsorbent. The usage of the Empty Fruit Bunches as AC also helps in resolving problem of Empty Fruit Bunches agricultural left-over product.

Five trials of two different types of activated carbons were used, the first one maize cobs from vegetal source and second one activated carbon from animal source, both of them were tested the acetic acid adsorption. The activated carbon of maize cobs were prepared by chemical activation with  $ZnCl_2$  (zinc chloride). It demonstrated that the MAPZC5 activated carbon sample which was gotten from the solid part of the maize cobs had better adsorption characteristic than the measured manufacturing activated carbon from animal source. As a result, activated carbon of maize cobs can be considered as adsorbent to cleanse of the waste water contaminated by acetic acid (Dina et al., 2012).

Mundhe et al. (2015) examined the potential use of ACs biosorbent prepared from seeds of *Polyalthia longifolia* commonly called as Ashok for the elimination of acetic acid from aqueous solution. The experimental data have been assessed using Freundlich and Langmuir isotherm model. Maximum adsorption has been found to be 29.4 % at 30 °C for lower concentration at 0.100 gm adsorbent dose.

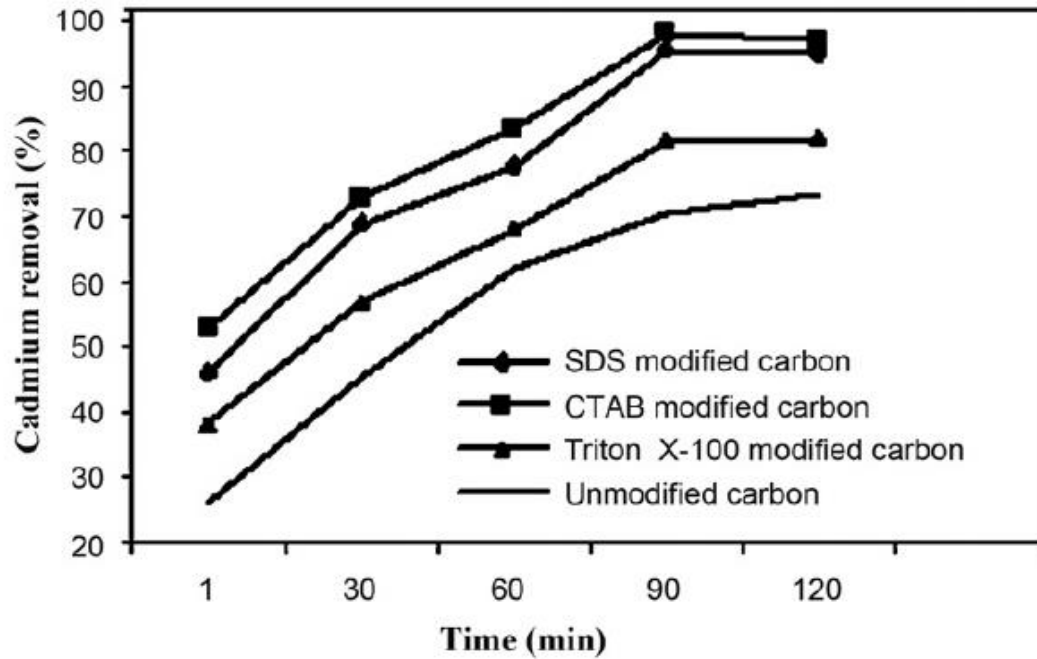
#### **2.6.2.2 Modified Activated Carbon**

Despite the fact that activated carbon is inexpensively readily available resources like saw dust, dates , coke, papaya wood, peat, coconut shells and rice husk have been effectively utilized as adsorbents for elimination of toxic material (Arulanantham et al,1989 ; Montanher et al.,2005; Asma et al., 2005; Nadeem et al., 2006; San et al., 2003; Al-ghouti et al., 2010) . Modified activated carbon indicated enhanced removal efficiency due to enhancement in the

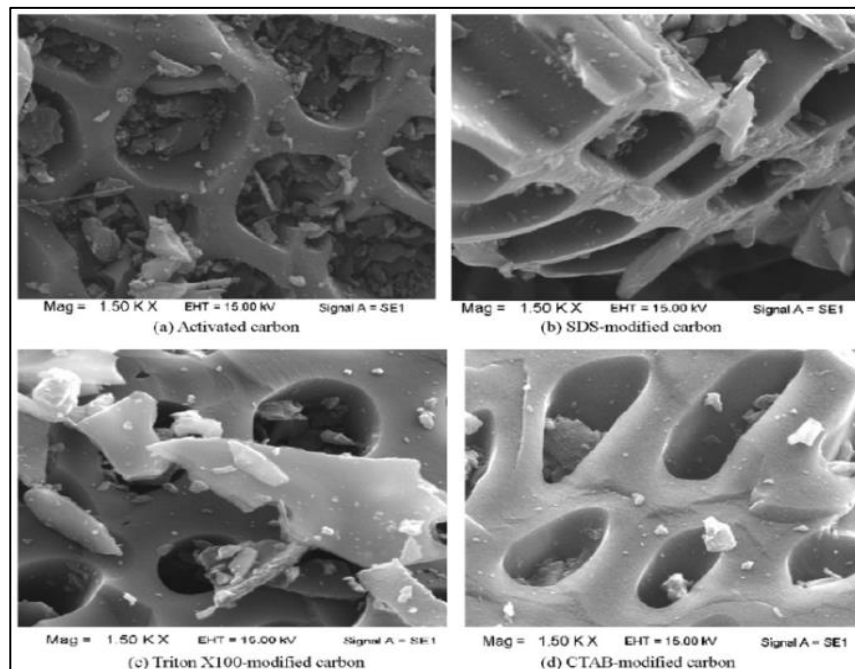
active surface of this adsorbing material. It had proved that from waste of husk and pods can create high quality microporous activated carbons by applying simple steam pyrolysis process (Nadeem et al., 2006; Warhurst et al., 1997).

Adsorbents with surface modification are not only greater in terms of elimination efficiency than the non treated adsorbents but moreover enhancing the adsorption selectively of certain toxic materials (Nadeem et al., 2006). The adsorptive material surface can be modified with hydrophilic groups that can have positive charge (cationic), negative charge (anionic), no charge (non- ionic) and have both charges negative and positive (Zwitterionic) which usually leads to structured molecular assemblies depending on the nature of the group (Nadeem et al., 2006).

Nadeem et al. (2009) utilized modified activated carbon for cadmium sorption from prepared aqueous solution. The modified activated carbon were prepared with negative charge (ionic) surfactant called sodium dodecyl sulphate (SDS) and positive charge (cationic) surfactant called cetyltrimethyl ammonium bromide (CTAB), compared it with commercially nonionic Triton-X 100 and compared it with unmodified activated carbon. The research revealed that treated carbon had greater porosity and enhanced surface area compared with unmodified activated carbon and it were accomplished 98% removal of cadmium with the cationic surfactant treated carbon, while the anionic modified carbon achieved slightly less efficiently and the unmodified carbon performing the least Fig 6&7.



**Figure 7:** Surfactant modification effect of on cadmium elimination (Nadeem et al., 2009).



**Figure 8 :** Adsorbent SEM images (a) activated carbon AC, (b) modified activated carbon SDS, (c) modified carbon Triton X-100 and (d) modified carbon CTAB (Nadeem et al., 2009).

Immediate sorption of two types of phenolic compounds (2-nitrophenol) and (4-nitrophenol) on a mixture of geo-compounds were founded on activated carbon and surfactant-modified pillared-clay, by using batch tests the sorption of two phenolics compound (2-nitrophenol) and (4-nitrophenol) on these sorbents was inspected in both single and dual constituent systems from the prepared aqueous solutions. In single-constituent systems, sorption isotherms were analyzed with the Freundlich equation for (2-nitrophenol) and (4-nitrophenol) as a function of pH (Hamidouche et al, 2015).

The effectiveness of the degradation the diesel oil under the aerobic conditions was reduced in the existence of Triton X-100 surfactant by approximately 25%, instead of 80% without surfactant to 60% with surfactant. And regarding the anaerobic conditions the effect of Triton X-100 surfactant was not observed. Through the 'central fission' mechanism Triton X-100 was almost certainly degraded. Privileged degradation of Triton X-100 above diesel oil was the reason behind reduction on diesel oil biodegradation effectiveness.

### **3. Methodology:**

The assessment and treatment of the formation produced water from the North Field was conducted in three phases:

- (1) Field sampling
- (2) Produced water characterization and analysis.
- (3) Produced water treatment using
  - (i) Sand filtration
  - (ii) Activated carbon filtration
  - (iii) Modified Activated carbon filtration.

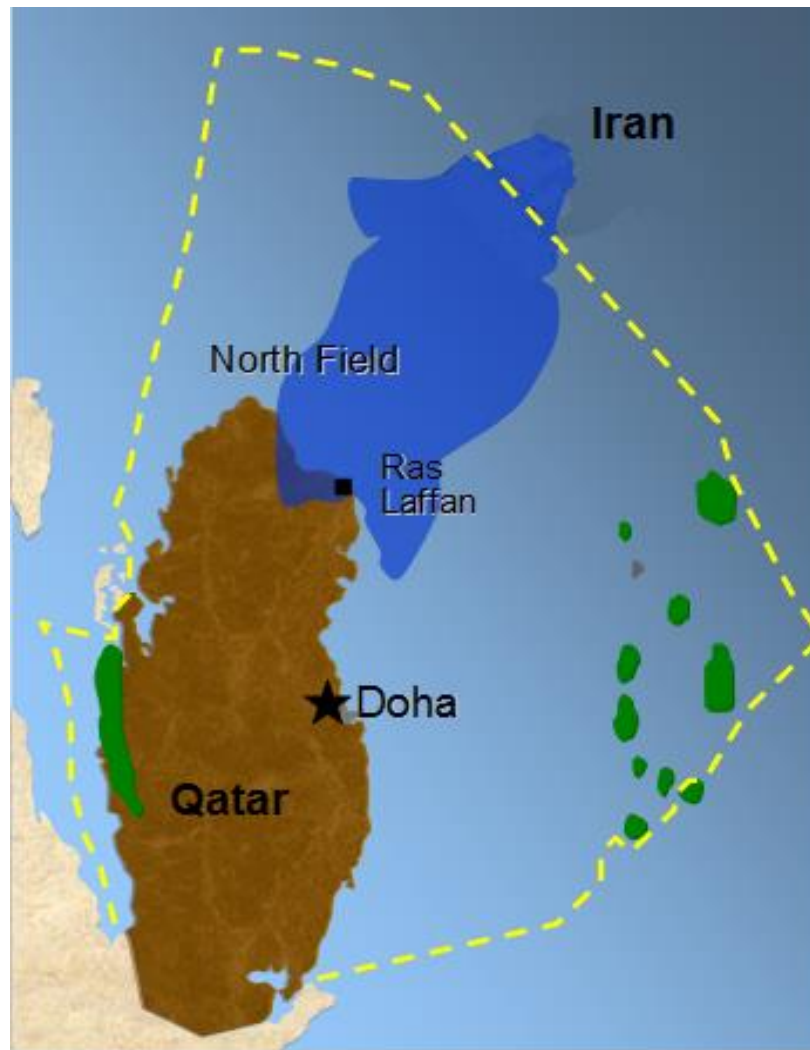
### **3.1 Sampling:**

#### **3.1.1 Produced Water sampling:**

Representative samples of the produced water were prepared by collecting a grab sampling set of produced water samples from LNG liquefied Natural Gas plant in Qatar at North Field during different time in 10 days from the locations shown in the map in Fig.8. One sample per day was collected in 20-liter containers. Therefore, the total volume of samples collected in a 10-days period was 200 L approximately, (10 days  $\times$  20 liters = 200 liters). Fig.9 shows the process of collecting water samples, mixing the total volume in order to get homogeneous content and stored in a big storage 200 L container.

### 3.1.2 Sand and Clay sampling:

The sand sample was collected from (Umm Saied sand dune, local sand) by Millipore water and dried overnight in an oven (Binder Company) at 110°C. Raw clay was collected from local plantation, crushed and grinded.



