

Removal of Iron and Manganese from Marginal Quality Brackish Water for Sustainable Reverse Osmosis Desalination

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Abstract: Membrane based solutions are the main strategy for desalination of brackish and saline water. The treatment of the former type of water is sometimes complicated by the presence of organic contaminants, soluble iron and manganese salts. The presence of these pollutants accelerates membrane fouling and degradation and consequently limits successful application of membrane based interventions. Moreover, upstream pretreatment system is adversely affected due to shorter operation cycles and the possibilities of material and functional failure. Thus, it is deemed necessary to incorporate iron and manganese removal unit according to sound criteria achieving optimal performance and cost merits. This paper addresses the application of simple iron and manganese removal unit based on sodium hypochlorite and potassium permanganate oxidants. The factors affecting the chemical oxidation of iron and manganese in synthetic brackish water and raw well water were experimentally investigated to come-up with an optimized pretreatment scheme for brackish water with and without organic contaminants. Moreover, the financial impact of the stated interventions on brackish water, containing iron and manganese, RO desalting economics is discussed. It is shown that the capital cost for RO plant with iron and manganese removal unit is about 14% more than that for conventional RO plant. Also, the estimated cost of water production by RO using an iron and manganese removal unit as a pretreatment is about \$ 0.6 /m³ as compared to about \$ 1.04/m³ in case of using conventional pretreatment only.

Key words: Brackish water • Iron and manganese • Reverse osmosis • Cost

INTRODUCTION

Low quality brackish water may be characterized by the presence of iron (Fe) and / or manganese (Mn) salts and organic contaminants. Iron is found in brackish ground water at varying concentrations, usually up to 4 mg/l and in some cases up to 15 mg/l [1-3].

The presence of small concentrations of iron and manganese is supposed to complicate brackish water desalination. In the pretreatment process, iron may be precipitated within the filtration medium in the presence of air (above pH=7) thus, adversely affecting filtration and backwashing processes. In addition, the passage of iron and manganese salts to the membrane modules and the increasing concentration of these salts in the boundary layer in the concentrate compartment results in rapid fouling and deterioration of membrane performance (e.g. increase of pressure drop, decrease of flux and poor product quality) according to two mechanisms, the first is related to formation of iron precipitates especially in the

presence of organic contaminants and the second is related to accelerated catalytic degradation of the membrane substrate [4-6]. In general, the overall impact of iron and manganese salts on brackish water reverse osmosis (RO) desalination comprises complication of the pretreatment and desalination processes, shorter life of membrane material and membrane modules and consequently limited plant availability and costly operation [7,8].

In groundwater, Fe and Mn are usually present as Fe⁺² and Mn⁺² ions in soluble forms. The removal of Fe from groundwater is relatively easier than Mn. In general, the removal processes are either physico-chemically or biologically based interventions. The physico-chemically based processes include oxidation with an oxidizing agent such as oxygen, chlorine, ozone or potassium permanganate followed by physical separation of suspended matters by clarification and/or filtration [5, 6, 8]. Recently, various treatment technologies have been employed to enhance water quality. These

methods include ion-exchange [9], Nanofiltration (NF) and UltraFiltration (UF) combined with chemical oxidation [1, 10]. Biological removal of Fe and Mn has been also reported to be successful on the experimental level [11].

In view of the above mentioned considerations, incorporation of iron and manganese removal within the matrix of pretreatment train seems mandatory for desalination unit sustainability and cost effective desalination [10, 11]. This paper is an endeavor to come up with an appropriate process design for iron and manganese removal as an essential component in brackish water RO desalination system in the presence of those components.

Rational for the Selection of Iron and Manganese Removal Pretreatment System:

Design of RO system for desalination of brackish water containing iron and manganese should satisfy the following criteria:

- Incorporation of iron and manganese removal unit within the conventional scheme with minimum footprint.
- Compatibility of the conditions of upstream pretreatment with those downstream conditions required for optimal desalting operation.
- Reliability and compatibility of the process with the site prevailing infrastructure and expertise.
- Minimum impacts on desalination economics.

