Magnesium Salt Recovery from Concentrate and Use in Treatment of Saline Water

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Abstract. Magnesium salt was recovered from artificial concentrate and used in the removal of contaminants (PO_4, Turbidity and NO_3) from saline water that has high initial magnesium concentration (artificial brackish and sea water) at pH 11. Solar panels were used to enhance and expedite the precipitation process. PO_4 removal efficiency increased as Recovered Magnesium Salt (RMS) increased, with the highest removal reaching 99.7% at a dose of 200 mg/l (RMS), initial PO_4–P concentration of 20 mg/l, and water salinity of 40,000 mg/l. Removal efficiency of PO_4 increased as the salinity of water increased. However, beyond 10,000 mg/l salinity, the improvement was practically non-existent. Removal efficiency for turbidity and NO_3 also improved as the dose of RMS increased. There was no correlation between TDS concentration and turbidity or NO_3 removal efficiency. Turbidity removal efficiencies reached a value of 90% at a dose of 200 mg/l RMS for initial turbidity value of 50 NTU, and water salinity of 40,000 mg/l. NO_3 removal efficiency ranged from 38.4% to 99.2%. The study also evaluated the effect of anti-scalant use on the removal efficiency of PO_4, turbidity, and NO_3 using RMS. Results have shown, using 2 anti-scalants (Phosphonic acid and a proprietary anti-scalant (AS-4100)), that the negative effect disappears after two hours of anti-scalant addition.

1 Introduction

Magnesium precipitated from sea water as magnesium hydroxide has been shown to be an effective coagulant for the removal of contaminants in waters. They also have been used in the recovery of nitrogen and phosphorous present in wastewater [1-6]. Magnesium hydroxide ($Mg(OH)_2$) when precipitated at pH values higher than 10.5 can be used as a coagulant that can remove colloidal particles by sweep flocculation [7].
Magnesium present in sea water can be concentrated by solar desalting. This can be achieved by inducing the depositing of $CaCO_3$, calcium sulfate ($CaSO_4$), and sodium chloride (NaCl), thus forming a bittern (liquid bittern (LB) or if further evaporation is allowed dry bittern (DB) with high concentrations of magnesium salts and limited amount of potassium (K) and sodium (Na) salts [8].

The recovery of magnesium salts from the concentrate and their use in the pretreatment of saline water will contribute to the reduction of concentrate management cost. Magnesium

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salts recovered from sea water (liquid bittern or dry bittern) have been used as coagulant to treat turbidity and other contaminants in fresh water resources [3, 6, 9-11]. Others conducted experiments to determine the possibility of recovering magnesium salt from concentrate water [12, 13]. Ding et al. used magnesium hydroxide as a coagulant to treat orange wastewater [14]. The effect of mixing speed and retention time on continuous coagulation of magnesium hydroxide was studied. Sorour et al. studied the recovery of calcium and magnesium from concentrated water and seawater using precipitation/ chelation units [15]. The extraction of calcium using sodium carbonate from concentrate water was 93.2% and sea water was 96.6% at pH between 9 - 9.2. Magnesium extraction with sodium hydroxide was 74% from concentrate water and 99.6% from sea water at pH 12. Sorour et al. studied the recovery of salt from seawater and RO brines using chemical precipitation [16]. Turek et al. explained the mechanism of recovery $Mg(OH)_2$ and $CaCO_3$ salts from sea water by using electrodialysis and electrodialysis reversal methods to achieve zero liquid discharge [17].

Magnesium recovered from seawater [18] or bittern [19,20] to recover phosphorus from municipal wastewater by struvite ($MgNH_4PO_4.6H_2O$) was investigated. Alrowaished et al. proposed the use of solar panels to evaporate concentrate water and extract minerals and salts [21]. Many other researchers have recommended the reuse of concentrate through recovery of salts, which reduces the negative effects on the environment, reduce the amount of waste and can be considered as a new source of salts [22-24].

In the present study, magnesium salts recovered from the concentrate was used to remove contaminants from saline water. Magnesium present in artificial concentrate (prepared in the lab) was recovered and used as a coagulant. Magnesium salt was recovered (will be referred to as Recovered Magnesium Salt (RMS)) in dry form after evaporation using solar panels to speed up the evaporation process.

2 Methods

Artificial seawater (40 g/L TDS) was prepared by adding, for every 1.0 liter of solution, the following quantities of salts to distilled water: 30.9 g NaCl, 2.38 g MgSO4, 1.42 CaSO4, 3.8 g $MgCl_2$, 0.28 g CaCO3, and 1.14 g KCl. In the first step, this artificial seawater was placed in basins containing a heat exchanger to accelerate the evaporation process. The heat exchanger was heated using solar panels that absorb solar radiation to heat oil which heats water into the solar system and convert it into steam. As evaporation proceeds, the concentration of salts increases and start to precipitate according to their solubility. The sequence of salt precipitation is assumed as follows: precipitation of CaCO3 and CaSO4 salts first, then the precipitation of NaCl, KCl salts, and finally the precipitation of the highly soluble MgSO4 and MgCl2 salts. In the second step, and after the first five salts precipitated, the liquid over them was decanted and dried using solar energy. This dry salt was assumed to be recovered magnesium salt (RMS) and used in the coagulation process. The RMS was assumed to be mostly $MgCl_2$. In the third step, magnesium chloride salt or RMS was used in the pre-treatment of artificially prepared saline water, with 3 different salinities (2000 mg / l, 10000 mg / l and 40,000 mg / l).

Three different concentrations of phosphate were added to each concentration of water and treated using different concentrations of recovered magnesium salt (RMS). Phosphate concentrations were 5 mg / L, 10 mg / L and 20 mg / L as PO_4. Phosphate was added as KH_2PO_4 compound.

