

Experimental Study of Effluent Salty Wastewater Treatment from a Solar **Desalination Pond**

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Abstract

In this research, the quality of the wastewater discharged into the environment has been investigated. The effluent from solar desalination pond contains large amounts of TDS (3.68 grams per liter) and TH (6.50 grams per liter). Since the use of filter is not economical in this case, three types of commercial coagulants such as aluminum sulfate, ferric chloride and ferric sulfide have been used in this study. The main parameters such as effectiveness of three inorganic coagulants, ammonium sulfate, ferric sulfate, and ferric chloride, which separately help to remove hardness, have been studied. According to the results, using laboratory test, 25/g of ferric sulfate as coagulant is best coagulant mass and the ratio of 4 to 3 for auxiliary coagulant (sodium carbonate and sodium hydroxide) to coagulant will be best ratio. Also, the mixing rate of 120 rpm in the first reactor will give the best mixing speed. These conditions will lead to 0.348 grams per liter of TDS, 0.345 grams per liter of TH and 0.195 grams per liter of calcium hardness and 300 micro Siemens electrical conductivity of the purified sample.

Keywords

Inorganic Coagulants, Softening Process, Total Dissolved Solids, Total Hardness Removal, Wastewater Treatment

1. Introduction

Water shortage includes water stress and water crisis. The concept of water stress is new, relatively. The meaning of water stress is hardness in finding sources of fresh water for use, which is caused by depletion of resources [1]. A water crisis is a situation in which potable and unpolluted water in an area is less than its demand. The usual approach of ranking countries is based on amount of water resources available per year per [2]. For example, according to the Fallen mark water stress index, a country or region is said to have "water stress" when its annual water resources are less than 1700 cubic meters per person per year [3]. At a level between 1700 and 1000 cubic meters per person per year, periodic or limited water shortages can be expected. When water resources are less than 1000 cubic meters per person per year, the country is facing "water shortage" [4]. FAO affiliated with the United Nations states that by 2025, 1.9 billion people will live in countries or regions with absolute water shortage and two-thirds of the world's population will be under stressful conditions [5]. Another measure, as part of a broader assessment of water management in 2007, aimed to relate water availability and how resources are used. Therefore, water shortage was divided into two "physical" and "economic" parts. Physical water scarcity is when there is not enough water to meet all demands, including water needed for effective ecosystem functioning [6]. Arid regions often suffer from physical water shortages. Sometimes it seems that water is abundant, but somewhere resources are overused, such as when hydraulic infrastructure for irrigation is overdeveloped. Signs of physical water shortage are: environmental degradation and reduction of underground water. It should be known that water stress damages living organisms because every organism needs water to live [7]. Lack of economic water is caused by the lack of investment in water or the inability of humans to meet its demand. Symptoms of economic water shortage include the lack of infrastructure with people often needing to fetch water from the river for domestic and agricultural use. As large parts of Africa experience economic water scarcity, increasing water infrastructure in these regions can help reduce poverty. The critical conditions often arise for communities that are economically poor and politically weak and live in dry environments [8]. In other countries, like India, people are also suffering from water shortage. As in India water scarcity is a big problem. People go to well to get water for their daily needs. They provide water from 40 to 50 kilometers away from their village. Fifty years ago, when the population on the planet was less than half its current population, it was common knowledge that water was an infinite resource. People weren't as rich as they are today, consumed fewer calories and ate less meat, so less water was needed to produce food. They needed a third of the volume of water we currently extract from the river [9]. Today, the competition for water resources is much more intense. The reason is that there are currently more than seven billion people on earth, the consumption of meat and vegetables and water is increasing, and competition for water in the industrial, urban and biofuel sectors is increasing. The total amount of fresh water resources has also decreased due to climate changes that have caused the retreat of natural glaciers, reduced river flow and shrinking of lakes. Many over-pumped aquifers (groundwater aquifers) do not refill quickly [10]. To avoid a global water crisis, farmers must work to increase productivity and meet growing demands for food production, while industries and cities seek to find ways to better use water. The use of wastewater has attracted attention of those industries that have felt the lack of water. Water contains dissolved solids and salt. The water flow from the multi-purpose poly distillation unit is revealed from reject flow section for the feed flow of the reverse osmosis unit. Most of the industries close to sea discharge wastewater from the salty water of the desalination units directly into the sea, and this factor causes water salinity and shock to aquatic life and organisms [11]. In the basic softening process, pre-treatment is used and for this purpose they are used to produce salt and drinking water. During the pre-treatment process, the total hardness is due to the presence of magnesium and calcium salts, it is also possible to produce sodium chloride salt from the effluent. The removal of total water hardness is a function of several factors such as the speed of mixing in the reactor, the amount of sodium carbonate, the amount of sodium hydroxide and also the amount of added coagulant to the process [12]. In this study, three commercial coagulants (with a concentration of 10 g/liter), ferric sulfate 98% by weight, ferric chloride 97% by weight, and aluminum sulfate (alum) 98%, individually and in combination, were used for flocculation. In order to find the optimal amounts of main coagulants and auxiliary coagulants, we have used laboratory test, and then according to the optimal mass of coagulants and auxiliary coagulants obtained, we have used an appropriate amount of them in the pre-treatment reactors. Therefore, experiments have been conducted with the aim of finding the optimal values of the above factors.

