MEMBRANE TE[illegible] HARVESTING FOR

by

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TEKNOLOGI MEMBRAN DALAM PEROLEHAN MIKROALGA UNTUK PENGHASILAN BIOBAHAN API

ABSTRAK

Mikroalga telah muncul sebagai salah satu alternatif yang menjanjikan sumber lipid untuk digunakan dalam penghasilan biodiesel kerana kadar pertumbuhan dan pengeluaran yang tinggi untuk menghasilkan biojisim berbanding penjanaan lain bahan suapan biodiesel. Dalam kajian ini, *Chlorella vulgaris* telah dipilih sebagai model mikroalga. Isu yang paling penting yang perlu ditangani adalah proses perolehan biojisim *Chlorella vulgaris* yang ketara lebih mahal daripada pengkulturan alga. Oleh itu, perolehan *Chlorella vulgaris* merupakan penyelidikan yang penting dalam usaha untuk membangunkan proses yang sesuai dan ekonomi untuk spesies mikroalga supaya penghasilan biodiesel ini berdaya saing. Kajian terperinci mengenai keberkesanan penurasan membran untuk pemisahan biojisim *Chlorella vulgaris* daripada media kultur telah dijalankan. Asetat selulosa membran hidrofilik dengan diameter liang 1.2 μm mempamerkan prestasi terbaik di antara empat membrane yang diuji (nitrat selulosa, polipropilena dan polivinildiflorida) dari segi fluks penelapan. Keadaan-keadaan optimum yang dicapai adalah 1.5 bar tekanan transmembran (TMP) dan 0.4 ms^{-1} halaju aliran silang (CFV). Tambahan pula, 0.75% natrium hipoklorida (NaOCl) pada 60 °C telah dijalankan sebagai proses pembersihan membran. Ketebalan pengutuban kepekatan (CP) telah didapati sangat bergantung kepada caj permukaan membran dan bilangan kitaran pembersihan membran. Perkaitan mikroalga-membran telah berjaya dicapai melalui pendekatan XDLVO. Akhir sekali, kaedah mikropenurasan telah dibandingkan dengan kaedah pengemparan dan pengentalan untuk menentukan kaedah yang paling berkesan untuk

memisahkan biojisim *Chlorella vulgaris* daripada media kultur. Antara tiga kaedah-kaedah perolehan yang dinyatakan dalam kajian ini, didapati bahawa membran mikropenurasan adalah proses perolehan yang lebih berkesan kerana ia membolehkan pengendalian kultur dengan jumlah yang besar pada kos tenaga yang rendah. Profil asid lemak (FAME) yang sama telah diperolehi bagi semua kaedah perolehan, yang menunjukkan bahawa komponen utama adalah asid palmitik (C16:0), asid oleik (C18:1) dan asid linoleik (C18:2). Walau bagaimanapun, jumlah individu bagi FAME adalah lebih tinggi untuk mikropenurasan berbanding pengemparan dan pengentalan; pengentalan adalah yang paling teruk dalam hal ini dengan menghasilkan jumlah FAME yang paling rendah (41.61 ± 6.49 mg/g dw). FAME tak tepu (C16:1, C18:1, C18:2, C18:3) mendominasi dalam FAME profil (>70%) untuk semua kaedah perolehan yang digunakan dan dengan itu menjadikan biojisim *Chlorella vulgaris* adalah spesis yang baik untuk penghasilan biodiesel.