**Figure 9:** Map sampling location sites in RasLaffan industrial city.



**Figure 10:** (a) 10-containers of produced water samples, (b) and (c) Pouring samples in the big drum (d) mixing the collected samples for homogeneity, (e) collecting samples for testing (f) collecting 4 containers each (20 liters) for carrying out sand filtration experiments.

## 3.2 Sand Filtration Column Preparation

Sand filtration column was prepared as per the following procedure: first, the sand sample collected from Um Saied sand dunes was washed by Millipore water and dried overnight in an oven (Binder Company) at 110°C. The sand was then sieved to < 1mm using sieves from Test Sieve- Tokyo.



The collected clay was crushed and grinded using a ball mill (Brand Retsch PM 400) for 45 min. The grinded clay powder was then sieved to  $< 250 \mu\text{m}$  by using a sieve shaker (Brand Haver & Boecker). A combination of sand plus 2 % clay mix was prepared by first weighing 9800 g of sand using a top-loading weighing Balance (Brand Kern) plus 200 g clay powder weighed by an analytical balance (Brand Sartorius).

Four polyvinyl chloride (PVC) columns plus four replicate columns (120 cm “length” x 10 inch “diameter”) were prepared by alternatively placing 4 layers of cotton and 5 layers of sponge, in the bottom of the each columns to prevent the sand and clay to leached out to the receiving containers. Each column was then filled using 10 kg of the sand 2% clay mixed powder prepared earlier. The column content was then washed twice using 5 L of Millipore water (Q-Pod). After that, 25 L of Millipore water and the produced water samples were filtered and collected from each column at a rate of  $0.3 \text{ m}^3/\text{h}$  in 25 liters’ container. Figure 10 shows the steps for sand filtration column preparation and filtration (Fig.10).



**Figure 11:** (a) Sand and Clay mixed 10 kg (b) cotton and sponge layers (c) placing cotton and sponge layers at the bottom of the column, (d) adding the sand/clay mixed (e) Sand filtration stage with Millipore water followed by produced water for the 4 replicates, (f) collecting 4 controls and samples.

### 3.3 Mixing the filtered Produced water after the sand filtration:

Collecting four liters from each single filtered produced water container (25 liters) and theirs controls for carrying out full chemical and physical characterization analysis tests for both controls and filtered produced water. The second stage was mixing the four containers each one 25 liters (total 100 liters) to make sure of the homogeneity before splitting them in

two containers each one 50 liters to conduct the next step filtration by activated carbon and modified activated carbon (Fig. 11).



**Figure 12:** Mixing the four containers and splitting them in 50 liter's container.

### **3.4 Activated Carbon Filtration Column Preparation**

The activated column filtration column was prepared as per the following procedure: Commercial granular activated carbon (Hobby Company) was washed by Millipore water and dried overnight in an oven (Binder Company) at 110°C. Four glass columns 250 ml (20 cm “length” x 5 cm “diameter”) were filled by the activated carbon with fixed weight of 100 g using an analytical balance (Brand Sartorius) and glass wool in the bottom to prevent activated carbon leaching. The columns were washed by two liters of Millipore water. After that, two liters of Millipore water was passing through each columns as control samples then produced water samples after the sand filtration was passed through each the four columns with a rate of 0.3m<sup>3</sup>/h and collected in glass bottles (Fig. 12).



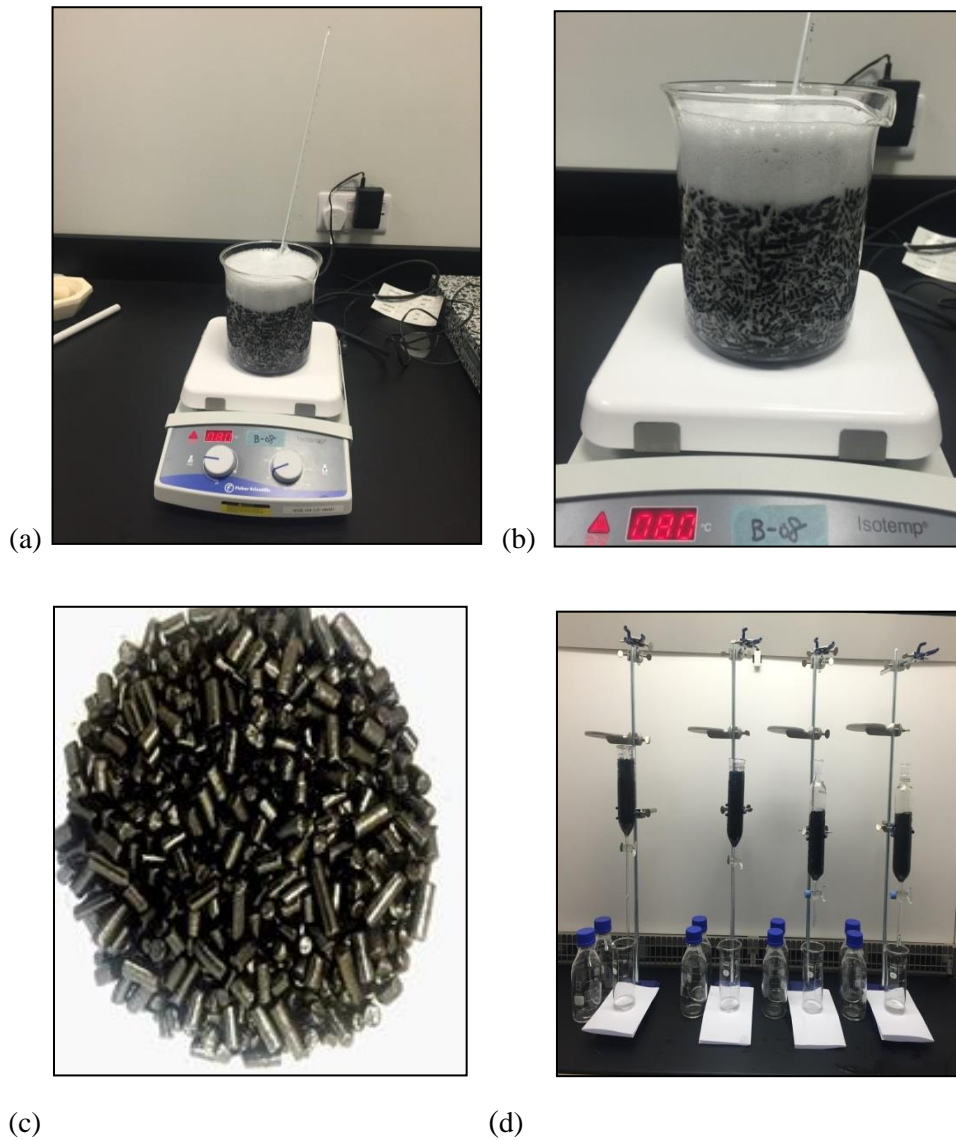
**Figure 13:** Activated carbon filtration columns.

### **3.5 Modified Activated Carbon filtration Column preparation:**

Modified activated carbon filtration columns were prepared as per the following procedures: granular activated carbon (Hobby Company) was washed by Millipore water and dried overnight in an oven (Binder Company) at 110°C. The Microemulsion was prepared as the following : Surfactants Triton X-100 (non-ionic), (ISO – Octylphenoxy polyethoxyethanol) were obtained from BDH Company, then placed in orbital shaker with controlled temperature from Fisher Scientific Company with 160 rpm, at temperature  $80 \pm 0.5$  °C for 6 hours and left to gain the room temperature. Each 100 g of sample was filtered by filter Whattman-42 without rinsing, and dried in an oven overnight at 110°C (Nadeem et al. 2006).

Four glass columns 250 ml (20 cm “length” x 5 cm “diameter”) were filled by the 100 g of weighing by an analytical balance (Brand Sartorius) and glass wool in the bottom to

prevent the modified activated carbon leaching then washed by five liters of Millipore water. After that, two liters of Millipore was pass through each columns as control samples then two liters of produced water samples (after the sand filtration) was passed through each of the four columns with a rate of  $0.3\text{m}^3/\text{h}$  and collected in glass bottles. Figure 13 shows the preparation of modified activated carbon (Microemulsion) column preparation.



**Figure 14:** (a), (b) preparation of Microemulsion, (c) Modified activated carbon (d) filtration columns with Modified activated carbon.

### 3.6 Samples Analysis

Parameters for comprehensive physical and chemical characterizations of the produced water are listed in Table 25.

**Table 25** : Measured parameters of the produced water along with method reference and the technique / instrument used for measurement.

<b>Parameter</b>	<b>Method</b>	<b>Techniques</b>
<b>pH</b>	EPA 150.1	Electrometric By PH Meter (TOA DKA Company)
<b>COD</b>	EPA 410.4	Spectroscopy By Hach DRB 200 digester / Hach DR 6000
<b>TOC</b>	EPA 415.1	IR By TOC-L (Total Organic Carbon Analyzer)
<b>TC/NPOC</b>	EPA 415.1	Total Organic Carbon, Combustion or Oxidation;
<b>TN</b>	ASTM D5176-08	Total Nitrogen( Chemically bound ) in Water by  (Pyrolysis and Chemiluminescence) Detection
<b>Salinity</b>	*	By Calculation from Conductivity.
<b>Conductivity</b>	EPA 120.1	Electrometric By Conductivity Meter (TOA DKA Company )
<b>TSS</b>	EPA 160.2	Gravimetric by filtration with filter Paper Whatman 0.45
<b>HEM (Oil &amp;</b>	EPA 1664 A	Gravimetric Method, Extraction by Hexane.
<b>B.T.E.X</b>	EPA 524.2	By GC-MS ( HP 5973),Burge and trape and headspace
<b>Sulfide</b>	EPA 376.1	Titrimetric by MetrohmTitrino with stirrer with Iodine
<b>Silica</b>	EPA 370.1	Spectroscopy by UV-Visible.
<b>Phosphate</b>	EPA 300	By IC Water 717, Autosampler 432 and
<b>Sulphate</b>	EPA 300	By IC Water 717, Auto sampler 432 and conductivity detector.
<b>Chloride</b>	EPA 300	By IC Water 717, Auto sampler 432 and conductivity detector.  For high range (Titration with silver nitrate).
<b>Formate</b>	*	By IC Metrohm 881 compact IC pro
<b>Acetate</b>	*	By IC Metrohm 881 compact IC pro
<b>Propionate</b>	*	By IC Metrohm 881 compact IC pro
<b>Phenol</b>	EPA 420.1	Spectroscopy by UV-Visible (4 Amino Anti Pyrine).
<b>Aluminum</b>	EPA 200.7	
<b>Arsenic</b>	EPA 200.7	
<b>Barium</b>	EPA 200.7	

<b>Boron</b>	EPA 200.7
<b>Cadmium</b>	EPA 200.7
<b>Calcium</b>	EPA 200.7
<b>Cobalt</b>	EPA 200.7
<b>Chromium</b>	EPA 200.7
<b>Copper</b>	EPA 200.7
<b>Iron</b>	EPA 200.7
<b>Lead</b>	EPA 200.7
<b>Manganese</b>	EPA 200.7
<b>Magnesium</b>	EPA 200.7
<b>Molybdenum</b>	EPA 200.7
<b>Nickel</b>	EPA 200.7
<b>Potassium</b>	EPA 200.7
<b>Sodium</b>	EPA 200.7
<b>Strontium</b>	EPA 200.7
<b>Vanadium</b>	EPA 200.7
<b>Zinc</b>	EPA 200.7

Spectroscopy By ICP-OES,  
(Perkin Elmer Optima 5300DV) in ESC.

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### 3.7 Materials, Chemicals and Reagents:

The main materials used in this project are: local sand from Umm Saied sand dune, raw clay collected from local plantation, commercial granular activated filter carbon (Hobby company), Millipore water with conductivity 0.055  $\mu\text{s}/\text{cm}$  , Surfactant TritonX-100 (ISO – Octylphenoxypolyethoxyethanol) from BDH.

## 4. Results and Discussion

### 4.1 Chemical and Physical Characterization of Produced Water Samples:

The following sections discuss the main physical and chemical properties measure of the produced water samples as collected before treatment with sand, activated carbon and modified carbon filtration. The comparison with produced water from gas fields worldwide is challenging for two main reasons; first, the difference in some physical and chemical properties due to the nature of geographical site and/or due to the different operational technologies compared to what is processed in Qatar, and secondly, due to the limitation of published data of produced water associated with gas field production compared to that of oil production worldwide.