Three different values of turbidity were added to each concentration of water and treated using different concentrations of RMS. The turbidity values were 10 NTU, 25 NTU and 50 NTU.

Three different concentrations of nitrogen were added to each concentration of water and treated using different concentrations of magnesium chloride, to obtain the optimum dose of

magnesium chloride to treat each concentration of nitrogen. Nitrogen concentrations were 25 mg / l, 50 mg / l and 100 mg / l as N. Nitrogen was added as KNO_3 compound.

Three concentrations of RMS were used on each sample and each concentration of saline water, phosphate, turbidity and nitrogen. These concentrations were as follows: (50 mg/l, 100 mg/l and 200 mg/l) to determine the optimum dose of it to use as a pre-treatment.

A six beaker Jar test apparatus was used in this evaluation. Rapid mixing for 60 seconds with 300 rpm and two different slow mixing times (10 minutes and 30 minutes) with 30 rpm were used. All jar test experiments were conducted at pH 11.

3 Results and discussion

Magnesium recovered from artificial concentrate (RMS) was used in different doses to treat different concentrations of phosphate, turbidity and nitrogen for different water salinities. The results are summarized next.

3.1 Phosphate Removal

Figure 1 shows the results obtained when treating different concentrations of phosphates by different doses of RMS at salinity of 2000 mg/l after 30 min precipitation.

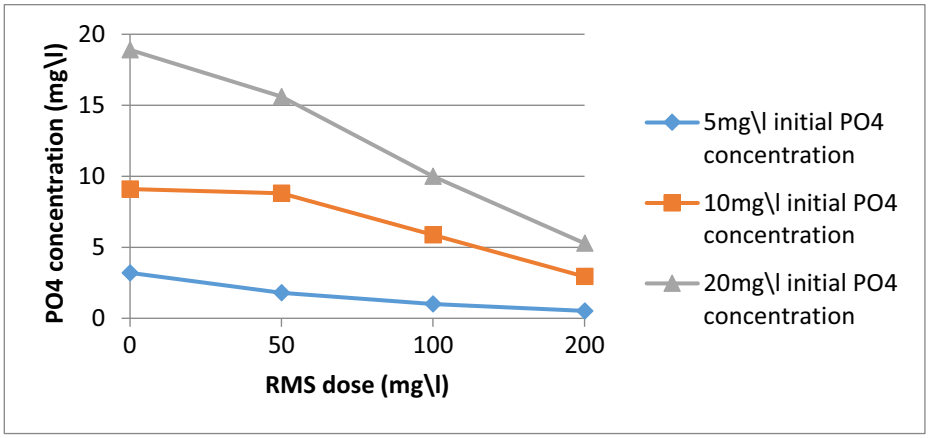

Fig. 1. RMS dose vs PO_4 concentration for three curves (5, 10 and 20 mg/l initial PO_4 concentrations) for **2000 mg/l salinity.**

The results show that the increase in RMS dose increases the removal efficiency of phosphate.

Figure 2 shows the results obtained when treating different concentrations of phosphates by different doses of RMS at salinity of 10000 mg/l after 30 min precipitation.

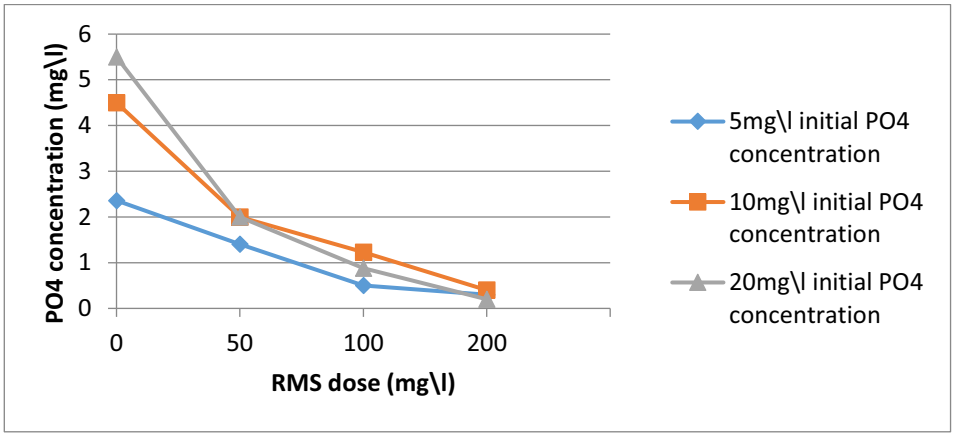

Fig. 2. RMS dose vs PO_4 concentration for three curves (5, 10 and 20 mg/l initial PO_4 concentrations) for **10000 mg/l salinity.**

The results show that as water salinity increased, phosphate removal is more efficient, due to the presence of more magnesium chloride in saline water.

Figure 3 shows the results obtained when treating different concentrations of phosphates by different doses of RMS at salinity of 40000 mg/l after 30 min precipitation.

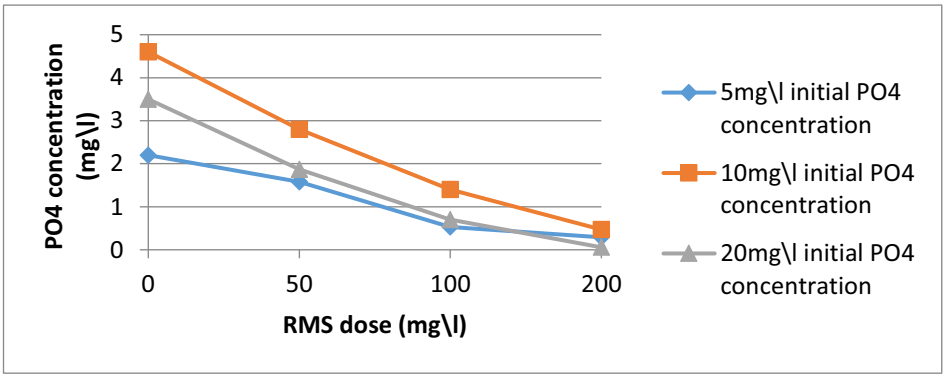

Fig. 3: RMS dose vs. PO4 concentration for three curves (5, 10, and 20 mg/l initial PO4 concentrations) for **40000 mg/l salinity**.

