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Case Report

Electrochemical Pretreatment as a Suggested Alternative, More Compatible with Environment and Sustainable Development in RO Desalination System

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Abstract: RO processes have more promising future perspectives. Nevertheless, there are some constraints that require certain efforts to be spent on research and development. First of all, pretreatment step must be optimized for minimum environmental impact by eliminating chemicals additives as can as possible. This review study focuses on RO technology and introduces electrocoagulation as a suggested alternative which can play an important role for many tasks in a manner more compatible with environmental and sustainable development, depending on clean and economic energy.

Keywords: RO Desalination, Electrocoagulation, Silica Removal, Total Hardness, Chlorination, Boron

1. Introduction

Nations of the world are faced with the challenge of supplying the ever-increasing water demand, and desalination seems to be a promising solution to address this challenge. However, constant improvement of available technologies in order to reduce the cost of this solution, and the development and use of new environmentally friendly technologies and energy sources in a sustainable manner should be pursued. [1]

Desalination techniques are mainly classified into two types: (1) processes based on physical change in the state of the water or distillate through evaporation, and (2) processes using a membrane that employ the concept of filtration. Based on installed capacity, the leader in the market place is the membrane desalination process of reverse osmosis (RO). [2]

For several years, membrane research has focused on replacing some of the chemical pretreatment options with physical processes. Over time, RO technology has also improved to require less chemical conditioning of the feed water. [3]

In the long run the pre-treatment of the feed water must be performed in an environmentally friendly manner. Therefore alternatives to conventional chemical pre-treatment must be identified. [4]

The pre-treatment process improves the quality of the raw feed water to ensure consistent performance and the desired output volume of the desalination process. Almost all desalination processes require pre-treatment of some kind. The level and type of pretreatment required depends on the source and quality of the feed water and the chosen desalination technology. For source water of poor quality, pretreatment can be a very significant portion of the overall plant infrastructure. The potential influences on public health and the environment from the pretreatment process operations are associated with the chemical conditioning (addition of biocides, coagulants, flocculants, antiscalants, etc.) of the source water prior to pre-treatment and with the disposal of the residuals formed during the pre-treatment process.

Pretreatment, when required, normally involves a form of filtration and other physical-chemical processes whose primary purpose is to remove the suspended solids (particles, silt, organics, algae, etc.) and oil and grease contained in the source water when membrane desalination is used for salt separation. For thermal desalination processes it protects downstream piping and equipment from corrosion and from

formation of excessive scale of hard deposits on their surface (scaling). Biofouling is most often mitigated using an oxidant although non-oxidizing biocides are also utilized. Potential public health effects associated with pre-treatment are typically associated with the by-products formed during the chemical conditioning process and their potential propagation into the finished fresh water. [5]

2. RO as a Major Desalination Technique

Traditionally, the use of multi-stage flash (MSF), multi-effect distillation (MED), electrodialysis (ED), and reverse osmosis (RO) processes has received significant attention in attempts to improve the reliability and the performance of freshwater production processes.

Current research on desalination processes, however, addresses important topics associated with lowering the cost and enabling a more environmentally friendly operation.

Overall, consideration of total water production costs, the land scarcity of a nation, and promotion of an environmentally friendly operation suggests that the use of RO processes will be the most economic technology for large scale seawater desalination processes in the near future. [6]
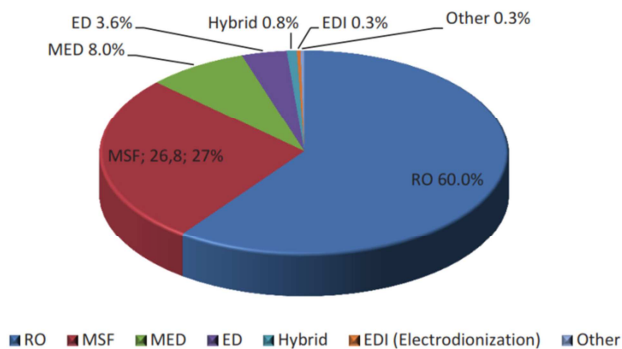

Figure 1. *Desalination technology market (IDA in Koschikowski, 2011) [7].*
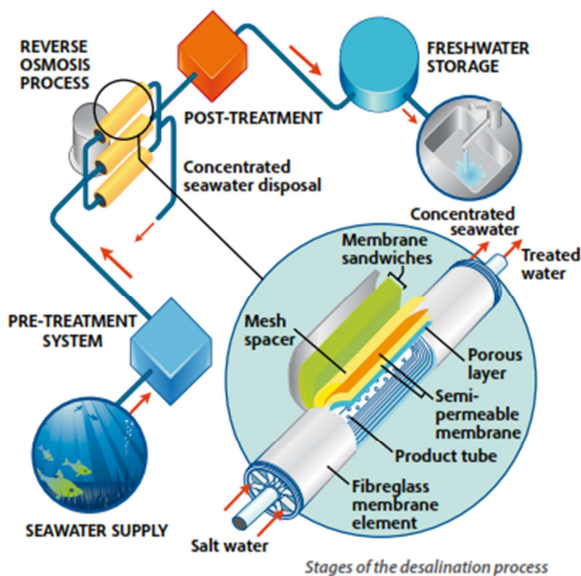

Figure 2. *Stages of RO desalination process [9].*

According to the precedent comments, it is possible to infer that, during the coming years, RO systems will continue their development growing in the market share of desalination technologies. So, the future of water desalination is, in great measure, associated to improve reverse osmosis processes. Meanwhile, other new desalination principles become applied generating new technologies to produce desalinated water with significant advantages over those applied nowadays. [8]

Reverse osmosis has several advantages over distillation, including:
- Less energy required.
- Its discharge has lower thermal impacts since the feed water does not have to be heated.
- Fewer corrosion problems.
- Higher recovery rates.
- Less surface area than distillation plants for the same amount of water production.

But it also has several disadvantages:
- It is generally more sensitive to poor water quality, resulting in the need to shut down facilities during severe storms or periods of high runoff when there are increased amounts of suspended particulates in feed water.
- It usually required more frequent cleaning and maintenance, often using various chemicals and cleaning agents, and often requiring full or partial shutdowns during cleaning.
- The membranes are sensitive to fouling due to bacterial contamination or other causes, which may require more frequent replacement and result in higher costs.
- It requires more extensive pretreatment, often with the use of biocides, coagulants, and other compounds.
- The process and its use of cleaning agents generate wastes that may include toxic chemicals, metals, and other constituents that are either discharged to surface waters or are separated and sent to a wastewater treatment facility or landfill. [10]

Pretreatment process:

Membrane desalination is used to desalinate water from many sources including brackish surface water from rivers and lakes, brackish groundwater from wells, municipal and industrial wastewater, and seawater from open ocean intakes and beach wells. Because of the great variability of the water quality depending on its source (brackish water or seawater) and the type of intake (open or subsurface) simple generalizations about pre-treatment requirements are not definitive.

