

Pretreatment of Brackish Water Using DC-Electrocoagulation - Method and Optimization

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ABSTRACT: *Electrochemically generated iron can remove most contaminants present in water and waste water, by precipitation, adsorption, electrostatic interaction, and complex formation (generally called electrocoagulation- EC). In the present paper, pretreatment of brackish water having high total hardness (TH), alkalinity (A), SO_4^{2-} and Cl^- ions, is studied by application of a DC-electrical current to the iron electrodes. Operating parameters such as electrical current density, volume flow, surface area of electrodes, distance between the two electrodes, water temperature, aerating flow, retention time, contact time of produced sludge before and after the process, addition of coagulant aid (bentonite) and the colloidal additive (clay particles) were optimized. The results of this study for a brackish sample with 11.8 TH, 5.6 HCO_3^- (A), 12.4 SO_4^{2-} , and 23.5 Cl^- meq/lit indicate that the process is able to lower more than %94 the (TH), %92 (A), %50 SO_4^{2-} and %43 Cl^- .*

KEY WORDS: *Pretreatment, Brackish water, Electrocoagulation, Electrochemical removal, Bentonite, Clay*

INTRODUCTION

The rapid growth of population and the consequent shortage of fresh water sources, has made the importance of water supply felt more and more seriously. Good quality water is needed for drinking and also for agricultural and most industrial purposes. That is why the methods for supplying high quality water especially, drinking water in the large scale, are considered very important.

The brackish and brine waters though expensively available, contain high quantities of TH, A and TDS and thus can not be used directly. High concentration of ions,

such as Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} , Cl^- and HCO_3^- are the most considerable as well as the prevailing problems in the extent of chemical treatment of brackish or salty waters. Relating to the desired quality, the output water in the present process, can be used directly, or it can be piped to membrane plants as reverse osmosis (RO) and / or electrodialysis (ED), or ion exchange plants, for providing highly pure and potable water with less cost and problems. The researchers believes that, this is an effective step towards to make cheaper process of desalination of brackish and salty waters. The RO is a

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modern method for the desalination of salty or brackish waters and since it is a membrane process, it is necessary to pretreat the input water to the plant.

When the necessary technology of pretreatment was not adopted, the serious scale frequently formed inside of RO and lead to operating difficulties and loss of efficiency. In recent years, the electrocoagulation(EC) as a new method of desalination of brackish water has been studied and the technical feasibility has been confirmed [1].

The EC not only can efficaciously reduce the turbidity of water but also can remove some kind of ions like Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-} , retard and so on existing in the water the scale in RO [2].

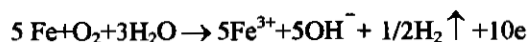
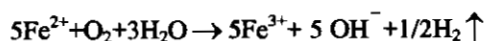
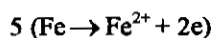
The EC treatment process to be used is the CURE process developed by Clean UP and Recovery (CURE) Corporation, Denver, Colorado[3]. The EC treatment has been reported as an inexpensive method for separation of solids and oils from tar sand processing wastewaters[3]. The electrochemical technology(DC-EC) used to treat textile wastewater and for removing heavy metals from contaminated ground water [4,5]. The CURE electrocoagulation system was evaluated for removal of low levels the radionuclides uranium, plutonium and americium as well as other contaminants in wastewater[6]. The alternating current electrocoagulation (AC-EC) process has been successfully applied for effective coagulation of ultra-fine solid suspension, metal ions and oil emulsions [7,8]. The economic aspects of EC process have been discussed for achievement to new inexpensive method of wastewater treatment [1,6,7].

Mechanism of removing ions

The mechanisms of coagulation have been studied very extensively [9,10]. In this method a wide variety of aluminium and iron salts was used. In the DC-EC method aluminium electrodes have been used without aeration. This method is electrolysis process. The iron electrodes with aeration prefer to use because they are more economic than aluminium. In this method Fe^{2+} oxidize completely to Fe^{3+} and also cathodic reduction is possible due to aeration.