Results show that the increase in RMS doses leads to a higher removal efficiency of phosphate. The higher the concentration of salts, the more efficient of phosphate removal due to the presence of magnesium chloride in saline water.

One can conclude from the previous results that the removal efficiency of phosphate is increased by increasing the dose of magnesium chloride and the presence of magnesium chloride increases in water as salt concentration increases. For the best removal efficiency, wait 30 minutes after treatment.

Table 1 summarizes the effect of initial salinity on phosphate removal for (5, 10 and 20) mg/l initial PO_4 concentrations for three concentrations (2000, 10000, 40000 mg/l salinities). The results showed that an improvement on the removal efficiency of metals, total suspended solids and phosphate.

Table 1. Effect of initial salinity on phosphate removal for (5, 10 and 20) mg/l initial PO_4 concentrations for three concentrations (2000, 10000, 40000 mg/l salinities).

PO_4 before treatment (mg\l)	RMS dose (mg\l)	PO_4 after treatment (mg\l) Salinity = 2000 mg/l	PO_4 after treatment (mg\l) Salinity = 10000 mg/l	PO_4 after treatment (mg\l) Salinity = 40000 mg/l
5	0	3.20	2.36	2.20
	50	1.80	1.41	1.58
	100	1.00	0.50	0.53
	200	0.52	0.30	0.29
10	0	9.10	4.50	3.60
	50	8.80	2.00	2.80
	100	5.87	1.23	1.40
	200	2.93	0.40	0.47
20	0	18.9	5.50	3.50
	50	15.6	2.00	1.87
	100	10.0	0.88	0.70
	200	5.28	0.20	0.06

Table 1 shows that when the water salinity increased from 2000 mg/l to 10,000 or 40,000 mg/l, the phosphate removal efficiency dramatically increased. However, when salinity increased from 10,000 mg/l to 40,000 mg/l, the phosphate removal efficiency did not improve dramatically, and in some cases deteriorated. One possible explanation is that the sedimentation time provided in this case (30 minutes) was not capable of removing all the phosphate-chloride precipitates at the high salinity water.

3.2 Turbidity Removal

The turbidity was removed using RMS at different concentrations of turbidity and salinity. Figure 4 shows the results obtained when treating different concentrations of turbidity by different doses of RMS at salinity of 2000 mg/l after 3 hr precipitation.

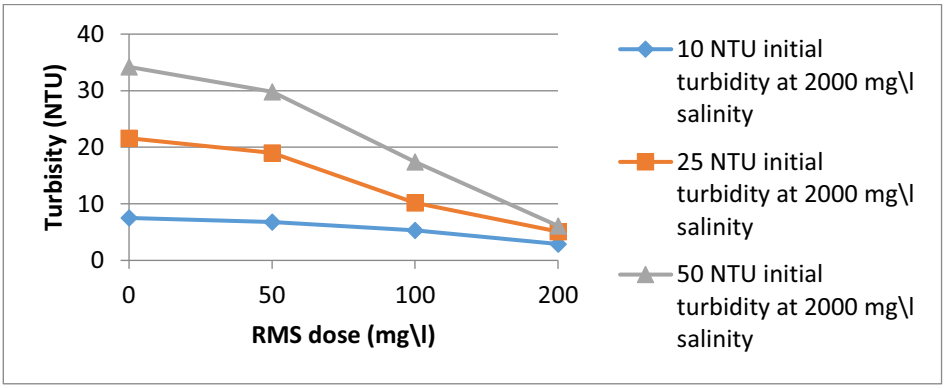

Fig. 4. RMS dose vs. turbidity for three curves (10, 25 and 50 NTU initial turbidity values) for 2000 mg/l salinity after 3 hr precipitation.

The results show that the removal efficiency using recovered magnesium salt (RMS) to remove turbidity achieved best results after 3 hr precipitation.

Figure 5 shows the results obtained when treating different concentrations of turbidity by different doses of RMS at salinity of 10000 mg/l after 3 hr precipitation.

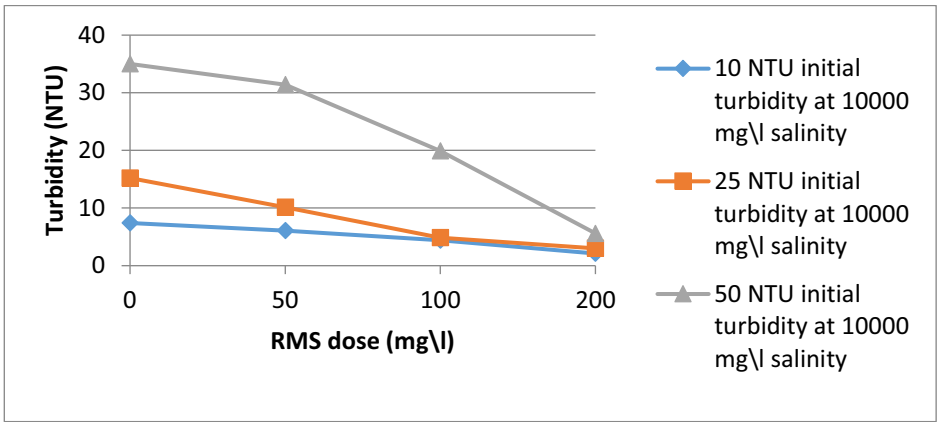

Fig. 5. RMS dose vs. turbidity for three curves (10, 25 and 50 NTU initial turbidity values) for 10000 mg/l salinity after 3 hr precipitation.