For membrane desalination facilities the pre-treatment processes must address:

Membrane fouling and scaling from metal oxides, colloids, and inorganic salts; Fouling or plugging by inorganic particles; Biofouling by organic materials; Chemical oxidation and halogenation by residual chlorine; Chemical reduction of chlorine. Effects of other constituents such as oil, aquatic organisms and heavy metals.

Membrane desalination requires a higher degree of pre-treatment than thermal desalination processes.

An inadequate pretreatment system may severely impact RO system performance. In fact, most RO system failures are usually the result of a poorly designed/performing pretreatment system. It is of critical importance that the pretreatment system performance is satisfactory for the service intended. [5]

In general RO membranes are manufactured from two materials - cellulose acetate (CA) and polyamide (PA). Alterations to these materials' basic chemistry give rise to a variety of membrane sub-classifications.

The scaling of RO membranes is closely linked to the system's recovery and cross flow. As a general rule, the higher the recovery of the system, the more likely scaling will occur. Therefore, sufficient control and monitoring of the RO and its pre-treatment are vital.

Chemical pre-treatment to RO systems is primarily concerned with the prevention of scaling by poorly soluble salts and the minimization or control of biological growth. The source of the feed water and the membrane type dictate the chemical additions necessary. Chemical additions should always be kept to a minimum, where possible, because over addition can increase the feed TDS to the RO system, and therefore the RO permeate's TDS. [11]

a. Conventional approach:

After screening trash from the intake seawater as an initial pretreatment step, coagulation, flocculation, media filtration, and cartridge filter steps are usually included in the pretreatment process to improve the feed water quality for the RO process.

Key issues to be considered in the pretreatment step are as follows:

- Preventing bacterial growth and bio-fouling in the RO membrane.
- Inhibiting scale formation in the RO membrane.
- Regulating the water pH to adequate values in the RO membrane.
- Destabilization and agglomeration of colloidal particles and dissolved organics.
- Removal of suspended solids.
- Preventing a sudden appearance of particulate matter in the feed water for the RO membrane.
- Neutralizing the residual active chlorine.

In order to resolve the problems mentioned above, the following approaches are recommended, respectively:

• Sodium hypochlorite (NaOCl), Cl_2, $KMnO_4$ or O_3 can be used to control bio-fouling. H_2SO_4 can be applied to assist the biocide action of NaOCl.

• Sodium hexametafosphate is usually dosed to control scaling. H_2SO_4 can be used to help the action of the scale inhibitors.

• H_2SO_4 can be dosed to regulate the pH for polyamide-type RO membranes.

• Ferric or alum salts are often used to coagulate and flocculate colloidal particles and dissolved organics.

• Anthracite (~1 mm) is often applied during the granular media filtration process to remove suspended solids. The media backwashing process with air is followed by the granular media filtration process to remove captured particles from the filters.

• Cartridge filters are usually tasked with preventing the sudden appearance of particulate matter.

• Sodium metabisulfite ($NaHSO_3$) is primarily used to neutralize the residual active chlorine, especially for a polyamide-type RO membrane. [6]

b. Membrane approach:

The idea of alternative pretreatment is to replace conventional chemical pretreatment by physical alternatives which provide the same or even better feed water quality, especially for the demanding RO membranes. The most promising technology is membrane pretreatment with ultra- or nanofiltration. These have pore sizes small enough to remove most troubling substances from the intake water. [12]

Compared to the ultrafiltration (UF) pretreatment process, there are several major disadvantages of conventional pretreatment processes; significant differences between conventional and UF pretreatments, summarized in Table 1, which affect RO membrane fouling during the RO membrane lifetime. From the table, it can be seen that the UF pretreatment system is more efficient than the conventional one.

*Table 1. Comparison of conventional and UF membrane pretreatments [6].*

UF membrane pretreatment	Conventional pretreatment	
Stable and constant water quality (SDI < 2.0)	Unstable and fluctuating water quality depending on raw seawater (Silt Density Index, SDI < 4.0)	Treated water quality
20% higher	100%	Average RO flux
Lower fouling potential	High fouling potential	RO membrane fouling rate
4 – 12 times per year	1 – 2 times per year	RO membrane cleaning frequency
UF/NF membranes: 5 – 10 years, Cartridges: often not needed	Filters: 20 – 30 years, Cartridges: 2 – 8 weeks	Typical life time
33% lower	100%	RO membrane replacement rate
0 – 25% higher	100%	Capital cost
30 – 60% smaller	100%	Footprint
Higher than conventional	Lower than UF	Energy consumption
Lower	High	Chemical dosing rate
Shorter	Long	Intake line
Lower	High	Operation/management costs
Better boron control	------	Miscellaneous

But UF/MF pretreatment usually requires chemically enhanced backwash and periodic cleaning of the membranes and is therefore not entirely chemical free. [13]

In fact, both conventional and membrane treatment are involved in chemicals addition, and need backwash processes. [14]

For instance: Figure 3. Shows red brines containing ferric sulphate from filter backwash at Ashkelon RO desalination plant; backwash with 6500 m^3 in 10–15 min every hour. [4]
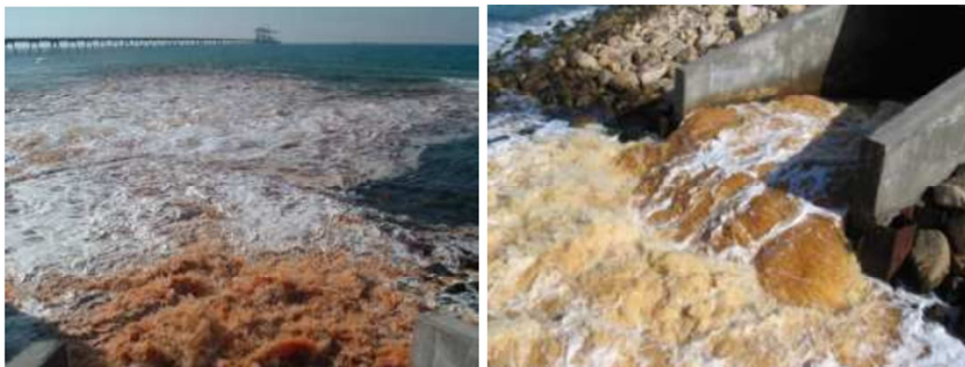
Figure 3. Ashkelon (Israel), RO plant with negatively buoyant brine discharge during backwash through an open channel at the coast into the Mediterranean [15].

