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Applied Investigation of Effluent Wastewater of Desalination Systems: South Pars Gas Company

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Abstract:

The purpose of this pretreatment process is softening the wastewater as much as possible to prepare the feed stream for salt production units and also the first stage of processes related to zero discharge desalination (ZDD). The basic parameters such as the effectiveness of three commercial mineral coagulants, Aluminum Sulfate, $Al_2(SO_4)_3$, Ferric Sulfate, $Fe_2(SO_4)$ and Ferric Chloride, $FeCl_3$, individually in removing of the total hardness, the optimized amounts of Sodium Carbonate and Sodium Hydroxide and the optimum mixing rate of the first reactor are investigated in the laboratory. The effluent waste water of the desalination systems of the gas complexes is treated in the proposed treated waste water process to produce potable water and salt at final stages and its superiority of this wark. Main properties of clarified produced water such as total hardness, alkalinity and total dissolved solid, pH, temperature, electrical conductivity; Calcium hardness and Magnesium hardness are evaluated in each run. Comparing the results reveals the optimum values of the basic conditions such as the amount of soda, sodium carbonate, coagulant and mixing rate of first pretreatment reactor to improve the performance of zero discharge desalination process.

Keywords: mineral coagulant; petrochemical complex; sea ecosystem; strategic utility unit; total hardness removal; wastewater treatment; ZDD.

1. Introduction

Direct drainage of the concentrated brine wastewater of desalination units to sea, could cause salinity and thermal shocks to aqua environment (Banasiaka et al., 2007; Kaghazchi et al.,2010; Kim et al., 2009; Sadek, 2010; Sadrzadeh and Mohammadi, 2008). But if the concentrated brine wastewater is pretreated in basic softening process, it can be used in order to production of salt and potable water. During pretreating process, total hardness which is caused by Mg^{2+} salts and Ca^{2+} salts, are removed and production of Sodium Chloride salt becomes possible (Johnson et al., 2008). Usage of Sodium Carbonate and Sodium Hydroxide or Calcium Hydroxide in wastewater, vanishes the temporary and permanent hardness as Magnesium Hydroxide and Calcium Carbonate compounds. These particles are small and time is needed for the sedimentation. By using mineral coagulants in special conditions the required time for coagulation, flocculation and sedimentation steps (Liu et al., 2010; Mu et al., 2009; Rizzo et al., 2008), are short enough and also the turbidity of the product is minimized. (Ma et al., 2007; Pour rezaei et al., 2010). Determination of the optimized amounts of Sodium Carbonate, Sodium Hydroxide, suitable conditions of the pretreatment process, type and dosage of coagulant, have to be studied and evaluated to reach the higher yield and minimize total hardness.

Published papers in the field of pretreatment process of wastewater from a desalination unit are scarce in the literature. However there are many papers about the performance of coagulants and polymers in the initial pretreatment of feed water for desalination units (Ma et al., 2007; Tili et al., 2003). The researchers surveyed a material used to avoid fouling of membrane (Tili et al., 2003;

Farahbod et al. 2012). In the feed stream of the reverse osmosis (RO) unit, phosphate inhibitors are used and they found that Polyacrylate inhibitor, RP12000, is the proper matter to avoid fouling of membrane (Kim, 2011; Gnanadason et al., 2011; Farahbod et al., 2012). The coagulation and powdered activated carbon adsorption are two options of the pretreatment micro filtration (Farahbod et al., 2012). The optimized dosage of coagulant is investigated by considering the key parameters of the raw water. They knew that properties of raw water are tremendously varied with seasons and rain fall. Results of their experiments showed that adding Polyaluminum Chloride was critical to maintain high water flux in the membrane system. Moreover there are researches about the best type of coagulants and coagulation mechanisms in pretreatment of water (Macedonio et al., 2011; Nan et al.,2009). The scientists used Magnesium and Zinc compounds comparing with the aluminum and ferric salts and showed that the efficiency of Zinc sulfate is higher than other coagulants in Silica removal therefore that produced water used for reboilers (Cui et al., 2011; Jeawoo and Hyo-Taek, 2011).

Beltran et al. investigated the proper coagulant for treatment of the textile wastewater on 2009 (Xiaosheng and Gianluca, 2010). The scientists studied the efficiency of the enhanced pretreatment process of ground water with high content of Mg^{2+} by $AlCl_3$, $FeCl_3$ and Polyaluminum Chloride (PAC) (Yana et al., 2009; Johir et al., 2009). They dedicated that the efficiency of the enhanced softening affected severely by the content of the raw water, for example the quantity of natural organic matter (NOM), total hardness of water, dosage of coagulant and their type. They concluded that PAC is the most effective and the produced water has the appropriate pH lower than 10. Wang et al. 2009 surveyed the coagulation performance of the Aluminum salts and the effect of total hardness on this performance (Wang et al., 2009; Ryabtsev et al., 2003). They revealed that the high hardness affects the coagulation efficiency and kinetics. In 2010 they studied the effect of ionic strength in addition to the total hardness on the coagulation performance to vanish humic acid (HA) (Wang et al., 2009). The researchers studied the softening process of the potable water before distribution (Gao et al., 2009). They used pellet reactor and Sodium Hydroxide to pretreat and reached the water with low total hardness. In this paper the pretreatment process of wastewater stream exited from a MED desalination unit carried out, experimentally.