The **pH** value measured for the three water samples are shown in Table 26. The values are reproducible and show that the produced water is acidic with mean value of 4.43. This value is consistent with what has been reported earlier for produced water from gas platform production (pH values ranges between 3.5-5.5 ) (Veil et al, 2004).

**Conductivity** of the formation-produced water is a reflection of total dissolved of cations and anions present in the water. The mean value conductivity of the current study is 7035  $\mu\text{S}/\text{cm}$  (Table 26) which is within the range (4200  $\mu\text{S}/\text{cm}$  - 180000  $\mu\text{S}/\text{cm}$  ) as comparison studies of natural gas /produced waters by Ahmadun et al., 2009.

Table 26 shows salinity measured values for the three replicates which are reproducible and the mean value is round 4502.4 mg/l compared with previous study for Hibernia produced



water which showed that the salinity is ranging between 46–195 ‰. (Ayers and Parker, 2001).

The measured mean values of the **chloride** content in the formation-produced water samples is 2921 mg/l as shown in Table 26, which is matching the previous studies of produced water from natural gas field by Ahmadun et al. (2009) and Fillo & Evans (1992) for chloride concentration which was ranged between 1400-190,000 mg/l. Moreover matching the oilfield –produced water chloride and the concentration range between 80-200,000 mg /l) as shown by Tibbetts et al. (1992).

The current average value of the measured **sulfate** was 46.13 mg/l as shown in Table 26 which is consisted with the following previous studies and reviews findings studies of Shepherd et al. ,1992, ; Fillo et al.,1992 ; Johnson et al. ,2008 found the Sulfate concentration in natural gas formation-produced water were ranged between 1.0 – 47 mg/l. The sulfate content in oil field -produced waters studies (Tibbetts et al. (1992) also shows the sulphate results in the range between <2-1650 mg/l. One more study for the shale gas produced water the sulphate content was in the range between undetected -3663 mg/l as shown by McIntosh et al., 2002; McIntosh and Walter, 2005.

The mean value of the current study of **phosphate** concentration is 2.06 mg/l as shown in Table 26 .Phosphates are low in most of the produced water as evidence from apparently the study on produced water by (Johnsen et al. 2004) and Shale gas produced water study by (McIntosh et al., 2002; McIntosh and Walter, 2005) have shown the sulfate concentration is 0.35 mg/l and between ND -5.3 mg/l respectively.

326.3 mg/l is the mean value of **sulfide** as shown in Table 26 which is a little bit higher than the study of Witter and Jones (1999) for California offshore wells which were range between

48–216 mg/L sulfide. In the other hand the writer (Neff, 2002) said the Produced water from sour oil/gas wells may contain high concentrations of sulfide.

The most abundant content of **metals and cations** were found in the current study are sodium (1198 mg/l), calcium (285 mg/l ), potassium (100.9 mg/l), magnesium (45 mg/l), strontium ( 13.18 mg/l), boron (5.7 mg/l) and iron (4.15mg/l) as shown in Table 26. The study by Johnson et al. (2008) demonstrated metals in natural gas produced water from two different studies (Fillo & Evans, 1990; USEPA,2000) and found the most concentrated metals and cations are matching sodium, calcium, magnesium, potassium, strontium and iron as agreed against the current study (Tables 8&9).

The Mean value of the **TSS** is 21.33 mg/l as shown in Table 26. The comparison studies of natural gas produced waters by Ahmadun et al. (2009) and Tibbetts (1992) have shown similar TSS mean value (21 mg/l) in current study on produced water (Table10).

Organic acids in formation-produced water from three production facilities on the Norwegian continental shelf (Røe Utvik ,1999), in Mexico Gulf off the Texas and Louisiana coast, and in the Basin of Santa Maria at California coast (MacGowan and Surdam , 1988) (Table 15) are in line with the mean results of formate (<1 mg/l), acetate (370 mg/l) and propionate (17.5 mg/l) of the current study results for organic acids (Table 26).

The current study mean value of **phenol** is 1.96 mg/l as shown in Table 26, demonstrates the agreement with the total phenol in produced water worldwide which is between 0.4-23 mg/l (Neff, 2002) and total phenols in formation-produced waters from Norwegian Sector of the North Sea and Gulf coast of Louisiana the range from 0.36 to 16.8 mg/L and 2.1 to 4.5 mg/L, respectively (Neff, 2002; Johnsen et al., 2004).

Organic compounds such as volatile organic compound represented by benzene, ethylbenzene, toluene and xylene (**BTEX**) were measured and summarized in Table 26. The current study data shows that concentration of benzene (Mean value is 11170 ppb) was most abundant among the BTEX group. Secondly, is the ethylbenzene with mean value 4648.6 ppb followed by xylenes meaning concentration of 1156.8 ppb and the lowest concentration among the BTEX group was toluene with Mean value of 378.17 ppb. The sequence of BTEX concentration is agreement with the study by Dórea et al. (2007) for oil field produced water collected from Permian Basin which found that the benzene is the most abundant with concentration range between 1.5-778.5 ppm. Secondly ethylbenzene, third xylenes, finally toluene. The toluene mean value of the current study is very high in line with the mean value of Dórea et al., (2007) study.

Content of BTEX in oil field formation-produced water collected from Gulf of Mexico showed that the benzene is the most abundant with concentration range between 0.44-2.80 ppm, secondly toluene, third xylenes, finally ethylbenzene. and for Indonesia produced water the BTEX concentration showed that the benzene is the most abundant with concentration ranged between 0.084-2.30 ppm, secondly toluene third ethylbenzene, finally xylenes (Neff, 2002). The concentrations of the BTEX in oil field produced water collected from the Bonsucesso plant effluent. State of Sergipe in Brazil have shown that the highest concentration is the benzene within the range from 1.291 to 1.511 ppm (Khan et al., 2016) (Table 16) which is also, perfectly matched the data with previous study by Neff, 2002 on Gulf of Mexico and Indonesia produced water .

The results also show that BTEX concentration exceeds phenol concentrations (Mean value for the phenol is 1.96 mg/l). This is in accordance with previous studies Lee & Neff 2011);

Li, 2013) which is due to the relatively higher solubility of BTEX in water compared to phenol (Cavalcanti et al., 2012).

The mean value of TOC is 2405.6 mg/l in produced water for the current study (Table 26) compared with concentration ranges of total organic carbon (TOC) in several classes of naturally occurring water worldwide ranges from < 0.1 to more than 11,000 mg/L (Neff, 2002) and is greatly inconstant from one well to another. However, with some exemptions like formation-produced water from Louisiana production wells contains 67–620 mg/L TOC (Veil et al., 2005).

The current study mean value of COD is 10496.6 mg/l as shown in Table 26, it is also in line with the comparison study by (Ahmadun et al., 2009) for natural gas produced waters for COD concentration range was between 2600 mg/l to 120,000 mg/l .

The current study mean value of **BOD** is 1034 mg/l value as shown in Table 26 is also holds good and agreed with the below study by (Fillo & Evan, 1990) Table 12, on the basis of establishment by Produced water from mostly gas production platforms contained higher content of BOD than from oil production platform. Studies of natural gas produced waters for BOD concentration the results was range between 75-2870 mg/l (Fillo & Evan, 1990).

The current study mean value of **oil and grease** is 40.5 mg/l as shown in Table 26 is very much comply with the varied studies on produced water in table 14 . The comparison studies of natural gas produced waters by Ahmadun et al. (2009) for oil & grease concentration was range between 6-60 mg/l and 2.3 –38.8 mg/l. In another review study for natural gas produced water the oil and grease range was between 2.3- 60 mg/l (Shepherd et al.1992) and (Johnson et al. (2008).A research in the western United States for formation-produced water

showed the content of the oil and grease (HEM) range between 40 mg/L to 2,000 mg/L (Benko and Drewes,2008).

The total nitrogen mean concentration is (47.4 mg/l) for the current study as shown in Table 26, It is also falls within the below different studies. Mean concentrations of nitrate, nitrite & ammonia of several produced water samples from 50 platforms discharging to the hypoxic zone of Mexico Gulf at Louisiana coast (Veil et al. 2005; Bierman et al. 2007) table 19. As stated by (Lee & Neff, 2011), the total nitrogen as ammonia & ammonium concentration in mostly gas production is 57 mg/l.

The mean value of the CI (Corrosion Inhibitor) in current study of produced water is 623.3 ppm as shown in Table 26 which is much higher compared to (Johnsen et al. 2004) study which range between 25-100 ppm. The concentration of KHI and MEG in current study is very low because the samples were collected before the injection season in winter.

**Table 26:** Produced water Chemical and physical characterizations from Natural gas production in the North filed of State of Qatar.

Parameter	Unit	produced water (R1)	produced water (R2)	produced water (R3)	Mean	SD
PH	NA	4.43	4.43	4.44	4.43	0.01
COD	ppm	10370	10440	10680	10496.67	162.58
TOC	ppm	2424	2401	2392	2405.67	16.50
BOD	ppm	1034	1076	992	1034.00	42.00
Salinity	ppm	4528	4460.8	4518.4	4502.40	36.35
Conductivity	µs/cm	7075	6970	7060	7035.00	56.79
TSS	ppm	25	21	18	21.33	3.51
HEM	ppm	36.4	40.4	44.8	40.53	4.20
Sulfide	ppm	349	324	306	326.33	21.59
Silica	ppm	1.9	2.0	2.09	2.00	0.10
Phosphate	ppm	2.13	2.07	1.98	2.06	0.08
Sulphate	ppm	46.3	45.92	46.16	46.13	0.19
Chloride	ppm	2913	2933	2917	2921.00	10.58
Formate	ppm	0.39	0.32	0.33	0.35	0.04
Acetate	ppm	373	368	365	368.67	4.04
Propionate	ppm	18.2	16.2	17.7	17.37	1.04
Phenol	ppm	1.92	1.905	2.04	1.96	0.07
Aluminum	ppb	4.16	9.17	17.52	10.28	6.75
Arsenic	ppb	5.47	7.00	9.23	7.23	1.89
Barium	ppb	60.93	60.03	60.58	60.51	0.45
Boron	ppb	5665.38	5717.93	5850.66	5744.66	95.49
Cadmium	ppb	0.05	0.05	0.05	0.05	0.00
Calcium	ppb	283547.66	285227.87	287920.52	285565.35	2205.88
Cobalt	ppb	7.54	7.34	6.24	7.04	0.70
Chromium	ppb	30.46	29.89	30.59	30.31	0.37
Copper	ppb	0.66	0.57	0.64	0.62	0.05
Iron	ppb	4262.88	4035.3	4134.41	4144.20	114.11
Manganese	ppb	259.04	255.21	260.53	258.26	2.74
Magnesium	ppb	44354.25	46476.78	44362.22	45064.42	1223.15
Molybdenum	ppb	5.53	5.53	5.5	5.52	0.02
Nickel	ppb	7.35	7.09	6.8	7.08	0.28
Potassium	ppb	101024.28	100956.16	100786.56	100922.33	122.42
Sodium	ppb	1215547.0	1182652.96	1196301.16	1198167.04	16526.21
Strontium	ppb	13128.02	13103.48	13313.63	13181.71	114.90
Vanadium	ppb	2.58	2.52	ND	2.55	0.04
Zinc	ppb	5.25	4.98	4.7	4.98	0.28
Corrosion Inhibitor	ppm	609.6	620.1	640.23	623.31	15.57
KHI	%	0.27	0.27	0.27	0.27	0.00
MEG	%	0.33	0.33	0.33	0.33	0.00
Benzene	ppb	8031	16069	9410	11170.00	4298.32
Ethyl benzene	ppb	4084	5415.5	4446.5	4648.67	688.39
Toluene	ppb	262	289.5	283	278.17	14.37
Xylene	ppb	1055.5	1201.5	1213.5	1156.83	87.96
TN	ppm	47.6	47.51	47.13	47.41	0.25

ND: Not detected, below the detection limit.

