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Prospection on water pollution by crude oil at Ajdabiya Libya

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Abstract
Among water pollution sources, the petrochemicals wastes and pollutants, are dumped without treatment in the sea, lakes and ground in Libya. The objective of our present research, is to study the impact of waste from crude oil extraction on the environment of the Libyan region of Ajdabiya. The monitored physicochemical indicators are: Temperature (°C), pH, electrical conductivity (CE), TDS, CL-, NO_3-, SO_4^{2-}, HCO_3-, Na+, Mg^{2+}, K+, Ca^{2+}, Salinity, Total Hardness (TH).
The mineralization faithfully follows the rates of dissolved salts. The electrical conductivity varies from 7880 to 46700 µs/cm and far exceeds the Libyan irrigation standards (>2700µs/cm). Concerning the nitrate their contents range from 230 to 1210 mg/L and clearly reflect the crude oil pollution origin.
The Piper diagram and Wilcox-Riverside projections shows that the waters associated with crude oil have a chloride-sodium and potassium or sulphated sodic and slightly bicarbonated sodium or potassium facies. Moreover, the hydro physicochemical plot shows that the quality of the water associated with the oil of Ajdabiya Libya is poor and above all a degraded quality.

Keywords: Hydrochimestry, Waters, Crude oil, Pollution, Ajdabiya, Libya

1. Introduction
Oil is a natural resource that is an important resource for many countries in the Gulf, Africa, Asia and America [1-2]. Unfortunately the history of oil in the African region is fraught with problems identified by the Extractive Industries Assessment Report (EIR) which has highlighted social and environmental problems [3-4]. Several marine, coastal and continental ecosystems have been damaged by oil activities around the world and especially Libyan cities, such as the city of Ajdabiyia [5-8].
The purpose of this present work is to evaluate the degree and the modalities of pollution generated by the extraction, transport and refinement of oil in Libya. Thus, to provide decision-makers with scientific and technical support to initiate a continuous decision-making dynamic aimed at protecting the marine and coastal environment that is vital for the whole country.
Indeed, the present study proposes to validate a physicochemical monitoring [9-11] intended to describe and evaluate the nature, the quality and quantity of ecotoxic generated by the oil industry in the Libyan region of Ajdabiya.
In fact, the waters associated with the oil production industry are highly polluted and have an environmental impact on groundwater, surface water and oceans. We will also look for ways to reduce their consequences [12-13].

2. Materials and Methods
2.1. Field of Study
Ajdabiya is the capital of Al Wahat district, located in north-eastern Libya. It is located about 160 km south of Benghazi, on the coastal highway leading to Tripoli in the Gulf of Sirte. It was from 2001 to 2007 the capital of the district of the same name, Ajdabiya which has about 76968 inhabitants (Fig.1-2) [14].

2.2. Water sampling and analysis
For all sampling area **(Tab.1),** the parameters studied and the methods used are as follows:
- Temperature (T °C) is measured on site by a thermometer probe ;
- The pH was measured directly after sample collection using a Model 3310 pH meter;

- The electrical conductivity of the water samples was measured directly after sample collection using a Conductimeter Model Consort. Electrical conductivity EC is expressed in ds/m or µs/cm at 25 °C;
- Total Dissolved Solute TDS in mg/L and Salinity in g/L ;
- Estimate of calcium and magnesium ($Ca^{+\ 2}$, $Mg^{+\ 2}$). Calcium and magnesium ions were estimated by plating the EDTA solution, which is a stable compound with calcium and magnesium ions using the Eriochrome black T reagent, Murexid [15-16];
- Determination of chloride (Cl-). Chlorides are measured by the method of Mohr (AFNOR T90-014). The chlorinated water samples were calibrated with 0.014M silver nitrate using potassium chromate as a reagent in a neutral or alkaline medium [17].
- Determination of sulfates SO_4^{2-}. The method used was based on the fact that the sulfate ions are deposited in the 1: 1 HCl acid medium in the presence of barium chloride due to the formation of barium sulfate in the form of single crystals of barium sulfate. Absorption can be measured by UV.V is Spectrophotometer [18];
- Determination of carbonate and bicarbonate (HCO_3^-, CO_3^{2-}). Carbonates and bicarbonates were estimated by the concentration of HCL (0.05 N) [19];
- Determination of sodium and potassium (Na^+, k^+). Each element was estimated to have distinct radii when excited by a flame (photovoltaic) using a flame photometer [20].
- Total hardness TH, calcium or magnesian hardness, alkalinity, bicarbonate and carbonates are measured by volumetric method of hydrochloric acid (0.05N) titration method (AFNOR T90-036).