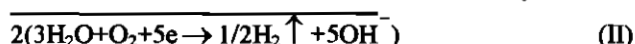
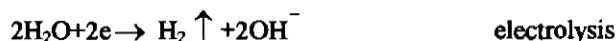
The produced Fe^{2+} from anode as a result of aerating oxidize immediately to Fe^{3+} .

The anode reactions are: (25°C)

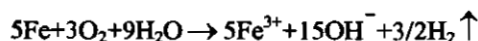


(I)

The cathode reactions are: (25°C)



The overall reaction (I+II) is as below, and that is as a result of both factor of electrolysis and aeration [2, 11,12].



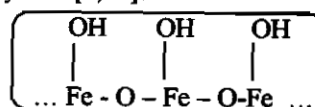
In this condition the various species produced such as $\text{Fe}(\text{OH})_3$, $[\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3]$, FeOOH include highly charged polymeric ions as same as $[\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_4]^{4+}$, $[\text{Fe}(\text{OH})_4]^{5+}$ [2, 10,11,13].

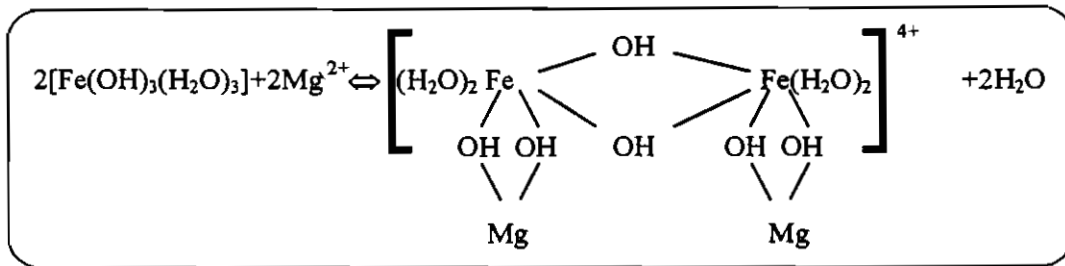
The overall removal mechanisms

Wastewater treatment terminology often includes adsorption, co-precipitation, surface complexation and electrostatic attraction. Frequently the processes overlap and distinction becomes difficult. For sake of this discussion and to describe why the proposed treatment scheme works, two simple terms will be used; pre-precipitation and adsorption. Adsorption includes surface complexation and electrostatic attraction.

One of the main species in solution is $[\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3]_2$, that can attract Mg^{2+} as following reactions by surface complexation, electrostatic attraction and pre-precipitation, similar to aluminium[2].

As a result of dewatering, $\text{Fe}(\text{OH})_3$ is converted to FeOOH (hydrous ferric oxide), which is a monomer of hydroxy polymer [5,11]:





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[5]. For securing the sufficient quantity of colloidal and suspended matter simple additive like clay is used[10].
- 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 [2,5].

Experiment using EC

Experimental device

The electrochemical cell or EC-chamber consists of a fiberglass body containing a number of steel and / or iron plates, which act as electrodes. Inside the cell, the

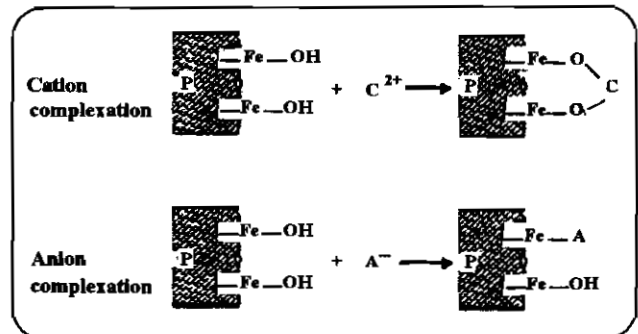


Fig.1: Formation of a surface complex for ions removal
P= interior of suspended particle

electrodes are separated by a small and the given distance and the brackish water flows through the gaps in contact with the electrodes. The capacity of EC-chamber is 5 lit and total area of electrode plates is 0.18 m².

