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SHMP as Antiscalant for Treating Brackish Water using Reverse Osmosis

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Abstract: One of the most genuine issues found in desalination utilizing reverse osmosis (RO) is concentrate or administration of brine. This concentrate can be utilized as a raw material for production of minerals. The antiscalants present in the RO handle ought to be removed after the process of salt crystallization. The precipitation of the amount of sulfate and carbonate from calcium can be modulated by the antiscalants in the process of reverse osmosis. However, the modulation of calcium phosphate has not been highlighted in literature. This gap in the literature instigated us to explore the activity of the antiscalants in the scaling of calcium phosphate in the RO blocks by a mild method. Nowadays, most RO desalination plants are utilizing phosphorus-based antiscalants to prevent scaling and to realize tall layer execution, as measured by diminished transmembrane weight, salt entry, and expanded saturate stream. In any case, phosphorus antiscalants in brine disposal can be an natural issue that ought to be considered and considered when introducing a desalination plant. Sodium Hexametaphosphate (SHMP) is reckoned excellent antiscalant agent which utilizes to deal with scaling in RO films. The sodium hexametaphosphate solution is prepared by mixing in sodium hexametaphosphate vessel and dosed to the feed water through. However, the apparatus containing sodium hexametaphosphate was highly prone to contamination by bacteria. The amount of bacteria within the apparatus after 36 days of makeup was far too high to be analysed as it reached a value of beyond Too Numerous To Count (TNTC). The polyphosphate can be transformed into orthophosphate in presence of sodium hexametaphosphate solution. The conversion is influenced by parameters like temperature, concentration and different nutrients responsible for the growth of microbes. Thus a study was conducted for the detection of free phosphate in a solution of sodium hexametaphosphate. Since hydrogen sulfide (H_2S) can be generated in raw water, the use of chlorine was averted completely. The tanks and injection lines containing sodium hexametaphosphate solution was disinfected using sodium metabisulfite (SBS). The optimum concentration of sodium metabisulphate solution required for sterilization along with reducing the formation of the free phosphate was studied. The reaction of the SBS in the apparatus containing sodium hexametaphosphate solution was studied. Furthermore the interaction between the SBS with the sodium hexametaphosphate solution in connection with the Microguard Filter (MGF) influencing the efficacy and output of the RO system was studied.

Keywords: Antiscalant, Sodium Metabisulfite (SBS), Sodium Hexametaphosphate (SHMP), Reverse Osmosis (RO)

1. Introduction

Water is an integral component for the living organisms. The percentage of fresh water available for the global population is hardly 3%. The demand for clean water throughout the world has been growing exponentially, which requires efficient techniques to meet the same. It's assessed that less than one percent of the international water supply is effectively available which maintains the adequate quality of water. There will be a dearth of the supply of fresh water in the coming decades as predicted by different studies. Since water availability consolidates both water quality and sum, diminishment in jeopardizing water due to water defilement development reduces the available water. Different organisations have been established across the world to authorise and authenticate the techniques used for cleaning water. The drawbacks associated with the techniques adopted while producing clean water should be meticulously addressed. Almost sixty seven percent water is lost during the purification procedure which can be recovered by utilizing modified water treatment techniques. Thus water purification procedure should be efficiently managed and the people should be made aware about the conservation of water.

RO plays a primary role in the arena of freshwater and supply water. The technique of inorganic scaling is an unflinching issue inside the RO desalination arrangement. There are multiple techniques for modifying the scaling of the RO systems like improvement of the materials present in the scaling layer, pretreatment of the hard water, modification of the antiscalants and standarisation of the methods of operation. The modulation of the layer scaling by investigation of different antiscalants is a cheap and facile process among the aforementioned techniques. Different types of antiscalants along with their utilization in the control of the scaling in the RO layer has been intensively studied in the present research. There are numerous drawbacks associated with the antiscalants for decreasing the scaling on the RO film, like movement of the bacteria, control of the effective doses, the proper concentration and fouling caused by the antiscalants. Thus there is an increasing demand for the search of environmentally acceptable antiscalants with high potency. The integration of the antiscalants with different established pretreatment agents and their optimization is pivotal for preventing the scaling.

The membrane filtration technique utilized within the desalination industry boasts natural benefits and energy effectiveness, in this manner it is favored over the thermal desalination procedures (Ashfaq, Al-Ghouti, Qiblawey, Zouari, Rodrigues & Hu, 2019). Despite its predominant qualities, the execution and treatment effectiveness of the layer filtration strategy is still undermined by natural, inorganic, colloidal

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and natural film fouling (Ashfaq, Al-Ghouti, Al Disi & Zouari, 2020). Depending on their feedwater concentration, these foulants frequently display at the identical time and associated with one another (Ashfaq, Al-Ghouti, Qiblawey, Rodrigues, Hu & Zouari, 2019b). Feedwater contains all foulant sorts, counting natural, inorganic, microbial, and colloidal foulants (Ashfaq et al., 2020). Subsequently, examination of the intuitive between these foulants is vital to way better understand the component and related seriousness of membrane fouling. (Liu, Xu, and Das 2019) worked on investigating the effectivness of biological fouling and scaling stated that organic foulants boost scaling by minimizing nucleation time, thereby increasing flux decline. Another study illustrates that the microorganisms in reverse osmosis systems affect biofouling and intensifies microorganic fouling by secreting carbohydrates and extracellular polymeric substances (EPS) (Butt, Rahman & Baduruthamal, 1997). Moreover, in regions where seawater temperature matches the optimal range for microbial growth, as in the Middle East, biofouling in the desalination industry is particularly problematic and common (Al-Ahmad, Abdul Aleem, Mutiri & Ubaisy, 2000). Biofouling affects 82% of RO plants and 70% of the seawater RO plants worldwide and cannot be avoided because of the rapid growth rate of microorganisms (Ashfaq, Al-Ghouti, Qiblawey, Zouari, et al., 2019).