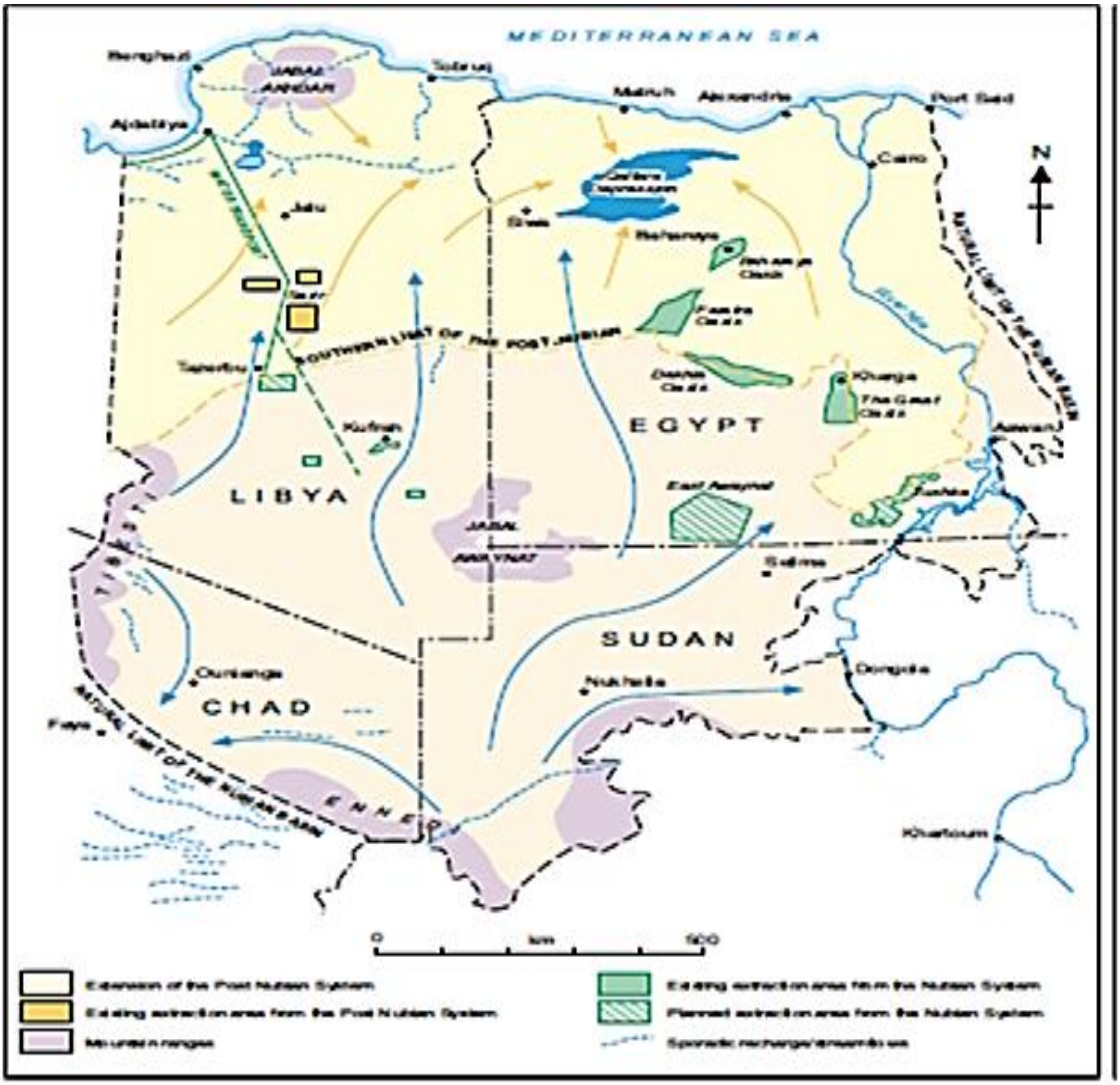

Fig 1: Spatial distribution of Al Wahat oil fields and strata in the Nubian Basin [1].

