Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1138893

57 (2016) 24116–24123
November

Pilot study on treating with the micro-alkalized makeup water of recirculated cooling water system by an integrated membrane process

Huiming Zeng, Liang Lv*, Yuechao Wu, Yulin Wang, Jianjun Chen, Rui Fan, Xiaoli Shen

College of Chemical and Materials Engineering, Quzhou University, 78 Jiu Hua Bei Da Dao, Ke Cheng District, Quzhou City, Zhejiang 324000, China, email: weimingzeng2015@126.com (H. Zeng), Tel. +86 570 8026667; Fax: +86 570 8026552; emails: Lianglv_qzxy@126.com (L. Lv), 490280706@qq.com (Y. Wu), 57185975@qq.com (Y. Wang), 408630041@qq.com (J. Chen), 286289882@qq.com (R. Fan), 942884865@qq.com (X. Shen)

Received 17 August 2015; Accepted 3 January 2016

ABSTRACT

In the pilot-scale study, a kind of pretreated wastewater from the pickling process in a steel wire rope manufacturer was reused by a novel integrated membrane process (Reverse osmosis and R-HCO_3 anion-exchange resin combined in series), and the operating parameters for the system had been optimized. After the pretreatment process through neutralization, coagulation, clarification sand filtration, and ultra-filtration in sequence, the wastewater was treated with the integrated membrane process. The integrated membrane process can remove most of inorganic and organic ions and realize the micro-alikalization for product water, which can facilitate the zero liquid discharge for cooling water system. Furthermore, the operating parameters of this process were optimized as well: when the pH of inlet water was 8.57, the dosage of scale inhibitor agent was 2.5 mg/L, the optimized operating trans-membrane pressure was 1.32 MPa, the flux was 39.87 L/(m^2 h), and water recovery rate was 55%. The filtering flow of the resin bed was 20–30 m/h, and the regeneration agent (0.7 mol/L $NaHCO_3$) consumption ratio is 3.2.

Keywords: Recirculated cooling water; Makeup water treatment; Integrated membrane process; Micro-alkalinity process

1. Introduction

The increasingly severe shortage of fresh water makes the value of the reclaimed water as industrial water much more important [1–3]. The reclamation of the IND not only cuts down the discharge of the wastewater, but also saves much fresh water source. In addition, it was better to reuse the industrial water further more and to achieve the liquid zero discharge [4,5].

The recirculated cooling water system is one of the biggest industrial water users, transferring the waste heat of the industrial system to the atmosphere by evaporation. Generally, as the cooling water recirculates and evaporates, there are three main problems, such as pipe corrosion, scaling, and microbial contamination. At present, the prevalent method to prevent heat exchange tubes from corrosion, scaling, and microbial contamination is the supplementation of

---

*Corresponding author.

chemical inhibitor [6], which may cause environmental pollution too. Researches on synergistic effects of the multicomponent mixture between corrosion inhibitor and scaling inhibitor become a hotspot, as that can sharply decrease the dosage. In addition, the application of environment friendly chemical inhibitors, such as polyepoxysuccinic acid and polyaspartic acid, can be potentially used as scale inhibitors [7]. Alternatively, the physical approaches, including high frequency electromagnetic, electrostatic, and ultrasonic treatment, are also utilized for the treatment of recirculated cooling water [8]. Unfortunately, these efforts have not effectively solved these tough problems.

The well-treated reclaimed water is a kind of perfect makeup water in the recirculated cooling water system [9]. With the development of water treatment technologies, especially the membrane technology, the feasibility of using the reclaimed water from different industrial processes is well verified, but it demands strict pretreatment process [10,11]. Nanofiltration (NF) and reverse osmosis (RO) can partially or completely remove the organic compounds and mineral salts, exhibiting as the core treating unit to treat the wastewater [8,12]. A new process of treatment with makeup water of the recirculated cooling water system by NF and ion exchange hybrid technology has been studied [13–15]. It potentially solves these three main problems without any inhibitor injection or wastewater effluent by adjusting the water quality of the makeup.

