MODELING, SIMULATION AND DESIGN OF MEMBRANE BASED PALM OIL MILL EFFLUENT (POME) TREATMENT PLANT FROM PILOT PLANT STUDIES

CHONG MEI FONG

UNIVERSITI SAINS MALAYSIA

2007

MODELING, SIMULATION AND DESIGN OF MEMBRANE BASED PALM OIL MILL EFFLUENT (POME) TREATMENT PLANT FROM PILOT PLANT STUDIES

by

CHONG MEI FONG

Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy

February 2007

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my beloved husband Mr. Chong Kin Yuen for his endless love, understanding, prayers and patience that supported me through the whole course of study. I would like to express my special appreciation to my parents, Mr. Chong Chew Yee and Mrs. Choo Chau Meng as well as my wonderful siblings, my brother and sisters.

I wish to express my sincere gratitude and appreciation to my main supervisor Prof. Abdul Latif Ahmad who provided an enthusiastic, motivating and critical atmosphere during the course of my study. I would like to express my genuine appreciation to my most respectful co-supervisor, Prof. Subhash Bhatia for his inspiration and enthusiasm throughout this research work. It was a great pleasure to me to conduct this research under his constructive comments.

I am very much indebted to Yayasan Felda for their financial assistance in supporting this project and to the Ministry of Science, Technology and Innovation for granting me the PASCA scholarship. My special acknowledgment to the Dean and Deputy Dean, School of Chemical Engineering for their continuous support on post-graduate affairs. The greatest appreciation goes to all the technicians in the laboratories and the staff of the School of Chemical Engineering for their full cooperation, especially Mr. Nur Najib and Mr. Aziz. The merit also goes to Mr. Raja and Mr. Chua of United Oil Palm Sdn. Bhd. for their warm cooperation and assistance in providing me the POME samples.

I would like to express my special appreciation and sincere salutation to my closest friends Ms. Ong Ai Lien and Mr. Lau Kok Keong for their support, inspiration, understanding and encouragement. Deepest appreciation also goes to Dr. Ooi Boon Seng, Dr. Suzylawati, Dr. Ali Akbar, Dr. Habibollah Younesi, Mr. Derek Chan, Mr. Chai Siang Piao, Ms. Wong Cheng Teng, Ms. Sim Jia Huey, Ms. Leo Choe Peng, Ms. Chan Choi Yee, Ms. Loh Siew Chun, Ms. Tan Lian See, Ms. Ivy Tan, Ms. Minoo Tasbihi and all the postgraduate students.

Finally but definitely not the least, I also wish to express my appreciation to countless individuals who have contributed directly or indirectly towards accomplishment of my research work.

Chong Mei Fong

February 2007

TABLE OF CONTENTS

Page

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

A	area	[m^2]
ACC	annualized capital cost	[RM/yr]
$A_{channel}$	area of membrane channel per module	[m^2]
$A_{H_2SO_4}$	volume of H_2SO_4 titrated for sample	[mL]
A_p, A_m, A_s	Hamaker constant of the solids, solvent and polymer respectively	[J]
ARR_{GAC}	annual replacement rate for GAC	[RM/yr]
ARR_{memb}	annual replacement rate for membrane	[RM/yr]
A_t	total membrane area	[m^2]
a	osmotic constant	[m^3.Pa/g]
a_m	effective monomer size	[nm]
B	ball constant	[$(m/s)^2$]
$B_{H_2SO_4}$	volume of H_2SO_4 titrated for blank	[mL]
$BOD_{insoluble}$	insoluble BOD	[mg/L]
$BOD_{soluble}$	soluble BOD	[mg/L]
BOD_{total}	total BOD	[mg/L]
b_{BOD}	coefficient of Eq. (3.4)	[dimensionless]
b_i	coefficient of Eq. (3.3)	[dimensionless]
$b_{O\&G}$	coefficient of Eq. (3.2)	[dimensionless]
b_R	fitting parameter in Eq. (3.14)	[dimensionless]
b_{ss}	coefficient of Eq. (3.1)	[dimensionless]
C	specific wet cake scrolling rate	[m^2s]
C	concentration	[kg/m^3]
C_b	bulk feed concentration	[kg/m^3]
C_{bi}	solute bulk feed concentration	[kg/m^3]
C_{bi_o}	initial solute bulk feed concentration	[kg/m^3]
$COD_{insoluble}$	insoluble COD, mg/L	[mg/L]
$COD_{soluble}$	soluble COD, mg/L	[mg/L]
COD_{total}	total COD, mg/L	[mg/L]
C_{chem}	chemical cost	[RM]
C_{CIP}	cost of Clean In Place (CIP) or back-flush for the membrane system	[RM]
$C_{cleaning}$	chemical cleaning cost	[RM]
$C_{control}$	control & automation cost	[RM]

C_{e_i}	equilibrium liquid phase concentration of solute	[mg/L]
C_{elec}	electrical cost	[RM]
C_{equip}	total equipment cost	[RM]
C_{Fert}	profit generated via fertilizer sale	[RM]
C_{fi}	solute feed concentration	[mg/L]
C_{flocs}	flocs' solid concentration in the dry basis	[m^{-3}]
C_{frame}	framework cost	[RM]
C_{GAC}	activated carbon granular replacement cost	[RM/yr]
C_g	concentration in the gel layer	[kg/m^3]
C_i	solute concentration	[kg/m^3]
$\overline{C_i}$	average value of solute bulk feed and permeate concentration	[kg/m^3]
C_i^0	initial liquid phase concentration of solute	[mg/L]
C_L	aggregate structure prefactor	[dimensionless]
C_{labor}	labor cost	[RM]
$C_{ma\,\mathrm{int}\,enance}$	maintenance cost	[RM/yr]
$C_{material}$	material cost	[RM]
C_{memb}	membrane replacement cost	[RM/yr]
C_p	permeate concentration	[kg/m^3]
C_p	specific heat capacity	[J/kg^{o}C]
C_{pi}	solute permeate concentration	[kg/m^3]
$C_{piping\ \&\ valves}$	piping, valves & fittings cost	[RM]
$C_{O\&G}$	oil and grease concentration	[mg/L]
$C_{operating}$	total operating cost	[RM/yr]
CRF	capital recovery factor	[dimensionless]
C_{si}	equilibrium concentration of solute	[mg/L]
C_{ss}	suspended solids concentration	[mg/L]
$C_{ss,F}$	suspended solids concentration in the filtrate	[mg/L]
$C_{ss,S}$	suspended solids concentration in the supernatant	[mg/L]
C_{total}	total cost	[RM]
C_{wi}	solute wall concentration	[kg/m^3]
C_1	base cost of reference equipment	[RM/unit]
C_2	equipment cost	[RM/unit]

c_{chem}	unit cost for polymers	[RM/kg]
c_{elec}	electricity rate	[RM/kwh]
c_{Fert}	unit selling price for fertilizer	[RM/kg]
c_{GAC}	unit cost for activated carbon granular	[RM/kg]
c_{HNO_3}	unit cost for nitric acid	[RM/kg]
c_{memb}	unit cost of membrane	[RM/m^2]
c_{NaOH}	unit cost for sodium hydroxide	[RM/kg]
c_{total}	total treatment cost per cubic meter	[RM/m^3]
D	impeller diameter	[m]
D_{bi}	solute diffusivity in the concentration polarization layer	[m^2/s]
DCC	direct capital cost	[RM]
D_{si}	surface diffusivity coefficient of solute	[m^2/s]
D_{sc}	scaling length	[nm]
D_{vi}	molecular diffusion coefficient of the solute	[m^2/s]
d	inner diameter of membrane tube	[m]
d_a	agitator diameter	[m]
d_{am}	arithmetic mean floc diameter	[µm]
d_F	fractal dimension	[dimensionless]
d_h	hydraulic diameter	[m]
$\overline{d_i}$	arithmetic mean diameter of flocs in size class i	[µm]
d_p	particle diameter	[m]
$\overline{d_{pi}}$	average particle size for each pair of consecutive sieves	[µm]
d_s	polymer dosage	[mg/L]
d_t	diameter of the tank	[m]
E_f	fluid collection efficiency of an aggregate, dimensionless	[dimensionless]
e	elementary charge	[Columb]
F	Driving forces	[kWs/m.mole]
F_T	correction factor	[dimensionless]
G	global average fluid velocity gradient or shear rate	[s^{-1}]
g	earth gravity	[m/s]
H	effective filtration thickness	[m]
$H_{(x,y)}$	unretarded geometric functions	[dimensionless]
h	tank height	[m]

