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Ultrafiltration using gas sparging technique for treatment of natural rubber effluent

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ABSTRACT Physical and chemical properties of natural rubber effluent have been identified to contain large amounts of non-rubber compounds and chemicals which can seriously damage or kill the natural flora and fauna of the waters when the effluent is discharged untreated. This paper presents the application of membrane technology for the treatment of natural rubber processing effluent that involves gas injection technique. During the experiments, permeate was collected and analysed for several characteristics such as total solids (TS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen and ammoniacal nitrogen (NH_3-N). The results show that the use of gas sparging technique was able to increase total permeate flux 8.3% and 145.3% compared to non-gas sparged technique condition. In terms of permeate quality, reductions achieved for total solid (TS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen and ammoniacal nitrogen (NH_3-N) were 95%, 67%, 77%, 51%, 74% respectively. For non-gas sparged technique conditions, permeate fluxes declined sharply with time due to accumulation of foulant on the membrane surface. However both conditions showed increase of total permeate flux with transmembrane pressure and feed flowrate.

ABSTRAK Sifat-sifat fizik dan kimia daripada pembuangan sisa pemprosesan getah asli terbukti mempunyai kandungan sejumlah bahan bukan getah dan juga bahan kimia yang tinggi. Kandungan ini dapat membawa kemusnahan yang serius kepada flora dan fauna yang terdapat di dalam sungai apabila sisa pemprosesan tersebut dibuang tanpa diolah terlebih dahulu. Kajian ini bertujuan untuk menerangkan penggunaan teknologi membran untuk merawat sisa-sisa pemprosesan getah asli yang melibatkan teknik "gas sparging". Semasa pemprosesan, hasil permeat dikumpul dan dianalisa untuk menentukan beberapa sifat-sifat khas seperti jumlah pepejal (TS), keperluan oksigen kimia (COD), keperluan oksigen biokimia (BOD), jumlah nitrogen (TN) dan nitrogen amonia (NH_3-N). Hasil yang diperolehi menunjukkan bahawa penggunaan teknik "gas sparging" boleh meningkatkan jumlah fluks permeat dalam julat 8.3% hingga 145.3% jika dibandingkan dengan keadaan tanpa "gas sparging". Untuk kualiti permeat, penurunan kandungan jumlah pepejal (TS), keperluan oksigen kimia (COD), keperluan oksigen biokimia (BOD), jumlah nitrogen (TN) dan nitrogen amonia (NH_3-N) adalah pada 95%, 67%, 77%, 51%, dan 74%. Untuk keadaan tanpa penglibatan teknik "gas sparging", penurunan fluks permeat terhadap waktu sangat cepat disebabkan penimbunan kotoran di atas permukaan membran. Disamping itu pengaruh tekanan dan kelajuan alir masuk terhadap fluks permeat yang dihasilkan meningkat baik pada keadaan melibatkan teknik "gas sparging" maupun keadaan tanpa melibatkan teknik "gas sparging".

(Natural rubber effluent, crossflow ultrafiltration, gas sparging technique)

INTRODUCTION

Malaysia is a major producer of agricultural products. Although processing of agricultural products plays an important role in the economic development of Malaysia, it has also been identified as one of the major sources of pollution in this country. One such agricultural product is natural rubber processing effluent which can seriously damage or kill the natural flora and fauna of the waters when this effluent is discharged untreated. Currently most of the natural rubber effluent treatment in Malaysia uses anaerobic/facultative ponding system. This system is popular due to its simplicity in operation and low operating cost. Although this system is effective in removing most of the pollutants from natural rubber effluent, this system needs ample land for its construction and is not suitable for factories in the urban area because it emits offensive smell especially when it rains [1].

There is an emerging trend towards the use of the other technologies such as membrane technology to enhance treatment process performance [2-4]. Nowadays, industries avoid use of dead end filtration mode or conventional mode which causes build up of debris on the membrane surface, thus effecting a reduction in fluid permeation. Conversely, crossflow filtration employs tangential flow across the membrane surface [5]. There are now four commonly accepted categories or classes of pressure driven membrane filtration processes, defined on the basis of size as shown in Table 1[6].

Recently, the use of membrane filtration that involves gas sparging technique is being studied for the treatment of natural rubber effluent [7,8]. The aim of this study is to investigate the performance of membrane filtration with gas sparging technique to treat natural rubber effluent, including to assess the effects of operating conditions on total permeate fluxes.

