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Treatment of natural rubber wastewater by membrane technologies for water reuse

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Abstract. A series of laboratory scale experiments were performed to investigate the feasibility of membrane separation technology for natural rubber (NR) wastewater treatment and reuse. Three types of spiral wound membranes were employed in the cross-flow experiments. The NR wastewater pretreated by sand filtration and cartridge filtration was forced to pass through the ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes successively. The UF retentate, which containing abundant proteins, can be used to produce fertilizer, while the NF retentate is rich in quebrachitol and can be used to extract quebrachitol. The permeate produced by the RO module was reused in the NR processing. Furthermore, about 0.1wt% quebrachitol was extracted from the NR wastewater. Besides, the effluent quality treated by the membrane processes was much better than that of the biological treatment. Especially for total dissolved solids (TDS) and total phosphorus (T-P), the removal efficiency improved 53.11% and 49.83% respectively. In addition, the removal efficiencies of biological oxygen demand (BOD) and chemical oxygen demand (COD) exceeded 99%. The total nitrogen (T-N) and ammonia nitrogen (NH_4-N) had approximately similar removal efficiency (93%). It was also found that there was a significant decrease in the T-P concentration in the effluent, the T-P was reduced from 200 mg/L to 0.34 mg/L. Generally, it was considered to be a challenging problem to solve for the biological processes. In brief, highly resource utilization and zero discharge was obtained by membrane separation system in the NR wastewater treatment.

Keywords: natural rubber wastewater; ultrafiltration; nanofiltration; reverse osmosis; quebrachitol

1. Introduction

Natural rubber (NR) latex, which mainly consists of rubber particles and skim serum, is a colloid obtained from the tree *Hevea brasiliensis*. Skim serum is the main source of the effluent in the NR processing plant. In addition to water, it contains large quantities of valuable constituents such as proteins, resins, carbohydrates and mineral matter (White and De 2001). It was reported that quebrachitol (2-O-methyl-L-inositol) is the largest single non-rubber component present in the latex and about 0.1wt% quebrachitol can be extracted from the skim serum (Gopalakrishnan *et al*. 2010, Jiang *et al*. 2014, Wu *et al*. 2016). Quebrachitol is an optically active cyclitol, which serves as a starting material for the synthesis of a wide variety of bioactive material (Kiddle 1995). The other natural organic resources in the skim serum have great potential for industrial applications in the production of fertilizer. However, there is no corresponding record for the industrial application of skim serum, which is only treated as an industrial effluent.

Since the natural rubber processing needs large quantities of water, which are used to dilute the field latex and clean the materials and machineries (Sulaiman *et al*. 2010), it produced large amounts of wastewater, The wastewater can combine with the skim serum form the NR processing effluent and then result in more serious pollution. Currently, the activated sludge process is the most commonly used method for treating NR wastewater to allow wastewater discharge within law requirements (He 2007, Mohammadi *et al*. 2013). The organic matters in the skim serum were consumed by microorganisms rather than utilized in the biological processing (Bernardes 2014). This is a waste of valuable resources and leads to undesirable eutrophication and malodor problems due to the biodegradation of the organic matters (Mohammadi *et al*. 2013).

The membrane acts as a semi-permeable barrier and possesses different perm-selectivity for different compounds depending on the membrane pore size (Bernardes 2014, Judd and Judd 2012). Generally, membranes can perform all kinds of separations that conventional separation processes such as distillation, adsorption and extraction can (Cartinella *et al*. 2006, Gopal *et al*. 2006, Melita *et al*. 2014). In addition, membrane processes also can be combined with other physical or biological treatment processes to meet specific requirements (Yahiaoui *et al*. 2013, Sulaiman *et al*. 2010). After a rapid growth over the past few decades, membrane separation process which was accepted as a versatile separation process has been introduced in industrial operations instead of conventional treatments for wastewater treatment to meet today's international standards (Fersi *et al*. 2005, Ghaffour *et al.* 2009).The application of membrane separation process not only enables high removal efficiencies, but also

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allows recycle of valuable resources (Gopal *et al*. 2006, Fersi *et al*. 2005, Collins *et al*. 2009). In a previous paper, we reported the successful use of membrane separation processes for extracting quebrachitol from NR wastewater (Jiang 2014). In the present study, experiments were performed to investigate the feasibility of membrane separation processes for NR wastewater reuse and a comparison was also proposed with the conventional activated sludge system. It will be very interesting to see if the NR wastewater treatment can be combined with the recycle of the waste organic resources in the wastewater. It will considerably reduce the wastewater treatment cost and enhance the usefulness of natural rubber latex as a renewable resource.