## 4.2 Produced Water Treatment Results:

The objective of water treatment is to study the feasibility of its reuse in well injection or for domestic use such as irrigation. The treatment includes the removal of hydrocarbons and heavy metals.

### 4.2.1 Sand Filtration Results:

Slow Sand filtration treatment was applied with flow rate of  $0.3 \text{ m}^3 / \text{h}$ . After the sand filtration, the **pH** value of the filtered produced water increased from mean value 4.4 (acidic media) to mean value 7.5 (neutral media) as shown in Table 27. The pH results of filtered water are always greater than those of the raw water, this referred to attribute to the presence of alkaline salts in the former (Gherairi et al., 2013). And due to the high chloride concentration in the sand dune, as proved by Al-Awajy et al. (1992) study to determine the the salt content in Saudi sand dune , they found that the sand dune salt composition have high chloride and sulphate  $\text{Cl}/\text{SO}_4(=18.0)$  and low calcium and magnesium  $\text{Ca}/\text{Mg} (=0.6)$  equivalent ratios.

The water **conductivity** increased after the sand filtration from mean value  $7035 \text{ } \mu\text{s}/\text{cm}$  to  $8710 \text{ } \mu\text{s}/\text{cm}$  as shown in Table 27. Gherairi et al. (2013) mentioned that the conductivity usually after the sand filtration becomes high and differed significantly due to the existence of a high content of salts and directly linked to initial salinity of the sand and usually conductivity becomes high in the first waters because it is the beginning point of leaching of the soluble salts then after while reduces. Which agreed with domestic waste water treatment study conducted by Gherairi et al. (2013), the conductivity of the filtered water at beginning

become higher and stable at 3.5 mS/cm for two weeks. However, from the 14<sup>th</sup> to the 42<sup>nd</sup> day, the conductivity of the water reduced to 1.2 mS/cm.

Filtration by sand filter achieves a significant reduction of **TSS** (total suspended solids) values, TSS reduced from average value 21.3 ppm to less than 5 ppm after the sand filtration as shown in Table 27 and the average removal efficiencies for the TSS was > 76 % which agrees with liming wastewater treatment study conducted by Abul Hashem et al. (2016) and the removal efficiency of TSS was 81%.

There was a small reduction observed for the mean value of **COD** concentration of the current raw produced water from mean value 10496 mg/l to mean value 9450 mg/l after the sand filtration as shown in Table 27. The average removal efficiencies for the COD is 10.3 % which is a low percentage compared to previous studies. (Gherairi et al., 2013) study for treatment of domestic wastewater by using bi-layer filtration system made of sand from a sand dune and activated carbons. The filtering yield for the COD for the sand only range found between 79.1 and 95.3 % (Table 27). Another study by Zipf et al. (2016) which aimed to determine the effectiveness of slow sand filtration system treatments applied on greywater and followed by activated carbon filtration, the average removal efficiencies for the COD was 56 %, for the sand filtration only. The variation in the average removal efficiencies for the COD between the current study 10.3 % and the above two studies may be referred to the nature of the chemical characterization of the filtered raw water and the initial COD concentration as both of them were applied for the domestic wastewater and greywater, compared to the complicated chemical composition of the current produced water and high initial COD 10496 mg/l.



There is no any significant change in **TOC** (Total Organic Compound) concentrations after the sand filtration and the mean value before the filtration is 2405.6 mg/l and after the sand filtration the mean value is 2424 mg/l as shown in Table 27. However the TOC reduction approved after the sand filtration in previous studies, for example in previous study to investigate the possible efficiency of coarse and fine sand filtration for eliminating organic compounds from processing wastewater in turkey, effluent of the Sand filtration was verified and the elimination of total organic compound (TOC) and Biological oxygen demand (BOD5) was more than 94% and column operation was at low and medium hydraulic loading rates ( $6132\text{L}/\text{m}^2/\text{day}$ ) (Young et al in 2007).

Sand filtration is also able to remove the **Oil & grease (HEM)**. Sand filter achieve a significant reduction in oil and grease concentration by Hexane extractable Material (HEM) method , oil and grease concentration reduced from average value 40.5 mg/l to average value 1.2 mg/l after the sand filtration as shown in Table 27, and the average removal efficiencies for the oil and grease for current study is more than 97 % , which agreed with previous study conducted by Multon and Viraraghavan (2006) on produced water, the primary oil and grease (O&G) content was 264 and final O&G was 13.3 mg/l with O&G removal efficiencies recorded at 95.8 %.

The removal efficiency of sulfide for the current study is > 99%. The Sulfide concentration for the produced water reduced from average value 326.3 mg/L to 0.03 mg/l after the sand filtration as shown in Table 27, which is totally agreed with sulfide removal efficiency of Abul Hashem et al. (2016) study for liming waste water treatment which was also 99%.

There is small reduction in **chloride** concentration after sand filtration from mean value 2921 ppm to mean value 2584.2 ppm. Whereas the Sulphate concentration increased little bit from mean value 46.3 ppm to average 54 ppm as shown in Table 27, addition sulphate leaching from the sand dune it is self , as proved by Al-Awajy et al. (1992) study to determine the salt content in Saudi sand dune , they found that the sand dune salt composition have high chloride and sulphate  $Cl/SO_4$  (=18.0) and low calcium and Magnesium  $Ca/Mg$  (=0.6) equivalent ratios and there is no significant change in the phosphate concentration.

There is no any significant change in **formate** concentration and regarding the **acetate and propionate** concentration before and after the filtration. The average values for the acetate and propionate before the filtration were 368.6 and 17.3 mg/l respectively and after sand filtration 339.8 and 16.5 mg/l respectively and removal efficiency 7.8 % and 4.5% respectively as shown in Table 27.

There is a slight reduction in **phenol** concentration after sand filtration from average concentration 1.96 mg/l to average value 1.39 mg/l with removal efficiency of 28.8 % as shown in Table 27. It is quit low compare to a study conducted by P.J. Welz et al., (2012) to evaluate the elimination of the phenolic components from wastewater of winery by three types of columns, the first one normal sand columns, second biological sand filters and third sand microcosms column, and the removal efficiency of the normal sand columns from abiotic was 52%.

There is a significant reduction after sand filtration in the following **metals** concentration Aluminum, Boron, Cobalt, Chromium, Iron, Manganese and Potassium from 10.3, 5744.6, 7.04, 30.3, 4144.2, 258.2 and 100922.3 ppb respectively to < 1, 4907, 0.56, 0.75, 22.35, 10.7

and 86863.3 ppb and the high significant removal efficiency is for the Iron, Chromium and Manganese, >99%, 97.5 % and 95 % respectively. There is a significant increasing after sand filtration for the following metals concentration Barium, calcium, copper, Zinc and Magnesium from 60.5, 285565.3, 0.62, 45064.4 and 4.98 ppb respectively to 522.2, 495914.6, 113.9 and 5292 ppb respectively as shown in Table 27. There is no significant change after sand filtration in concentration the following metals Arsenic, Cadmium, Molybdenum, Nickel, Sodium and Vanadium.

The clean quartz sand has a negative charge ; cations such as iron, manganese, and aluminum are attracted to the sand particles due to two forces mass attraction force and centrifugal force phenomenon, mass attraction which is extent and reduce with the sixth power of the distance between particles and the centrifugal force, inversely proportionate to the second power of the distance, and their impact accordingly reaches deeper into the body of the passing liquid and this force forces the contamination particles to come into direct contact with the adsorption surface (Scholz, 2016).

Regarding the Additives treatment chemicals (CI, KHI and MEG) . The corrosion inhibitor after the sand filtration dropped from average value 623.3 mg/l to average value 36.66 mg/l and the average removal efficiency 94 % as shown in Table 27. The corrosion inhibitor which is used in current study source to protect produced water pipe lines is commercial mixture product consist of the following chemical composition ethanediol,2.5 Furandione,dihydro-3-(tetrapropenyl) reaction product with triethylenetetraamine, Alcohols,C8-10,ethoylated) mainly consist of amid ( Nitrogen compounds).

There are a significant reduction in the B.T.E.X concentrations for the Benzene, Ethyl Benzene and xylene from average value 11170, 4648.6 and 1156.8 ppb respectively and after

sand filtration average became 766, 6.46 and 38.18 ppb respectively with removal efficiency 93%, 99% and 96.7 % and no significant change in Toluene concentration as shown in Table 27. As the B.T.E.X is volatile organic compound apart of the VOCs will release during the mixing and sand filtration process.

There is significant reduction in the **Total Nitrogen (TN)** compound for the produced water from average value 47.4 mg/l to average value 17.18 mg/L and the elimination efficiency of the TN (total nitrogen) is 63.7 % (Table 27), compared to the study conducted by Lahbib et al. (2016) which used combined treatment using a multi-soil-layering system with sand filters (MSL-SF) showed very high efficiency in the removal of the TN by 92.93 % for the Hydraulic Loadings rate HLR-100. The TN removal mechanism could be referred to secondary adsorption on the sand particles, the clean quartz sand is a negatively charge, adsorb the positive then the positive adsorb the negative (secondary adsorption), the negatively charged particles such  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{PO}_4^{3-}$  are eliminated by the secondary adsorption after the initial positive ion adsorption.



**Figure 15:** Produced water (PW) before and after sand filtration (SF).

**Table 27:** Chemical and physical characterization of Produced water after the Sand filtration.

Parameter	Unit	Sand Filter (R1)	Sand Filter (R2)	Sand Filter (R3)	Mean	SD	SF%
pH	NA	7.54	7.79	7.43	7.59	0.18	-71.13
COD	ppm	9400	9600	9300	9433.33	152.75	10.13
TOC	ppm	2383	2433	2456	2424.00	37.32	-0.76
Conductivity	µs/cm	8500	8810	8820	8710.00	181.93	-23.81
TSS	ppm	5	5	5	5.00	0.00	76.56
HIM	ppm	1.2	1.3	1.1	1.20	0.10	97.04
Sulfide	ppm	0.03	0.03	0.03	0.03	0.00	99.99
Silica	ppm	0.848	0.848	0.94	0.88	0.05	55.99
Phosphate	ppm	2.5	1.7	1.7	1.97	0.46	4.53
Sulphate	ppm	379	312	419	370.00	54.06	-702.14
Chloride	ppm	2582	2583	2587.7	2584.23	3.04	11.53
Formate	ppm	0.39	0.32	0.33	0.35	0.04	0.00
Acetate	ppm	313.298	323.98	382.215	339.83	37.09	7.82
Propionate	ppm	15.247	16.773	17.7	16.57	1.24	4.57
Phenol	ppm	1.392	1.416	1.368	1.39	0.02	28.80
Aluminum	ppb	ND	ND	ND	#DIV/0!	#DIV/0!	100.00
Arsenic	ppb	5.95	6.98	5.12	6.02	0.93	16.82
Barium	ppb	655.41	415.62	495.73	522.25	122.08	-763.04
Boron	ppb	4850	5002	4869	4907.00	82.82	14.58
Cadmium	ppb	0.15	0.23	0.03	0.14	0.10	-173.33
Calcium	ppb	449454	503736	534554	495914.67	43085.76	-73.66
Cobalt	ppb	0.58	0.59	0.52	0.56	0.04	92.00
Chromium	ppb	0.43	1.34	0.48	0.75	0.51	97.53
Copper	ppb	132.37	124.74	84.65	113.92	25.63	-18175.94
Iron	ppb	17.46	28.14	21.45	22.35	5.40	99.46
Manganese	ppb	7.67	12.21	12.46	10.78	2.70	95.83
Magnesium	ppb	53366	55000	50412	52926.00	2325.43	-17.45
Molybdenum	ppb	0.55	0.55	0.55	0.55	0.00	90.04
Nickel	ppb	10.49	12.53	8.93	10.65	1.81	-50.42
Potassium	ppb	87793	87550	85247	86863.33	1405.05	13.93
Sodium	ppb	1138533	1140287	1262204	1180341.33	70900.57	1.49
Strontium	ppb	13854	14257	14378	14163.00	274.36	-7.44
Vanadium	ppb	1.62	2	2.21	1.94	0.30	23.79
Zinc	ppb	154.18	156.79	132.16	147.71	13.53	-2868.05
Corrosion Inhibitor	ppm	35.1	36.73	38.16	36.66	1.53	94.12
KHI	%	0.1	0.1	0.1	0.10	0.00	62.96
MEG	%	0.01	0.01	0.01	0.01	0.00	96.97
Benzene	ppb	1006	519	773	766.00	243.58	93.14
Ethyl benzene	ppb	7.66	4.3	7.43	6.46	1.88	99.86
Toluene	ppb	353	158.64	315	275.55	103.01	0.94
Xylene	ppb	43.04	24.56	46.95	38.18	11.96	96.70
TN	ppm	17.2	17.5	16.84	17.18	0.33	63.77

ND: Not detected, below the detection limit.