(Mangal et al. 2021) studied the effectiveness of 8 different types of antiscalants for hindering the scaling by calcium phosphate in absence of acids, during reverse osmosis. It has been revealed from literature that the issue of scaling by calcium phosphate is debatable. Although, some groups have reported high rate of calcium phosphate scaling at similar parameters (temperature, concentration of phosphate and calcium, pH), other groups have reported the same at lesser rate. There was a remarkable decrease in the flux in presence of the amorphous phase of calcium phosphate introduced in the membranes of the reverse osmosis system. 85% of the synthetic concentrate was obtained. However, the surface of the membrane of TW30-1812-50 RO system was found to be covered by granules of amorphous calcium phosphate particles during the experiments in presence of antiscalants at a concentration of 33.3%. In the study by (Ashfaq et al., 2020) scalants are compounds that reason of inorganic fouling and mineral scaling in reverse osmosis systems. The scalants used in his study are alkaline and non-alkaline scales calcium sulfate, calcium carbonate, strontium sulfate ($SrSO_4$) and barium sulfate ($BaSO_4$). Other scales include calcium fluoride (CaF) and silica (SiO_2) which are equally problematic. According to (Ashfaq et al., 2020) that the supplement of antiscalants prevents these scalants, from causing inorganic fouling or scaling in reverse osmosis plants. Also the (Ashfaq et al., 2020) in the article related to the subject that these antiscalants are instrumental in maintaining high recovery rates, maximized energy consumption and reverse osmosis plant longevity. While the article given by (Saleem & Zaidi, 2020) related to organic polymers resembling poly maleic acid but the study extended to add polyacrylic acid (PAA) and poly maleic acid (PMA) are the key components in the commercial antiscalant market. In the research paper written by (Van Driessche, Stawski & Kellermeier, 2019) that the interaction amongst antiscalants and biofoulant in reverse osmosis systems has not been adequately investigated, especially considering the vast variety of bioprocesses involved and their influence on the production of minerals. Van Driessche et al., 2019 reported that the metabolic activities of the bacteria can directly develop supersaturation environments for the minerals and bacterial cells and EPS indirectly as a template for nucleation. Given that carbonates, sulfates and other minerals behave like scalants in reverse osmosis plants, these microorganisms-scalant interactions may lead to further membrane fouling.(Al-Roomi and Hussain 2016) classified the antiscalant into two categories namely antiscalants devoid of phosphorus and antiscalants containing phosphorus. The antiscalants containing phosphorus existed as phosphates as well as phosphonates. (Finch and Rashchi 2000) reported a process to characterize the compounds [sodium hexametaphosphate (SHMP) and sodium tripolyphosphate] that contain orthophosphate particle ($PO_4$3-) group from P–O group. The phosphonates contain one or more C-PO(OH)2 groups and are more active than phosphates as they are in the vicinity of the covalent bong formed by carbon and phosphorus(Nowack 2003). The geometry of a few ordinary phosphonates follow the patterns of ordinary polyphosphates. Both phosphonates and phosphates can be utilized as complexing specialists in numerous cases based on their capacity to form complexes.(Finch and Rashchi 2000) Rashchi and Finch, 2000 stated that the phosphate was found to accelerate the activity of scaling at a faster pace by forming soluble metal complexes. In any case, it has been revealed from the literary works of Al-Roomi and Hussain, 2015; Li et al., 2017 that the hydrolysis of phosphates to orthophosphate is facile in presence of calcium particles which in turn boosts the process of biofouling. Thus compared to phosphates, phosphonates have a broader possibility of applications since it retards the process of biofouling to greater extent (Matin et al. 2019) (Tong et al. 2019). The chemical compositions are the basis of classifications of the mineral scaling process. Thus the mineral scaling has been classified as silica based scaling and metal-ion based scaling. The compounds [calcium sulfate, calcium carbonate, strontium sulfate

($SrSO_4$) and barium sulfate ($BaSO_4$)] used in metal ion based scales are obtained through the process of crystallization (Martin et al, 2019). The collision between the particles is initiated under the condition when the concentration of the salt is more than that of the salts soluble in the solvent. The particles form clusters leading to the generation of a micronuclei. The nucleation centres are generated at the micronuclei and the particles align forming an order to create steady cores. Thus the growth of the crystal from the cores is known as scale arrangement.

(Topçu et al. 2017) have categorized the silica-based scaling as metal scaling and silica scaling. The process of silica-based scale faces limitations due to silica polymerization and the aggregation of shapeless colloidal silica. These conditions depends on different parameters like temperature, pH and ionic quality, silica concentration(Bush et al. 2018).

Silica polymerization is formed by elimination of water from the molecules to form Si–O–Si anhydrides which arranges to form the polymers. Thus the molecule of $Si(OH)_4$ initially dimerises to form $Si(OH)_3$-O-$Si(OH)_3$ followed by oligomers, colloidal polymers and finally polymers of $(SiO_2)_n$.When the silica compounds come in vicinity of multivalent cations the solubility of the silica derivatives is diminished. Thus metal silicates precipitate out during the process.

Fouling

Fouling is a long standing problem in the inverse osmosis plants used for the purification of water as the removal of pollutants is hindered by fouling. The films used in switch osmosis is highly contaminated due to fouling which affects the potency of the process. The contaminants include organic materials, colloidal particles and suspended solids (Winter, 1995). There are four different types of fouling process in switch osmosis namely biofouling, inorganic or scaling, natural and particulate fouling. Biofouling is still a challenging problem as the biological particles cannot be discarded through the process of pre-treatments. Apart from biofouling, the other types of components responsible for fouling can be removed by well-developed pre-treatment techniques. The components responsible for fouling the membranes in switch osmosis are removed effectively through pretreatment procedures.

There is an inter-relation between the parameters used for estimating the fouling of membranes and water encompassing the characteristics like electrical conductivity of the materials to their properties in their dissociated forms. The parameters are collectively termed as Potential Fouling Water Quality Parameters (PFWQPs). The properties like turbidity, solids which remain suspended and dissolved elements of PFWQP can be eliminated by standard pre-treatment procedure. However, the pharmaceutical companies are still demanding the recognition of other parameters like compounds affecting the endocrine, microorganisms and colloidal particles as PFWQP for removal by a secondary pre-treatment procedure. The elimination of these foulants through pre-treatments can aid in the treatment of water and furthermore make is economical. Different foulants and their available pre-treatments for reverse osmosis will be taken up in this study. Ahmed et al., 1989 studied the fouling issue for a switch osmosis plant at Ras Abu Jarjur in the Kingdom of Bahrain. The ground water of the area is contaminated with significant amount of H_2S and experiments were conducted to resolve this issue. The group found that the SHMP in the tanks were the major source of normal interaction which was obtained from the TBC values inside the SHMP tanks. Since free phosphate (orthophosphate) is toxic for living things, the orthophosphate was converted to SHMP. SHMP is a polyphosphate whose conversion into orthophosphate is affected by parameters like pH, concentration and temperature. Chlorine was restricted in the process of conversion due to the presence of H_2S in the water.

The SHMP tanks and infusion lines were sterilized with sodium metabisulfite (SBS). There has been investigation of the optimal amount of SBS to be added to the apparatus containing SHMP, such that the reversal to form orthophosphate is limited. Thus the amount of SBS within the SHMP tanks has to be estimated based on the Micron Observe Channel (MGF) condition and operation of the turn around osmosis.