2. Materials and methods

2.1 Wastewater

The wastewater was supplied from a raw NR factory. In the NR processing, field latex was coagulated by formic acid in the coagulation tank. Skim serum collected by squeezing the completely coagulated latex was used in the membrane experiments, owing to its high pollution load. It contains a small amount of uncoagulated rubber and various non-rubber constituents which originated from field latex. In addition, some chemicals such as ammonia and formic acid were introduced in the NR processing. The effluent from the NR processing plant was also collected to determine the pollutant parameter values. It contains skim serum and large quantities of cleaning water, which were used to cleaning the latex coagulum, coagulation tank and plant floor. It would be treated by an anaerobic-aerobic treatment system. The main characteristics of both effluents are presented in Table 1.

2.2 Wastewater analysis

The following parameters were measured: pH, total dissolved solids (TDS), conductivity, chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids (SS), total nitrogen (T-N), ammonia nitrogen (NH_4-N), and total phosphorus (T-P). All analyses were performed as per the Water and wastewater monitoring and analysis methods (2009).

2.3 Membranes

Spiral wound membranes purchased from General Electric Company (GE, USA) were employed in the cross-flow filtration experiments. The base material is tetrafluorometoxil (TFM) and each membrane is 45.72 mm diameter and 304.80 mm length, with an effective surface area of 0.32 m^2. Other physical properties of the membranes are listed in Table 2.

2.4 Experimental procedure

Experiments were carried out in batches using a laboratory scale membrane system as shown in Fig. 1, which consists of sand filtration, cartridge filtration, UF, NF and RO processes. First, a pressure sand filter was used for the removal of suspended solids. Furthermore, the skim serum was clarified by a cartridge filter with a pore size of 0.22 μm before passing through the UF membrane. The UF membrane with a molecular weight cut-off (MWCO) of 1000 Daltons can reject most of the organic matters in the skim serum, which was proposed as NF pretreatment. The retentate from UF module was collected and processed into fertilizer or recirculated to the feed tank. The UF permeate was forced to pass through the NF and RO membranes successively. The NF retentate, which was rich in quebrachitol, was used to extract quebrachitol by crystallization (Jiang *et al*. 2014). The permeate produced by the RO module was collected for analyzing. In the experiments, the default operating pressure of UF was 20 bar, both the NF and RO experiments were performed at 30 bar.

Table 1 Characteristics of NR wastewater

Parameters	Skim serum	Effluent
pH	4.42	5.7
TDS (g/L)	4.68	3.32
Conductivity ($ms \cdot cm^{-1}$)	9.35	6.65
BOD (mg/L)	6952	1748
COD (mg/L)	26160	6632
SS (mg/L)	213	468
T-N (mg/L)	405	322
NH_4-N (mg/L)	391	311
T-P (mg/L)	200	96

Table 2 Membranes characteristics

Process	Model	Cut-off	Max. pressure
UF	GE1812C-34D	1 kDa	27.60 bar
NF	DL1812C-34D	150-300 Da	41.00 bar
RO*	SE1812C-34D	Non-porous membrane	41.00 bar