#### 4.2.2 Activated Carbon and Modified Activated Carbon Results:

After the sand filtration the four containers mixed to gather to sure the homogeneity of the filtered water and split them in two containers to conduct activated carbon and modified activated carbon filtrations.

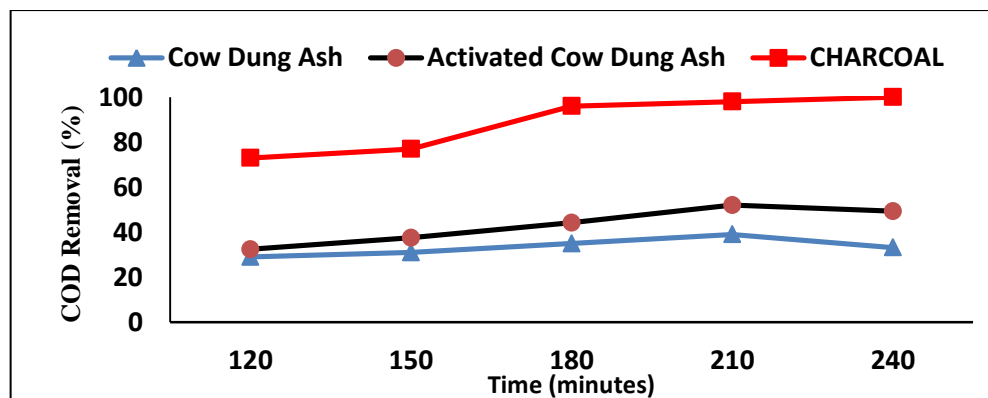
After the activated carbon filtration, **pH** value slightly increased from mean value 7.59 to mean value 8.23, on another hand after the Modified activated carbon filtration there was no any significant change in the pH value before and after filtration as shown in Table 28.

The incensement of the pH after the activated carbon filtration had been approved by (Farmer et al, 1996), granular activated carbon adsorption systems exhibitions increment in the adsorbed waste water pH, this raise could be as result in contact between the anions and protons in the filtered water and the activated carbon surface. The interaction can be defined as an ion exchange phenomenon, in which the activated carbon surface sorbs the corresponding hydronium ions and anions from the solution. These researches have presented that the anion sorption and resulting pH increase is independent of the raw material used for the activated carbon manufacturing, the pH incensement usually occur with new , acid washed and reactivated, granular carbons.

The **COD** concentration after the AC filtration reduced from the average 9433.3 mg/l to the average value 7200 mg/l as shown in Table 28, and COD removal efficiency 23.7% slightly low compare to previous studies exhibited below except the study for the Wastewater from Sugar industry by using activated carbon prepared from Bagasse fly ash, and the removal efficiency was 27 % (Lakdawala and Patel,2012), whereas the COD average value after the modified activated carbon increased form the average value 9433.3 mg/l to value10625 mg/l as shown in table 30, could be due to leaching of the

surfactant Triton -100 from the filtration columns, as the control samples also showed high COD concentration, another explanation could be refer to the increase in chloride concentration after the MAC filtration as the Chlorides could be oxidized by dichromate and cause a positive interference (USEPA,COD,1993). The reduction of COD after the AC filtration had been exhibited in many studies, (Nurshazwani,2015) demonstrated study to examine removal of COD by using activated carbon prepared from sugarcane bagasse (SCAC) for adsorptive elimination of COD from leachate of Landfill located at Sahom, Perak, Malaysia elimination percentage of COD was 77.8%.

Comparison of study between three types of activated carbon, (CDA) cow dung ash, (ACDA) Activated cow Dung Ash and commercially charcoal (CHAR) were evaluated for the elimination of organic pollution from the leachate of landfill with identified initial concentration (COD) Chemical Oxygen Demand. The influence of several factors like adsorbents amount, pH, time and temperature was examined also findings showed that up to 79% elimination of COD could be accomplished by using (ACA) activated cow dung ash, whereas (CA) cow dung ash exhibit 66% elimination of COD, and charcoal (CHAR) eliminate 94% of COD as shown in Fig.15 (Kamalpreet et al., 2016).



**Figure 16:** COD removal by three different adsorbents at fixed dose (Kamalpreet et al., 2016).

Another research demonstrated harmonization with the research above where complex of rice hull/Mn Fe<sub>2</sub>O<sub>4</sub> adsorbent was applied. Initial COD concentration of the waste water was 2088mg/L and the elimination efficiency of COD was 73% (APHA, 2005). Lv et al. (Lv et al., 2009) used bamboo ash activated carbon to reduce the COD concentration from cotton fabric manufacturing wastes water and the elimination efficiency of COD was 72%. Table 24 demonstrates previous studies data regarding the COD removal efficiency by using different types of Activated carbon.

There is similarly reduction percentage for the **TOC** concentration after activated carbon and modified activated carbon filtration, the TOC reduced from the average value 2424 mg/l to the mean value 1680.7 mg/l and the TOC removal efficiency is 30.7 % as shown in Table 28&30, and regarding the modified activated carbon is reduced from the average value 2424 mg/l to the average value 1670.7 mg/l with removal efficiency 31.1 % as shown in Table 29&30. Compared with the research carried out by (Luukkonen et al, 2014) to examine the elimination of remaining total organic carbon (TOC) from make-up water of power plant by using commercial activated carbon from four different sources and all demonstrated similarly efficient removing from 41.7% to 44.8%.

Water characteristics study for one year from (2000–2001) conducted to monitor the Rusko waste Water treatment factory , the result showed that the treatment process removed 53% of TOC, starting with TOC average 5.5 mg/l for the raw water and after treatment the TOC became on average of 2.6 mg/l (Myllykangas et al., 2002).

Regarding the **organic acids (formate, acetate and propionate)** there were significant reduction in concentration of the acetate and propionate after activated carbon filtration,



before the filtration the average values for the acetate and propionate were 339.8 mg/l and 16.57 respectively and after the Ac filtration the average values were 55.6 mg /l and 1.87 mg/l respectively with elimination effectiveness for the acetate 83.6% and for the propionate 88.7 % as shown in Table 28&30. Whereas after the modified activated carbon there was reduction in acetate concentration only from 339.8 mg/l to 258.1 mg/l with removal efficacy 24 % only as shown in Table 29&30.

Compared to previous studies, (Mundhe et al., 2015) investigated the potential use of ACs biosorbent prepared from seeds of *Polyalthia longifolia* for the elimination of acetic acid from aqueous solution. The experimental data have been assessed using Freundlich and Langmuir isotherm model. Maximum adsorption has been found to be 29.4 % at 30 °C for lower concentration at 0.100 gm adsorbent dose.

Five trials of two different types of activated carbons were used and approved the efficiency of AC to remove the acetic acid, the first one maize cobs from vegetal source and second one activated carbon from animal source, both of them were tested the acetic acid adsorption, The activated carbon of maize cobs were prepared by chemical activation with ZnCl<sub>2</sub> (zinc chloride). It demonstrated that the MAPZC5 activated carbon sample which was gotten from the solid part of the maize cobs had better adsorption characteristic than the measured manufacturing activated carbon from animal source. As a result, activated carbon of maize cobs can be consider as adsorbent to cleanse of the waste water contaminated by acetic acid (Dina et al., 2012).

There were a significant reduction after Activated carbon filtration in the following **metals** concentration iron, nickel ,zinc ,copper, boron and barium from 22.3,10.6,147.7 , 113.9, 4907,522.2 ppb respectively to < 1, <1,11.2,36.3,3312.5 and 474.5 ppb respectively.

And the removal efficiency is 100% ,100% ,92.6% ,68.1%,32.5% and 9.1% respectively as shown in Table 28&30, whereas the modified activated carbon got higher removal efficiency than the activated carbon filtration for zinc , copper and Boron except for Barium which got less removal efficiency than the activated carbon filtration and the concentration of Iron, Nickel ,zinc ,copper and boron reduced to <1, <1,<1,79.5 and 538 ppb with removal efficiency 100% ,100% ,100 % ,30.4 % and 89 % as shown in Table 29 &30. (Wahi et al., 2009) inspected the capability of (AC) activated carbon was prepared from empty fruit bunches (EFB) of palm oil to eliminate many metals and for Cu (II) the removal efficiency was only 25%.

(Anirudhan & Sreekumari, 2011) examine the adsorptive elimination of heavy metal ions from manufacturing waste water using coconut buttons waste as the activated carbon. The research indicated that the activated carbon removal efficiency for copper Cu (II) ions concentration from manufacturing waste water.

Regarding the modified activated carbon by using commercially nonionic Triton-X 100 surfactant previous study approved removing the Cadmium ions from aqueous solutions and due to the low cadmium concentration in current produced water samples after the sand filtration it difficult to confirm the removal efficacy of the cadmium. As the treated carbon had greater porosity compared with unmodified activated carbon , has higher removal efficiency than the activated carbon filtration for zinc, copper and Boron. (Nadeem et al., 2009) which agreed with current study findings.

There is a significant reduction in the **B.T.E.X** compound concentration after the activated carbon filtration for the benzene, ethyl benzene toluene and xylene from 766,6.46,275.5 and 38.18 ppb to 5.43,1.49,1.85 and 1.15 ppb with removal efficiency

99.3% ,76.9 % ,99.3% and 97% respectively as shown in Table 28& 30, Whereas after the modified activated carbon the **B.T.E.X** (benzene, ethyl Benzene toluene and xylene) reduced from 766,6.46,275.5 and 38.18 ppb respectively to < 0.5 ppb for all them with removal efficiency > 99 % as shown in Table 29 &30, Which already approved through several previous studies for example. A research carried out by (Aleghafouri et al., 2015) to look at the B.T.E.X adsorption from diethanolamine (DEA) solution by using three types of commercially granular activated carbons (AC). The adsorption of BTEX from diethanolamine (DEA) solution were carried out to eliminate benzene, toluene, ethyl benzene and metaxylene (BTEX) from Diethanolamine solvents and the equilibrium batch adsorption studies for BTEX removal were fit into Langmuir, Freundlich and Sips model isotherms to obtain the best fitted model. Another research conducted by Doyle et al. (Doyle et al., 1997) tried a combination of a modified polymer, bentonite or organoclay and bed adsorption column packed by activated carbon. The researchers reported that their system could eliminate hydrocarbons steadily and effectively resulting in reduced total petroleum hydrocarbons and soluble hydrocarbons such as B.T.E.X: benzene, ethyl benzene, toluene and xylene to (Lower detection limit) non-detectable limits.

There is small reduction in the **Total Nitrogen (TN)** compound concentration before and after Activated and modified activated carbon, the removal efficiency of the activated carbon is 3.2% and for the activated carbon is 6.1% as shown in Table 28, 29 &30.