MEMBRANE TECHNOLOGY IN MICROALGAE HARVESTING FOR BIOFUEL PRODUCTION

ABSTRACT

Microalga has emerged as one of the most promising alternatives sources of lipid for use in biodiesel production because of their high growth rates and productivity to produce biomass compared to other generations of biodiesel feedstocks. In this study, *Chlorella vulgaris* was selected as the model microalga. The most important issue to be addressed is the recovery process of *Chlorella vulgaris* biomass that can be substantially more expensive than the culturing of the microalgae. Therefore, *Chlorella vulgaris* harvesting is an important research area in order to develop an appropriate and economical process for microalgae species so that the production of this biodiesel is competitive. Detailed studies on the effectiveness of membrane filtration for the separation of *Chlorella vulgaris* biomass from the culture medium had been carried out. The hydrophilic cellulose acetate membrane with pore diameter of 1.2 µm exhibited the best performances among four membranes tested (cellulose nitrate, polypropylene and polyvinylidenefluoride) in terms of permeation flux. The optimal conditions achieved were 1.5 bar of transmembrane pressure (TMP) and 0.4 ms^{-1} of crossflow velocity (CFV). In addition, 0.75% sodium hypochloride (NaOCl) at 60 °C was performed as the membrane cleaning process. The concentration polarization (CP) thickness was found to be strongly depended on the membrane surface charge and the number of membrane cleaning cycles. The microalgae-membrane interaction was successfully achieved by XDLVO approach. Finally, the microfiltration method was compared with centrifugation and coagulation method to determine the most efficient method for separating *Chlorella vulgaris* biomass from the culture medium. Of the three

harvesting methods described in this work, it was found that the membrane microfiltration was more effective in harvesting process because it allowed the handling of large volumes of culture at a low energy costs. Similar fatty acid (FAME) profiles were obtained for all of the harvesting methods, indicating that the main components were palmitic acid (C16:0), oleic acid (C18:1) and linoleic acid (C18:2). However, the amounts of the individual FAME were higher for microfiltration than for centrifugation and coagulation; coagulation performed the most poorly in this regard by producing the smallest amount of FAME (41.61 ± 6.49 mg/g dw). The unsaturated FAME (C16:1, C18:1, C18:2, C18:3) were predominant in the FAME profile (>70%) for all harvesting methods applied and thus making *Chlorella vulgaris* biomass a good species for biodiesel production.

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LIST OF ABBREVIATIONS

AB	Acid-base interactions
BBM	Bold's Basal Medium
CA	Cellulose acetate
CD	Convection-Diffusion
CDE	Convection-Diffusion-Electrophoretic
CFF	Crossflow filtration
CFV	Crossflow velocity
C-K	Carman-Kozeny
CN	Cellulose nitrate
CO_2	Carbon dioxide
CP	Concentration polarization
CPO	Crude palm oil
DI	Deionized
DLVO	Derjaguin-Landau-Verwey-Overbeek
DW	Distilled water
EOM	Extracellular organic matter
EPA	Eicosapentaenoic acid
EPS	Extracellular polysaccharide
ES	Electrostatic repulsion
FAME	Fatty acid methyl ester
ME	Mixed ester
MF	Microfiltration
MPOB	Malaysian Palm Oil Board
NOM	Natural organic matter
PAC	Polyaluminum chloride
PC	Polycarbonate
PES	Polyethersulfone
POME	Palm Oil Mill Effluent
PP	Polypropylene
PVC	Polyvinylchloride
PVDF	Polyvinylidenefluoride

SEM	Scanning electron microscope
SFA	Saturated fatty acid
SMP	Soluble microbial products
sp.	species
TMP	Transmembrane pressure
UF	Ultrafiltration
UFA	Unsaturated fatty acid
vdW	van-der-Waals interaction
XDLVO	Extended DLVO