The solubility and ionic properties of the antiscalants which are ionic in nature are highly affected by the pH, thereby impacting the operation of the system (Prihasto et al., 2009; Qin et al., 2005;(Tong et al. 2019). For instance, the soluble carbonate salts depends drastically on the pH values. The carbonates alters into bicarbonates with the decrease in the pH values and the slobility increases (Prihasto et al., 2009; (Tong et al. 2019). Another study revealed that pH affected the rate of scaling in reverse osmosis (Qin et al. 2005). They studied the scaling process in a nickel-plating company and found that moo bolster pH evolved in a moo fouling process of the reverse osmosis layer at the scaling end. Alternately, the solubility of the amorphous SiO_2 at acidic and neutral pH is moderate which enhances when the pH value is within 8-9 (Milne et al., 2014;(Tong et al. 2019)). Thus pre-treatment based on pH to eliminate silica was studied by (Bush et al. 2018). They reported that pre-treatment techniques like acidification and alkalization were effective for averting the silica scaling when the pH value is maintained at a level higher than 10 or lower than 5. The arrangement of the ionic species in H3SiO4 and H2SiO4 along with the polymerization of silica in acidic condition lowers its solubility (Bush et al. 2018)(Tong et al. 2019). The ionic scalants get deprotonated with the increase in the value of pH. The interaction between the compounds responsible for scaling and antiscalants influence the performance of the antiscalants (Ang et al. 2016).

Rahardianto et al. (2008) has reported that the influence of pH at values (pH = 6.4 and pH = 7.9) on antiscalant performance in reverse osmosis with high gypsum scaling was not substantially remarkable. This was attributed to the fact that the antiscalant was completely ionized at pH value higher than 6.0. (Ruiz-Agudo et al. 2016)has indicated that the bond of a commercial copolymer behaving as antiscalant formed by a combination of copolymer (allyl sulfonic acid /maleic acid) with phosphonate groups and complex Ba2+ ion augmented with heightening the pH. The enhancement in the deprotonation of the acidic counterpart at pH 10 as compared to pH 6 resulted in this phenomenon. Again the effect of pH was studied in bolster water by adding Ca2+ ions on the bovine serum of egg whites (BSA) by modulating the polyaspartic corrosive particles (PASP)(Yang, Liu, and Li 2010). They found that the fouling diminished at pH value of 7.0 as compared to that of 4.9, which is the isoelectric point of BSA. The electrostatic repulsion between the BSA and the absorbed BSA on the RO layer hindered the deposition of the BSA at the neutral pH. The complex formed by the BSA and Ca on the surface of the film is made stable by PASP added to water due to the formation of BSA–Ca–PASP complexes which are soluble in water at the desired pH(Yang, Liu, and Li 2010).

Inhibitor

Ituen et al., 2017 studied a variety of inhibitors used to examine both the arrangement of scale and disintegration of the surface layer. They studied various disintegration and scale edge inhibitors such as characteristic phosphonate and common phosphine. They also investigated the destructive nature of the polycarboxylic acids. Disintegration and scale inhibitors are divided into as either phosphorus-free inhibitors and phosphorus-containing inhibitors. The phosphorus-free inhibitors are predominantly used around the world as its operation is cheap. Nevertheless, these inhibitors are non-biodegradable, thus polluting the world along with biofouling of film systems. Consequently, there has been a prominent demand for effective environmental friendly and scale inhibitors with adequate potency. The efficacy of the presently available inhibitors (hydroxylic, carboxylic, and acylamido) have been thwarted due to strong molecular chelation.

The organic materials synthesized by living organisms are potential disintegration and scale inhibitors as they contain broad entireties of these valuable bunches. Extracellular polymeric substances (EPS) are a mixture of polymers with high molecular weight containing proteins, polysaccharides, glycoproteins, lipids and humic acid like substances which possess the ability to interact with the solid surfaces by forming a layer (Wang et al., 2018). Thus the EPS film prevent the molecules like oxygen and chloride to reach the surface of the metals. The proteins and humic acid like materials complexes with the Ca and hinder the scaling. There are two types of EPS: EPS which remain linked to the cells and are difficult to dissolve and EPS which are easily removed from the cells (s-EPS). The s-EPS have superior performance between the two like high capacity to transfer protonic particles, biosorption of solids and good biodegradability. Additionally, the s-EPS are cheap and bio-renewable, making them a better choice as scale inhibition and anti-corrosion agents.

The EPS of Bacillus cereus (B. cereus) have the capability to adsorb into multiple surfaces like carbon steel, stainless steel (SS), conveyer belts and floors. The corrosion of the SS was retarded by the biofilm formed by B. cereus in seawater containing 90% of the EPS (S. Li et al. 2019). Complexes are formed by the interaction of the s-EPS of B. cereus and hinder the arrangement of the calcium carbonate. However, the application of the s-EPS as scale inhibitors are very scarce. This study focused the s-EPS induced biomineralization obtained from B. cereus. The corrosion activities were examined on 316L SS in commercial seawater. The s-EPS is a potent candidate for preventing double bio-functional erosion along with inhibiting scaling in seawater environment.

Mungal M N et al (2020) reported that antiscalants (A/S) or scale inhibitors containing phosphonate, sulphonate or carboxylic groups may chelate with groups like zeolites, alum and carbon. The scale inhibitors are classified as antiscalants or edge inhibitors. The edge inhibitors are potent in their activity. The most prevalent chelating agents is EDTA (tetra sodium salt of ethylene diamine) used for controlling the hardness (at pH > 6.0). Antiscalants form salts by scaling the minerals. The A/S hinder the formation of valuable stones like pearls and do not move out into the suspension. Certain scale inhibitors are equipped with dispersants that aids in increasing the rate of suspension. The antiscalants can increase the softness when the hardness of the water is lower than 100 ppm. A/S was designed using flush cycle which operates automatically in the RO/NF system after the shutdown of the system. This thwarted the scaling by concentrated salts on the side of the membrane surface rejected by the feed. Antiscalants can be used either alone or with acid feeds. When corrosive agent is added to an A/S, as in LSI it is an excellent tool. The value of 1.0 is satisfactory in spite of the fact that a few A/S producers claim an LSI with a value of 2.7 is worthy when utilizing their prescribed item. The dose of A/S lies between a value of 2 to 10 ppm, depending on the potential of scale-forming in the RO bolster water, item water recuperation, and proposals from the A/S manufacturer. The greatest benefit of a better LSI venerate is that the RO/NF system would be able to perform at higher efficacy thus decreasing the cost. The higher improvement stems from the higher salt concentration within the feed–reject channel. The sparingly dissolvable salts can supersede their solvency limits at a faster rate. The long performance recovery is a choice when enhancing the production by integration of a second-pass reverse osmosis plant until the sustained water is perfectly purified.

Sodium hexametaphosphate (SHMP) could be an edge operator that determined from the lack of hydration of orthophosphoric destructive. The compound is utilized to curb the scaling of compounds like metallic sulfate and calcium carbonate. It is most broadly utilized since it offers awesome obstacle at a moo taken a toll. It depends on the sulfate and calcium concentration along with that of CF and the estimation is inside the run of 2–5 ppm. The precipitation of the calcium sulfate by SHMP is around 150% based on the submersion control. However, the organophosphates are an superior to SHMP based on their capability to hydrolyse faster, but are more expensive. The organophosphates hinder the scaling and diffuse faster as compared to SHMP. In this line, polyacrylic acids (PAA) are better at retarding scaling and exhibit uniform distribution as compared to SHMP.