In order to save the fresh water and achieve zero discharge of wastewater in a steel wire rope factory, the wastewater from the iron wire pickling process was pretreated with neutralization, clarification, sand filter, and UF process firstly, and then post-treated by RO membrane and a kind of anion-exchange resin bed in order. The reclaimed water was taken to the recirculated cooling system as the makeup water. In this paper, the RO system operating parameters have been optimized, the product water quality from RO and the resin bed has been analyzed, and the contamination of the RO membrane has been studied as well.

2. Design and principle

Fig. 1 shows the schematic of pretreatment process for treating with the raw wastewater.

The raw wastewater came from the process of pickling iron wire in a steel wire rope manufactory, and the iron wire was pickled by hydrochloric acid for the removal of rust. Generally, the rust was dissolved in the acidic wastewater so that a high amount of ferric ion and a trace amount of lead ion appeared in the wastewater. In the pretreatment process, the NaOH was added to neutralize the feed solution for the precipitation of the ferric ion and lead. Then, the coagulants, including PAC (aluminium polychloride) and PAM (polyacrylamide), were added to clarify the water. Finally, the product water from clarification tank was filtered by sand filter and UF (ultrafiltration) to remove the residual flocs and Fig. 2 shows the schematic of the integrated membrane process, which was comprised of RO membrane and ion exchange resin, for producing the makeup water of the recirculated cooling water system.

The pretreated wastewater was chosen as feedwater in the pilot test. After flowing into the cycling water tank, it was drawn into the fiber filter and the RO membrane module by a multi-stage pump. About 15% (v/v) feedwater permeated through the RO membrane in a cycle, and the other was divided into two parts: one went back into the cycling tank and the other was discharged. The ratio between the volume of these two streams was about 16:1. Subsequently, the water quality in the cycling tank was stabilized so that the RO membrane ran stably. After the treatment with the product water of the RO membrane by a special ion-exchange resin—$RHCO_3$, the outlet water went into the recirculated cooling water system. The process could remove Ca^{2+}, Mg^{2+} ions, N, P or other organic nutrient compounds, and transform the anion (i.e. Cl^-, SO_4^{2-}) into HCO_3^-. Consequently, the recirculated cooling water could be alkalized in a certain degree. Meanwhile, metal corrosion, scaling of heat exchanger tube as well as microbial pollution could be hindered without any chemical agent injection.

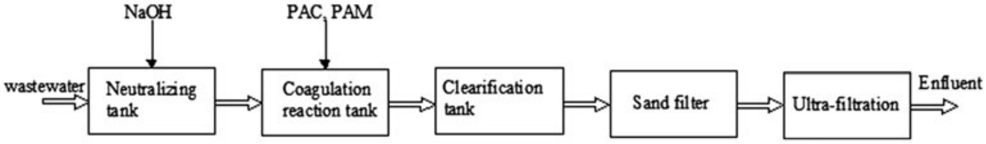

Fig. 1. Schematic of pretreatment process for treating with the raw wastewater.