LIST OF SYMBOLS

Symbol	Description	Unit
A	Effective Hamaker constant	-
A_e	Effective surface area of the membrane	m^2
A_r	Arrhenius constant	s^{-1}
a_c	Radius of the colloid (microalgae)	m
C_b	Concentration in bulk, $x = 0$	g/ℓ
C_f	Feed concentration	g/ℓ
C_i	Concentration of solute	g/ℓ
C_p	Concentration of solute in permeate	g/ℓ
C_w	Concentration at the membrane wall, $x = d$	g/ℓ
D	Diffusivity of the charged solute	m^2/s
D_f	Fractal dimension	-
d	Thickness of the CP layer	nm
d_m	Mean pore size of membrane	m
d_p	Mean particle size of the layer	m
Ea	Activation energy	kJ/mol
E_c	Energy barrier for cleaning	kcal/mol
F	Faraday constant, 96,500	C/mol
f	Frictional coefficient	-
h	Surface-to-surface separation distance	m
$h(t)$	Layer height	m
I	Ionic strength	mol/ℓ
J	Permeability	m/s
J_d	Flux decline	$ℓ/h.m^2$
J_i	Initial flux	$ℓ/h.m^2$
J_p	Permeate flux	$ℓ/h.m^2$
J_r	Flux recovery	$ℓ/h.m^2$
J_s	Flux of the microalgal suspension at steady state	$ℓ/h.m^2$
J_{w0}	Initial pure water flux	$ℓ/h.m^2$
J_{w1}	Final water flux before removing the cake layer	$ℓ/h.m^2$
J_{w2}	Final water flux after removing the cake layer	$ℓ/h.m^2$
J_{wc}	Final water flux through the cleaned membrane	$ℓ/h.m^2$

K	Equilibrium constant	-
k_b	Boltzmann's constant, 1.38×10^{-23}	J/K
k_0	Cleaning rate constant	-
L	Thickness of membrane	mm
MW	Molecular weight	g/mol
N_A	Avogadro's number, 6.022×10^{23}	mol^{-1}
P_{in}	Inlet pressure	bar
P_{out}	Outlet pressure	bar
P_{perm}	Permeate pressure	bar
R	Universal gas constant	J/mol.K
R_a	Roughness	µm
R_b	Resistance caused by pore blocking	m^{-1}
R_c	Resistance of the cake layer	m^{-1}
R_{cp}	Resistance caused by concentration polarization	m^{-1}
R_m	Intrinsic resistance of the membrane	m^{-1}
R_{m*}	Membrane resistance in modeling part	m^{-1}
R_{max}	Maximum fouling resistance	m^{-1}
R_{mb}	Membrane resistance after blocking	m^{-1}
R_s	Residue resistance at a given t_c	m^{-1}
R_{st}	Stokes radius of solute molecular	m
R_T	Total filtration resistance	m^{-1}
r_a	Aggregate radius	m
r_p	Primary particle radius	m
r_L	Specific cake resistance	m^{-2}
T_c	Cleaning temperature	°C
T	Temperature	K
t	Time of extraction	min
t_c	Cleaning time	min
U	Total interaction energy between membrane and particle	J
x	Distance from the bulk to the membrane	m
Y	Oil extraction yield	%
Y_T	Percent oil yield at temperature T	%
Y_u	percent unextracted oil	%
y_0	Minimum separation distance between the two surfaces	m

z_i	Valence of the ion *i*	-

Greek letters

ΔG	Free energy of adhesion	mJ/m^2
ΔH	Enthalpy change	kJ/mol
ΔS	Entropy change	1/mol.K
Δt	Time period	s
ΔV	Permeate volume	mℓ
α	Specific resistance of the layer	m^{-2}
α_m	Specific membrane resistance before blocking	m^{-2}
α_{mb}	Specific membrane resistance after blocking	m^{-2}
ρ	Density of microalgae	$cell/m^3$
ψ	Electric potential of the charged surface	mV
μ	Viscosity	kg/m.s
μ_i	Electrophoretic mobility of the charged solute	$m^2/V.s$
ζ	Zeta potential of the fouled surface	mV
ζ_c	Zeta potential of the colloid	mV
ζ_m	Zeta potential of the membrane	mV
κ	Reciprocal of the Debye length at 25°C	s^{-1}
ε	Porosity of the layer	-
ε_a	Aggregate porosity	-
ε_m	Porosity of the membrane before blocking	-
ε_{mb}	Porosity of the membrane after blocking	-
$\varepsilon_r\varepsilon_0$	Dielectric permittivity of the fluid	-
ε_t	Overall cake porosity	-
λ	Correlation length for molecules in aqueous systems	m
γ	surface energy	mJ/m^2
χ_{mean}	Mean particle size deposited on the cake layer at a specific height	m