The atomic weight of PAA is very high which also has high anti-scaling properties. The multivalent cations (Al) or the cationic polyelectrolytes cause precipitation and sleet and thereby foul the layers. The inhibitors mixed inhibitors obtained by combining PAA with atomic weight (6,000–25,000 Da), moo with atomic weight (2,000–5,000 Da) along with organophosphates exhibit good dispersive properties and behave as good inhibitors. Accurate dosing of antiscalants are required for preventing fouling, as higher or lower dose have the capability to foul. A higher dose of antiscalants causes biofouling with the formation of complexes of hard ions. The organic substances are a good source of food for the microorganisms.

Successful assessment of inhibition performance can suggest a better guidance for the selection of antiscalants and its amounts for its effective deployment in procedure. The point by point operation strategies for the assessment of scale restraint execution are separated into two major categories encompass both inactive and energetic strategies . The static methods comprises of the static jar test (Yu et al. 2006), bubble, turbidity method (Rabizadeh et al., 2017) and conductivity method (Goh et al., 2018), using the relentless composition and precipitation technique. The foremost common inactive strategy is the inactive jolt test due to its clear operation. The clear restraint proficiency is assessed specifically by alteration in the concentration of the solute. The effects of the antiscalants can be observed by using X-ray diffraction and electron microscopy. These analytical methods are also used for detection the alteration of the scale in the morphology of the crystal and also examine the distortion in the crystal. Thus its impediment is that diverse conditions appear between the inactive jostle test and viable applications. In this way the gotten comes about and conflicting with numerous commonsense conditions and are not totally pertinent. Impressive contrasts from down to earth application conditions moreover exists in other inactive strategies. In spite of the fact that the comes about from these strategies are improper for commonsense applications, they are reasonable as pre-evaluation approaches. In a varieties of articles related to the given authors that(Al-Roomi et al., 2015; Al-Roomi and Hussain, 2015, 2016) worked broadly on the energetic strategies which found to be able to supply valid comes about for the down to earth pertinence of antiscalants by recreating the viable conditions. A RO unit in the laboratory scale is used for mimicking the RO handle for examining the prevention of scaling in the active RO framework. The resistance in the scaling can be examined by making a comparative study on the alteration in the flux of the substrate either with the antiscalant expansion or without the same. The surface film can be visualized through an electron microscope for the analysis of the surface of the scale and thickness of the surface. These parameters influence the activities of the antiscalants in the RO(Thompson et al. 2017). The operational parameters like nourish spacer, crossflow speed and counting weight can be modified using the RO diversion tests. The results from the simulation tests of dynamic RO has been more promising.

As of now, AFCs are utilized to decrease the quantity of suspended solids and adsorbing biological phenomena, in show disdain toward of is special plans work to empty hydrocarbons inside the feed water. Clarify the typical arrange of a high brackish RO plant. In the work done by (Kah et al., 2011) regarding the RO desalination execution is subordinate on the quality of the feed water and the advantage life of the membrane surfaces. Generation decay takes after a anticipated way, but the rate of decay is straight forwardly influenced by the adequacy of pre-treatment and strategy of operation and support. Thus, and, according to (Devin, 2012) that suitable monitoring and support will bring the decrease near to the targeted value. The remedial measures to move forward RO Piece execution are coordinates within the pre- treatment system. In any case, the ultimate alteration happens within the RO generation area, where the chief cleaning degree is the RO membranes cleaning program. The manufacturer's rules are broadly utilized.

In any case, as more information got to be accessible, it transpired that the manufacturer's cleaning rules were not reliably compelling. Hence, modern cleaning programs were defined that utilized prescribed chemicals congruous with the RO films. It is customary hone to perform a 5000 ppm SBS dousing for 72 hours taken after by flushing with essential water at whatever point there's a fast decay in generation of any RO Square.

SHMP could be a potential source of oxygen consuming microscopic organisms in its free phosphate shape. Without observing, it may increment bacterial stack on the RO block when injected as an antiscalant. Introducing cartridge watch channels within the RO shock treatment line does not specifically eliminate bacterial action so it could be a tried-and-true defense against inorganic foulants from the SBS tanks. Previously, the common hone was to arrange the cartridge components utilized within the MGF vessel. But due to the swelled taken a toll of these components, different strategies are attempted to clean these elements.

Literature recommends continuing operation exploiting the subsequent protocols and procedures: 1) Regular sterilization of Dual Media Filters; 2) Routine restoration of ACFs; 3) Regular MGF and well collector pipe sterilization; 4) Use of SBS for shock treatment of RO membranes; 5) Use of SBS for regular RO membrane sterilization; 6) Routine SHMP tank sterilization. ACFs are employed to absorb H2S gas for a limited time until saturation.

A study completed in xxxx explored the xxxxxxx and concluded xxxxxx. Then discuss what was lacking in the study/ say how new evidence has come to light and reference. What is the difference between the previous experiment design and this this design?The current aims to update those finds by investing the xxxxxx

2. Materials and Methods

The Test Skid Unit

This test skid is an experimental tool used to simulate realistic RO conditions on small scale for comparison. The brackish RO desalination test skid used extracted its raw and highly brackish ground feed water from high saline deep wells and contained approximately 2 – 5 ppm of dissolved sulfides. The test utilized 3 filtration processes and a unit of RO blocks as illustrated in Figure 1. In this investigation, the Dual Media Filters, MGF and well collector pipes were regularly sterilized to avoid any bacterial or biological growth colonies. ACFs were routinely restored by 2 ppm and may goes to 4000 ppm. SBS was used for shock treatment of RO membranes and RO membrane sterilization. Additionally, SHMP tanks were also regularly sterilized. These processes were standardly employed as recommended. Zero pre-chlorination and a closed pressurized structure was kept up to the gas stripping system of hydrogen sulfide in the post treatment zone to dodge discuss oxidation. Broken up sulfides might oxidize to natural sulfur and may attrack colloidal fouling within the plant. This test skid takes after the central plan and operation of a ordinary high brackish RO

