SILICA REMOVAL IN INDUSTRIAL EFFLUENTS WITH HIGH SILICA CONTENT AND LOW HARDNESS

Isabel Latour, Ruben Miranda, Angeles Blanco*

Department of Chemical Engineering, Faculty of Chemistry, Complutense University of Madrid – Avda. Complutense s/n, 28040 Madrid (Spain). Phone: +34 913944247. Fax: +34 913944243. E-mail*: ablanco@ucm.es

ABSTRACT

High silica content of paper mill effluents is limiting their regeneration and reuse after membrane treatments such as reverse osmosis (RO). Silica removal during softening processes is a common treatment; however, the effluent from the paper mill studied has a low hardness content which makes necessary the addition of magnesium compounds to increase silica removal. Two soluble magnesium compounds ($MgCl_2·6H_2O$ and $MgSO_4·7H_2O$) were tested at five dosages (250-1500 mg/L) and different initial pHs. High removal rates (80-90%) were obtained with both products at the highest pH tested (11.5). With these removal efficiencies, it is possible to work at high RO recoveries (75-85%) without silica scaling. Although pH regulation significantly increased the conductivity of the waters (at pH 11.5 from 2.1 mS/cm to 3.7-4.0 mS/cm), this could be partially solved by using $Ca(OH)_2$ instead of NaOH as pH regulator (final conductivity around 3.0 mS/cm). Maximum chemical oxygen demand (COD) removal obtained with caustic soda was lower than with lime (15% vs. 30%). Additionally, the combined use of a polyaluminum coagulant during the softening process was studied; the coagulant, however, did not significantly improve silica removal, obtaining a maximum increase of only 10%.

Keywords: silica removal, magnesium, softening, co-precipitation, membranes fouling, effluent reuse, paper recycling

1. INTRODUCTION

Nowadays sustainable water management in paper mills is a must. One of the alternatives to improve sustainability is the reduction of the fresh water consumption through the regeneration and reuse of the effluent after an advanced treatment, usually including a reverse osmosis (RO) (Negaresh et al. 2013). With this treatment, it is possible to obtain high quality water to replace fresh water use at critical points, such as in the high pressure showers of the paper machine, where the highest quality is required (Ordoñez et al. 2010). Nevertheless, one of the bottlenecks for the implementation of this technology is the silica scaling on reverse osmosis membranes, which is very hard to remove once it is formed (Koo et al. 2001; Hater et al. 2011). This limitation is more important in deinking paper mills because they have high silica content in the effluent which is ranging from 50 to 250 mg/L as SiO_2 (Huuha et al. 2010; Latour et al. 2013). This causes severe scaling problems in RO membranes and other processes due to its low solubility 100-140 mg/L (as SiO_2) at 25ºC (Sheikholeslami and Tan 1999). Silica scaling on RO treatments limits its recovery efficiency and the viability of the treatment (Salvador Cob et al. 2012), but it is not the only reason for the growing interest on silica removal, there is also stringent limits on the effluent quality set by the environmental legislation for silica: 50 mg/L in Finland, Canada or United States (Huuha et al. 2010). Therefore there is a real industrial challenge in the paper sector, especially in recycling paper mill, the removal of silica from the effluent.

In deinking paper mills, silica mainly comes from sodium silicate, which is a process additive used in deinking and bleaching steps to achieve the optical properties required in the final product (Ferguson 1992a; Ferguson 1992b). Due to its variety of functions, its removal in origin is very difficult. Although some alternatives have been studied (Hamäläinen et al. 2007), there is still not a satisfactory solution.

Silica and silicates derive from the orthosilicic acid. This is a weak polyprotic acid with pK_a values of 9.9, 11.8 and 12 (Ning 2002). Orthosilicic acid only remains monomer at 25ºC when the concentration is less than 2 mM. It polymerizes when its concentration in the solution is higher, resulting larger molecules which can reach a colloidal size. The rate of silicic acid polymerization is strongly pH-dependent. The reaction is very fast in neutral and slightly alkaline solutions, and extremely slow at low pH values of 2-3

(Ning 2002). More complex colloids can also be formed by its combination with organic and inorganic compounds. Silica and silicates chemistry is complex as different species with different behaviour can be found in the system. The most common classification of silica related species is based on their size, in this sense they can be classified as soluble, colloidal or particulate. Soluble silica includes polysilicic acid, small molecules as dimers, trimers or oligomers. Colloidal silica is used to address more highly polymerized species or particles larger than 50 Å, although sometimes this denomination also includes species down to 10-20 Å. This category includes the colloidal particles formed by the combination with organic and inorganic species (Sheikholeslami and Tan 1999). On the other hand, particulate silica is larger than colloidal size silica.

Silica scaling can occur through different mechanisms. First, deposition of silica compounds such as pure quartz scales, calcium silicate, magnesium silicate, and aluminum silicate when their solubility is exceeded. Colloidal silica deposition can also be found. In this case colloids are formed in the bulk solution and then accumulate on the membrane surface blocking the pores. Finally, biogenic silica scaling caused by microorganisms can also appear on the membranes (Sheikholeslami and Tan 1999; Sheikholeslami and Bright 2002).

There are several silica removal processes but chemical methods are the most frequently used (Sheikholeslami et al. 2001; Zeng et al. 2007). Among them, silica removal during softening processes or by coagulation at high pH are the two most commonly used as they are able to treat large volumes of water at moderate costs. Both treatments are efficient with high silica concentrations such as those typically found in paper mill effluents.

The drawback of silica removal by coagulation for high silica loaded effluents is the cost of the treatment due to the high dosages of coagulant required (Hermosilla et al. 2012; Latour et al. 2013). On the other hand, silica removal during softening is promising although it is necessary to ensure that there is enough hardness present in the water in order to obtain high silica removal rates. Though calcium and magnesium are proven to be functional for silica removal, the higher ratio Mg/Ca, at constant total hardness, the higher silica removal is achieved (Chen et al. 2006). This is the reason

why this study is focused on improving silica removal during the softening process by the addition of magnesium salts.

In the literature, there are several theories regarding the silica removal mechanisms (Sheikholeslami and Bright 2002; Chen et al. 2006; Parks and Edwards 2007; Hsu et al. 2008). Two main mechanisms have been proposed and probably both could occur simultaneously: adsorption of silica into fresh precipitated $CaCO_3$ and $Mg(OH)_2$ and co-precipitation of silica to form calcium and magnesium silicates with different stoichiometries.

