Original Article

EVALUATION OF INDUSTRIAL WATER QUALITY AND THE EFFICIENCY OF THE DESALINATION UNIT IN REMOVING SOME HEAVY MINERALS IN EFFLUENTS OF IRAQI NORTH OIL COMPANY

[1]Ahmed Yashar Kader, [1]Fadam Muteb Abdoon and [2]Abdul Majeed Khorsheed Ahmed
[1] Department of Chemistry, College of Science, Tikrit University, Tikrit, Iraq.
[2]Department of Chemistry, College of Education for Pure Science, Kirkuk University, Kirkuk, Iraq

DOI: 10.47750/pnr.2022.13.S08.110

Abstract

Improving the quality of industrial water specifications is important in the operational units of oil companies, so this research aims to study the specifications and quality of industrial water used in crude oil primary treatment units and the efficiency of the desalination unit. Water samples were collected from the Zab River, a water source for the company, treated water used in oil units, salt removal unit discharge water, tank drainage, industrial wastewater and injection water in the fields. Some heavy elements (Iron, Vanadium, nickel, Chromium and lead) were estimated. By using Atomic Absorption Technology (ASS). The alkaline elements (sodium, calcium and potassium) were determined using the Atomic Emission Technique (AES), where the results were for sodium (1320-2.16) ppm, calcium (17.06-2.15) ppm, and potassium (213.5-2.24) ppm. The results we obtained for Iron were between (10.7-0.17) and for Chromium between (0.32-0.11) with concentrations ppm, and they did not show any concentration of nickel, Vanadium and lead in ppm concentrations. The pH function was between (8 - 6) and electrical conductivity (46400-394) µs. The total hardness (20200-109) ppm and total dissolved solids (24128-146) ppm.

Keywords: Heavy Metals, Alkaline Elements, Discharge of the salt removal unit, Injection water, (ASS) Spectrophotometry,(AES) Spectroscopy.

1-INTRODUCTION

Water is one of the most important materials used in industrial and commercial activities, which is later disposed of as waste. It is called industrial wastewater. Industrial wastewater can contain heavy metals, pollutants, fats, oils, detergents, acids and drugs(1). Water is an easy and inexpensive source to obtain. Therefore, it is used in washing the facility as a solvent, energy production, distillation, filtration, and service uses(2). It is used in many industries, including the paper and cardboard industry, the chemical industry, the mining industry, mineral processing, the pharmaceutical industry, the manufacture of thermal and nuclear plants and in the petroleum industries(3). As for the petroleum industries, water has many uses, can be classified according to use, and also varies water specifications according to its use(4). It is used in washing and cleaning raw materials and equipment for workers. Water is used to heat or cool fluids (heat exchangers). It is used in the production of steam to operate steam turbines (steam boilers). • It is used as a primary treatment in washing oil in emulsification and salt removal units(5). as injection water for fields. Raw water contains mud, dust, plankton, bacteria, dissolved salts and heavy elements with different concentrations, so it needs preliminary treatments before using it in the operational units[6]. Therefore, it is important to treat water from pollutants and impurities in the water because it causes many problems, such as excessive corrosion in pipes and equipment. It also causes mineral deposits and blockages in pipes[7]. Therefore, the water is treated to eliminate some impurities through (filtration, sedimentation, adding alum, chlorine injection, and removing hardness)[8]. Oil refining produces a huge amount of gaseous, liquid and solid pollutants. Crude oil contains various heavy metals accompanying it from the extraction field. Thus, crude oil is initially treated by washing the oil with water to remove salts and emulsify in salt removal units[9]. In this process, part of the minerals accompanying the crude oil is disposed of: the minerals in the form of dissolved salts in crude oil. It will be present in the residues resulting from the desalting unit, and the complex part (organic mineral compounds) will resist the process and remain in the crude oil[10]. Therefore, the wastewater from the desalination unit is highly saline and contains high concentrations of heavy metals and toxic pollutants. Therefore, the washing water is treated before it is released to the sea or water bodies at the treatment plants of the oil company or the refinery, or it can be treated for reuse for injection in the fields[11].

