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Electrocoagulation (with Iron electrodes) as a pre-treatment part of brackish groundwater desalination system

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Abstract:

TH (total hardness) and pH reduction is an essential pretreatment step in water desalination plant (thermal or membrane especially RO), in order to minimize precipitation of salts, and reduce operation/maintenance costs. This research studies the effect of using electrocoagulation technique as brackish groundwater pretreatment, to improve water quality by reducing (TH, pH, electrical conductivity), considering TH as a basic studied parameter. Among four metallic electrode types (aluminum, chromium, stainless steel, iron), Iron has the best performance for TH removal, it has been demonstrated that 8 iron electrodes with: monopolar system, (4A) current intensity, (40min) retention time, (3h) later sedimentation time, can slightly reduce conductivity, while achieve 75% TH removal rate, and pH reduction more than 2.4 degree without any acidic addition (so we could eliminate the traditional acidification step prior to RO membrane since the preferred pH is about 5.5 to 6.5), resulting in less secondary pollution, with electrical consumption about 4.4 Kw.h/m^3.

Key words: *Brackish groundwater, Electrocoagulation, Iron electrodes, pH reduction, TH removal.*

1. Introduction

Water, as a precious natural resource, plays an important part in people's life on the planet. The demand for clean and fresh water is ever increasing for many reasons including population growth, industrial development and severe draught in some parts of the globe, so desalination has been developed to turn salt water into fresh water.

One of the main conventional processes used is: reverse osmosis (RO) [1].The most important factors affecting RO membrane process are membrane fouling and/or scaling, resulting in a higher operational cost. Membrane fouling/scaling causes a permeate flux decrease during constant operating conditions [2].

RO membranes are very sensitive to fouling caused by:

- Suspended solids – plugging.
- Biological matter.
- Chemical scaling.
- Colloidal material.

They require an efficient pre-treatment of the feed water by:

- Filtration to decrease turbidity and fouling index.
- Chemicals addition, to limit biofouling.
- Acid or anti-scalant addition to increase solubility of salts of calcium (bicarbonates, sulphates), barium sulphate and strontium sulphate [3] [4].

Scaling formed by the precipitation of salts on the membrane surface is often caused by calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), silica (SiO_2), and iron hydroxide $Fe(OH)_3$. Therefore, a lower consumption rate of treatment chemicals would reduce the scaling and fouling problems due to chemicals, also one of key issues to be considered in the pretreatment step is: Regulating pH to adequate values in RO membrane [2].

Water hardness creates a lot of problems for life and industry, so its removal is essential.
For this purpose, there are various techniques, 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. There are also various techniques for the removal of water hardness each with its own special advantages and disadvantages. Electrochemical or electrocoagulation method due to its simplicity has gained great attention and is used for removal of various ions and organic matters [5].

2. A brief description of electrocoagulation mechanism

Interest in improving physical- chemical treatment, along with increasing environmental awareness, is fuelling 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 [6]. 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 [7].

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 [4] [6].

By mixing the solution, hydroxide species are produced which cause the removal of matrices by adsorption and coprecipitation [8]. 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: $Fe + 3H_2O \rightarrow 1.5H_2 + Fe(OH)_3$
[6] [9]
So in general, at the anode, sacrificial metal (M), Al or Fe, is dissolved:

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

In conclusion, the formation of metal hydroxide flocs proceeds according to a complex mechanism which may be simplified as: [10]

$$M^{3+} \Rightarrow \text{monomeric species} \Rightarrow \text{polymeric species} \Rightarrow \text{amorphous } M(OH)_3$$

The electrode connections in an electrocoagulation reactor can be monopolar or bipolar. A simple arrangement of the electrode connections is shown in (Fig.1) [9] [11].

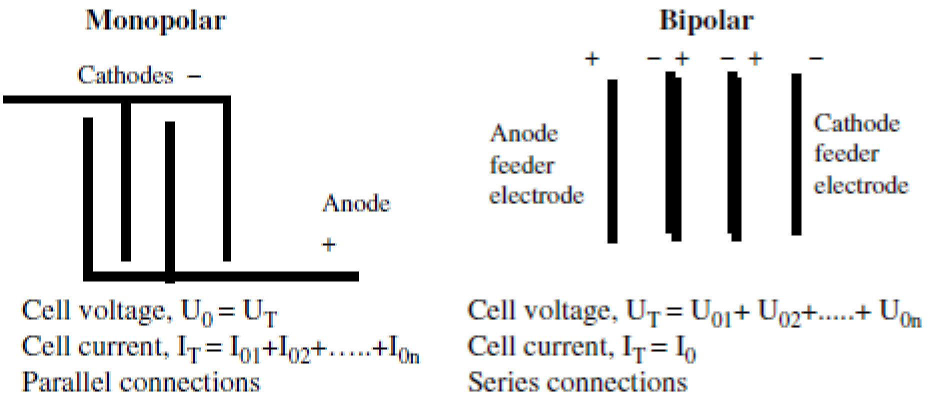

Fig.1. Monopolar and bipolar electrode connections in the EC reactor

3. Materials and methods

3.1. Water samples:

The raw water samples were original obtained from Kafar Hamra brackish groundwater wells (Aleppo City - Syria), at pH and TH values of (7.78 to 8.02), and (1165 to1200) mg/l$CaCO_3$ respectively, Electrical conductivity values were about 1.911 to 1.945 ms/cm (at 21 -22 C°).

