

Potassium permanganate as pre-oxidant in a reverse osmosis water plant

Rafael Marín Galvín (*) and José Miguel Rodríguez Mellado

Departamento de Química Física y Termodinámica Aplicada, Facultad de Ciencias, Universidad de Córdoba, Avda. S. Alberto Magno s/n, 14004-Córdoba (SPAIN)

Abstract

This paper deals with the use of potassium permanganate (KMnO_4) as pre-oxidant in the reverse osmosis water plant of Marbella (Spain) during the summer of 1997. This facility usually treats shallow coastal marine raw water extracted at a depth of 10 m, containing a high amount of algae. These algae have caused heavy fouling rates in the reverse osmosis (RO) membranes and problematic operation of the plant. The use of KMnO_4 as pre-oxidant in dosages of about 0.45 to 0.8 g/m^3 has greatly improved the process through elimination of algae and organic matter in the water. Finally, the use of the reactant only increased the cost of water production by between 3 and 5 \$US/1000 m^3 (depending of the specific dosage used).

Introduction

KMnO_4 was introduced as a water treatment chemical by Sir Alexander Houston in London as early as 1913. In the USA this was already used in 1927 and 1928 in Rochester, NY, and Buffalo, NY, respectively (Welch, 1963; Shrode, 1972). In Spain the first experiments were carried out in Cáceres in 1984 intended to oxidise Fe and Mn in anoxic raw waters used for drinking water production (Catalán et al., 1984).

KMnO_4 is a very effective pre-oxidant for the following:

- oxidation of divalent Fe and Mn (Adams, 1960; Humphrey and Eikleberry, 1961; Marín Galvín and Rodríguez Mellado, 1996);
- oxidation of unspecific organic matters (Ma, 1990; Marín Galvín, 1997);
- removal of algae and their metabolites (AWWA, 1982; Carbonell Padrino and Martínez Ramírez, 1996);
- disinfection better than chlorine on some micro-organisms such as viruses (Welch, 1963);
- reduction of the final dose of chlorine;
- reduction in trihalomethane (THM) formation and other chlorinated organic compounds (Armenter et al., 1997; Colthurst and Singer, 1982; Marín Galvín, 1997; Singer et al., 1982);
- finally, reduction in tastes and odours in final drinking waters (Cherry, 1962; AWWA, 1982; Marín Galvín, 1997).

All the evidence summarised above is based on results obtained when treating raw continental water (i.e., not saline waters extracted from reservoirs, rivers and underground waters) intended for drinking water production. Nevertheless, the use of KMnO_4 to treat marine raw waters has only been employed to date in raw waters with high amounts of divalent iron and manganese (Pujadas, 1984), with good results.

This paper reports on the first results of a more complete investigation, focused on the use of KMnO_4 as pre-oxidant in an

RO membrane facility, in order to improve the general operation of the plant, as well as to safeguard the quality of influent marine waters rich in algae and unspecific organic matter.

Materials and methods

Marine raw waters used in this study were abstracted through pumping from an open conduit inlet located at a depth of 10 m and distance of 500 m from the coastline in Marbella (Spain). This raw water is also used to feed the RO plant of the Western Sun Coast (Málaga): the RO plant is the biggest in Europe and the 6th biggest in the world, producing 55 000 m^3/d of soft drinking water (Velasco López, 1997).

Water samples were analysed according to *Standard Methods*, 1989 and Marín Galvín, 1995; organic matter was analysed by the heat acidic medium permanganate method (COD-Mn), and total-P by the ascorbic-molybdate method. The membrane filtration technique was employed to investigate total and faecal coliform numbers.

Laboratory tests with KMnO_4 used the solid commercial product (AQUOX™) in a 0.1% w/w solution: 1 ml of this solution added to 1 000 ml of raw water implied a dose of 1 mg/l or 1 g/m^3 of product. All experiments were done in triplicate. Conversely, full-scale plant tests also used the commercial product but dosed directly as solid product.

Results and discussion

Table 1 shows the average quality of marine raw water investigated corresponding to a period between 23 June and 19 September 1997. During this period the water showed algal bloom characteristics due to the presence of the following phytoplankton species: Rhodophyta (red algae), Chlorophyta (green algae), diatoms (*Navicula* and *Rivularia*) and *Rhodomonas* (dinoflagellates). This bloom caused severe fouling of RO membranes as well as a high level of COD-Mn (greater than 5 $\text{mg O}_2/\text{l}$ - maximum level established in the Spanish criteria for drinking waters) in the final treated water. Due to these problems the effectiveness of KMnO_4 to remove algae and organic matter in order to improve the operation of the RO plant, was investigated.

* To whom all correspondence should be addressed.