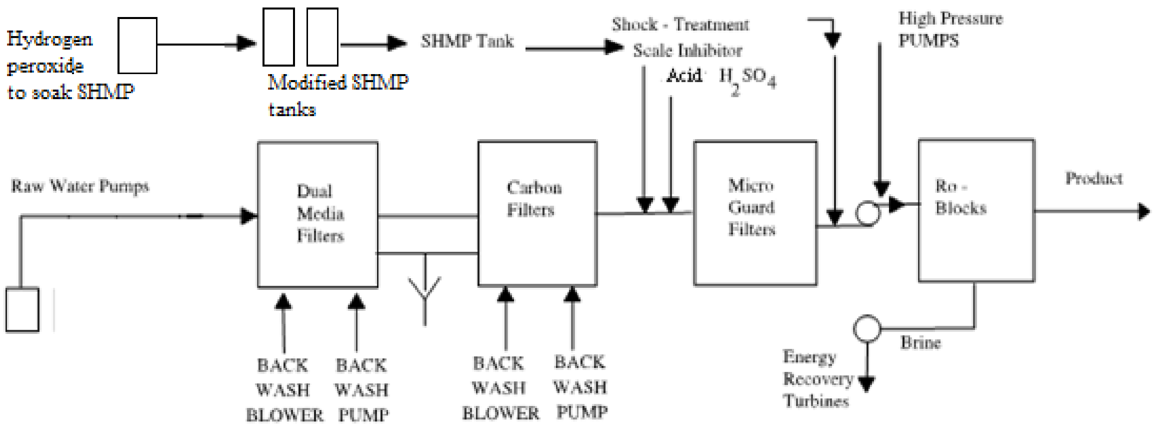


Figure 1: Layout of test skid used to simulate RO conditions

Pre- Treatment System

The pre-treatment process involves thorough filtration of feedwater obtained with raw water pumps. The first filtration started at the Dual Media Filters and were periodically chlorinated offline. Thereafter, the raw water passed via the Activated Carbon Filters (AFCs). The AFCs and sulphuric acid were dosed. Pre-treatment chemicals were dosed, then dosed by SHMP in the in-line mixer. This was done to control both alkaline and non-alkaline scaling. Micron Guard Filtration was the final pre-treatment process before the feedwater entered the RO membrane. Polypropylene filters of 1-5 micro pore sized and 10 micron pore size utilized in a while, indeed littler pore sizes are exploited to maintain a strategic distance from infiltration of substances that cause unmistakable fouling. The resultant bolster water was considered totally congruous with the RO films and pressurized by tall weight pumps at that point encouraged into the RO Blocks.

The over-all recovery 68-72% and expected to increase if required to 80%. Produced water was sent to draw back tanks and after that injected to furthermore acidity with sulfuric corrosive to pH 4.5. This was done to release H2S gas for following expulsion inside the gas stripping towers. The degasified water is at that point infuse with the post-treatment Cl2. The third arrange rejected concentrated brine stagging system This was done to discharge H2S gas for ensuing removal within the gas stripping towers. Once the product is ready to move for production would be chlorinated to disinfection.

The test skid operation and execution were considered palatable as SHMP and SBS blend. SHMP was dispersed within the dechlorinated water in numerous concentrations of 10 ppm and 7%. One of the earliest issues recognized was the over-the-top bacterial development within the Dual Media Filters and ACFs. Trial to use Hydrogen peroxide (H2O2) to long term disinfect the vessel successful and the additional vessel for SHMP solution was fabricated here to prolong the disinfect and kept biological accepted to operate the sodium hexametaphosphate away from bacteria breakthrough. The hydrogen sulfide gas smell and expanding sums of Dissolved oxygen (DO) within the pre-treatment system displayed. Examinations and studies were executed to investigate fitting arrangements. The findings come about in early alterations to the pre-treatment framework which are presently connected to the plants. It is obvious now that sterility must be kept up through each treatment organize by portray as it were restrained algal development and extra measures ought to be implemented to direct bacterial action.

As a result, the following protocols were formulated and enforced for the continual sterilization of DMF exploiting 1000 ppm, Cl2 injection to two DM/F on daily base and pressurized air with backwashing and lengthier rinse duration to make sure thorough Cl2 removal prior to placing the filter online; shorter filter component substitution of the MGF (day cycle) was used here to play further clean the items. The sodium bisulfite was increased to 10000ppm. Including SBS, a well-known bactericide, to control oxygen consuming levels and dispense with time devouring offline chlorine sterilization of the SHMP vessels ; Micron guard cartridge filters were installed in the RO shock treatment line. MGF vessels was pressurized in this trial and make it to undergo chlorine sterilization for the period of planned maintenance outages.

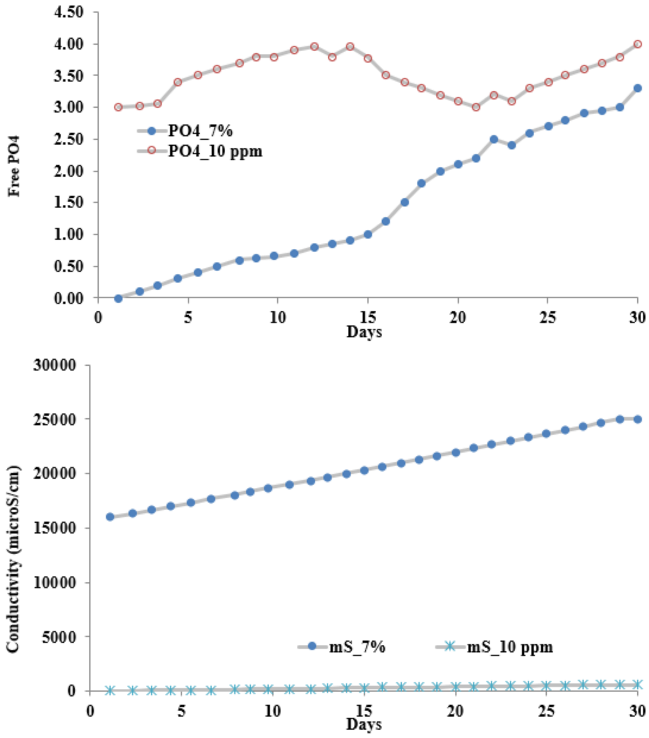
SHMP and SBS

As the SHMP tank is designed to supply the unit with SHMP solution varying form different percentage aiming to sustain the flow of the stream with sterilized antiscalant and maintain the flow to zero bacterial and biological material. To mimic the SHMP vessel, a variety of concentrations of sodium bisulfite were added to a seven percent of SHMP solution and studied to determine for free phosphate, EC, pH and TBC. Eventually, the RO Blocks present a decline in production, elevated deferential pressure, and salt passage. When the foulants affected the conditions and the MGF cartridge elements started to get deteriorated, along with high ΔP and low rate of flow, the aerobic bacteria was eliminated from SHMP tanks entering the system by a modified method. This modification involved the daily add-on of 0.25% solution in SHMP tanks flow into the system to improve water quality, stabilize the flow rate and lower ΔP. Furthermore, MGF vessels will be hold close online for 16 weeks after the shutdown, yielding in a significant progress. Visual inspection also illustrated that the elements were clean for four weeks with only a faint odor, which could be attributed to the presence of the anaerobic bacteria in the untreated water and infection during installation of the elements. To maintain a clean system and eliminate the odor at the bottom of the MGF vessel, soaking the vessel up to the outlet header with five percent H_2O_2 for four hours prior to element installation was proposed. Earlier, the use period of MGFs was more than four weeks. However, because of low flow, elevated SDI and differential pressure, the service period was reduced.