pH and Electrical conductivity were measured with Labor- pH- meter 766, Opt - Knick › - and Labor- conductivity meter 703, Opt - Knick › (www.Knick.de). TH was measured as mg/l $CaCO_3$ by using Spectro Direct/pc spectroII_5b - Lovibond®, Tintometer®, Analysis No. 200, 201 - Metallphthalein^3 - Wavelength (λ) = 571 nm - (The method was developed from a titration procedure).

3.2. Electrocoagulation reactor:

The using reactor is a simple cubic glassy cell with a lower drainage valve and 8 metallic 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.2).

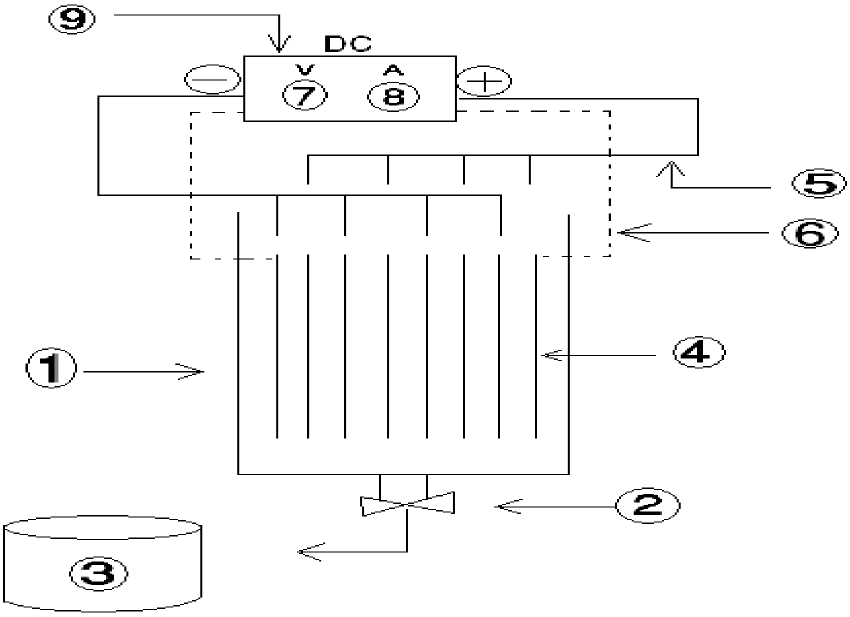

Fig. 2. EC reactor 1-EC cell 2-discharge valve 3-cylindrical sedimentation tank 4-electrode 5-anodes-cathodes connections (monopolar system) 6-bipolar system (if used) 7-digital Volt meter 8-digital Amper meter 9-DC power supply.

DC power supply is an electrical transformer which turns AC into DC, provided with current intensity control system within (0 – 10) A, the input voltage is 220V-AC while the output voltage-DC is variable according to many factors such as: applied intensity, brackish water conductivity, electrodes configuration (number and spaces), and these factors have also been considered when we designed the electrical transformer.

We fixed chosen intensity values, then read the equivalent voltages, so the basic electrical parameter in this study was current intensity (A). The volume of each batch is 3.6 L, then EC process is followed by sedimentation step (for 3 hours) in a cylindrical tank.

4. Results and discussion

4.1. The effect of electrode type:

The comparison was between four metallic electrodes types: (aluminum, chromium, stainless steel X8Cr17, iron) with low current intensity just (1A), constant electrocoagulation retention time (15min).

The results shown on table 1, Fig.3, demonstrate that iron electrodes had the best TH removal rate, and pH reduction, but the efficiency at all cases was low, and the treated water became slightly red with Iron.

Table 1: Treatment efficiency between 4 electrode types

Raw groundwater characteristics : TH= 1165 mg/l $CaCO_3$ - pH= 7.78		
Electrode type	**Potential difference (V)**	**TH mg/l$CaCO_3$**
Aluminum	4	1150
Chromium	5.75	1075
Stainless steel	5.5	1050
Iron	4	975