According to these criteria, relatively complicated processes such as biological and electrochemical oxidation have been excluded. Simple chemical treatment based on using metered doses of hypochlorite or permanganate has been selected for reliable cost effective reduction of iron and manganese salts. Realization of this approach necessitated identification of the appropriate dosage of oxidants on the experimental level as described below.

MATERIALS AND METHODS

Materials: Chemical oxidation experiments were conducted using simulated brackish water of salinity up to 4000 mg/l using sodium chloride. The following salts were used: ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) as iron and manganese sources, respectively. Potassium permanganate (KMnO_4) and sodium hypochlorite (NaOCl) were used as oxidants. All chemicals used such as sodium bicarbonate (for pH adjustment) and urea (as a model organic contaminant) were of laboratory grade. Also, raw ground

Table 1: Characteristics of raw ground water at typical well south of Cairo

parameter	Value
pH	7.7
Total dissolved solids (TDS),mg/l	1550
Alkalinity, mg/l (as CaCO_3)	1200
Hardness, mg/l (as CaCO_3)	939
Mg^{2+} , mg/l	167
Ca^{2+} , mg/l	99.5
CO_3^{2-} , mg/l	120
HCO_3^- , mg/l	488
SO_4^{2-} , mg/l	164.7
Fe^{2+} , mg/l	0.3
Mn^{2+} , mg/l	0.94

water sample taken from a working treatment plant at Beny Swif - Egypt was employed for experimental verification. Its chemical and physical characteristics are presented in Table 1.

Methods: Experiments were conducted on the prepared synthetic brackish water with the required salinity and pH. Addition of urea and oxidant doses has been undertaken as follows:

- Oxidation of iron (4.5 mg/l) in distilled water using KMnO_4 (5-10mg/l).
- Oxidation of manganese with or without iron content (1.8 mg/l) in NaCl solution (4000mg/l) using KMnO_4 (0.5-4 mg/l).
- Oxidation of iron (4.2mg/l) for different NaCl solutions (0-4000mg/l) using NaOCl (3.12-7.2 mg/l) as active chlorine.
- Oxidation of iron in the presence of Urea (50 mg/l) using NaOCl (3.12mg/l) as active chlorine.

The batch oxidation tests were conducted by shaking 250 ml sample (in 500 ml conical flask) for 15 and 30 minutes for Fe and Mn, respectively. Samples were left to settle for 45 minutes prior to filtration. The raw ground water sample taken from the working treatment plant at Beny Swif was tested for the oxidation treatment using different doses of KMnO_4 up to 2.5 mg/l and pH of 7.7 (raw groundwater) and adjusted pH (8.4).

Analysis: The liquid samples, after filtration through filter paper (Whatman No. 42), were quickly acidified before analysis. Fe and Mn were analyzed using the atomic absorption spectrophotometer, Perkin Elmer model (1100 B) for iron and manganese determination before and after the treatment according to Standard Methods for the Examination of Water and Wastewater [12].

RESULTS AND DISCUSSION

Iron Removal from Synthetic Brackish Water Using KMnO₄:

For the tested synthetic brackish water with iron content of 4.5 mg/l, the effect of KMnO₄ dose (5-10 mg/l) and pH (7-8.5) on iron removal is depicted in item 1 in Table 2. It is obvious that 98.2 % to 99.3 % iron efficiency could be achieved above pH 7 using the specified oxidant dose. This may be attributed to the role of dissolved oxygen and relatively alkaline conditions of the synthetic brackish water on iron removal. This result is supported by the fact that Fe can be oxidized in alkaline ground water by aeration. Consequently, lower doses of oxidant may be used for partial or complete aeration.