h_o	minimum separation distance between particle surfaces	[nm]
ICC	indirect capital cost	[RM]
i	interest rate	[%]
J_i	flux of solute	[kg/m^2.s]
J_v	volumetric flux of permeate	[m^3/m^2.s]
$J_{v,ss}$	volumetric flux at steady-state	[m^3/m^{2}s]
J_w	flux of solvent	[m^3/m^2.s]
$J_{v,ss}$	volume flux of permeate at the steady-state condition	[m^3/m^2.s]
K	Debye-Hückel parameter	[J/m^{3}C]
K_B	Boltzmann constant	[J/K]
K_b	total back transport coefficient	[m^2]
K_i	Freundlich capacity parameter	[(mg/g)/(mg/L)$^{1/n}$]
k	mass transport coefficient	[m/s]
k_{avg}	sludge average permeability constant	[m^2]
k_{fi}	external mass transfer coefficient of solute	[m/s]
L	effective compacting bowl length	[m]
L	bed length	[m]
L	phenomenological coefficient	[dimensionless]
L_B	length of used bed	[m]
L_C	clarification length	[m]
L_{jj}	straight phenomenological coefficient	[dimensionless]
L_{jk}	cross phenomenological coefficient	[dimensionless]
L_p	hydraulic permeability constant	[m/Pa.s]
$\overline{L_p}$	specific hydraulic permeability constant	[m/Pa.m.s]
l	membrane thickness	[m]
M_{bt}	total back transport mass up to time t	[kg]
m	mass fluid flow	[kg/s]
m	solute molar mass	[g/mol]
m_C	mass flow rate of the centrate	[kg/s]
m_F	mass flow rate of the feed slurry	[kg/s]
m_{Fert}	mass flow rate of fertilizer	[kg/s]
m_{HNO_3}	mass of acid needed per small module for membrane cleaning	[kg/module]
m_i	solute molar mass	[g/mol]
m_i	salt concentration	[mol/m^3]

m_{NaOH}	mass of caustic needed per small module for membrane cleaning	[kg/module]
m_{poly}	mass of polymers needed per day	[kg/day]
m_S	mass flow rate of dry sludge or cake	[kg/s]
N	rotational speed	[rpm]
N_{AV}	Avogadro's number	[mol^{-1}]
$N_{cleaning}$	number of membrane cleaning cycle per year	[yr^{-1}]
N_i	number concentration of particles or aggregates in section i	[m^{-3}]
$N_{memb,yr}$	membrane life	[yr]
N_p	number of pressure vessels/modules connected in parallel	[dimensionless]
N_p	power number of agitator	[dimensionless]
N_s	number of small module connected in series	[dimensionless]
N_{yr}	plant life	[yr]
N_1	reference agitator speed	[rev/s]
N_2	agitator speed	[rev/s]
n	number of membrane tube inside the small membrane module	[dimensionless]
n	number concentration of particles or aggregates	[m^{-3}]
Δn	conveyor differential speed	[1/s]
$1/n_i$	Freundlich intensity parameter	[dimensionless]
n_m	motor efficiency	[dimensionless]
n_p	pump efficiency	[dimensionless]
n_x	number of tank	[dimensionless]
n_y	number of batch of polymer solution prepared in a tank per day	[day^{-1}]
P	pressure	[Pa]
$\overline{P}$	local solute permeability constant	[m/m.s]
ΔP	trans membrane pressure	[bar]
P_{ap}	atmospheric pressure	[bar]
$P_{agitator}$	power needed for the agitator	[W]
ΔP_c	pressure drop across the gel layer	[bar]
P_{ij}, P_{ii}	solute permeability constant	[m/s]
P_{in}	inlet pressure	[bar]
P_m	permeability coefficient	[m^2]
P_{out}	outlet pressure	[bar]

P_{pump}	power of the pump	[W]
Q	volumetric flow rate	[m^3/s]
Q_C	volume flow rate of centrate	[m^3/s]
Q_F	volume flow rate of feed	[m^3/s]
Q_L	radial liquid flow	[m^3/s]
Q_p	permeate flow rate	[m^3/s]
q, η	constant in Eq. (3.61)	[dimensionless]
q_{e_i}	solid phase surface loading of solute at equilibrium	[mg/g]
q_i	solid phase loading of solute on the GAC particle	[mg/g]
q_i^0	solid phase surface loading corresponding to C_i^0	[mg/g]
q_T	total mass of adsorbate	[mg/g]
q_1	reference equipment capacity/size	[m^3 or m^2]
q_2	equipment capacity/size	[m^3 or m^2]
R	true rejection	[dimensionless]
R	particle radius	[m]
R^2	coefficient of determination	[dimensionless]
R_a	scale up ratio	[dimensionless]
R_{COD}	COD removal	[dimensionless]
Re	Reynolds number	[dimensionless]
$R_{F/S}$	ratio of suspended solids concentration in the filtrate to the supernatant	[dimensionless]
R_g	ideal gas constant	[8.314 m^3.Pa/mol.K]
R_g	gel layer resistance	[m^{-1}]
R_H	hydraulic resistance	[m^{-1}]
R_i	intrinsic rejection of the solute	[dimensionless]
R_m	resistances due to the membrane	[m^{-1}]
R_o	observed rejection	[dimensionless]
R_s	solids recovery	[%]
r	water recovery	[%]
r	radial axis of GAC particle	[m]
$\bar{r}$	mass mean aggregate radius	[µm]
r_{ci}, r_{cj}	floc collision radius	[µm]
r_{d_a/d_t}	geometric proportion of tank diameter to agitator diameter	[dimensionless]
r_i	particle radius at size class i	[µm]

r_o	composite radius of a particle with adsorbed polymer layers	[µm]
r_{oi}, r_{oj}	primary particles radii	[µm]
r_t	total water recovery	[%]
r_1	bowl radius	[m]
r_2	pond surface radius	[m]
S	specific rate constant of fragmentation	[s^{-1}]
S_{ci}	Schmidt number of the solute	[dimensionless]
Sh_i	Sherwood number of the solute	[dimensionless]
s	distance between particles centers	[nm]
T	temperature	[^oC]
TCC	total capital cost	[RM]
T_{ci}	cold fluid inlet temperature	[^oC]
T_{co}	cold fluid outlet temperature	[^oC]
T_{hi}	hot fluid inlet temperature	[^oC]
T_{ho}	hot fluid outlet temperature	[^oC]
ΔT_{lm}	log mean temperature difference	[^oC]
ΔT_m	corrected mean temperature difference	[^oC]
t	time	[s]
t_b	break-point time	[s]
t_d	saturation time	[s]
t_d	number of working days per year	[day/yr]
t_h	total operation hour per day	[hr/day]
t_t	time equivalent to the total capacity of the bed	[s]
t_u	time equivalent to the usable capacity of the bed up to the break-point time	[s]
U	overall heat-transfer coefficient	[J/ ^oC m^2]
U	superficial velocity	[m/s]
V	tank volume	[m^3]
$\overline{V}$	partial molar volume	[m^3/mol]
V_{Ai}	molar volume of the solute	[m^3/kmol]
V_{base}	volume of reference tank	[m^3]
V_{column}	volume of GAC column	[m^3]
V_{GAC}	volume of the activated carbon granular	[m^3]
V_{poly}	volume of polymer solutions required per day	[m^3/day]
V_s	influent water approach velocity	[m/s]

V_g	total volume of gel layer up to time t	[m^3]
V_p	total volume of permeate up to time t	[m^3]
V	volume of the suspension	[J]
V_T	net interaction energy between two primary particles	[J]
V_{edl}	electrical double layer repulsion	[J]
V_s	energy of steric repulsion or bridging attraction	[J]
V_{vdw}	Van der Waals energy	[J]
v	superficial velocity	[m/s]
v	cross-flow velocity	[m/s]
v	kinematic viscosity	[m^2/s]
v, u	particle or aggregate volumes	[m^3]
x	coordinate perpendicular to the membrane	[dimensionless]
x^*	dimensionless boundary layer thickness	[dimensionless]
x_C	solids concentration of the centrate in weight basis	[kg/kg]
x_F	solids concentration of the feed slurry in weight basis	[kg/kg]
Δx_i	increment of weight fraction in each pair	[dimensionless]
x_S	solids concentration of dry sludge or cake in weight basis	[kg/kg]
x_W	moisture content	[kg/kg]
Z_i	mass fraction of solute	[dimensionless]
z	gel layer thickness	[m]
z	coordinate along the longitudinal bed axis	[m]
z_c	valence of counter ions	[dimensionless]
z_i	valence of electrolyte ions	[dimensionless]