On the other hand, different authors studied the addition of coagulant to assist silica removal during the softening process (Sheikholeslami and Bright 2002; Al-Rehaili, 2003; Cheng et al. 2006; Zeng et al. 2007), yet, there is no agreement on whether coagulant addition significantly improves silica removal. Al-Rehaili (2003), for example, found necessary the addition of coagulants such as alum, sodium aluminate or ferric chloride to improve the performance of the lime-soda ash process on silica removal. However, Sheikholeslami and Bright (2002) found that the addition of alum and ferric chloride only slightly increase silica removal during the softening process. Furthermore, Chen et al. (2006) studied that the addition of a polyaluminum chloride improved silica removal at pH 10 but it decreased at higher pH due to the anphoteric properties of the aluminum hydroxide.

This paper aims to generate new knowledge on the mechanisms and the efficiency of silica removal by softening in the effluent of a deinking paper mill with high silica content and low hardness. These conditions differ from the ones considered in previous studies in which silica was removed during de softening process (Chen et al. 2006; Parks and Edwards 2007; Hsu et al. 2008). In those cases, the water to be treated had low silica content and high hardness. Due to the low calcium and magnesium contents of the effluent, two magnesium soluble salts ($MgCl_2·6H_2O$ and $MgSO_4·7H_2O$) were used to improve silica removal efficiency. In this study the dosage, the operating pH and the pH regulator were optimized. Moreover, the combination of $MgCl_2·6H_2O$ with a polyaluminum nitrate sulphate coagulant was also studied to reduce treatment cost. The final objective of the present work is to achieve the silica removal necessary (80-90%)

to increase RO recovery from 20% to 60-80%, to be able to make the effluent reuse process technically and economically feasible.

2. MATERIALS AND METHODS

2.1. Water Samples

This study was carried out with the effluent of a Spanish paper mill using 100% recovered paper to produce newsprint. The mill has an integrated wastewater treatment plant consisting of a primary treatment by dissolved air flotation and a secondary treatment based on an aerobic digestion of the waters on a moving bed biofilm reactor (MBBR), followed by a secondary dissolved air flotation. Water samples were taken after these treatments, before the effluent discharge to an urban wastewater treatment plant. Samples were stored at 4ºC during the tests and no sets of trials longer than five days were carried out. Table 1 summarizes the main characteristics of the effluent. Dissolved fraction was obtained by centrifugation at 2000 g during 15 min.

Table 1 Characteristics of the paper mill effluent.

RAW WATER	
pH	8.3
Conductivity (mS/cm)	2.20
Cationic Demand (meq/L)	0.74
Total Solids (mg/L)	1986
Total Suspended Solids (mg/L)	83
BOD_5 (mg/L)	150
Turbidity (NTU)	120
Total Alkalinity (mg/L $CaCO_3$)	675
DISSOLVED FRACTION	
Total Solids (mg/L)	1894
Silica (mg/L SiO_2)	180
COD (mg/L)	450
Sulphates (mg/L)	239
Chlorides (mg/L)	126
Calcium (mg/L)	33.5
Magnesium (mg/L)	2.8
Turbidity (NTU)	7.9

2.2. Chemicals

Two magnesium compounds, $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$, and two different pH regulators, NaOH and $Ca(OH)_2$, were tested. The four of them, reagent grade, were supplied by PANREAC. A polyaluminum nitrate sulphate coagulant (PANS combined with a quaternary polyamine hybrid coagulant) supplied by Sachtleben Chemie (Germany) was also used. This coagulant has 3.2% aluminum content and 1.8 wt.% polyamine active content. Magnesium compounds, pH regulators and the coagulant were prepared at 10 wt./v.% with distilled water on a daily basis.

2.3. Methodology for jar-tests

For each magnesium compound 5 dosages were tested (from 250 to 1500 mg/L) at 3 different pHs: 10.5, 11 and 11.5. First, the best magnesium compound was selected using NaOH as pH regulator. Then the pH regulator was optimized, comparing the efficiency of NaOH and $Ca(OH)_2$. Finally, the effect of the polyaluminum coagulant on the softening treatment with the most efficient magnesium salt was assessed.

Fig. 1 summarizes the jar-test methodology followed to study the efficiency of the different treatments. First, the pH of the samples was adjusted by adding NaOH 10 wt./v. % to 250 ml of sample. After 1 min of mixing at 800 rpm, the magnesium compounds were added from and mixed with the waters during 15 min at 800 rpm. After this period, the waters were allowed to settle for 1 h. Finally, the clarified waters and their dissolved and colloidal material (DCM) fraction, obtained by centrifugation at 2000 g during 15 min, were characterized for different analytical parameters. All trials were carried out at room temperature (20ºC ±2 ºC) by duplicate, and the average error between replicates was always under 5%.

The optimization of the pH regulator was carried out following the same jar-test methodology but, in this case, the study was only carried out with the most efficient magnesium salt according to the previous results obtained, i.e. $MgCl_2 \cdot 6H_2O$. Three different dosages (500, 1000 and 1500 mg/L) were tested with the two pH regulators.

Finally, the effect the combination of a polyaluminum coagulant with the magnesium compound was studied. In this case, $MgCl_2 \cdot 6H_2O$ dosages were tested at 250 mg/L and 750 mg/L. The coagulant dosage used was fixed according with preliminary tests

(Latour et al. 2013) and it was 125 mg/L at the three initial pHs tested. The objective was to partially replace the magnesium salt with the coagulant. For that purpose lower dosages were used. As shown in Fig. 1 after the addition of the magnesium salt and mixing, 125 mg/L of coagulant were added and mixed during 2.5 minutes at 800 rpm. Then samples were allowed to settle for 1 hour as in the rest of studies.