*RO with a nominal rejection of 98.5% of NaCl

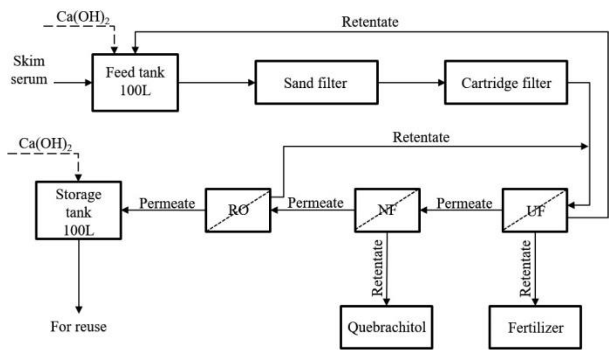

Fig. 1 Schematic diagram of the laboratory scale membrane system

3. Results and discussion

3.1 Effect of the transmembrane pressure on permeate flux in membrane processes

Permeate flux is an important parameter in the design and economic feasibility analysis of membrane separation processes (Fersi and Dhahbi 2008). Transmembrane pressure (TMP) plays an important role in permeation and separation. The relationship between permeate flux and TMP for clean water and skim serum was studied in the experiments. The TMP was varied from 6 to 22 bar in the UF experiment, and from 18 to 34 bar in the NF and RO experiments. As shown in Fig. 2, the NF membrane showed the largest permeate flux. The average clean water fluxes of the UF, NF and RO membranes were 1.69, 4.51 and 2.40 $L.h^{-1}.m^{-2}.bar^{-1}$, respectively. The permeate flux declined 20.84%, 20.01% and 49.57% in the case of NR wastewater, respectively. Results also show that the permeate flux increases obviously with increasing TMP in each membrane experiment. As expected, TMP has a significant influence on the permeate flux.

3.2 Effect of the transmembrane pressure on conductivity

The conductivity which is usually used to monitor the retentate rate and permeate quality, was measured after membrane treatment in this study. The effect of TMP on conductivity is illustrated in Fig. 3. With increasing TMP in the experiments, the conductivity of UF, NF and RO permeate decreased 19.35%, 16.55% and 18.52% within the pressure range studied, respectively. It indicated an increase of the retentate rate. This is because permeate flux increased with increasing TMP in the membrane process, and more solutes were gathered at the surface of the membrane. The concentration gradient causes the solutes tend to diffuse back to the bulk solution. It contributed to the decrease of the concentrate of the permeate and increase of the retentate rate (Dong 2007).

3.3 Effect of the volume reduction factor (VRF) on permeate flux

The volume reduction factor (VRF) is defined as the initial volume of the effluent divided by the retentate volume. In the membrane processes, due to the concentration polarization and membrane fouling caused by high COD value and high salt concentration, the permeate flux decreases with the VRF increasing, which is considered as the major drawback in various industrial applications (Fersi *et al*. 2005, Kumar *et al*. 2015). Fig. 4 shows the effect of the VRF on the permeate flux. The UF, NF and RO experiments were performed at 20, 30 and 30 bar, respectively. The corresponding initial permeate flux was 19.40, 116.23 and 35.25 $L.h^{-1}.m^{-2}$, respectively. With the VRF increasing, the UF permeate flux decreased slightly, and only a 22.22% reduction of the initial flux was obtained when the VRF reached the final value (VRF=8.42). However, in the case of NF, a rapid permeate flux decline was observed for 1.38-3.13 VRF range. It represented a 57.86% decline of the initial permeate flux when the VRF is 3.13. It can be concluded that VRF has a significant influence on concentration polarization which decreases the permeate flux sharply. In the RO process, it could be seen that an increase in VRF value to 9.33 decreases flux to 54.01% of the initial permeate flux. The permeate flux became stable till the VRF reached a value of 4.19.

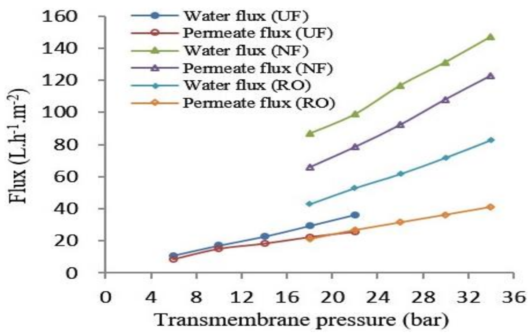

Fig. 2 Effect of transmembrane pressure on permeate flux for clean water and natural rubber wastewater