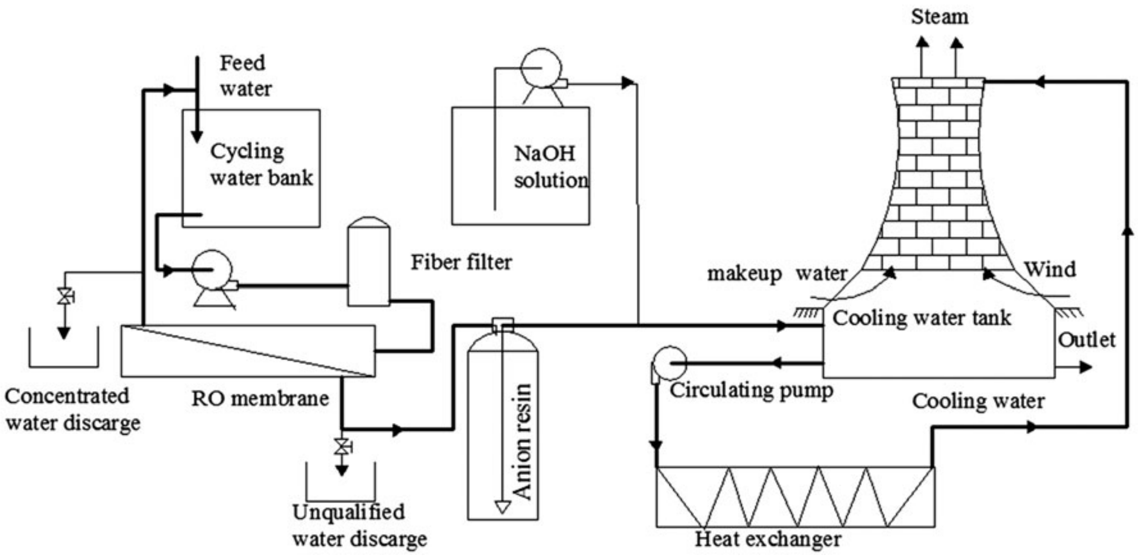

Fig. 2. Schematic of pilot of the integrated membrane at pilot scale for producing makeup water of the recirculated cooling water system.

2.1. *Production of makeup water*

When all of the organic and most of the inorganic salt in the feed water have been removed by the RO membrane at first, only a small amount of NaCl permeated through the membrane, and then can be transformed into HCO_3^- after reacting with the special anion resin—$RHCO_3$, which realizes the micro-alkalization for the makeup water The reaction can be shown below:

$$RHCO_3 + A^- = RA + HCO_3^- \quad (1)$$

A^-: Single-charged anion.

2.2. *Stability of water quality in re-circulating cooling system*

According to the equation of bicarbonate hydrolysis, the concentrated factor of the cooling water was equal to that of the total alkalinity. The relationship between theoretical pH value and total alkalinity of cooling water solution is expressed in Eq. (2):

$$[H^+] = \frac{(K_W + K_H^* P_{CO_2}^* K_1) + \sqrt{(K_W + K_H^* P_{CO_2}^* K_1)^2 + 8B_T K_H^* P_{CO_2}^* K_1 K_2}}{2B_T} \quad (2)$$

where K_W denotes equilibrium constant for pure water, K_H^* is Henry coefficient of CO_2 gas, K_1 and K_2 denote the first- and second-order dissociation of H_2CO_3, respectively. $P_{CO_2}^*$ presents the partial pressure of gaseous carbon dioxide in the atmosphere, and B_T denotes total alkalinity of the cooling water.

Theoretically, the pH of the cooling water was determined by the total alkalinity when cooling water and the atmosphere reached to vapor liquid equilibrium. Thereby, the pH value of cooling water can be controlled by adjusting the total alkalinity of the recirculated cooling water.

2.3. *Prevention of scaling, corrosion, and microbial contamination*

The RO membrane can remove all the mineral ions which causes scaling (such as calcium and magnesium), nutrition element and almost of corrosive anions. Moreover, chlorine, nitrate, and phosphate anions had been turned into alkaline anions, which could facilitate the passivation of the metal pipe and prevent the cooling system from corrosion or sludge.

3. Experimental apparatus and methods

The schematic of the makeup water treatment system is composed of three sections: a pretreatment system, a desalination and micro-alkalization system, and a simulated recirculated cooling water system. The pretreatment system included neutralization, coagulation, and UF sections. The desalination and micro-alkalization system included a fiber filter and a RO module, six 20-inch fiber filtrating unit was fixed in the container. There were one 4,040 stainless steel pressure vessel and one Φ 250 × 500 mm ion exchange bed produced by grass fiber-reinforced plastics. The specifications of the RO module and the resin are shown in Tables 1 and 2. The simulated recirculated cooling water system, including spray cooling tower, recirculated water loop, and aerator (air fan) was used to simulate the heat exchange and the mass transfer procedure between gaseous CO_2 and recirculated water.