MATERIALS AND METHODS

Experimental setup

The schematic diagram of the experimental setup is shown in Figure 1. All experiments were carried out at room temperature. This pilot scale system utilises a PVDF vertical tubular membrane with MWCO 100,000. It has an internal diameter of 12.5 mm, length 1.2 m, and effective surface area of 0.0471 m2. The natural rubber effluent solution was driven from feed tank by a gear pump and circulated through the membrane module with upward flow. The gas was directly injected to the inlet (bottom) of the membrane through a solenoid valve. Permeate was weighed using an electronic balance where the mass was recorded every five seconds and then recycled back to the feed tank to maintain a constant feed concentration. After each experimental run, the membrane was immediately washed with 1.0 % sodium hydroxide solution and then flushed with distilled water. After cleaning the flux was checked to ensure that the intrinsic membrane resistance had recovered to its original value.

Operational parameters

In order to evaluate the stability and capability of membrane processes, experiments were carried out at different operational conditions and parameters. The range of transmembrane pressure (TMP) was varied from 7.50 psig to 13.00 psig, flowrate gas sparging from 0 -500 ml/min and liquid feed flowrate between 1000 ml/min to 1600 ml/min. All experiments were carried out at room temperature. Each experiment was run for 4 hours with interval of 30 minutes for sampling under both gas sparged and non-gas sparged conditions.

Sampling and analytical methods

Skim natural rubber latex serum derived from coagulation of skim latex was obtained from a factory. Due to the milky nature of the skim latex serum, it is necessary to store it overnight before use. Effluent sample and permeate were collected to be analyzed for pH, total solid (TS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen and ammonia nitrogen (NH_3-N). The analyses were performed in accordance with procedures described in the standard methods for examination of water and wastewater.

Table 1. Classification of pressure driven membrane filtration processes.

Membrane Process	**Pore Size (μm)**	**Separation Capability**	**Pressure (bar)**
Reverse Osmosis	<0,001	Dissolved salts and low molecular weight substances (up to 100 daltons)	7-70
Nano Filtration	0,0008 - 0,009	2-valent metal ions, 3-and more valent ions, molecules of low molecular weight (200-300 daltons), viruses	5-15
Ultra Filtration	0,005 - 0,05	Particles size over 1 μm, some viruses, bacterias, dissolved substances with molecular weight between 10 000 - 500 000 daltons	0,5-5
Micro Filtration	0,05 - 5	Colloids, protozoa (Ciptosporidium, Giardia)	0,5-3

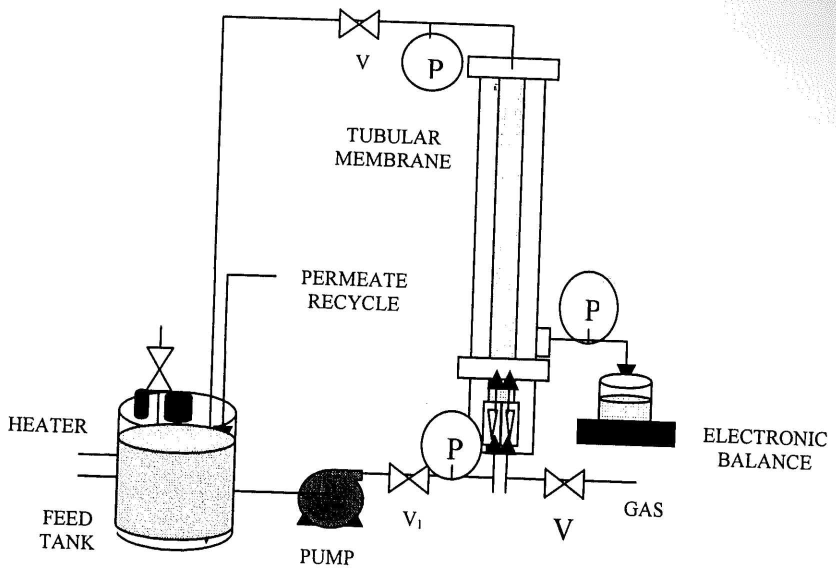


Figure 1. Schematic of semi pilot scale ultrafiltration system.

RESULTS AND DISCUSSIONS

Permeate quality achieved

The characteristics of effluent after treatment which involved gas sparging technique and non-gas sparging technique are shown in Table 2. The results in Table 2 show that the characteristics of permeate quality are not distinctly different, probably due to the fact that the same membrane was used. However the total nitrogen content in the permeate under gas sparged condition was higher than the under non-gas sparged condition. This is probably due to some of the nitrogen gas being soluble in the feed stream during the experimental run. Consequently, the dissolved total nitrogen in permeate under gas sparging was higher than non-gas sparged condition.