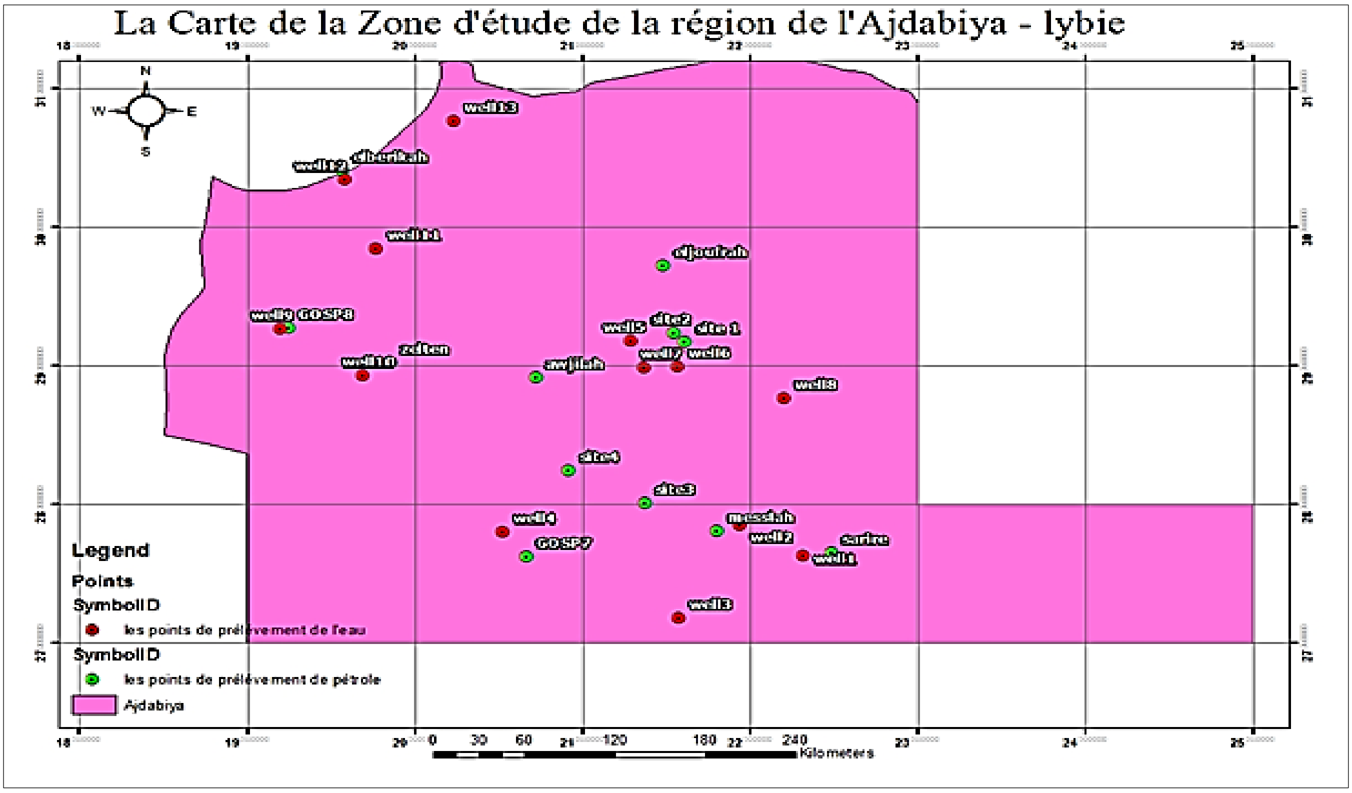

Fig 2: Map of the Study Area Ajdabiya – Libya

Table 1: Geolocation of water sampling stations associated with crude oil in Ajdabiya-Jalo.