Greek Letters

τ	residence time	[s]
δ	adsorbed polymer layer thickness	[nm]
δ_{pol}	thickness of concentration polarization layer	[m]
ρ	suspension density	[kg/m^3]
ρ_b	density of the ball	[kg/m^3]
ρ_{cake}	cake density	[kg/m^3]
ρ_L	liquid density	[kg/m^3]
ρ_l	density of the fluid at the measuring temperature	[kg/m^3]
ρ_p	particle density	[kg/m^3]
ρ_w	density of water	[kg/m^3]

α	collision efficiency factor	[dimensionless]
α_{Sc}	numerical constant	[dimensionless]
η	absolute liquid viscosity	[Pa.s]
φ	conveyor speed	[1/s]
ω	angular velocity of bowl	[1/s]
ε	porosity of the GAC bed	[dimensionless]
$\bar{\varepsilon}$	average turbulent energy dissipation rate	[m^2/s^3]
ε_o , ε_r	dielectric constant of a vacuum and the solvent	[C/mV]
ζ	exponent	[dimensionless]
γ	activity coefficeint	[dimensionless]
γ	breakage distribution function	[dimensionless]
σ	reflection coefficient	[dimensionless]
σ_i	reflection coefficient	[dimensionless]
ϕ	osmotic function	[dimensionless]
π	osmotic pressure	[Pa]
π	spreading pressure	[N/m]
$\Delta\pi$	osmotic pressure difference across the membrane	[bar]
π_i^0	spreading pressure of the solute at equilibrium	[N/m]
μ	viscosity	[Pa.s]
μ	chemical potential	[J/mol]
μ_w	viscosity of water	[Pa.s]
β	collision frequency factor	[m^3/s]
υ_i	floc volume fraction in size class i	[dimensionless]
λ_R	characteristic wavelength of interaction	[nm]
ψ_{oi} , ψ_{oj}	surface potential	[mV]
Γ / Γ_o	fractional polymer surface coverage	[dimensionless]
Φ_{so}	polymer volume fraction at a single saturated surface	[dimensionless]

Subscripts

b	bulk
i	dissolved organic solutes
$i=1$	carbohydrate constituents
$i=2$	protein
$i=3$	ammoniacal nitrogen
in	inlet stream
j	membrane stage
m	total number of stage in membrane system
m	membrane wall

out	outlet stream
p	permeate
$poly$	cationic or anionic polymer
r	retentate stream
$recycle$	recycle stream
ss	suspended solids
$sys1$	first membrane system
$sys2$	second membrane system
w	water

LIST OF ABBREVIATION

ACC	Annualized Capital Cost
Ag_2SO_4	Silver Sulfate
Al	Aluminum
Alum	Aluminum Sulfate
ATH	N-Allylthiourea
BOD	Biological Oxygen Demand
Ca	Calsium
CF	Concentration Factor
CIP	Clean In Place
COD	Chemical Oxygen Demand
CPO	Crude Palm Oil
CRF	Capital Recovery Factor
CSTR	Continuous Stirred Tank Reactor
C/S	Carbon Steel
Cu	Copper
DCC	Direct Capital Cost
DLVO	Derjaguin Landau Verwey Overbeek
DOE	Department of Environment
DP	Dosing Pump
EDCs	Endocrine Disrupting Compounds
EQA	Environmental Quality Act
Fe	Iron
FELDA	Federal Land Development Authority
FFB	Fresh Fruit Bunch
FPCDSD	Film-Pore-Concentration Dependent Surface Diffusion
GAC	Granular Activated Carbon
H_3BO_3	Boric Acid
HDPE	High Density Polyethylene
$HgSO_4$	Mercuric Sulfate
HNO_3	Nitric Acid
HSDM	Homogeneous Surface Diffusion Model
H_2SO_4	Sulfuric Acid
IAST	Ideal Adsorbed Solution Theory
ICC	Indirect Capital Cost

K	Potassium
K_2Cr_2O	Potassium Dichromate
KHP	Potassium Hydrogen Phthalate
KOH	Potassium Hydroxide
LDM	Linear Driving Force Model
M	Mixer
MCL	Maximum Contaminant Level
MF	Microfiltration
Mg	Magnesium
MINLP	Mixed-Integer Nonlinear Programming
Mn	Manganese
MWCO	Molecular Weight Cut Off
$Na_2B_4O_4$	Sodium Tetraborate
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NF	Nanofiltration
NH_3-N	Ammoniacal Nitrogen
NOM	Natural Organic Matter
O_2	Oxygen
ODE	Ordinary Differential Equation
PBM	Population Balance Model
PDM	Pore Diffusion Model
PEO	Polyethylene Oxide
PFD	Process Flow Diagram
PhACs	Pharmaceutically Active Compounds
POME	Palm Oil Mill Effluent
PVDF	Polyvinylidene Diflouride
RO	Reverse Osmosis
SOCs	Synthetic Organic Chemicals
SOP	Standard Operating Procedure
SS	Stainless Steel
TCC	Total Capital Cost
TiO_2	Titanium Dioxide
TNT	Trinitrotoluene
TP	Transfer Pump
UASB	Up-flow Anaerobic Sludge Blanket

UF	Ultrafiltration
USEPA	U.S. Environment Protection Agency
V	Valve
VOCs	Volatile Organic Compounds
WR	Working Reagent
Zn	Zink

PEMODELAN, SIMULASI DAN REKABENTUK LOJI RAWATAN KUMBAHAN KILANG KELAPA SAWIT (POME) BERASASKAN MEMBRAN DARIPADA KAJIAN LOJI PANDU

ABSTRAK

Tanpa rawatan, pembuangan kumbahan kilang kelapa sawit (POME) ke persekitaran mengakibatkan masalah pencemaran yang serius dan rawatan POME berasaskan membran telah dicadangkan sebagai salah satu penyelesaiannya. Projek penyelidikan ini telah mencadangkan rekabentuk optimum bagi loji rawatan POME berasaskan membran berdasarkan data ujikaji yang diperolehi dari kajian loji pandu.

Proses pemberbukuan terus telah membuktikan bahawa polimer organik berkembar dapat menggantikan Alum dalam rawatan POME dengan kos 3.6 kali lebih rendah. Dos optimum polimer kation ialah 300 mg/L pada adukan 200 putaran per minit untuk 3 minit dan dos optimum polimer anion ialah 50 mg/L pada adukan 150 putaran per minit untuk 1 minit. Proses pemberbukuan terus menunjukkan kecekapan rawatan yang tinggi dengan penyingkiran pepejal terampai, Keperluan Oksigen Kimia (COD), minyak & gris serta perolehan semula air yang masing-masing sebanyak 99.7%, 58.0%, 99.7% dan 82.1%.

POME ialah sistem bahan terlarut berbilang dan model pengangkutan yang dibangunkan untuk sistem bahan terlarut berbilang termasuk (1) Model Pengimbangan Populasi untuk pemberbukuan terus, (2) model yang bergandingan antara Model Resapan Permukaan Homogen dengan Teori Larutan Terjerap untuk penjerapan karbon berbutir teraktif, (3) model yang bergandingan antara Analisis Pengangkutan Balik dengan Teori Penurasan untuk sistem penurasan ultra (UF) dan (4) model yang bergandingan antara Model Spiegler-Kedem Lanjutan dengan Model Pengutuban Kepekatan untuk sistem penurasan osmosis balikan (RO). Parameter untuk model-

model ini telah dinilai berdasarkan data ujikaji yang diperolehi dari kajian loji pandu. Keputusan simulasi menunjukkan persetujuan yang setara dengan data ujikaji.

Tiga rekabentuk loji rawatan POME berasaskan teknologi membran berskala industri yang berbeza telah dicadangkan melalui integrasi model-model pengangkutan berdasarkan imbangan jisim, analisis saiz dan kos alatan serta kajian pengoptimuman. Rekabentuk A, B dan C dibezakan oleh sistem penurasannya. Rekabentuk A mengandungi sistem penuras seramik UF dan penuras polimer RO manakala Rekabentuk B mengandungi sistem penuras polimer UF dan penuras polimer RO. Dalam Rekabentuk C, sistem penuras polimer RO dua-laluan telah digunakan. Dalam proses pra-rawatan, bahan enapcemar diperolehi semula sebagai baja organik dan sistem membran digunakan untuk perolehan semula dan penulenan air.