☎ 34-57-218617/18/19; fax 34-57-218606; e-mail QFIROMEJ@uco.es
Received 3 December 1997; accepted in revised form 24 April 1998

TABLE 1 AVERAGE QUALITY OF MARINE RAW WATER STUDIED		
Parameters	Units	Concentration
Temperature	°C	23
COD-Mn	mg/l O ₂	12.5
Chloride	g/l of Cl	19.45
Conductivity	mS/cm	58.98
pH	pH units	8.1
Iron	mg/l of Fe	<0.010
Manganese	mg/l of Mn	0.030
Total phosphorus	mg/l of P	0.038
Total coliforms	colonies/100 ml	100
Faecal coliforms	colonies/100 ml	0

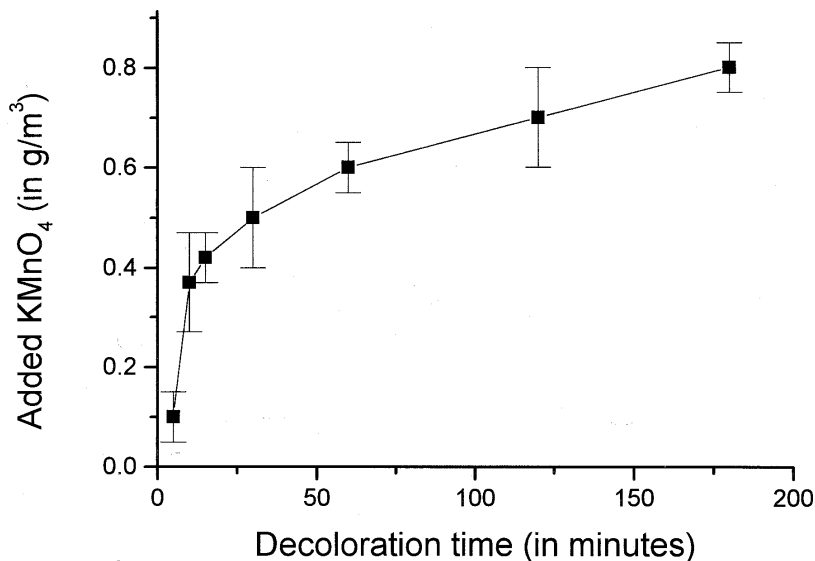


Figure 1
Average curve
decoloration vs. time

Laboratory tests

The use of KMnO₄ is dependent on the time elapsed between addition to raw water and the subsequent treatment process applied to water (e.g. settling, filtration,...). In this case, the correct use is when the KMnO₄ carries out its oxidant action before introducing the water to the membranes.

A typical parameter in the use of KMnO₄ is the immediate KMnO₄ demand of water after 15 min (IPD₁₅). This was determined by dosing different amounts of KMnO₄ solution to 1 000 ml of raw water and reading which dose produces the disappearance of pink colour in 15 min (disappearance of pink colour denotes that the concentration of KMnO₄ is lower than 0.050 mg/l) (Shrode, 1972; Welch, 1963). Results indicated an IPD₁₅ ranging between 0.45 and 0.7 g/m³ according to the varying quality of the marine raw water.

For operational purposes, it is very important to know the evolution of decoloration with time for different KMnO₄ doses: therefore, depending on the flow pumped towards the RO plant both the hydraulic time (from 1 to 3 h) and the dose of KMnO₄ changed. Fig. 1 shows the average decoloration vs. time curve for all the laboratory experiments carried out. These data show the optimal dose to apply for each specific hydraulic time.

In this way, the waters dosed with KMnO₄ after 1, 2 and 3 h

of contact time and decoloration doses of 0.6, 0.7 and 0.8 g/m³, respectively, were analysed. The averaged results (see Table 2) for marine raw water indicated that after 1 h of pre-oxidation with 0.6 g/m³ of KMnO₄, the COD-Mn value was reduced to 50% (average), the total coliform number being zero and total-P was reduced from 0.038 mg/l to <0.005 mg/l.

Full-scale plant tests

As noted above, concurrent with a strong period of algal bloom experienced in the marine raw water, the increasing fouling of the RO membranes provoked a reduction of 50% in the time of the operative cycles. This circumstance was associated with increases of the (SDI) values (a fouling index of the RO membranes) of raw water up to more than 5 units, as well as high values of the COD-Mn (from 25 to 37 mg/l).

When a dosage of 0.7 to 0.8 g/m³ of KMnO₄ was added to raw water during abstraction, the organic matter in the water was oxidised by KMnO₄ along the pipeline feeding the RO plant (1.5 to 2.5 h of hydraulic time) and it did not show any pink colour in the inlet to the RO plant.