Stations	Latitude	Longitude	Stations	Latitude	Longitude
Well 2	27°51'18.12"N	21°56'49.03"E	Well SEP	28°59'44.44"N	21°34'29.73"E
Well 3	27°10'52.51"N	21°34'55.18"E	Well 249	28°59'12.19"N	21°22'32.48"E
Well 4	27°47'56.12"N	20°31'54.67"E	Well 256	28°45'50.37"N	22°12'26.00"E
Well 5	29°10'45.26"N	21°17'56.09"E	Well D44	29°15'50.42"N	19°12'27.11"E
Well 6	28°59'44.44"N	21°34'29.73"E	Well G128	28°56'47.46"N	19°42'23.98"E
Well 7	28°59'12.19"N	21°22'32.48"E	Well G144	29°50'29.70"N	19°46'38.06"E
Well 8	28°45'50.37"N	22°12'26.00"E	Well G36	30°20'30.24"N	19°35'34.61"E
Well 9	29°15'50.42"N	19°12'27.11"E	Well tank	30°45'44.17"N	20°14'22.06"E
Well 10	28°56'47.46"N	19°42'23.98"E	Well S1	27°51'18.12"N	21°56'49.03"E
Well 11	29°50'29.70"N	19°46'38.06"E	Well S2	27°10'52.51"N	21°34'55.18"E
Well 12	30°20'30.24"N	19°35'34.61"E	Well S3	27°47'56.12"N	20°31'54.67"E
Well 13	30°45'44.17"N	20°14'22.06"E	Well S4	29°10'45.26"N	21°17'56.09"E

Fig 3: Spreading and storage areas for crude oil waste in Libya.

Fig 4: Methods of assaying and analyzing petroleum waste.

3. Results and Discussion

In the initial production of oil fields, the oil is not associated with water, but after a period of production, begins the emergence of water with oil extracted. The amount of water is gradually increased due to the upward water creep and in the final phase of the field operation, the proportion of produced water can reach 90% and more [25-26].

In the tanks, there is always water that is below the tank is the water associated with the oil. The water that accompanies the oil is characterized by a huge amount of dissolved mineral salts. It is a salt water, see very salty ranging from a few hundred thousand to more than 600000 ppm. The salinity varies in Libya from 25 to 117,5 g / L and comes from a salt-laden oil of 25000 to 117500 mg / L (Tab. 3). Nitrates (234 to 609 mg / L); sulphates (278 to 2609 mg/L); Total Hardness (572 to 9820 mg / L) are present at levels exceeding acceptable standards [27].

Table 3: Descriptive statistics of physicochemical crude oil waste of Ajdabiya

Variables	Observations	Minimum	Maximum	Mean	Standard deviation
T°C	42	21	46	33,3714	6,71
pH	42	6,2	7,96	7,2195	0,41
CE µS/cm	42	12654	66925	36855,5476	19135
TDS mg/L	42	8225	48432	24075,0952	12649
TH mg/L	42	572	9820	4095,9762	2435
Na^+ mg/L	42	723	37320	9941,3786	10894
Mg^{2+} mg/L	42	219	1009	622,5048	208
Ca^{2+} mg/L	42	464	5820	1894,0714	1434
K^+ mg/L	42	19,5	1140	403,3238	373
CL- mg/L	42	2800	70421	27537,1667	17119
SO_4^{2-} mg/L	42	278	2609	1238,2333	640
NO_3- mg/L	42	234	609	402,1190	108
HCO_3- mg/L	42	410	6561	799,1024	923
$CaCO_3$ mg/l	42	28,8	4032	1829,5262	1121
Salinity g/L	42	25	117,50	76,1429	19

The salinity of the water associated with the oil may be due to the phenomenon of ion exchange between them and clay minerals where the water can be impregnated with dissolved saline rocks. The water associated with the oil is greater than 1 g/cm^3 and the density increases with the increase of the concentration of the salts. The viscosity of the water associated with the oil is lower than the viscosity of the oil itself, which is an essential factor in the movement of the joint. The associated oil and water have less viscosity than oil, and the blend has greater mobility and movement than oil during oil well production. There may be joint motion in the porous medium between oil and water and move faster toward the well.