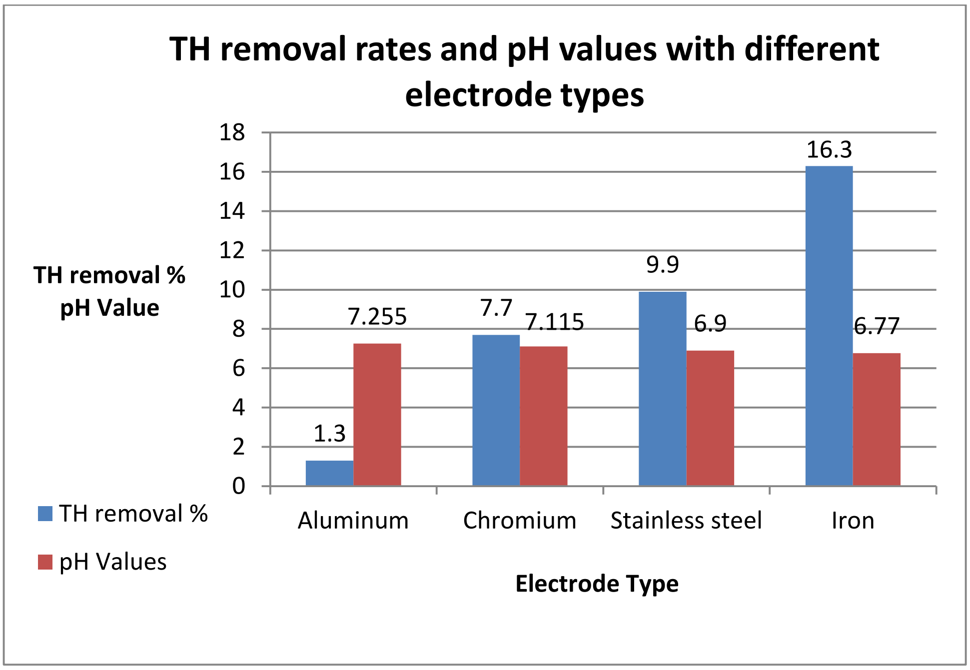

Fig.3. TH removal and pH reduction comparison between 4 electrode types

4.2. The effect of current intensity and retention time (using iron electrodes):

For the best electrode type (iron), we worked on tow similar experimental series:

At the first one: variable current intensity (2 – 4 – 6 – 8) A, with constant electrocoagulation retention time (15min), then we applied retention time of (10 – 20 – 30 – 40) min, with constant current intensity (2A). Table 2, Fig. (4, 5, 6, 7).

Table 2. TH values with different (current intensity, retention time) values

Raw groundwater characteristics : TH= 1200 mg/l $CaCO_3$ - pH= 8.02				
Sample	**Retention time (min)**	**Current intensity (A)**	**Potential difference (V)**	**TH mg/l$CaCO_3$**

1	15	2	4	850
2	15	4	6	700
3	15	6	7.25	500
4	15	8	9	400
5	10	2	4	900
6	20	2	4	700
7	30	2	4	600
8	40	2	4	500