Mixing was carried out in a multiposition magnetic stirrer OVAN MulitMix Heat D. pH was measured using a GLP 22 pH meter (Crison, S.A), according to Standard Method 4500, and conductivity was determined with a GLP 31 conductivity meter (Crison, S.A.), according to the ISO 7888. Reactive silica was measured by flow analysis and photometric detection through silicomolybdate and reduction to molybdenum blue, using a FIA Compact (MLE GmbH) according to DIN EN ISO 16264 and expressed as mg/L of SiO_2. Chemical oxygen demand (COD) was measured according to the Standard Method 5220-D (Alkalinity was measured by titration with sulphuric acid 0.1 N using a pH electrode connected to an automatic titrator, model Compact I (Crison Instruments S.A.) to reach pH 4.5, according to the EPA 310.1 (1983) method. Sulphate content was determined using Nanocolor® sulphates method (Macherey-Nagel GmbH). Calcium and magnesium content were measured using a direct air-acetylene flame atomic absorption method according to ISO-7980:1986 in a SpectraA 220 spectrophotometer supplied by Varian. Finally, turbidity was measured with a LP 2000-11 nephelometer, supplied by Hanna Instruments, according to ISO 7027.
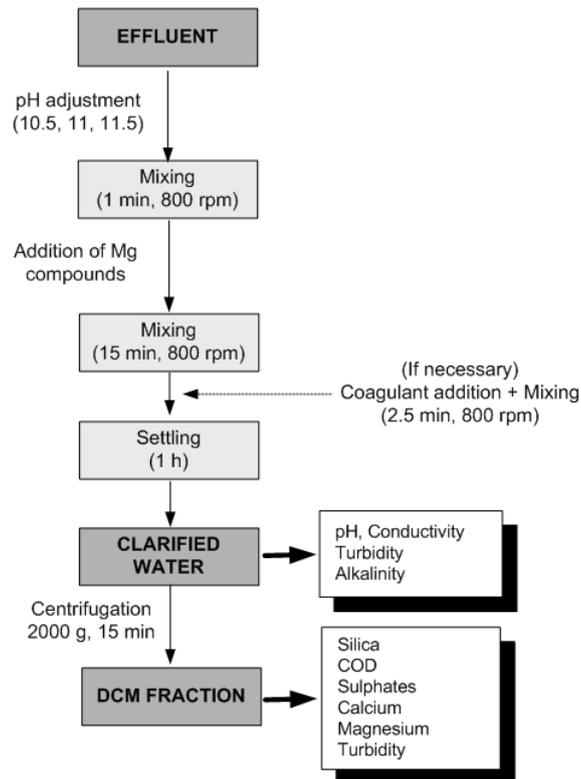
Fig. 1 Methodology for the evaluation of silica removal during softening.

.

3. RESULTS AND DISCUSSION

3.1. Selection of the pH and magnesium compound

Fig. 2 shows silica removal rates obtained with different dosages of $MgCl_2 \cdot 6H_2O$ and $MgSO_4 \cdot 7H_2O$ at three initial pHs (10.5, 11 and 11.5). Experiments at initial pH=8.3 (pH of the waters without any pH adjustment) and 9.5 were also carried out, however, as silica removal rates were lower than 20% even at the highest magnesium chloride dosage tested (1500 mg/L), the results are not shown. Due to the high silica removal rates required to achieve the objectives of the present work, these pHs were discarded, and only pHs ≥ 10.5 were further studied. The maximum removal rates were achieved at the highest pH (11.5) and dosage (1500 mg/L), being $MgCl_2 \cdot 6H_2O$ more efficient (90% silica removal) than $MgSO_4 \cdot 7H_2O$ (77% silica removal) at these conditions. With 90% silica removal it would be possible to work on RO membranes at 80-85% without silica scaling problems. Besides, it is worth to mention that silica removals around 60% are also a treatment option as they would be high enough to work at intermediate RO recoveries (60-75%), with the additional advantage of lower pH adjustment (pH=11 and

8

1000-1500 mg/L of the magnesium species) or a lower magnesium compound dosage (dosages $\geq$ 750 mg/L at pH=11.5), which are translated in lower chemical costs, lower conductivity and possibly avoiding the need of RO rejects post-treatment.
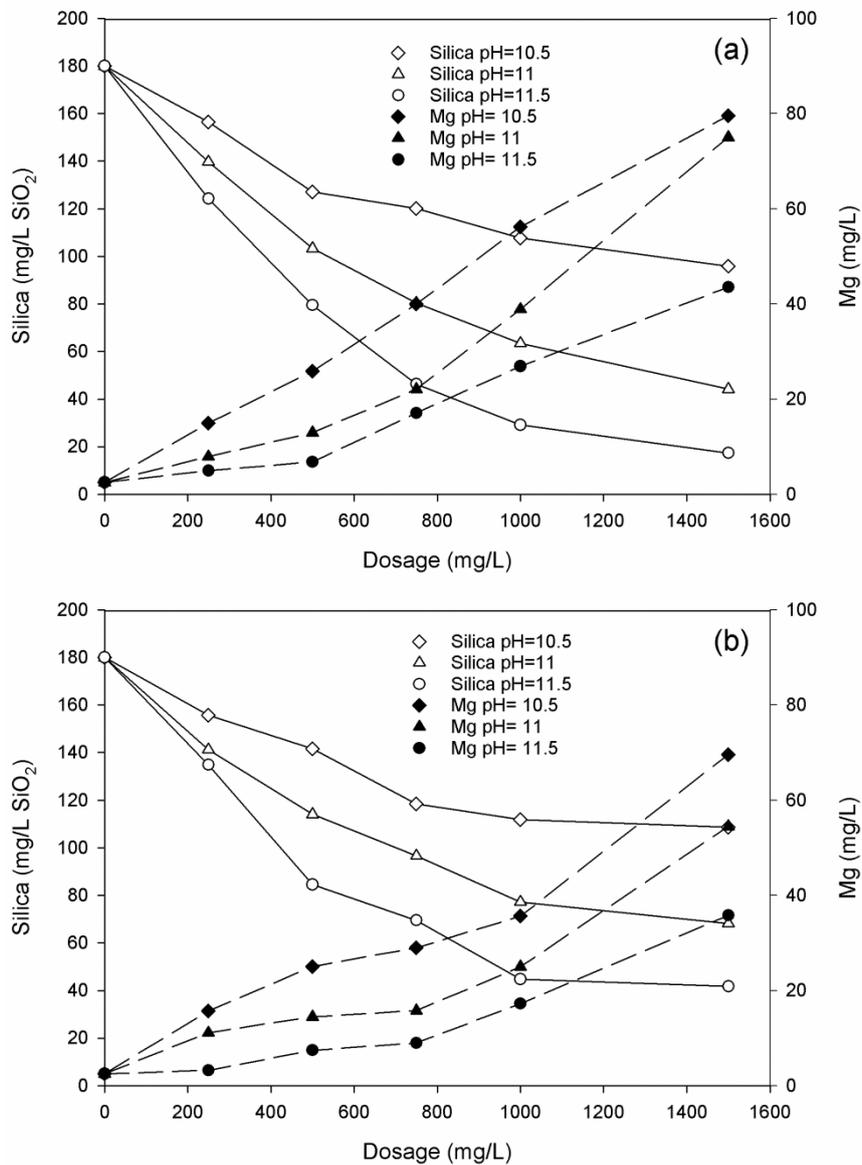

Fig. 2 Silica removal vs. dosage of (a) $MgCl_2 \cdot 6H_2O$ and (b) $MgSO_4 \cdot 7H_2O$, at different initial pHs.