2. Materials and Method

2.1. Test Method

First, the temperature, pH, total amount of dissolved solids in water, total hardness and alkalinity of a 6-liter sample of the saline effluent from the multi-stage distillation unit of the petrochemical complex were measured, and then this sample was sent into the first pre-treatment reactor. After that, temperature and pH are measured before and after coagulant injection. Then calculated amounts of sodium hydroxide with a purity of 99.4% by weight and sodium carbonate with a purity of 99.2% are added to the process and the solution is stirred for 2 minutes at different speeds. After 2 minutes, open connecting valve between the first and second reaction parts so that the solution is transferred to the second pre-treatment reaction part. There, the solution is stirred for 8 minutes with a mixing speed of 50 rpm. The following chemical reactions in the coagulation stage for each of the coagulants, it is as follows. The coagulation mechanism of calcium hydroxide carbonate with each of the coagulants is shown in reactions (1) to (3). The precipitation of calcium sulfate and calcium chloride from the effluent was separated.

$$\operatorname{Al}_{2}(\operatorname{SO}_{4})_{3} + 3\operatorname{Ca}(\operatorname{HCO}_{3})_{2} \leftrightarrow 2\operatorname{Al}(\operatorname{OH})_{3} + 3\operatorname{CaSO}_{4} + 6\operatorname{CO}_{2}$$
(1)

$$\operatorname{Fe}_{2}(\operatorname{SO}_{4})_{3} + 3\operatorname{Ca}(\operatorname{HCO}_{3})_{2} \leftrightarrow 2\operatorname{Fe}(\operatorname{OH})_{3} + 3\operatorname{CaSO}_{4} + 6\operatorname{CO}_{2}$$
(2)

$$\operatorname{FeCl}_{3} + 3/2\operatorname{Ca}(\operatorname{HCO}_{3})_{2} \leftrightarrow \operatorname{Fe}(\operatorname{OH})_{3} + 3/2\operatorname{CaCl}_{2} + 3\operatorname{CO}_{2}$$
(3)

During these reactions, carbonate hardness is removed and produces products in the form of sediment and gas, which are removed from the effluent phase. Using carbonate and sodium hydroxide as a coagulant will remove hardness temporarily and permanently and turn it into magnesium hydroxide and calcium carbonate. These particles are small and need a long time to settle. By using inorganic coagulants in special conditions, time required for coagulation and flocculation stages as well as sedimentation is short, and as a result, product limitations are minimized. The determination of optimal amounts of sodium hydroxide and sodium carbonate, as well as the optimal and natural conditions of the pretreatment process, depend on the type and dosage of coagulants. The performance of coagulants should be checked and evaluated so that the total hardness is minimized and the resulting effluent is more transparent.

2.2. Experimental Investigation

The coagulation method with mineral coagulants has been used to separate the present ions in the wastewater and obtain magnesium and calcium hardness. This process takes place in two stirred reactors under the name of coagulation stage (first reactor), flocculation stage (second reactor) and precipitation stage. The reactors are insulated thermally and equipped with a stirrer with the ability to determine the speed of the stirrer. The conical shape at the end of the reactor is considered to be easier to empty and help to settle faster, as well as creating an effective fluid vortex effect. The reactor cycle in the coagulation stage is faster and time is slower compared to the flocculation reactor. In this stage, the goal is to break the bond of inorganic coagulants and make effective contact between the ions dissolved in the effluent and the coagulant ions. In order to effectively remove ions that cause hardness, sodium carbonate and sodium hydroxide are used in this step, and pH regulation is also effective in this step. It is necessary that pH of the effluent is between 7 and 8. The nature of the coagulants in the water causes a decrease in the expected pH. The specific volume of effluent, coagulant, sodium carbonate and sodium hydroxide calculated by laboratory test is poured into the first reactor and mixing is done with a fast cycle for a short period of time.