As the first and the largest desalination plant in Ashkelon Site has been initially operated in July 2005 a phenomenon of reddish brine has been observed. This happens almost every hour for 10–20min while untreated backwash water, with high ferric concentration, up to 42 mg/L, is discharged with the brine as shown in Fig. 4. High ferric concentration and high loads are due to usage of ferric sulfate as coagulant additive.

The discolored plume has been observed at a distance of 3 km from the outfall along the seashore, in "Yam Shikma" marine reserve area as a function of the weather conditions. [16]
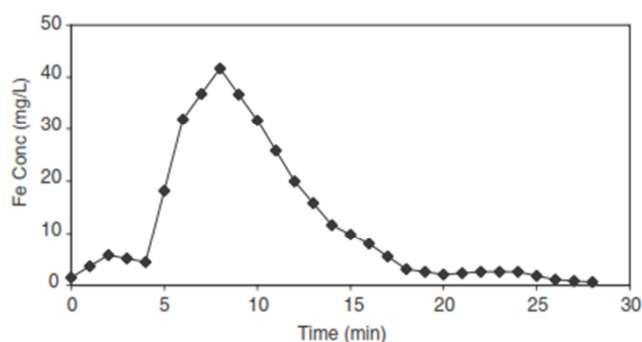
Figure 4. Ferric (Fe) concentration in the brine during sand-filter backwash.

c. UV treatment:

The use of UV irradiation as alternative pretreatment method is also suggested.

A wavelength of 200-300 nm damages the DNA structure of microorganisms and can be applied for disinfection of the intake water. Easy handling and the avoidance of storage and disposal of chemicals are advantages of UV pretreatment. But on the other side, highly reactive substances like free radicals are produced which may form by-products in unknown variety and quantity. So it must be supposed that UV treatment is not an effective pretreatment method. [12]

3. Electrochemical Technique as a Reliable Water Treatment

Electrochemistry is moving fast from traditional roles. Thus it can be a real alternative to many hazardous, difficult and expensive processes in a broad range of industries. It is likely that electrochemistry will play a more important role in development of cleaner and more efficient processes in all industries which manufacture or use chemical as it can contribute to the solution of environmental challenges.

It can deal with many pollutants: gases, liquids, and solids, and can treat from milliliters to millions of liters. [17]

Electrochemical treatment techniques have attracted a great deal of attention because of their versatility and environmental compatibility. In the last decade, electrochemical treatment has frequently been used to treat various industrial wastewaters successfully. It uses the electron as the main reagent, which is a "clean reagent". [18]

The advantages of using electrons as reagent to produce chemical changes are: i) the cost competitive situation with respect to alternative processes, ii) selective chemistry, iii) broad applicability, iv) less pollution than most competing processes, v) lower temperature requirements than those of equivalent counterparts, especially high temperature techniques, vi) the required equipment and operation are generally simple and, if properly designed, inexpensive as compared with conventional technologies and vii) the main electrochemical parameters, current (I) and potential (E), are particularly suited for data acquisition, process automation and control. [17] In recent years, EC (as an electrochemical technique) has been successfully tested to treat various industrial wastewater such as decolorization of dye solutions and textile wastewaters, treatment of electroplating and polishing wastewaters, removal of arsenic and fluoride ions from industrial wastewater, electrochemical degradation of

organics, treatment of chromium (VI) from wastewater, removal of colloidal particles, removal of phenolic compounds, clarification of potable water, removal of phosphate, removal of boron and petrochemical wastewater treatment [19], as well as it has been used in brackish water treatment. [14]

Electrocoagulation (EC) mechanism:

Interest in improving physical-chemical treatment, along with increasing environmental awareness, is fueling the drive to minimize the use of chemical products in water treatment. Electrocoagulation (EC) is a process that does not require the addition of any chemical coagulants, the coagulant is generated in-situ through the dissolution of sacrificial anodes that are connected to an electric current [20].

It involves dissolution of metal from the anode with simultaneous formation of hydroxyl ions and hydrogen gas occurring at the cathode.

Highly charged cations destabilize any colloidal particles by the formation of polyvalent polyhydroxide complexes. These complexes have high adsorption properties, forming aggregates with pollutants. Evolution of hydrogen gas aids in mixing and hence flocculation. Once the floc is generated, the electrolytic gas creates a flotation effect removing the pollutants to the floc - foam layer at the liquid surface.
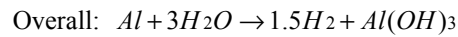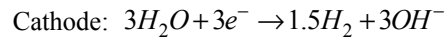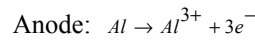
There are a variety of ways in which species can interact in solution:

1. Migration to an oppositely charged electrode (electrophoresis) and aggregation due to charge neutralisation.

2. The cation or hydroxyl ion (OH^-) forms a precipitate with the pollutant.

3. The metallic cation interacts with OH^- to form a hydroxide, which has high adsorption properties thus bonding to the pollutant (bridge coagulation).

4. The hydroxides form larger lattice-like structures and sweeps through the water (sweep coagulation).

5. Oxidation of pollutants to less toxic species.

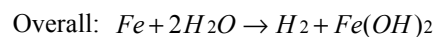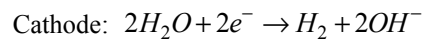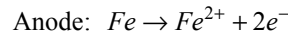6. Removal by electroflotation and adhesion to bubbles [21].

Aluminum and iron are the materials of choice because they produce a higher valence. Hydroxyl ions and hydrogen gas form at the cathode, and metal ions are released at the anode by electrolytic oxidation of the metal electrode [20].