Fig. 3, shows the mmol of silica removed per mmol of initial magnesium contents. This ratio is almost the same for both magnesium species, what would explain that silica removal rates with $MgSO_4 \cdot 7H_2O$ were lower than those obtained with $MgCl_2 \cdot 6H_2O$ as $MgSO_4 \cdot 7H_2O$ has a magnesium content of 9.9 wt.% versus 12.0 wt.% of $MgCl_2 \cdot 6H_2O$. It was observed that as pH was increased more silica was removed per mmol of

magnesium. With 250 mg/L of the magnesium salts this ratio increased from 0.8 at pH=10.5 to 1.20 at pH=11 and 1.50 at pH=11.5. As dosage increased these differences between the ratios at the three pHs became smaller. The explanation is that, despite the increase in silica removal with the dosage there was an excess of magnesium in the water. Therefore, the final concentration of magnesium in the effluent increases with the dosage and decreases with pH. In these conditions precipitation of magnesium hydroxide and magnesium silicates are favoured (Al-Mutaz and Al-Anezi 2004).
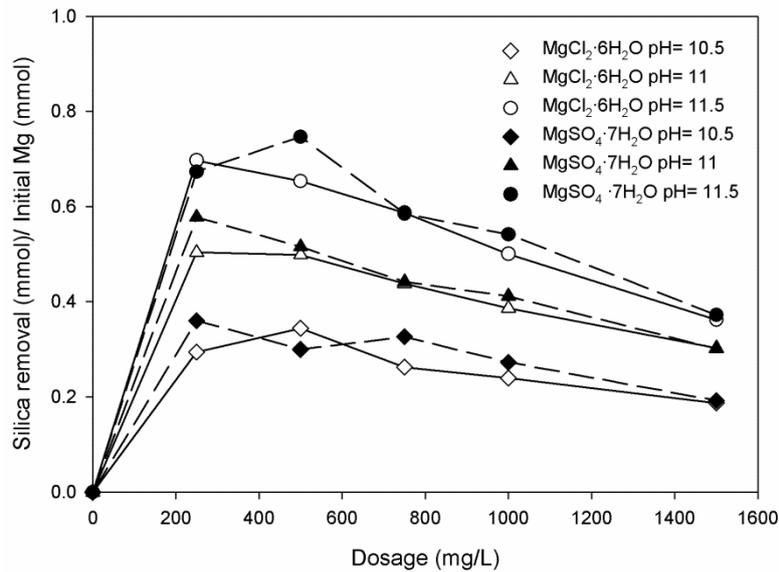
Fig. 3 mmol of silica removed per mg/L of initial magnesium at different initial pHs with $MgCl_2 \cdot 6H_2O$ or $MgSO_4 \cdot 7H_2O$.

Silica is removed at high pHs by two main mechanisms: precipitation of calcium and/or magnesium silicates with different stoichiometries and by adsorption/enmeshment in freshly precipitates of $Mg(OH)_2$ and/or $CaCO_3$. However, depending on the pH one mechanism is more important than the other, although both usually occur simultaneously. If silica is removed through the formation of magnesium silicates such as Mg_2SiO_4 (forsterite) or $MgSiO_3$ (enstatite) the ratio mmol Si removed/mmol Mg removed would be 0.5 and 1, respectively. If adsorption on magnesium hydroxide were the main mechanism involved this ratio would be smaller. Chen et al. (2006) and Hsu et al. (2008) reported that 0.04 mmol Si were removed per mmol of Mg removed. Fig. 4 shows the ratios mmol Si removed/mmol Mg removed at the three pHs and dosages tested. For both products the Si:Mg removed decreased with the dosage indicating that

the precipitation of $Mg(OH)_2$ was favoured at higher magnesium concentrations. On the other hand, the ratio Si:Mg increased with pH and thus the precipitation of magnesium silicates. These results were in agreement with the fact that the $SiO_4{}^{4-}$ becomes more predominant at pHs higher than 11, which would favour the precipitation of forsterite (Sheikholeslami and Bright 2002). Regarding the values of the Si:Mg ratio for the two magnesium salts tested, with $MgCl_2 \cdot 6H_2O$ the Si:Mg varied between 0.2-0.4, what indicates that Mg_2SiO_4 (forsterite) was the precipitated compound. This ratio is lower than 0.5 due to the precipitation of $Mg(OH)_2$ which, as mentioned before, removes silica in a ratio 0.04 Si:Mg. With $MgSO_4 \cdot 7H_2O$ the ratio Mg:Si was higher and varied between 1and 0.5. In this case, the ratio 1:1 points at the precipitation of $MgSiO_3$ (enstatite) apart from the other two species. According to the Si:Mg ratios obtained, despite the fact that precipitation of $Mg(OH)_2$ contributed to the removal of silica, the precipitation of silicates was the main silica removal mechanism.
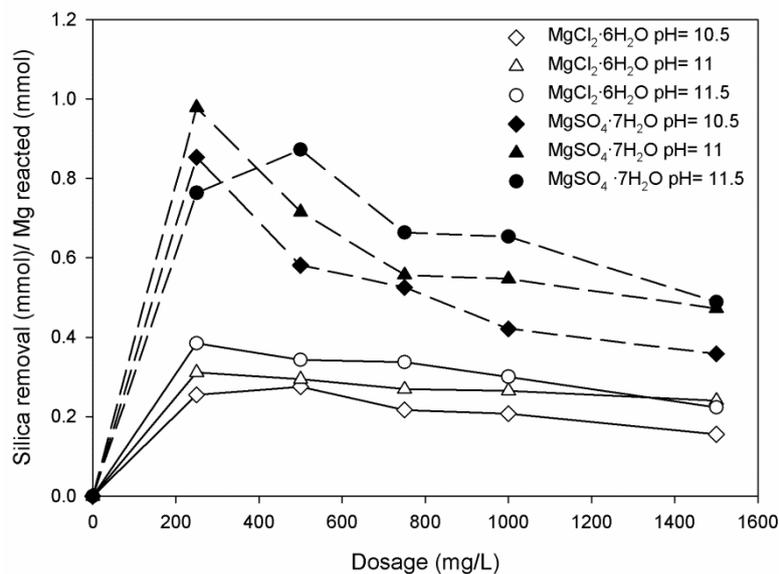

Fig. 4 mmol of silica removed per mmol of magnesium reacted at different initial pHs with $MgCl_2 \cdot 6H_2O$ or $MgSO_4 \cdot 7H_2O$.