In this experimental study the wastewater of South Pars Gas Company is softened by Sodium Carbonate and Sodium Hydroxide. Three types of usual mineral coagulants are investigated, named; Ferric Sulfate, Aluminum Sulfate and Ferric Chloride. Softening process is occurred in three steps; Coagulation, flocculation and sedimentation steps. Main items such as efficiency of three types of current coagulants, speed of agitation and appropriate amount of Sodium Carbonate, the optimum ratio of Sodium Hydroxide to coagulant and Sodium Carbonate to coagulant are investigated. Three commercial mineral coagulants, Aluminum Sulfate, $Al_2(SO_4)_3$, Ferric Sulfate, $Fe_2(SO_4)$ and Ferric Chloride, $FeCl_3$, are used in this paper to improve coagulation step in pretreatment process. Properties of mother wastewater and also produced water are evaluated and analyzed in each run.

1.1. Practical desalination Unit of South Pars Gas Company

Approximately, 1030 ton/hr flow rate of sea water is fed to each of desalination unit although each unit has designed for 1100 ton/hr of sea water. About 28% of the feed is produced as sweet water and high saline water is drained to the sea as brine wastewater. So, the total flow rate of brine wastewater is 3700 ton/hr, approximately. Salinity of the brine wastewater is 54500 ppm and total hardness is about 50696.3 ppm as $CaCO_3$.

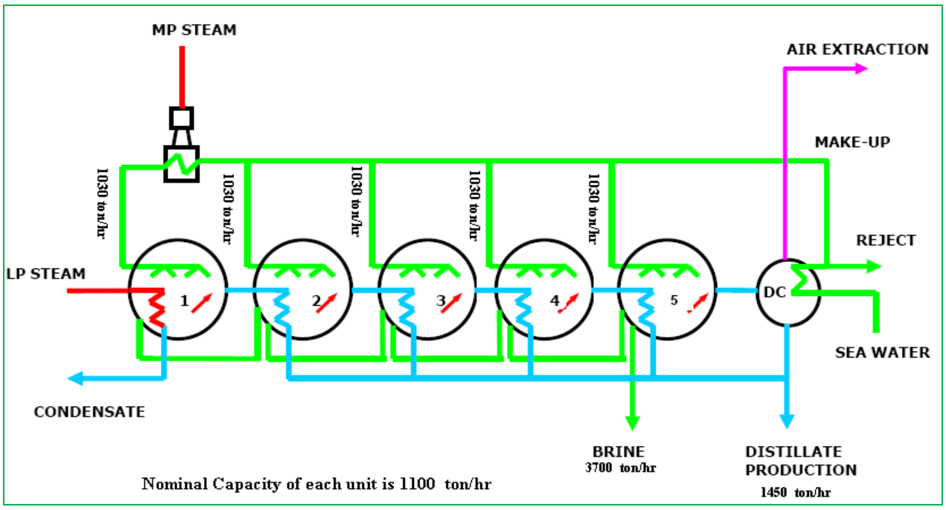


Figure1- A schematic of MED desalination of South Pars Gas Company

2. Experimental Section

2.1. Experimental Study

The proposed softening process for wastewater of desalination unit of South Pars Gas Company is investigated experimentally in laboratory scale. In following, the experimental apparatus and the experimental procedure are described.

2.2. Experimental Apparatus

Batch softening process is held in two pretreatment reactors. Main bodies of these reactors are polyethylene containers and each one with 8 liters capacity. Both of them are equipped by an agitator and connected in series through 1.5 inches PVC tube. The first reactor is about 40 cm higher than the second one, so the outlet stream of the first reactor is drained to the second one by gravitational force, easily. Each reactor can be drained through a PVC globe valves and one PVC valve, installed between them, is to control the flow rate. Length of mixer is about 40 cm and is made from high corrosion resistance stainless steel rod; the cross shape blades have right angle to horizontal so that it mixes the coagulants, Sodium Carbonate and Sodium Hydroxide with wastewater. The speed of mixer in the first reactor is more than the speed in the second one. The speed is changed from 50, 70, 90,120, 140, 160, 180 and to 200 rpm for 2 minutes and the slow speed of mixer in the second reactor is 50 rpm for 8 minutes. Temperatures of the first and second reactor are measured by thermometer. These two reactors are fixed and set up in one table. Figure 2 shows a schematic of this experimental set up.

3. Results and Discussion

3.1. Mixing rate of first reactor

Operating conditions of the two pretreatment reactors are effective on the coagulant performance. One of these importances is the rate of mixer in the coagulation step and in the first reactor.