Table (1) show the range of concentration of heavy metal in seawater and freshwater[12]

Element	Conc. In seawater In ppm	Conc. In freshwater In ppm
Fe	0.03-70	10-1500
Cr	0.2-50	0.1-6
Ni	0.13-43	0.02-27
Pb	0.03-13	0.06-120
V	2.5-250	0.9-130

Table (2) Concentration of Nickel and Vanadium in crude oil for some country fields [12]

Element	Canada	Kuwait	South Louisiana	Prudhoe bay
Ni	65.4	7.7	2.2	10
V	192.6	28	1.9	20

Department of Energy (DOE) prepared for the US Department of Energy In 2004, the study was conducted on the water associated with oil from extraction wells to evaluate this water (NETL).To discuss its physical and chemical properties and its potential impact on the environment, as well as to discuss many options. The water accompanying the oil from the field contains heavy elements with different concentrations, as the study showed Energy Technology Lab United States. It was found that these properties differ according to the geographical location and the geological layers and contain heavy metals.

Table (3) concentration of heavy metals in water associated with crude oil[13]

Element	Zn	Fe	Pb	Ni	Cd	Cu	Mn
Conc.(ppm)	1.2	4.9	0.19	1.7	0.023	0.45	0.12

Water is used at a rate of (4-6)% of the amount of crude oil, and a demulsified is added to get rid of the emulsified water as the oil and water enter a container containing the electrode and generate a high voltage (12000-19600)V that causes the water membranes to break, collect and precipitate to the bottom due to the density difference and discharge It is distinguished by its green color and pH(6.5-8.5) and has an oily smell[14].

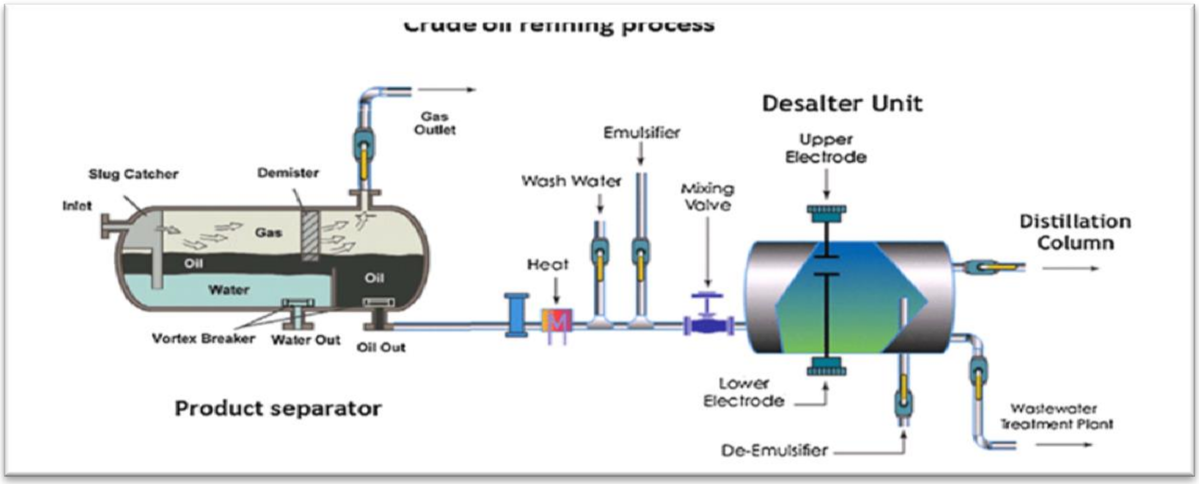

Figure: (1) Salt removal unit

There are many techniques for the determination of heavy metals in water. Atomic absorption technology[15]. Ultraviolet and visible spectroscopy technology[16]. Flow injection technique[17]. HPLC technique[18]. Atomic absorption is a simple, available, and less expensive analytical technique regarding material use and device requirements and achieves high repeatability, accuracy, and reproducibility.