**Figure 17:** Produced water (PW), Sand filtration (SF), activated Carbon (AC) and modified Activated carbon (MAC).

**Table 28:** Filtered Produced water chemical and physical characterization after the Activated Carbon filtration.

Parameter	Unit	AC1	AC2	AC3	AC4	Mean	SD
pH	NA	8.25	8.2	8.21	8.26	8.23	0.02944
COD	ppm	7450	6850	7250	7250	7200	251.66115
TOC	ppm	1588	1679	1745	1711	1680.75	67.45060
Conductivity	µs/cm	8954	8925	9008	8998	8971.25	38.74167
Phosphate	ppm	0.1	0.1	0.1	0.1	0.1	0.00000
Sulphate	ppm	367.2	373.9	368.8	366.3	369.05	3.39460
Chloride	ppm	2536	2589	2607	2571	2575.75	30.30264
Formate	ppm	0.404	0.393	0.327	0.338	0.3655	0.03863
Acetate	ppm	55.919	55.739	55.063	55.733	55.6135	0.37701
Propionate	ppm	1.884	1.899	2.055	1.642	1.87	0.17053
Aluminum	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Arsenic	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Barium	ppb	476	466	492	464	474.5	12.79323
Boron	ppb	3240	3290	3420	3300	3312.5	76.32169
Cadmium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Calcium	ppb	465400	452600	475600	472600	466550	10237.67552
Cobalt	ppb	ND	ND	ND	ND	ND	#DIV/0!
Chromium	ppb	ND	ND	ND	ND	ND	#DIV/0!
Copper	ppb	36.6	42.3	31.89	34.49	36.32	4.42766
Iron	ppb	ND	ND	ND	ND	ND	#DIV/0!
Lead	ppb	ND	ND	ND	ND	ND	#DIV/0!
Manganese	ppb	40	41	36	41	39.5	2.38048
Magnesium	ppb	63600	61800	65400	64800	63900	1587.45079
Molybdenum	ppb	9.77	9.75	8.16	10.55	9.5575	1.00337
Nickel	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Potassium	ppb	91889	91879	92200	92474	92110.5	284.48609
Sodium	ppb	1226000	1144000	1189000	1198000	1189250	34033.07215
Strontium	ppb	13620	13840	13900	14300	13915	283.49015
Vanadium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Zinc	ppb	12.33	15.75	8.54	8.54	11.29	3.46882
Benzene	ppb	6.61	10.13	2.21	2.78	5.4325	3.69113
Ethyl benzene	ppb	1.55	1.59	1.41	1.42	1.4925	0.09106
Toluene	ppb	2.11	3.21	1.02	1.07	1.8525	1.03513
Xylene	ppb	1.21	1.26	1.07	1.07	1.1525	0.09743
TN	ppm	16.44	16.91	16.77	16.4	16.63	0.24967

ND: Not detected, below the detection limit.

**Table 29:** Filtered Produced water chemical and physical characterization after the Modified Activated Carbon filtration

Parameter	Unit	MAC1	MAC2	MAC3	MAC4	Mean	SD
pH	NA	7.97	7.99	7.97	7.9	7.96	0.0395
COD	ppm	10800	10900	9900	10900	10625.00	485.6267
TOC	ppm	1708	1683	1603	1689	1670.75	46.4067
Conductivity	µs/cm	9474	9469	9489	9490	9480.50	10.5987
Phosphate	ppm	0.1	0.1	0.1	0.1	0.10	0.0000
Sulphate	ppm	192	192	190	190	191.00	1.1547
Chloride	ppm	3048	3060	3030	3030	3042.00	14.6969
Formate	ppm	1	1.1	2	1.5	1.40	0.4546
Acetate	ppm	266.4	254.9	257.9	253.3	258.13	5.8369
Propionate	ppm	15.9	16.8	16.9	16.7	16.58	0.4573
Aluminum	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Arsenic	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Barium	ppb	527	530	526	536	529.75	4.5000
Boron	ppb	536	532	554	530	538.00	10.9545
Cadmium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Calcium	ppb	537200	538300	535400	539600	537625.00	1778.3419
Cobalt	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Chromium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Copper	ppb	77	79	78	83	79.25	2.6300
Iron	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Manganese	ppb	40	41	36	41	39.50	2.3805
Magnesium	ppb	63600	61800	65400	64800	63900.00	1587.4508
Molybdenum	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Nickel	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Potassium	ppb	94453	96619	94065	94016	94788.25	1236.0554
Sodium	ppb	116200	113800	119800	122000	117950.00	3656.5011
Strontium	ppb	15240	15320	15600	15600	15440.00	187.6166
Vanadium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Zinc	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Benzene	ppb	0.5	0.5	0.5	0.5	0.50	0.0000
Ethyl benzene	ppb	0.5	0.5	0.5	0.5	0.50	0.0000
Toluene	ppb	0.5	0.5	0.5	0.5	0.50	0.0000
Xylene	ppb	0.5	0.5	0.5	0.5	0.50	0.0000
TN	ppm	16.12	15.99	16.3	16.1	16.13	0.1284

ND: Not detected, below the detection limit.

**Table 30:** Comparison of the removal efficiency among Activated Carbon and modified Activated Carbon .

<b>Parameter</b>	<b>Unit</b>	<b>AC %</b>	<b>MAC %</b>
COD	ppm	23.67	-12.63
TOC	ppm	30.66	31.07
Conductivity	µs/cm	-3.00	-8.85
Phosphate	ppm	94.92	94.92
Sulphate	ppm	0.26	48.38
Chloride	ppm	0.33	-17.71
Formate	ppm	-5.43	-303.85
Acetate	ppm	83.63	24.04
Propionate	ppm	88.72	-0.01
Aluminum	ppb	NA	NA
Arsenic	ppb	100.00	100.00
Barium	ppb	9.14	-1.44
Boron	ppb	32.49	89.04
Calcium	ppb	5.92	-8.41
Copper	ppb	68.12	30.43
Iron	ppb	100.00	100.00
Manganese	ppb	-266.42	-266.42
Magnesium	ppb	-20.73	-20.73
Molybdenum	ppb	-1637.73	100.00
Nickel	ppb	100.00	100.00
Potassium	ppb	-6.04	-9.12
Sodium	ppb	-0.75	0.07
Strontium	ppb	1.75	-9.02
Zinc	ppb	92.55	100.00
Benzene	ppb	99.29	99.93
Ethyl benzene	ppb	76.91	92.26
Toluene	ppb	99.33	99.82
Xylene	ppb	96.98	98.69
TN	ppm	3.20	6.13

NA: Not applicable.

**Table 31:** Comparison of the removal efficiency among Sand filtration (SF), Activated Carbon (AC) and modified Activated Carbon (MAC)

Parameter	Unit	SF %	AC %	MAC %
COD	ppm	10.13	23.67	-12.63
TOC	ppm	-0.76	30.66	31.07
Conductivity	µs/cm	-23.81	-3.00	-8.85
Phosphate	ppm	4.53	94.92	94.92
Sulphate	ppm	-702.14	0.26	48.38
Chloride	ppm	11.53	0.33	-17.71
Formate	ppm	0.00	-5.43	-303.85
Acetate	ppm	7.82	83.63	24.04
Propionate	ppm	4.57	88.72	-0.01
Aluminum	ppb	100.00	NA	NA
Arsenic	ppb	16.82	100.00	100.00
Barium	ppb	-763.04	9.14	-1.44
Boron	ppb	14.58	32.49	89.04
Calcium	ppb	-73.66	5.92	-8.41
Chromium	ppb	97.53	100.00	100.00
Copper	ppb	-18175.94	68.12	30.43
Iron	ppb	99.46	100.00	100.00
Manganese	ppb	95.83	-266.42	-266.42
Magnesium	ppb	-17.45	-20.73	-20.73
Molybdenum	ppb	90.04	-1637.73	100.00
Nickel	ppb	-50.42	100.00	100.00
Potassium	ppb	13.93	-6.04	-9.12
Sodium	ppb	1.49	-0.75	0.07
Strontium	ppb	-7.44	1.75	-9.02
Zinc	ppb	-2868.05	92.55	100.00
Corrosion Inhibitor	ppm	94.12	0.15	0.15
KHI	%	62.96	0.00	0.00
MEG	%	96.97	0.00	0.00
Benzene	ppb	93.14	99.29	99.93
Ethyl benzene	ppb	99.86	76.91	92.26
Toluene	ppb	0.94	99.33	99.82
Xylene	ppb	96.70	96.98	98.69
TN	ppm	63.77	3.20	6.13

NA: Not applicable.



## **4.2.3 Mechanism of Adsorption:**

### **4.2.3.1 Sand filtration:**

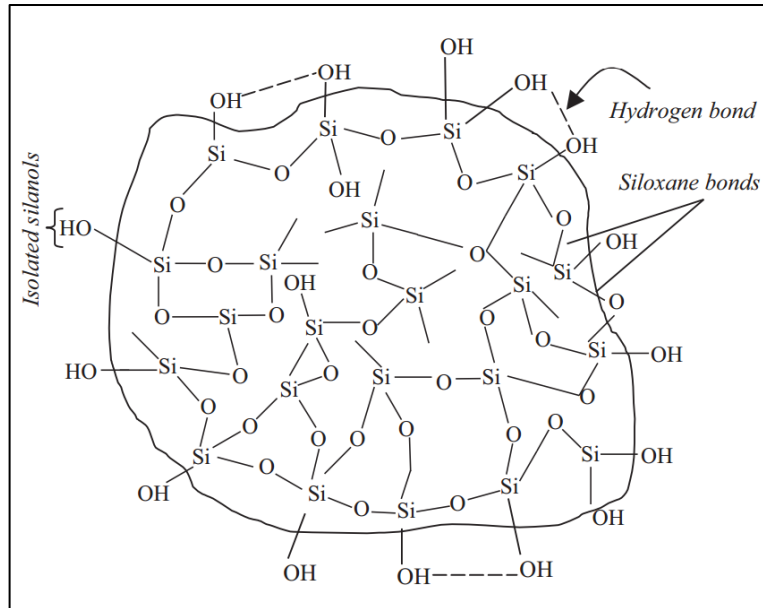
Sand filtration performed to achieve high removal efficiency for the total suspended solids with more than 77% and it is achieved by straining mechanisms as the large suspended matters particles that cannot go through the gaps between the sand grains are removed for the grain size of 0.15 mm, the diameter of the smallest pores are still a little over 20  $\mu\text{m}$  and are therefore removed whatever over this size and incapable to keep hold of the colloidal matter with size 0.001-1  $\mu\text{m}$ . Therefore the macro compounds (complexes) such as corrosion inhibitor and KHI kinetic inhibitor which has been eliminated by 94.1% and 62.9% respectively and could be eliminated by straining mechanisms (Huisman & Wood,1974; Bourke,1995; Scholz, 2016). The sand filtration also performed high removal efficiency for oil and grease as more than 97% could be due to straining mechanisms too .

Sand filtration demonstrated high removal efficiency for the metals and cations with positive charge such as iron, chromium and manganese and the removal efficiencies were as the follows 99.5%, 97.5% and 95.8% respectively; the removal effectiveness was achieved by mass attraction mechanisms (electrostatic interaction). The sand consists of silica (silicon dioxide, or  $\text{SiO}_2$ ), usually in the form of quartz. The quartz crystals is a negatively charge and attracts positive particles in the water therefore there was high removal percentage for the following metals iron, chromium and manganese and existent of 2% clay in sand filter bed contributed in metals adsorptions (Huisman & Wood,1974; Bourke,1995; Scholz, 2016). The negative charges particles or partially organic source (Polar), colloidal matter, and other impurities with negative charged such as anions like

phosphate, sulphate, chloride,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  are eliminated by the secondary adsorption after the initial positive adsorption, therefore more than 93% of the BTEX is removed except for toluene, 63.7% of total nitrogen, 11.5% of chloride and 4.5% of phosphate.

The silica surface includes functional groups such as silanol groups that spread over the matrix of the silica as shown in Fig17. The silanol group is very active and reacts with several polar organic compounds and many functional groups. The surface characteristics of the RD are determined by presence of silanol groups on its surface. Enough concentration of these groups makes the surface of the RD hydrophilic. The OH groups perform as the centres for adsorption during their specific interaction with adsorbates capable of creating a hydrogen bond with the OH groups (of water molecules) (Zhuravlev, 2000) OH groups on the RD are divided into the following: (i) isolated free silanol ( $-\text{SiOH}$ ), (ii) geminal free silanol ( $-\text{Si}(\text{OH})_2$ ) and (iii) vicinal or bridged or OH groups bound through the hydrogen bond. Furthermore, on the RD surface there exist surface siloxane groups or  $\text{Si}-\text{O}-\text{Si}-$  bridges with oxygen atoms on the surface.