By mixing the solution, hydroxide species are produced which cause the removal of matrices by adsorption and coprecipitation [19, 22]. The REDOX reactions at the anode and cathode are as follows:
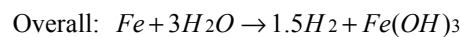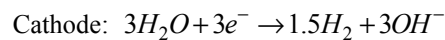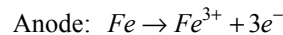
Example 1: Aluminum anode

Anode: $Al \rightarrow Al^{3+} + 3e^-$

Cathode: $3H_2O + 3e^- \rightarrow 1.5H_2 + 3OH^-$

Overall: $Al + 3H_2O \rightarrow 1.5H_2 + Al(OH)_3$

Example 2: Iron anode

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall: $Fe + 2H_2O \rightarrow H_2 + Fe(OH)_2$

Or

Anode: $Fe \rightarrow Fe^{3+} + 3e^-$

Cathode: $3H_2O + 3e^- \rightarrow 1.5H_2 + 3OH^-$
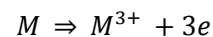
Overall: $Fe + 3H_2O \rightarrow 1.5H_2 + Fe(OH)_3$

[20, 22]

Electrocoagulation is the electrochemical production of destabilisation agents (such as Al, Fe) [23], so (in general) at the anode, sacrificial metal (M), Al or Fe, is released:

$$M \Rightarrow M^{3+} + 3e$$

In conclusion, the formation of metal hydroxide flocs proceeds according to a complex mechanism which may be simplified as: [14]

$$M^{3+} \Rightarrow monomeric\ species \Rightarrow polymeric\ species$$

$$\Rightarrow amorphous\ M(OH)_3$$
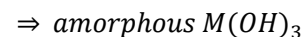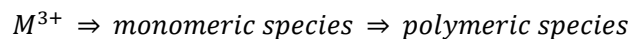
Moreover, the adsorption rate of produced hydroxides by this process is 100 times as much as hydroxides produced through chemical processes and they do not produce secondary pollutants. [24]

The electrode connections in an electrocoagulation reactor can be monopolar or bipolar. A simple arrangement of the electrode connections is shown in (Fig. 5) [23].
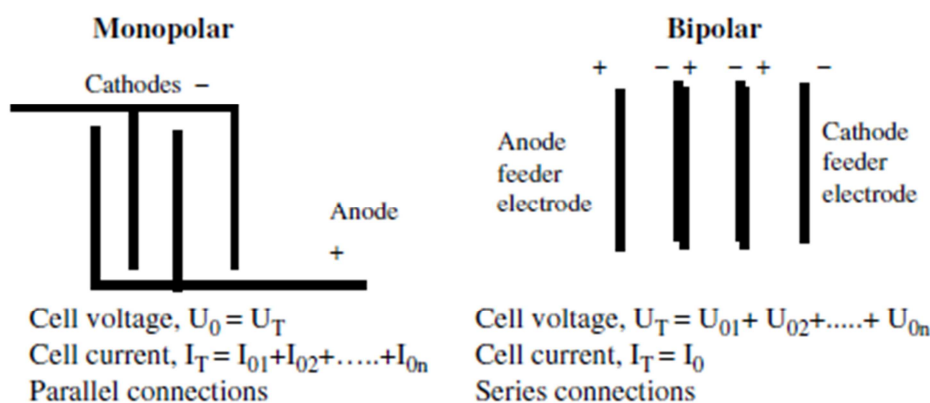

Figure 5. Monopolar and bipolar electrode connections in the EC reactor.

4. Some Major Environmental Challenges in RO System and the Role of EC Technique

4.1. Acidification

Acid is normally used to adjust the pH to slightly acidic values in order to enhance the coagulation-flocculation process and can also be used for scale control. The pH value of the concentrate may therefore be slightly acidic (pH 6-7) as compared to ambient levels of around 8. [13]

The feed water's pH will typically be adjusted to approximately 6.0, at which point the majority of the carbonate within the water can be found either as bicarbonate or carbon dioxide (CO_2) - these do not form scales with calcium.

Acid addition is a simple system, using the pH of the water as feedback to meter the dosage of acid required. However, this potentially creates two problems, firstly, the CO_2 created will freely pass into the RO permeate, which will then require degassing downstream. Secondly, large doses of acid will increase the feed TDS to the system. If hydrochloric acid is used, it will increase the permeate TDS because the added chloride is poorly rejected by the membrane. Sulphuric acid, on the other hand, will not affect the permeate TDS as badly because sulphate is well rejected by RO membranes. However, if the dosage of the acid is too high, precipitation of calcium sulphate becomes a risk. [11]

For instance, sulfuric acid increases the concentration of the SO_4, ion from 3020 to 3050 mg/l, an increase of about 1% above the natural concentration of seawater (based on technical information from the Hydranautics company and its rodesign simulation package). [25]

Electrocoagulation can be a clean alternative for acidification step; since it is able to reduce pH without acid, so chemical additives for this purpose can be avoided.

(Case study 4.2.3 explains more details concerning this point). [14]

4.2. Scaling

Membrane scaling is caused by the precipitation of salts originally present in feed water. [26]

4.2.1. Silica Scaling

Silica can be found in surface and groundwater as particulates, colloids, polymers, or dissolved in the form of acids or hydroxides. Dissolved silica in water is normally measured as SiO_2 despite the fact that the exact form of dissolved silica is not known.

Efficient operation of the reverse osmosis (RO) process for desalination of brackish water requires the reduction of silica in feed water to safe levels in order to avoid scale formation. [27]

Silica concentrations in source waters can range between 1 and 60 ppm to even 300 ppm in some volcanic regions.

Table 2. *Typical concentration of dissolved silica in natural waters [28].*

ppm	Natural Waters
1 - 3	Lakes
3 - 15	Major rivers
1 - 10	Seawater
2 - 60	Wells
50 - 300	Wells in volcanic and oil fields

Control of silica level in reverse osmosis (RO) feed water is extremely important in order to avoid membrane scaling, especially for hollow fiber membranes.

Silica scale is difficult to remove through periodic membrane cleaning operations, leading to reduced capacity and quicker membrane replacement.

Also for industrial purposes silica concentration in feed water to high pressure boilers should be less than 8 mg/L to prevent silica scale; and to reduce the possibility of silica scaling in the steam turbines, silica concentration in steam should be less than 20 ppb.

Several treatment processes can be used for removal of silica from water. Such processes include: cold softening using lime and iron salts, cold softening using lime and soda ash, hot softening using lime and soda ash, and ion ex-change [27].

But those methods have negative environmental effects, and required more chemical involving, so electrocoagulation has come as a suggested alternative more effective, simple, and clean.