Figure 1 depicts the effect of KMnO₄ dose (0.5-4 mg/l) on manganese residual content for the treatment of Mn (1.8 mg/l) with or without Fe content

(3.8 mg/l) in NaCl solution (4000 mg/l) and at pH (8.5). The results show that for both cases, KMnO₄ dose of 2 mg/l achieves maximum Mn removal efficiencies of 98.8 % and 97.8 %, respectively which indicates that the presence of Fe enhances Mn removal as previously reported by Ellis *et al.* [3]. For iron removal, the lowest residual iron content of about 0.05 mg/l have been reached using KMnO₄ dose of 1 mg/l manifesting removal efficiency of 98.7 % as shown in item 2 in Table 2.

Chemical Oxidation of Synthetic Ground Water Using NaOCl:

For feed iron concentration of 4.2 mg/l, the lowest residual iron content of about 0.03 mg/l has been reached using 4.75 mg/l of active chlorine at pH=7.5 in distilled water. The effect of water salinity (1000 - 4000 mg/l) is considered almost insignificant regarding residual iron content for all active chlorine doses as shown in item 3 in Table 2.

Table 2: Results of the experimental treatment using different oxidants for Synthetic brackish water

Feed concentration (mg/l)					Effluent concentration (mg/l)	
Fe	Mn	NaCl (mg/l)	pH	Oxidant dose (mg/l)	Fe	Mn
1-Iron removal from synthetic brackish water using KMnO ₄						
4.5	-	0	7	5	0.04	-
				7.5	0.05	
				10	0.03	
4.5	-	0	8	5	0.04	-
				7.5	0.06	
				10	0.07	
4.5	-	0	8.5	5	0.05	-
				7.5	0.08	
				10	0.03	
2- Iron and manganese removal from synthetic brackish water using KMnO ₄						
-	1.8	4000	8.5	0.5	-	1.4
				1		1
				2		0.04
				3		0.11
				4		0.17
3.8	1.8	4000	8.5	0.5	0.06	0.82
				1	0.05	0.34
				2	0.16	0.02
				3	0.09	0.0
				4	0.03	0.03
3- Iron removal from synthetic brackish water using NaOCl at different NaCl solutions						
4.2	-	0	7.5	3.12	0.09	-
				4.75	0.03	
				7.2	0.05	
4.2	-	1000	7.5	3.12	0.01	-
				4.75	0.02	
				7.2	0.01	
4.2	-	1500	7.5	3.12	0.01	-
				4.75	0.01	
				7.2	0.06	
4.2	-	2000	7.5	3.12	0	-
				4.75	0.05	
				7.2	0.08	
4.2	-	4000	7.5	3.12	0.1	-
				4.75	0.07	
				7.2	0.05	
4- Iron removal from synthetic brackish water using NaOCl in the presence of Urea (50 mg/l)						
4.5	-	0	7.5	3.12	0.03	-
		1000			0.02	
		2000			0.03	
		3000			0.16	
		4000			0.24	

Table 3: Typical capital cost estimates for brackish water RO desalting system (3000 m³/day) [1]

Item	Cost (\$ 1000)	
	RO without Fe & Mn removal unit	RO with Fe & Mn removal unit
1- Conventional pretreatment	380	280
2- Fe & Mn removal unit	-	360
3-RO desalination unit	1500	1500
Total plant cost	1880	2140

Table 4: Typical Water Production Cost (\$ /m³) [1, 13,14]