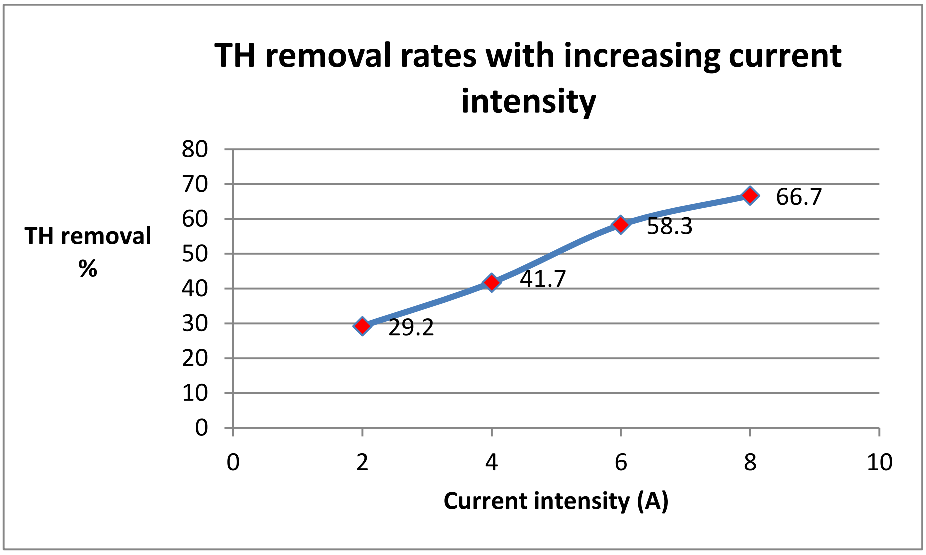

Fig.4. TH removal by increasing current intensity

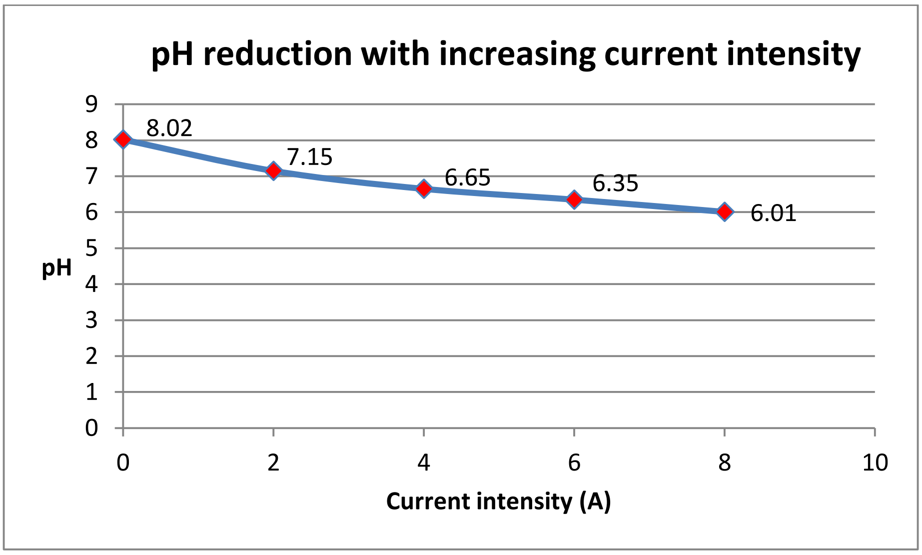

Fig.5. pH values with increasing current intensity

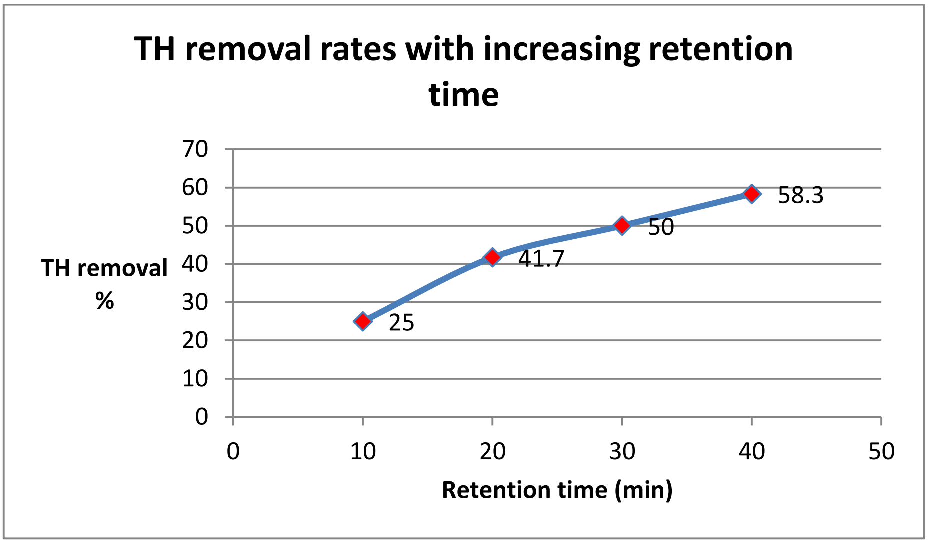

Fig.6. TH removal by increasing retention time

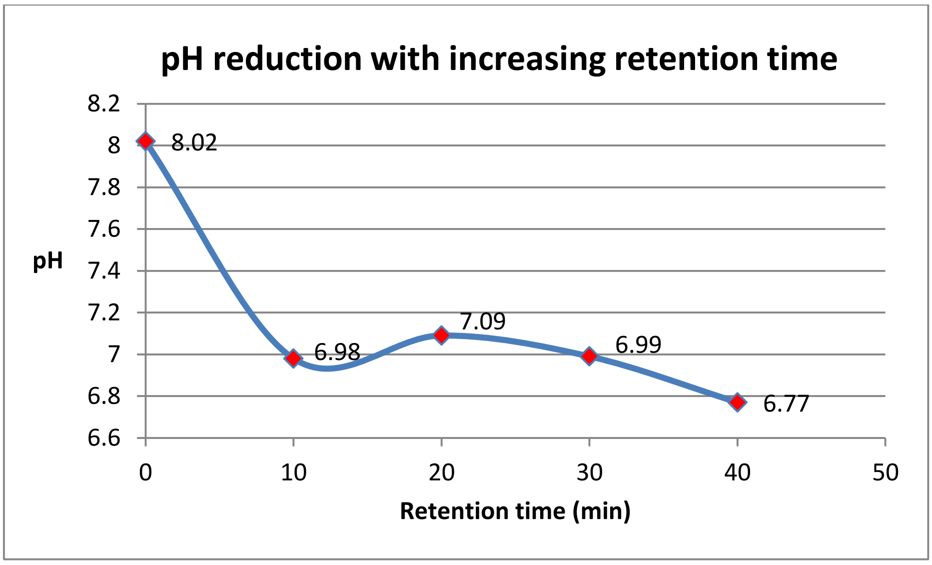

Fig.7. pH values with increasing retention time

At the second one: the applied intensity values are (1 – 5 – 10) A, with constant electrocoagulation retention time (15min), then we applied retention time of (10 – 20 – 40) min, with higher constant current intensity of (4A) to get more efficiency, Table 3, Fig. (8, 9, 10).