The use of KMnO₄ was continuously maintained for 120 h (15 to 19 September). In this period the time of service of the RO membranes increased to the original values as found during the absence of algal blooms, and the SDI values became lower than

Time (h)	Dose	COD-Mn	Residual Mn	Colour	Total-P	Total coliforms
1	0.6	6	0.045	<2	<0.005	0
2	0.7	5.9	0.040	<2	<0.005	0
3	0.8	5.9	0.035	<2	<0.005	0

COD-Mn: mg/l O₂; Mn: mg/l; Colour: Hazen units; Total-P: mg/l; Total coliforms: colonies/100ml

3 units. At the same time, the pre-oxidised water showed a constant residual concentration of Mn lower than 0.050 mg/l and a COD-Mn value lower than 5 mg/l.

Finally, the average costs of treatment with KMnO₄ increased the total costs of drinking water treatment by only between 3 and 5 \$US/1 000 m³ (depending on specific dosage, and approximately never more than 10% over total costs). Table 3 shows an estimation of costs.

Conclusions

The dosing of KMnO₄ as pre-oxidant in low dosages has proved its effectiveness in order to eliminate the problems caused by algal blooms in marine raw water, to be treated in an RO plant. The additional costs of treatment can be estimated to be about 5 to 10% with respect to the usual RO treatment costs. Nevertheless, new experiments are being carried out to optimise the process.

Acknowledgements

Authors wish to express their acknowledgements to Mr. J. Velasco López and Mr. A. Muñoz Rizos of DECOSOL, exploiter company of the Reverse Osmosis Water Plant of Marbella (Spain). Also, partial financial support was obtained from Junta de Andalucía (Research Group FQM-0198) .

References

- ADAMS B (1960) Manganese removal by oxidation with potassium permanganate. *J. AWWA* **52** 219-228.
- ARMENTER J LI, CRISTIÁ J and MATÍA LI (1997) Pretreatments options for water with high disinfection byproducts formation potential. Paper presented at XX11 IWSA Congr., Madrid. Special Subject 15. SS15-1, SS-15-8.
- AWWA (1982) Permanganization of Denver's Raw Water Reservoir. *AWWA Res. Found. Res. News* (August) 2-4.
- CARBONELL PADRINO MO V and MARTÍNEZ RAMÍREZ E (1996) El permanganato potásico como algicida. *Química e Industria*, Setiembre 549-552.
- CATALÁN LAFUENTE J, GARCÍA MARTÍNEZ E, GARZA MONJE J and BOTAS LAMAS T (1984) Aplicación del permanganato potásico, KMnO₄, al tratamiento de aguas blancas. *Tecnología del Agua* **17** 95-98.

	Percentage	\$US/1 000 m ³
Chemicals	20%	8
Electric power	40%	16
Membranes replacement	40%	16
Permanganate	(+10%)	(+4)
Total	-	44

- CHERRY AK (1962) Reduction for tastes and odours - KMnO₄ and activated carbon. *Water Works Eng.* (March) 182-185.
- COLTHURST JM and SINGER PC (1982) Removing trihalomethane precursors by permanganate oxidation and manganese dioxide adsorption. *J. AWWA* **74** (2) 78-83.
- HUMPHREY SB and EIKLEBERRY MA (1961) Iron and manganese removal using KMnO₄. *Water & Sewage Works* **108** 176-180.
- MA J (1990) Effectiveness and mechanism of potassium permanganate oxidation for the removal of micropollutants from polluted water. Doctoral Dissertation, Harbin Univ. of Archit. and Eng., PR China.
- MARÍN GALVÍN R (1995) *Análisis de Aguas y Ensayos de Tratamiento: Principios y Aplicaciones*. Ed. GPE, S.A. Barcelona (Spain).
- MARÍN GALVÍN R (1997) Permanganato potásico en potabilización de aguas. Reducción de materias orgánicas y subproductos de desinfección. *Química e Industria* **44** (6) 24-30.
- MARÍN GALVÍN R and RODRÍGUEZ MELLADO JM (1996) Potabilización de aguas con permanganato potásico. *Ingeniería Química* **325** 75-82.
- PUJADAS A (1984) Pretratamientos del agua en los sistemas de Ósmosis Inversa. *Tecnología del Agua* **17** 55-59.
- SHRODE LD (1972) Potassium permanganate: Use in potable water treatment. *Water and Sewage Works*, ref. núm. R10-R19.
- SINGER PC, BORCHAD JH and COLTHURST JM (1982) The effects of permanganate pretreatment on trihalomethane formation in drinking water. *J. AWWA* **72** (10) 573-578.
- STANDARD METHODS (1989) *Standard Methods for the Examination of Water and Wastewaters* (17th edn.) AWWA, Washington DC (USA).
- VELASCO LÓPEZ J (1997) Planta Desaladora de la Costa del Sol Occidental. *RETEMA-Medio Ambiente*, Enero. 37-45.
- WELCH WA (1963) Potassium permanganate in water treatment. *J. AWWA* **55** 735-741.

