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Membrane Separation as a Cleaner Processing Technology for Natural Raw Rubber Processing

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ABSTRACT

Natural rubber (NR) processing had long been a process utilizing a lot of water, discharging effluent with high organic load, creating waste and malodour. In the wake of global consciousness about environment and the scarcity of water, the NR processing, raw as well as rubber product manufacturing need to be reengineered and made environmentally and economically viable. In view of this, Malaysian Rubber Board (MRB) created a paradigm shift in raw rubber processing by investigating the use of membrane separation technology to overcome some of its pertinent problems. This paper outlines the use of membrane separation technology as an alternative method to promote cleaner processing and to extract useful biochemical as a value-added product. References were made to the current R&D projects as well as give an overview of the projects that could be undertaken in the near future so as to make NR industry to be environmentally friendly and economically viable and to achieve a zero discharge through the application of membrane separation technology.

Keywords: Raw rubber processing, effluent, membranes separation, cleaner production, value-added products

1.0 INTRODUCTION TO ON RAW NR PROCESSING

Raw rubber processing includes latex and coagulated rubber lump (cup-lump) processing [1]. Each of this processing varies considerably from one another as they are used for different applications. Figure 1 shows different type of raw rubber processing and their usage in making various rubber products.

1.1 Latex Processing

Latex exudes from the rubber tree once it is tapped. The latex flows into a cup attached to the tree below the tapping cut by gravity and remains un-coagulated for about 4 hours after tapping. It is then collected and bulked in tanks. The addition of 0.1% ammonia into the latex collecting tank keeps the latex in liquid form until it arrives at the latex processing factory. At the factory, it is concentrated

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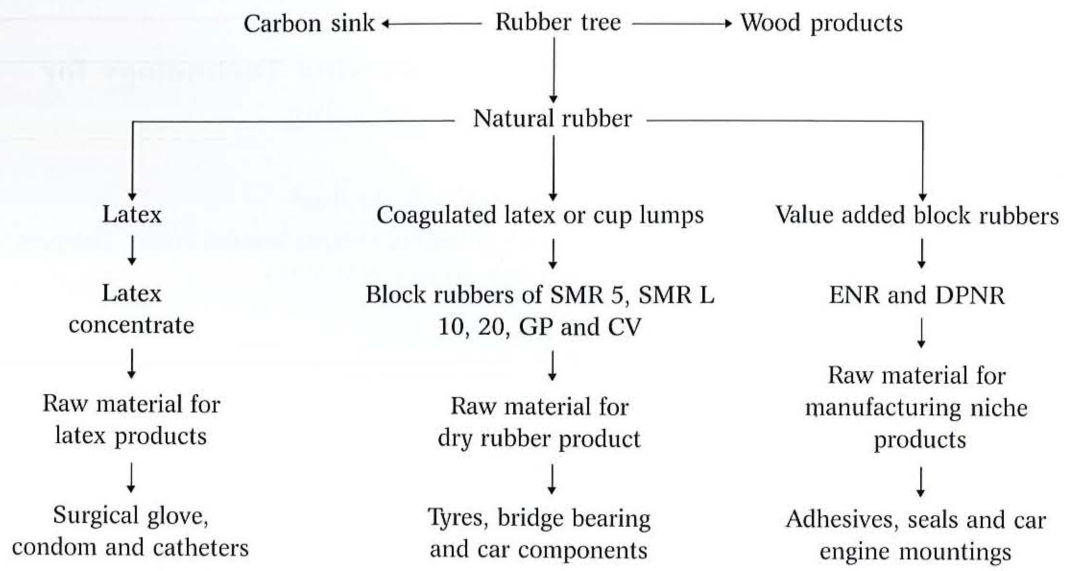


SMR: Standard Malaysian Rubber; CV: Constant viscosity; GP: General purpose; ENR: Epoxidised NR; DPNR: Deproteinised NR

Figure 1 Types of raw rubber processing and their usage in making various rubber products

from latex with dry rubber content (DRC) of 30% to a latex concentrate of 60% DRC. It serves as the main raw material for natural rubber latex product manufacturing factories that produce examination gloves, condoms and latex thread. Centrifugation is the preferred method and accounts for some 95% of the total concentrate produced in Malaysia. Centrifugation produces skim latex as a by-product. Skim rubber processing involves the recovery of 4-5% of dry rubber by cheap grade sulphuric acid coagulation. Once the skim rubber is recovered, the effluent consisting of sulphuric acid contaminated serum with a high biological oxygen demand (BOD) is discharged into the effluent anaerobic ponds (Figure 2). Factories which do not have proper maintenance of the effluent ponds bring about environmental problems such as malodour from the release of hydrogen sulphide gas from the effluent pond. In addition, raw rubber processing uses a high amount of water (Figure 3). The effluent treatment pond takes the bulk of the effluent discharged during processing. Biological treatment system incurs high cost to comply with the stringent environment regulatory requirement standards set by the Malaysian Department of Environment (DOE) [1-3].