Table 3. TH values with different (current intensity, retention time) values

Raw groundwater characteristics : TH= 1200 mg/l $CaCO_3$ - pH= 7.99				
Sample	**Retention time (min)**	**Current intensity (A)**	**Potential difference (V)**	**TH mg/l$CaCO_3$**
9	15	1	3.5	1100
10	15	5	6.75	550
11	15	10	10.5	300
12	10	4	6	700

13	20	4	6	500
14	40	4	6	300

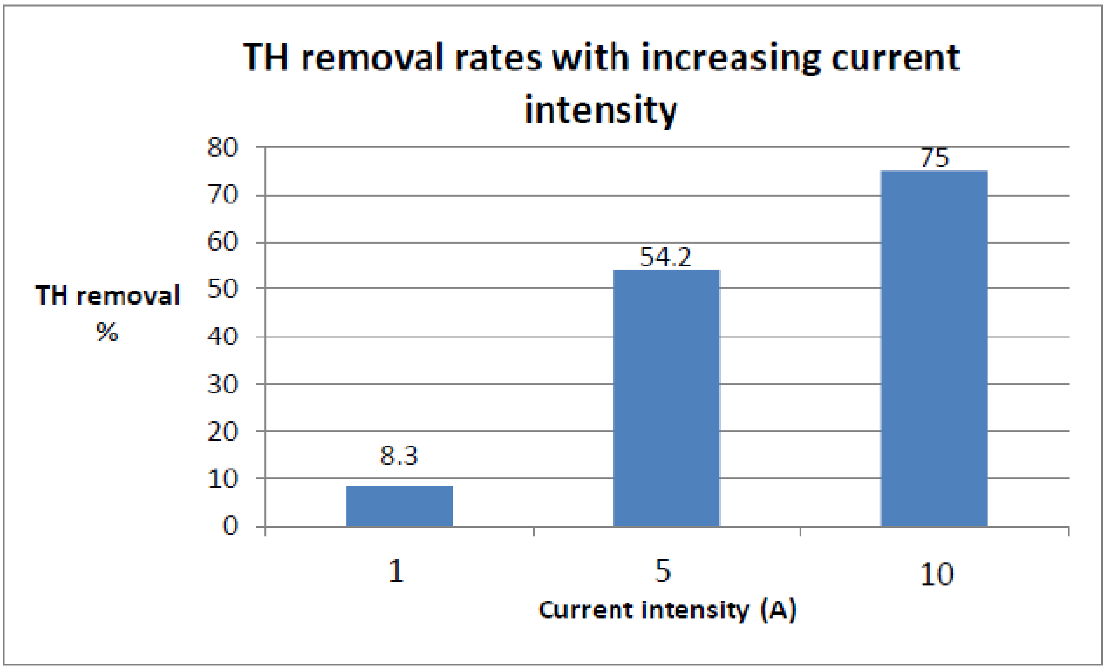

Fig.8. TH removal with increasing current intensity

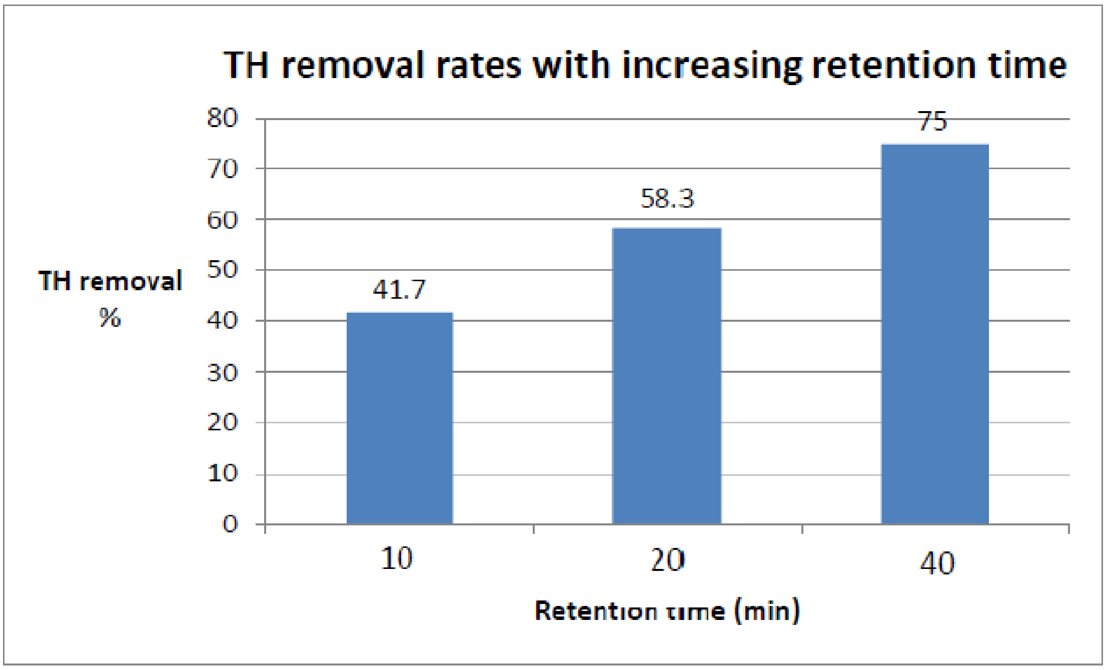

Fig.9. TH removal with increasing retention time

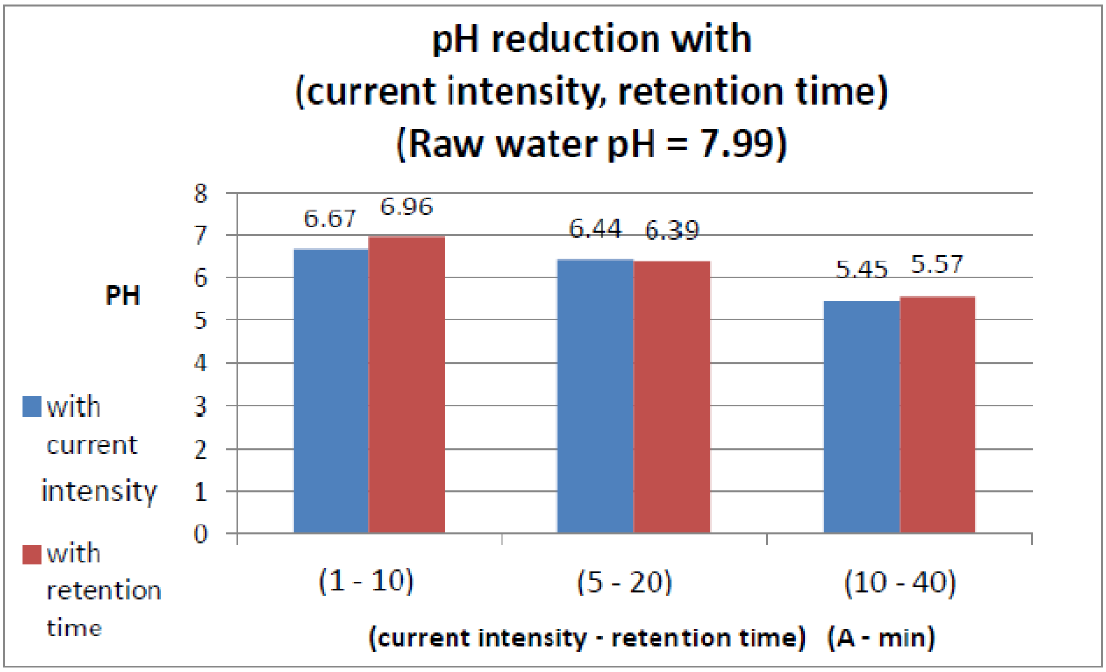

Fig.10. pH reduction with increasing (current intensity - retention time)

So EC technique (with iron electrodes) is effective for TH and pH reduction, since increasing current intensity or retention time leads to higher TH removal rates and lower pH values, because the more intensity and / or retention time, the more coagulant agent is produced according to Faraday law:

$$C = 1.040 \times I \times (P - 1) \times t/V$$

[C: dissolved metal (Fe) mg/l, I: intensity (Amper), P: electrodes number, t: time (hour), V: volume (m^3)].

Furthermore water temperature increases due to increasing current intensity and / or retention time, somehow the rise of temperature may has some effect on EC performance as the result of increasing mobility and contact of ions together and with hydroxy polymer, and / or because increasing the kinetic of removal reactions.