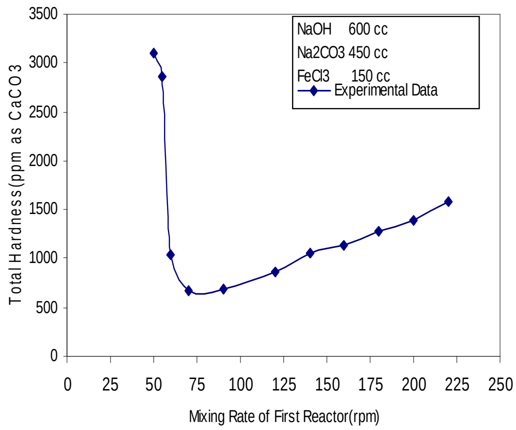
In this step, coagulant is combined with sediments which are removed from water, so the appropriate mixing rate is the most important parameters for proper collision. In this study, the mixing rate of first reactor is investigated for each coagulant with the fix dosage of Sodium Carbonate and Sodium Hydroxide.

Figure 2. Picture of pretreatment set up

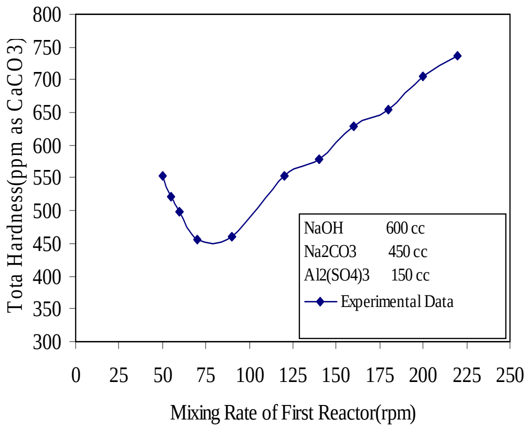
Experimental data for total hardness versus mixing rate of the first reactor are shown in Figures 3. The results indicate that about 70 rpm is the best mixing rate for the first pretreatment reactor and the total hardness reaches to the lowest amount.

Figure 3-a, also indicates that using the $FeCl_3$ as mineral coagulant, the total hardness in 70 and 90 rpm are the same approximately but the total hardness of the clarified water in 70 rpm is less. Furthermore the value of Calcium hardness in 70 rpm is less, so this can be concluded that the optimum speed of agitator to vanish the Calcium ions is 70 rpm. The trend of changes of the total hardness in the speeds higher than 70 rpm is demonstrated in Figure 3. Amount of sedimentation in speeds lower than 70 rpm is less than ones which are measured in speeds higher than 70 rpm. In Figure 3-c, the value of total hardness is minimum by using the $Fe_2(SO_4)_3$ as a mineral coagulant, in 70 rpm and about 453 ppm as $CaCO_3$. The slope of curve in Figure 3 (a, b and c) is positive at mixing rates higher than 70 rpm, in first reactor. The collision between particles and attraction between them are two major factors which affect the quality of coagulation and flocculation, 70 rpm provides the best collision and attraction between particles. In Figure 3- b, when $Al_2(SO_4)_3$ is used as coagulant, It seems that in low speeds, power of mixing is not enough to make the required fluctuation for suitable collision between ions, so the amount of total hardness is higher than 550 ppm as $CaCO_3$. By increasing the speed of the mixer to 70 rpm, the amount of total hardness decreases to about 460 ppm as $CaCO_3$. But in higher ranges of speed of mixer, turbulences avoid forming of complexes so total hardness increases again.

According to Figure 3-b it can be concluded that a value of the total hardness of clarified water is minimum when the mixing rate of the agitator is 70 rpm in the first reactor.



(a)



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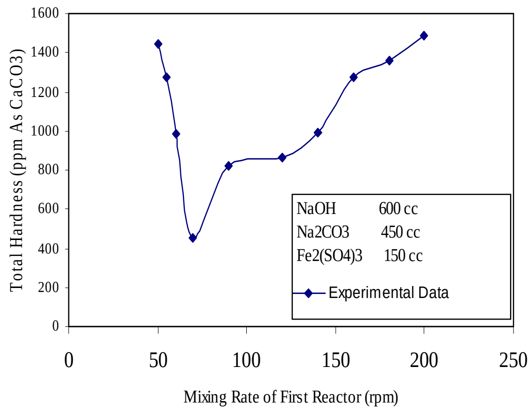


(c)

Figure-3 (a, b and c). Optimum mixing rate in the first pretreatment reactor for $FeCl_3$ (a), $Al_2(SO_4)_3$ (b) and $Fe_2(SO_4)_3$

Also the Calcium hardness is measured in this research and the trends of variation of Calcium hardness for each coagulant are shown in Figure 4. 450 cc of Sodium Carbonate, 600 cc Sodium Hydroxide and 150 cc of each coagulant are used in experiments which the effect of the speed of agitation and the type of coagulant are determined. Moreover, residence time for first reactor is 2 minutes and in the second reactor is 8 minutes in all experiments. Considering the Figure 4 the trend of values of Calcium hardness versus mixing rate in first reactor for $Al_2(SO_4)_3$, 70 rpm is the best speed for proper interactions and collisions for ions to sediment Calcium carbonate. Before this speed, the Calcium hardness is about 306 ppm as $CaCO_3$, in 70 rpm the amount is decreased to about 225 ppm as $CaCO_3$ and in higher agitator speed, the Calcium hardness increases to about 270 ppm as $CaCO_3$. Although the difference between minimum and maximum of values of Calcium hardness is about 81 ppm as $CaCO_3$ however the purpose of this research is finding the optimum speed of the agitator in the first reactor, so 70 rpm is the best. According to the Figure 4, when $FeCl_3$ is used as a coagulant, the minimum amount of Calcium hardness is reached in 70 rpm. Difference between Calcium hardness in 90 rpm and 70 rpm is sensible but increasing of Calcium hardness in speeds higher than 90 rpm is moderately. Also 70 rpm is the best mixing rate in the first reactor when $Fe_2(SO_4)_3$ is used.