Many studies had proved the high efficiency of electrocoagulation in silica removal from brackish water (it could be total removal). Figure 6 shows the importance of this technique, also Case study 4.2.3 explains more details concerning this point. [14]
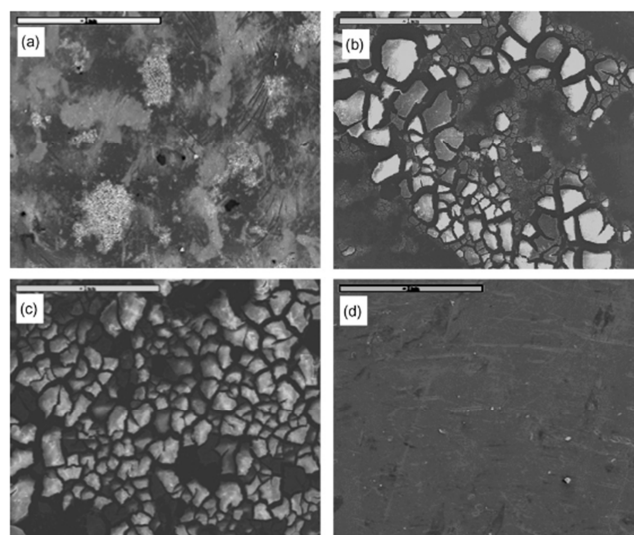
Figure 6. *The SEM images of membrane autopsy for water samples containing (a) 100 mg/L, (b) 200 mg/L, (c) 500 mg/L of feed dissolved silica concentrations. Part (d) is the figure for water sample (feed silica concentration = 200 mg/L) pretreated with electrocoagulation [29].*

4.2.2. Total Hardness TH

Water hardness creates a lot of problems for life and industry. Except calcium and magnesium, iron, manganese and strontium and some other metals can cause water hardness too, but their amount in comparison to the amount of calcium and magnesium can be ignored. [24]

Scaling from calcium carbonate, which is relatively insoluble at normal pH values, can be prevented by adjusting the pH of the feed stream to between 5.5 and 6 through acidification.

Water softening chemicals can be used to remove sulphate ions from the feed water. In cases where this is impractical, sodium hexametaphosphate may be added to prevent calcium sulphate precipitation. [26]

Considering problems of water hardness, its removal is essential.

There are various techniques for the removal of water hardness, such as using chemical substances and ion exchange resins.

Applying each of these techniques has undesirable effects on the quality of product water. In the process of ion exchange, sodium concentration of water increases that is harmful for patients with hypertension or cardiovascular diseases who have to consume sodium limit diet. Ion exchange processes cannot be applied for removal of water hardness in large water treatment plants.

Using lime for softening causes an increase in permanent water hardness. On the other hand, great amount of produced sludge causes clogging of filters and water distribution systems.

Using these appliances requires skill and addition of specified amount of lime and sodium carbonate to the system. In the process of liming, coagulants such as alum or ferric chloride are used to increase the weight of insoluble particles and consequently sedimentation velocity. This technique in addition to its economic cost, has undesirable health effects such as increasing the risk of Alzheimer disease, moreover, lime increases water pH. In order to improve the efficiency of chlorine in the process of disinfection, water pH after hardness removal should be decreased to <7.8 and this requires increase in acid consumption.

Coagulants in addition to increasing the amount of sludge production, increase the total solids in the effluents. Adsorption process is also used for hardness removal. This process due to adsorbent loss during the process and the necessity of backwashing has also gained less attention. Use of membranes, has the problem of scaling and frequent membrane fouling. [24]

4.2.3. Case Study

Many of Kafar Hamra groundwater wells (in Aleppo city – Syria) suffer from high content of salts, high total hardness (TH), silica, electrical conductivity, which make water unsuitable for drinking and cause difficulties to some local industries, and desalination facilities at industrial structures which need large amount of water for the production line (e.g. dye works).

This study tests the ability of using electrocoagulation technique as brackish groundwater pre-treatment to reduce its total hardness, silica compounds, electrical conductivity, and pH, with Aluminum electrodes in monopolar system, and makes a comparison with another study of similar brackish water using chemical pre-treatment prior to RO step.

Methods and results

The using reactor is a simple cubic glassy cell with a lower drainage valve and 8 Aluminum electrodes, (1mm thickness and constant space distance 2 cm), connected to DC electric power supply with high-low current intensity, and digital Amper-Volt meter. All electrodes were of identical size at 16 cm×20 cm (*W×H*) with approximately electro-active area of 16 cm×10.5 cm. (Fig. 7).
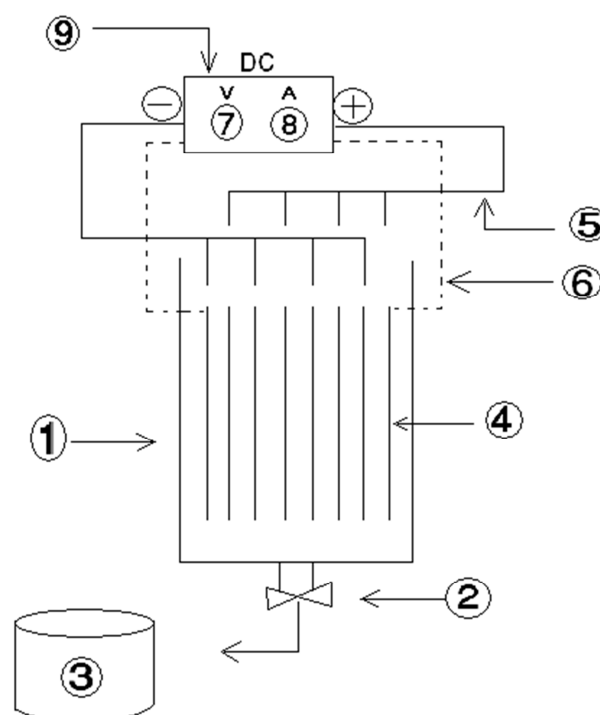
Figure 7. EC reactor 1-EC cell 2-discharge valve 3-cylindrical sedimentation tank 4-electrode 5-anodes-cathodes connections (monopolar system) 6-bipolar system (if used) 7-digital volt meter 8-digital amper meter 9-DC power supply.

The most important results (with Aluminum electrodes) were:

(1) – Increasing current intensity or retention time led to higher TH, SiO_2, Si, SO_4, and electrical conductivity removal rates.

(2) – Increasing retention time led to more pH reduction, but high intensity did not reduce pH, so medium values are preferred concerning all parameters.

(3) – Aluminum concentration in the treated water was about 0.2 mg/l and did not exceed 0.43 mg/l.