In case of iron electrodes:

The removal mechanism often includes adsorption, co-precipitation, surface complexation and electrostatic attraction [12], and many components may be produced such as: [10]

$$Fe(OH)^{2+}, Fe(OH)_2^{+}, Fe_2(OH)_2^{4+}, Fe(OH)_4^{-}, Fe(H_2O)_2^{+}, Fe(H_2O)_5OH^{2+}, Fe(H_2O)_4(OH)_2^{+},$$
$$Fe(H_2O)_8(OH)_2^{4+}, Fe_2(H_2O)_6(OH)_4^{2+}$$

One of the main species in solution is $[Fe(OH)_3(H_2O)_3]_2$, that can attract Mg^{2+} as following reactions by surface complexation, electrostatic attraction and precipitation. As a result of dewatering, $Fe(OH)_3$ is converted to FeOOH (hydrous ferric oxide), which is a monomer of hydroxy polymer. (Fig.11).

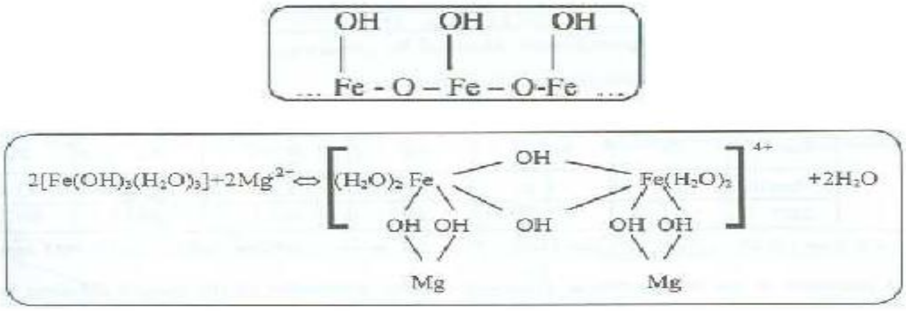

Fig.11. Side of interaction's mechanism

In this case, the removal is occurred in accordance with two manners:

a) The formation of a surface complex by connection of hydroxy polymer to a suspended particle.
b) The role of hydroxy polymer in the removing process is conducted via gathering ions and increasing of local concentration and then, it will perform "chemical reactions". As the hydrous ferric oxide in combination with various surface complexes contains area of apparent positive and negative charge and the opposite charge "attract", they are strong enough to remove some dissolved species and ions from the aqueous phase (Fig.12) [12].