1.2 Block Rubber Processing

Besides latex processing, NR processing includes raw rubber processing as well. Raw rubber is the latex that is left to undergo natural coagulation on the latex collection cup, attached to individual rubber trees known as cup-lumps as well as late-drips found in the latex cups and hardened rubber stripped from tapping cut known as tree laces. These materials are brought to the raw processing factory as field grades which are turned into technically specified block rubbers known as Standard Malaysian Rubber (SMR) of various grades such as SMR 10 (0.1% dirt content), SMR 20 (0.2% dirt content) and SMR GP (general purpose).

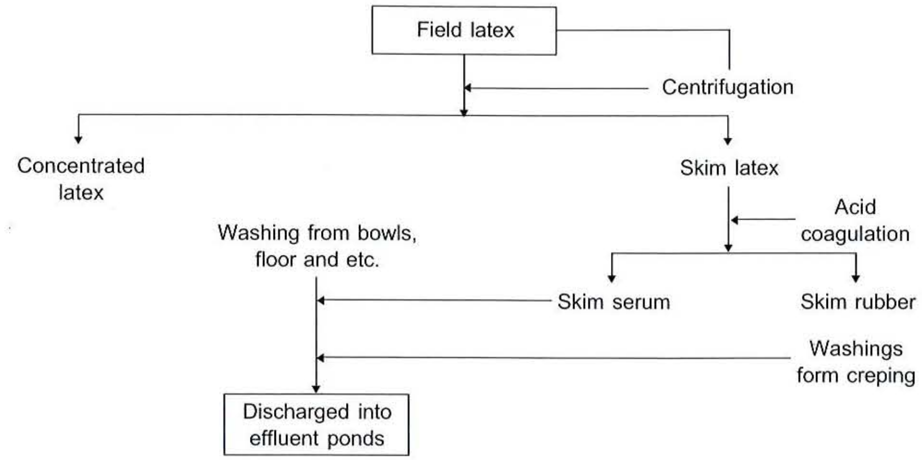


Figure 2 Sources of effluent during latex processing

1.3 Status NR Processing

Natural rubber (NR) processing has long been utilizing excessive water, discharging effluent of high organic load, creating waste and malodour (Figures 2 and 3). In the wake of global consciousness on environment and the expected scarcity for water, the raw NR processing, and rubber product manufacturing need to be reengineered and made environmentally friendly and economically viable.