The RD surface is terminated by OH groups and oxygen bridges, which act as adsorption sites. In the adsorption process. The surface characteristics of the RD depend on these groups and, at a sufficient concentration, the surface of the RD becomes hydrophilic. Other important groups are the OH groups, which act as centers for adsorption through the formation of hydrogen bonds with the adsorbate (Zhuravlev, 2000). Moreover, the RD consists of siloxane groups or  $-\text{Si}-\text{O}-\text{Si}-$  bridges with oxygen atoms on the surface that might act as an adsorption site.



**Figure 18:** Structure of silica surface depicting the various types of bonds and silanol groups present on diatomite [Si–O–Si: the Siloxane Bond] (Zhuravlev, 2000 ;Aue et al,1961).

#### 4.2.3.2 Activated carbon and modified activated carbon:

Activated carbon filtration found is more efficient to remove COD and TOC with 23.7% and 30.7% respectively among the three media. Regarding the removal efficiency of the AC for the organic acid was the highest for the acetate and propionate with 83.6% and 88.7% respectively and for the inorganic ions- phosphate the removal efficiency was 94.9%. Also the AC showed removal for some metals such as zinc, copper, boron, nickel, iron and chromium and highest removal efficiency more than 97% for the all B.T.E.X compound except for the ethyl benzene was 76.9%.

Modified Activated Carbon found is more efficient to reduce the TOC with 31.1% whereas the COD concentration increased by 12.6%. MAC showed also removal efficiency for the inorganic ions phosphate and sulphate with 94.9 and 48.4% respectively. For the metals

MAC was more efficient than the AC to reduce the zinc, molybdenum and boron concentration and less efficient than AC to reduce copper and acetate (Organic acid), Regarding the B.T.E.X removal efficiency is similar to AC more than 98% except for the ethyl benzene was 92.3% higher than AC 76.9%

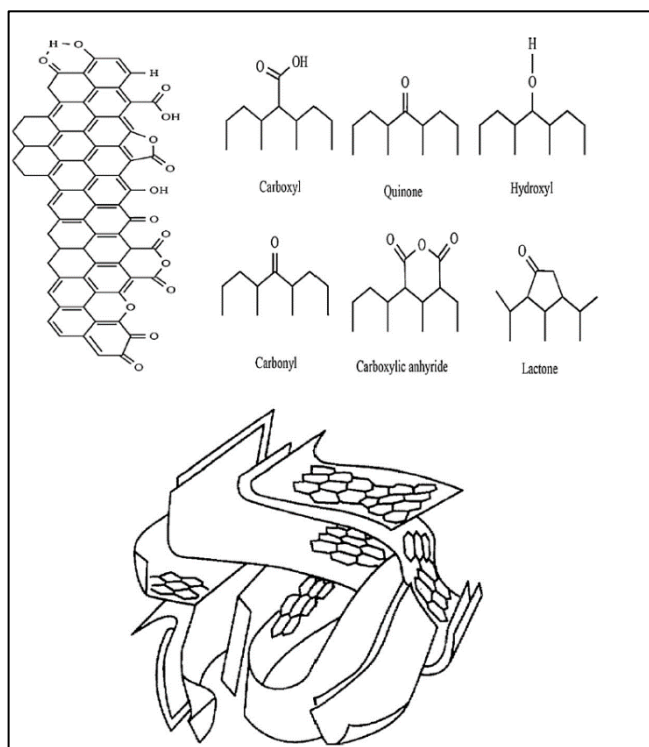
Activated carbon is especially efficient at eliminating of heavy metals and a big range of organic compounds from waste water (Marsh & Rodríguez ,2006) due to Activated carbon has various of unique characterization, for example, high grade of surface reactivity, high adsorption ability, extended surface area, and microporous structure, (Bhatnagar et al.,2013).

Adsorption by activated carbon is combination of physical, chemical and exchange adsorption physical is relatively weak inter-molecular attraction forces (Van der Waals) forces, chemical adsorption occurs by chemical interaction between adsorbate and adsorbent and the exchange adsorption by charged sites on the surface (Marsh & Rodríguez , 2006).

Activated carbons, however, are widely used as adsorbents. They represent extremely versatile adsorbents of industrial significance and are widely used in many applications which are concerned principally with the removal of undesirable species from liquids or gases. The surface functional groups anchored on/within carbons were found to be responsible for the variety in physicochemical and catalytic properties of the matters considered (Shen et al., 2016).

The heteroatoms on the surface of Activated carbon take an important role on its application. The heteroatoms of porous carbon surface mostly contained nitrogen ,oxygen, , halogen ,hydrogen ..etc. , which are bonded to the edges of the carbon layers and govern the surface chemistry of Activated carbon (Elsayed et al, 2004). Among these heteroatoms, the oxygen-containing functional groups (also denoted as surface oxides) were the broadly

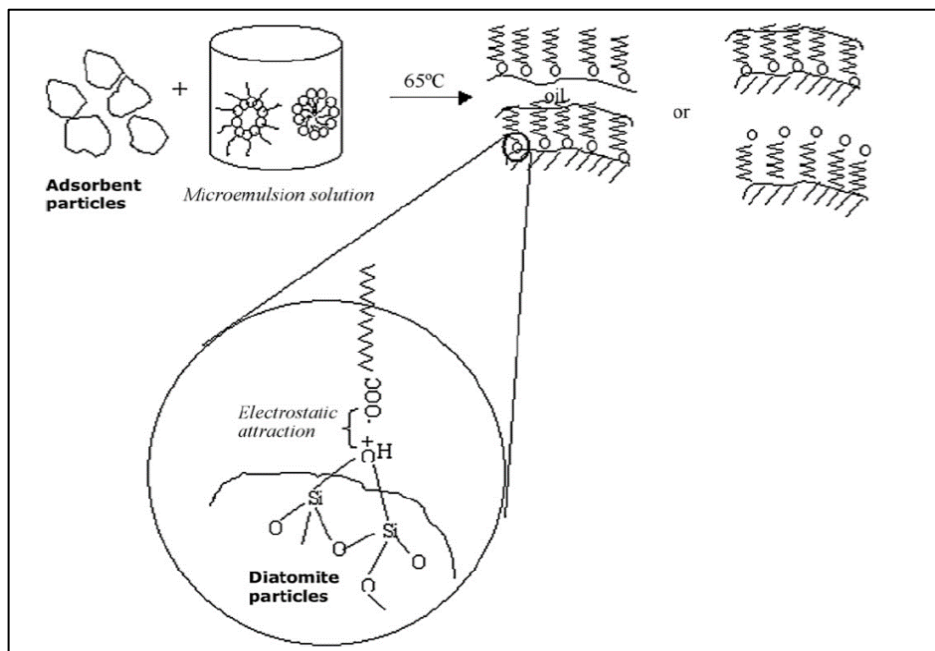
recognised and the most common species formed on the surface of carbons, which significantly influenced their performance in conversion systems, catalytic reactions, and adsorptions (Li et al, 2002). Carboxyl, carbonyl, phenol, quinone and lactone groups on carbon surfaces were shown in Fig. 18. Fig. 18 also shows an average structure of Activated Carbon, consisting of aromatic sheets and strips, containing several slit shaped voids, i.e., the micropores. Most possibly, these non-polar formations can play a part in the interaction of carbon surface with H<sup>+</sup>/OH<sup>-</sup> ions and decrease the strength of the present functional groups.



**Figure 19:** Simplified schematic of some acidic surface groups bonded to aromatic rings on AC. (Shen et al , 2016).

By using microemulsion modified adsorbent, the following advantages are expected: (a) using no liquid organic solvents; decreasing the effect on the global warming, (b) running

the treatment process at ambient conditions, (c) using the local resources, (d) producing less waste and (e) having lower operating and capital costs. In previous studies by (Khraisheh & Al-Ghouti, 2005) they studied the colour adsorption by calcined diatomite from wastewaters through modification with microemulsions. It was concluded from the FTIR and pH analysis that the major mechanism of the reactive yellow dye (RY) molecules onto the microemulsions is by an electrostatic attraction between the carboxylate anion and the dye. In the case of the MB and reactive black (RB), the adsorption mechanism could be a combination of different mechanisms such as electrostatic attraction, capturing by microemulsion micelles in the pores of the calcined diatomite or the hydrophobic attraction. The adsorption capabilities were higher than unmodified calcined diatomite. In the case of adsorption of the MB molecules, a high adsorption capability onto the microemulsions was obtained.



**Figure 20:** Schematic showing the interaction of the surfactant on the surface of the RD (Khraisheh & Al-Ghouti, 2005).

## 5. Conclusions and Recommendations

### 5.1 Conclusions

This project would end up with following conclusion:

- Chemical and physical composition of the formation-produced water from Northfield offshore gas production platform in Qatari has been examined and the result were compared with the chemical composition of other field produced water, the concentration were within the range among other field except for sulfide, and treatment chemical production(additive chemicals) concentrations.
- Sand filtration showed higher removal efficiency for the flowing parameters TSS, Corrosion inhibitor and total nitrogen with 77.5%, 94.1% and 63.7% respectively. The highest metals removal was for iron and manganese and regarding the B.T.E.X it showed high removal efficiency more than 95% except for the toluene was 26.7% .The COD removal efficiency after sand filtration is 10.2% the lowest among the others media .as shown in Table 31.
- Activated carbon filtration is found more efficient to remove COD and TOC with 23.7% and 30.7% respectively among the three media. Regarding the removal efficiency of the AC for the organic acid was the highest for the acetate and propionate with 83.6% and 88.7% respectively and for the inorganic ions the phosphate removal efficiency was 94.9%.

Also the AC showed removal for some metals such as zinc, copper, boron, nickel, iron and chromium and highest removal efficiency more than 97% for the B.T.E.X except for the ethyl benzene was 76.9% as shown in Table 31.

- Modified Activated Carbon found is more efficient to reduce the TOC with 31.1% whereas the COD concentration increased by 12.6%.MAC showed also removal efficiency for the inorganic ions phosphate and sulphate with 94.9 and 48.4% respectively. For the metals MAC was more efficient than the AC to reduce the zinc, molybdenum and boron concentration and less efficient than AC to reduce copper and acetate (Organic acid) , Regarding the B.T.E.X removal efficiency is similar to AC more than 98% except for the ethyl benzene was 92.3% higher than AC 76.9% as shown in Table 31.

## 5.2 Recommendations

There are several areas for further studies and applications could be applied on produced water such as:

- Study other chemical, physical and biological characterization such as NORM, microbiology survey, TPH...etc.
- Study produced water characterization during winter season when there are additional antifreeze chemicals or hydration inhibitor injection such as MEG and KHI.
- Applied High Hydraulic Loadings sand, Activated carbon, or others media filtration treatment system techniques.
- Applied different pilot scale studies such as phytoremediation, microbial bioremediation treatments...etc.



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## Appendix:

**Appendix A:** Produced water Chemical and physical characterizations from Natural gas production in the North field of State of Qatar (4 Replicates).