At last, these components were splashed in 5000 - 6000 ppm chlorine arrangement for 24 hours taken after by water streaming, which reestablished the components. When these renewed elements were installed, silt density index (SDI), ΔP, and flow rates were measured

4.0 Behavior of SHMP Solution

SHMP was dissolved in the chlorine free water with a variety of concentrations ranging from ten ppm and seven percent. The yields are presented in Figure 2 and illustrate the behavior of SHMP in raw brackish water. Approximately 25% of unique polyphosphates solution returns to orthophosphate at 10 ppm to be available in the mix solution. Free phosphate returned in high solution mixed concentration (seven percent) and no increment of free phosphate is watched amid this period. The pH and electrical conductivities readings were steadily increment with time, but more variations happen in more strength. TBC increment is very fast in both concentrations (Ten ppm and seven percent). It appears that TBC elevation is independent of free phosphate concentration. These results propose that an environment for total bacterial growth persists regardless of SHMP concentration.



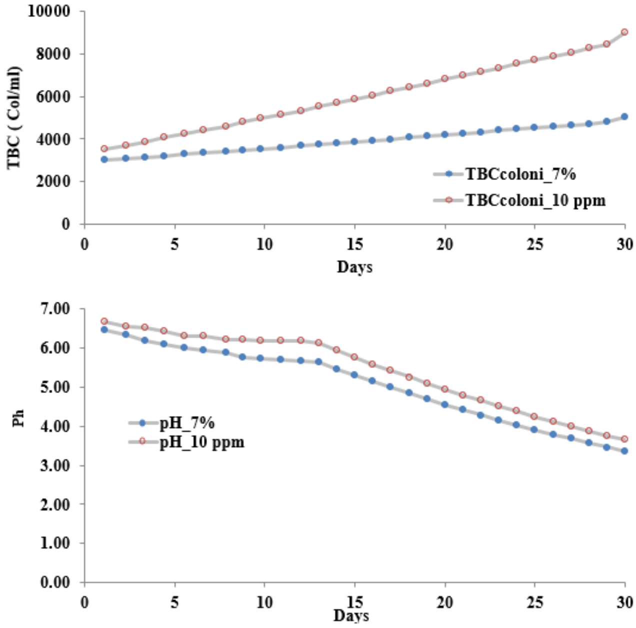


Figure 2: Behaviour of SHMP in Raw Brackish water

SBS

The results indicate that low strength and concentration, less than 0.1%, of SBS may perhaps not persist its continuous way to sterilize a SHMP solution (Figure 3). A concentration of at least 0.25% of SBS is required maintain a sterilized SHMP tank. Increased concentrations of SBS decreased the value of pH within a span of few days and extended to pH reading of 4 within 5 to 6 days. Additionally, conductivities increase precipitously in a higher SBS concentration. Thus, best possible SBS concentration is concluded as 0.25%, where the addition of SBS does not significantly affect the SHMP solution but still achieves a sterilized condition (Figure 3).

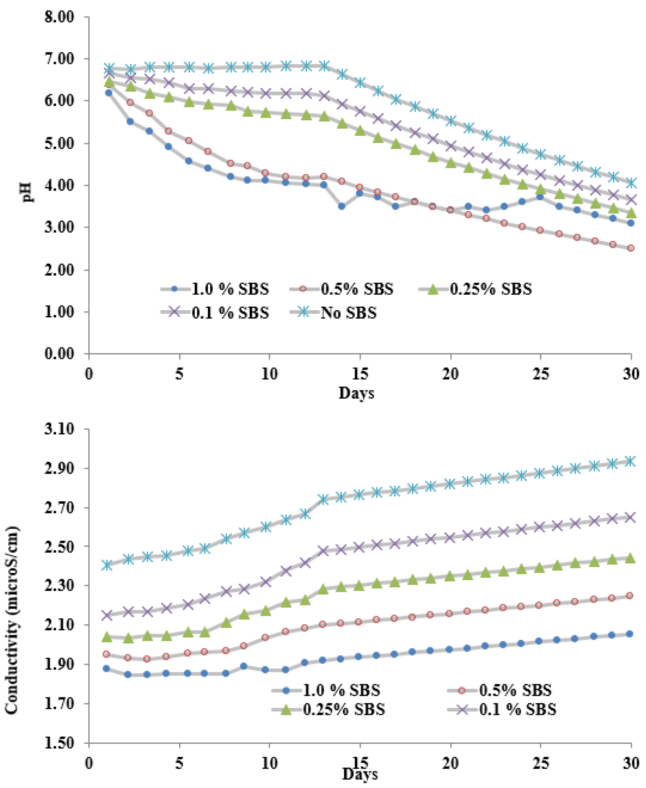


Figure 3 conductivity and pH

The reverse osmosis has become popular in the field of desalination based on its cheap value and ease of operation. It has become a demanding topic of research for further development in desalination of water.(M'nif et al. 2007) The desalination by reverse osmosis is carried out for both brackish water (BW) (water from marshes, estuaries, mangroves etc.) and seawater as feed.(Zhang et al. 2013) The membrane of the reverse osmosis possesses the capability to discard he amount of inorganic salts. Thus this technique has become very popular for the treatment of brackish water.(Malaeb and Ayoub 2011) Nevertheless, the technique of reverse osmosis is economically viable only when the purification of the BW exceeds 70%. Conversely, the concentration of the sparingly soluble salts is directly proportional to the recovery rate of the BW, leading to the precipitation of the salts on the membrane which augments the scaling.(Jawor and Hoek 2009) There is excess concentration of near saturated level of mineral salts ($BaSO_4$, $CaSO_4$ and $CaCO_3$) in the BW feeds, which enhances the probability of the membrane fouling.(Zhao, Zou, and Mulcahy 2012) These slats surpass their solubility level and precipitate even when small amount of water is extracted.(Pérez-González et al. 2012)

The formation of the scales in the membranes of water purification systems occur through a combination two different processes: surface crystallization (crystals precipitate on the surface of the membrane) and bulk crystallization (crystals precipitate in the solution).(Antony et al. 2011) The formation of the scale on the membranes is dictated by properties of the surface of the membranes and methods of operation.(Rahman and Amjad 2010) The heterogeneous nucleation process of crystal formation is thermodynamically favoured leading to the formation of crystals at low supersaturation levels. The scaling occurs on the membranes when the solubility product of the ionic salts in the solution either become equal or lesser than that of the ionic product leading to a supersaturated condition. Apart from the supersaturated condition, the kinetics of precipitation also influences the degree of scaling.(J. Au, M. Kim, A. Rahardianto, Y. Cohen 2007) The scaling in RO systems used for BW is due to the high concentration of CO_3^{2-}, Ca^{2+}, SO_4^{2-} ions. The fouling is mainly caused by the $CaSO_4$ and $CaCO_3$ salts.(Ochando-Pulido, Victor-Ortega, and Martínez-Ferez 2015) $CaCO_3$ salt is mainly responsible for the formation of scales in BW, surface water and all types of inland water.(Amjad and Koutsoukos 2010) The other slats responsible for fouling are $BaSO_4$ and $SrSO_4$ which are generally present in a concentration of less than 0.5 mg/L(Hegab and Zou 2015) and silica present in the groundwater which creates hard scales on the membranes.(Greenberg, Hasson, and Semiat 2005)