(4) – Table (3): shows a comparison between chemical treatment of similar water (from groundwater wells near Riyadh - Saudi Arabia) at Salbukh plant and electrochemical treatment cases of electrocoagulation study (with Aluminum) regarding only specific parameters:

Table 3. *Comparison between chemical and electrochemical pretreatment.*

Parameter	Chemical treatment	*EC (2A, 30min)	EC (4A, 30min)	EC (12A, 30min)
TH	62.1% Removal	32.2% Removal	37.4% Removal	55.5% Removal
SiO2	71.6% Removal	95% Removal	More than 95% removal	More than 95% removal
SO4	12.5% Increasing	10.3% Removal	14.3% Removal	39.3% Removal
Electrical conductivity	0.05% Reduction	17.1% Reduction	22.2% Reduction	35.4% Reduction
pH	8.13 to 6.19 With H2SO4 acid	7.80 to 6.79 No acid	7.97 to 6.68 No acid	8.01 to 8.27

*EC: Electrocoagulaion

With electrical consumption as shown in table (4): (regarding 30 min electrocoagulation time)

Table 4. *Electrical consumption of the 3 previous electrochemical study cases.*

Current intensity (A)	2	4	12
Electrical consumption Kw/m^3	1.3	3.75	21.25

(5) – More over:

Whence electrochemical pretreatment (with Electrocoagulation) was effective in TH, Silica, SO$_4$ removal, also achieved preferred pH for desalination units, with less chemical additions, so it can be considered more economical, environmental friendly, and had less secondary pollution, since it eliminates the extra using of chemicals, especially at acidification step, and minimize the need of more cleaning solutions during the traditional backwashing processes at membrane techniques, where SO$_4$ (included in H$_2$SO$_4$ and other chemical coagulants) may be a problem leads to CaSO$_4$ probable precipitations which resulting in technical difficulties, and more O&M costs.

Regarding the secondary pollution, it had been noticed that electrochemical sludge is much smaller and cleaner than chemical one, and we may get some benefits from it by reusing as a source of another new chemicals making.

Figure 8: shows the big difference between EC sludge volume before and after dewatering step (only by natural evaporation):
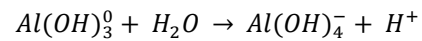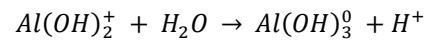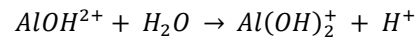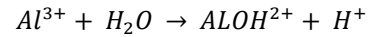

Figure 8. *Sludge resulting from EC treatment using Aluminum electrodes.*

In case of Al electrodes:
Monomeric species such as: Al(OH)$^{2+}$, Al(OH)$_2{}^+$, Al$_2$(OH)$_2{}^{4+}$, Al(OH)$^{4-}$

And polymeric species such as: Al$_6$(OH)$_{15}{}^{3+}$, Al$_7$(OH)$_{17}{}^{4+}$, Al$_8$(OH)$_{20}{}^{4+}$, Al$_{13}$O$_4$(OH)$_{24}{}^{7+}$, Al$_{13}$(OH)$_{34}{}^{5+}$ are formed during the EC process.
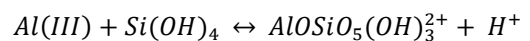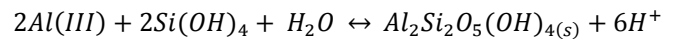
Formation rates of these different species depend on pH of the medium and types of ions present, and play an important role in the EC process. (Moving from the first to fourth equation is accompanied with lowering pH).

$$Al^{3+} + H_2O \rightarrow ALOH^{2+} + H^+$$

$$AlOH^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3^0 + H^+$$

$$Al(OH)_3^0 + H_2O \rightarrow Al(OH)_4^- + H^+$$

In particular for the electrocoagulation with aluminum anodes, formation of stable hydroxyaluminosilicates (HAS) has been known as an important process in the presence of silicic acids:

$$nAl_{(aq)}{}^{3+} \overset{OH^-}{\longleftrightarrow} [Al(OH)_3]n \overset{Si(OH)_4}{\longleftrightarrow} (AlO)_n(SiO)_{n/2}(OH)_{2n}$$
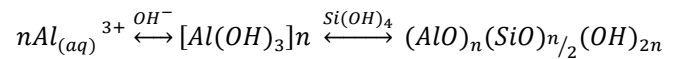
Formation of HAS between Al(III) and Si(OH)$_4$, exemplified by the following known reactions may occur:

$$2Al(III) + 2Si(OH)_4 + H_2O \leftrightarrow Al_2Si_2O_5(OH)_{4(s)} + 6H^+$$

$$Al(III) + Si(OH)_4 \leftrightarrow AlOSiO_5(OH)_3^{2+} + H^+$$

The low solubility of these HAS suggests that precipitation will occur and eventually forms the sediment observed in the electrocoagulation reactor.

Therefore, electrocoagulation with aluminum anodes takes advantage of fact that Al and Si(OH)$_4$ are effective mutual scavengers in the process of removing dissolved silica from

the solutions.

Furthermore: we can gain very important advantage from EC technique's by-products, such as H_2 gas as a great power source:

$$Al + 3H_2O \rightarrow 1.5H_2 + Al(OH)_3$$
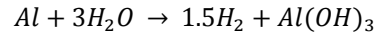
$1m^3$ treated water could produce 4.88 m^3 hydrogen (in case of 12 A, 30 min operational factors).
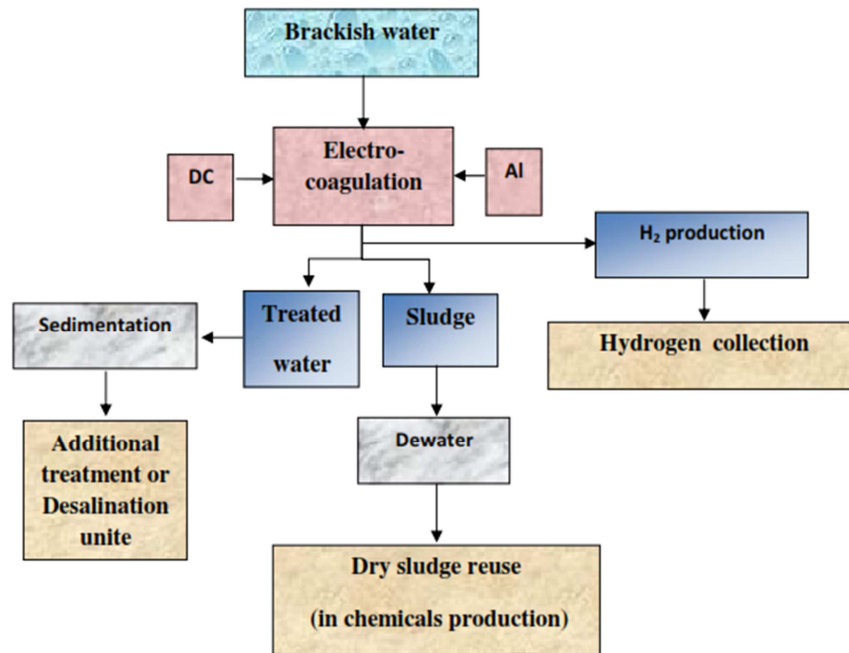

Figure 9. The integral treatment approach with Aluminum electrodes [14, 22].

4.3. Disinfection Matters (Chlorine and Chlorination by-Products)

Disinfection is a common unit process used in water supply treatment. Chlorination is traditionally the most dominant method of disinfection.