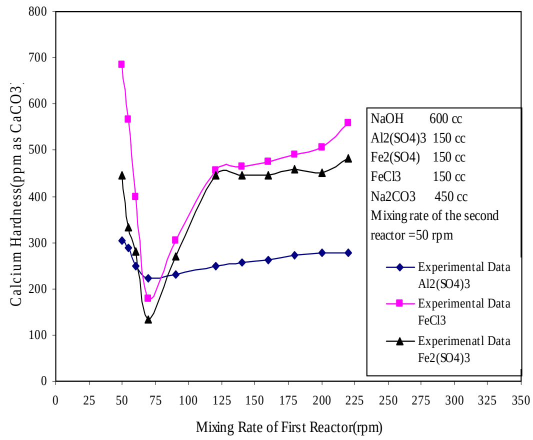


Figure- 4. Effect of mixing rate in the first reactor on the Calcium hardness

3.2. Different Amounts of Sodium Carbonate (Na2CO3)

Sodium Carbonate is used for removing permanent Calcium hardness; therefore the appropriate amount of Sodium Carbonate is investigated as one of the major factors in efficiency of softening process. In all related experiments, 150 cc of each coagulants and 600 cc of Sodium Hydroxide are used by the optimum mixing rate in the first reactor for 2 minutes and 50 rpm in the second reactor with 8 minutes residence time. Figure 5, shows the performance of three types of coagulants regard to removing of total hardness in various amounts of Sodium Carbonate. Although the performance efficiency of $FeCl_3$ is lower than $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ in total hardness removal. This is revealed that total hardness removal by $Fe_2(SO_4)_3$, is more efficient till the amount of Sodium Carbonate becomes near 1500 cc. Using $Al_2(SO_4)_3$ as a mineral coagulant, is suitable for values of Sodium Carbonate higher than 1500 cc. Maximum softening for $Fe_2(SO_4)_3$ is 0.9911 which can be reached by using 450 cc of Sodium Carbonate however at the same conditions amount of total hardness removal is 0.991058 and 0.991 by using $Al_2(SO_4)_3$ and $FeCl_3$, respectively. Also the peak of curve for $Al_2(SO_4)_3$ is 0.9985 by using 2900 cc of Sodium Carbonate. It shows that by adding 2450 cc more Sodium Carbonate the total hardness removal increases just about 0.74%. Therefore it is clear that reaching this value of softening is not cost beneficial. Although the charge density of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ are equal but since the molecular weight of $Fe_2(SO_4)_3$ is higher, so the tendency of $Fe_2(SO_4)_3$ in removing total hardness is higher than the other. The molecular weight and charge density of $FeCl_3$ is the lowest one so this cannot be the suitable coagulant.

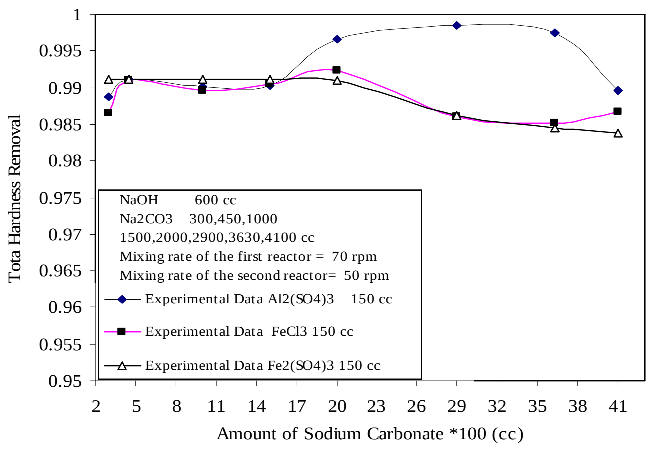


Figure- 5. Effect of various amounts of Sodium Carbonate on total hardness.

Equations 1, 2 and 3 show the reactions related to the coagulation step.

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \leftrightarrow 2Al(OH)_3 + 3CaSO_4 + 6CO_2 \quad (1)$$

$$Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 \leftrightarrow 2Fe(OH)_3 + 3CaSO_4 + 6CO_2 \quad (2)$$

$$FeCl_3 + \frac{3}{2}Ca(HCO_3)_2 \leftrightarrow Fe(OH)_3 + \frac{3}{2}CaCl_2 + 3CO_2 \quad (3)$$

pH is an important factor to control coagulation process. In Figure 6 the amounts of pH of clarified water in each test are shown for three types of coagulants. As shown in Figure 6, by using Sodium Carbonate near 1500 cc, the trend of changes of pH values for three coagulants is 11.3 to 11.48. So, according to the Figure 6 the variation of pH is not severely.