Keputusan imbangan jisim pada optimum membuktikan bahawa kualiti air yang diperolehi semula untuk semua rekabentuk mematuhi piawai pelepasan kumbahan yang dikuatkuasakan oleh Jabatan Alam Sekitar. Air terawat untuk Rekabentuk C mematuhi piawai kualiti air minuman Agensi Perlidungan Alam Sekitar, Amerika Syarikat. Analisis saiz dan kos alatan pada keadaan optimum menunjukkan bahawa jumlah kos rawatan untuk Rekabentuk A adalah yang tertinggi (RM 115.11/m^3) dan ini diikuti oleh Rekabentuk B (RM 23.64/m^3) dan Rekabentuk C (RM 7.03/m^3). Oleh itu, Rekabentuk C telah dipilih sebagai rekabentuk yang paling optimum.

Keuntungan pengendalian semetrik tan tandan buah kelapa sawit segar (FFB) yang telah diproses ialah RM 209.77. Dengan penjimatan kos melalui kitar semula air, jumlah kos rawatan untuk Rekabentuk C hanya 1.5% daripada keuntungan pengendalian (RM 3.22/tan FFB terproses). Rekabentuk loji rawatan POME berasaskan membran berskala industri yang kos effektif, boleh laksana dan menjanjikan telah dicadangkan dalam projek penyelidikan ini.

MODELING, SIMULATION AND DESIGN OF MEMBRANE BASED PALM OIL MILL EFFLUENT (POME) TREATMENT PLANT FROM PILOT PLANT STUDIES

ABSTRACT

If untreated, the discharge of Palm Oil Mill Effluent (POME) into the environment leads to serious pollution problems and the membrane based POME treatment process has been suggested as a solution. The present research proposed the membrane based POME treatment plant design based on the experimental data obtained from the pilot plant study.

The proposed direct flocculation process has proven that the organic dual polymers could replace Alum in POME treatment with 3.6 times lower cost. The optimum cationic polymer dosage was 300 mg/L at stirring of 200 rpm for 3 min and the optimum anionic polymer dosage was 50 mg/L at stirring of 150 rpm for 1 min. The direct flocculation shows high treatment efficiency with 99.7%, 58.0%, 99.7% and 82.1% of suspended solids, Chemical Oxygen Demand (COD), oil & grease removal and water recovery respectively.

POME was considered as a multiple solute system and the transport models developed for the multiple solutes system include (1) Population Balance Model for direct flocculation, (2) coupled model of Homogeneous Surface Diffusion with Adsorbed Solution Theory for granular activated carbon adsorption, (3) coupled model of Back Transport Analysis with Filtration theory for ultrafiltration (UF) membrane system and (4) coupled model of Extended Spiegler-Kedem Model with Concentration Polarization Model for reverse osmosis (RO) membrane system. The model parameters were evaluated from the experimental data obtained from the pilot plant study. The simulation results show a good agreement with the experimental data.

Three different types of designs for industrial scale membrane based POME treatment plant were proposed by the integration of the transport models via mass balance, equipment sizing, costing and optimization analysis. Designs A, B and C were distinguished by the membrane systems proposed. Design A consisted of UF ceramic membrane and RO polymeric membrane system whereas the Design B consisted of UF polymeric membrane and RO polymeric membrane system. In the Design C, two-pass RO polymeric membrane system was employed. In the pretreatment process, sludge was recovered as an organic fertilizer and the membrane system was used for the recovery and purification of water.

The mass balance results at optimum condition proved that the quality of the recovered water for all the designs met the effluent discharge standards imposed by the Department of Environment. The treated water of Design C met the drinking water quality standard of U.S. Environment Protection Agency. The sizing and costing analysis at the optimum condition show that the total treatment cost for Design A was the highest (RM 115.11/m^3), followed by Design B (RM 23.64/m^3) and Design C (RM 7.03/m^3). Therefore, the Design C was chosen as the optimal design.

The operating profit gained per ton of Fresh Fruit Bunch (FFB) processed is RM 209.77. With cost saving due to water recycling, the total treatment cost of Design C is only 1.5% of this amount (RM 3.22/ton FFB processed). A cost effective, feasible and promising industrial scale membrane based POME treatment plant design is proposed in the present research.

CHAPTER 1

INTRODUCTION

Malaysia is the largest producer and exporter of palm oil; contributing more than 50% of world production and 60% of world export (Malaysian Palm Oil Board, 2005). In year 2005, approximately 14.96 million ton of crude palm oil (CPO) were produced, that amounted to approximately 44.88 million ton of Palm Oil Mill Effluent (POME) discharged into the rivers of Malaysia (refer to Fig. 1.1). With this statistics, the palm oil industry in Malaysia is identified as the industry that produces the largest pollution load into the rivers of Malaysia (Malaysian Palm Oil Promotion Council, 2005). Therefore, a great action needs to be taken to reduce or eliminate the pollution caused by the discharge of POME into the environment in order to guarantee the sustainable development of palm oil industry in Malaysia as the world largest producer and exporter.

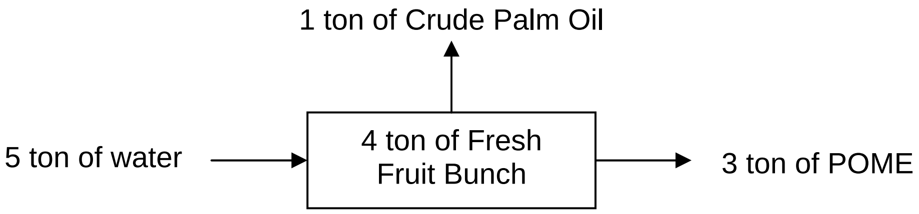

Fig. 1.1: POME generation and amount of water requirement per ton of crude palm oil produced (Ma, 1999).

1.1 Palm Oil Mill Effluent (POME)

The production of palm oil results in the generation of huge quantities of highly polluting wastewater termed as Palm Oil Mill Effluent (POME). The POME is thick brownish viscous liquid waste and is non-toxic as no chemicals are added during oil extraction but has an unpleasant odor. It is predominantly organic in nature and highly polluting (Ma, 2000). POME is a colloidal suspension of 95-96% water, 0.3-0.4% oil and 4-5% total solids including 1-2% suspended solids. The distribution of chemical constituents of POME has been determined and analyzed by several researchers (Ho *et al*., 1984; Chow, 1991; Ma, 2000) and is summarized in Table 1.1.

Table 1.1: Characteristic and distribution of chemical constituents of Palm Oil Mill Effluent (POME) (Ho *et al*., 1984; Chow, 1991; Ma, 2000).

Parameter	Mean Value	Parameter	Mean Value
pH	4.7	Protein, mg/L	16,000
Temperature, ^{o}C	85	Phosphorous, mg/L	180
Oil and grease, mg/L	4000	Potassium, mg/L	2270
Biological Oxygen Demand (BOD), mg/L	25 000	Magnesium, mg/L	615
Chemical Oxygen Demand (COD), mg/L	50 000	Calcium, mg/L	439
Total Solids, mg/L	40 500	Boron, mg/L	7.6
Suspended Solids, mg/L	18 000	Iron, mg/L	46.5
Ammoniacal nitrogen, mg/L	35	Manganese, mg/L	2.0
Total Nitrogen	750	Copper, mg/L	0.89
Carbohydrate Constituents, mg/L	10,000	Zinc, mg/L	2.3

The high content of COD and BOD in POME as shown in Table 1.1 indicate that the POME has an extremely high content of degradable organic matters, which is due in part to the presence of suspended solids, oil & grease and dissolved organic solutes of carbohydrate constituents, protein and ammoniacal nitrogen. The un-extracted oil & grease is generally contained inside the suspended solids which comprised of cell walls, organelles and short fibers. Thus, the removal of suspended solids will actually remove the oil & grease and insoluble portion of the COD and BOD simultaneously. The soluble portion of the COD and BOD are contributed by the dissolved organic solutes of carbohydrate constituents, protein and ammoniacal nitrogen. The total nitrogen includes the nitrogenous compound of protein and ammoniacal nitrogen.

From the environmental point of view, the discharge of untreated POME characterized by the extremely high content of degradable organic matters based on the characteristic as shown in Table 1.1 into the water streams or rivers will definitely lead to severe pollution to the rivers, destruction to the aquatic habitats and deterioration of ecosystem. In addition, the conventional biological POME treatment of anaerobic ponding system produces unpleasant odor of biogas which contains methane, carbon dioxide, hydrogen sulphide and other gasses (Mahabot and Harun, 1986). Thus, proper POME treatment is urgently needed to ensure the sustainable economic growth of palm oil industry in Malaysia besides protecting the environment.

1.2 Environmental Regulatory Control for POME Discharge

The government decided that the environmental control of palm oil industry warranted a licensed approach that would permit intimate control of individual factories. It also provides a mechanism for allowing variable effluent standard to be applied based on the demands of current environment circumstances. The environmental quality regulations for the crude palm oil industry were the first set of regulations promulgated under the Environmental Quality Act (EQA), 1974 for control of industrial pollution sources which is enforced by the Department of Environment, (DOE) Malaysia (Thani *et al*. 1999).