However, there are serious safety concerns and great ecological risks involved in the use of chlorine. Other methods, such as ozonation, UV radiation and ClO_2 application, are still more expensive or less convenient than chlorination. [30]

Humic and fulvic acids and other related substances that constitute NOM can react with chlorine (and other disinfectants) to produce a wide range of halogenated by products. In the presence of high bromide, as found in seawater and many brackish waters, the bromide is oxidised to bromine or hypobromite, which will take part in the halogenation reactions and produce organobromine products. Data from studies on the chlorination of seawater show that the yield of disinfection by-products (DBPs) in the form of trihalomethanes (THMs) is dominated by the brominated THMs, particularly bromoform and to a lesser extent chlorodibromomethane. The WHO guideline values for these two substances are both 100 µg/liter while the guideline values for the other THMs are 200µg/liter for chloroform and 60µg/liter for bromodichloromethane. Numerous other organobromine and organochlorine compounds are also formed at low levels and there are studies underway that continue to identify more of them. There may also be small quantities of iodinated THMs present, but there are no guideline values for these substances and there is limited data on their presence in disinfected fresh waters, and some on their occurrence in disinfected waters with high salt content. [5]

In RO desalination plants operating with polyamide membranes dechlorination is necessary to prevent membrane oxidation. Therefore the issue of chlorine discharge is restricted to the smaller portion of plants which use cellulose acetate membranes. Regarding these plants residual chlorine is released to the environment with the effluents where it reaches values of 100–250 µg/l, representing 10–25% of the dosing concentration. Assuming a product-effluent-ratio of 1:2 the specific discharge load of residual chlorine per m^3 of product water is 0.2–0.5 g/m^3. For a plant with a daily desalination capacity of 24,000 m^3, for instance, this means a release of 4.8–12 kg of residual chlorine per day. Again, the problem of chlorine discharge is restricted to plants with cellulose acetate membranes. In contrast, the release of chlorination by-products is an issue at all RO plants regardless of the material of their membranes, as by-products form up to the point of de-chlorination. [4]

Chlorine is proven to be toxic at concentrations of a few micrograms only. The photosynthesis process of plankton can be seriously reduced at concentrations of only 20 µg/l. At levels of 50 µg/l the composition of marine organisms can change and their variety is reduced. The known lethal values for fish species range between 20 and several hundred µg/l. Fig. 10. Depicts toxic chlorine concentrations for a range of species by means of the LC_{50} indicator. It can be seen that the reported chlorine concentrations in MSF effluents and in the

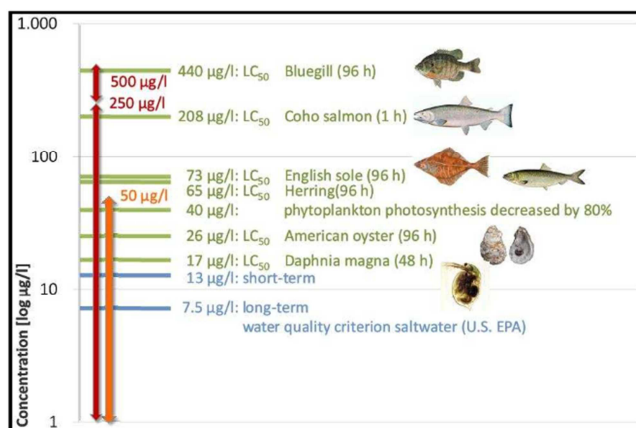mixing zone are acutely toxic for many of the examined marine organisms.

Figure 10. Chlorine toxicity levels for a range of marine species [12].

Alternative chemical methods have been investigated to control biofouling in SWRO plants, including monochloramine (NH_2Cl), Ozone (O_3), or copper sulfate ($CuSO_4$). None of these has gained wide acceptance over chlorine use. [13]

Dechlorination:

Chlorine is one of the most hazardous pretreatment chemicals. In cases where its application cannot be prevented, dechlorination is a simple and effective method to avoid adverse effects. This step should be a compulsory part of the environmental strategy and not only an operational necessity in RO plants in order to protect the membranes. [12]

The removal of chlorine is performed with sodium bisulfite, which is continuously added to reach a concentration three to four times higher than the chlorine concentration (1500–4000 µg/L). The corresponding amount per cubic meter of product water is 4.5–12 g/m^3. As this substance is a biocide itself and harms marine life through depletion of oxygen, overdosing should be prevented. [4]

It has been reported that electrochemical disinfection can destroy a wide variety of microorganisms from viruses through bacteria and algae to larger species such as *Euglena*. The electrochemical process has the potential to be developed as a robust, cost-effective and environmental friendly alternative of disinfection.

For example: Only thirty minutes are required for electrocoagulation to achieve total *E. coli* cells removal. Also electrocoagulation has shown the same efficiency toward algae and coliforms in two kinds of surface waters. The main mechanisms of electrocoagulation are charge neutralisation of microorganisms by electrical field and metallic cations followed by their flotation or sedimentation.

During electrochemical disinfection, water is forced through a disinfector that is equipped with electrodes on which current is charged. This practice is different from conventional electrochlorination, which relies on the production of a concentrated chlorine solution by electrolysing a side-stream of salt water.

The great effectiveness of electrochemical disinfection has been demonstrated in several liquid media.

A number of theories have been proposed to explain electrochemical major bactericidal actions, including destruction caused by the electric field and generation of energy rich but short-lived intermediate electrochemical products.

Increasing attention has been recently given to free radicals, such as •OH- and O_2•-, that could be produced during electrolysis, for their possible role in the electrochemical's strong killing actions, although more evidence remains to be collected. [30]

4.4. Boron Rejection

Desalination of brackish and/or saline groundwater presents other challenges such as the presence of naturally occurring contaminants in groundwater that are not removed effectively by RO desalination, including boron.

High boron concentrations are commonly observed in coastal aquifers due to boron desorption from marine sediments and at near-neutral pH, boron occurs primarily as uncharged $B(OH)_3^0$, which is not efficiently adsorbed and can accumulate in groundwater. [31]

Boron concentration in water product is the main challenge for membrane's manufacturers because its ion flows easily through them.