Item	Cost (\$ /m ³)	
	RO without Fe & Mn removal unit	RO with Fe & Mn removal unit
1- Operating Cost (\$/m ³)		
- Labor (\$/m ³)	0.10	0.1
- Membrane replacement (\$/m ³)	0.42	0.084
- Maintenance (\$/m ³)	0.063	0.071
- Chemicals (\$/m ³)	0.1	0.15
- Electricity (\$/m ³)	0.15	0.20
Total Operating Cost (\$/m ³)	0.833	0.605
2- Depreciation (\$/m ³)	0.209	0.238
3- Total Production Cost (\$/m ³)	1.042	0.843
Basis of Cost Estimates		
- Annual production (m ³ /yr)	900,000	900,000
- Membrane cost	20% of RO capital cost	20% of RO capital cost
- Membrane life	1 years	5 year
- Maintenance cost	3% of total capital cost	3% of total capital cost
- Electricity	2 kWh/m ³ (at \$0.05/kWh)	3 kWh/m ³ (at \$0.05/kWh)
- Annual depreciation	10% of capital cost	10% of capital cost

The presence of urea doesn't affect the residual iron concentration at NaCl concentration less than 2000 mg /l where, iron removal efficiencies range from 99.5% to 99.6%. On the other hand, iron removal efficiency drops to 94% at 4000 mg/l of NaCl concentration as depicted in Figure 2.

Indicators of Raw Ground Water Treatment: Treatment results of raw ground water sample taken from a working treatment plant are illustrated in Figure 3. It is shown that the best result of iron removal is attained at KMnO₄ dose of 1 mg/l at both tested pH values of 7.7 and 8.4. For Manganese, the best condition is attained at pH = 8.4 and KMnO₄ dose of 1.5 mg/l.

Proposed Integrated Scheme for the Desalination of Marginal Quality Brackish Water: The conventional RO desalination scheme for brackish water is illustrated in Figure 4. The material balance for plant production and water quality is based on the following:

- Plant capacity: 3000 m³/d
- Raw water quality: (TDS = 4000mg/l, Fe =3.8 mg/l, Mn = 1.8 mg/l).
- Required water quality: (TDS = 500 mg/l, Fe < 0.1 mg/l, Mn <0.05 mg/l).
- Number of RO units /stage: 2 brine stages (RO1, RO2).
- Recovery of RO1, RO2: 70%, 60.7%, respectively.

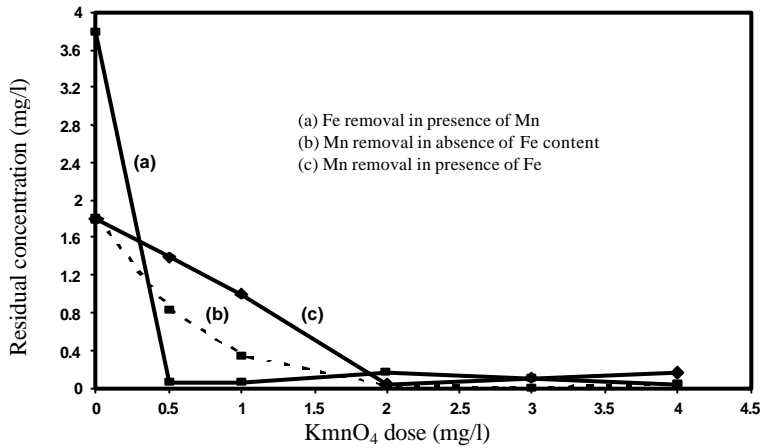


Fig. 1: Effect of KMnO₄ dose on iron and manganese removal Initial Fe & Mn concentrations (3.8, 1.8 mg/l), respectively NaCl (4000 mg/l), pH (8.5)