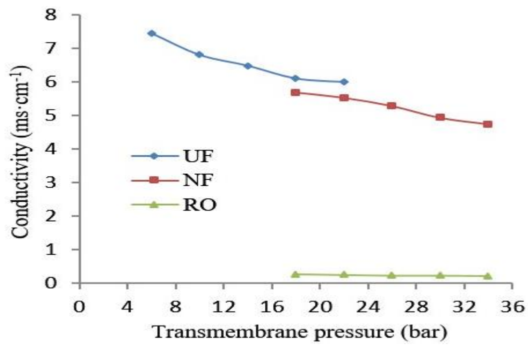

Fig. 3 Effect of transmembrane pressure on conductivity in the membrane experiments

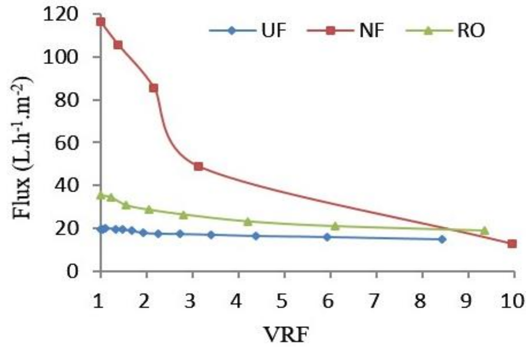

Fig. 4 Effect of the volume reduction factor on permeate flux in the membrane experiments

3.4 Permeate quality achieved

The main characteristics of the feed and permeate samples are presented in Table 3. For comparison, the NR wastewater treated by a conventional activated sludge system was also analysed. As shown in Table 3, except for the pH, all the other parameters show that the effluent quality treated by the membrane processes was much better than that of the biological treatment, even though the concentration of the skim serum is much higher than the effluent from the NR processing plant.

The removal efficiencies of some parameters for both processes are presented in Fig. 5. Compared with the biological treatment, higher removal efficiency was achieved by using membrane processes. The TDS and T-P removal efficiency improved 53.11% and 49.83% respectively. The removal efficiency of BOD and COD exceeded 99%, and both the T-N and NH_4-N had approximately similar removal efficiency (93%). Generally, T-P removal efficiency was relatively low because of the limit of the biological processes, the removal efficiency was 50% (from 96 mg/L to 48 mg/L) in the experiments. For the membrane separation treatment, a significant reduction of T-P was obtained, the T-P decreased from 200 mg/L to 0.34 mg/L.

The results indicate that the membrane processes contributed to a significantly excellent removal efficiency of all parameters and the permeate has extremely favourable analytical characteristics to be reused in the NR processing.

As described in the previous paragraphs, the membrane separation system exhibited a better performance in the effluent treatment compared with the biological treatment. However, it has no effect on the pH. On the contrary, the effluent pH decreased from pH 4.42 to 3.15 after treated by the membrane processes. This is because the RO membrane rejected dissolved ions but not dissolved CO_2, HCO_3^- was rejected by the RO membrane, resulting in lower $[HCO_3^-]$ in permeate than that in feed. In order to remain a constant p*Ka*(*Ka*=$[HCO_3^-][H^+]/[H_2CO_3]$), eventually higher $[H^+]$ or lower pH in permeate than that in feed was obtained (Qin e*t al*. 2005). So the treated effluent is limited in the application of washing latex coagulum and preparing acid solution, but not suitable for irrigation or discharge owning to its low pH. Considering the more extensive application, the effluent needs to be adjusted to neutral pH.

3.5 pH adjustment

In the present study, the effluent pH was adjusted to neutral using calcium hydroxide in the pre- or post-treatment. As shown in Fig. 6, the initial effluent pH values have significant influence on the calcium hydroxide dosages. When the effluents were adjusted to neutral, the calcium hydroxide dosage of effluent A (pH 4.04) nearly double of effluent C (pH 4.90). After treated by membrane system, the pH of effluent B decreased from 4.39 to 3.47, while the calcium hydroxide dosage decreased 87.5%.

In the pre-treatment, the adjustment of pH is a slow reaction process owning to the complicated chemical compositions. In order to get the constant neutral effluent after the pre-treatment, the pH of skim serum must be adjusted to near 8.5 in advance and waiting for 12 hours. Even so, salts still precipitated out of the UF permeate continually in the membrane processes and made it difficult to perform the NF experiment.