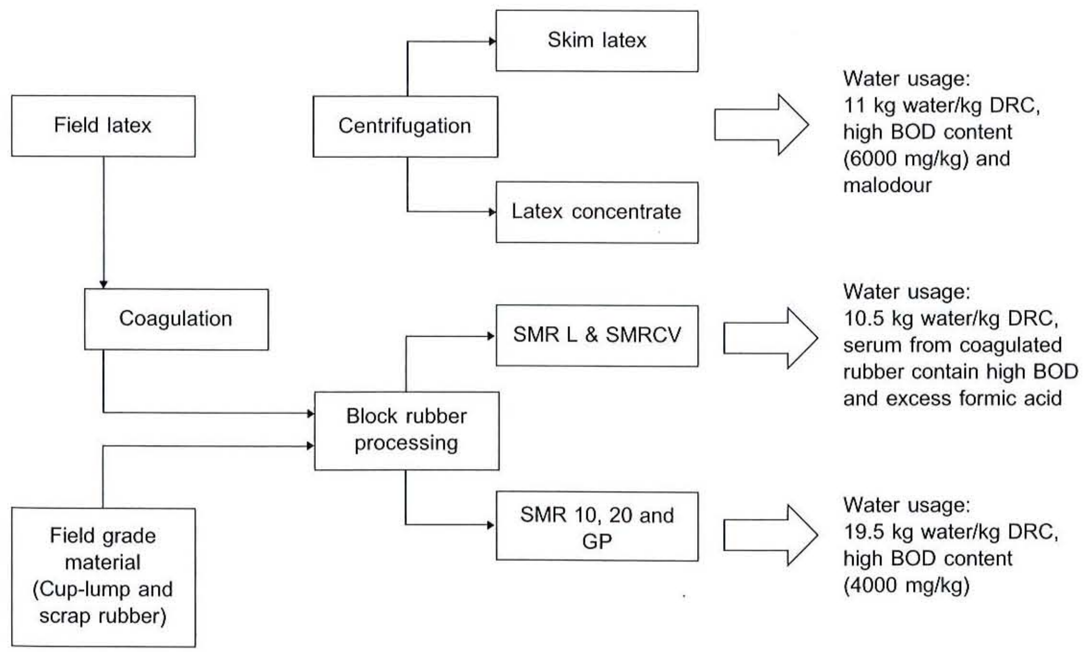


Figure 3 Status of raw NR processing

This paper outlines the use of membrane separation technology as an alternative method to promote cleaner processing technique in the raw rubber processing and also to extract useful biochemicals as value-added products from the waste. References are made to the current R&D projects in the Rubber Research Institute of Malaysian Rubber Board as well as give an overview of the projects that could be undertaken in the near future so as to make NR industry a sustainable industry.

2.0 METHOD/THEORY

2.1 The Need to Explore New Processing and Effluent Treatment Technique

NR processing and waste water treatment need to be re-engineered to make the transformation from consuming excessive water to a minimal amount. Approximately 10.5 kg of water per kg of block rubber processing and 19.5 kg of water per kg of latex processing is utilized and discharging effluent with 4000 mg/kg and 6000 mg/kg respectively (Figure 3). Subsequently, a cleaner production technology should be formulated to minimize waste, and recover value-added products from waste. This is necessary because water could become a scarce commodity in the future. The present high usage of water in NR processing could pose a major problem in sustaining the industry. Technology needed for recycling waste water should be fully exploited. Other effluent treatment systems should also be explored since using biological treatment alone would become outdated and not effective and would become less efficient in complying with the future stringent DOE requirements. Treated water quality should be for home consumption standards. All rubber and products should comply with ISO 14000, eco-labeling and life cycle audit criteria, soon. Minimizing and utilizing of waste and effluent should be fully exploited to recover value-added products to achieve 'zero discharge' and to maximize revenue [2, 4-6].

2.2 Utilization of Membrane Separation Technology for NR Processing

A paradigm shift is necessary to exploit other effective waste treatment and resource recovery technologies. This will prepare the NR industry for more stringent demands in environmental management. In view of this, the membrane separation technology which is fast gaining importance globally could become one of the available options to be exploited for our needs. To achieve continued sustainability of the NR industry and to cater for the future environmental regularity requirements, the MRB has embarked in carrying out the following R&D projects to evaluate the use of membrane separation technology [2].

2.3 An Alternative Method of Latex Processing Leads to 'Zero Discharge'.

An alternative method of concentrating field latex which could produce latex concentrate and a clear serum and not skim latex as a by-product was explored. Thus membrane separation technology become a viable option to concentrate NR field latex since aqueous phase make up about 60% of the latex by weight. The rubber hydrocarbon make up to about 35-38% with a molecular weight distribution of latex particles ranging from 300 000 to about 10 million Dalton and the rest are non rubber solids. R&D was carried out for the last 3 years to establish the possibility of using ultrafiltration as an alternate method of concentrating NR field latex using locally fabricated ultrafiltration system as shown in Figure 4. Thus attempts were also made to identify a suitable composite preservation system between two available options and to study the effects of feed flow-rate and trans-membrane