Alkalinity is an important parameter to understand silica removal mechanism during the softening process as it allows monitoring the precipitation of $Mg(OH)_2$, $CaCO_3$ and different calcium or magnesium silicates. As mentioned, in this particular case, silica removal through the precipitation of calcium carbonate or/and calcium silicates was not significant given the low average value of calcium removed (only 10 mg/L) under the

different operational conditions, so much so taking into account the high dosages of Mg tested and the higher efficiency of Mg compared to Ca on silica removal. The results show that alkalinity followed the same tendency for both magnesium salts: it increased with the pH, as there were more hydroxide groups in the water, and decreased with magnesium dosage because more magnesium was available to precipitate with hydroxides forming $Mg(OH)_2$ or silicates. The final alkalinity of the water with the maximum dosage tested (1500 mg/L) was around 1000 mg/L $CaCO_3$ at pH=10.5, 1100 mg/L $CaCO_3$ at pH=11 and 1150 mg/L $CaCO_3$ at pH=11.5.

Conductivity is also critical for working at high RO recoveries. As mentioned, usual recoveries in RO systems for this application are around 60-80%, thus the conductivity in the RO rejects are 2-4 times higher than the feed water. In the specific case of this paper mill, the discharge limit value for conductivity in the effluent is 7.5 mS/cm, therefore higher values in the rejects would make necessary the post-treatment of these RO rejects, this increasing the cost of the treatment chain.

Although the conductivity of the treated water was mostly increased due to pH regulation, the addition of magnesium salts also had a contribution to such rise. The conductivity increase caused by higher dosages of the magnesium salt was, however, lower at high pHs. This was because at higher pHs, the softening process was favoured, thus more magnesium in form of magnesium hydroxide and magnesium silicate were removed and, in to a lesser extent, calcium carbonates and silicates. The increase in conductivity, compared with the blank value at each initial pH, was 0.7 mS/cm at pH 10.5, 0.6 mS/cm at pH 11 and 0.4 mS/cm at pH 11.5 for $MgCl_2·6H_2O$. In the case of $MgSO_4·7H_2O$ this increase was 0.4 mS/cm, 0.3 mS/cm and 0.1 mS/cm for pH=10.5, 11 and 11.5 respectively. This increase was smaller with $MgSO_4·7H_2O$ compared to $MgCl_2·6H_2O$. This is in agreement with the bibliography in which it was reported that the conductivity of 10 wt./vol.% dissolutions of $MgCl_2·6H_2O$ and $MgSO_4·7H_2O$ are 108 mS/cm and 42.7 mS/cm respectively (Wolf 1966; CRC 2013).

In correspondence with alkalinity, pH decreased with the different treatments. This decrease was always more pronounced with $MgCl_2·6H_2O$ for all the dosages and pHs tested. pH decrease was also more significant in those trials carried out at higher initial pH. The pH fall for the maximum dosage of the magnesium compound was 0.4 at an

initial pH= 10.5, 0.7 at initial pH=11 and 0.9 at initial pH= 11.5 with $MgCl_2 \cdot 6H_2O$. In the case of 1500 mg/L of $MgSO_4 \cdot 7H_2O$ the decrease was 0.3, 0.5 and 0.7 at an initial pH of 10.5, 11 and 11.5 respectively. This is in agreement with the highest magnesium content of $MgCl_2 \cdot 6H_2O$ and the highest silica removal achieved with this salt. To avoid scaling phenomena when mixing with other process waters, the pH of the treated water should be 7.5±1.0. In addition, the discharge limit of this paper mill establishes that the pH value of the final effluent, including RO rejects, should lie between 6.5 and 9.5. With all the treatments the final pH was above the limit, being necessary to carry out a pH adjustment before discharge.

Another important paramether to consider when using membrane technologies is COD, since it contributes to the organic fouling of the membranes. The maximum COD removal efficiencies achieved with 1500 mg/L of $MgCl_2 \cdot 6H_2O$ were 2% at pH=10.5, 10% at pH=11 and 14% at pH=11.5. Magnesium sulphate was slightly more efficient than magnesium chloride in COD removal, achieving the following COD removals at the maximum dosage (1500 mg/L): 11 % at pH=10.5, 14% at pH=11 and 16% at pH=11.5.

Regarding turbidity, there was not a clear relaation between the pH and the magnesium compound dosage and turbidity. Turbidity of clarified waters varied from 70 to 170 NTU, depending on the treatment, and dissolved turbidity of clarified waters from 7 to 15 NTU.

When selecting the best treatment for silica removal, the counterion of the magnesium salt used should be also taken into account as it could affect the membrane performance or the entire process. The use of magenisum sulphate could cause scaling problems due to the precipitation of calcium sulphate as initial sulphate content in the effluent was already high (239 mg/L). On the other hand, the use of chlorides could cause corrosion problems. In the particular case of the paper mill studied, there is a discharge limit of 1000 mg/L for sulphates and 2000 mg/L for chlorides. As $MgCl_2 \cdot 6H_2O$ was more effective than $MgSO_4 \cdot 7H_2O$ on silica removal and, in this particular case, higher concentrations of chlorides are allowed in the effluent, the former was selected to optimize the pH regulator and to study the synergistic effect of the use of a coagulant and a magnesium salt.