The condition under which the rate of deposition of the salt near the membrane becomes more than that of the rate of removal, initiates the formation of the fouling layer.(Qureshi et al. 2013) The permeate water flux is drastically reduced due to the fouling of the membranes as the water has to permeate through a denser layer due to the enhancement of the membrane hydraulic resistance.(Tay and Song 2005) Moreover, the diffusion of the salts in the opposite direction is prevented by the deposited layer on the membrane which ultimately decreases the propelling force for the reverse osmosis and also augments the osmotic pressure.(Herzberg and Elimelech 2007) The diminishing of flux through the membrane is both irreversible or reversible based on the level of fouling.(Kanani, Sun, and Ghosh 2008) The water diffusion of water through the membrane is subsequently diminished with the progress of scaling. Thus the pressure of the system has to be amplified for maintain the flux, which in turn enhances the consumption of energy.(Butt, Rahman, and Baduruthamal 1997) Additionally, the membrane has to be cleaned at regular intervals which decrease the durability of the membrane and also enhances the maintenance cost.(Lu et al. 2006) thus the budget of the RO plant is elevated to about 15%. The fouling is also affected by the morphology and geometry of the spacers.(A.I. Radu, M.C.M. van Loosdrecht 2013) The formation of scale is boosted by spacers.(Mitrouli et al. 2012) The generation of nucleus leading to the growth of the crystals are boosted in the areas near the spacer, so scales are formed even though the saturation level of the feed water is low.

A common problem in the field of water transport, thermal desalination plants, plants producing gas and oil and reverse osmosis is the formation of calcium carbonate scales.(Zeino et al. 2018) The densely packed $CaCO_3$ salt binds strongly to the surface of the membrane.(Muryanto et al. 2014) The fouling by the $CaCO_3$ salt is highest for the stream of concentrate at the final part of the membrane system in the RO systems.(Khan et al. 2014) The degree of precipitation of the $CaCO_3$ is influenced by the parameters like the concentration of the ions responsible for scaling, pH, temperature and pressure.(Mpelwa and Tang 2019) The presence of high amount of concentration of the ions responsible for scaling causes a condition of supersaturation. The rate of precipitation is enhanced with elevated temperature which reduces the solubility of $CaCO_3$.(Issabayev et al. 2018) The rate of loss of CO_2 is augmented under the condition when the pressure is lowered boosting the precipitation process of $CaCO_3$. In this line the precipitation process is faster under alkaline condition, since the solubility of $CaCO_3$ is substantially reduced at higher pH.(Sousa, Signorelli, and Bertran 2016)

Extensive studies have been carried worldwide to decrease the rate of scaling to improve the efficacy of the RO system and improve the economic aspect. The industrial plants reduce the rate of scaling by modulating the process of operation and RO system and pretreating the feed water. The pH of the feed water and the concentration of the mineral salts is decreased by pretreatment process. Another commonly used technique is the introduction of inhibitors for controlling the scaling.(Lee, Kim, and Lee 1999) The inhibitors are organic compounds which block the active sites of crystal growth through adsorption.(H. Li et al. 2011) However, these antiscalants cannot hinder the salt crystallization when the salt approaches the solubility limit, but encumber the accumulation of the crystals on the surface of the membrane.(Drak et al. 2000) The accumulation is thwarted due to the electrostatic repulsion between the compounds with similar charges.(J. Rieger, E. Hadicke 2001) A small concentration in ppm scale added to the feed water is capable of preventing the fouling, which establishes the antifouling action and take place devoid of any chemical reaction between the salt and the antiscalants.(C. Wang, Zhu, and Wang 2010) The antiscalants interact with the polyvalent cations through the formation of stable complexes.(Eriksson, Merta, and Rosenholm 2007)

Antiscalants are compound to reduce the fouling of membranes. The influence of the type of scale inhibitors and pH of the solution was studied in reverse osmosis of BW, which indicated that the antiscalants affected the shape and size of the salt crystals. Additionally, it was found that the decrease in larger amount of flux was caused by the crystals with smaller sizes.(Mulder 1991) The presence of divalent anions and cations (Mg^{2+}) as antiscalants hindered the process of precipitation of the $CaCO_3$ salt, by retarding the initiation process of crystallization by 1 order along with altering the prominent phase to aragonite from calcite.(F. Wang and Tarabara 2007)

The companies use polyacrylamide (PAM), polyacrylic acid (PAA), polymaleic anhydride(Shen Z et al. 2012) and inorganic polyphosphates as chemical additives (antiscalants) for hindering the process of crystal growth to prevent the formation of scale.(Hasson and Cornel 2017) The antiscalants used commercially are categorized as polycarboxylates, phosphonates and phosphates based on the presence of the main functional groups. These compounds are used as inhibitors of scale deposition(Ketrane et al. 2009) which alter the morphology of the nucleus of the crystal by retarding their growth.(Issabayev et al. 2018) Among these inorganic polyphosphates are commonly used as they are cheap and effective. The hydrolysis rate of the linear polyphosphates is sluggish at low temperature and pH value 7, which is enhanced at elevated temperature due to the cleavage of the long chain polyphosphates into smaller chain molecules.("Efficiency of Five Scale Inhibitors on Calciumcarbonate Precipitation Fromhardwater: Effect of Temperature and Concentration," n.d.) A cyclic polyphosphonate called sodium hexametaphosphate (SHMP) is a type of scale inhibitor which has six phosphate groups in its structure. This compound has been reported to inhibit the scaling on the membranes used in reverse osmosis for desalination(Rahman 2013) and cooling water.(Abd-El-Khalek and Abd-El-Nabey 2013) An interaction takes place between the cationic ions and the anions like carbonate, inhibitor and the bicarbonate during the process of inhibition of the scaling activity. A compatible interaction between the parameters is required for efficient inhibition. However, the hydrolysis of the SHMP should be averted in the dosing tank as it produces $Ca_3(PO_4)_2$ which further increases the scaling activity. The hydrolysis of the SHMP is shown in equation:

$$PO_3{}^{-} + H_2O \rightarrow H_2PO_4{}^{-} \rightarrow HPO_4{}^{2-} \rightarrow PO_4{}^{3-}$$

$$3Ca^{+} + 2PO_4{}^{3-} \rightarrow Ca_3(PO_4)_2$$

The inhibition efficacy of $CaCO_3$ scale was studied by SHMP de Morais et al(de Morais et al. 2020) and the effect of pH was studied at extreme condition of pressure and temperature. The $CaCO_3$ formed a mixture of cubic orthogonal crystals (calcite) and needle shaped crystals (aragonite) in all values pf pH in absence of SHMP.(Sergeeva, Vikulina, and Volodkin 2019) However, alteration of pH in presence of SHMP led to the formation of crystal with different morphology below a pH value of 6.5. This modification was attributed to the effective interaction between the Ca ions and SHMP, which enhanced the inhibition characteristics of scaling up to 75%. However, there was no change in the crystal morphology above pH 6.9.