In the experiment, the RO membrane operating parameters such as flux, trans-membrane pressure (TMP), dosage of scaling inhibitor, and water recovery rate had been optimized by monitoring the flux and TMP. Initially, the operating parameters were determined by reference or former experimental data: the flux was set at 30 L/(min m^2) and then increased step by step until the line between flux and TMP curved down; Afterwards, the optimized flux and TMP were achieved, while other parameters such as quantity of cycling flow of 18 L/min, dosage of scaling inhibitor of 3 mg/L, and the recovery rate of 70% were optimized by the same method.

The parameters, including pH, the conductivity, chloride ion, and alkalinity of product water from the RO membrane and the $RHCO_3$ anion-exchange resin bed were analyzed by the meters or the Chinese national standard methods (GB/T 15453 2008).

Additionally, in order to analyze the reaction mechanism of the $RHCO_3$ resin, the chemical cleaning effluent of the exchangeable anion (HCO_3^- and CO_3^{2-}) in the $RHCO_3$ resin has been analyzed.

4. Results and discussion

4.1. The water quality of the membrane inflow

After the pretreatment, the pH, the total suspended solid, the turbidity, and the total iron in the wastewater changed, which were accorded with the inflow standard of the membrane. The quality of product water from the pretreatment system is listed in Table 3.

The data in Table 3 indicate that the product water from the pretreatment system contains high salinity in the view of high TDS. During the pretreatment process, hydrochloric acid as the cleaning reagent for steel and the quicklime as the neutralizing agent are employed, and the product water contains high amount of the chloride ion and the hardness. Therefore, the desalination process was necessary for the recirculating cooling makeup water treatment.

Table 1
Properties of the RO membrane module

RO membrane	Area (m^2)	Fixed inflow pressure (MPa)	Fixed flux (m^3/d)
BW30-4040	8.1	1.55	9.08

Table 2
Properties of ion-exchange resins used in this work

Resin	Matrix and porosity	Functional group
Hydrolite-213FC	Polyacrylic-DVB, gel	Quaternary ammonium

Table 3
Quality of product water after the pretreatment

Parameters	pH	Turbidity (NTU)	Conductivity (μs/cm)	TDS (mg/L)	Total hardness as $CaCO_3$ (mg/L)	Total alkalinity as $CaCO_3$ (mg/L)	Cl^- (mg/L)
Value	7.7–9.0	0.7	1,500–3,000	421.5	110.7–300.0	100.0–250.0	192.4–421.0

Table 4
Optimization of operating parameters of the RO module

Items	Flux (L/(m^2 h))	TMP (bar)	Permeability (L/(m^2 h bar))	pH	Scaling inhibited reagent (mg/L)	Recovery (%)
Values	39.87	13.20	3.02	8.57	2.5	55

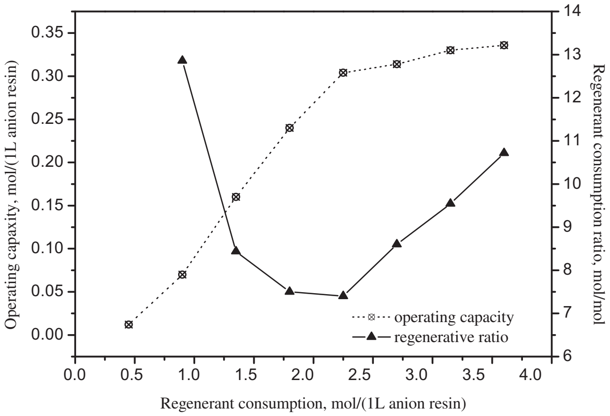

Fig. 3. Variation in the operating capacity and the regenerant consumption ratio of the $RHCO_3$ ion-exchange resin with the regenerant consumption.