2- Experimental Part

2-1- **Equipments**

1- atomic absorption spectroscopy (AAS) :-

a- Flame atomic absorption spectroscopy (FAAS)

b- Flameless Atomic absorption spectrophotometer (GFAAS) or Electrothermal Atomic Absorption Spectrometry (ETAAS)

2- Flame photometer

3- pH meter

4- Electrical Conductivity meter

5- Total Dissolved Solids meter

Figure: (2) SHIMADZU AA7000 Atomic Absorption Spectrophotometer

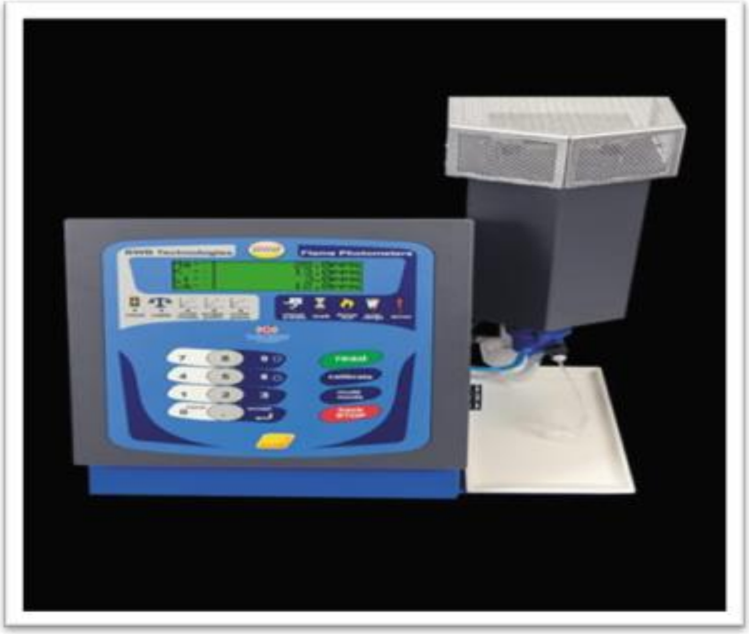

Figure: (3) flame photometer BWB Technologies

2-2 Procedures

The original standard solution (1000 µg/ml in 2% HNO3) was used to determine the metals. Prepare several standard solutions by diluting the original standard stock solution (C1 V1 = C2 V2) (1000 µg/ml → 100 µg/ml → 10 µg/ml → 1 µg/ml).

2 ml of concentrated nitric acid was added to 98 ml of sample to determine alkaline and heavy elements in water samples by sample digestion method.