Parameter	Unit	produced water (R1)	produced water (R2)	produced water (R3)	produced water (R4)	Mean	SD
PH	NA	4.42	4.43	4.43	4.44	4.43	0.01
COD	ppm	10520	10370	10440	10680	10502.50	133.26
TOC	ppm	2407	2424	2401	2392	2406.00	13.49
BOD	ppm	1350	1034	1076	992	1113.00	161.68
Salinity	ppm	4556	4528	4460.8	4518.4	4515.80	39.99
Conductivity	µs/cm	7120	7075	6970	7060	7056.25	62.90
TSS	ppm	19	25	21	18	20.75	3.10
HEM	ppm	39.7	36.4	40.4	44.8	40.33	3.46
Sulfide	ppm	375	349	324	306	338.50	30.05
Silica	ppm	1.98	1.9	2.0	2.09	1.99	0.08
Phosphate	ppm	2.65	2.13	2.07	1.98	2.21	0.30
Sulphate	ppm	47.22	46.3	45.92	46.16	46.40	0.57
Chloride	ppm	2829	2913	2933	2917	2898.00	46.80
Formate	ppm	0.4	0.39	0.32	0.33	0.36	0.04
Acetate	ppm	373	373	368	365	369.75	3.95
Propionate	ppm	17.9	18.2	16.2	17.7	17.50	0.89
Phenol	ppm	2.08	1.92	1.905	2.04	1.99	0.09
Aluminum	ppb	5.48	4.16	9.17	17.52	9.08	6.01
Arsenic	ppb	5.80	5.47	7.00	9.23	6.88	1.70
Barium	ppb	61.07	60.93	60.03	60.58	60.65	0.46
Boron	ppb	5550.72	5665.38	5717.93	5850.66	5696.17	124.42
Cadmium	ppb	0.05	0.05	0.05	0.05	0.05	0.00
Calcium	ppb	291857.7	283547.66	285227.87	287920.52	287138.44	3625.24
Cobalt	ppb	7.51	7.54	7.34	6.24	7.16	0.62
Chromium	ppb	30.78	30.46	29.89	30.59	30.43	0.38
Copper	ppb	0.99	0.66	0.57	0.64	0.72	0.19
Iron	ppb	4200.45	4262.88	4035.3	4134.41	4158.26	97.32
Manganese	ppb	255.78	259.04	255.21	260.53	257.64	2.56
Magnesium	ppb	45231.86	44354.25	46476.78	44362.22	45106.28	1002.20
Molybdenum	ppb	5.53	5.53	5.53	5.5	5.52	0.02
Nickel	ppb	6.32	7.35	7.09	6.8	6.89	0.44
Potassium	ppb	101019.67	101024.28	100956.16	100786.56	100946.67	111.17
Sodium	ppb	1238917.2	1215547.0	1182652.96	1196301.16	1208354.58	24438.10
Strontium	ppb	13199.51	13128.02	13103.48	13313.63	13186.16	94.24
Vanadium	ppb	2.53	2.58	2.52	ND	2.54	0.03
Zinc	ppb	7.93	5.25	4.98	4.7	5.72	1.49
Corrosion Inhibit	ppm	641.1	609.6	620.1	640.23	627.76	15.51
KHI	%	0.27	0.27	0.27	0.27	0.27	0.00
MEG	%	0.33	0.33	0.33	0.33	0.33	0.00
Benzene	ppb	30099	8031	16069	9410	15902.25	10094.25
Ethyl benzene	ppb	13857	4084	5415.5	4446.5	6950.75	4638.35
Toluene	ppb	669.5	262	289.5	283	376.00	196.02
Xylene	ppb	1303	1055.5	1201.5	1213.5	1193.38	102.47
TN	ppm	47.14	47.6	47.51	47.13	47.35	0.25

ND: Not detected, below the detection limit.

**Appendix B: Chemical and physical characterization of Produced water after the Sand filtration . (4 Replicates)**

Parameter	Unit	Sand Filter (R1)	Sand Filter (R2)	Sand Filter (R3)	Sand Filter (R4)	Mean	SD
pH	NA	7.48	7.54	7.79	7.43	7.56	0.1597915
COD	ppm	9500	9400	9600	9300	9450	129.09944
TOC	ppm	2322	2383	2433	2456	2398.5	59.410998
Conductivity	µs/cm	8640	8500	8810	8820	8692.5	152.61608
TSS	ppm	5	5	5	5	5	0
HEM	ppm	1.2	1.2	1.3	1.1	1.2	0.0816497
Sulfide	ppm	0.03	0.03	0.03	0.03	0.03	0
Silica	ppm	0.876	0.848	0.848	0.94	0.878	0.0433897
Phosphate	ppm	0.1	2.5	1.7	1.7	1.5	1.0066446
Sulphate	ppm	376	379	312	419	371.5	44.245527
Chloride	ppm	2587.08	2582	2583	2587.7	2584.945	2.8638145
Formate	ppm	0.4	0.39	0.32	0.33	0.36	0.0408248
Acetate	ppm	292.031	313.298	323.98	382.215	327.881	38.580167
Propionate	ppm	13.519	15.247	16.773	17.7	15.80975	1.8316767
Phenol	ppm	1.596	1.392	1.416	1.368	1.443	0.1038653
Aluminum	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Arsenic	ppb	7.83	5.95	6.98	5.12	6.47	1.1835821
Barium	ppb	692.66	655.41	415.62	495.73	564.855	131.12803
Boron	ppb	5089	4850	5002	4869	4952.5	113.37401
Cadmium	ppb	0.31	0.15	0.23	0.03	0.18	0.1194432
Calcium	ppb	437561	449454	503736	534554	481326.25	45704.222
Cobalt	ppb	2.26	0.58	0.59	0.52	0.9875	0.8488963
Chromium	ppb	3.98	0.43	1.34	0.48	1.5575	1.6681402
Copper	ppb	325.2	132.37	124.74	84.65	166.74	107.69345
Iron	ppb	33.81	17.46	28.14	21.45	25.215	7.2282986
Manganese	ppb	66.55	7.67	12.21	12.46	24.7225	27.971766
Magnesium	ppb	59806	53366	55000	50412	54646	3929.2099
Molybdenum	ppb	0.55	0.55	0.55	0.55	0.55	0
Nickel	ppb	20.97	10.49	12.53	8.93	13.23	5.3664141
Potassium	ppb	96838	87793	87550	85247	89357	5117.5777
Sodium	ppb	1112158	1138533	1140287	1262204	1163295.5	67182.606
Strontium	ppb	14162	13854	14257	14378	14162.75	224.01097
Vanadium	ppb	3.95	1.62	2	2.21	2.445	1.032618
Zinc	ppb	267.49	154.18	156.79	132.16	177.655	60.900318
Corrosion Inhibitor	ppm	38.23	35.1	36.73	38.16	37.055	1.475274
KHI	%	0.1	0.1	0.1	0.1	0.1	0
MEG	%	0.01	0.01	0.01	0.01	0.01	0
Benzene	ppb	5664	1006	519	773	1990.5	2457.062
Ethyl benzene	ppb	5.39	7.66	4.3	7.43	6.195	1.6238329
Toluene	ppb	157.08	353	158.64	315	245.93	102.87293
Xylene	ppb	29.68	43.04	24.56	46.95	36.0575	10.64999
TN	ppm	19	17.2	17.5	16.84	17.635	0.9491575

ND: Not detected, below the detection limit.

## Appendix C: Chemical and physical characterization of control water after the Sand filtration.

Parameter	Unit	SF-Control 1	SF-Control 2	SF-Control 3	SF-Control 4	Mean	SD
pH	NA	7.61	7.58	7.19	7.39	7.44	0.19
COD	ppm	8.00	5.00	6.00	6.00	6.25	1.26
TOC	ppm	0.70	1.40	1.40	1.70	1.30	0.42
BOD	ppm	3.00	15.00	11.00	7.70	9.18	5.08
Conductivity	µs/cm	2120.00	1902.00	2150.00	2070.00	2060.50	110.70
TSS	ppm	5.00	5	5	5	5	0
HEM	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Sulfide	ppm	0.03	0.03	0.03	0.03	0.03	0.00
Silica	ppm	14.51	13.96	12.15	12.15	13.19	1.22
Phosphate	ppm	0.10	0.10	0.10	0.10	0.10	0.00
Sulphate	ppm	1573.00	1356.00	1492.00	1530.00	1487.75	93.86
Chloride	ppm	0.45	0.64	14.50	0.73	4.08	6.95
Formate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Acetate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Propionate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Phenol	ppm	0.01	0.01	0.01	0.01	0	0
Aluminum	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Arsenic	ppb	2.56	0.51	0.49	2.62	1.55	1.21
Barium	ppb	10.74	10.80	10.57	10.76	10.72	0.10
Boron	ppb	219.00	222.00	214.00	221.00	219.00	3.56
Cadmium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Calcium	ppb	576615.00	577572.00	573411.00	577015.00	576153.25	1869.81
Cobalt	ppb	0.46	0.25	0.30	0.32	0.33	0.09
Chromium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Copper	ppb	16.91	21.75	16.77	16.33	17.94	2.55
Iron	ppb	24.89	18.39	21.88	20.15	21.33	2.77
Lead	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Manganese	ppb	10.19	10.89	10.36	10.44	10.47	0.30
Magnesium	ppb	5341.00	5279.00	5202.00	5169.00	5247.75	77.39
Molybdenum	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Nickel	ppb	9.47	9.99	9.31	10.04	9.70	0.37
Potassium	ppb	3622.00	3558.00	3501.00	3483.00	3541.00	62.75
Sodium	ppb	917.00	893.00	838.00	838.00	871.50	39.90
Strontium	ppb	2656.00	2642.00	2587.00	2741.00	2656.50	63.72
Vanadium	ppb	7.00	7.11	6.99	7.16	7.07	0.08
Zinc	ppb	40.48	41.24	39.74	41.53	40.75	0.80
Corrosion Inhibitor	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
KHI	%	ND	ND	ND	ND	#DIV/0!	#DIV/0!
MEG	%	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Benzene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Ethyl benzene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Toluene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Xylene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
TN	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!

ND: Not detected, below the detection limit.

**Appendix D:** Chemical and physical characterization of controls water after Activated carbon filtration.

Parameter	Unit	Control AC1	Control AC2	Control AC3	Control AC4	Mean	SD
pH	NA	8.44	8.23	8.55	8.53	8.44	0.15
COD	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
TOC	ppm	1.23	1.83	0.41	1.13	1.15	0.58
Conductivity	µs/cm	39.64	55.18	38.10	43.42	44.09	7.73
Phosphate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Sulphate	ppm	202.00	206.00	201.00	208.50	204.38	3.50
Chloride	ppm	339.00	339.00	339.00	339.00	339.00	0.00
Formate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Acetate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Propionate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Aluminum	ppb	76.50	61.51	64.34	53.06	63.85	9.70
Arsenic	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Barium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Boron	ppb	7.89	5.00	5.00	6.69	6.15	1.41
Cadmium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Calcium	ppb	3510.00	2470.00	3630.00	3780.00	3347.50	595.34
Cobalt	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Chromium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Copper	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Iron	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Lead	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Manganese	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Magnesium	ppb	759.00	444.00	715.00	674.00	648.00	140.36
Molybdenum	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Nickel	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Potassium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Sodium	ppb	6530.00	1790.00	5890.00	5850.00	5015.00	2172.46
Strontium	ppb	57.95	35.81	56.53	54.46	51.19	10.35
Vanadium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Zinc	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Benzene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Ethyl benzene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Toluene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Xylene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
TN	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!

ND: Not detected, below the detection limit.

**Appendix E:** Chemical and physical characterization of controls water after Modified Activated carbon filtration.

Parameter	Unit	Control MAC1	Control MAC2	Control MAC3	Control MAC4	Mean	Stdev
pH	NA	7.28	7.21	7.31	7.23	7.26	0.05
COD	ppm	35800	38000	31400	35500	35175	2752
TOC	ppm	2361.00	2239.00	2234.00	2430.00	2316.00	96.05
Conductivity	µs/cm	87.24	91.58	72.12	91.58	85.63	9.24
Phosphate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Sulphate	ppm	39.10	38.20	31.80	38.50	36.90	3.42
Chloride	ppm	36.80	31.90	31.90	32.00	33.15	2.43
Formate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Acetate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Propionate	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Aluminum	ppb	73.00	50.19	80.10	52.06	63.84	14.98
Arsenic	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Barium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Boron	ppb	312.00	342.00	293.00	336.00	320.75	22.59
Cadmium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Calcium	ppb	10650.00	1095.00	8880.00	10650.00	7818.75	4559.50
Cobalt	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Chromium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Copper	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Iron	ppb	109	109	135	96	112	16
Lead	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Manganese	ppb	12	12	10	11	11	1
Magnesium	ppb	1410.00	1470.00	1370.00	1480.00	1432.50	51.88
Molybdenum	ppb	7	7	7	8	7	0
Nickel	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Potassium	ppb	33866	39029	27885	41447	35557	6013
Sodium	ppb	1420.00	1510.00	1270.00	1610.00	1452.50	144.31
Strontium	ppb	139.00	148.00	102.00	139.00	132.00	20.45
Vanadium	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Zinc	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Benzene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Ethyl benzen	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Toluene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
Xylene	ppb	ND	ND	ND	ND	#DIV/0!	#DIV/0!
TN	ppm	ND	ND	ND	ND	#DIV/0!	#DIV/0!

ND: Not detected, below the detection limit.