Effect of gas sparging on total permeate flux

A typical graph showing the variation of permeate flux with time at a constant feed flowrate (1400 ml/min) for different gas sparging flowrates is given in Figure 2. The effect of flowrates of gas sparging on total permeate flux at different transmembrane pressure is shown in Figure 3. Both graphs show that permeate fluxes increased significantly for different flowrates of gas sparging and transmembrane pressure. In Figure 2 it can be seen that permeate flux is found to decrease with time as the retained particles accumulate on the membrane surface and start to show the effect of fouling. Accumulation of cells, cell debris, or other rejected particles on the membrane surface occurs as external fouling or cake formation and is

Table 2. Characteristics of permeate after ultrafiltration.

Parameters	Feed	WGS	%Removal	NGS	%Removal
pH	3.75	4.46	+16	4.42	+15
Total Solid (TS)	7100	370	95	300	96
COD	3998	1332	67	1337	67
BOD_5	3642	853	77	1012	72
Total Nitrogen	596	295	51	240	60
NH_4-N	435	115	74	110	75

WGS = under gas sparging condition
NGS = under non-gas sparging condition
(all values except pH are expressed in mg/l)

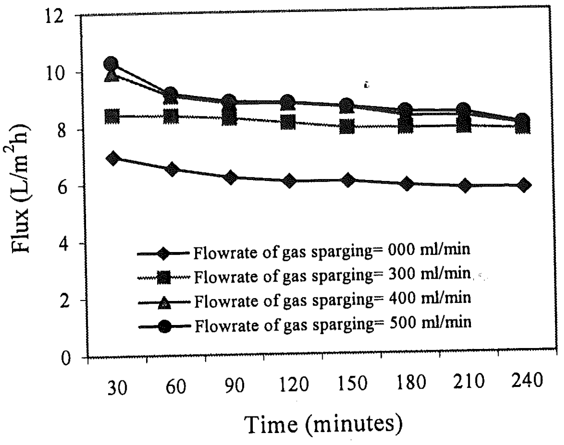


Figure 2. A typical graph showing variation of permeate flux with time at different flowrates of gas sparging and a feed flowrate of 1400ml/min and TMP of 13.00 psig.

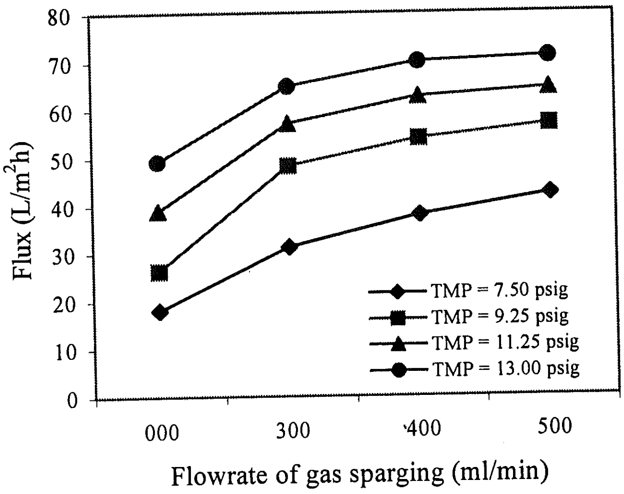


Figure 3. A typical graph showing the effect of gas sparging flowrate on total permeate flux at feed flowrate of 1400ml/min and different TMP.

usually reversible. From both figures it is shown that the use of gas sparging technique can enhance permeate flux. During gas sparged condition, the cake layer formation on the membrane surface was disrupted, leading to some of cthe ell debris or foulant to be swept away from the membrane surface.

The use of gas sparging technique also promotes turbulence in the feed stream thus reducing cake layer formation on the membrane surface. The permeate fluxes that are obtained are also higher due to the increase in turbulence in the feed stream. The use of gas sparging technique in upward crossflow when compared with the normal or conventional crossflow under non-gas sparged operation shows increases in the total permeate flux in the range of 8.3% to 145.3%. In Figure 3 it can be seen that the highest total permeate flux was obtained at gas sparging flowrate of 500 ml/min and at transmembrane pressure of 13.00 psig. In Figure 3 it is also shown that further increase in flowrate of gas sparging did not result in further increase of total permeate flux. This probably due to flow pattern changes inside the membrane where voids start to occupy more space than the liquid, thus resulting in total permeate flux decrease.