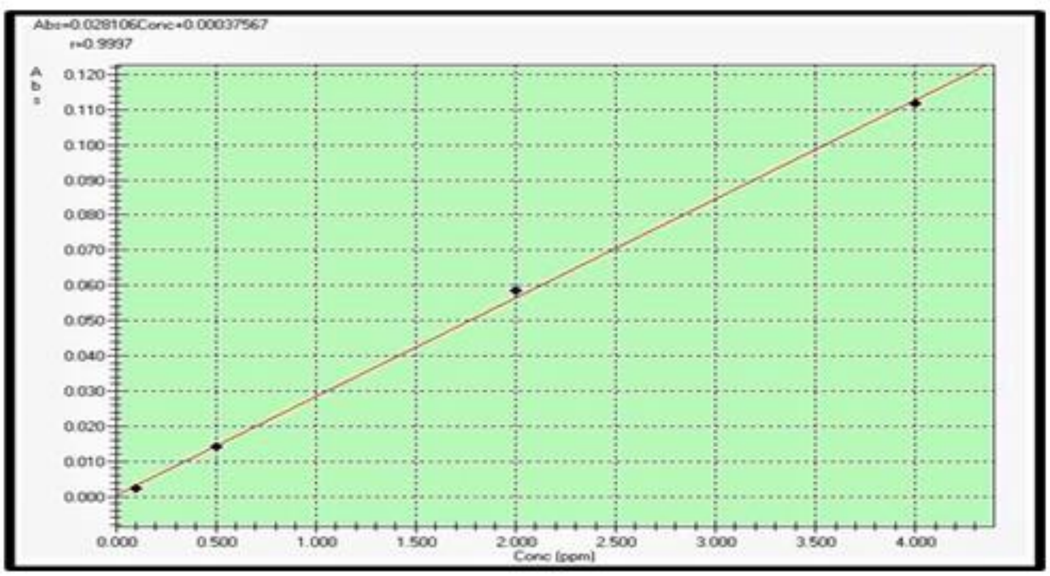

Fig (4): Calibration curve of lead

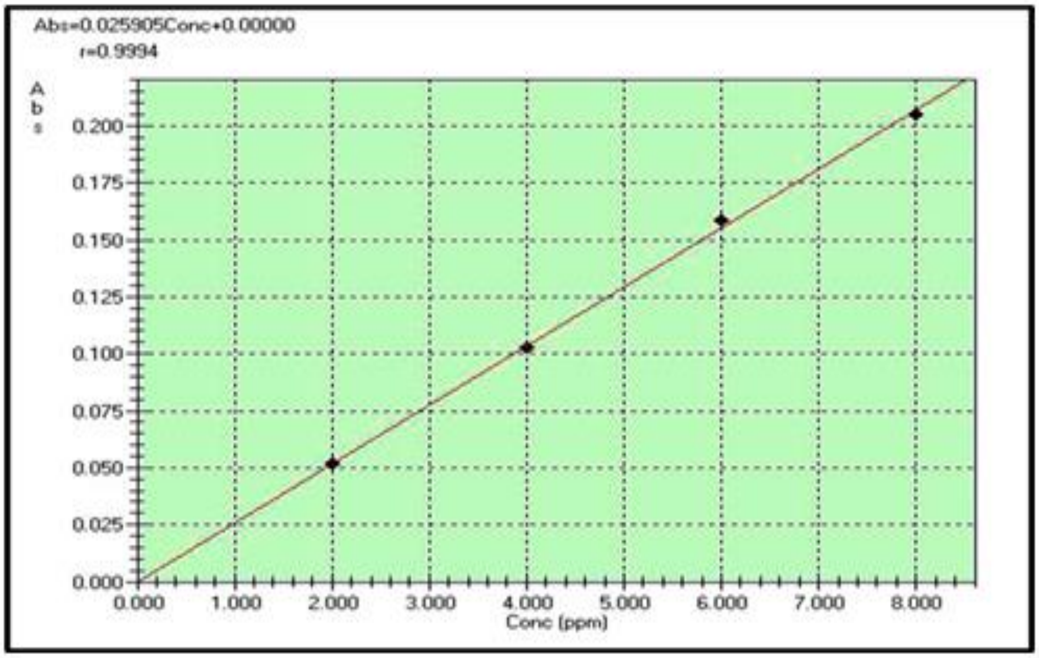

Fig (5): Calibration curve of Iron

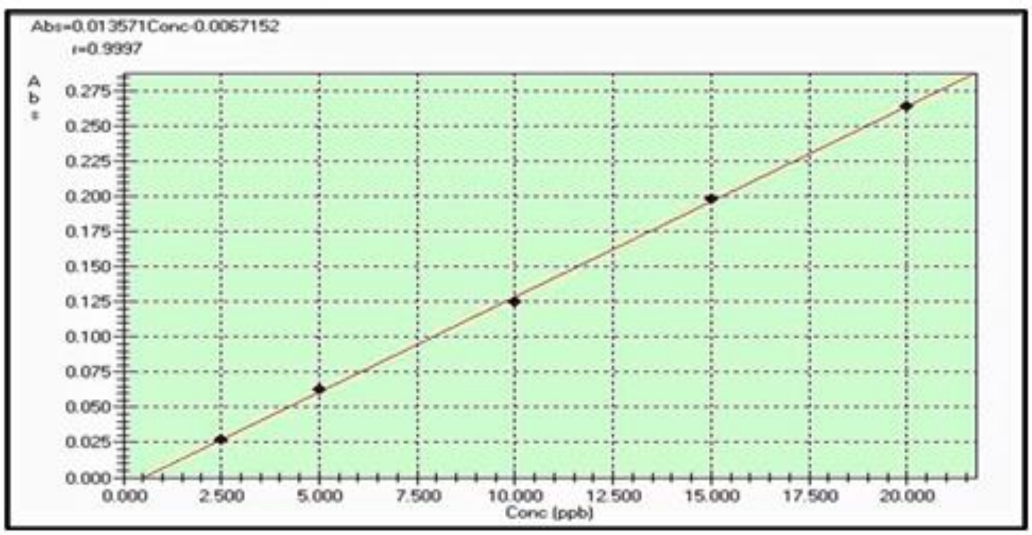

Fig (6): Calibration curve of Vanadium

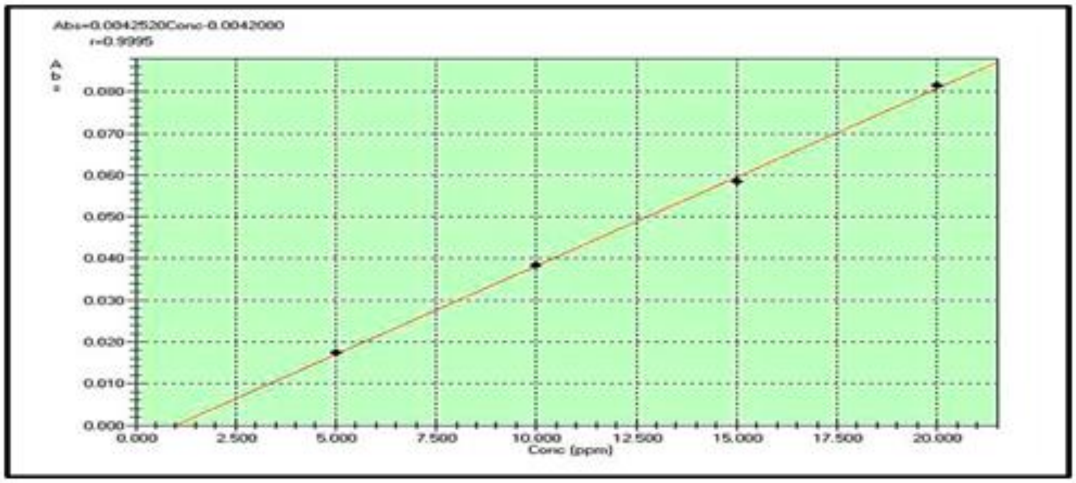

Fig (7): Calibration curve of Ni

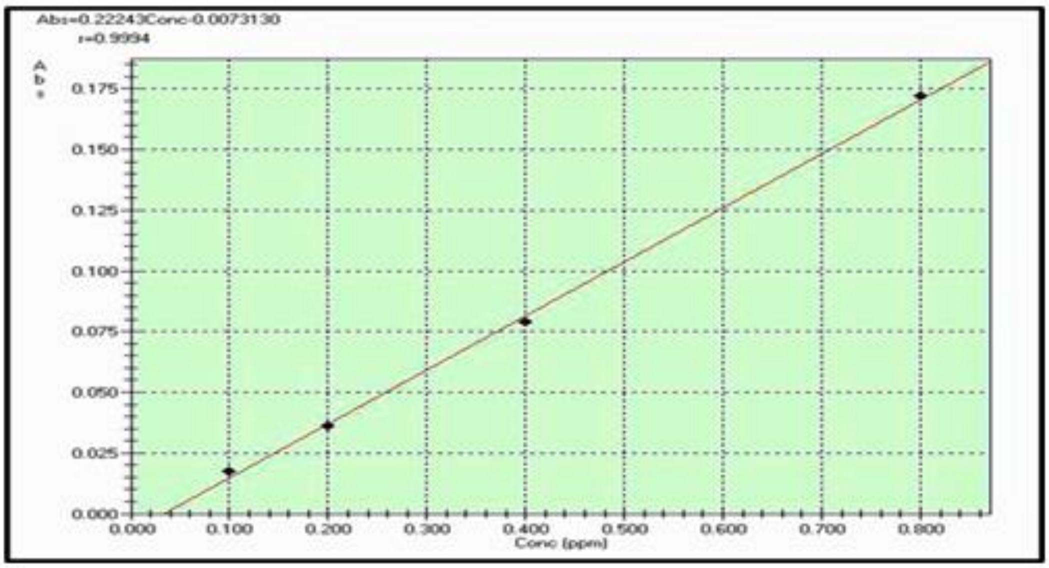

Fig (8): Calibration curve of Chromium

- The electrical conductivity of the models was measured after washing the electrode with distilled water and calibrating the device with calibration solution, then taking the results in µS/cm.
- Using a soluble solids meter, the total dissolved solids concentration was measured in water samples after washing the electrode several times and taking concentrations in units of mg/L.
- The pH function was measured using a pH meter for water models after calibrating the device using buffer solutions.

3- RESULTS AND DİSCUSSİON

3-1 Results

Heavy metals were estimated in water models. The concentrations are estimated in units ppm, as shown in Table(4).

Table (4): The concentrations of heavy metals

Samples	Conc. Pb	Conc. V	Conc. Ni	Conc. Cr	Conc. Fe
Zab River	nil	nil	nil	0.3	0.3
treated water	nil	nil	nil	0.11	0.17
Industrial Waste water	nil	Nil	nil	0.14	0.27
Wastewater from the desalination unit	nil	nil	nil	0.33	10.7
Injection water	nil	nil	nil	0.18	0.51
Wastewater from oil tanks	nil	nil	nil	0.23	0.15