In addition to increased precipitation time, the increase in magnesium chloride doses leads to better results in the removal efficiency of turbidity.

Figure 6 shows the results obtained when treating different concentrations of turbidity by different doses of magnesium chloride at salinity of 40000 mg/l after 3 hr precipitation.

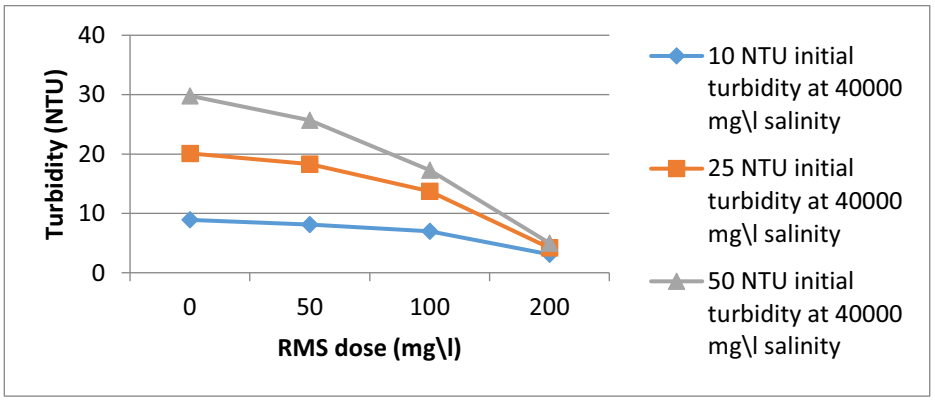

Fig. 6. RMS dose vs. turbidity for three curves (10, 25 and 50 NTU initial turbidity values) for 40000 mg/l salinity after 3 hr precipitation.

Previous results show that turbidity needs time for precipitation to show better removal efficiency results. This means that in addition to increase the dose of magnesium chloride, increased in precipitation time is needed [6].

Table 2 summarizes the effect of initial salinity on turbidity removal for (10, 25 and 50) NTU initial turbidity values for three concentrations (2000, 10000, 40000 mg/l salinities) after 3 hr precipitation.

Table 2. Effect of initial salinity on turbidity removal for (10, 25 and 50) NTU initial turbidity values for three concentrations (2000, 10000, 40000 mg/l salinities) after 3 hr precipitation.

Turbidity before treatment (NTU)	$MgCl_2$(mg\l)	Turbidity after treatment (NTU) Salinity 2000 mg/l	Turbidity after treating (NTU) Salinity 10000 mg/l	Turbidity after treatment (NTU) Salinity 40000 mg/l
10	0	7.5	7.40	8.9
	50	6.8	6.10	8.1
	100	5.3	4.40	7.0
	200	2.9	2.11	3.1
25	0	21.6	15.20	20.1
	50	19.0	10.13	18.3
	100	10.2	4.84	13.7
	200	5.1	3.00	4.2
50	0	34.2	35.0	29.8
	50	29.8	31.4	25.7
	100	17.4	19.9	17.3
	200	6.1	5.6	5.0

3.3 Nitrogen Removal.

Different concentrations of nitrogen were treated using different doses of RMS. Figure 7 shows the results obtained when treating different concentrations of nitrogen by different doses of RMS at salinity of 2000 mg/l after 30 min precipitation.

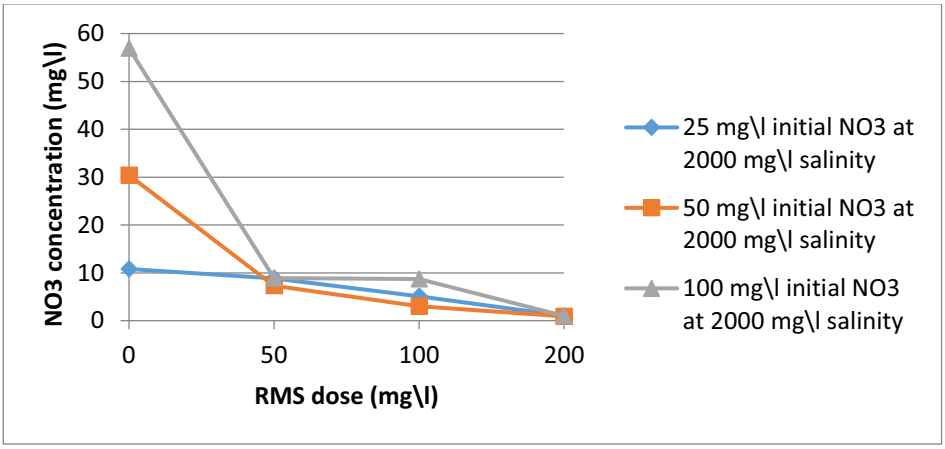

Fig. 7. RMS dose vs. NO_3 concentration for three curves (25, 50 and 100 mg/l initial NO_3 concentrations (measured as nitrate)) for 2000 mg/l salinity**.**

The results show high removal efficiency of nitrogen using RMS. When RMS was added, it reacts with NO_3 and formed large flocs that precipitated with high efficiency.

Figure 8 shows the results obtained when treating different concentrations of nitrogen by different doses of RMS at salinity of 10000 mg / l after 30 min precipitation.