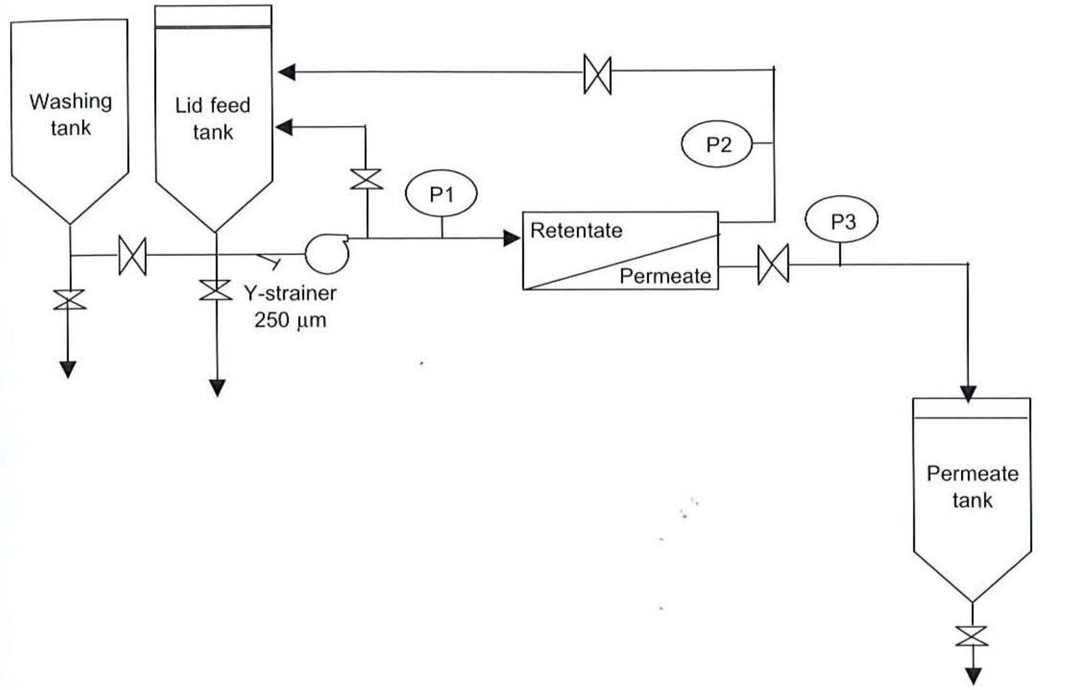


Figure 4 Schematic diagram of an ultrafiltration system to concentrate preserved NR field latex

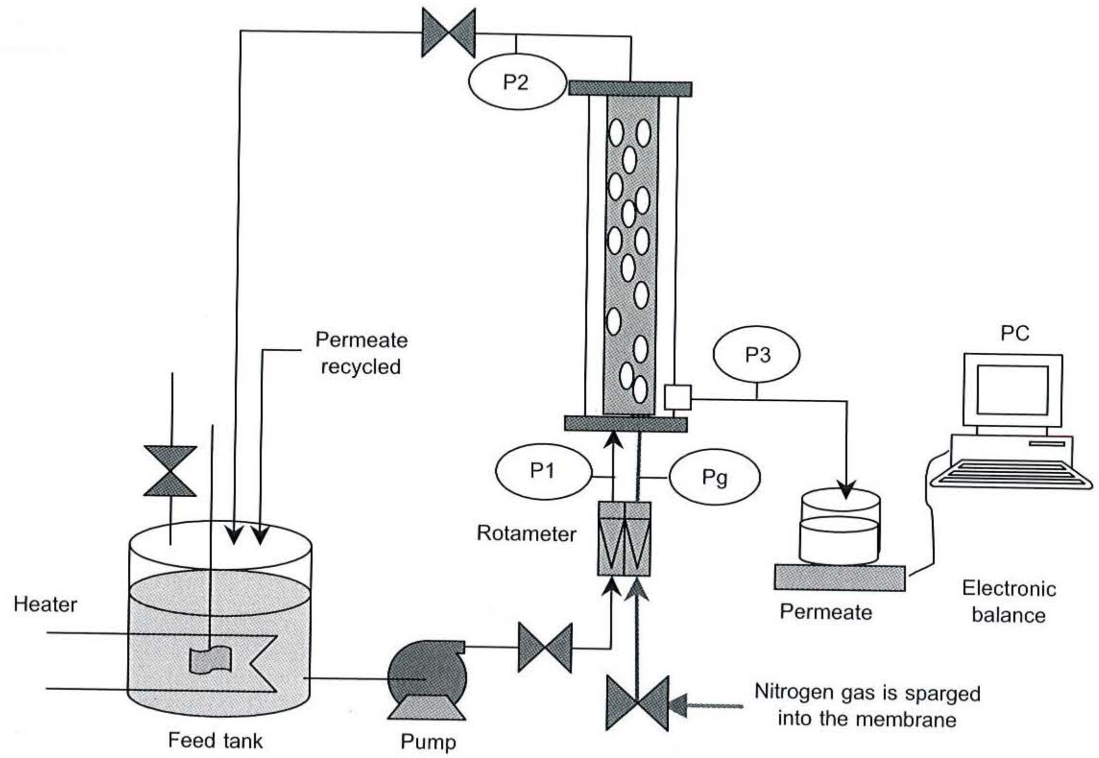
pressure (TMP) on permeate flux. TMP is the average value of inlet pressure P1 and outlet pressure P2. The optimum TMP for the concentration process and the degree of concentration achievable was also identified [7]. Field latex was successfully concentrated from a DRC of 30% to 50% obtaining a clear serum as by-product instead of skim latex.