Experimental method

By Na₂SO₄.10H₂O, CaCl₂.2H₂O, MgCl₂.6H₂O,NaHCO₃ and distilled water the testing sample is prepared:

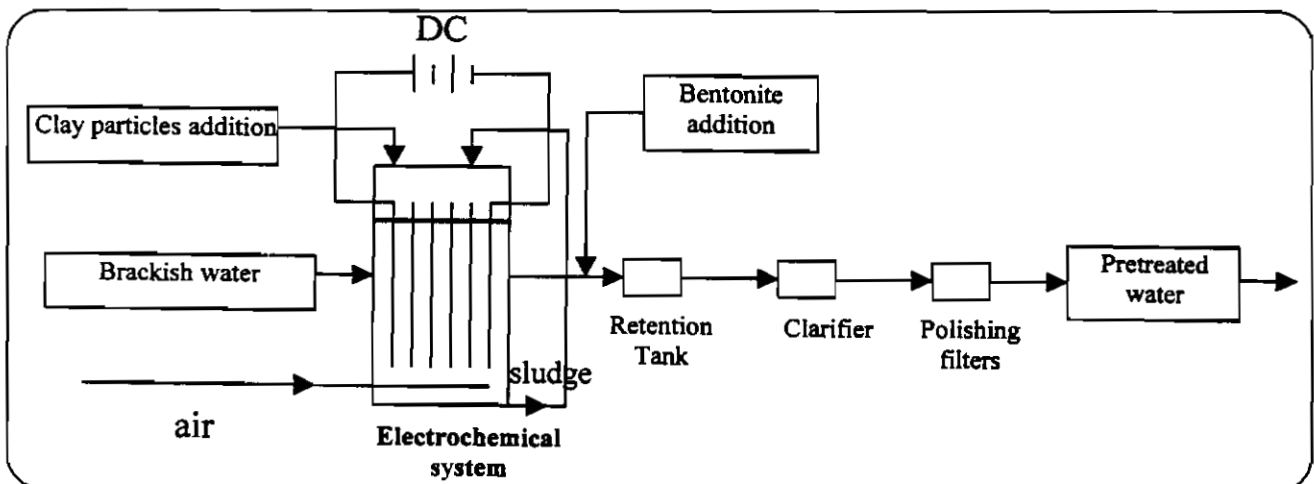


Fig.2: Process Flow diagram

Ions	Ca ²⁺	Mg ²⁺	Na ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
Meq/lit	5.57	6.2	30.41	5.61	23.54	12.4
ppm	111.6	75.03	699	342.2	835.6	595.2

$$H_{Ca} = 278.4 \text{ ppm CaCO}_3 ; H_{Mg} = 308.6 \text{ ppm CaCO}_3 ; TH = 11.77 \text{ meq/lit} = 587 \text{ ppm CaCO}_3 ; TDS = 4183 \text{ ppm CaCO}_3$$

The used quantities of the clay particles as a colloidal matter and the bentonite as a coagulant aid, are 0.9 ppm and 40 ppm, respectively. Before performing process, the clay particles are added, and bentonite soil is added after the performing process and before the filtration.

For the performance of DC-EC process, a DC power supply, connection wires and a electrochemical cell, which is connected to a aerating pump equipped with a flow meter are used. The DC power supply is connected between the cell's two end electrodes. As current flows from an electrode to other through the process water, an electrochemical reaction occurs where the positively charged sides, the anodes, give off ferrous ions. Iron addition is controlled simply by varying the cell power.

The aerating must be performed so fast that the solution won't turned into green in other words, all of Fe²⁺ must be oxidated to Fe³⁺. For the analysis of TH and SO₄²⁻ titration by EDTA(volumetric back titration) was used. In the other hand analysis of Cl⁻ and HCO₃⁻ have been done by Mohr and standard acid titration method respectively. After the sedimentation of sludge, the output water is filtered, carefully by the clarifier system and / or the filter paper which diameter of its holes is 0.45 μm. It is worth to mention that, all of the used clay particles and bentonite would remain in the sludge.