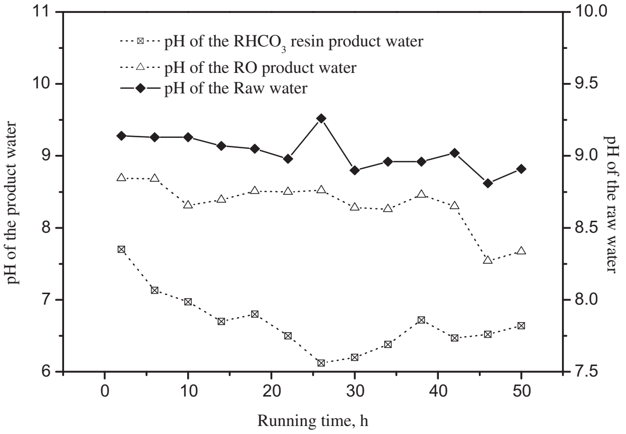

Fig. 4. Variation in the pH in the raw water, the product water of RO, and the $RHCO_3$ resin.

4.2. *Optimization of operating parameters for desalinating and micro-alkalizing system*

4.2.1. *Optimization of operating parameters for RO process*

In the experiment, based on strict monitoring of the product water quality and the TMP, the operating parameters such as the flux, TMP, the pH of influent, the dosage of scaling inhibited reagent and the water recovery rate, for RO module was optimized step by step. The results were listed in Table 4.

4.2.2. *The optimized operating parameters of the $RHCO_3$ anion-exchange resin regenerated*

In this case, $RHCO_3$ anion-exchange resin (600 mL) was used for the removal of Cl^- ion which permeated from the RO module. When the $RHCO_3$ resin was exhausted, it was regenerated by 0.7 mol/L $NaHCO_3$ solution. The regenerating reagent reverse-flowed the resin bed at rate of 5 m/h. The discharged wastewater had been gradient recovered in eight parts, where the content of Cl^- ions was analyzed. The corresponding relationship between dosage of regenerating agent and the recovery of the working exchangeable capacity or the regeneration agent consumption ratio (the regeneration agent consumption per 1 mol recovery of the exchangeable capacity) is shown in Fig. 3.

Fig. 3 shows that the working exchangeable capacity increased slowly before the consumption of regeneration agent went to 2.25 mol per liter of resin, the regeneration agent consumption ratio reduced to the lowest port of which the data were 7.5 mol/mol. Therefore, the optimized consumption ratio of regenerant solution was 3.2 L $NaHCO_3$ per liter of $RHCO_3$ resin.

4.3. *Product water quality*

The pH, conductivity, alkalinity, and Cl^- in the inflow water, the product water of RO module, and the $RHCO_3$ resin were detected. The sampling frequency was two times per day. The variations are shown in Figs. 4, 5, and 6, respectively.

It can be seen in Fig. 4 that the pH declined in gradient after being filtrated by RO membrane and the $RHCO_3$ resin bed. The variation trend in the raw water was similar to the outflow of the RO membrane, but the pH of the resin bed product water was independent on inflow. Comparing to Cl^-, RO membrane had higher removal ratio to CO_3^{2-}, HCO_3^-, or SO_4^{2-}; the alkalinity of the water had been cut down by the RO membrane, so that the pH became lower and the variation trend was similar to the alkalinity. The alkalinity of $RHCO_3$ resin product water rose up due