The pH does not show significant variations and the waters are generally acidic to slightly basic ranging between 5.57 and 7.86 (Tab.3) following their contamination by petroleum residues.

Electrical conductivity. The supply of pure water without salt is bad. When pure water is free of salts, bases and acids, it increases the electrical conductivity in the water [15]. This fact makes it possible to introduce the quantity of salts into the water. Any water has an electrical conductivity, but the removal of the ionic concentration of the water decreases its conductivity. The electrical conductivity is measured in µs / cm and varied from 12654 and 66925 µs/cm (Tab.3).

The Total dissolved solutes (TDS) is an important indicator of the suitability of water for various uses. The more soluble salts, the less soluble is water. If the water contains less than 1 mg / liter, the water is unacceptable and this water is not valid. For many uses, the concentration of dissolved salts in water varies considerably from one region to another [28]. In water polluted by oil it varies from 8225 and 48432 mg/L and is far from norms.

Total Hardness TH varied from 572 to 9820 mg/L and is linked to calcium and magnesium concentrations.

Calcium and magnesium with bicarbonate and carbonate and sulphate or silica components are insulation materials for heat in boilers and in household and industrial appliances. But combined with fatty acid ions give undesirable deposits lead to distortion of basins and walls in bathrooms and toilets. The high level of magnesium also causes intestinal diarrhea, especially for new users who do not know this water.

Chlorides with a concentration greater than 100 mg / L for salt water, lead to physiological complications and various diseases. The food industry usually requires less than 250 mg / L and the textile, paper and synthetic rubber industries require less than 100 mg / L of chloride. With 2800 and 70421 mg / L of chlorides the waters associated with oil exceed the norms of agricultural irrigation.

Sulphates also combine with calcium to be an adhesive that limits the thermal conductivity in the tubes. Therefore, it is prohibited for certain industries such as sulphate level higher than 250 mg / L. The sulphate level of 500 mg / L or more gives the water a bitter taste. Water containing more than 1000 mg / L of sulphates causes damage to physical health. The waters studied had between 278 and 2609 mg / L of sulphates and are widely polluted.

Bicarbonate when heated with water vapor gives carbon dioxide and carbonate and the latter combines with alkaline earth elements and the head of calcium and magnesium and forms a crust composed of Calcium and magnesium carbonate leads to reduced thermal conductivity through the walls of the conduction tubes and reduces the flow of fluid in these tubes and sometimes clogged completely. For many industries, the level of carbonate, bicarbonate or alkalinity is generally high.

Concerning the nitrate contents (Tab.3), the values oscillate between 234 mg / L and 609 mg/L and clearly reflect a nitrogen pollution of petroleum origin [27].

The Piper diagram (Fig. 5) shows that globally the waters associated with petroleum have a chloric sodium facies and potassium or sulphated sodium and slightly bicarbonated sodium or potassium. Moreover, the projection of hydrophysicochemical data in the Wilcox diagram and Riversade (Fig. 5), shows that the water quality associated with Ajdabiya Libya oil is poor and above all a deteriorated quality at because of the alkalizing power of sodium (SAR). These waters are classified in group C4S4 and outside this grid and are unfit for irrigation.