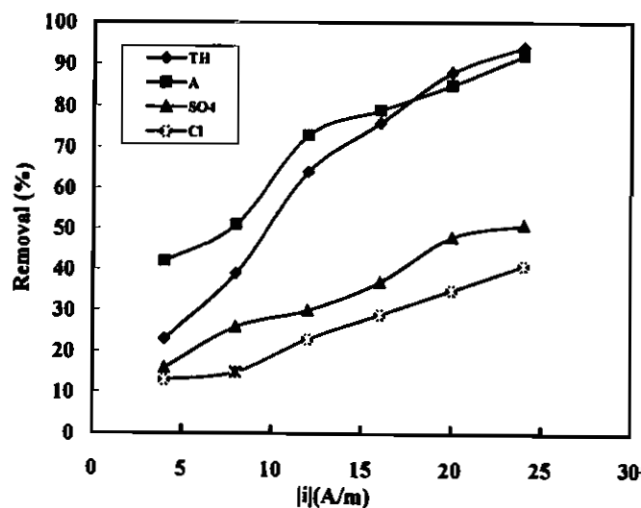
RESULTS AND DISCUSSION

Among of the effective factors on the process, the current density (ampere over square meter of electrodes total area) and volume flow are the most important. The cost of process is determined by the consumption of electrode and electrical energy, which is economic due to the main advantages of method [2,3]. On the other hand, the most the change in the efficiency is related to the changes of these two parameters: a) the electrical energy, b) electrodes consumption. Therefore the effect of these

two parameters on the removal efficiency is studied first and then the effect of the other parameters such as chemical consumption will be discussed:

Effect of current density on the removal efficiency

As the diag. 1 shows, the removal percents are increased by increasing of $|i|$, which is due to decreasing of oxidized iron.

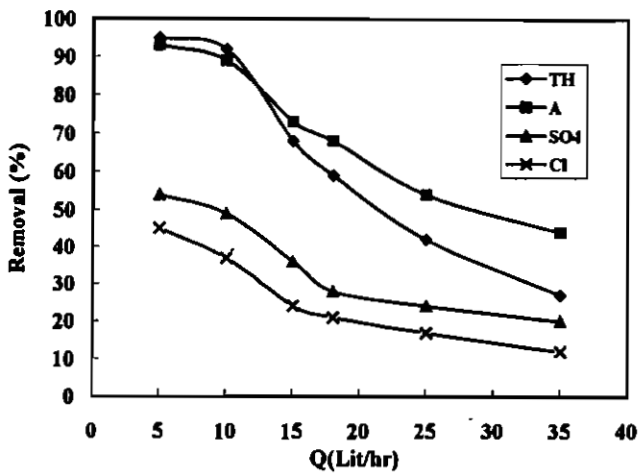


Diag. 1: Effect of current density on the removal efficiency: (Q) Volume flow: 10 hr/ lit, (d) Distance: 1.5 cm, (T) Temperature: 25 °C, (c.t) First contact time with produced sludge from preceding process: 10min (TH: Total hardness, A: Alkalinity)

Effect of volume flow on the removal efficiency

As the diag. 2 shows, the removal percents are decreased by increasing of Q, which is because of decreasing the oxidized iron.

From two diagrams, it observed that, (a) As the result of increasing $|i|$ and decreasing Q, the more coagulant agent is produced according to the Faraday's law, and from two diagrams, it observed that, (a) As the result of increasing $|i|$ and decreasing Q, the more coagulant agent



Diag. 2: Effect of volume flow on the removal efficiency:
 $|i| : 22 A/m^2, d : 1.5 \text{ cm}, T : 25^\circ C, c.t_1 : 10 \text{ min}$

is produced according to the Faraday's law, and therefore the removal percent is increased. (b) In two processes with different Q and $|i|$, if the consumption coulombs become equal, the removal efficiency in foregoing process will be equal.