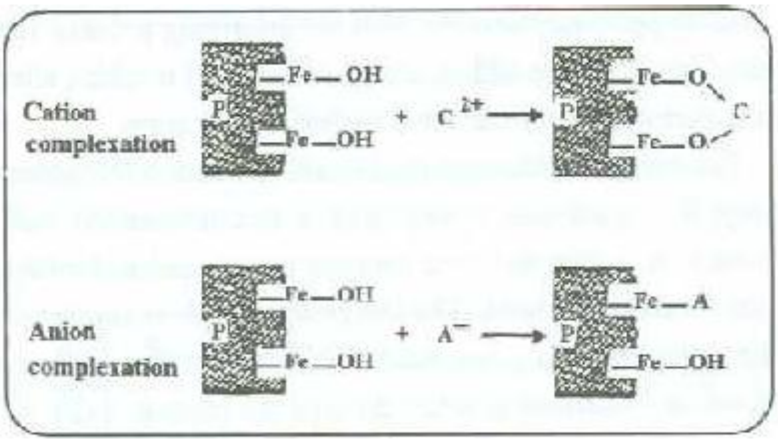

Fig.12. Formation of a surface complex for ions removal, P = interior of suspended particle

For the two previous experimental series we measured the electrical conductivity of raw water and best TH removal's samples (within temperature degree of 21-22 C°), table.4 shows the efficiency of electrocoagulation on electrical conductivity reduction.

Table 4. Electrical conductivity reduction for the best samples

Series No.1	**Sample**	Raw water	4	8
	Conductivity ms/cm	1.945	1.651	1.669
Series No.2	**Sample**	Raw water	11	14
	Conductivity ms/cm	1.911	1.584	1.598

4.3. pH behavior during sedimentation (storage) time:

Since electrocoagulation is a pre-treatment step, it is important to study the storage time (including sedimentation period) prior to the next step (which is the main desalination unite). It has been noticed that pH value is seriously affected by sedimentation time. Table.5 and Fig.13 demonstrate that pH behavior changes according to electrode type. It has the same increasing trend by raising sedimentation time with aluminum, chromium, and stainless steel electrodes, while there is a decreasing trend when using iron.

According to Faraday Law, (Fe) has a higher released ions into treated water, so maybe the high presence of Fe^{3+} and OH^{-} ions (in case of iron) leads to more $Fe(OH)_3$ precipitate, hence: more free OH^{-} ions are reduced by time, resulting in further pH reduction.

Table 5. pH changes with sedimentation time and different electrode types – for initial pH=7.78

Electrode type	Aluminum	Chromium	Stainless steel	Iron
Sedimentation time (hour)	**pH**			
2	7.21	7.09	6.875	6.83
3	7.255	7.115	6.90	6.77
5	7.29	7.19	7.00	6.785
12	7.49	7.37	7.19	6.69

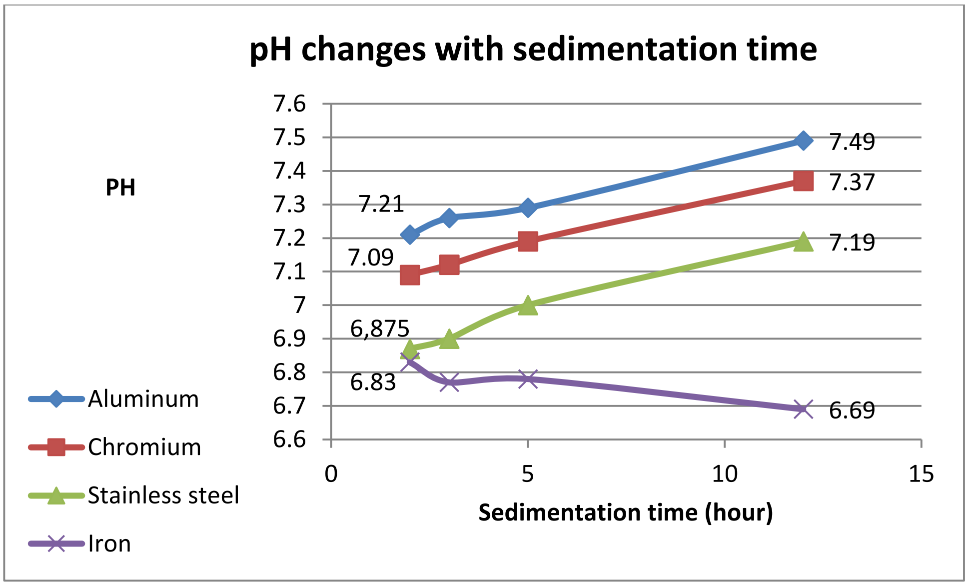

Fig.13. pH behavior with sedimentation time for different electrode types - initial pH=7.78

To make sure, about pH behavior during sedimentation period (in case of iron electrodes), we measured pH changes of the best previous samples (from table 2,3,4 and Fig.5,7,10) with higher storage (sedimentation) time and we got the same conclusion. Table 6 and Fig.14.