2.4 Membrane Separation Technology to Treat NR Latex Processing Effluent

A joint study was carried out between MRB and Chemical Engineering Department of University of Malaya to evaluate the use of membrane separation to treat NR latex processing effluent. Treatment of the effluent was carried out using a small-scale cross flow ultrafiltration pilot plant (Figure 5) fabricated locally using a tubular membrane installed vertically with a 100 kD molecular weight cut-off (MWCO) with an effective membrane area of 0.047 m^2. The feed which is a latex processing effluent circulated upward through the membrane module using a gear pump. Nitrogen gas was directly injected to the inlet (bottom) of the membrane through a solenoid valve. This gas sparging technique was to reduce fouling of the membrane and to enhance flux. Permeate was the treated effluent collected directly into a container on the weighing balance. The permeate mass was recorded and was characterized for effluent testing parameters [8].

2.5 Evaluation of the Use of Membrane Separation to Treat Latex Processing Effluent

During the treatment of latex processing effluent by ultrafiltration, percentage reductions of 92, 96, 67, 72, 60 and 75 were achieved for suspended solids, total solids, COD, BOD, total nitrogen and ammonia-cal nitrogen, respectively. Although the percentage reductions were good for other



P1 - Inlet pressure gauge, P2 - Outlet pressure gauge, P3 - Permeate pressure and Pg- pressure of sparged gas

Figure 5 Schematic diagram of an ultrafiltration system to treat latex processing effluent [8]

parameters, the values for COD and BOD are far off from the Effluent Discharge Standards of DOA (Standard values of prescribed premises occupied used for production of concentrated latex). COD and BOD need to be further reduced to comply with the Effluent Discharge Standard of Department of Environment. Other modern technologies which incorporate both membrane separation technology and biological treatment need to be investigated to reduce the BOD and COD [2].

3.0 RESULTS AND DISCUSSION

3.1 Constrains Using Ultrafiltration to Concentrate NR Field Latex

By utilising membrane separation technology in particular, ultrafiltration latex could be concentrated by separating the serum as a clear solution from the latex to make latex concentrate (Figure 4 and 6). The latex concentrate goes to latex product manufacturing factory as a raw material and the serum subsequently could be utilized for useful biochemical extraction. Serum contains many useful biochemicals. The single largest component of latex serum is a water-soluble carbohydrate, quebrachitol, which is a chemical feedstock for the synthesis of a range of bioactive material [4]. If all the serum from natural rubber latex processing could be exploited, the income from biochemical extraction may well exceed that from the sale of rubber. Since the whole latex, i.e. serum as well as latex

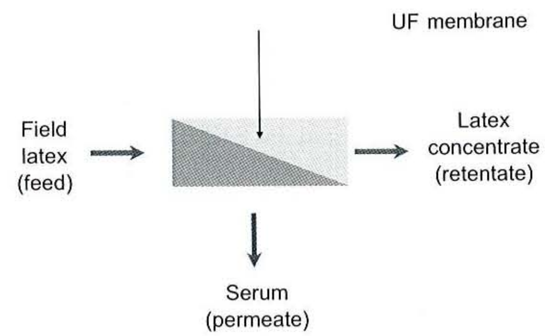


Figure 6 Schematic diagrams showing the use of membrane separation to concentrate field latex

concentrate, would be fully utilized by pharmaceutical and latex product manufacturing industry, this will lead to a 'zero discharge scenario' [1, 3, 5, 6].