Effect of transmembrane pressure on total permeate flux

A typical graph that shows the effect of transmembrane pressure (TMP) on total permeate flux at a constant feed flowrate using gas sparging technique is given in Figure 4. The transmembrane pressure is calculated as the average of the value before and after the membrane module minus the

pressure of permeate. The applied transmembrane pressure was varied from 7.50 psig to 13.00 psig. These results show that the total permeate fluxes increase approximately linearly with increase in transmembrane pressure and then decrease gradually.

Let us take the case of feed flowrate of 1400 ml/min as an example. Initially, from TMP of 7.50 to 9.25 psig, the increase in the total permeate flux was obtained 34.7%. When TMP was increased from 9.25 to 11.25 psig, increase in the total permeate flux is 13.2%. Further increase in TMP from 11.25 to 13.00 psig, resulted in the total permeate flux of 10.1%. This shows that higher transmembrane pressure resulted in higher total permeate flux and then further increase in transmembrane pressure the total permeate flux decline gradually. Eventually, a limiting permeate flux was reached where any further increase in transmembrane pressure no longer resulted in further increase in permeate flux. This is probably due to the cake layer or deposited layer on the membrane surface becoming more compact thus resulting in higher resistance towards permeate flow.

Effect of the feed flowrate on total permeate flux

A typical graph showing the effect of feed flowrate at a constant flowrate of gas sparging (500 ml/min) on total permeate flux at different transmembrane pressure for 240 minutes is given in Figure 5. The figure generally showed a linear increase in total permeate flux with an increase in feed flowrate. However there was a sudden sharp decrease at a feed flowrate of 1600 ml/min. This phenomena was probably due to reduction in the driving force acting on permeable solution causing the concentration of rejected solute on the membrane surface being higher than that in the bulk solution.

This is the so-called concentration polarization phenomenon, which results in fouling and solute adsorption on the membrane as well as a flux decline. As a consequence, less solution can pass through membrane and the rest remains as retentate. The figure also shows the maximum total permeate flux occured at feed flowrate of 1400 ml/min.

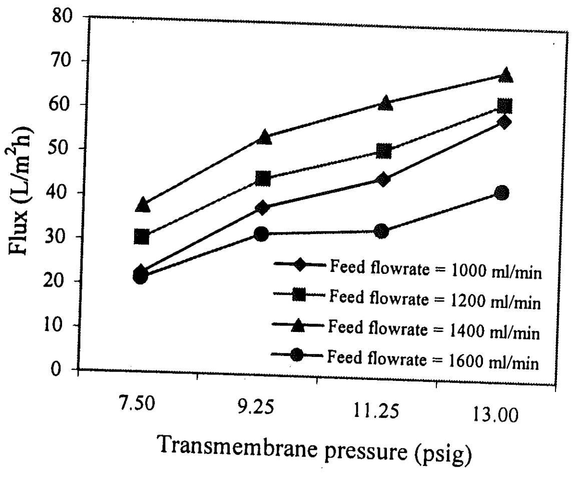


Figure 4. **A typical graph showing effect of transmembrane pressure on total permeates flux at feed flowrate of 1400 ml/min for 240 minutes.**

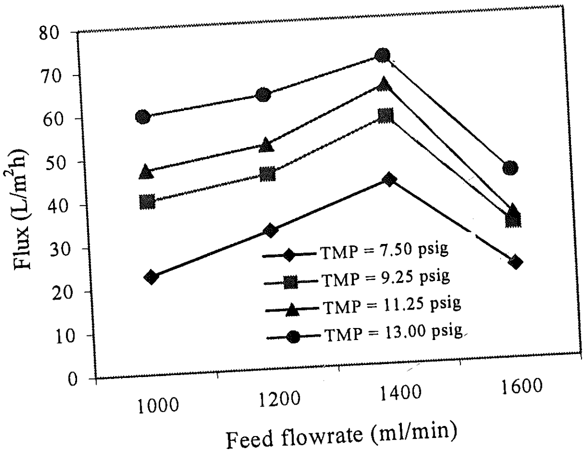


Figure 5. A typical graph showing effect of feed flowrate on total permeate flux at all TMP for 240 minutes under gas sparging condition.

Cake layer resistance

A typical graph showing the effect of different flowrate of gas sparging on cake layer resistance at a constant feed flowrate and at transmembrane pressure of 13 psig for 240 minutes is given in Figure 6. It can be seen that, increase in flowrate of gas sparging can reduce cake layer resistance. Reduction of cake layer resistance due to cake layer formation on membrane surface small that caused by some of cake layer on membrane surface had swept away. For non-gas sparging condition the cake resistance is high. However when the gas is injected into the feed stream, it disrupts concentration polarization and causes increased turbulence in feed stream thus sweeping away foulant into the retentate. Images of cake layer formation that was taken using scanning electron microscope (SEM) can be seen in Figure 7a and Figure 7b respectively. From the images, the cake layer that was formed on membrane surface under non-gas sparged condition was more distinct than under gas sparged condition.