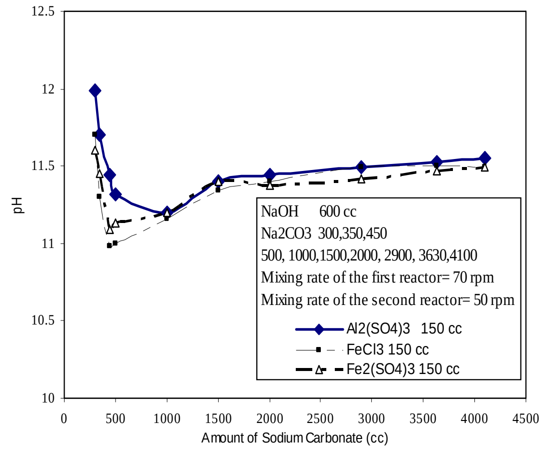
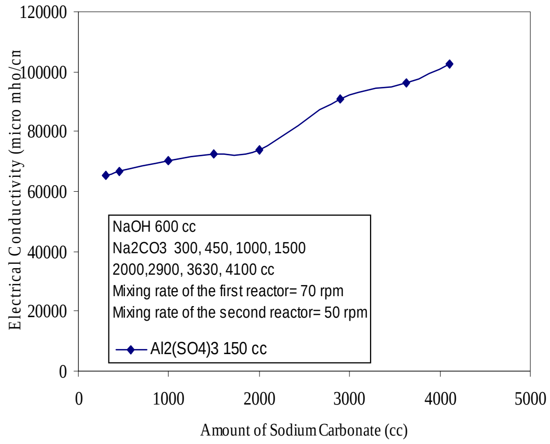


Figure- 6. Variations of pH of clarified water due to amount of Sodium Carbonate for three coagulants

3.3. Electrical Conductivity (EC)

One of the other important factors measured in this study is electrical conductivity of the clarified water. This factor can be an indicator for performance evaluation of coagulants in total hardness removal. In Figure 7 a, b and c, the performance of three types of coagulants by different amounts of Sodium Carbonate is shown in terms of electrical conductivity. This is concluded that the electrical conductivity is at minimum when the ratio of Sodium Carbonate over coagulant is 3. Moreover, it can be concluded that in low amounts of Sodium Carbonate below 2900 cc, electrical conductivity (EC) of clarified water decreased comparing the value of EC for mother wastewater. However in amounts 2900, 3630 and 4000 cc of Sodium Carbonate the values of EC increase, even more than EC of mother wastewater.



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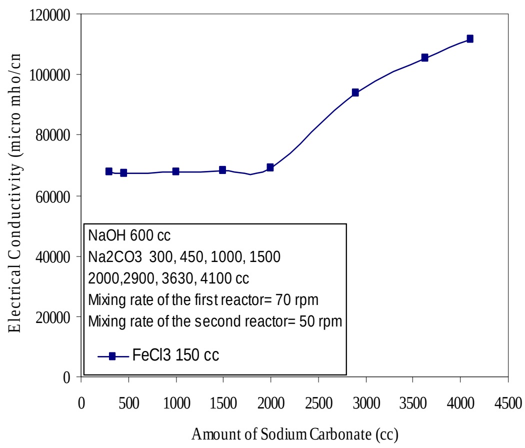

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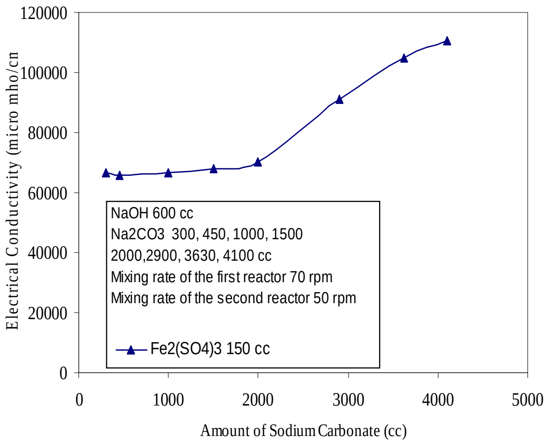
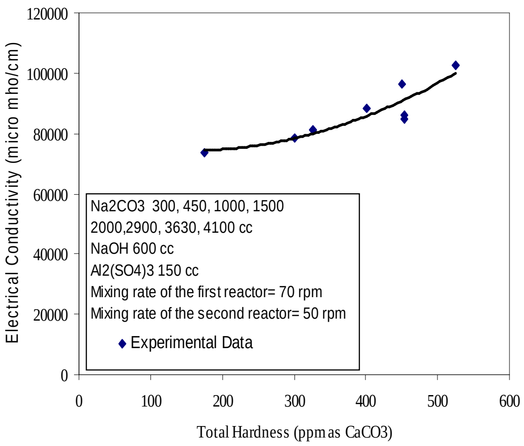


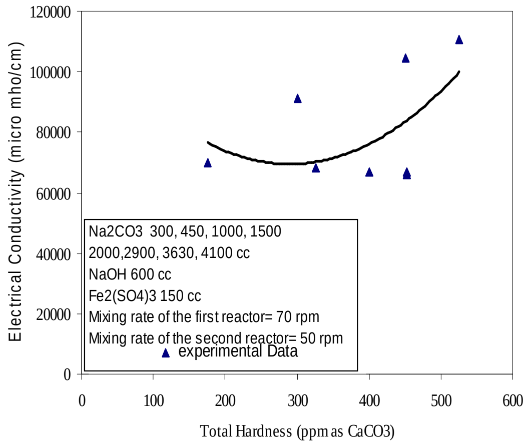
(c)

Figure- 7. Effect of amount of Sodium Carbonate on EC of the clarified water for three types of coagulants, a, b and c.