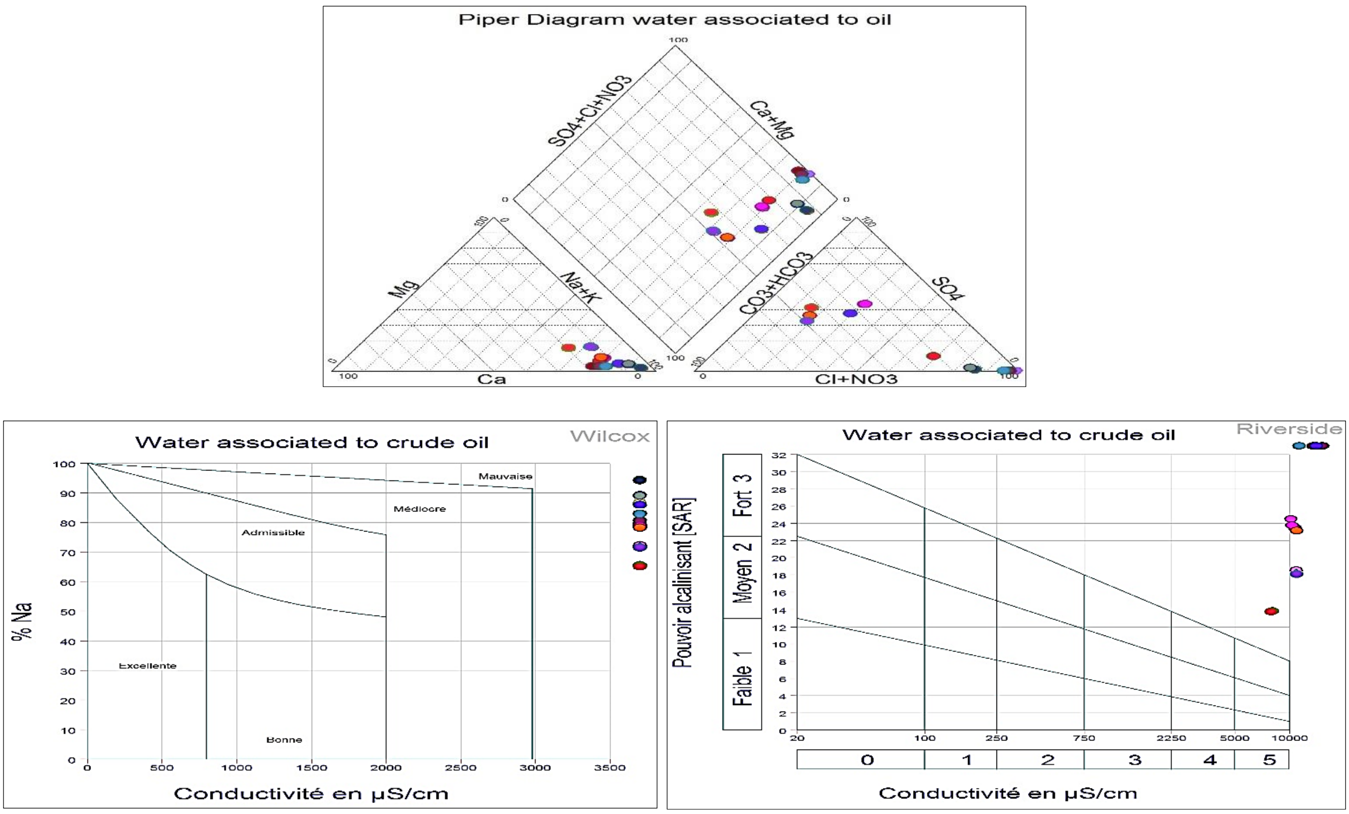

Fig 5: Hydrochemical Facies of water assiociated to crude oil in Ajdabiya, Libya.

4. Conclusion

All water studies and research have identified water needs in light of Libya's population increase, which is expected to reach about 14 million by 2025. Total freshwater resources are around 4.5 billion cubic meters and the total needs of this population are about 7.6 billion. The expected deficit is about 1.3 billion cubic meters. To compensate for this deficit, groundwater resources must be studied and rationalized. This study aims to explore and analyze water resources in order to assess their quality and validity [33]. Clouds are not well distributed and precipitation is random [34].

Large-scale oil pollution has led to a deterioration of water quality. In addition to increased salinity of the waters due to several factors such as the intrusion of salt water from layers carrying salt water to fresh rolling classes or the entry of seawater or salt water to proximity.

The objective of this study is to evaluate the chemical content of associated water for oil production and collected in the evaporation ponds in the Ajdabiya area. The evaluation of the chemical properties and heavy elements of the oil in the Libyan desert.

For the water quality in the Fezzan area, 82% of the wells studied are low to moderate saline, not exceeding 480 mg / L. 16% of these salt wells are high, reaching 1440 mg / L. The ratio of 2% of these salt wells is very high at 3692 mg / L.