In conclusion, the poor controllability made it unfeasible to adjust effluent pH in the pre-treatment. Therefore, adjusting the effluent pH to neutral in the post-treatment is a more appropriate choice. It not only requires less calcium hydroxide but also has a constant pH. Furthermore, it is unnecessary to worry about the scale formation on membrane surfaces.

3.6 Extraction of quebrachitol and preparation of fertilizer

The NF retentate, which is rich in quebrachitol, was concentrated on a rotary evaporator after decolorized using activated carbon, and then kept at 4℃ for 12 hours to promote crystallization. The resulting crude extract thus obtained was recrystallized several times. Finally, about 0.1% (by weight) of quebrachitol was obtained from the skim serum.

The UF retentate, which contains large amounts of proteins was mixed with the edible fungi residue and inoculated microorganisms in the composting process, in order to make it harmless and useful.

Table 3 Effluent quality of the membrane and biological processes

Parameters	serum	Membrane treatment	Effluent	Biological treatment
pH	4.42	3.15	5.7	7.94
TDS (g/L)	4.68	0.39	3.32	2.04
Conductivit (ms·cm^{-1})	9.35	0.77	6.65	4.08
BOD (mg/L)	6952	17.5	1748	44
COD (mg/L)	26160	80	6632	172
SS (mg/L)	213	--	468	18
T-N (mg/L)	405	28.7	322	31.4
NH_4-N (mg/L)	391	26.5	311	30.2
T-P (mg/L)	200	0.34	96	48

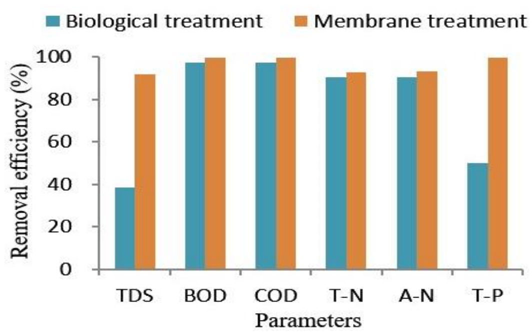

Fig. 5 Comparison of the membrane and biological systems for removal efficiency of respective parameters

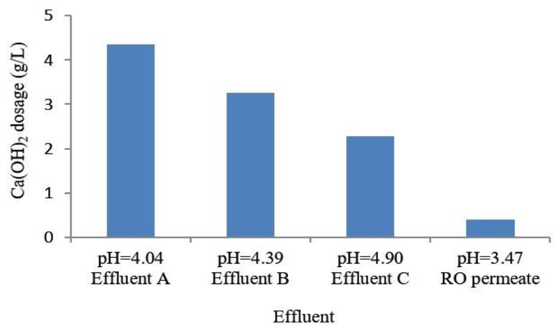

Fig. 6 Effluent pH adjustment

4. Conclusions

The experimental results obtained from the laboratory scale tests reveal that the membrane processes are suitable as advanced treatments of NR wastewater for reuse, and efficiently solved the odor problem. About 0.1wt% quebrachitol was extracted from the skim serum. The effluent quality treated by the membrane processes was much better than that of the biological treatment. Especially for the TDS and T-P, the removal efficiency improved

53.11% and 49.83% respectively. The removal efficiencies of BOD, COD and T-P exceeded 99%.

Although high quality effluent can be obtained using the membrane processes, the production efficiency was noted to be very low due to the low permeate flux of the UF membrane with a MWCO of 1000 Daltons. In order to improve the production efficiency, the UF membrane should be cut out or replaced with a high permeability UF membrane in the further studies. However, The UF membrane with a MWCO of 1000 Daltons is necessary for extracting quebrachitol (Jiang 2014). Consideration must be given to both production efficiency and quebrachitol extraction. If we skip the UF step in the experimental procedure, it will largely improve the efficiency of the membrane processes, and only NF retentate need to be performed by UF so as to extract quebrachitol successfully. Accordingly, the workload of the UF membrane will decrease greatly.

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