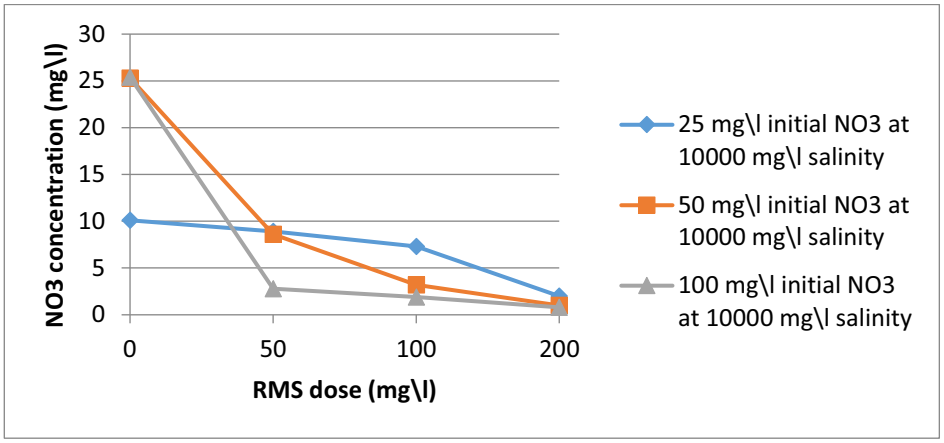

Fig. 8. RMS dose vs. NO_3 concentration for three curves (25, 50 and 100 mg/l initial NO_3 concentrations) for 10000 mg/l salinity.

Removal efficiency increases with the increase in RMS dose. The magnesium dose increases with increase in water salinity because saline water contains magnesium as one of its components.

Figure 9 shows the results obtained when treating different concentrations of nitrogen by different doses of RMS at salinity of 40000 mg/l after 30 min precipitation.

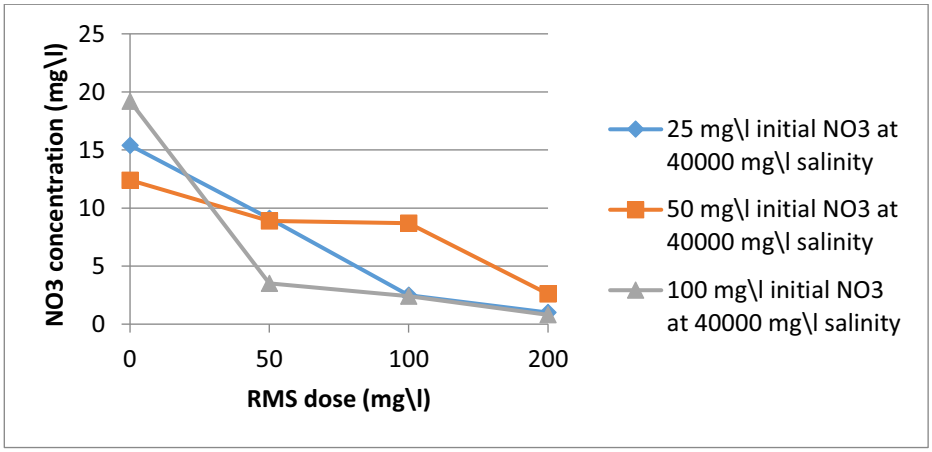

Fig. 9. RMS dose vs. NO_3 concentration for three curves (25, 50 and 100 mg/l initial NO_3 concentrations) for 40000 mg/l salinity**.**

Previous results confirm that the increased dose of magnesium chloride with the presence of nitrate leads to a higher precipitation efficiency of nitrogen [20].

Table 3 summarizes the effect of initial salinity on NO_3 removal for (25, 50 and 100) mg\l initial NO_3 concentrations for three concentrations (2000, 10000, 40000 mg/l salinities) after 30 min precipitation. Table 3 shows that when the water salinity increased from 2000 mg/l to 10,000 or 40,000 mg/l, the nitrogen removal efficiency dramatically increased. However, when salinity increased from 10,000 mg/l to 40,000 mg/l, the nitrogen removal efficiency did not improve dramatically, and in some cases deteriorated. One possible explanation is that the sedimentation time provided in this case (30 minutes) was not capable of removing all the nitrogen-chloride precipitates at the high salinity water.

Table 3. Effect of initial salinity on nitrogen removal for (25, 50 and 100) mg\l initial nitrogen concentrations for three concentrations (2000, 10000, 40000 mg/l salinities) after 30 min precipitation.

Nitrogen before treatment (mg\l)	$MgCl_2$(mg\l)	Nitrogen after treatment (mg\l) Salinity 2000 mg/l	Nitrogen after treatment (mg\l) Salinity 10000 mg/l	Nitrogen after treatment (mg\l) Salinity 40000 mg/l
25	0	10.8	10.1	15.4
	50	8.8	8.9	9.1
	100	5.1	7.3	2.5
	200	1.0	2.0	1.0
50	0	30.4	25.3	12.4
	50	7.3	8.6	8.9
	100	3.0	3.2	8.7
	200	0.9	1.0	2.6
100	0	56.9	25.4	19.2
	50	8.9	2.8	3.5
	100	8.7	1.9	2.4
	200	1.0	0.8	0.8

1.4 Treatment with and without antiscalant.

Two types of antiscalant were used in the experiments, with 20 mg/l dose. The first one was Phosphonic acid antiscalant which is an organic compounds of the form of $R\text{-}PO_3H_2$. The two most widely used Phosphonic acids are (methylene Phosphonic acid $CH_2\text{-}N\text{-}CH_2\text{-}CH_2\text{-}(PO_3H_2)_3$ and (Hydroxyethylene diphosphonic acid $CH_3\text{-}C\text{-}OH\text{-}(PO_3H_2)_2$). The antiscalant used in this study was methylene Phosphonic acid.