3.2. Optimization of the pH regulator

As high pHs are required for silica removal, the selection of the pH regulator is a key factor to be considered, both in terms of costs and dissolved solids increase. The use of lime milk instead of caustic soda was analyzed. The main advantages of lime milk compared to caustic soda are that it is cheaper and contributed less to the increase of conductivity. Additionally it improved COD removal which was very low when NaOH was used as pH regulator. On the other hand, the volume of sludge generated was higher than in the case of NaOH.

As shown in Fig. 5, the maximum removal rates obtained with NaOH at each pH were 77 % and pH 10.5, 84% at pH 11 and 91 % at pH 11.5 with 1500 mg/L of $MgCl_2·6H_2O$ in all the cases. Silica removal was increased when lime was used instead of NaOH. However, the difference in performance of the two products was less noticeable at higher pHs. Silica removal rates of lime were similar at the three pHs tested. With this pH regulator the maximum removal rates achieved were 87%, 90% and 93% at pH= 10.5, 11 and 11.5 respectively with 1500 mg/L of $MgCl_2·6H_2O$. This is very important given the low dosage of pH regulator needed and therefore, the low increase in conductivity of the treated water. The higher removal rates obtained with lime milk seem to be due to the precipitation of $CaCO_3$, which also favours the removal of silica (Sheikholeslami and Bright 2002). Another possibility is that silica was also removed through the formation of calcium silicates. It is interesting to notice that with 500 mg/L of $MgCl_2·6H_2O$ the silica removal obtained at pH 11 with both pH regulators was higher than the one obtained at pH 11.5. This is because silica solubility increases with pH, and the removal rates achieved at that pH were not higher enough to compensate the increase in the initial silica concentration at this pH.
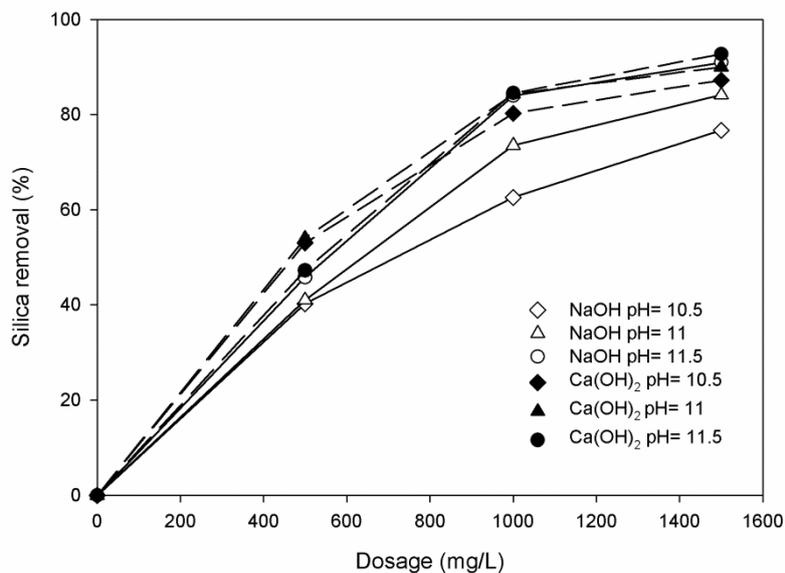
Fig. 5 Silica removal versus MgCl$_2$·6H$_2$O dosage at different initial pHs with Ca(OH)$_2$ or NaOH as pH regulators.

Regarding the conductivity of the treated waters it was always higher with caustic soda than with lime at all pH and dosages (Fig. 6). At pH 10.5, conductivity of the treated water varied between 3.9-4.8 mS/cm with caustic soda and only 3.0-3.3 mS/cm with lime milk depending on the magnesium salt dosage. At pH 11 the conductivity ranges were 4.3-4.5 mS/cm for caustic soda and 2.7-2.9 mS/cm for lime milk. Finally, at pH 11.5 maximum increases in conductivity were obtained, 4.6-4.8 mS/cm for caustic soda and 2.8-3.1 mS/cm for lime milk. The use of lime milk would allow working at 70% recovery in the RO membranes without any post-treatment of the rejects for all dosages at the three pHs tested as the conductivities of the rejects would be lower than the discharge limit (7.5 mS/cm).
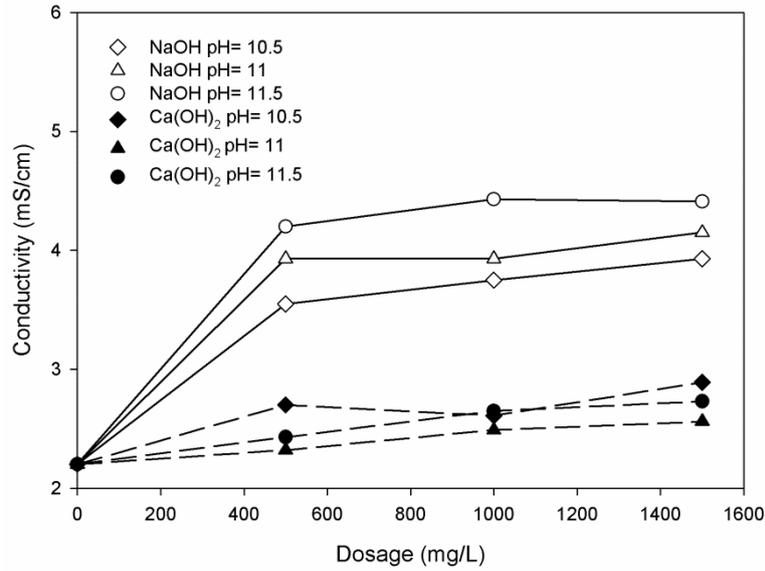
Fig. 6 Conductivity of treated waters vs. MgCl$_2$·6H$_2$O dosage at different initial pHs with Ca(OH)$_2$ or NaOH as pH regulators.

Although the use of lime milk can increase the turbidity of the waters, this effect was not relevant for the reuse of this effluent. The final turbidity with lime milk was higher than with caustic soda for all the dosages at the three pHs. The maximum turbidity was observed for the two pH regulators at pH 10.5 and 1500 mg/L. Under these conditions. the final turbidity of the water was 180 NTU with caustic soda and 640 NTU with lime milk. In addition, the final turbidity at pH 11.5 and 1500 mg/L of MgCl$_2$·6H$_2$O, where maximum silica removal was obtained, was 140 NTU with caustic soda and 320 NTU with lime milk. High turbidity treated water could cause problems before a RO or UF unit. This limitation, however, could be solved with the use of a dissolved air flotation unit (DAF) or by increasing the settling time. In this respect, the use of a coagulant or small dosages of a flocculant would be enough for reducing turbidity without limiting the process feasibility and at a very low cost.