The Environmental Quality (Prescribed Premises) (Crude Palm Oil) Order 1977, prescribed factories that process oil palm fruit or oil palm fresh fruit bunches into crude oil as “Prescribed Premises” which shall require a license under Section 18 of EQA 1974 for the occupation or use of their respective premises. This order imposed few conditions for factories owners to obtain the license for factories operation that includes ensuring acceptable condition of effluent discharge, proper waste disposal and air emission control throughout the operation (Environmental Quality Act 1974, 2005).

The Environmental Quality (Prescribed Premises) (Crude Palm Oil) Regulations 1977, promulgated under the enabling powers of Section 51 of the EQA 1974, are the governing regulations and contain the effluent discharge standards. Other regulatory requirements are to be imposed on the individual palm oil mills through conditions of license. The current effluent discharge standards ordinarily applicable to crude palm oil mills are shown in Table 1.2 (Environmental Quality Act 1974, 2005).

Table 1.2: Effluent discharge standards for crude palm oil mills (Environmental Quality Act 1974, 2005)

Parameter		Parameter Limits (Second Schedule)	Remarks
Biological Oxygen Demand (BOD; 3-Day, 30°C)	mg/L	100	
Chemical Oxygen Demand (COD)	mg/L	*	
Total Solids	mg/L	*	
Suspended Solids	mg/L	400	
Oil and Grease	mg/L	50	
Ammoniacal Nitrogen	mg/L	150	Value of filtered sample
Total Nitrogen	mg/L	200	Value of filtered sample
pH	-	5 – 9	
Temperature	°C	45	

Note: *No discharge standard after 1984

1.3 Conventional Biological Treatment System for POME

The biological treatment system with emphasis on anaerobic digestion is the most conventional POME treatment system adopted in most of the palm oil mills in Malaysia. However, coping with the increasing production in most palm oil mills, the under-sized biological treatment system is unable to cope with the increased volume of POME (Ismail, 2005). The biological treatment relies on bacteria to break down the organic matters into simple end products of methane, carbon dioxide, hydrogen sulphide and water. The organic matters digestion by the bacteria requires long treatment period and thus, large treatment area is required.

The biological treatment system requires proper maintenance and monitoring as the bacteria is very sensitive to the changes in the environment. Great care needs to be taken to ensure a conducive environment for the bacteria to grow during the digestion process (Ma, 2000). Attentions from skilled operators as well as the commitment from the management are also required. Unfortunately, these issues are always ignored by the mill owners because the effluent treatment is often viewed as a burden and given the lowest priority.

Therefore, an efficient treatment system is urgently desired as an alternative to the conventional biological treatment to ensure the final discharge of the treated water is meeting the effluent discharge standards imposed by the DOE, Malaysia.

1.4 Membrane based POME Treatment Pilot Plant

Membrane separation technology is recognized as an efficient, economical and reliable technology that exhibits high potential to be applied in POME treatment (Ismail, 2005). POME contains valuable plant nutrients in substantial amount. The membrane separation technology coupled with pretreatment recovers these nutrients as fertilizer and recycle clean water to achieve zero discharge. Consequently, the treatment of POME using membrane technology will be efficient, innovative and attractive to the mill owners. In addition, the membrane technology also supports the Clean Development Mechanism (CDM) issue under the Kyoto Protocol to reduce global green house gases emission.

The investigation on the feasibility and suitability of the membrane separation technology in POME treatment is carried out in a pilot plant with the capacity of 450L/hr (Ismail, 2005). This pilot plant was designed and fabricated locally; consists of two stages of treatment. This includes series of pretreatment processes followed by the membrane separation processes. The Process Flow Diagram (PFD) of the membrane based POME treatment pilot plant is shown in Fig. 1.2. As shown from Fig. 1.2, the pretreatment processes in the pilot plant involve coagulation by using Aluminum Sulfate (Alum), flocculation by using cationic polymer (flocculent), sludge dewatering by filter press and granular activated carbon (GAC) adsorption. The membrane separation processes in the pilot plant involve ultrafiltration (UF) membrane system and reverse osmosis (RO) membrane system.

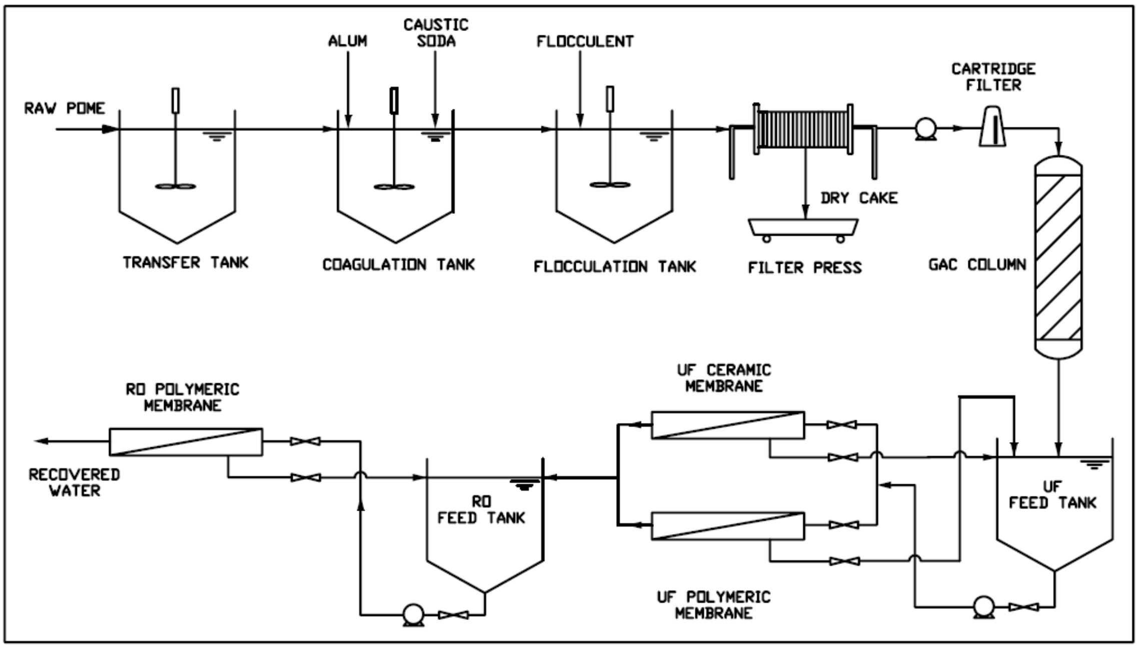

Fig. 1.2: Process Flow Diagram (PFD) for the membrane based POME treatment pilot plant

1.4.1 Coagulation and Flocculation Process

The chemical pretreatment of coagulation and flocculation is used to remove the suspended solids of POME and once the suspended solids is removed, the oil & grease, insoluble COD and BOD will be removed simultaneously. The Alum is added into the raw POME as coagulant and the suspended solids in the mixture is allowed to coagulate to form microflocs at the pH of 6.04. The pH is adjusted by using the alkaline solution of caustic soda. Alkaline solution is used in this case because both raw POME and Alum are acidic in nature. However, these microflocs are too fine to be removed by using the filter press. Therefore, long chain cationic polymer is used to chain, capture and flocculate these microflocs to form large and dense flocs suitable to be dewatered by using the filter press at high water recovery.

1.4.2 Sludge Dewatering by Using Filter Press

After the coagulation and flocculation process, the dense flocs containing captured suspended solids are termed as sludge while the remaining liquid with low suspended solids concentration is termed as supernatant. The mixture of sludge and supernatant is fed into the filter press. The filter chambers can hold a predetermined press volume and are wrapped with porous filter cloths which allow the permeation of supernatant while preventing the passage of the sludge. The applied pressure to the filter press causes the supernatant to pass through the filter cloth while the sludge remains in the chamber as cake. The filter press is operated in a batch mode as after each cycle of operation (when the chambers of the filter press are full with cake), the filter press has to be stopped so that the chambers can be emptied and cleaned. Therefore, filter press is only suitable for low capacity sludge dewatering (as used in this pilot plant) and it is not suitable for large capacity sludge dewatering with continuous mode.

1.4.3 Granular Activated Carbon (GAC) Adsorption

The pretreated POME fed into the Granular Activated Carbon (GAC) column as shown in Fig. 1.2 is the supernatant collected from the filter press unit. The GAC adsorption is used to remove the dissolved organic solutes present in the pretreated POME which generally contributed to the brownish color and the unpleasant odor. The dissolved organic solutes present can be grouped into three major groups which are the carbohydrate constituents, protein and ammoniacal nitrogen. The removal of these dissolved organic solutes will actually remove the soluble COD and BOD present in the pretreated POME.