Effect of retention time on the removal efficiency

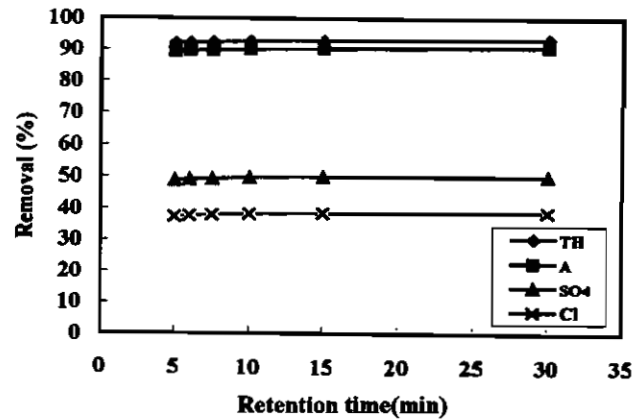
The amount of consumption coulomb or produced iron in the all of stages, must be equal. Therefore, only the effect of retention time on the removal efficiency is considered. According diag. 3 the removal percents are increased 1.5–2% by increasing retention time 5 to 30 min.

Effect of distance between the two electrodes on the removal efficiency

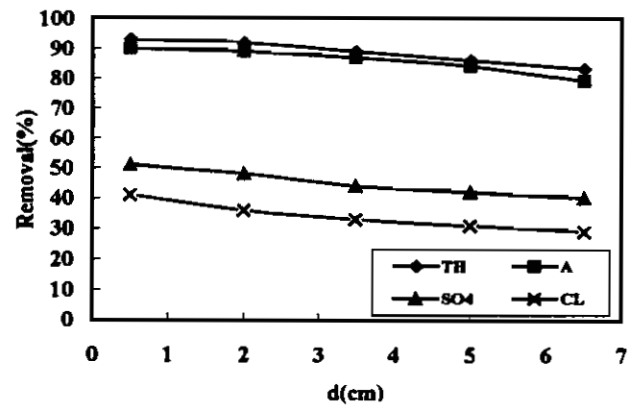
In the result of increasing distance, the electrical current is decreased (according to $R = \rho d/A$) and so the given amounts of solution of NaCl is added to stabilize the current density. The more accumulation of the ions with hydroxy polymer, in the other words, increasing of local concentration, and the increase of electrostatic intractions are the reasons for the increasing removal in the less distance, (Diag.4).

Effect of the total area of electrodes on the removal efficiency

The amount of consumption coulomb or produced iron,



Diag. 3: Effect of retention time on the removal efficiency:
 $|i| = 22 A/m^2, d = 1.5 \text{ cm}, T = 25^\circ C, c.t_1 = 10 \text{ min}, q = 1425 \text{ C/lit}, A_{tot} = 0.18 \text{ m}^2$

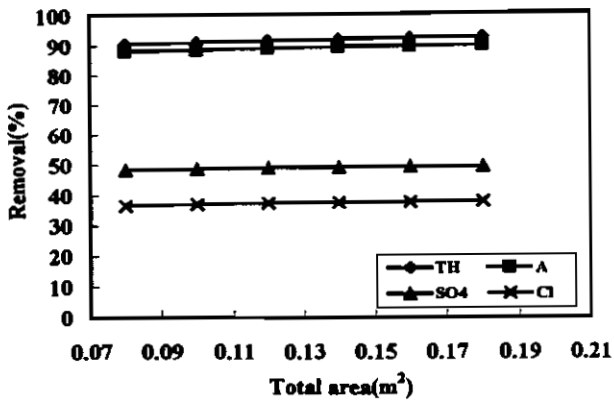


Diag. 4: Effect of distance between the two electrodes on the removal efficiency: $|i| = 22 \text{ A/m}^2, Q = 10 \text{ lit/hr}, T = 25^\circ C, c.t_1 = 10 \text{ min}$

must be equal in the all of stages and just as it is observed, there is direct relation between removal efficiency and total area of electrode. It is because of the more and quicker distribution of flocculant agent in the volume unit. In spite of consumption of the same electrical energy and to obtain desired removal efficiency, it could be increased Q , by increasing of total area of electrodes, proportionately, (Diag.5). Because,

$$\begin{array}{c} \downarrow \uparrow \quad \uparrow \downarrow \quad \uparrow \\ \downarrow R = \rho d / A_{tot} \uparrow \rightarrow E = Ri \rightarrow q = it \rightarrow Q = V/t \downarrow \end{array}$$