Concentration of NR latex by ultrafiltration (UF) is a viable option to solve environment related problems inherent with the current mode of concentration using centrifugation. Using the correct membrane material and operating condition, it is possible to obtain a clear serum as permeate. By using the ultrafiltration system as shown in Figure 4, the concentration of field latex was increased from 30% to 50%. The increase in DRC per square meter of membrane area per hour (m^2/hr) was 28%. An increase in the membrane area would increase the level of concentration within a short period of time and precaution should be taken to control the rise in temperature with a suitable cooling system [7]. The membrane cleaning procedure produces a mean flux recovery of 82%. From the results of the flux recovery, the cleaning procedure was satisfactory although the procedure completely did not eradicate the permanent fouling of the membrane [5-7].

3.2 Recovery of Waste Latex (Skim Latex) via Ultrafiltration

To change the field latex concentration process from centrifugation to membrane separation is not a realistic endeavour. The existing latex concentrate factories has already invested heavily in purchasing centrifuges costing close to RM300,000.00 each, and converting it to a membrane latex concentrator would not be economical. Moreover, latex glove manufactures are more accustomed to film properties of centrifuged latex.

Centrifuged latex consists of latex particles of within a narrow range where smaller particle and most of the non-rubber are separated and goes into the skim latex fraction during centrifugation, unlike ultrafiltered latex where all the particles are retained and the film properties is yet to be evaluated. Even if the properties of this latex are comparable to that of centrifuged latex, it would take quite awhile to change the mind set of latex dipped goods factory owners and their established customers [9, 10]. In addition, environmental degradation at the latex concentrate factories originate from skim latex processing. Skim latex is produced as a by-product from centrifugation process to concentrate field latex.

An immediate measure to solve the environmental problems faced by the latex concentrate factories is to recover the NRSL by concentrating it using UF. MRB has successfully carried out R&D work to concentrate NRSL that was obtained as a by-product via the centrifugation process, where the DRC was increased from 5% to about 30% (same as the DRC value of field latex) [9,10]. Latex free, clear serum which was not contaminated by any acid was obtained from this UF process. This serum has potential to be turned into fertilizers as the low-end product. On the higher end; it can be used to extract value-added bio-chemicals such as industrial protein and quebrachitol [7, 8]. The concentrated skim latex can be recycled to the oncoming field latex for producing latex concentrate by centrifugation process (Figure 8).The other option is to be used as a new raw material. Concentrated skim latex is being currently evaluated as a new value-added raw material for making niche rubber products which requires softness. Therefore, UF has prevented the NRSL being turned into a waste latex and scrap rubber and from discharging acid tainted effluent. Instead, it has produced two new valuable raw materials [9, 10].

Therefore, the ideal option is to change the current method of skim latex processing. Since environmental degradation in the latex concentrate factory originates from the processing of skim latex by acid coagulation, it would be to eliminate skim latex coagulation by sulphuric acid. A more realistic way is to add value to skim latex by concentrating it by ultrafiltration. By using the ultrafiltration system as shown in Figure 4, several runs were carried out to concentrate skim latex that was obtained as a by-product from a centrifugation process. The DRC of the skim latex was increased from 5% to about 30% (same as the DRC value of field latex) which is 95% m^2/hr (an increase in TSC of 95% per hour if the membrane area is 1 m^2). The concentration process was carried out at a constant TMP of 2 bar. This was achieved within a shorter period of time because of better average flux due to lower solid content of skim latex. A clear serum was obtained as a by-product. This serum was further processed to extract protein and quebrachitol (Figures 6 and 7).

The advantages of skim latex recovery by concentrating it via ultrafiltration includes the high investment cost incurred during the purchase of centrifuging machineries that costs over RM 0.3 million each, can still be used; environmentally friendly: Prevents the discharge of effluent with high sulphate content to the treatment pond; malodour from the release of hydrogen sulphide gas during bio-degradation at effluent pond could be prevented; reduction in effluent treatment costs; quality latex recovery of by membrane separation increases profit since the cost of sulphuric acid for coagulating skim latex is eliminated; recovery of latex worth more than RM 60 million annually, (based on the 2005 concentrate latex production figure); increase of revenue from value-added products recovered from serum; cost for water is reduced as water could be recycled; 'zero discharge' during NR latex processing.

3.3 Membrane Bioreactor

The project relates to the advanced effluent treatment technology using a membrane bioreactor (MBR) system for rubber product manufacturing industries - a combination of two basic processes (biological degradation and membrane separation) into a single process where suspended solids and microorganisms responsible for biodegradation are separated from the treated wastewater by membrane filtration unit [11].