It has been pointed out that high boron content in the Gulf seawater explains why the use of RO processes are not too much extended in those regions. [8]

In terms of key contaminants of direct interest for health and environment, the most important is probably boron, which can be of significance in reverse osmosis plants since the rejection ratio of boron (probably mostly as borate) is less than that for most other inorganics. The current WHO guideline value for boron (borate) in drinking water is 0.5 mg/litre, however, this is due to be reconsidered under the rolling revision of the Guidelines (WHO, 2004). Although a health based guideline might possibly be 1 mg/litre or higher, there are plants that are sensitive at 0.5 mg/litre. The latter might become the principal issue for residual boron i.e. its effect as an herbicide if present in sufficient amount in irrigation water, particularly in areas where rainfall is so low as to not cause leaching of salts from soils. [5]

EC has been proven as an effective method for boron removal [23], and many studies demonstrated that chemical adsorption with freshly formed $Al(OH)_3$ flocs played a dominant role in the removal of boron. [14]

Using Aluminum electrodes in monopolar system could achieve 97% removal rate. [23]

Many studies aim to explore the mechanisms of boron removal by electrocoagulation (EC). The results demonstrate that adsorption and precipitation of boron by Al flocs are dominant mechanisms in boron removal using EC. The Al flocs that result from the EC process are found to be mainly composed of polymeric Al_{13} polymers (43%) and to have a long-lasting positive charge. These characteristics of the flocs contribute to the high levels of boron removal observed using EC. The maximum boron adsorption of the Al flocs is 200 mg g^{-1}. [32]

5. Future Ideas for Desalination and Sustainable Development Planning

By employing intelligent planning and the appropriate technologies, it is possible to minimize the adverse effects of seawater desalination plants on the environment. The environmental awareness of the planners, the designers, the decision-makers and the public during the early stages of planning and construction, will enable the construction of environmentally friendly plants. [25]

Research and development efforts in RO desalination are concentrated on the following aspects
• Decrease sensitivity of membranes regarding fouling (smoother surfaces, negative charged or neutral membranes).
• Increase rejection rate of salts.
• Develop new membranes that would be resistant to oxidising agents.
• Improve energy recovery.
• Improve boron rejection. [33]
• The pre-treatment process itself can be advanced to further reduce the use of chemicals. [4]

Also, areas of current and future research on solar thermal desalination focus on the following three aspects: (1) enhancing solar energy collection, (2) improving the technology of desalination techniques, and (3) better matching the solar field and desalination unit. These areas of investigation directly relate to the economic performance improvement of the system. [2]

5.1. Renewable Energy Considerations

Since electricity is the first essential requirement of electrocoagulation, its production is very vital for the whole technique. Solar energy is an important source for this production, and fortunately: places of water shortage are the most solar energy enrichments. [14]

For example each square kilometer of land in the Middle East and North Africa (MENA) receives every year an amount of solar energy that is equivalent to 1.5 million barrels of crude oil. Up to now, this tremendous energy resource is completely untapped. The technology to harvest, store and convert it to useful energy is present state of the art: concentrating solar power (CSP). As an example, a concentrating solar power plant of the size of Lake Nasser in Egypt (Aswan) would harvest the energy equivalent to the present Middle East oil production.

The solar electricity generating potential was thoroughly assessed for each country of the MENA region within the MED–CSP study that was sponsored by the German Federal Ministry for the Environment. Excluded were all areas that are not feasible for CSP operation or already used otherwise. According to that study, the coastal economic solar electricity generating potential amounts to 5,700 TWh/y, while the total economic CSP potential of the MENA region amounts to 630,000 TWh per year, (for comparison: the present world electricity demand is about 18,000 TWh/y). Using only one part out of thousand of this resource, CSP has the potential to cope with both the growing electricity demand and the growing freshwater deficit in MENA via solar powered electricity generation and seawater desalination.

Concentrating solar power technology offers a unique opportunity for competitive, secure and sustainable energy for electricity and seawater desalination in the Middle East and North Africa. CSP is present state of the art, the resources are almost unlimited, and the necessary investments are affordable. The resources exceed by far the present Middle East oil exports and are still untapped.

CSP is of vital importance for the MENA region, as it is the only available resource that is large and affordable enough to cope with the challenge of growing electricity consumption and increasing shortage of potable water.

It will, however, take at least a decade to introduce noticeable CSP shares into the energy portfolio. Therefore, MENA governments must establish adequate conditions to initiate market introduction, now.
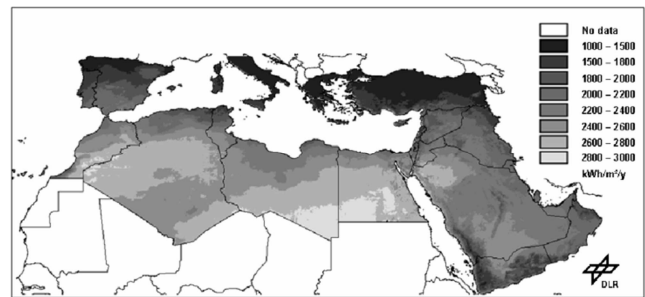
Figure 11. Annual direct normal solar irradiance in MENA and Southern Europe in kWh/m²/y [34].

5.2. Enhanced CSP/RO Plant

A future advanced RO plant would run completely with electricity from concentrating solar power plants. During operation there is no use of fossil energy carriers and consequently no emissions to the atmosphere.

In the future advanced CSP/RO plant, the use of chemicals and the concentration of brines will be avoided to a great extent by increased filtering and diffusion, and energy input will be delivered by solar energy. [4]

Moreover, alternative energy sources can be used for desalination and can reduce the cost of desalination. Specifically, renewable solar energy can be used as an alternative fuel for electric or thermal plants; and renewable wind energy and nuclear energy can be used to generate electricity for use in desalination plants. [35]

6. Conclusions and Recommendations

As discussed above, there are several operational / environmental issues facing desalination technique, especially RO system.

The major aspects concerning pretreatment step are: acidification, anti-scaling, chlorination, and boron rejection. All of these factors are involved in many technical and environmental problems, for their extremely chemicals usage.

So it is the time to suggest an alternative pretreatment which minimize chemical additives, called "Electrocoagulation".

Electrocoagulation is an effective treatment method depends on clean and economic energy, and it has been demonstrated (in many researches) as a promising solution for pretreatment aspects mentioned above.

However, more R&D efforts have to be spent in the field of employing this technique as a pretreatment part in RO system for:

- pH adjustment without acidification.
- TH, Silica, and electrical conductivity reduction with no chemicals addition, resulting in less sludge and less backwash processes.
- Electrical disinfection prior to membrane step, instead of chlorination.
- Boron removal, since it is difficult task for RO membrane.
- H_2 production, since it is an important by-product of the whole process, so it can be considered as a great energy source too.

Finally

More arid and semi-arid areas = more fresh water shortage, but also = more CSP (concentrating solar power).

In another expression: Less fresh water = More sun rays (solar energy).

So if we could employ this sun renewable power in electricity production we can apply electrocoagulation economically in a manner compatible with sustainable development rules.

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