Regarding COD, higher removal rates were obtained with lime milk than with caustic soda at the three pH and dosages. For both pH regulators, COD removal increased by increasing the pH and dosage (Fig. 7). However a maximum COD removal of around 30% was obtained with lime milk and only 15% with caustic soda. This maximum removal obtained with caustic soda was smaller than those achieved with lime milk at

lower pHs and the same dosage of MgCl$_2$·6H$_2$O. This removal rates were 19% and 23% at pH 10.5 and 11 respectively.
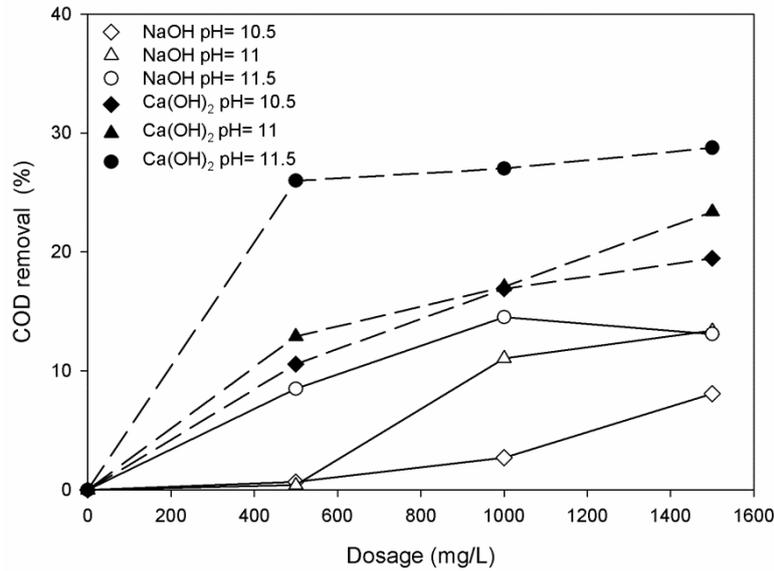

Fig. 7 COD removal vs. MgCl$_2$·6H$_2$O dosage at different initial pHs with Ca(OH)$_2$ or NaOH as pH regulators.

As it has been demonstrated, despite sludge generation being higher with lime than with caustic soda, it is preferred as pH regulator for the following reasons: silica and COD removal efficiencies with lime were higher than with caustic soda, the conductivity of the treated waters was considerably lower and lime milk is considerably cheaper than caustic soda.

3.3. Silica removal with MgCl$_2$·6H$_2$O assisted by the addition of a polyaluminum coagulant

Coagulation and particularly, coagulation with aluminum based salts, has been recently recognized as an efficient silica removal technique for the application considered in this work (Hermosilla et al. 2012; Latour et al. 2013). In view of that, the synergistic effect of silica removal with magnesium chloride and the subsequent addition of a polyaluminum nitrate sulphate coagulant were studied. The selected polyaluminum based coagulant (PANS) showed to be very efficient for silica removal in the same effluent of previous studies carried out by the authors (Latour et al. 2013). The approach

followed was to obtain similar removal efficiencies lowering the dosage of $MgCl_2 \cdot 6H_2O$ by a polyaluminum coagulant while determining if there are any other synergistic effects in other quality parameters of the treated water. A fixed dosage of 125 mg/L of the polyaluminum coagulant was tested to enhance silica removal with $MgCl_2 \cdot 6H_2O$ which was used at 250 mg/L and 750 mg/L dosages. These dosages enabled intermediate efficiencies on silica removal.

As shown in Fig. 8, the silica removal rates obtained with 250 mg/L of magnesium chloride and the coagulant were 27%, 30% y 43% at pH 10.5, 11 and 11.5 respectively. With 750 mg/L the values of removal were 54% at pH 10.5, 59% at pH = 11 and 77% at pH 11.5. Zeng et al. (2007), achieved around 64% silica removal combining 750 mg/L of $MgCl_2 \cdot 6H_2O$ with 150 mg/L of a zinc coagulant ($ZnSO_4 \cdot 7H_2O$). Although in this study the operational pH was not indicated it was said that 600 mg/L of NaOH were added.

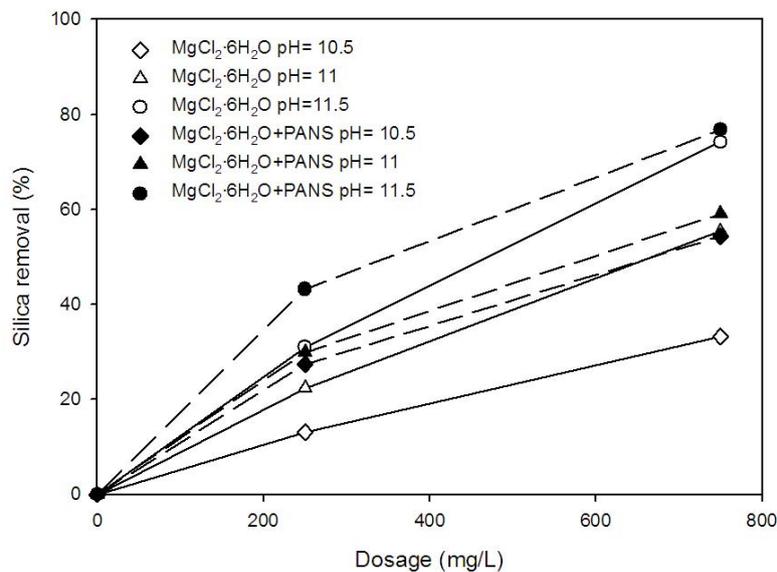**Fig. 8** Silica removal vs. $MgCl_2 \cdot 6H_2O$ dosage at three pH with and without further coagulation treatment.