The graphite atomic absorption technique was used to determine Vanadium, and this technique has High sensitivity technology and can read low detection limits (in ppb). The highest concentration was in the drainage water of the salt removal unit (156) ppb, and the lowest concentration was in the treated water (8) ppb.

Table (5):Operation Condition

Metals	Flame Type	Wavelength Nm	Lamp Current Ma
Pb	Air/Acetylene	217	10
Ni	Air/Acetylene	232	12
Fe	Air/Acetylene	248.3	10
Cr	Air/Acetylene	357.9	10

Using the atomic emission device, the alkaline elements sodium, calcium and potassium were estimated at concentrations of ppm, as shown in Table (6)

Table (6): Concentration of Alkaline Elements

Samples	Conc. K	Conc. Ca	Conc. Na
Zab River	2.24	2.15	2.16
treated water	2.11	2.36	3.15
Wastewater Industrial	2.03	1.15	1.25
the Wastewater from desalination unit	42.3	10.76	766
Injection water	213.5	17.06	1320
Wastewater from oil tanks	3	2.36	3.52

The pH function of samples of sap water, industrial wastewater, injection water and treated water was between (7-8.5). As for the wastewater of the desalination unit, the acidity function appears to be 6.5, indicating the presence of sulfur compounds transferred from crude oil to water, causing its transition to acidity. It is also characterized by green color and smells of sulfur.

Table (7): showing total soluble solids results and electrical conductivity

Samples	T.D.S(PPM)	Conductivity µs/Cm
Zab River	169	394
treated water	146	348

Waste water Industrial	278	612
desalination unit Waste water from	24128	46400
Injection water	230	537
Waste water from oil tanks	9402	18080

3-2 DISCUSSION

Knowing water specifications is important and treating water from impurities and salts is necessary because it passes through various equipment and pipes that cause corrosion and calcification problems if not treated. The results that we obtained, as shown in Table (4), show an increase in water concentrations, the discharge of the salt removal unit and then the water of the tanks, and this indicates the disposal of some heavy metals that are in the form of dissolved salts and not the organometallic complex (porphyrin metal). Furthermore, an increase in the concentrations of alkaline elements, electrical conductivity, and solids in a wastewater model of a desalting unit, As shown in Tables (6) and (7), indicates the unit's efficiency in removing salts.

4-CONCLUSION

The efficiency of the desalination unit in removing heavy metals from crude oil is the percentage removed from the oil. This percentage is too small and does not fulfil the primary purpose of the desalination unit, which is to eliminate heavy metals so as not to poison the expensive catalysts used in the catalyst units.

The Zap water specifications appear good, reducing the use of expensive materials to treat it. The specifications of treated water, industrial wastewater and injection appear within the required specifications.