2.3. Laboratory Equipment

The wastewater treatment process was carried out in two pretreatment reactors. The two conical reactors made of polyvinyl chloride with a capacity of 10 liters were connected consecutively as pre-treatment. The first reactor equipped with a mixer is called a coagulation reactor or a fast reactor. The 6 liters of wastewater, sodium hydroxide and sodium carbonate were added to the reactor along with coagulation. The coagulation mechanism happened with a high speed of the mixture in 2 minute intervals in this reactor. The second slow reactor or coagulation reactor was also equipped with a metal mixer, and the stages of coagula-

tion (8 minutes) and sedimentation are performed in this reactor. The second reactor had two discharge paths, one for the clear flow above the effluent and the other for sediment effluent. **Figure 1** shows the schematic of each of the reactors. The reactions related to the injection of aluminum sulfate, ferric sulfate and ferric chloride are given in the form of relations (1), (2) and (3).

3. Results and Discussion

Experiments were conducted in order to investigate the effect of changing the mixing speed in the first reactor, the type and amount of inorganic coagulants on the quality of the purification process. The amount of carbon dioxide and total hardness, total dissolved solids, temperature, pH, chemical oxygen requirement, biochemical oxygen requirement, calcium and magnesium hardness, sedimentation time and electrical conductivity were considered to provide the quality of the purification process. Three types of common mineral coagulants, aluminum sulfate, trivalent ferric chloride, and trivalent ferric sulfate have been used. The used solutions for each of the coagulants as well as sodium hydroxide and sodium carbonate were made by dissolving 10 grams of each solid in 1 liter of distilled water and then a certain volume was used. We inject 6 liters of wastewater along with soda and different amounts of coagulants obtained by the laboratory test into the first tank and the mixer starts working with a certain speed for 2 minutes. The coagulant is added during the start of the mixer. After that, the entire material is discharged to the second reactor and mixed at 50 rpm for 8 minutes. Then the stirrer is turned off and the effluent is given some time until the clear solution is separated from the coagulated materials containing polluting ions and the turbidity of the clear solution reaches 0.3. The clear solution as a result of pretreatment is discharged and tested.

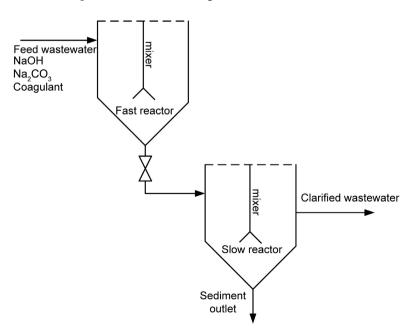


Figure 1. Schematic of the reactors of the pretreatment unit.

3.1. Speed of Mixing in the First Reactor

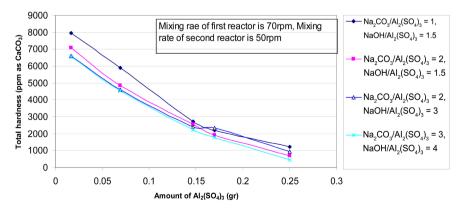
The operating conditions of the two reactors have an effect on the performance of the pretreatment process, and the speed of mixing in the coagulation stage in the first reaction station is one of the most important conditions. In this step, the coagulant is combined with the ions that are supposed to be removed from the water. Therefore, it is obvious that the optimal mixing speed is considered a very important factor to create a suitable interaction between materials. In this study, the speed of mixing in the first pre-treatment reaction, which includes 6 liters of wastewater, has been investigated for each coagulant with different amounts of sodium and soda. In the first coagulation reactor, it is combined with sediments separated from water, so the optimal mixing speed is the most important parameter in creating optimal interactions. The mixing speed of the fast reactor was investigated with different revolutions, 50, 55, 60, 70, 90, 120, 140, 160, 180 and 200 rpm.