1.4.4 Ultrafiltration (UF) Membrane System

Ultrafiltration (UF) membrane system is used to remove the remaining dissolved organic solutes which are unable to be adsorbed by the GAC. The UF will retain soluble macromolecules of dissolved organic solutes (mainly carbohydrate constituents, protein and ammonical nitrogen) and everything larger while passing solvent and other small soluble species; thus able to reduce the soluble COD and BOD concentration in the pretreated POME. As shown from Fig. 1.2, the pilot plant investigation for UF membrane system is based on two types of UF membrane material which are the ceramic and polymeric type.

The ceramic membrane is investigated because of its general characteristics of being chemically inert, allowing long term cleaning with aggressive solutions, stable at high temperature; withstand high pressure and resistance to mechanical strength (Baker, 1997; Sondhi and Bhave, 2001). Such ceramic membrane characteristics allow separation of high fouling load of POME with prolonged membrane lifespan. However, this type of membrane requires complex membrane cleaning procedure with much amount of cleaning reagent. In addition, the UF ceramic membrane is expensive (10 times higher) as compared to the UF polymeric membrane.

The polymeric membrane can be available easily as it is widely used in the membrane system. The UF polymeric membrane is much cheaper than the UF ceramic membrane and it requires simple membrane cleaning procedure with less amount of cleaning reagent. However, this type of membrane is unable to cope with high temperature (>80 ^{o}C), and pressure as well as strong mechanical strength. The UF polymeric membrane is not chemically inert and unable to withstand long term cleaning with aggressive solutions. Therefore, such polymeric membrane used for separation of high fouling load of POME is not durable and require frequent replacement.

The investigation of both types of ceramic and polymeric membrane in the pilot plant allows the quantitative comparisons of both membranes as they exhibit specific advantages and disadvantages. Though the ceramic membrane has prolonged lifespan, the total cost can be more expensive as its membrane cost is much expensive and requires much amount of cleaning reagent. On the other hand, though the polymeric membrane requires frequent replacement, the total cost can be cheaper as its membrane cost is much cheaper and requires less amount of cleaning reagent. Therefore, proper evaluation of the performance for both UF ceramic and polymeric membrane based on the pilot plant coupled with cost analysis is required so that both types of membrane material can be compared quantitatively.

1.4.5 Reverse Osmosis (RO) Membrane System

The final unit operation involved in the membrane based POME treatment pilot plant is reverse osmosis (RO) membrane system. The permeate collected from the UF membrane system is fed into the RO membrane system to remove micro-molecules of dissolved organic solutes (mainly carbohydrate constituents, protein and ammonical nitrogen) which have passed through the pores of UF membrane for further soluble COD and BOD reduction. Tubular polymeric membrane is used in this process for the benefit of resistance to membrane fouling due to good fluid hydrodynamics outweighs the high cost (Baker, 1997). The concentrated retentate of UF and RO membrane system in the pilot plant is drained of after each experimental run. However, for actual industrial treatment plant, the concentrated retentate of UF and RO membrane system are recycled back to the treatment system to increase the overall utilization of the POME.

1.4.6 Overall Performance of the Pilot Plant

The overall performance of the membrane based POME treatment pilot plant shows a very promising result. The recovered water/treated POME not only complied with the effluent discharge standards set by the DOE of Malaysia, but the recovered water was crystal clear and could be recycled as process, utility or boiler feed water. The high content of organic nutrient in the dry cake from the filter press could be converted into organic fertilizer (Ismail, 2005). The overall treatment efficiency in terms of pH, BOD_3, COD, suspended solids and oil & grease based on the study of the pilot plant is summarized in Table 1.3.

Table 1.3: Overall treatment efficiency for membrane based POME treatment pilot plant (Ismail, 2005).

Parameter	**POME**	**Stage 1**	**Stage 2**	**Stage 3**	**Stage 4**	**Discharge Standard**
pH	4.1	6.0	6.0	6.1	6.5	5 – 9
BOD_3, mg/L	20 200	6 100	4 600	3 900	73	100
COD, mg/L	43 200	13 300	9 300	7 900	187	NR
Suspended Solids, mg/L	19 000	45.54	24.72	0.60	ND	400
Oil and Grease, mg/L	3 200	30	4	1	ND	50

Stage 1=Coagulation and Flocculation; Stage 2=GAC Adsorption; Stage 3=UF Membrane System; Stage 4=RO Membrane System; ND=Not Detectable; NR=Not Required

1.5 Problem Statement

The results obtained from the membrane based POME treatment pilot plant study by Ismail (2005) are promising and attractive to the palm oil mill owners as the treatment system offers water recycling and sludge recovery as organic fertilizer; which achieving zero discharge. Therefore, there is an urgent need to develop and design an industrial scale membrane based POME treatment plant suitable for a typical palm oil mill in Malaysia based on the findings obtained from the pilot plant studies.

The re-evaluation of the systems/processes in the pilot plant found that the coagulation and flocculation process for POME treatment seems to be quite expensive. The optimum Alum dosage of 15,000 mg/L POME treated and polymer dosage of 300 mg/L POME treated are needed to obtain the desired results (Ismail, 2005). Based on the preliminary cost analysis using the optimum dosage for Alum and polymer, the treatment cost for coagulation and flocculation without consideration of the alkaline solution used for pH adjustment could be RM 18.30/m^3 POME treated (calculated based on the Alum and polymer unit cost of RM 1.00/kg and RM 11.00/kg respectively; source from Envilab Sdn. Bhd., Malaysia). According to the operation hours of approximately 5000 per year (source from Alfa Laval (Malaysia) Sdn. Bhd.), the total treatment cost of coagulation and flocculation for a typical POME flow rate of 27 m^3/hr based on the palm oil mill capacity of 36 tons/hr (181,400 tons/yr) Fresh Fruit Bunch (FFB) processed is RM 2.49 millions per year. This treatment cost is too high to convince the mill owners and thus a more economical treatment process for coagulation and flocculation is needed for membrane based POME treatment before the complete treatment plant can be designed.

The study of the membrane based POME treatment pilot plant by the previous researchers (Ismail, 2005) is solely relies on the experimental evaluation. The performance for each of the system/process in the pilot plant actually deals with specific internal mass balances as well as their equilibrium relationships, transport and thermodynamic properties which can be represented by the transport models. The transport models available in the literature mostly deal with the single solute system. However, the membrane based POME treatment system deals with the complex system of POME which is multiple solutes. Therefore, the transport models suitable for multiple solutes system which are representing the systems/processes in the pilot plant need to be developed in order to effectively evaluate the performance of the treatment system based on the transport phenomena. The transport models are also needed for mass balance calculation to estimate the performance, size and cost of the industrial scale membrane based POME treatment plant.

The study of the membrane based POME treatment pilot plant is confined to only one mode of operation or design. However, several different modes of operation and designs can be obtained by placing the unit operations/systems in different orientations. The experimental study of the pilot plant for different designs based on different orientations of the unit operations is impossible as the pilot plant does not provide such flexibility in addition to large experimental works involved. Unfortunately, the different designs of membrane based POME treatment system are needed to compare and evaluate the most suitable industrial scale plant design for a typical palm oil mill in Malaysia. Thus, a study based on the integrated transport models developed for multiple solutes POME system is needed to evaluate the performance of the industrial scale membrane based POME treatment plant of different design configurations. Several different designs can be obtained by integrating each transport model representing each unit operation/system through mass balance analysis at different orientations.

The evaluation of the membrane based POME treatment pilot plant through experimental study unable to provide information on the optimum operating and design parameters for the industrial scale treatment plant. This information is important and essential before a decision can be made. Therefore, optimization based on minimization of the total treatment cost coupled with mass balance, sizing and costing analysis is needed for all the proposed designs in order to obtain the optimum operating and design parameters. The final treatment plant design can be chosen by comparing the total treatment cost of the proposed designs obtained from the optimization study.