The second one which is available in the local market was AS-4100, the most important characteristics of this product are that it is considered as an antifouling in the RO for low TDS feed water. Proved to be effective as an antifouling for silica and calcium scales (calcium carbonate and calcium sulfate) in all types of water. In addition, it's approved in drinking water applications and effective against all common composition salts.

The results of phosphate removal using RMS with and without Phosphonic acid antiscalant and the effect of phosphonic acid and AS-4100 antiscalants when directly added, after an hour and thirty minutes and after two hours were shown in figures (10, 11 and 12) with salts concentration of 10,000 mg /l.

The use of RMS with phosphonic acid and AS-4100 antiscalants leads to reduction in the effective removal of phosphate and limitation in precipitation. Results show that phosphonic acid antiscalant has a higher effect than AS-4100 antiscalant on phosphate removal efficiency; this can be attributed to the presence of phosphorus in phosphonic acid antiscalant. The effect of phosphonic acid and AS-4100 antiscalants disappears after two hours from the addition.

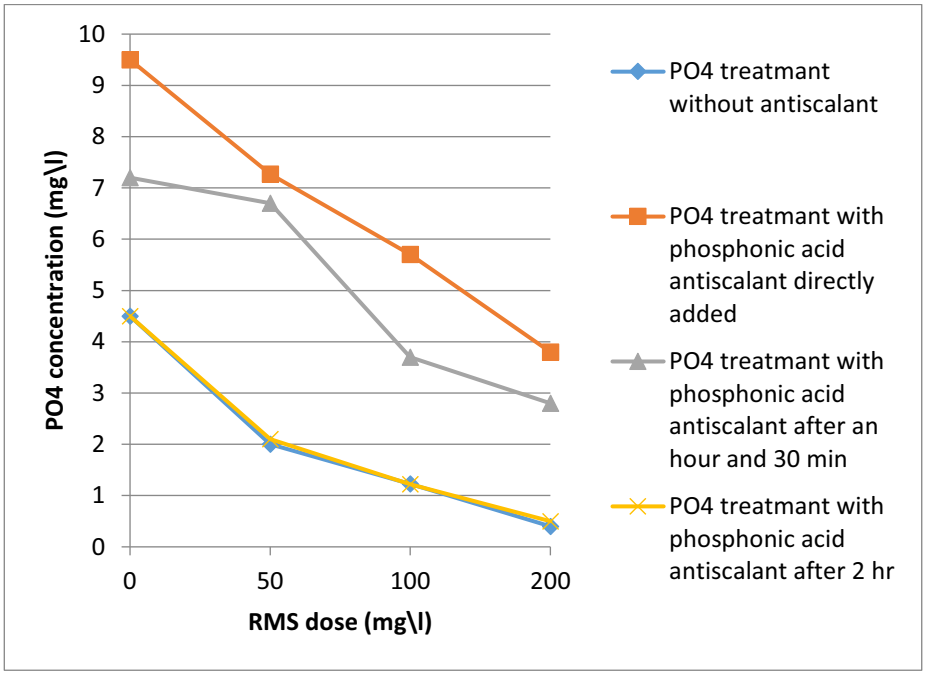

Fig. 10. RMS vs. PO_4 – P concentration for three curves (50, 100 and 200 mg/l initial RMS doses) for 10000 mg/l salinity.

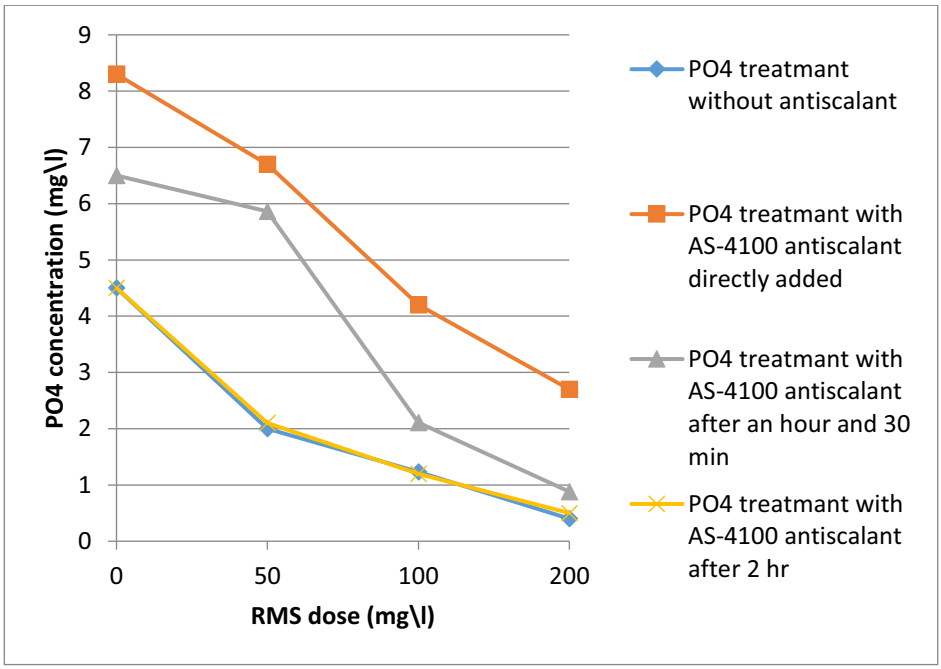

Fig. 11. RMS vs. PO_4 – P concentration for three curves (50, 100 and 200 mg/l initial $MgCl_2$ concentrations) for 10000 mg/l salinity.