There is a relation between total hardness of the clarified water and electrical conductivity, so for three coagulants in different amounts of Sodium Carbonate, Figures 8, a, b and c are shown. Figure 8-a shows that when $Al_2(SO_4)_3$ is used as a mineral coagulant, both total hardness and electrical conductivity are at minimum when 450 cc Sodium Carbonate is used, and then this indicates the best fraction of $Na_2CO_3 / Al_2(SO4)_3$ is 3. Also, Figure 8-c shows the trend of electrical conductivity versus total hardness when the coagulant is $FeCl_3$. Electrical conductivity is from 65000 to 67000. However EC and TH have sensible increase in amounts of Sodium Carbonate more than 2000 cc. Comparing results in Figure 8 shows, by using 450 cc Sodium Carbonate and 150 cc of each coagulant, the EC and TH are in the minimum quantities.



(a)



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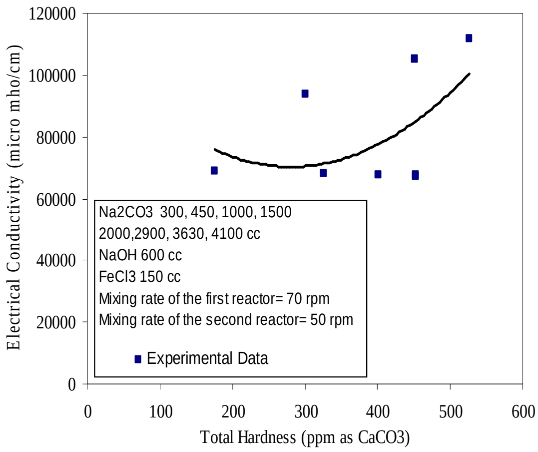

(c)

Figure- 8. Relation between the TH and EC in variant amount of Sodium Carbonate when a) $Al_2(SO_4)_3$,b) $Fe_2(SO_4)_3$,c) $FeCl3$ is as a coagulant.

Samples of wastewater before and after sedimentation step are shown in Figure 9 (a, b and c) for three mineral coagulants by mixing rate of 70 rpm in the first reactor and fraction of Sodium Carbonate and Sodium Hydroxide per coagulant is 3 and 4 respectively.

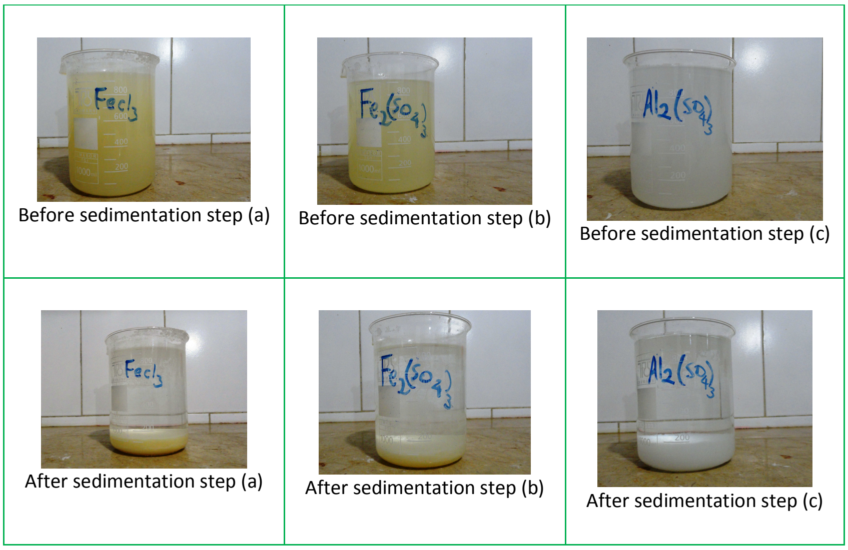

Figure-9. Samples of wastewater with three mineral coagulants (a, b, c) (mixing rate of 70 rpm in the first reactor and fraction of Sodium Carbonate and Sodium Hydroxide per coagulant is 3 and 4 respectively)

3.4. Various Fractions of Sodium Carbonate and Sodium Hydroxide

One of the important parameters in coagulation process is minimum amount of coagulant. This parameter has more effectiveness particularly while the efficiency of softening process is dependent on the amounts of Sodium Carbonate and Sodium Hydroxide. Therefore this is concluded that finding the appropriate amounts of Sodium Carbonate and Sodium Hydroxide is possible considering the amounts of coagulant, fractionally. According to this concept, four fractions is investigated for each mineral coagulant, $Al_2(SO_4)_3, FeCl_3$ and $Fe_2(SO_4)_3$.