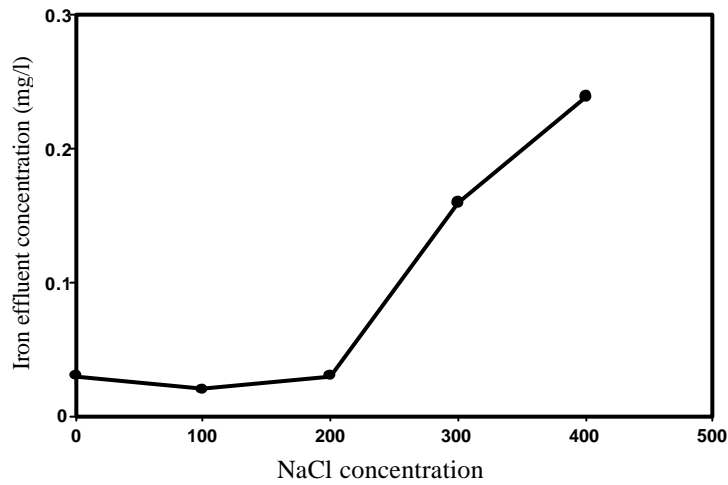


Fig. 2: Effect of NaCl concentration on iron removal in the presence of urea (50 mg/l) Initial Fe concentration (4.5 mg/l) NaOCl dose (3.12 mg/l), pH (7.5)

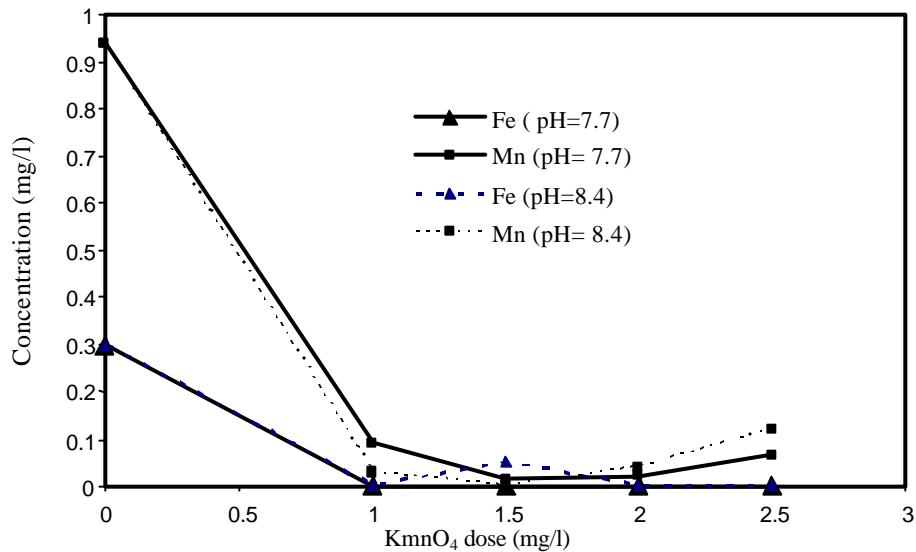


Fig. 3: Effect of KMnO₄ dose on iron & manganese removal in raw ground water at pH 7.7 & 8.4 . Initial Fe & Mn concentrations (0.3 & 0.94 mg/l), respectively

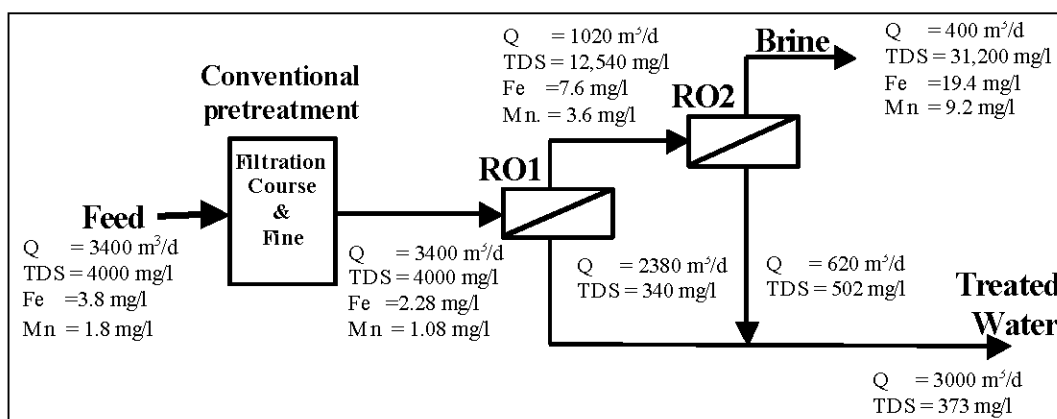


Fig. 4: RO desalting system for brackish water containing iron and manganese with conventional pretreatment