REFERENCES

1- Pal, P. (2017). Industrial water treatment process technology. Butterworth-Heinemann.

2- Guyer, J. P., & PE, R. (Eds.). (2018). An Introduction to Industrial Water Treatment. Guyer Partners.

3- Chesnutt, T. (2021). The economics of sustainable industrial water use, reuse, and the value of water. Sustainable Industrial Water Use: Perspectives, Incentives, and Tools, C. Davis and E. Rosenblum (eds.), IWA Publishing, London.

4- Hansen, É., Rodrigues, M. A. S., Aragão, M. E., & de Aquim, P. M. (2018). Water and wastewater minimization in a petrochemical industry through mathematical programming. Journal of Cleaner Production, 172, 1814-1822.

5- Zhang, N., Yang, X., Wang, Y., Qi, Y., Zhang, Y., Luo, J., ... & Jiang, W. (2022). A review on oil/water emulsion separation membrane material. Journal of Environmental Chemical Engineering, 107257.

6- Ihsanullah, I., Sajid, M., Khan, S., & Bilal, M. (2022). Aerogel-based adsorbents as emerging materials for the removal of heavy metals from water: Progress, challenges, and prospects. Separation and Purification Technology, 120923.

7- Buckley, T., Xu, X., Rudolph, V., Firouzi, M., & Shukla, P. (2022). Review of foam fractionation as a water treatment technology. Separation Science and Technology, 57(6), 929-958.

8- Martínez Moya, S., & Boluda Botella, N. (2021). Review of Techniques to Reduce and Prevent Carbonate Scale. Prospecting in Water Treatment by Magnetism and Electromagnetism. Water, 13(17), 2365.

9- Abed, S. M., Abdurahman, N. H., Yunus, R. M., Abdulbari, H. A., & Akbari, S. (2019, November). Oil emulsions and the different recent demulsification techniques in the petroleum industry-A review. In IOP Conference Series: Materials Science and Engineering (Vol. 702, No. 1, p. 012060). IOP Publishing.

10- Dando, D. A., & Martin, D. E. (2003). A guide for reduction and disposal of waste from oil refineries and marketing installations (Vol. 6, No. 03). Brussels, Belgium: CONCAWE.

11- Dold, P. L. (1989). Current practice for treatment of petroleum refinery wastewater and toxics removal. Water Quality Research Journal, 24(3), 363-390.

12- Ware, K. D. (1993). Heavy Metals and the Petroleum Industr. TEXAS UNIV AT AUSTIN.

13- Veil, J. A., Puder, M. G., & Elcock, D. (2004). A white paper describing produced water from production of crude oil, natural gas, and coal bed methane (No. ANL/EA/RP-112631). Argonne National Lab., IL (US).

14- Zolfaghari, R., Fakhru'l-Razi, A., Abdullah, L. C., Elnashaie, S. S., & Pendashteh, A. (2016). Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. Separation and Purification Technology, 170, 377-407.

15- Radulescu, C., Dulama, I. D., Stihi, C., Ionita, I., Chilian, A., Necula, C., & Chelarescu, E. D. (2014). Determination of heavy metal levels in water and therapeutic mud by atomic absorption spectrometry. Romanian Journal of Physics, 59(9-10), 1057-1066.
16- Kulkarni, S., Dhokpande, S., & Kaware, J. (2015). A review on spectrophotometric determination of heavy metals with emphasis on cadmium and nickel determination by UV Spectrophotometry. International Journal Of Advanced Engineering Research And Science (IJAERS), 2(9), 35-38.
17- Faraji, M., Yamini, Y., Saleh, A., Rezaee, M., Ghambarian, M., & Hassani, R. (2010). A nanoparticle-based solid-phase extraction procedure followed by flow injection inductively coupled plasma-optical emission spectrometry to determine some heavy metal ions in water samples. Analytica chimica acta, 659(1-2), 172-177.
18- Vogl, J., & Heumann, K. G. (1997). Determination of heavy metal complexes with humic substances by HPLC/ICP-MS coupling using on-line isotope dilution technique. Fresenius' journal of analytical chemistry, 359(4), 438-441.