Comparing these results with the ones obtained with magnesium chloride used alone, it can be observed that silica removal increased with the addition of coagulant and this increase was higher at pH 10.5 (around 10%) while it was 5% at pH 11 and 11.5. Regarding COD removal, the addition polyaluminum coagulant did not have a

significant effect onthe results, being the differences smaller than 2%. On the other hand, conductivity was increased by de addition of the coagulant. It varied between 3.93 mS/cm at (pH 10.5 and 250 mg/L) and 4.63 mS/cm (pH 11.5 and 750 mg/L). When coagulant was not added it varied between 3.67 mS/cm (pH 10.5 and 250 mg/L) and 3.61 mS/cm (pH 11.5 and 750 mg/L). The final conductivity of the water was around 1 mS/cm higher when $MgCl_2 \cdot 6H_2O$ was combined with coagulant than with $MgCl_2 \cdot 6H_2O$ alone for the same silica removal. Finally, the addition of coagulant failed to remove any dissolved turbidity though around 50 NTU were removed in the clarified fraction.

4. CONCLUSIONS

High silica removal rates (80-90%) were obtained by adding soluble magnesium compounds (1500 mg/L) at high initial pH (11.5) to the effluent. These silica removal rates would allow working in RO membranes at high recoveries (75-85%) without silica scaling problems. $MgCl_2 \cdot 6H_2O$ is preferred to $MgSO_4 \cdot 7H_2O$ because it is slightly more efficient on silica removal, due to its higher Mg content.

High pH required for high silica removal efficiencies is directly translated into an important increase of the conductivity of the waters that may require a further post-treatment. This problem could be partially solved using $Ca(OH)_2$ instead of NaOH as pH regulator (final conductivity around 3 mS/cm vs. 4 mS/cm). Additionally, the use of $Ca(OH)_2$ has the advantage of a lower cost, lower settling time, slightly higher silica removal (2-10%, depending on the initial pH) and an additional 15% COD removal.

The combination of $MgCl_2 \cdot 6H_2O$ with a polyaluminum based coagulant did not improve silica removal significantly (a maximum increase of 10% was achieved). On the other hand, conductivity of the treated waters increase and the COD removal was not affected at all. Therefore, the use of the coagulant is not recommended.

According to the obtained ratios of Si removed/mmol Mg removed (around 0.5 and 1), it can be ascertained that the main mechanism involved on silica removal was the co-precipitation of silica with magnesium. These Si:Mg ratios are compatible with the formation of Mg_2SiO_4 (forsterite) or $MgSiO_3$ (enstatite).

Acknowledgments

References

Al-Mutaz IS, Al-Anezi IA (2004) Silica removal during lime softening in water treatment plant. International Conference on Water Resources and Arid Environment, King Saud University, Riyadh, December 5-8

Al-Rehaili AM (2003) Comparative chemical clarification for silica removal from RO groundwater feed. Desalination 159:21-31

American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF) (2005) Standard Methods for the Examination of Water and Wastewater, 21st edn. American Public Health Association (APHA), Maryland (United States)

Chen S, Chang T, Lin C (2006) Silica pretreatment for a RO brackish water source with high magnesium. Water Sci Technol Water Supply 6:179-187

Ferguson L (1992a) Deinking chemistry: Part 1. Tappi J 75:75-83

Ferguson L (1992b) Deinking chemistry: Part 2. Tappi J 75:49-58

Hamäläinen H, Aksela R, Rautiainen J, Sankari M, Renvall I, Paquet R (2007) Silicate-free peroxide bleaching of mechanical pulps: Efficiency of polymeric stabilizers, Proceedings TAPPI of International Mechanical Pulping Conference, 215−236, Minneapolis, United States, May 6-9

Hater W, Kolk CZ, Dupoiron C, Braun G, Harrer T, Götz T (2010) Silica scaling on reverse osmosis membranes- Investigation and new test methods. Desalin Water Treat 31:326-330

Haynes WN (ed) (2013) CRC Handbook of Chemistry and Physics, 94th edn. CRC Press, Boca Raton (United States)

Hermosilla D, Ordóñez R, Blanco L, de la Fuente E, Blanco A (2012) pH and particle structure effects on silica removal by coagulation. Chem Eng Technol 35:1632-1640

Hsu H, Chen S, Lin C, Chang T (2008) Silica pretreatment for RO membrane by softening-adsorption. J Environ Eng Manage 18:99-103

Huuha TS, Kurniawan TA, Sillanpää MET (2010) Removal of silicon from pulping whitewater using integrated treatment of chemical precipitation and evaporation. Chem Eng J 158:584-592

Koo T, Lee YJ, Sheikholeslami R (2001) Silica fouling and cleaning of reverse osmosis membranes. Desalination 139:43-56

Latour I, Miranda R, Blanco A (2013) Silica removal from newsprint mill effluents with aluminum salts. Chem Eng J 230:522-531

Negaresh E, Antony A, Cox S, Lucien FP, Richardson DE, Leslie G (2013) Evaluating the impact of recycled fiber content on effluent recycling in newsprint manufacture. Chemosphere 92:1513-1519

Ning RY (2002) Discussion of silica speciation, fouling, control and maximum reduction. Desalination 151:61-73

Ordoñez R, Hermosilla D, San Pío I, Blanco A (2010) Replacement of fresh water use by final effluent recovery in a highly optimized 100% recovered paper mill. Water Sci Technol 62:1694-170

Parks JL, Edwards M (2007) Boron removal via formation of magnesium silicate solids during precipitative softening. J Environ Eng 133:149-156

Salvador Cob S, Beaupin C, Nederlof MM, Harmsen DJH, Cornellisen ER, Zwijnenburg A, Genceli Güner FE, Witkamp GJ (2012) Silica and silicate precipitation as limiting factors in high-recovery reverse osmosis operations. J Membrane Sci 423-424:1-10

Sheikholeslami R, Al-Mutaz IS, Koo T, Young A (2001) Pretreatment and the effect of cations and anions on prevention of silica fouling. Desalination 139:83-95

Sheikholeslami R, Bright J (2002) Silica and metals removal by pretreatment to prevent fouling of reverse osmosis membranes. Desalination 143:255-267

Sheikholeslami R, Tan S (1999) Effects of water quality on silica fouling of desalination plants. Desalination 126: 267-280

Wolf V (1966) Aqueous Solutions and Body Fluids. Their Concentrative Properties and Conversion Tables. Harper & Row, Publishers, New York (United States)

Zeng YB, Yang CZ, Pu WH, Zhang X (2007) Removal of silica from heavy oil wastewater to be reused in a boiler by combining magnesium and zinc compound with coagulation. Desalination 216:147-159