Results about appropriate fractions for $Al_2(SO_4)_3$ are shown in Figure 10 and indicate that $Na_2CO_3 / Al_2(SO4)_3 = 3$ and $NaOH / Al_2(SO_4)_3 = 4$ achieve the best total hardness removal.

It seems that the effectiveness of Sodium Carbonate, Sodium Hydroxide and each coagulant in removing hardness of South Pars Gas water, depends on the ratio of Sodium Carbonate to coagulants and also the ratio of Sodium Hydroxide to each coagulant. Since one of the main purposes in all pretreatment processes is the limit of appropriate amount of coagulant, so the mentioned fractions are assumed according to the optimum amount of coagulant. In this paper the limit optimum amount of each coagulant is assumed 150 cc in each test. Experiments are done to study about the appropriate fractions of $Na_2CO_3 / Coagulant$ and $NaOH / Coagulant$ which the results are demonstrated in Figures 10, 11, 12, and 13.

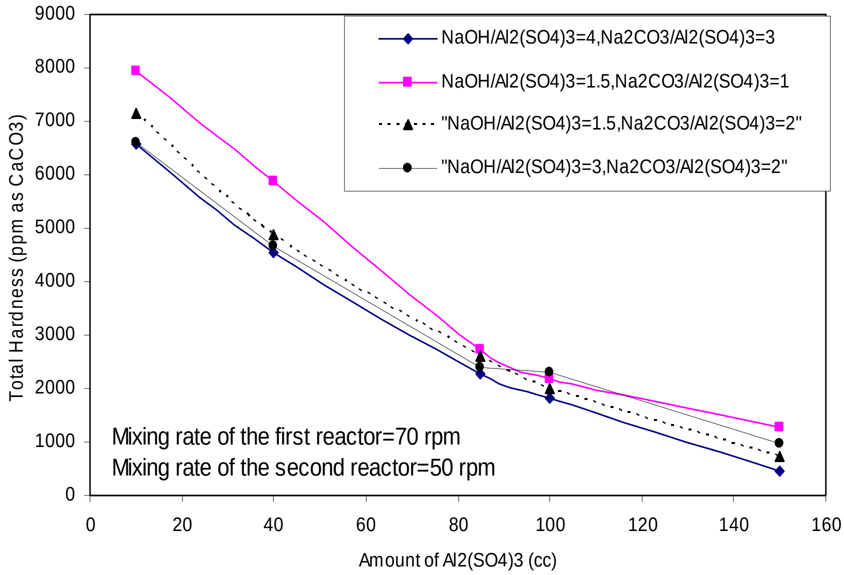

Figure- 10. Effect of fractions of $Na_2CO_3 / Al_2(SO4)_3$ and $NaOH / Al_2(SO_4)_3$ on the total hardness of the clarified water.

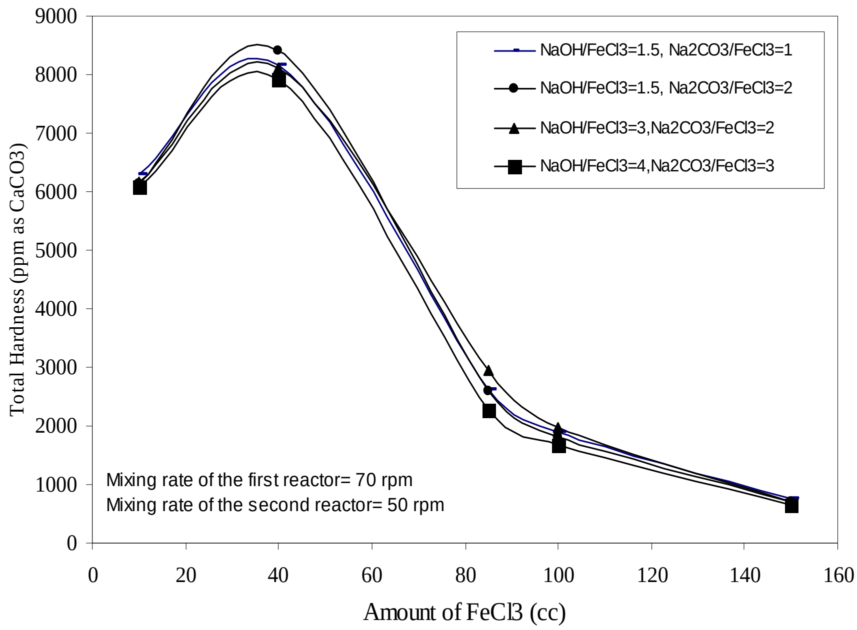

Figure- 11. Effect of fractions of $Na_2CO_3 / FeCl_3$ and $NaOH / FeCl_3$ on the total hardness of the clarified water.