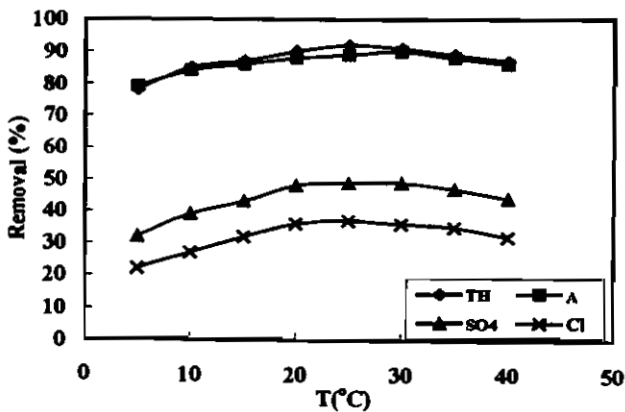
it is obvious the A_{tot} increased from 0.18 m^2 to 0.324 m^2 ($\times 1.8$), Q can be increased from 10 lit/hr to 18 lit/hr ($\times 1.8$).



Diag. 5: Effect of the total area of electrodes on the removal efficiency: $|i| = 22 \text{ A/m}^2$, $Q = 10 \text{ lit/hr}$, $T = 25^\circ\text{C}$, $c.t_1 = 10 \text{ min}$

Effect of temperature on the removal efficiency

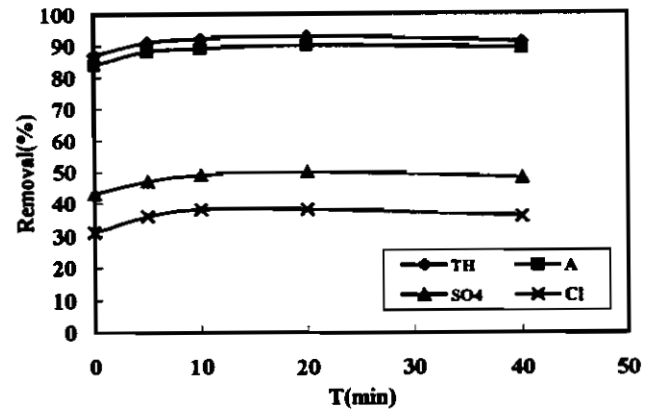
As it is specified (diag. 6), the rise of temperature has some effect in the increasing of the efficiency, that is as the result of increasing mobility and contact of ions together and with hydroxy polymer and /or because increasing the kinetic of removal reactions. Although, the increasing of mobility prevents the better accumulation, but this parameter have not preference over former parameter. On the other hand, because of the formation of unsuitable floc and/or increasing the solubility of precipitates, in the high temperatures the removal efficiency, is decreased.



Diag. 6: Effect of temperature on the removal efficiency: $|i| = 22 \text{ A/m}^2$, $Q = 10 \text{ lit/hr}$, $d = 1.5 \text{ cm}$, $c.t_1 = 10 \text{ min}$

Effect of the contact time of produced sludge before process on the removal efficiency

As the diag.7 shows, the first contact time with sludge,



Diag. 7: Effect of the contact time of produced sludge before process on the removal efficiency:

$|i| = 22 \text{ A/m}^2$, $Q = 10 \text{ lit/hr}$, $d = 1.5 \text{ cm}$, $T = 25^\circ\text{C}$

which is hydroxy polymer and ferric hydroxide, can remove the targets. Because, the concentration of ions is much in the raw water and discrepancy of concentration is the main factor of motive in the removal. But, if the contact time to be more than the amount of optimum, the removal efficiency will decrease, because the capacity of sludge for removal will be completed and the removed targets in the former process is released from sludge gradually.