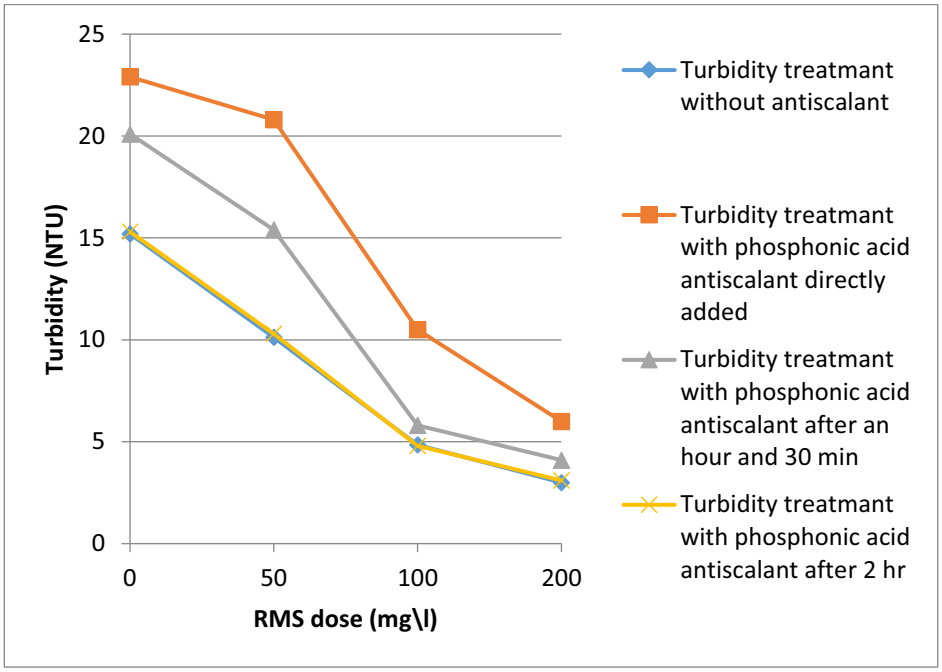

Fig. 12. RMS vs. turbidity value for three curves (50, 100 and 200 mg/l initial $MgCl_2$ concentrations) for 10000 mg/l salinity

The results of turbidity removal using RMS with and without antiscalants are shown in figures (13, 14 and 15) with salts concentration of 10,000 mg/l.

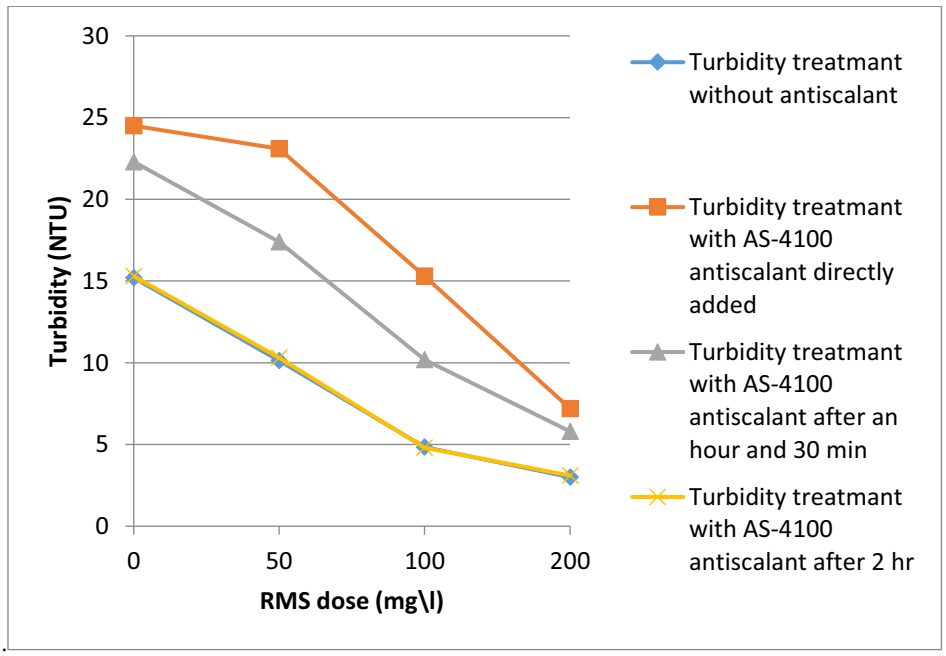

Fig. 13. RMS vs. turbidity value for three curves (50, 100 and 200 mg/l initial $MgCl_2$ concentrations) for 10000 mg/l salinity

The effect of antiscalant on the removal of turbidity was negative. It reduced the removal efficiency compared to the removal without an antiscalant. The results showed that AS-4100 antiscalant has a higher effect than phosphonic acid antiscalant on turbidity. The effect of phosphonic acid and AS-4100 antiscalants disappears after two hours from the addition.

The results of nitrogen removal using RMS with and without phosphonic acid and AS-4100 antiscalants are shown in figures 14 and 15 with salts concentration of 10,000 mg / l.