This promising new effluent treatment technology with high biomass concentration (8000 mg/l-12000 mg/l) able to treat wastewater to the highest tertiary standards with fewer steps, lesser sludge produce due to high sludge age, and use smaller land area than the conventional systems and also enables high wastewater recycling. In addition, high sludge retention time in this system is capable to provide better support for the growth of the slow-growing nitrifying bacteria than the conventional activated sludge system. Hence, this system provides greater potential for the oxidation of ammonium nitrogen to nitrate nitrogen [12].

From 2002 to 2005, Malaysian Rubber Board (MRB) carried out a joint R&D work with Chemical Engineering Department of University of Malaya using MBR in treating latex processing effluent. Reduction in COD and BOD were much lower than DOE Standard's requirement (< 50 mg/L) [11]. The BOD_3 and COD removal efficiency of treated effluent from MBR process were observed at 97% and 98%, respectively [10] and removal efficiency is higher compared to using UF alone. The schematic

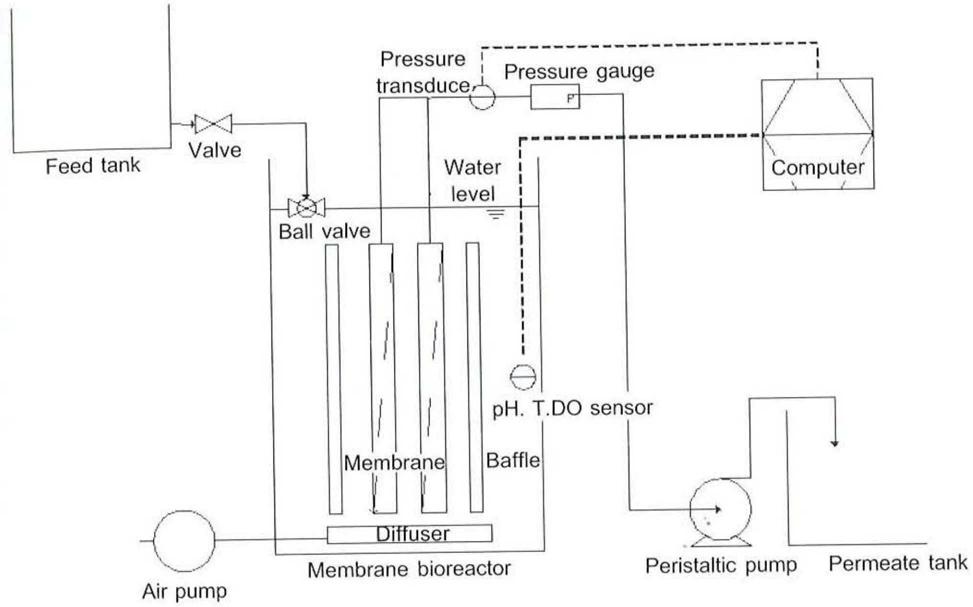


Figure 7 Semi-pilot plant model of MBR used for treating latex processing effluent [11]

diagram of the semi-pilot model is as shown in Figure 7. The treated water passing through flat sheet UF membrane can be recycled back to the factory. This system gives an option for recycling water. MRB is currently involved in R&D work in scaling up of this technology to be used in treating effluent from latex product manufacturing industry [12].

3.4 Zero Discharge Scenarios at Natural Raw Rubber Processing Factories Utilizing Membrane Separation Processes (MSP)

Membrane separation process could revolutionize raw rubber processing. Latex processing had been successfully transformed to achieve discharge status by the recovery of skim latex and turning it into skim latex concentrate and skim serum; value added raw materials. Now there is an option for latex processing for by-passing centrifugation process and straight go for the production of latex concentrate and serum using ultrafiltration. The MBR usage could be exploited in the future to recycle water in the block rubber processing.

4.0 CONCLUSION

MRB being the guardian of the NR industry in Malaysia incorporates R&D projects that would help sustain the growth of rubber industry in the country. The R&D projects in the mid-stream sector of the industry (processing and effluent management) are geared towards a cleaner processing technique: minimizing waste and isolating value-added products from the waste. It also includes improving the effluent treatment system so that water which is considered to be a valuable commodity in the future could be recycled and reused. The new latex processing technology and skim latex recovery with the value-added product recovery from serum using membrane separation technique is currently being up-scaled in a commercial factory. With early signs showing promising results from the up-scaling of these projects together with membrane bioreactor which promotes water recycling, it would not be long for the mid stream processing activities of the NR Industry in Malaysia to fully achieve zero discharge status.

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