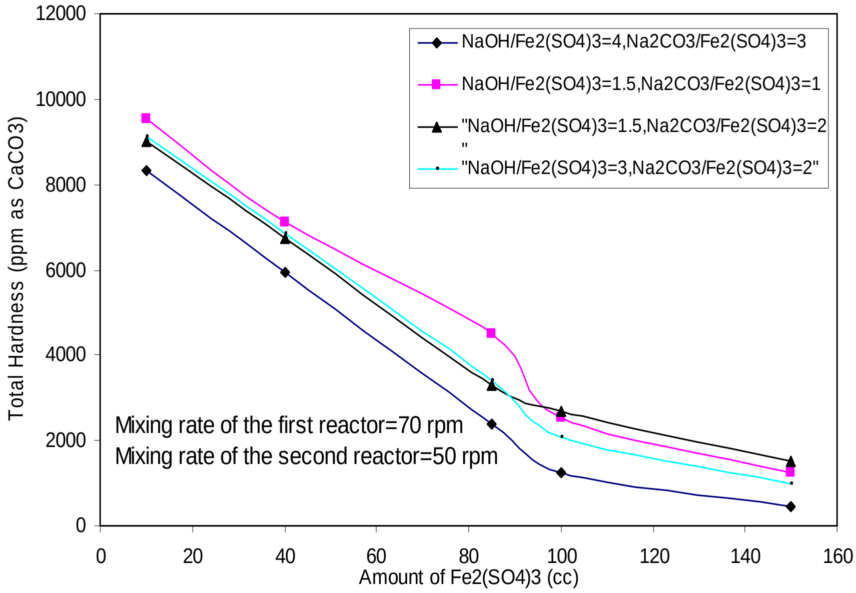

Figure- 12. Effect of fractions of $Na_2CO_3 / Fe_2(SO_4)_3$ and $NaOH / Fe_2(SO_4)_3$ on the total hardness of the clarified water.

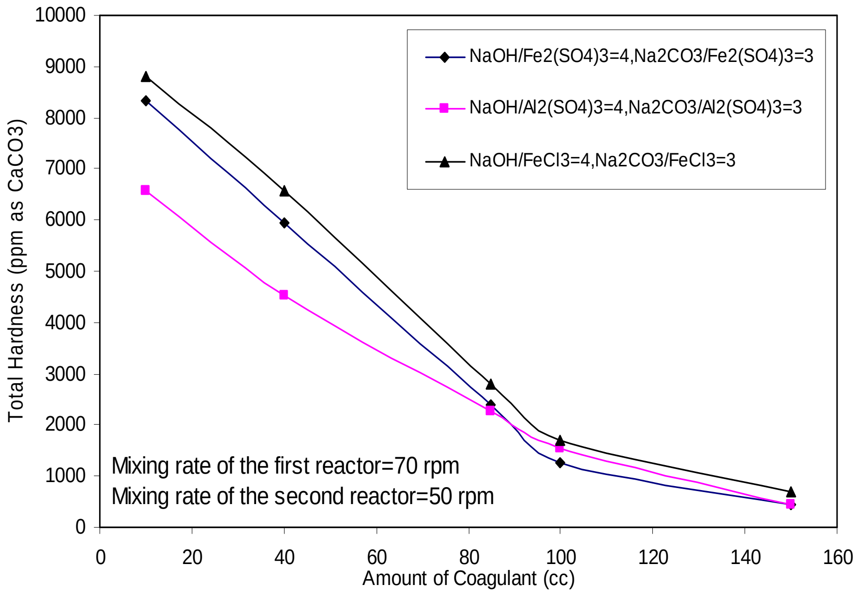

Figure- 13. Comparison between the effectiveness of three coagulants with the appropriate fractions of $Na_2CO_3 / Coagulant$ and $NaOH / Coagulant$

4. Conclusions:

A pretreatment process is suggested for softening of brine waste water of South Pars Gas Company. Currently direct drainage of the wastewater of desalination units to sea could cause salinity and thermal shocks to sea ecosystem. The purpose of this pretreatment process is softening the wastewater as much as possible to prepare the feed stream for salt production factories. The suggested pretreatment process can be the first stage of processes related to ZDD processes. Performance of three types of commercial coagulants, Aluminum Sulfate, $Al_2(SO_4)_3.14H_2O$, Ferric Chloride , $FeCl_3$ and Ferric Sulfate, $Fe_2(SO_4)_3$, are considered. Permanent hardness of the raw water is higher than temporary hardness. Sodium Carbonate is used for removing permanent Calcium hardness; therefore the appropriate amount of Sodium Carbonate is one of the major factors in efficiency of softening process. Therefore amount of Sodium Carbonate is investigated experimentally in this research. Therefore variations of total hardness of clarified water with different mixing rates of first tank reactor and with various fractions of Sodium Carbonate and Sodium Hydroxide for each coagulant are presented separately. Comparing the results the optimum values of the major parameters are determined. Experimental results approve that $Fe_2\ (SO_4)_3$ is the best mineral coagulant in the same condition among the $FeCl_3$ and $Al_2\ (SO_4)_3$ and this coagulant removes hardness more efficiently. The best mixing rate speed in the first reactor is obtained as 70 rpm. Moreover this is suggested that finding the optimum fractions of Sodium Carbonate to coagulant and Sodium Hydroxide to coagulant is more effective than considering to the amount of Sodium Carbonate and Sodium Hydroxide individually. The experimental results show the appropriate fraction of $Na_2CO_3 / Coagulant$ is 3 and $NaOH / Coagulant$ is 4. The experiments indicate that by using $Fe_2(SO_4)_3$, the percentage of total hardness removal reaches to 99.11 approximately.

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