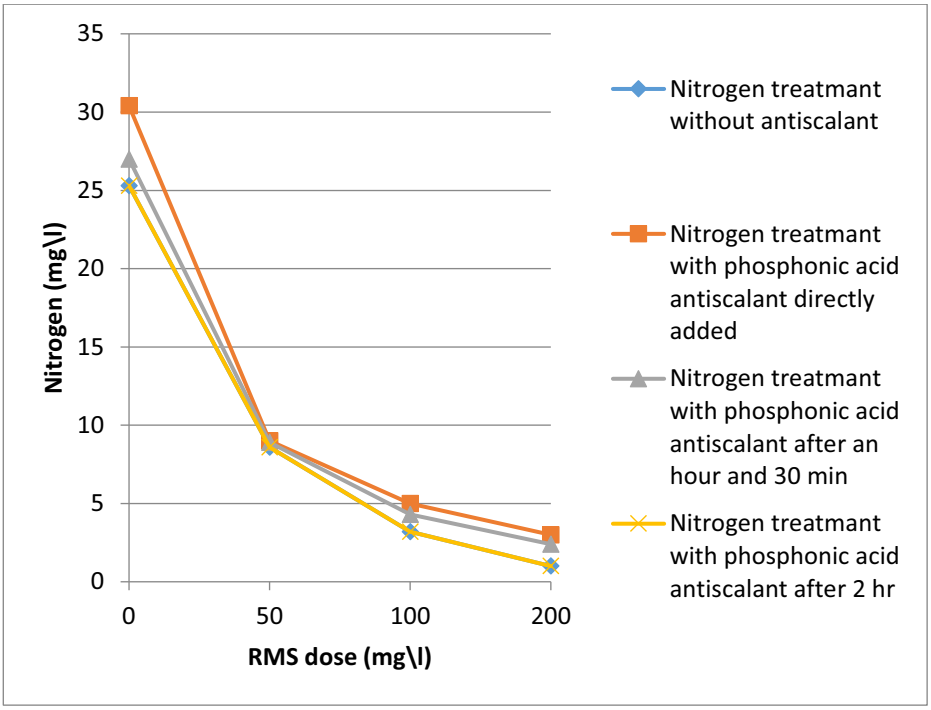

Fig. 14. RMS vs. nitrogen concentration for three curves (50, 100 and 200 mg/l initial RMS dose) for 10000 mg/l salinity.

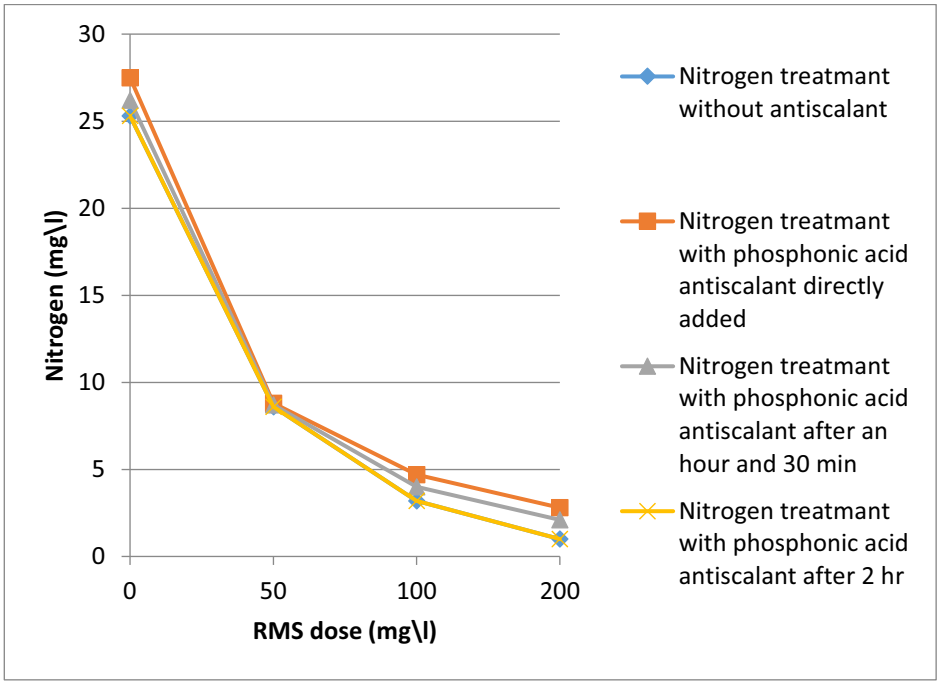

Fig. 15. $MgCl_2$vs. nitrogen concentration for three curves (50, 100 and 200 mg/l initial $MgCl_2$ concentrations) for 10000 mg/l salinity.

The results show that the use of antiscalant leads to a reduction in the effectiveness of removal due to the fact that the antiscalant reduces the precipitation and increases the solubility of salts. However, the effect of antiscalant was relatively small and the effect of phosphonic acid was higher than AS-4100 antiscalant. The effect of phosphonic acid and AS-4100 antiscalants disappears after two hours from the addition. The antiscalant mechanism is represented in delaying the formation of scales on the membrane surface. The scale may consist of mineral fouling such as $CaSO_4$, $CaCO_3$, $BaSO_4$, $SrSO_4$, CaF_2, and silica. As the presence of antiscalant in the feed water delay the reaction between calcium magnesium and bicarbonate, which leads to delay in the formation of scales during the desalination process. The antiscalant absorbs the nucleus of the solid calcium materials and prevents the growth and formation of crystals on the membrane surface.

4 Conclusion

The following conclusions can be drawn from the present study:
- Magnesium salt recovered from artificial concentrate has been shown to be effective in the removal of PO_4, Turbidity and NO_3 from saline water that has high initial magnesium concentration (artificial brackish and sea water).
- PO_4 removal efficiency increased as Recovered Magnesium Salt (RMS) increased, with the highest removal reaching 99.7% at a dose of 200 mg/l (RMS), initial PO_4-P concentration of 20 mg/l, and water salinity of 40,000 mg/l.
- Removal efficiency of PO_4 increased as the salinity of water increased up to 10,000 mg/l salinity. However, there was no correlation between TDS concentration and turbidity or NO_3 removal efficiency.

- Removal efficiency for turbidity improved as the dose of RMS increased, reaching a value of 90% at a dose of 200 mg/l RMS for initial turbidity value of 50 NTU, and water salinity of 40,000 mg/l.
- Removal efficiency for NO_3 improved as the dose of RMS increased, ranging from 38.4% to 99.2%.
- The use of anti-scalant use showed negative effect on the efficiency of RMS, but this negative effect disappeared after two hours of anti-scalant addition.

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