3.2. Optimum Ratios of Sodium Carbonate and Sodium Hydroxide to Coagulant Powders

It seems that the effect of soda, soda and coagulant in removing wastewater hardness depends on the ratio of soda to coagulant and soda to coagulant. On the other hand, since one of the main goals of the pretreatment process is limited to the minimum and optimal amount of coagulant used, this study was conducted with the aim of finding the minimum and optimal amount of coagulant, which according to the tests, the minimum optimal amount of coagulant is 25 grams per Liter is considered. At this stage, Laboratory test (1 liter volume) was used to determine the optimal mass of coagulant and auxiliary coagulant. Experiments were conducted to find the appropriate ratio of soda to coagulant and soda to coagulant, so that the results are shown in **Figures 2-4**.

Figure 2 shows that with the increase of aluminum sulfate, the total hardness decreases significantly.

Figure 4 shows that with the increase of ferric sulfate, the total hardness decreases significantly.





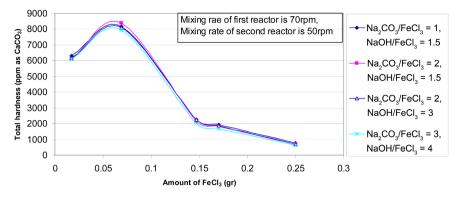


Figure 3. Total hardness changes according to different amounts of ferric chloride.

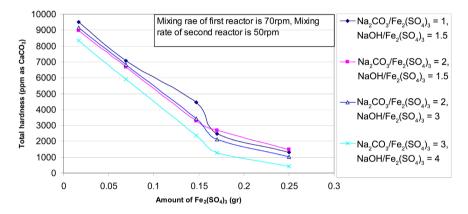


Figure 4. Total hardness changes according to different amounts of ferric sulfate.

The results of the tests in Figure 5 show that the total hardness value when the amount of aluminum sulfate coagulant is 25 g in different ratios of Na₂CO₃ and NaOH to coagulant is around 500 to 1000 mg/liter of carbonate equivalent, also in Figure 3 when the amount of chloride if ferric is equal to 25.0 grams, the total hardness in different proportions of soda and coagulant is about 500 mg/liter carbonate equivalent. Figure 4 indicates that the amount of total hardness in 25/g of ferric sulfate coagulant reaches the limit of 400 mg/liter. The laboratory results show that the convergence of the total hardness value when using 25.0 g of ferric sulfate coagulant is higher than the other two coagulants, which can be an expression of the stronger bond of that coagulant with calcium and magnesium ions in the range of ratios tested for the profit is to the contracting party. According to the fact that in the test, the consumption of each of the coagulants, including ferric sulfate, ferric chloride, and aluminum sulfate, should be determined, so we are looking for this, to examine the purity of each of the coagulants. Since the optimal amount of coagulant is evaluated at 25/g and in this mass amount of coagulant, the total hardness removal percentage decreased by 99.11%, so the amount of 25/g of coagulant is considered as the optimal amount of coagulant used. Also, since the ferric sulfate coagulant had the best effect in reducing the total hardness level for the effluent from Jar, this type of coagulant has a better performance than other coagulants. Therefore, since the purpose

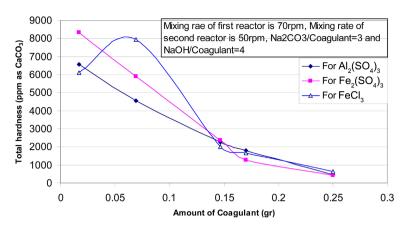


Figure 5. Total hardness changes according to different amounts of coagulants.

of this study is to design a unit for the pretreatment of the effluent from the desalination units and discharged to the marine ecosystem, it has been sought to consider a pretreatment unit that has been examined in this study as a pretreatment reactor. For better dissolution and mixing operations between coagulant and waste water, as well as waste, the de-reactor is used as a pre-treatment unit in the waste water. Also, since many articles consider the amount of coagulant injected into the reactor in the form of a solution in the range of 8 to 15 grams per liter of distilled water, in this study, considering that 25.0 grams of coagulant is examined and since 6 liters of wastewater were used in each coagulant. It takes 25/g to be converted into milliliters of the complexing agent dissolved in one liter of distilled water. Since 10 grams per liter of distilled water has been used for 6 liters of waste water, so 25/g per liter of waste water in the first reactor can be calculated in milliliters to convert it into a function for treating 6 liters of waste water in the first reactor. Therefore, 25/g of each of the coagulants used in the Laboratory test will be equivalent to 150 ml of the coagulant solution that will be injected into the effluent in the first reactor.