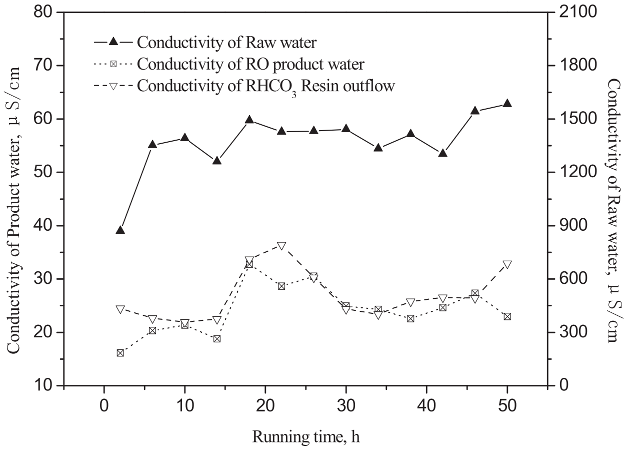

Fig. 5. Variation in the conductivity in the raw water, the RO product water, and the $RHCO_3$ resin product water.

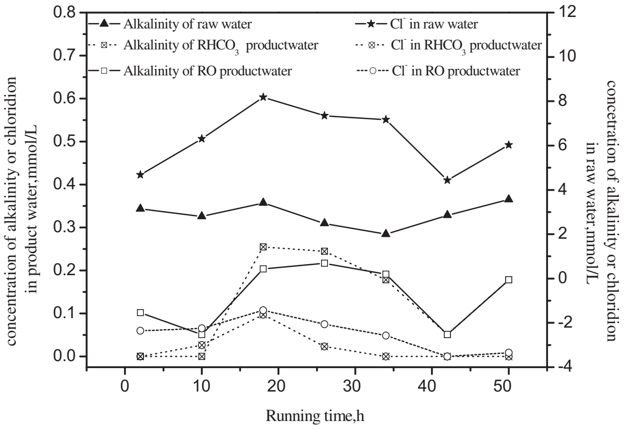

Fig. 6. Variation in the alkalinity and Cl^- in the raw water, the product water of RO, and the $RHCO_3$ resin.

to the Cl^- being exchanged into HCO_3^-, while the pH went lower.

In order to find out the exchanging mechanism among the Cl^-, HCO_3^-, and $RHCO_3$, three tests had been carried out. The first one was added with 1,000 mL alkalinity NaOH with 0.01 mol/L and 5 mL $RHCO_3$ resin, the second one was added with 4.25 mL Na_2CO_3 with 1 mol/L and 5 mL $RHCO_3$ resin, and the third one was add with 500 mL $NaHCO_3$ with 0.01 mol/L and 5 mL $RHCO_3$ resin. The initial and final solutions, which were sampled before reaction, were analyzed in 3 h. The results were listed in *A*, *B*, and *C* items and then the resin was analyzed by 50 mL Na_2SO_4 with 1 mol/L (Table 5).

The data shows that the pH and the $1/2CO_3^{2-}$ or OH^- of the soak solution came down after the reaction, while the $1/2CO_3^{2-}$ and HCO_3^- kept constant except in the NaOH solution. The mechanism was shown below:

$$2RHCO_3 + OH^- \rightarrow R_2CO_3 + HCO_3^- + H_2O \tag{3}$$

$$2RHCO_3 + CO_3^{2-} \rightarrow R_2CO_3 + 2HCO_3^- \tag{4}$$

$$2RHCO_3 + HCO_3^- \rightarrow R_2CO_3 + HCO_3^- + H_2CO_3 \tag{5}$$

The variation trends of the three kinds of water were consistent, and comparing to the inflow, the product water of RO membrane was cut down at 98% in conductivity or salt. And the reaction in $RHCO_3$ resin made the conductivity of the product water slightly lower, due to the formation of weak acid H_2CO_3.

Fig. 6 demonstrates that variation trends of Cl^- and alkalinity of the inflow water, RO product water, and $RHCO_3$ product water were similar, and the product water varied slightly. It illustrated that the product water could be impacted by the raw water quality, but the RO membrane and the resin bed made the influence lower. The RO membrane removed about 99.2% of Cl^- and 95% of alkalinity, and the $RHCO_3$ resin bed removed about 50% of the residue of Cl^-, but the alkalinity increased slightly. It is presented that product water of the treatment system included trace amounts of Cl^- and alkalinity, which accorded with the makeup demand of the macro-alkalization process.