1.6 Research Objectives

The research objectives for the present study are as follows:

1. To propose and investigate a cost effective POME pretreatment method of direct flocculation by using only polymer based coagulant/flocculants (cationic and anionic polymers) in bench scale or jar test analysis; replacing the current coagulation and flocculation system in the pilot plant using Alum and polymer.
2. To develop and analyze the transport models to obtain model parameters for different processes/operations in the pilot plant. The direct flocculation process, GAC adsorption, UF and RO membrane system are considered for modeling. The modeling and simulation analysis of all the transport models are based on the experimental data and analysis of suspended solids, carbohydrate constituents, protein and ammoniacal nitrogen which are correlated with COD, BOD and oil & grease of POME at different stages of treatment.
3. To propose and evaluate different designs of industrial scale membrane based POME treatment plant by integrating all the transport models through mass balance, sizing and costing analysis.
4. To optimize the operating and design parameters for all the proposed designs of membrane based POME treatment plant based on total treatment cost minimization.
5. To propose the final design of industrial scale membrane based POME treatment plant based on the total treatment cost comparisons between the different proposed designs. The parameter sensitivity and feasibility analysis for the final design of industrial scale membrane based POME treatment plant are also evaluated.

1.7 Research Scope

The main focus of the present study is the design of industrial scale membrane based POME treatment plant at optimum condition which is suitable for a typical palm oil mill in Malaysia. Based on the analysis of the pilot plant, the main systems/processes considered in the industrial scale plant design are the coagulation and flocculation process, sludge dewatering process, GAC adsorption, UF and RO membrane system.

The coagulation and flocculation process in the pilot plant using Alum and polymer was very expensive and cost ineffective. Therefore, the direct flocculation using cationic and anionic polymers was investigated to evaluate the possibility to completely replace the metal based Alum with water soluble organic based polymer. The direct flocculation process studied in the present research was the single and dual polymer systems. In the single polymer system, only cationic polymer was added to remove the high content of suspended solids by inducing flocs formation. In the dual polymer system, cationic polymer followed by anionic polymer was added into the POME system. The dual polymer system was employed when the single polymer system failed to achieve the desired flocculation. The performance of the single and dual polymer system was investigated based on the removal efficiency of suspended solids and COD as well as the water recovery. Finally, the treatment cost of direct flocculation process was compared with the coagulation and flocculation process to analyze the cost effectiveness of both processes.

The correlations between the indirect indicators of COD, BOD, oil & grease, total nitrogen with the multiple solutes of suspended solids, carbohydrate constituents, protein and ammoniacal nitrogen were obtained based on the POME characteristic analysis. The transport models representing the processes/operations in the pilot plant were evaluated based on the mass transport phenomena of these multiples solutes.

The transport models investigated were: (a) Population Balance Model (PBM) for flocculation process, (b) coupled model of Homogeneous Surface Diffusion Model (HSDM) with Ideal Adsorbed Solution Theory (IAST) for granular activated carbon (GAC) adsorption, (c) coupled model of Back Transport Analysis with Filtration Theory for ultrafiltration (UF) membrane system and (d) coupled model of Extended Spiegler-Kedem Model with Concentration Polarization Model for reverse osmosis (RO) membrane system. The investigation of these transport models included parameters estimation based on literature and experimental data, modeling and simulation study to predict and evaluate the performance of the operations/processes and comparisons of the simulated results with the experimental results obtained from the pilot plant study.

Three different designs for industrial scale membrane based POME treatment plant were proposed by placing the transport models representing the operations/processes at different orientations. These transport models were inter-connected to form a complete industrial scale design through the mass balance analysis based on the multiple solutes of suspended solids, carbohydrate constituents, protein and ammoniacal nitrogen. The major unit operations in all the designs were cationic and anionic polymer flocculation tanks, Dry Solids Decanter, GAC column, UF membrane system and RO membrane system. Each of the unit operation was represented by its own transport model which was already tested and validated based on the pilot plant analysis.

It must be noted that the sludge dewatering system using Dry Solids Decanter was being considered in the industrial scale designs because the filter press was not suitable for high capacity dewatering process with continuous mode. In contrast, the capacity of the decanter was too large to be installed in the pilot plant. The minimum feed capacity of the decanter available in the market is 2 m^3/hr and the pilot plant available has the capacity of only 450 L/hr. Thus, the filter press was used in the pilot plant for sludge dewatering to separate the supernatant from the sludge after the direct flocculation process. The characteristic of the supernatant and cake obtained from the filter press was assumed to be identical with the supernatant and cake obtained from the Dry Solids Decanter. As the sludge dewatering process only involved liquid and solid phase separation, the investigation based on merely simple mass balance without the consideration of transport model was adequate. However, detailed sizing based on the mass balance results of the decanter was needed to determine the operating parameters and performance of the decanter.

The sizing and costing for all the proposed designs were determined based on the mass balance calculations. The costing of the proposed designs allowed the estimation of the total treatment cost for each of the proposed design. The total treatment cost of each proposed design was then minimized through optimization study using the sequential quadratic programming method subject to the constraints imposed to the variables of the systems. Throughout the optimization study for each of the designs, the mass balance, sizing and costing were recalculated simultaneously based on the optimum design and operating parameters to obtain the minimum total treatment cost. The performance of the proposed designs was compared based on the total treatment cost to obtain the final design for the industrial scale membrane based POME treatment plant. Finally, parameter sensitivity and feasibility analysis for the final design of industrial scale membrane based POME treatment plant were carried.

1.8 Organization of the Thesis

Chapter 1 (Introduction) presents a brief introduction about the generation and characteristic of the Palm Oil Mill effluent (POME) as well as the environmental regulatory control for POME discharge. The conventional biological treatment system for POME and the membrane based POME treatment pilot plant are discussed in this chapter. This chapter also includes problem statements that provide some basis and rationale on the necessity of this research study. The research objectives of the present study are presented with the research scope and the overall content of this thesis is summarized in the last section of this chapter.

Chapter 2 (Literature Review) elaborates some important information on the current POME treatment method and the processes of coagulation and flocculation, sludge dewatering, GAC adsorption, UF and RO membrane system which are available in the pilot plant. Information on process modeling, simulation and optimization for the design of industrial scale membrane based POME treatment plant are also discussed in detail.

Chapter 3 (Modeling and Simulation) discusses on the correlation of the multiple solutes of suspended solids, carbohydrate constituents, protein and ammoniacal nitrogen concentration in POME system with the indirect indicators of oil & grease, COD, BOD and total nitrogen concentration. Then, the development of the transport models representing the processes or systems in the pilot plant as listed below is discussed in detail.

a) Flocculation process - Population Balance Model (PBM).
b) Granular activated carbon (GAC) adsorption - coupled model of Homogeneous Surface Diffusion Model (HSDM) with Ideal Adsorbed Solution Theory (IAST).
c) Ultrafiltration (UF) membrane system - coupled model of Back Transport Analysis with Filtration Theory.
d) Reverse osmosis (RO) membrane system - coupled model of Extended Spiegler-Kedem Model with Concentration Polarization Model.

Chapter 4 (Design and Optimization of the Treatment Plant) proposes three different designs of industrial scale membrane based POME treatment plant. For every design, the major equipments in the flowsheet are represented by the transport models developed in Chapter 3 which are connected by mass balance analysis. The sizing and costing procedure is discussed in detail. The optimization study based on the total treatment cost minimization for each proposed design is also presented.

Chapter 5 (Materials and Methods) describes in detail all the materials and chemicals used in the present study. This is followed by the experimental procedure which includes analysis of sample, bench scale study, pilot plant Standard Operating Procedure (SOP) and pilot plant study.

Chapter 6 (Results and Discussion) is the core of this thesis with six main studies. In the first section, the raw POME characteristics based on the analysis methods are presented. The relationships and final correlations between the multiple solutes of suspended solids, carbohydrate constituents, protein and ammoniacal nitrogen with COD, BOD and oil & grease are presented and discussed. These final correlations are used throughout the modeling, simulation, design and optimization of the treatment plant. In the second section, the direct flocculation study using cationic and anionic polymers based on single and dual polymer systems are presented and discussed. The transport model developed for direct flocculation process is also presented and discussed. In the next sections, the transport models developed for GAC adsorption, UF and RO membrane system are discussed along with the parameters estimation based on literature and experimental data. The modeling and simulation study to predict and evaluate the performance of the operations/processes and comparison of the simulated results with the experimental results obtained from the pilot plant study are presented and discussed. In the last section of this chapter, mass balance results based on the proposed three designs of industrial scale membrane based POME treatment plant are presented. The sizing and costing for each of the designs are discussed and compared. It must be noted that though the transport model for sludge dewatering system using Dry Solids Decanter is not considered, the sizing of the decanter is presented and discussed in detail to investigate the characteristic and the performance of the decanter. Throughout the mass balance, sizing and costing calculation for each plant design, the optimization via total treatment cost minimization was implemented simultaneously to obtain the optimum operating and design parameters. Therefore, the calculated results for mass balance, sizing and costing presented in this section are based on the optimum condition obtained from optimization. The final treatment plant design was chosen by comparing the total treatment cost of the proposed designs. Finally, parameter sensitivity and feasibility analysis for the final design of industrial scale membrane based POME treatment plant were presented.