Table 1: The Analysis of High Brackish in Reverse Osmosis Plant Chemically

Item as ppm	Raw Water	RO Brine	Final Product
Dissolved O_2	0.12	-	-
TS	3.12	-	<0.05
TBC	2	29	2
TDS	12674	34365	282
Total Hardness	2249	7608	82
HCO_3	187	280	58
Ca	617	1718	21
PO_4	0.35	22.00	-
Na	3170	9024	87
K	136	378	253
Mg	293	801	1.97
Sr	22	59	0.31
Ba	0.27	0.48	-
NO_4	0.08	0.22	0.08
Ma	<0.03	0.05	<0.02
Cu	0.03	0.08	<0.02
Zn	0.07	0.08	<0.02
S_2O_3	1193	3054	<0.17
Cl	6836	18722	95
SO_4	610	1801	38
Oil	<0.10	<0.10	-

From table (1) that shows chemical analysis of highly brackish water used in reverse osmosis plants to show average temperature for raw water to reverse osmosis brine plus final product to be 30 ^{o}C. The total organic carbon for the raw water is always as 0.88 ppm while the rest is remained as not detected. The turbidity was showing Raw Water (0.16), RO Brine(0.25) and Final Product (1.7) while the silt density index (SDI) Raw Water (2.55), RO Brine(4.5) and Final Product (3.7). The conductivity are Raw Water (19245), RO Brine(46230) and Final Product 393). The pH for the Raw Water (6.85), RO Brine(6.35) and Final Product (8.30)

5.0 Discussion

Ashfaq et al, 2020 In this exploration, the cooperation's of seawater containing the antiscalants and calcium sulphate in the reverse osmosis system frameworks was analyzed. The collaboration of seawater scaling ions with scale inhibitor was researched by estimating the development of microscopic images of the antiscalants. The antiscalants were added as the only source of energy and carbon. In addition, the communication of calcium sulfate was checked using energy dispersive x-beam in electron microscopy. It was tracked down that few strains of the *Pseudomonas* species separated from the saline water equipped for utilizing antiscalants as an energy. It is noticeable that the development bends of the strains differ with the sort of the antiscalant contemplated. Additionally, the eventual outcomes of scaling collaboration displayed that the nearness of organisms incited/interceded precipitation of calcium sulfate on the switch osmosis film surfaces, in spite of the fact that, no precipitation was taken note on the control switch osmosis layers without microorganisms beneath the conditions that was planned for examination. In this way, the results of this investigation appeared that the nearness of scaling components in seawater turn around assimilation causes biofouling. Additionally, process of mineral scaling is enhanced due to biodegradation of the antiscalants and calcium sulfate precipitation. It has been reported that antiscalants can be biologically degraded by *Pseudomonas* to form carbon and energy. The rate of biodegradation was prominent for the case of various antiscalants. The biodegradation of calcium sulfate was found to be enhanced by each of the examined strains in solution. No precipitation was observed in controls of switch osmosis which were not inoculated with bacterial colonies. Thus, it can be concluded that microorganisms showed two perils in switch osmosis desalination systems. (I) The antiscalants were biodegraded which decreased their activity to control scaling and (II) calcium sulfate precipitated on the RO layers. Hence, the presence of microorganisms will enhance the biofouling and mineral scaling on the switch osmosis membranes. In like manner, it is basic to consider the cooperation between two foulants amidst the alteration of the control strategies of fouling. Assist investigation is being coordinated in analyzing these cooperation's in viewpoint and make film components fit for taking care of both scaling and organic fouling, at the same time.

The reestablished components were regarded worthy. Actually, reusing components for up to 12 cycles spared a significant sum of cash. Online tests utilizing 10 micron conjointly 5 micron and 1 micron cartridge components in channel lodgings appeared that the flotsam and jetsam accelerated and gathered in 1 Micron is higher than 5 Micron and 10 Micron channels. This, when executed within the invert osmosis plant with working conditions depended as nourish crude water. This might require more repetitive substitution of MGF components, but high-quality nourish water would certainly help in generation steadiness and reduce layer fouling. Besides, SHMP and H2SO4 determinations as of late implemented on the chemical manufacturer's especially moo press substance anticipated press sulfide arrangement. Interests, one shipment turned dim brown and was rendered off utilize and upkeep inside 10 days. Hence, by regularly cleaning MGF vessels with H2O2, maintaining a low iron content in SHMP and H2SO4 and adding SBS in SHMP tanks to prevent aerobic bacterial growth bettered the previously unpredictable performance of the MGF system.

Shock Treatment System utilizing SBS, a known bactericide, is commonly utilized within the water treatment plants. This framework is outlined for stun treatment of all pieces for 30 minutes to one hour. So, Sodium Bisulfite is ready each day within the stun treatment vessel with concentration 30000 ppm is dosed to each block either every day or on interchange days. Micron Guard Filter Cartridge are introduced within the stun treatment framework some time recently the RO Squares as an extra assurance against foulants. Filters 10 to 5 micrometer and 1 micrometer are utilized to assist diminish foulants.

6.0 Conclusion

The study encompasses the use of sulfuric acid and sodium hexametaphosphate (SHMP) in RO permeators. The major aim of the study was to search for a stable and feasible anti scaling agent. The experiment was carried out on a reverse osmosis slide of a working plant. The records were coordinated in a cluster of 2:1:1 for each test. The brackish saline water was transferred into the modules and the eliminated brine from these modules were transferred to the third module. The chemical testing has been elaborately discussed in the paper. Positive results were obtained from the experiments inside the plant due to positive impact of the advanced MGF. The membrane of the reverse osmosis was protected due to a reasonable distance from the contaminants absorbing the oxygen from the dosing lines and SHMP. The optimum concentration of SBS for controlling the microorganisms and preventing the reverse conversion of SHMP to orthophosphate was found to be 0.2%. However, the presence of the free phosphate has to be decreased in the future works. A modern line was exhibited for the dosing system of the SHMP during the annual shutdown of the plant. This study concluded the use of Cartridge Channels (5 Micron) substituting the Cartridge Channels (10 Micron). However, we found that fouling was a major issue in the RO plant which will be addressed subsequently in further studies.

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