Table 5
The analysis result of reaction soak solution and the disposal of the resin

Items		*A*	*B*	*C*	*a*	*b*	*c*
pH	Initial	12.10	10.85	8.66	8.27	8.27	8.27
	Final	10.43	10.15	7.93	11.87	9.63	8.80
$1/2CO_3^{2-}$ or OH^- (mmol)	Initial	9.66	4.22	0.50	0	0	0
	Final	1.83	2.62	0	3.31	1.69	0.57
$1/2CO_3^{2-}$ and HCO_3^- (mmol)	Initial	9.82	8.20	4.88	6.19	6.45	6.19
	Final	9.90	8.27	4.89	6.20	6.40	4.89

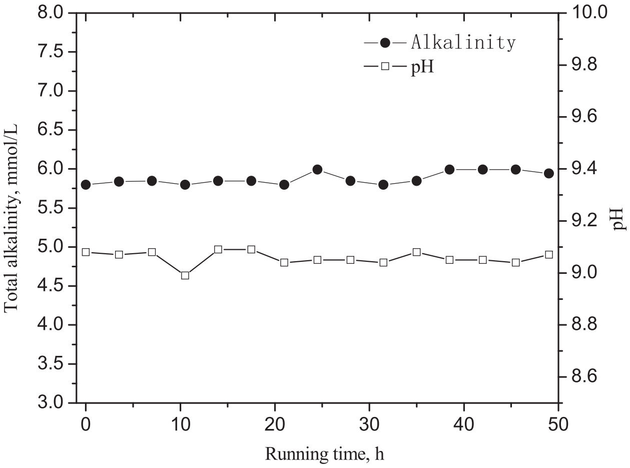

Fig. 7. Variation trend in the pH and alkalinity in simulated recirculated cooling water system.

4.3.1. The simulated recirculating cooling water quality

The product water of the $RHCO_3$ resin was injected in the simulated recirculating cooling water system as makeup. In this case, the cooling water system ran for 50 h continuously, and the alkalinity and the pH of cooling water were monitored at the interval of 2.5 h, which are shown in Fig. 7.

Fig. 7 indicates that the alkalinity and pH remain stable, although the product water from $RHCO_3$ resin varied. Because the makeup water would be concentrated more than 10 times in the simulated cooling system, then the recirculating cooling water was served as buffer solution which would lose some salt through wind or system leakage, and the alkalinity would keep quite steady. According to the Eq. (2), the pH of the buffer solution was determined by the alkalinity when the system remained in vapor liquid equilibrium.

5. Conclusion

The wastewater from iron acidic pickling process could be well treated by a series of pretreatment and subsequent integrated membrane process-RO membrane and $RHCO_3$ resin. The pretreatment process included neutralization, coagulation, clarification, sand filtration, and ultrafiltration. The operating parameters of RO membrane and $RHCO_3$ resin bed was optimized for facilitating the stable running of cooling water. Especially, the qualities of product water were impacted slightly by inflow, when treated with RO membrane and $RHCO_3$ resin bed. The pH of the resin product water was lower than that of inflow because the HCO_3^- in the water was absorbed to the H^+ in resin and then changed into H_2CO_3. The product water includes about 0.15 mmol/L alkalinity and 0.03 mmol/L Cl^-, which met the demand of micro-alkalization process, and the quality of the cooling water makeup with the product water keeps quite steady.

Acknowledgments

This work was partially supported by the National Natural Science Foundation (21271116, 21476127), the Public Technology Research Program of Zhejiang Province (2013C31108, 2013C33018, 2015C33231), the State Key Laboratory of Chemical Resource Engineering (CRE-2015-C-113), the Science and Technology Department of Quzhou City (2015Y010), and the Young Teachers Scheme of Quzhou University.