Chapter 7 (Conclusions and Recommendations) concludes the findings from the present research. The conclusions reflect the achievements of the listed objectives which were obtained throughout the study. Finally, recommendations for future study are listed. These recommendations are presented in view of their significance and importance related to the present research.

CHAPTER 2

LITERATURE REVIEW

This chapter provides a brief review on the current POME treatment methods and their limitations. An overview of the proposed membrane based POME treatment technology which covers the pretreatment processes (coagulation and flocculation, sludge dewatering and granular activated carbon (GAC) adsorption) and membrane separation technology (ultrafiltration (UF) and reverse osmosis (RO) membrane system) is presented. The description for the design of membrane based POME treatment plant with industrial scale via modeling, simulation and optimization studies is elaborated. A brief review on the transport models developed for the pretreatment processes and membrane separation technology is also addressed in this chapter.

2.1 Current POME Treatment Methods

The conventional treatment technology of POME employed in most of the palm oil mills in Malaysia is the combination of physical and biological treatment. The physical treatment is the primary treatment of screening, sedimentation and oil removal by using the oil traps. The biological treatment is the secondary treatment applied in the POME treatment for biodegradation of organic matters by microorganism digestion. The biological treatment system as summarized in Table 2.1 includes ponding system, Aerated Lagoon System, Conventional Anaerobic Digester, Anaerobic Contact Process, Up-flow Anaerobic Sludge Blanket (UASB) Reactor, Close Tank Digester and etc. The ponding system is the most widely used biological treatment for POME as 85% of Malaysia’s palm oil mills are applying this system. The thermal treatment of evaporation is also proposed in the secondary treatment of POME by Ma (1999). This method, however, is unsuccessful due to the generation of large amount of air pollutants as discussed in Table 2.1.

Table 2.1: Summary of various current POME treatment methods.

Ponding System (Chin and Wong, 1982; Chan and Chooi, 1982; Chin *et al.*, 1996)

- Combination of anaerobic, aerobic and facultative ponds or lagoons.
- About 85% of Malaysia's palm oil mills applying this system to treat POME.
- Main components of the system include de-oiling tank, acidification ponds, methanogenic ponds, facultative ponds and sand beds.
- Long treatment period of 45 to 60 days.
- High maintenance required due to huge treatment area.

Aerated Lagoon System (Thani *et al.*, 1999)

- Similar to the ponding system except the facultative lagoons are replaced with mechanically-aerated lagoons.
- Treatment period is usually between 15 to 20 days.

Conventional Anaerobic Digester (Lim *et al.*, 1983)

- Combines the anaerobic process in a digester tank with the aerated lagoons.
- The digester tank is a continuous stirred tank reactor (CSTR) with no solid recycle.
- Requires a longer treatment period (20 days) to prevent washout of microorganisms and to achieve desired treatment efficiency.
- High treatment cost.

Anaerobic Contact Process (Ibrahim *et al.*, 1984)

- Similar to the Conventional Anaerobic Digester except the raw wastewaters are mixed with recycled sludge solids and then digested in a continuously stirred digester tank (CSTR).
- Gas formation in the settling tank inhibits effective settling of the sludge and enhanced buoyancy of the suspended solids.

Up-flow Anaerobic Sludge Blanket (UASB) Reactor (Thani *et al.*, 1999, Najafpour *et al*., 2006)

- Combines the anaerobic process in a digester tank with the aerated lagoons.
- The digester tank is a UASB Reactor based on upward flow of wastewater through a suspended layer or sludge blanket of active biomass.
- Biochemical activity converts organic matter to methane and carbon dioxide gas.
- The biogas is collected and treated wastewater is discharged via an overflow weir.

Close Tank Digester (Mahabot and Harun, 1986)

- The digesters are operated as a conventional high-rate system.
- The treatment period is about 10 days.
- Biogas generated from the digester is compressed and discharged into the emitter utilized for heat and electricity generation and excess biogas is flared off.

Trickling Filter (Norulaini *et al.*, 2001)

- 50% of COD was achieved for the influent COD of 26,000mg/L.

Aerobic Lagoon System (Oswal *et al.*, 2002)

- Similar to aerated lagoon system except special species of microorganism is used.
- A tropical marine yeast (Yarrowia Lipolytica) is used for the degradation of POME in a lagoon.
- 95% COD removal was achieved at the retention time of 2 days.

Aerobic Rotating Biological Contactor (Najafpour *et al*., 2005)

- 88% COD removal for the retention time of 55 hours with the influent COD of 16,000mg/L.

Land Application System (Wood *et al.*, 1979; Eapen, 1977)

- Anaerobic digested POME is utilized as a source of organic fertilizer.
- The POME is pumped to distribution tanks and then applied directly as fertilizer onto the cropland by gravity flow or by pumping onto a system of inter-row flatbeds, long-beds or furrow.

Evaporation Process (Ma, 1999)

- Evaporation to remove solids content of POME.
- Energy obtained from burning unwanted fiber and shell.
- Generate large amount of air pollutants; creating another environmental problem.

The conventional biological POME treatment depends on the microorganisms to digest the COD and BOD. These microorganisms require intensive care as they are sensitive to the surrounding temperature and pH. Thus, skilled and experienced workers are needed for complete maintenance and control to ensure the biological treatment is implemented in an order manner. However, this issue is often neglected and the biological treatment fails to achieve the desired treatment efficiency. Consequently, the accumulation of excess suspended solids resulted dead spots and short-circuiting in the ponds. Digestion capacity becomes ineffective, hydraulic retention time is shortened, treatment efficiency is decreased and regular desludging becomes highly necessary. The oil gets accumulated on the surface of the ponds and sticky oily scum is formed. As a result, high labor cost is required to maintain the systems in the satisfactory conditions. The biological treatment also requires extensive treatment area and long treatment period (Thani *et al*., 1999; Mahabot and Harun, 1986; Ma, 2000).

Consequently, not all of the palm oil mills are meeting the Department of Environment (DOE) effluent discharge standards under the Environmental Quality Act 1974. The actual situation of POME treatment system using biological treatment is shown in Plate 2.1. Looking at the urge for solution of this problem, an alternative POME treatment system is proposed in the present research based on the membrane technology incorporated with pretreatment processes.

(a) (b)

(c) (d)

Plate 2.1: Conventional biological POME treatment (a) ponding system with accumulated suspended solids (b) open ditch with short-circuit (c) sticky oily scum (d) final discharge

2.2 Pretreatment Processes

The pretreatment processes employed for POME treatment in the present research are the coagulation and flocculation, sludge dewatering and granular activated carbon (GAC) adsorption. These processes are integrated in the membrane based POME treatment pilot plant to reduce the suspended solids content to an acceptable level in order to ensure the success of membrane separation technology. The pretreatment process is used to mitigate membranes fouling and degradation due to suspended solids loading during the operation and thus the membrane lifespan is prolonged (Ahmad *et al*., 2005).

2.2.1 Coagulation and Flocculation Process

Coagulation is defined as the destabilization of colloidal particles brought about by the addition of a chemical reagent called as coagulant. Flocculation is defined as the agglomeration of destabilized particles into microflocs and after into bulky floccules which can be settled called flocs. The addition of another reagent called flocculent or a flocculent aid may promote the formation of the flocs (Degrémont, 1979). The aim of applying coagulation and flocculation treatment is generally to remove the colloidal matters such as suspended solids present in the wastewater.

The most common coagulants used are hydrolysable metal cations such as lime, aluminum sulfate (Alum), ferric chloride and ferrous sulfate whereas polymers are employed as flocculent. These coagulants and flocculent are not only employed in POME treatment but they are used extensively in water and wastewater treatment (Vilgé-Ritter *et al*., 1999; Lee *et al*., 2000; Wang *et al*., 2006). Although inorganic coagulants are inexpensive and readily available, their usage requires high chemical cost due to high dosage. It also generates excessive volumes of phyto-toxic sludge and cannot be readily disposed. A large amount of caustic soda is needed to alter the solution pH to achieve its isoelectric point and coupling with flocculation is needed to improve the efficiency (Sarika *et al*., 2005).

The flocculent of organic macromolecules polymers offer significant advantages in coagulation-flocculation process. The concentrations needed are only a few milligrams per liter and they generate small quantity of non-hazardous sludge for easy disposal. On a price-per-weight basis, they are much more expensive than inorganic coagulants, but overall operating cost is lower because of a reduced dosage, elimination of for pH adjusting chemicals and reduced sludge disposal costs due to lower sludge volumes (Ravina, 1993).