Development of cake layer on membrane surface with time increases with cake layer resistance. Cake layer resistance increases with time as the retained particles accumulate on and within the membrane. Deposition and adsorption of small particles or macromolecules formed as internal fouling are usually irreversible. Flux decline in membrane filtration is a result of the increase in the membrane resistance due to the development of these additional resistances.

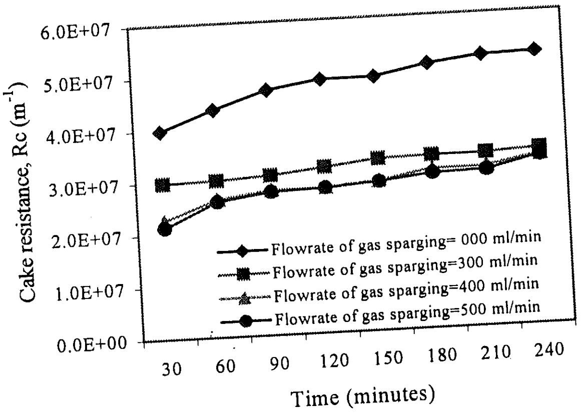
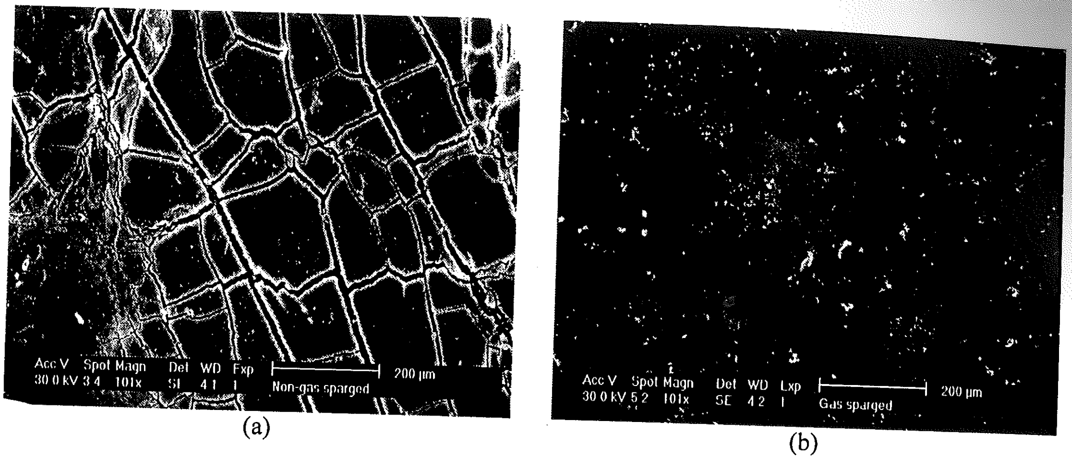


Figure 6. A typical graph showing effect of gas sparging on cake layer resistance at feed flowrate of 1400 ml/min and transmembrane pressure of 13 psig.



(a) (b)

Figure 7. SEM photograph of PVDF membrane after crossflow ultrafiltration of skim latex serum at feed flowrate of 1400 ml/min and transmembrane of 13 psig (a) under non-gas sparging condition and (b) under gas sparging condition.

CONCLUSIONS

In this work, the potential of ultrafiltration using gas sparging technique on permeate flux of natural rubber processing effluent was investigated and the following conclusions could be drawn:

1. Reductions achieved for permeate quality using gas sparged condition for total solids, COD, BOD, total nitrogen and NH_4-N were 95%, 67%, 77%, 51%, 74% respectively.
2. Reductions achieved for permeate quality for non-gas sparged condition for total solids, COD, BOD, total nitrogen and NH_4-N were 96%, 67%, 72%, 60%, 75% respectively.
3. Using gas sparing technique, the homogeneous liquid phase was changed to heterogeneous gas-liquid phase.
4. The technique of gas injection into the feed stream was found to effective in enhancing permeate flux and also it can last logger in usage of membrane.
5. Gas injection technique when compared with non-gas injection technique results in permeate flux increases in range 8.3% and 145.3%.
6. In this work the recommended optimal conditions under gas sparged condition are 500 ml/min, feed flowrate 1400 ml/min and transmembrane pressure 13.00 psig.

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