In Libya's arid and semi-arid regions in a paper on urban growth in the Sabha region, it was noted that the increasing reduction of the basin has resulted in an increase in the salinity of the water produced from the upper reservoir and c 'is the result of a local decrease in the groundwater level of aquifers that does not spread to several areas [9-10; 14; 35].

The concentration of soluble salts in oil-related waters exceeded the allowable limit. Thus the increase in these values and the concentration in the wells of the water used in the oil wells were not allowed for all the wells.

For positive ions, there are high concentrations of sodium, calcium, potassium and magnesium from water wells associated with oil. The calcium ion concentration for all the wells studied exceeded the standards.

The concentration of total dissolved solids and salinity in petroleum varies between 8225-48432 mg / L and 25000-117500 mg / L respectively, whereas these concentrations were 12000 to 54000 mg / L respectively in oil-related waters and used to maintain the pressure in the tank.

Most of the chemical properties of these waters were higher than the overall allowable rates for agricultural use, which may also be toxic to livestock and wildlife if consumed.

The biggest challenge for the oil industry and the environment is to reduce the threat of disposal of the large volume of water produced in the oil fields. Standard methods of chemical analysis to determine the contaminants used in this form of water. The water produced from groundwater trapped in the formations brought to the surface with the production of oil.

We have seen that oil is a continuum of molecules and that heavy fractions are the most complex part of petroleum products. Indeed, heavy cuts are composed of large molecules, very polar, rich in hetero elements and metals.

The current energy context nevertheless pushes the oil industry to direct its research toward the exploitation of heavy oil products. These products are therefore the subject of numerous studies aimed at optimizing their conversion into valuable products and limiting their impact on the environment.

The world faces a growing challenge of balancing the three essentials of life and economy: water, food and energy. There is a close relationship between energy and water. Water plays a central role in the production of oil and gas and vice versa. Fossil energy resources require extraction and water-based production. On the other hand, the supply of water for domestic purposes, industrial and agricultural uses energy in production, processing and distribution.

The oil and gas industry faces two major problems in water resource management. The first is to manage the water associated with oil production. The oil extracted from the wells is mixed with large quantities of water and, according to the global average, it extracts 3 to 5 barrels of water to each barrel of oil. This water for the oil is called the production of oil.

The water associated with oil "or" productive water "is estimated at 44 million barrels of water a day, assuming an average rate of four million barrels of water per million barrels of oil, with a production rate of only 11 million barrels a day.

Oil companies tend to inject oil fields through private wells similar to oil wells, but they are deeper to supply water to the bottom of the oil layer in order to increase pressure and push the oil upward to facilitate and increase the extraction and for this purpose requires pumping between 3 and 4 barrels of water to extract a barrel of oil.

This water is not directly usable. It is very salty and consists of a mixture of hydrocarbons, minerals, concentrated salts, additives and radioactive materials. Most of these waters are currently reused in wells after treatment to boost the pressure of the oil tank. In the case of dumping into the sea or being discharged to the surface without treatment, there will be a danger to the environment, where the polluting and harmful components of health cross the marine trophic chain or the groundwater. The use of this water for other purposes requires complex and expensive treatment, but it deserves to be studied and refined.

Since the mid-sixties and over the past three decades, groundwater has been used to inject oil fields in the southern and central and northern parts of the Eastern Region and, in fact, There are no precise figures or documented estimates of the volume of groundwater used in the injection of oil fields in the world, but the size of the production and the size of the fields; these are large quantities and some analysts attribute this to the fact that this large groundwater consumption may be the main reason for the drop in the groundwater level and the negative effects on water from natural springs and irrigation agricultural. It should be mentioned here that the use of groundwater was stopped and replaced by brackish water.

In conclusion of this study it is proposed to develop WWTPs for the treatment of water produced with the extraction of oil and its purification and re-injection into waterways. Thus, further reduce the amount of metal ions present in the treated water and the removal of metal ions and also reduce sulphate ions, nitrates, salinity and electrical conductivity [36-39].

Most countries already involved in offshore oil development have developed their own laws and standards at national and regional level. Instead of presenting final policy recommendations, we prefer to put in place tools and build a strong normative, regulatory and legal framework to protect the environment in Libya.

5. Acknowledgement

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