3.3. Removing the Total Hardness

The overall hardness is one of the main factors of wastewater quality, which depends on the amount of magnesium and calcium compounds in the wastewater. **Figure 4** and **Figure 5** show the effect of 150 cc of each coagulation at different speeds of the fast reactor mixer. The speed of mixing in this reactor helps to create proper bonds between the hardener ions in the effluent and the ions in the coagulants. Also, this mixing speed forms the optimal collision between coagulant ions and hardness agent ions in the effluent. According to **Figure 6**, the change does not follow a constant increasing or decreasing trend. The minimum value of total hardness is achieved at 120 rpm for all coagulations. All coagulants reduce the total hardness value from the initial value of about 50.6 grams per liter to less than 2 grams per liter at full mixer speed. Increasing the speed of the mixer from 50 rpm to 120 rpm decreases the total hardness, and increasing the speed from 120 to 200 rpm increases the total hardness. Also, ferric sulfate re-

moves the total hardness at 354 mg per liter, which is the best example of all coagulants. This is due to the increasing density and charge density of this compound in relation to the density and density of ferric chloride. Also, sulfate is heavier compared to chloride anion, as a heavier compound is formed when sulfate is coagulated with calcium and magnesium. Subsequently, a lower total hardness is obtained for the clear effluent by using ferric sulfate as a coagulant.

It seems that 120 revolutions per minute is the best mixing speed in the first reactor and the optimal collision and separation occurs at this speed.

3.4. The Amount of Carbon Dioxide Dissolved in the Wastewater for Different Amounts of Coagulant

Figure 7 shows the amount of carbon dioxide dissolved in the wastewater for different amounts of coagulants. As can be seen, when ferric sulfate is used as a coagulant, the interaction of the positive and negative ions of the coagulant, soda, and double-positive ions of calcium and magnesium are increased, as a result, the amount of clots produced is heavier, thus preventing them from being released. The carbon dioxide is sampled in the wastewater, the dissolution of this gas. For this reason, when 150 ml of ferric sulfate is used as a coagulant, the released carbon dioxide reaches 38 grams per liter, and when 300 and 450 ml of coagulant are used, the carbon dioxide dissolved in the wastewater will reach 25 and 20 grams per liter.

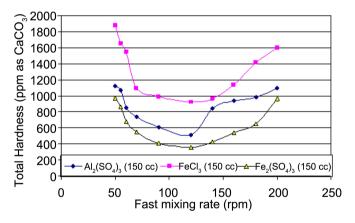


Figure 6. Total hardness versus mixing speed in a series reactor.

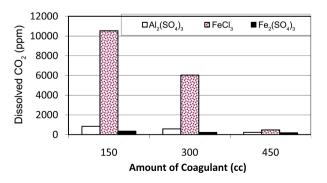


Figure 7. The amount of dissolved carbon dioxide for different amounts of coagulant.

Figure 7 shows that the highest amount of carbon dioxide dissolution is when ferric chloride is used as a coagulant. In the next step, the highest amount of dissolved carbon dioxide is related to the case when aluminum sulfate is used. Laboratory results show that the lowest amount of dissolved carbon dioxide is related to the use of ferric chloride.

4. Conclusion

The purpose of the proposed pre-treatment unit is to soften the effluent and provide nutrient flow for the units of the desalination unit. The main parameters such as the effectiveness of three inorganic coagulants, ammonium sulfate, ferric sulfate, and ferric chloride, have been studied separately. The proposed pre-treatment process is considered as the first process in the desalination process with zero output. In this study, the performance of three types of commercial coagulants such as aluminum sulfate, ferric chloride and ferric sulfide was investigated. According to the results, using laboratory test, 25/g of ferrous sulfate coagulant in one liter is the best coagulant mass and the ratio of 4 to 3 for auxiliary coagulant to coagulant will be best mixing speed. The results indicate that higher the amount of coagulant, the lower the total hardness and the total dissolved solids at low speeds of the fast stirrer. Also, the results indicate that the optimal amount of sodium carbonate and sodium hydroxide for 150 ml of ferric sulfate at 120 rpm is 600 and 450 ml, respectively.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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