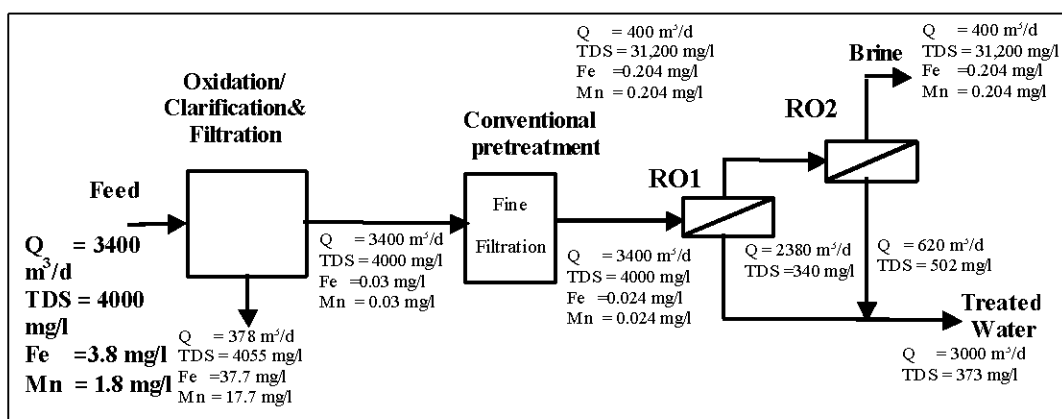


Fig. 5: Integrated pretreatment / RO desalting system for Brackish water containing iron and manganese

- TDS rejection of RO1, RO2: 91.5%, 96%, respectively.
- Removal of iron & manganese in the oxidation pretreatment before RO: (99.2 for Fe & 98.2 for Mn) and (20%) for fine filtration pretreatment.

The pretreatment is limited to chemical conditioning and filtration (coarse and fine filtration) prior to introducing water to RO membrane modules (maximum Fe and Mn removal approaches 40%) [1]. The proposed scheme for brackish water containing Fe and Mn shall incorporate Fe and Mn removal by oxidation, clarification and / or filtration (with water recovery of 90%) as an additional pretreatment to the conventional one as shown in Figure 5.

Economic Indicators for the Proposed Schemes:

In view of the experimental investigation results and based on updated cost data [13, 14] and collected data from the local market, the estimated costs for a

typical RO desalting plant (capacity of 3000 m³/d, salinity of 4000 mg/l and with Fe and Mn concentration of 3.8 mg/l and 1.8 mg/l, respectively) are typically given in Table 3. It is shown that the capital cost for RO plant with Fe and Mn removal unit is about 14% more than that for conventional RO plant. The production cost per cubic meter of produced water is depicted in Table 4. It is obvious that the cost is mainly affected by the cost of membrane replacement. Also, the estimated cost of water production by RO using an iron and manganese removal unit as a pretreatment is about \$ 0.6 /m³ as compared to about \$ 1.04/m³ in case of using conventional pretreatment only.

CONCLUSIONS

- The quality of brackish water could be improved by the use of proper pretreatment schemes prior to water desalting by RO.

- The experimental results for Fe & Mn oxidation show that lower doses of sodium hypochlorite or potassium permanganate (less than stoichiometric doses) could be used to achieve high removal efficiency by proper aeration, settling and filtration.
- Further investigations should be conducted to come up with the design parameters for the pretreatment options components and the integrated system for low quality brackish water desalting under varying conditions for water quality, plant capacity and site conditions.
- Economic analysis indicates the economic advantage of using the proposed scheme for iron and manganese treatment prior to RO desalting system.

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