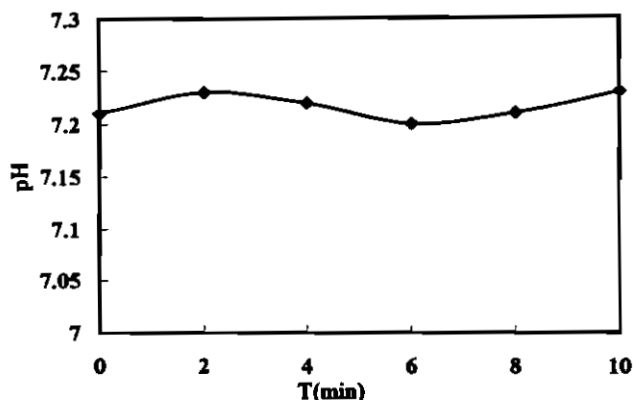
Effect of the contact time of produced sludge after process on the pH and the removal efficiency

By the increasing of sludge contact time after the process, the pH or some HCO_3^- is increased and removal efficiency is decreased so that in the range of 5 min to 25 min the removal efficiency of every ion is decreased about 20% and pH is increased from 8.6 to 9.0. In other words by the processing of time removed targets are released gradually, so the filtration must be performed immediately.

Because, as a result of performing of process, a much quantity of ions is removed, so its concentration is little in the finished water. Therefore, by reason of the difference of concentration the removed ions incline to return from sludge to water.

Relation of pH with process time

The HCO_3^- in sample can buffer the solution and



Diag. 8: Relation of pH with process time

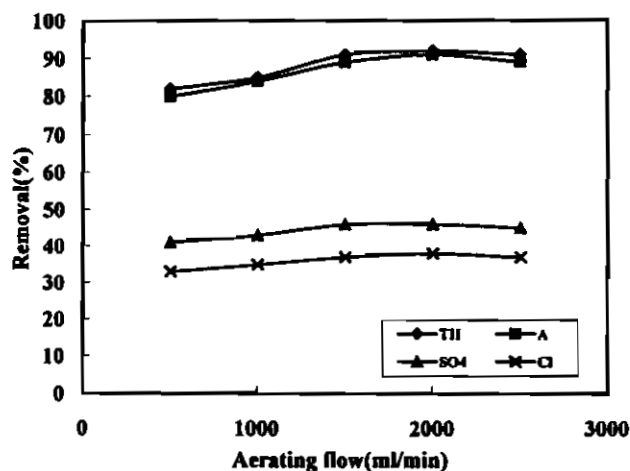
prevents the pH variation with time during the removal process. For this reason we prepared a sample similar to the testing sample without HCO_3^- . Our studies showed that the pH is nearly constant with time this means all of OH^- produced from cathode with Fe^{3+} is converted to $\text{Fe}(\text{OH})_3$, which is an important advantage of this method, (Diag.8).

Effect of aerating flow on the removal efficiency (for a 1 lit is considered)

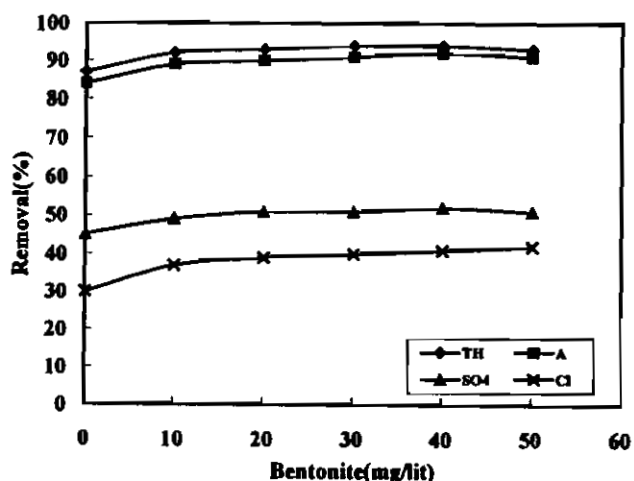
As the diag. 9 shows in the low and very high aerating flows, the removal efficiency is decreased, the reason for low aerating is that all Fe^{2+} is not converted to Fe^{3+} . The latter case is made by reason of very much increasing of the required velocity gradient for flocculation. In other words the large flocs are converted to the smaller flocs, and ionic motion increasing by high aeration flows therefore the surface complexation and ions accumulation with hydroxy polymer decreases, by reason removal process is not completed.

Effect of the addition of bentonite soil as coagulant aid in the removal efficiency

According to the diag. 10, addition of coagulant aid which causes the acceleration of flocculation and precipitation increases the removal efficiency. It is because of rapidly and densely formation of flocs. For instance, the bentonite soil accumulates the fine and light precipitates of CaCO_3 and magnesium complex, therefore it helps their precipitation.