References

[1] L. Yi, W. Jiao, X. Chen, W. Chen, An overview of reclaimed water reuse in China, J. Environ. Sci. 23 (2011) 1585–1593.

[2] X. Wang, X. Hu, H. Wang, C. Hu, Synergistic effect of the sequential use of UV irradiation and chlorine to disinfect reclaimed water, Water Res. 46 (2012) 1225–1232.

[3] T.M. Missimer, R.G. Maliva, N. Ghaffour, T. Leiknes, G.L. Amy, Managed aquifer recharge (MAR) economics for wastewater reuse in low population wadi communities, Kingdom of Saudi Arabia, Water 6 (2014) 2322–2338.

[4] B. Yang, L. Zhang, Y. Lee, D. Jahng, Novel bioevaporation process for the zero-discharge treatment of highly concentrated organic wastewater, Water Res. 47 (2013) 5678–5689.

[5] A.U. Shenoy, U.V. Shenoy, Continuous targeting and network design for zero wastewater discharge in water system integration, J. Cleaner Prod. 87 (2015) 627–641.

[6] F. Liu, X. Lu, W. Yang, J. Lu, H. Zhong, X. Chang, C. Zhao, Optimizations of inhibitors compounding and applied conditions in simulated circulating cooling water system, Desalination 313 (2013) 18–27.

[7] G. Cristofari, M. Znini, L. Majidi, J. Costa, B. Hammouti, J. Paolini, *Helichrysum italicum* subsp. *italicum* essential oil as environmentally friendly inhibitor on the corrosion of mil steel in hydrochloric acid, Int. J. Electrochem. Sci. 7 (2012) 9024–9041.

[8] L.D. Tijing, M.H. Yu, C.H. Kim, A. Amarjargal, Y.C. Lee, D.H. Lee, D.W. Kim, C.S. Kim, Mitigation of scaling in heat exchangers by physical water treatment using zinc and tourmaline, Appl. Therm. Eng. 31 (2011) 2025–2031.

[9] M.E. Walker, R.B. Theregowda, I. Safari, J. Abbasian, H. Arastoopour, D.A. Dzombak, M.K. Hsieh, D.C. Miller, Utilization of municipal wastewater for cooling in thermoelectric power plants: Evaluation of the combined cost of makeup water treatment and increased condenser fouling, Energy 60 (2013) 139–147.

[10] S.J. Altman, R.P. Jensen, M.A. Cappelle, A.L. Sanchez, R.L. Everett, H.L. Anderson, L.K. McGrath, Membrane treatment of side-stream cooling tower water for reduction of water usage, Desalination 285 (2012) 177–183.

[11] S. Barredo-Damas, M.I. Alcaina-Miranda, M.I. Iborra-Clar, J.A. Mendoza-Roca, Application of tubular ceramic ultrafiltration membranes for the treatment of integrated textile wastewaters, Chem. Eng. J. 192 (2012) 211–218.

[12] I.N. Widiasa, A.A. Susanto, H. Susanto, Performance of an integrated membrane pilot plant for wastewater reuse: Case study of oil refinery plant in Indonesia, Desalin. Water Treat. 52 (2014) 7443–7449.

[13] C. Ye, J. Lin, H. Yang, H. Zeng, Ion exchange equilibrium carbonate treatment for anticorrosion in open re-circulated cooling water system, Ind. Eng. Chem. Res. 49 (2010) 9625–9630.

[14] H. Zeng, J. Lin, C. Ye, Ion exchange softening and alkalization treatment for zerodischarge of circulating cooling water, J. Electrom. Anal. Appl. 1 (2009) 3–6.

[15] J. Lin, C. Ye, H. Zeng, F. Yu, X. Xiao, Nanofiltration and ion-exchange alkalinization for water conservation and zerodischarge in circulating cooling water system, Power Energy Eng. Conf. 1 (2009) 1–4.