Table 6. pH reduction with sedimentation time for different samples (iron electrodes)

Sample	4	8	11	14
Sedimentation time (hour)	**pH**			
3	6.01	6.77	5.45	5.57

7-7.5	5.28	5.65	5.03	5.08
11	5.14	5.34	4.98	5.06
29-30	5	4.88	4.82	4.88

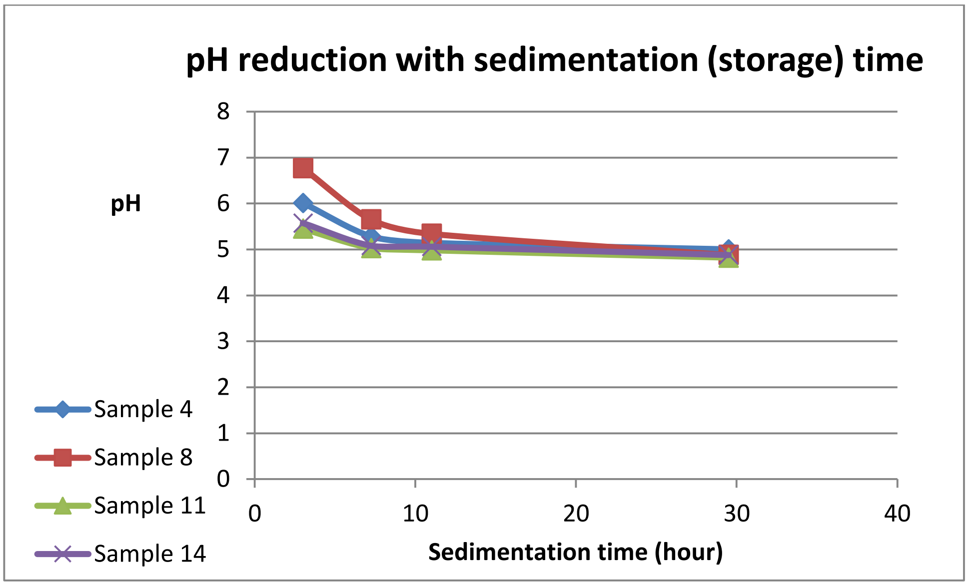

Fig.14. pH reduction with sedimentation time for different samples (iron electrodes)

There is always further pH reduction by increasing the time, so sedimentation (or storage) time must be controlled to get optimum pH for the next desalination process and avoid undesirable values.

Note: the applied sedimentation times were longer than the traditional practical values, because we considered both sedimentation and probable storage period.

4.4. Electrical consumption:

Considering best operational parameters obtained from table.3, for sample (14), (75% TH removal – more than 2.4 pH reduction): Iron electrodes, Current intensity I= 4 A, U= 6 Volt, T= 40 min retention time, with batch of V= 3.6×10^{-3} m^3, the electrical consumption per m^3 treated water will be:

E = (I × U × T) / V = (4×6×40/60)/0.0036 = 4444.4 w.h/m^3, about (4.4) KW to treat 1 m^3 for 75% TH removal, and pH reduction (more than 2.4 degree, from 7.99 to optimum pH degree 5.57) without any acidic addition.

From another point of view:

Since the total hardness removal amount is 900 g/m^3 (from 1200 to 300 mg/l$CaCO_3$), the electrical consumption per 1 g TH removal will be: E= 4444.4/900 = 4.9 w.h/g.

5. Conclusions

1. Among four metallic types, the best TH removal and pH reduction were achieved by using iron electrodes, (reduction from 1200 to 300 mg/l $CaCO_3$, which is suitable for RO membrane technique).
2. With iron electrodes:

- Increasing current intensity or retention time led to higher TH removal rates and lower pH values.
- Considering electrical conductivity there was a significant reduction.

- Using iron in electrocoagulation process resulting in large amount of total iron in the treated water (in some cases more than 150 mg/l) so it became red as an obvious disadvantage of this technique, (the total iron in the treated water was very high although the color could be disappeared by additional sedimentation).

3. At all cases the pH has been reduced by raising any of the two operational factors (current intensity-retention time), this reduction was done without any acidic addition, so it is more suitable and economical for desalination process, and some chemicals additives can be avoided.
4. There is a direct effect of sedimentation time on pH value, it tends to re-increase by increasing time (with aluminum, chromium, and stainless steel electrodes), while keeps decreasing with iron.

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