Diag. 9: Effect of aerating flow on the removal efficiency (for one liter of sample); $|\bar{i}| = 22 \text{ A/m}^2$, $Q = 10 \text{ lit/hr}$, $d = 1.5 \text{ cm}$, $T = 25^\circ\text{C}$, $c.t_1 = 10 \text{ min}$



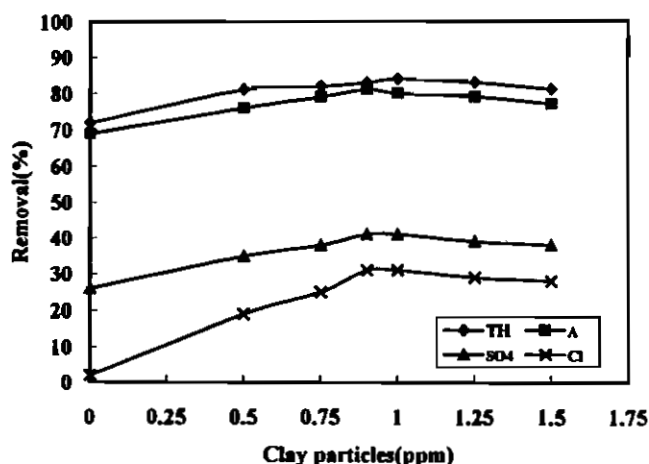
Diag. 10: Effect of the adding bentonite soil as coagulant aid in the removal efficiency: $|\bar{i}| = 22 \text{ A/m}^2$, $Q = 10 \text{ lit/hr}$, $T = 25^\circ\text{C}$, $d = 1.5 \text{ cm}$, $c.t_1 = 10 \text{ min}$

Effect of the addition of clay particles in the removal efficiency

According to the diag. 11, the colloidal and/or suspended clay particles are more effective on the removal process, especially, in decreasing of SO_4^{2-} and Cl^- .

CONCLUSIONS

The electrocoagulation process with iron electrodes and aeration is one of the most important methods for pretreatment or desalination of the much hard and



Diag. 11: Effect of the adding clay particles in the removal efficiency: $|i|=22 \text{ A/m}^2$, $Q=10 \text{ lit/hr}$, $d=1.5 \text{ cm}$, $T=25^\circ\text{C}$, $c.t_1=10 \text{ min}$

brackish water. The output water from process is post treated to drinking with less problems in the membrane plants because of deficiency of ions and non formation of scale. The best result is obtained by determination of optimum quantities of effective factors on the process for brackishwater with chemical specification 11.8TH, 5.6A, 12.4 SO_4^{2-} and 23.5Cl⁻ meq/lit. According to the results of this research, the optimum parameters in the conditions of $|i|=22 \text{ A/m}^2$ and $Q=10 \text{ lit/hr}$ to obtain the removal efficiency of 94% TH, 92% A, 50% SO_4^{2-} and 43%Cl⁻, are as follows:

1. Consumption of clay particles: 0.9 ppm
2. Water temperature :25-30 °C
3. Aerating flow :2000 ml / min for one liter of sample
4. Total area of electrodes :0.18 m² for one liter
5. Distance between the two electrodes :1.5 cm
6. The first contact time : 20min
7. The second contact time : less than 5 min
8. Consumption of bentonite soil : 40 ppm

Notations

W : electrical energy (watt. hr/lit)
 V : volume (lit)
 G : conductivity (1/Ω)
 E : voltage (volt)
 P : electrical power (watt)

R : electrical resistance (Ω)
 Q : volume flow (lit/hr)
 ρ : specific resistance (Ω. cm)
 $|i|$: current density (A/m²)
 A : area (cm² or m²)
 I : electrical current (ampere)
 d : distance between two electods (cm)
 Q : electricity consumption (coulomb)
 t : time (sec)
 c.t₁ : contact time (min)
 M : molecular wieght
 m : oxided iron mass
 n : oxidation number change

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